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Unified Theory of Resonance Energies, Ring Currents, and Aromatic Character in the $(4n + 2)\pi$-Electron Annulenes

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Abstract: It is demonstrated for the first time that, to high accuracy, there is an analytic relationship between the resonance energies (REs) and reduced ring currents (RCs) of the $(4n + 2)\pi$-electron annulenes—the original subjects of the Hückel rule—which leads naturally to a unified theory of aromatic character. The resonance energy is obtained as RE = $\pi^2 p_{rs}\beta/3N = \pi^2 E/6N^2$ where p_{rs} is the bond order, N is the number of carbon atoms, E is the total π-electron energy, and β is the resonance integral. The relationship between resonance energies and ring currents takes the form RE = π^2RC$/3S$ or RC = $3S$ RE$/\pi^2$ where S is the area of the ring. The available experimental evidence is shown to be in excellent agreement with this relationship. Attention is drawn to the present lack of integrity of our knowledge of nondissipative currents in organic molecules and bulk superconductors, and common facets of present theories are discussed.

While aromatic character has been of interest for some time,[1-6] attempts to quantify and more closely define the subject have considerably intensified in recent years. This is particularly true in the area of resonance energies, which are often interpreted in terms of aromatic character. The impetus for this revival of interest came from the work of Dewar,[7-12] in which he redefined the reference energy for calculation of the energy of aromatic stabilization. His method employs the appropriate number of localized single and double bond energies (taken from a series of polyenes) for the calculation of a reference energy which is defined to be the nonaromatic energy of the particular system.[7-12] With this definition the annulenes were found to possess a wide and continuous spectrum of resonance energies which included both positive (aromatic) and negative (antiaromatic[7,8]) values.[7-12] These quantities (which are now termed Dewar resonance energies) were first calculated by Dewar within the framework of the PMO theory and a π-electron SCF MO method.[8-12] More recently Hess and Schaad (HS)[13-17] have reparametrized the Hückel molecular orbital (HMO) method in a way which allows the calculation of Dewar resonance energies. A variation of this approach was introduced by Aihara (A-I and A-II)[18-20] and Gutman, Milun, and Trinajstic (GMT),[21] who utilized the π-bond energy of an infinitely large cyclic polyene in their definition of a reference structure. This procedure obviates the need for the utilization of a Kekule structure with distinct single and double bonds (which may not be unique), and ensures the correct asymptotic nonaromatic limit at infinitely large ring size. Finally, using a valence bond approach, Herndon[22-25] has introduced a structure-resonance theory based on Kekule structures which also allows the calculation of resonance energies.

The results of all of these methods are not only in good agreement with one another but have been demonstrated by the authors to provide a rather reliable index of the chemical stability and reactivity of the compounds studied.[9-25] Insofar as resonance energies serve as a criterion of aromatic character it may therefore be concluded that this aspect of the subject is now well understood. This in turn has led to a great improvement in our conception of the Hückel $(4n + 2)\pi$-electron rule.

The current state of affairs with other criteria of aromatic character is nowhere near as satisfactory. This is particularly true of the magnetic or ring current criterion of aromaticity.[2-4,6,26-40] Of all the criteria this one is most often employed, as some measure of the ring current is usually available from the ^{1}H NMR (and sometimes ^{13}C NMR[41-43]) chemical shifts[4] of the compound, and measurements of diamagnetic susceptibility exaltations[44] seem to be becoming quite routine.[45] In fact the magnetic criterion is often the sole piece of evidence for the aromatic character of new compounds, as resonance energies are extremely difficult to measure experimentally and are usually inferred from the observed chemical stability (which is not necessarily directly related to ground-state quantities such as resonance energy). There is now strong evidence to suggest that there is no relationship among these different criteria of aromatic character in the case of nonalternant hydrocarbons and heteroatomic systems.[26-30] *Even for the alternant hydrocarbons and annulenes there is as yet no demonstrated relationship between ring currents and resonance energies,* although the qualitative connection seems soundly based.[40] It is the purpose of this paper to show that there is in fact a direct mathematical dependence between these two quantities which allows the development of a unified theory of aromatic character in the $(4n + 2)\pi$-electron annulenes (which, after all, are the original subject of the Hückel rule).

Also included in the present work is a reconsideration of molecular ring currents[33,34] in the light of the microscopic theory of superconductivity as developed by Bardeen, Cooper, and Schrieffer (BCS).[46]

Theory

1. General. The Hückel molecular orbitals[11,47-49] for π-

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electron systems (HMOs) (ψ_k) are represented as a linear combination of atomic orbitals (ϕ_r):

$$\psi_k = \sum_r^N c_{kr}\phi_r \tag{1}$$

where N is the number of atoms in conjugation. The total π-electron energy (E) is given by

$$E = \sum_r^N q_r\alpha_r + 2\sum_{r<}^N \sum_s^N p_{rs}\beta_{rs} \tag{2}$$

where the electron density (q_r) and bond order (p_{rs}) are defined as

$$q_r = 2\sum_k^{\text{occ}} c_{kr}^* c_{kr} \tag{3}$$

$$p_{rs} = \sum_k^{\text{occ}} (c_{kr}^* c_{ks} + c_{kr}c_{ks}^*) \tag{4}$$

where α_r is the coulomb integral for atom r and β_{rs} is the resonance integral for the r–s bond. The mutual bond–bond polarizability ($\pi_{rs,tu}$) is given by

$$\pi_{rs,tu} = 2\sum_k^{\text{occ}} \sum_l^{\text{unocc}} \frac{(c_{kr}^* c_{ls} + c_{ks}^* c_{lr})(c_{kt}c_{lu}^* + c_{ku}c_{lt}^*)\beta^{-1}}{(\epsilon_k - \epsilon_l)} \tag{5}$$

where ϵ_k is the energy of orbital k.

2. Resonance Energies (REs) of the [$N = 4n + 2$]Annulenes. For the [$N = 4n + 2$]annulenes the HMOs may be written

$$\psi_k = \frac{1}{\sqrt{N}}\sum_r^N \exp\left\{\frac{2\pi i k r}{N}\right\}\phi_r,\ k = 0, \pm 1, \ldots, \pm\left(\frac{N}{2} - 1\right), \frac{N}{2} \tag{6}$$

whereas the orbital energies become

$$\epsilon_k = 2\beta\cos\left(\frac{2k\pi}{N}\right) \tag{7}$$

The total energy is therefore given by

$$E = 4\beta\sum_k^{\text{occ}} \cos\left(\frac{2k\pi}{N}\right) \tag{8}$$

$$= \frac{4\beta}{\sin(\pi/N)} \tag{9}$$

The bonding contribution (the atomic terms are omitted here and in subsequent discussion) from eq 2 simplifies to

$$E = 2Np_{rs}\beta \tag{10}$$

where r–s is taken here (and subsequently) to be a directly linked pair of atoms. The energy per bond (BE) is therefore found from

$$\frac{\text{BE}}{2\beta} = \frac{E}{2N\beta} = p_{rs} \tag{11}$$

where

$$p_{rs} = \frac{2}{N\sin(\pi/N)} \tag{12a}$$

At infinite ring size, the bond order (p_{rs}^{∞}) is given by

$$p_{rs}^{\infty} = 2/\pi \tag{13a}$$

The Dewar resonance energy (RE) may therefore be formed from

$$\text{RE} = N(\text{BE} - \text{BE}^{\infty})\beta \tag{14}$$

where BE^{∞} is the energy per bond at infinite ring size. Thus

$$\text{RE} = 2N(p_{rs} - p_{rs}^{\infty})\beta \tag{15}$$

From eq 12a, 13a, and 15, we obtain

$$\begin{aligned}\text{RE} &= 4\left\{\frac{\pi - N\sin(\pi/N)}{\pi\sin(\pi/N)}\right\}\beta \\ &= \frac{4}{\sin(\pi/N)}\left\{\frac{\pi^2}{6N^2} - \frac{\pi^4}{120N^4} + \ldots\right\}\beta \\ &= p_{rs}\left\{\frac{\pi^2}{3N} - \frac{\pi^4}{60N^3} + \ldots\right\}\beta\end{aligned} \tag{16}$$

3. Ring Currents (RCs) of the [$N = 4n + 2$]Annulenes. In our treatment of ring currents we adopt the McWeeny[34] formulation of the London[33] theory. In the present case the ring current intensity (I, in cgs units) is obtained from

$$I = [8\pi^2 c(e/hc)^2 H]\text{RC} \tag{17}$$

where H is the applied magnetic field (taken to be perpendicular to the plane of the ring), RC is the reduced ring current, and the other symbols have their usual meaning. RC is given by

$$\text{RC} = J_{rs}S \tag{18}$$

where S is the area of the ring and J_{rs} is the reduced bond current

$$J_{rs} = (p_{rs} + \beta\overline{\pi}_{rs,rs})\beta \tag{19}$$

where

$$\overline{\pi}_{rs,tu} = -2\sum_k^{\text{occ}} \sum_l^{\text{unocc}} \frac{(c_{kr}^* c_{ls} - c_{ks}^* c_{lr})(c_{kt}c_{lu}^* - c_{ku}c_{lt}^*)\beta^{-1}}{(\epsilon_k - \epsilon_l)} \tag{20}$$

is the imaginary mutual bond–bond polarizability, which in the present case may be simplified;

$$\begin{aligned}\overline{\pi}_{rs,rs} &= \frac{2}{N^2}\sum_k^{\text{occ}} \sum_l^{\text{unocc}} \left\{\frac{\sin\left[\frac{\pi}{N}(k + l)\right]}{\sin\left[\frac{\pi}{N}(k - l)\right]}\right\}\beta^{-1} \\ &= \frac{-2(N - 1)}{N^2}\frac{1}{\sin(\pi/N)}\beta^{-1} \\ &= \frac{(1 - N)p_{rs}\beta^{-1}}{N}\end{aligned} \tag{21}$$

and

$$\begin{aligned}\overline{\pi}_{rs,tu} &= -\frac{2}{N^2}\sum_k^{\text{occ}} \sum_l^{\text{unocc}} \left\{\frac{\sin\left[\frac{\pi}{N(k + l)}\right]}{\sin\left[\frac{\pi}{N(k - l)}\right]}\exp\left[\frac{2\pi i}{N}(k - l)\right]\right\}\beta^{-1} \\ &= \frac{2}{N^2}\frac{1}{\sin(\pi/N)}\beta^{-1} = \frac{p_{rs}\beta^{-1}}{N}\end{aligned} \tag{22}$$

where r–s and t–u are taken here (and subsequently) to be directly linked pairs of atoms. Therefore from eq 19 we obtain

$$J_{rs} = \frac{p_{rs}}{N}\beta = \overline{\pi}_{rs,tu}\beta^2 = \frac{E}{2N^2} \tag{23a}$$

$$= \frac{2\beta}{N^2\sin(\pi/N)} \tag{23b}$$

and

$$\text{RC} = \frac{p_{rs}S\beta}{N} = \overline{\pi}_{rs,tu}S\beta^2 = \frac{ES}{2N^2} \tag{24a}$$

$$= \frac{2S\beta}{N^2\sin(\pi/N)} \tag{24b}$$

which are equivalent to the London result.[33]

4. Relationship between Resonance Energies (REs) and Ring Currents (RCs) in the [$N = 4n + 2$]Annulenes. Clearly for large N it will be possible to truncate the expansion in eq 16 at the first term. Even for benzene the error is less than 2%. Adopting this simplification we obtain for the Dewar resonance energy

$$\mathrm{RE} = \frac{\pi^2 p_{rs}\beta}{3N} = \frac{\pi^2 E}{6N^2} \tag{25a}$$

$$= \frac{2\pi^2\beta}{3N^2 \sin(\pi/N)} \tag{25b}$$

Combining this with eq 23 and 24 we obtain

$$\mathrm{RE} = \frac{\pi^2 \mathrm{RC}}{3S} = \frac{\pi^2 J_{rs}}{3} \tag{26}$$

$$\mathrm{RC} = \frac{3S\ \mathrm{RE}}{\pi^2} \tag{27}$$

thus demonstrating the simple relationship between resonance energies and ring currents in the [$N = 4n + 2$]annulenes.

5. Resonance Energies (REs) and Ring Currents (RCs) in ($4n + 2$)π-Electron [N]Annulenes. In the preceding discussion, for concreteness, we have limited our arguments to the [$4n + 2$]annulenes. In this section we briefly indicate how the treatment may be extended beyond the [$4n + 2$]annulenes to include the $[4n]^{2+,2-}$; $[4n + 1]^-$; and $[4n + 3]^+$annulenes. In fact the results are entirely equivalent.

The bond orders for these systems (cf. eq 12a) are given by

$$p_{rs} = \frac{2}{N\tan(\pi/N)} \quad ([N = 4n]^{2+,2-}\text{annulenes}) \tag{12b}$$

$$= \frac{1}{N\sin(\pi/2N)} \quad ([N = 4n + 1]^-\text{annulenes and } [N = 4n + 3]^+\text{ annulenes})$$

The bond order at infinite ring size[19] (cf. eq 13a) is now replaced by

$$p_{rs}^{\infty} = \frac{2}{\pi}\cos\left(\frac{m\pi}{2N}\right) \tag{13b}$$

where m is the formal charge. Substitution of these expressions in eq 15 with subsequent expansion of the trigonometric functions (cf. eq 16) leads in all cases to our previous resonance energy result

$$\mathrm{RE} = \frac{\pi^2 p_{rs}\beta}{3N} \tag{25a}$$

$$= \frac{2\pi^2\beta}{3N^2\tan(\pi/N)} \quad ([N = 4n]^{2+,2-}\text{annulenes}) \tag{25c}$$

$$= \frac{\pi^2\beta}{3N^2\sin(\pi/2N)} \quad ([N = 4n + 1]^-\text{annulenes and } [N = 4n + 3]^+\text{annulenes}) \tag{25d}$$

A completely analogous substitution of eq 12b and 12c in eq 23a and 24a gives rise to the corresponding expanded expressions

$$J_{rs} = \frac{p_{rs}\beta}{N} \tag{23a}$$

$$= \frac{2\beta}{N^2\tan(\pi/N)} \quad ([N = 4n]^{2+,2-}\text{annulenes}) \tag{23c}$$

$$= \frac{\beta}{N^2\sin(\pi/2N)} \quad ([N = 4n + 1]^-\text{annulenes and } [N = 4n + 3]^+\text{annulenes})$$

$$\mathrm{RC} = \frac{p_{rs}S\beta}{N} \tag{24a}$$

$$= \frac{2S\beta}{N^2\tan(\pi/N)} \quad ([N = 4n]^{2+,2-}\text{annulenes}) \tag{24c}$$

$$= \frac{S\beta}{N^2\sin(\pi/N)} \quad ([N = 4n + 1]^-\text{annulenes and } [N = 4n + 3]^+\text{annulenes}) \tag{24d}$$

The main point for our purposes, however, is the total integrity of eq 24a and 25a which demonstrates that the relationship between ring currents and resonance energies (eq 26 and 27) is completely general for the ($4n + 2$)π-electron annulenes—thus encompassing all of the original subjects of the Hückel rule.

Table I. Resonance Energies for ($4n + 2$)π-Electron Annulenes (Units of β)

[N]annulene, [N]	unified theory	A-I[18-20]	A-II,[18-20] GMT[21]	HS[13-17]
$[3]^+$	0.731	0.692	0.536	
$[4]^{2+,2-}$	0.411	0.399	0.305	
$[5]^-$	0.426	0.418	0.317	
[6]	0.366	0.361	0.273	0.39
$[7]^+$	0.302	0.299	0.225	
$[8]^{2+,2-}$	0.248	0.246	0.186	
$[9]^-$	0.234	0.233	0.175	
[10]	0.213	0.212	0.159	0.26
$[11]^+$	0.191	0.190	0.143	
$[12]^{2+,2-}$	0.171	0.170	0.128	
[14]	0.151	0.150	0.113	0.23
[18]	0.117	0.117	0.090	0.22
[22]	0.096	0.095		0.22

Results and Discussion

The results of the unified theory are compared with other treatments of resonance energy[8-21] in Table I. It is clear that, for large N, the unified theory asymptotes toward the Aihara method (A-I),[18-20] but at lower values of N is intermediate between the results of Aihara (A-II),[18-20] GMT,[21] and HS.[13-17] The authors[8-21] whose work is cited in Table I have presented detailed comparisons of their results with the available experimental data and found excellent agreement. As the present study is in accord with the previous treatments, it seems that the unified theory also provides a good description of resonance energies.

However, an extra dimension is added to the resonance energy comparisons by our integration of this quantity with ring currents. Some time ago we developed a theory of aromatic character in the annulenes which was based on the experimental determination of ring currents from observed proton chemical shifts.[40] This analysis allowed the parametrization of β, the resonance integral, in the London equations[33] (for example, eq 24). At the time we termed this β_m, to denote its application to magnetic properties, and it seemed highly unlikely that such a parametrization would find utility in other areas (such as π-electron energies). Two different parametrizations were developed,[40] one based on the experimental diamagnetic susceptibilities of the benzenoid hydrocarbons (scheme A), which was taken from the work of O'Sullivan and Hameka,[50] and the other on an analysis of the ^{1}H NMR chemical shifts of *trans*-15,16-dimethyldihydropyrene[40,51] (scheme B). The results obtained with these two parametrization schemes (eq 25 and Table I) in resonance energy calculations via the unified theory are shown in Table II. The agreement with the available data is highly satisfactory, and provides strong support for the unification of the concepts of resonance energies and ring currents in the ($4n + 2$)π-electron

Table II. Resonance Energies for $[N = 4n + 2]$Annulenes (kcal/mol)

[*N*]annulene [*N*]	unified theory parametrization			Dewar[9] (SCF MO)
	A[a]	*B*[b]	expt[c]	
[6]	22.5	18.4	21.2 ± 0.9	22.1
[10]	13.1	10.7		9.9
[14]	9.3	7.6		3.9
[18]	7.2	5.9	4.9 ± 5.8	3.2
[22]	5.9	4.8		3.0

[a] Reference 40, $\beta = -61.4409$ kcal/mol. [b] Reference 40, $\beta = -50.3878$ kcal/mol. [c] References 52–55. See text.

annulenes. The experimental data are taken from the work of George, Trachtman, Bock, and Brett[52-55] as their homodesmotic reaction scheme is defined in accord with the Dewar resonance energy. In the case of [18]annulene,[56] however, we have adopted the more recent value of the heat of formation ($\Delta H_f(g$, 298 K$) = 124.0 \pm 5.5$ kcal/mol), which was obtained by Oth and co-workers.[57] A MINDO/3 SCF MO study of [18]annulene found $\Delta H_f(g$, 298 K$) = 129.3$ kcal/mol and a D_{3h} structure with bond length alteration.[58] Bond alternation was also found in the π-electron SCF MO study by Dewar[9] (Table II), the molecular mechanics calculation of Allinger and Sprague,[59] and the ring current analysis of proton chemical shifts.[40] In this latter work the ring current in [18]annulene was found to be approximately half the theoretical bond-equalized value,[40] and a similar reduction in the resonance energy from the unified theory is probably therefore in order, leading to a corrected resonance energy for [18]annulene of about 3.3 kcal/mol.

It is of interest to examine the behavior of the ring currents and resonance energies at large values of N in the hypothetical bond-equalized case. From eq 25a and 24a we obtain

$$\mathrm{RE} \approx \frac{2\pi}{3N}\beta \tag{28}$$

and

$$\mathrm{RC} \approx \frac{2S}{\pi N}\beta \approx \frac{Na^2\beta}{2\pi^2} \tag{29}$$

Thus

$$\mathrm{RE} \approx \frac{4\pi^3\mathrm{RC}}{3N^2a^2} \tag{30}$$

and

$$\mathrm{RC} \approx \frac{3N^2a^2\mathrm{RE}}{4\pi^3} \tag{31}$$

where a is the carbon-carbon bond length. Clearly *the ring current increases linearly with N whereas the resonance energy is inversely proportional to N*.

It is therefore essential to correct ring currents for differences in area before attempting to correlate resonance energies. This difference in behavior accounts for the fact that ring currents are detectable in large annulenes, although resonance energies are rapidly attenuated at ring sizes beyond benzene. In fact, of course, both quantities are quenched by the onset of bond alternation which we hope to treat in more detail in future publications. It is the presence of bond alternation which is presumably responsible for the correlation between proton chemical shifts in tetra-*tert*-butyldehydro[*N*]annulenes and HS resonance energies per π electron, which was recently pointed out by Hess, Schaad, and Nakagawa.[17]

Molecular Ring Currents and Superconductivity

The physical literature on the theory of superconductivity is replete with such statements as the following. "We have shown that interatomic currents induced in aromatic compounds may be characterized by saying that they behave like supercurrents . . ." (London[33,60]). "A superconductor thus behaves like a diamagnetic molecule of macroscopic dimensions" (Fröhlich[61]). "The diamagnetic ring currents of aromatic molecules such as benzene, naphthalene, etc., are nondissipative currents similar in many respects to the persistent currents of superconducting rings and have often been referred to as a form of superconductivity" (Little[62]). It is our purpose in this section to reconsider the McWeeny formulation[34] of the London theory of molecular ring currents[33] in the light of such statements. Particular attention is paid to the congruences between the MO theory of ring currents and the Bardeen, Cooper, and Schrieffer (BCS)[46] theory of superconductivity. Although a number of striking similarities between the two theories emerge in the ensuing discussion, it is concluded that a true understanding of the precise relationship between these two phenomena will require the further efforts of physicists and chemists—it is hoped that this study will stimulate such an endeavor.

We begin with an MO formulation of the Peierls[63] and Fröhlich[64] transition (referred to as a Jahn-Teller effect in chemistry[65]), and proceed from there to a discussion of the BCS superconducting ground state and its relationship to current-carrying states in $(4n + 2)\pi$-electron annulenes.

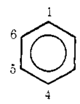
The Peierls and Fröhlich Transition (Jahn–Teller Effect). The phonon-mediated coupling of electrons which provides the accepted mechanism for superconductivity was first recognized by Fröhlich in his model of a one-dimensional superconductor.[64] It has subsequently been realized, however, that the instability found by Fröhlich does not correspond to the onset of superconductivity, but rather the transition to a nonmetallic (insulating) state of the linear chain. This latter effect is known as a Peierls[63] transition in which an energy gap is opened between the valence and conduction bands by a periodic distortion of the one-dimensional lattice.

The (commensurate) counterpart of this effect was recognized somewhat earlier in chemistry by Kuhn[66] (free-electron theory), Dewar[67] (MO theory), and others,[65,68-60] who considered the behavior of the bond lengths of polyenes at very long chain lengths. They found an energy gap at all chain lengths and that even in the case of the $(4n + 2)\pi$-electron annulenes bond length alternation should set in beyond a certain size. This behavior is entirely equivalent to the Peierls instability where a distortion of similar periodicity is predicted for a half-filled band structure.

The most convenient approach to this problem (at least in chemistry) has been provided by Binsch, Heilbronner, and Murrell.[71] These workers have shown that, by diagonalizing the bond-bond polarizability matrix ($\pi_{rs,tu}$, eq 5), it is possible to ascertain the likely symmetry of distortion (eigenvectors) and the energy gain (eigenvalues). That is, we solve the eigenvalue equation

$$\|\pi_{rs,tu} - \lambda_{rs}\delta_{rs,tu}\| = 0 \tag{32}$$

which is of the order of the number of π bonds in the molecule. The results for benzene (1) are shown in Table III. As may be



1

seen the largest eigenvalue (number 1) is associated with simple bond length alternation (b_{2u} distortion). The largest eigenvalue ($\lambda_{rs}^{\max}$) diverges as log n for the $[N = 4n + 2]$-annulenes.[70,71] The first few values are $-\lambda_{rs}^{\max}(\beta^{-1})[N]$: 1.0 [6], 1.342 [10], 1.560 [14], 1.722 [18], 1.850 [22]. The critical value of $\lambda_{rs}^{\max}$ is thought to be in the vicinity of $1.8\beta^{-1}$, al-

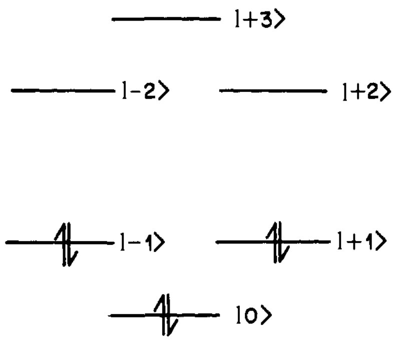


Figure 1. Benzene ground state with k values.

Table III. Eigenvalues and Eigenvectors of the Real Bond–Bond Polarizability Matrix ($\pi_{rs,tu}$) of Benzene

index	1	2	3	4	5	6
$\lambda_{rs}(\beta^{-1})$	1.0	0.222	0.222	0.0	0.0	0.0
bond r–s						
1–2	0.408	0.322	0.472	−0.527	0.407	0.238
2–3	−0.408	−0.575	0.052	−0.533	−0.132	0.445
3–4	0.408	0.243	0.524	−0.038	−0.393	0.587
4–5	−0.408	0.332	0.472	0.464	−0.114	0.521
5–6	0.408	0.575	0.052	0.470	0.424	0.314
6–1	−0.408	0.243	0.524	−0.025	0.685	0.173

though this number is highly dependent on the force constant parametrization scheme.[70,71]

BCS Ground State and the Energy Gap. In this section we seek analogy between the BCS superconducting ground state with its resultant energy gap[46,72] and the behavior of the $(4n + 2)\pi$-electron annulenes in the presence of an imaginary perturbation such as a magnetic field, as described by the McWeeny formulation[34] of the London theory.[33]

In the BCS theory[46] the ground state (Ψ_s) of a superconductor is given by

$$\Psi_s = \sum_{\mu} a_\mu \Psi_\mu \tag{33}$$

where Ψ_μ are the normal state configurations. A key feature of the BCS theory is the restriction placed on the configurations included in the superconducting ground state—only those configurations in which the spin-orbitals are occupied in pairs of opposite spin and momentum in eq 34 are admitted to the expansion in eq 33.

$$\Psi_\nu = k_1(1)\alpha(1);\ -k_1(2)\beta(2), \ldots \tag{34}$$

In the BCS theory the superconducting ground state is made up from a coherent linear combination of a very large number of such paired configurations.

Given the presence of an attraction between the pairs a bound state is possible.[73] In the normal state the phonon coupled electron-electron interaction (attractive) is overwhelmed by the coulomb term (repulsive). At sufficiently low temperature, however, the situation may be reversed, in which case the normal state is unstable with respect to the superconducting state. Transition to the superconducting state is accompanied by the formation of a gap in the density of states and the development of a highly correlated wave function; it is this condensation which accounts for the remarkable stability of the superconducting state against the scattering of electrons which is responsible for resistance in the normal state.

In the case of an organic molecule such as benzene the ground state is often approximated as a single configuration. Unlike the metallic situation, where the valence and conduction bands form a continuous distribution of energy levels, this is a reasonable approach for normal molecules. In the Hartree–Fock approximation the configuration is expressed as an antisymmetrized determinant of molecular orbitals. The HMO method is still simpler as electron-electron repulsion is omitted from the Hamiltonian which effectively precludes the correct description of electron spin. This is not so disastrous as it might seem in the present context, as the BCS attractive term is essentially spin independent,[72b] and the Block wave function, on which the BCS theory is based, takes no better account of the spin part of the wave function than the HMO method; in fact the two theories are identical in this respect.

Reference to the HMO wave function for benzene in Figure 1 shows that, at least in a formal sense, this could be associated with a BCS-type paired configuration. Nevertheless this does not seem to provide a true counterpart of a BCS wave function which is composed of a very large number of accessible configurations. A possible way out of this impasse is provided by eq 19, which gives the induced ring current. The second term in this equation, $\overline{\pi}_{rs,rs}$ (eq 21), does contain a sum over other configurations via virtual excitations (as does $\overline{\pi}_{rs,tu}$, eq 22). An analysis of these matrix elements as probabilities and probability amplitudes suggests that the zero-order virtually excited wave functions could be interpreted as BCS-type pair configurations.

While the above remarks do suggest that the London theory of molecular ring currents might provide a mechanism for superconductivity, London himself recognized that such an interpretation is not tenable from a formal point of view.[33] The London theory of molecular ring currents is based on the response of the orbital energies to the presence of a magnetic field. That is, the orbital energies of eq 7 are replaced by the perturbed energies

$$\epsilon_k = 2\beta \cos\left[\frac{2\pi}{N}(k + f)\right] \tag{35}$$

where

$$f = \frac{eSH}{hc} \tag{36}$$

For benzene f is equal to

$$f_{\text{benzene}} = 1.23 \times 10^{-9} H \tag{37}$$

with H in gauss. The London treatment is based on the assumption that f is much smaller than unity, which from eq 37 will be true for normal molecules in laboratory magnetic fields. On the other hand, for macroscopic materials, the critical field becomes extremely small[33] (ca. 10^{-7} G). It is therefore apparent that the London theory of molecular ring currents does not provide an analytical counterpart of bulk superconductivity, although the two phenomena are clearly related.

Nevertheless, the similarities mentioned above encouraged us to look for a closer analogue to superconductivity within the apparatus of the London–McWeeny theory of molecular ring currents. Given the complementary nature[74] of the Peierls[63] and superconducting[46] transitions in solid-state physics, we felt that it might be worthwhile to seek an eigenvalue problem bearing a similar relationship to the Binsch, Heilbronner, and Murrell[71] treatment of the second-order Jahn–Teller effect as expressed in eq 32. This would be provided by

$$\left\| \overline{\pi}_{rs,tu} - (\overline{\lambda}_{rs} - p_{rs})\delta_{rs,tu} \right\| = 0 \tag{38}$$

which from eq 21 and 22 may be reduced to

$$\left\| (p_{rs}/N)_{rs,tu} - \overline{\lambda}_{rs}\delta_{rs,tu} \right\| = 0 \tag{39}$$

This is similar to the eigenvalue equation implicated in the BCS theory.[46,75] All the matrix elements have a common value (p_{rs}/N), and the eigenvalue spectrum (shown for benzene in Table IV) has an energy gap (p_{rs}) between the ground state

Table IV. Eigenvalues and Eigenvectors of the Imaginary Bond–Bond Polarizability Matrix ($\overline{\pi}_{rs,tu}$) of Benzene

index	1	2	3	4	5	6
$\overline{\lambda}_{rs}(\beta^{-1})$	0.0	−0.667	−0.667	−0.667	−0.667	−0.667
bond r–s						
1–2	0.408	0.707	−0.408	−0.379	−0.132	−0.077
2–3	0.408	−0.707	−0.408	−0.379	−0.132	−0.077
3–4	0.408	0.0	0.816	−0.379	−0.132	−0.077
4–5	0.408	0.0	0.0	0.674	−0.603	−0.120
5–6	0.408	0.0	0.0	0.166	0.293	0.849
6–1	0.408	0.0	0.0	0.296	0.706	−0.498

and the manifold of excited states. Furthermore, the wave function is seen to remain rigid under the effect of the perturbation.[61,76] At infinite ring size the matrix elements become equal to $2/\pi N$ and the energy gap to $2/\pi$. We note that, unlike the solutions of eq 32, the eigenvalues of eq 39 are volume independent.

The physical significance of these results is difficult to interpret. If eq 38 does represent a superconducting state, it would suggest that, while the Peierls-Fröhlich-Jahn-Teller transition depends on virtual electric dipole transitions, the superconducting state arises from virtual magnetic dipole transitions. Alternatively it could be said that the Peierls-Fröhlich-Jahn-Teller transition arises from coupling to the real phonon field whereas the superconducting state arises from coupling to imaginary phonons, which would seem to require that the lattice be in some transition state with negative force constant.[77]

The above remarks, more than anything else, serve to emphasize the present lack of understanding of the relationship between lossless currents in organic molecules and bulk metals. Given the conductivity found for $(CH)_x$ particularly in the presence of dopants[78] and the superconductivity[79] observed in $(SN)_x$,[80] we believe that a true understanding of the relationship between these phenomena would be valuable in the design of new materials with desirable electronic properties.

Conclusion

We have shown for the first time that, to high accuracy, there is an analytic relationship between the ring currents and resonance energies of the (Hückel) $(4n + 2)\pi$-electron annulenes, as expressed in eq 26 and 27, which leads naturally to a unified theory of aromatic character. The available experimental evidence is consonant with the theory.

We have commented on the present lack of integrity of our knowledge of lossless currents in organic molecules and bulk superconductors and drawn attention to some common facets of present theories.

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Spin–Orbit Coupling in Metal–Anion Systems. The Colors of Post-Transition Metal Salts

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Abstract: A configuration-mixing model is developed for spin–orbit coupling in metal salts. The component excited configurations are of locally excited (LE) or charge transfer (CT) varieties. It is shown that the triplet ← singlet ($T_1 \leftarrow S_0$) transition of the nominal anion steals its intensity from local excitations in the case of light nontransition metal salts (e.g., $NaNO_2$) and from charge-transfer excitations in the case of heavy post-transition metal salts (e.g., $AgNO_2$). The model provides a simple rationalization of the colors and luminescences of post-transition metals in which neither the anion nor cation is separately chromophoric.

Introduction

The external heavy-atom effect is a valuable technique in the study of multiplicity-forbidden electronic transitions.[1] In particular, it has been used to interpret[2] the colors of post-transition metal salts in which neither the anion nor cation is separately colored. This interpretation, which constitutes a theory of color and luminescence for post-transition metal salts, suffered some defects.

(1) The data were qualitative. In the meantime, a considerable body of information on polarizations and oscillator strengths has been provided by Reznick et al.[3-5]

(2) The previous spin-orbital discussions[6] were "whole-molecule" in nature. The anion and cation systems were treated as a single unit. The resulting MO considerations, while substantiative of theory, were difficult to analyze for physical content.

(3) Too great a reliance was placed on computed quantities. Few experimental checks were available, and the computational results were indiscriminately used in spin-orbit considerations. The danger inherent in such an approach is demonstrated in Figure 1. The various data sets of Figure 1, when used in a perturbation-theory processing of spin-orbit coupling, yield quite different results, which is obviously unsatisfactory.

The present work proposes a rephrasing of the perturbation approach at the configuration, as opposed to the orbital, stage. Recent discussions of such an approach are available.[1,7,8] There is no doubt, in the present instance anyway, that the configuration mixing model is less satisfactory in a theoretical sense. It simply introduces (or reintroduces) the mixing of cation and anion wave functions at too late a stage and, because of the restricted number of locally excited (LE), charge transfer (CT), and retro-charge-transfer (RCT) configurations which may be considered, the degree of configuration mixing is almost certainly too limited. Nonetheless, the approach has certain advantages. Firstly, it facilitates the use of the empirical data, energies and intensities, which are available for the locally excited states of the anion and cation systems and for the CT states of the anion/cation system. Secondly, the results are more readily visualized, and may lead to conclusions concerning the origin of singlet-triplet enhancement (i.e., to the relative importance of the external heavy-atom effect in terms of either the spin-orbit coupling which the heavy-atom center mediates or the anion ↔ cation charge transfer which permits the anion electrons to participate in this coupling). Finally, by virtue of its inclusion of CT configurations at the very outset, it should permit some estimation of the degree, if any, to which anion $T_1 \leftarrow S_0$ transitions steal intensity from charge-transfer transitions.

The Configuration-Interaction (CI) Model

The zero-order wave functions are constructed from four MO functions: the LUMO and HOMO of the metal ion, $\varphi_{m'}$ and φ_m, respectively, and the LUMO and HOMO of the anion, $\varphi_{a'}$ and φ_a, respectively. These configurations are diagrammed in Figure 2.

The transition of interest is ${}^3\psi_{A*} \leftarrow {}^1\psi_0$. This transition, in zero order, is anion localized and is responsible for the color of post-transition metal salts.[2] In order for it to acquire transition probability, it must mix, under the influence of spin-orbit coupling engendered at the metal center, with $S_i \leftarrow S_0$ transitions. Consequently, we write the spin-orbit corrected ${}^3\psi_{A*}$ function as

$$\begin{aligned} {}^3\Psi_{A*} = {}^3\psi_{A*} + C_1{}^1\psi_0 + C_2{}^1\psi_{A*} + C_3{}^1\psi_{M*} \\ + C_4{}^1\psi_{CT} + C_5{}^1\psi_{RCT} \quad (1) \end{aligned}$$

where

$$C_i\ (i = 1, 2, 3, 4, 5) = \langle {}^1\psi_i|\mathcal{H}'|{}^3\psi_{A*}\rangle / [E_i{}^0 - E^0({}^3A*)] \quad (2)$$

where $\mathcal{H}'$ is the spin-orbit Hamiltonian and the eigenvalues $E_i{}^0$ refer to a nonrelativistic Hamiltonian. The spin-orbit-corrected ground state wave function is

$${}^1\Psi_0 = {}^1\psi_0 + C_6{}^3\psi_{A*} + C_7{}^3\psi_{M*} + C_8{}^3\psi_{CT} + C_9{}^3\psi_{RCT} \quad (3)$$

The transition moment of interest, ${}^3\Psi_{A*} \leftarrow {}^1\Psi_0$, in first order, is

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