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Foundations of conjugated-circuits models

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"Physical laws should have mathematical beauty."

P.A.M. Dirac

Abstract - A Simpson-Herndon model Hamiltonian defined on a space of orthogonal Kekulé structures is derived for 1-factorable polyhex species (e.g. benzenoid hydrocarbons) from either of two antecedent models. One antecedent model is the semiempirical valence-bond model treated in the simple resonance-theoretic approach of Pauling and Wheland; the other is the Pariser--Parr-Pople model treated within the bond-orbital resonance-theoretic approach of Živković. Finally the conjugated-circuit scheme of Randić is obtained, though in a modified form.

INTRODUCTION

In the mid fifties Simpson (refs. 1,2) proposed an elegant form of resonance theory. His argument was based upon orthogonal Kekulé structures that are exact. For example, for benzene the two Kekulé structures, usually depicted as in Figure 1, were conceived as being formed from symmetric and antisymmetric combinations of the exact $^1A_{1g}$ ground state and the exact lowest $^1B_{2u}$ excited state. Simpson noted that these two combinations would have the same symmetry properties as the two structures of Figure 1 and quite plausibly the same pattern for bond--orders and electron density. For other conjugated hydrocarbons the Kekulé structures were viewed as "coherent" states obtained by suitable unitary transformation of exact singlet eigenstates. The unitarity of these transformations guarantees the orthogonality of the resultant coherent Kekulé states. Finally Simpson assumed that a simple chemically appealling pattern of interaction amongst such exact Kekulé structures would provide quantitative estimates of the exact eigenenergies.

Fig. 1. The two Kekulé structures for benzene

Though Simpson occasionally used this scheme on a molecule or two of interest to him, the scheme seems to have been largely ignored for some time. One exception to this neglect is found in the Quantum Chemistry text (ref. 3) by McGlynn and co-workers, though even in their description of the use of this technique they caution the reader that "We cannot teach this art here; we can merely give examples..." The power and simplicity of the scheme was finally largely independently developed by Herndon (ref. 4) in 1973 when he systematically used the (appropriately parameterized) scheme to accurately reproduce by hand an otherwise computer--generated (ref. 5) list of 29 resonance energies. A notable simplification in Herndon's work was that the ground-state wavefunction could be closely approximated by the simple equally-weighted sum of (orthogonal) Kekulé structures. In fact with this ansatz the resonance energy could be developed (ref. 6) in terms of graph-theoretic invariants. Indeed Randić (ref. 7) independently noted that what has only more recently been realized (ref. 8) to amount to the same graph-theoretic resonance-energy expression could be obtained from a quantification of Clar's qualitative ideas (ref. 9) concerning aromaticity. This expression, and/or various extensions (ref. 10) of it, have now found numerous applications (ref. 11).

There are some points in this previous work that it would be desirable to clarify. Most particularly a systematic theoretical computationally amenable derivation of the Simpson-Herndon

Hamiltonian would be of utility. The simple pattern proposed for interaction matrix elements would be tested, and possibly corrected. Formulas, and ultimately values, for the interaction parameters would result. Further the way would be indicated for extensions to more general circumstances.

Here we initiate such a size-consistent theoretical derivation for 1-factorable polyhex species (ref. 12). It starts from approximate resonance-theoretic treatments of either the Pauling-Wheland valence-bond model (ref. 13) or the Pariser-Parr-Pople model (ref. 14). Thence in the next two sections we briefly review relevant points of these two treatments. To understand the basic many-body structure of the Hamiltonian and overlap operators it is crucial to develop more local("few-bond") operators acting on the space of Kekulé states. This problem is solved in section 4, then utilized in sections 5, and 6. In section 6 a size-consistent Simpson-Herndon model is derived by transforming "away" the non-identity overlap matrix. The result (up through third-order of off-diagonal "overlap") is found to yield new interactions. In section 7 we utilize Herndon's wavefunction ansatz to obtain a conjugated-circuits expression, now with parameters expressed in terms of the initial valence-bond or Pariser-Parr-Pople models.

VALENCE-BOND RESONANCE THEORY

The valence-bond model (ref. 13) of Pauling and Wheland has now been around for more than a half of a century. But especially for larger systems it is difficult to solve, and not fully understood, so that, e.g., it has only recently been suggested (ref. 15) to be involved in high-temperature superconductivity. Elsewhere (ref. 16) arguments have been marshalled to say that at least for benzenoids the approximation wherein the model is restricted to the subspace of Kekulé structures is quite reasonable. Further discussion concerning the validity of this assumption may be found in a forth-coming book (ref. 17).

Here we presume the restriction of the VB model to the subspace of Kekulé structures, these being valence-bond (or Rumer (ref.18)) structures with nearest neighbor spin-pairing exclusively. The overlap and Hamiltonian matrix elements are conveniently expressed (ref. 19) in terms of superposition diagrams obtained by superimposing the π-bonds of pairs of Kekulé structures. Thence in Fig. 2 are shown the three possible superposition diagrams arising from the Kekulé structures in Fig. 1.

Fig. 2. The three superposition diagrams for benzene

The overlap between two normalized Kekulé structures K and K' on an alternant system of 2M sites is

$$\langle K|K'\rangle = (1/2)^{M-i(K,K')-I(K,K')} \tag{2.1}$$

where i(K,K') is the number of small islands (each corresponding to a single common π-bond in K and K') in the superposition diagram of K and K', and I(K,K') is the number of big islands (each corresponding to a cycle of π-bonds alternately in K and K') in the superposition diagram. The interactions may be expressed (ref. 20) in terms of spin operators $\vec{s}_i$ for site i and an exchange parameter J, which is positive (antiferromagnetically signed). Interaction matrix elements between a nearest-neighbor pair of sites i and j then are nonzero only if i and j are in the same island of the associated superposition diagram, in which case

$$\langle K|2J\vec{s}_i\cdot\vec{s}_j|K'\rangle = -(3/2)\,J\langle K|K'\rangle \tag{2.2}$$

For more general circumstances (refs. 19,20) additional phases arise in (2.1) and (2.2).

The expressions of (2.1) and (2.2) determine the Hamiltonian and overlap matrices H and S of current interest. These are conveniently expressed if to every Kekulé structure $|K\rangle$ we identify a corresponding orthogonal one $|K)$, so that

$$(K|K') = \delta(K,K') \tag{2.3}$$

Then overlap matrix is represented in an operator-theoretic form

$$\underline{S} = \sum_{K,K'} \langle K|K'\rangle\, |K)(K'| \tag{2.4}$$

and the Hamiltonian matrix is represented as

$$\underline{H} = \sum_{K,K'} <K|H|K'> \, |K)(K'| \tag{2.5}$$

The Hamiltonian matrix elements $<K|H|K'>$ are a sum over nearest-neighbor pairs as in (2.2), and so bear some resemblance to the corresponding overlap matrix.

The structure of these matrices bears further elucidation. The exponent in (2.1) is 0 or greater; being 0 when there are only small islands. Each big island of 2m sites replaces m small islands and thence makes a contribution of m-1 to the exponent. Further for benzenoid structures (cut from the honeycomb lattice, without cutting "holes")(ref. 12) it is known (ref. 21) that all big islands are of size 4n+2, n=1,2,3,..., so that such a big island introduces a factor of s^n into the overlap where

$$s \equiv 1/4 \tag{2.6}$$

may be viewed as a type of local overlap. Then we can write

$$\underline{S} = \underline{1} + \sum_{N \geq 1} s^N \underline{S}^{(N)} \tag{2.7}$$

where $\underline{1}$ is the identity operator and

$$\underline{S}^{(N)} = \sum_{K,K'}^{|K \cup K'|_- = N} |K)(K'| \tag{2.8}$$

with $|K \cup K'|_-$ the sum over n-values for all the different big islands (of size 4n+2) in the superposition diagram between K and K'. Similar consideration of the Hamiltonian matrix elements reveals

$$<K|H|K'> = -(3/2) \cdot J \cdot \{M + |K \cup K|_+\} <K|K'> \tag{2.9}$$

where we recall that 2 M is the number of sites and $|K \cup K'|_+$ denotes the sum over weights for each big island in the superposition diagram, this weight being the number of nearest neighbor pairs of sites in the big island minus 2n+1 for that island (of size 4n+2).

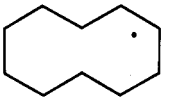

Fig. 3. The naphthalenic big island

Note for instance for the naphthalenic island of Fig. 3, this weight is 6 (since the two central sites are nearest neighbors, in benzenoids). Then we write

$$\underline{H} = -(3/2) \cdot J \cdot M \cdot \underline{S} + \sum_{N \geq 1} s^N \underline{H}^{(N)} \tag{2.10}$$

where

$$\underline{H}^{(N)} \equiv \sum_{K,K'}^{|K \cup K'|_- = N} |K \cup K'|_+ |K)(K'| \tag{2.11}$$

The crucial point to be utilized later is that both $\underline{S}$ and $\underline{H}$ may be expanded in overlap orders as in (2.7) and (2.10), with the higher orders presumably being of lesser importance.

BOND-ORBITAL RESONANCE THEORY

This approach applicable to Hückel, Hubbard or PPP models has recently been developed by Živković (ref. 22). His approach entails a wavefunction ansatz of the form

$$|\psi> = A \{\Phi_\alpha \Phi_\beta\} \tag{3.1}$$

where A is the system antisymmetrizer and Φ_σ is the factor for electrons of spin $\sigma = \alpha$ or β. Further he points out that each Φ_σ may be approximated in terms of states corresponding to Kekulé structures

$$|K_\sigma> \equiv \prod_i^* \{(1/\sqrt{2})(\chi_i + \chi_{i(K)}) \, \sigma\} \tag{3.2}$$

where the product is over all "starred" sites in the alternant structure, i(K) denotes the unstarred site π-bonded to site i in the Kekulé structure K, and the χ_i are orthonormalized atomic orbitals for site i. Variational optimization yields coefficients for $|K_\sigma>$ in the expansion of Φ_σ that are independent of the choice $\sigma = \alpha$ or β.

Something quite remarkable then occurs for the matrix problem to determine Φ_σ. First, Živković has shown (ref. 22) that the overlap matrix is exactly as in (2.4) and (2.7). That is, $<K_\sigma|K_\sigma'>$ is the same as $<K|K'>$ in (2.1). Second, the Hamiltonian matrix is nearly the same as in (2.5) and (2.10). That is, for the Hückel model $<K_\sigma|H_\sigma|K_\sigma'>$ is the same as $<K|H|K'>$ in (2.9) if one replaces J by the Hückel resonance integral β. For the Hubbard and PPP models an extra (near) constant multiple of $<K|K'>$ is added. Thence for benzenoids the same matrix diagonalization problem is obtained, though it represents an (apparently) quite different wavefunction ansatz and approach. It is motivated in terms of bond orbitals (the $(1/\sqrt{2})(\chi_i+\chi_j)\sigma$ built from orthogonalized atomic orbitals) in the presence of a mean field due to the electrons of the spin, whereas the VB approach is motivated in terms of strongly correlated singlet electron pairs (fundamentally in terms of nonorthogonal atomic orbitals).

An important difference between the VB and bond-orbital resonance theories occurs for nonbenzenoid alternants. For the simple VB resonance theories the basic matrix element formulas of section 2 remain unchanged, when big islands of size 4n occur. However, for the bond-orbital resonance theory such matrix elements are 0, and in some other cases an additional minus sign can appear in the analogy to (2.2). These features then account for Hückel's 4n+2 rule, and Živković then suggests that his version of resonance theory is superior, at least for non-benzenoids. Here we constrain our attention to benzenoids, whence the bond-orbital resonance-theoretic result is obtained from the Pauling-Wheland resonance theoretic result simply upon replacing J by β.

KEKULÉ-SPACE ALGEBRA

In performing detailed manipulations within the space spanned by Kekulé structures the algebraic structure of the associated operator space is of crucial significance. Especially the "local" operators affecting only a local subregion, identified to an embedded subgraph γ, are of interest. Here γ is presumed to be capable of carrying a local Kekulé structure, denoted κ' or κ, and the operator changing a local structure κ to κ' is denoted

$$\Lambda_\gamma(\kappa'|\kappa) \equiv \sum_{K'}^{\supseteq\kappa'} \sum_{K}^{\supseteq\kappa} |K')(K| \tag{4.1}$$

That is, if this operator is applied to a structure $|K)$ it gives a nonzero result only if κ on γ is a substructure in $|K)$, and if so it gives back the structure $|K')$ that is the same as $|K)$ except on γ where it coincides with κ'. For instance, with γ the left ring of naphthalene $\Lambda_\gamma(<|\,|>)$ changes the first Kekulé structure of Fig. 4 to the second, while if applied to the second or third it gives 0.

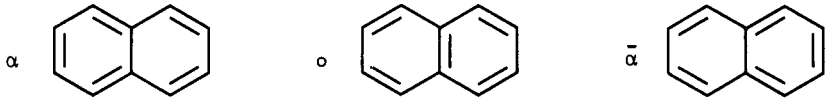

Fig. 4. The three Kekulé structures for naphthalene

Next we seek the result of multiplying two fundamental operators. In particular consider the product of $\Lambda_{\gamma_1}(\kappa_1'|\kappa_1)$ and $\Lambda_{\gamma_2}(\kappa_2'|\kappa_2)$. Following the notation of equation (4.1) with subscripts 1 and 2 now appended to the γ,κ,κ',K and K', one obtains the product of $|K_1')(K_1|$ with $|K_2')(K_2|$. Thence we consider the inner products $(K_1|K_2')$ with $\kappa_1 \subseteq K_1$ and $\kappa_2' \subseteq K_2$. Evidently the result must be nonzero only if the restrictions of κ_1 and κ_2' to $\gamma_1 \cap \gamma_2$ are the same. Moreover this restriction must be a Kekulé structure on $\gamma_1 \cap \gamma_2$, for otherwise κ_1 and κ_2, would both have different π-bonds incident from outside of $\gamma_1 \cap \gamma_2$ on single site(s) of $\gamma_1 \cap \gamma_2$. In this case we say κ_1 and κ_2 are compatible,

$$\kappa_1 \sim \kappa_2' \Leftrightarrow \kappa_1 \cap \gamma_2 = \kappa_2' \cap \gamma_1 \text{ is a Kekulé structure on } \gamma_1 \cap \gamma_2 \tag{4.2}$$

Also we introduce the Kronecker delta function $\delta(\kappa_1 \sim \kappa_2')$ that is nonzero only if $\kappa_1 \sim \kappa_2'$, in which case it is 1. Now if $\kappa_1 \sim \kappa_2'$, it has been noted that $\kappa_1 \cap \gamma_2$ is a Kekulé structure (on $\gamma_1 \cap \gamma_2$) and hence also must be the remaining portion (of κ_1)

$$\kappa_1/\gamma_2 \equiv \kappa_1 - (\kappa_1 \cap \gamma_2) \tag{4.3}$$

and likewise so must be κ_2'/γ_1. Evidently for $(K_1|K_2')$ to be nonzero, κ_1/γ_2 occurs in K_2'

and K_2 as well, while κ_2'/γ_1 occurs in K_1 and K_1' as well. Thus we have

$$\Lambda_{\gamma_1}(\kappa_1'|\kappa_1)\ \Lambda_{\gamma_2}(\kappa_2'|\kappa_2) =$$

$$\delta(\gamma_1 \sim \gamma_2)\ \Lambda_{\gamma_1 \cup \gamma_2}(\kappa_1' \cup (\kappa_2'/\gamma_1)\,|\,(\kappa_1/\gamma_2) \cup \kappa_2) \tag{4.4}$$

the fundamental relation enabling the manipulation of these operators.

Next several Hermitean operator sums are introduced. First

$$\Lambda(\xi) \equiv \sum_{C}^{\xi} \sum_{\kappa}^{C} \Lambda_C(\bar{\kappa}|\kappa) \tag{4.5}$$

where C is summed over all cyclic subgraphs of type ξ = 6, 10, 14a, 14b or 14c as shown in Figure 5, and $\bar{\kappa}$ denotes the Kekulé substructure on C that differs from κ in having single and double bonds interchanged.

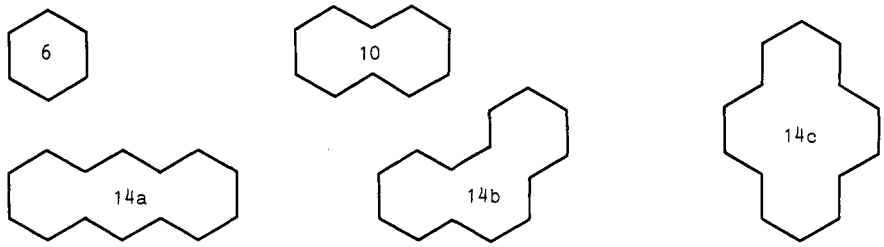

Fig. 5. The first five types of (feasible) cycles occurring in polyhex graphs

Second

$$\Lambda(\xi(m)) = \sum_{C(m)}^{\xi(m)} \sum_{\kappa(m)}^{C(m)} \Lambda_{C(m)}(\bar{\kappa}(m)\,|\,\kappa(m)) \tag{4.6}$$

where $\xi(m) \equiv \xi_1 x \ldots x \xi_m$ denotes a set of m types; $C(m) \equiv C_1 x \ldots x C_m$ indicates m disjoint cycles, the i^{th} C_i being of type ξ_i; and $\kappa(m) \equiv \kappa_1 x \ldots x \kappa_m$ indicates a collection of disjoint Kekulé structures, the i^{th} κ_i being on cycle C_i. Third

$$\Lambda(6') \equiv \sum_{C}^{6} \sum_{\kappa}^{C} \Lambda_C(\bar{\kappa}|\kappa)$$

$$\Lambda(10') \equiv \sum_{C}^{10} \{\Lambda_C(\bar{\alpha}|o) + \Lambda_C(\alpha|o) + \Lambda_C(o|\alpha) + \Lambda_C(o|\bar{\alpha}) \tag{4.7}$$

$$\Lambda(6,6') \equiv \sum_{C_1 x C_2}^{6x6} \sum_{\kappa_1 x \kappa_2}^{C_1 x C_2} \{\Lambda_{C_1 x C_2}(\kappa_1 x \bar{\kappa}_2\,|\,\kappa_1 x \kappa_2) + \Lambda_{C_1 x C_2}(\bar{\kappa}_1 x \kappa_2\,|\,\kappa_1 x \kappa_2)$$

where α, o, $\bar{\alpha}$ denote the three naphthalenic Kekulé structures of Fig. 4.

Such Hermitean operator sums are themselves closed under anticommutative multiplication. For instance

$$\{\Lambda(6),\ \Lambda(6)\} = 4\,\Lambda(6,6) + 2\,\Lambda(10) + 2\,\Lambda(6')$$

$$\{\Lambda(6),\ \Lambda(10)\} = 2\,\Lambda(6,10) + 2\,\Lambda(14a) + 2\Lambda(14b) + \Lambda(10')$$

$$\{\Lambda(6),\ \Lambda(6')\} = 2\,\Lambda(6,6') + 2\,\Lambda(6) + \Lambda(10') \tag{4.8}$$

$$\{\Lambda(6),\ \Lambda(6,6)\} = 6\,\Lambda(6,6,6) + \Lambda(14b) + 2\,\Lambda(6,10) + 2\,\Lambda(6,6')$$

as follows from the definitions (4.5)-(4.7) along with the basic relation of (4.4). As a consequence these operator sums form an algebra under anticommutation.

REPRESENTATION OF SYSTEM MATRICES

The various matrix operators of section 2 may now be represented in terms of the fundamental operator sums of section 4. The first two orders of the overlap matrix are

$$\underline{S}^{(1)} = \Lambda(6)$$
$$\underline{S}^{(2)} = \Lambda(10) + \Lambda(6,6) \tag{5.1}$$

recalling that cycles of size $4n+2$ contribute to order n, pairs of cycles of size $4n_1+2$ and $4n_2+2$ contribute to order n_1+n_2, etc. The first three orders of the Pauling-Wheland resonance-theoretic Hamiltonian matrix are

$$\underline{H}^{(1)} = -(3/2)\cdot J\cdot 3\,\Lambda(6)$$
$$\underline{H}^{(2)} = -(3/2)\cdot J\cdot\{6\,\Lambda(10) + 6\,\Lambda(6,6)\} \tag{5.2}$$
$$\underline{H}^{(3)} = -(3/2)\cdot J\cdot\{9\,\Lambda(14a) + 9\,\Lambda(14b) + 7\,\Lambda(14c) + 9\,\Lambda(6,10) + 9\,\Lambda(6,6,6)\}$$

where the integer preceding a Λ-operator is the common $|K \cap K'|_+$ value for the Kekulé structures yielding the cycles of that Λ-operator. This coefficient may be conveniently thought of as a sum of terms for the cycles contributing to the Λ-operator, such a term being the number of pairs of sites in the cycle that are nearest neighbors in the parent graph G minus half the size of the cycle.

It is also of utility to develop the inverse square root of the overlap in terms of Λ-operators. Generally square roots, especially for matrices, are not unique, though there is a "natural" choice described by Löwdin (ref. 23). If the nondiagonal part $\underline{S} - \underline{1}$ is sufficiently small, then Löwdin's expansion for this inverse square root

$$\underline{S}^{-1/2} = \underline{1} + \sum_{m\geq 1} \binom{2m}{m}(-1/4)^m\,(\underline{S} - \underline{1})^m \tag{5.3}$$

converges. Thence, with the use of (2.7),

$$\underline{S}^{-1/2} = \underline{1} + \sum_{m\geq 1} \binom{2m}{m}(-1/4)^m \sum_{i_1\ldots i_m} s^{i_1+i_2+\ldots+i_n}\,\underline{S}^{(i_1)}\ldots\underline{S}^{(i_m)} \tag{5.4}$$

With the identification of the coefficient of s^j as $(\underline{S}^{-1/2})^{(j)}$ one then has

$$(\underline{S}^{-1/2})^{(1)} = -(1/2)\,\underline{S}^{(1)}$$
$$(\underline{S}^{-1/2})^{(2)} = (3/8)\,\{\underline{S}^{(1)}\}^2 - (1/2)\,\underline{S}^{(2)} \tag{5.5}$$

Then upon substitution of (5.1) and use of (4.8) we obtain (after same manipulation)

$$(\underline{S}^{-1/2})^{(1)} = -(1/2)\,\Lambda(6)$$
$$(\underline{S}^{-1/2})^{(2)} = (1/4)\,\Lambda(6,6) - (1/8)\,\Lambda(10) + (3/8)\,\Lambda(6') \tag{5.6}$$

which are results of use in the next section.

A SIMPSON-HERNDON MODEL

A Simpson-Herndon model H may be obtained from either the Pauling-Wheland or bond-orbital resonance-theoretic model. In either case

$$H \equiv \underline{S}^{-1/2}\;\underline{H}\;\underline{S}^{-1/2} \tag{6.1}$$

where the desired structure-explicit formulas result upon expression in powers of the overlap factor s. For the VB case of Pauling and Wheland, one has

$$H = -(3/2)\cdot JM\cdot\underline{1} + \sum_{i,j,k\geq 1} s^{i+j+k}\,(\underline{S}^{-1/2})^{(i)}\,\underline{H}^{(j)}\,(\underline{S}^{-1/2})^{(k)} \tag{6.2}$$

so that we identify

$$H^{(1)} = \sum_{j=1}^{1}\sum_{i=0}^{1-j} (\underline{S}^{-1/2})^{(i)}\,\underline{H}^{(j)}\,(\underline{S}^{-1/2})^{(1-i-j)} \tag{6.3}$$

Then with the use of (5.2) and (5.6) along with the multiplication rules of (4.8) we find (after some manipulation)

$$H^{(1)} = -(3/2)\cdot J\cdot 3\,\Lambda(6)$$

$$H^{(2)} = -(3/2)\cdot J\cdot 3\{\Lambda(10) - \Lambda(6')\} \tag{6.4}$$

$$H^{(3)} = -(3/2)\cdot J\cdot\{3\Lambda(14a) + (3/2)\Lambda(14b) + 7\Lambda(14c) - 3\Lambda(10') + 3\Lambda(6)\}$$

Hence, summation with the weights s^i, leads to

$$H = -(3/2)\cdot J\cdot\{M\cdot\underline{1} + (51/64)\ \Lambda(6) - (3/64)\ \Lambda(6') + (3/16)\ \Lambda(10)$$
$$-(3/128)\ \Lambda(10') + (3/64)\ \Lambda(14a) + (3/128)\ \Lambda(14b)$$
$$+(7/64)\ \Lambda(14c)\} + \underline{O}(s^4) \tag{6.5}$$

Higher-order corrections could in principle be obtained following further the same approach. As noted in section 3 the primary difference for the bond-orbital resonance-theoretic case of Živković entails the replacement of J by β.

Our results of (6.4) and (6.5) differ notably in several ways from the earlier interaction proposed by Simpson (ref. 2) and by Herndon (ref. 4). First, there is the term $M\cdot\underline{1}$, which however may be argued to be subtracted off in computing a resonance energy. Second, there are novel terms involving $\Lambda(6')$ and $\Lambda(10')$, simply not appearing in the earlier empirical versions. Third, the three types of 14-cycle embeddings occur with different weights, also contrary to earlier treatments. Evidently these second and third features along with additional operators would appear in higher orders.

A CONJUGATED-CIRCUITS MODEL

As has been shown (ref. 8) elsewhere earlier empirical Simpson-Herndon model Hamiltonians lead to so-called conjugated-circuits models, when the assumption of a particular wavefunction ansatz is made. This (ref. 4) ground-state ansatz, which (for the nonorthogonal case) traces back to Pauling and Wheland (ref. 12), is

$$|\Psi) = \sum_K |K) \tag{7.1}$$

This assumption should be comparably reasonable for the present case, since the current model appears quantitatively similar to the earlier one. Then if one considers a 6-cycle contributing to $\Lambda(6')$, contributing Kekulé structures occur in pairs differing in conjugation only around that cycle and each member of the pair occurs with equal weight, so that

$$(\Psi|\Lambda(6')|\Psi) = (\Psi|\Lambda(6)|\Psi) \tag{7.2}$$

Similarly one finds

$$(\Psi|\Lambda(10')|\Psi) = 2(\Psi|\Lambda(10)|\Psi) \tag{7.3}$$

Thus

$$\frac{(\Psi|H|\Psi)}{-3J/2} = M(\Psi|\Psi) + (\Psi|\{(39/64)\ \Lambda(6) + (9/64)\ \Lambda(10)$$
$$+ (3/64)\ \Lambda(14a) + (3/128)\ \Lambda(14b) + (7/64)\ \Lambda(14c)$$
$$+ \underline{O}(s^4)\}|\Psi) \tag{7.4}$$

so that now it appears one is taking a matrix element over a Hamiltonian more like that of Simpson and Herndon, without $\Lambda(6')$ and $\Lambda(10')$ operators. Next we introduce conjugated-circuit counts

$$\#(\xi) \equiv \sum_K \#_\xi(K) \tag{7.5}$$

where $\#_\xi(K)$ is the number of cycles of type ξ = 6,10,14a,14b,14c that occur with alternating single and double bonds in Kekulé structure K. Evidently

$$\#(\xi) = (\Psi|\Lambda(\xi)|\Psi) \tag{7.6}$$

Now substracting off the $M\cdot\underline{1}$ - term to generate a resonance energy (RE) we have

$$RE = (\Psi|\{H - (3/2)\ J\ M\ \underline{1}\}|\Psi)/(\Psi|\Psi)$$
$$= -(3/2)\ J\{(39/64)\ \#(6) + (9/64)\ \#(10) + (3/64)\ \#(14a)$$
$$+ (3/128)\ \#(14b) + (7/64)\ \Lambda(14c) + \underline{O}(s^4)\}/\#(0) \tag{7.7}$$

where #(0) is the number of Kekulé structures.

The resultant expression (7.7) bears a closer resemblance to the usual conjugated-circuits expression than does our Hamiltonian of section 5 to the usual (ref. 4) Simpson-Herndon Hamiltonian. Still, the different 14-cycle embeddings have different coefficients. The ratio of the coefficient of #(10) to that of #(6) takes a value $3/13 \cong 0.23$ that is somewhat smaller than the empirically determined value (refs. 7,24) of 0.28. In fact the agreement for this ratio is rather close, since the present values are chosen to reproduce the results of a Pauling-Wheland or bond-orbital resonance-theoretic calculation, while the empirical ones were extracted from the MO-based values of Dewar and de Llano (ref. 5).

DISCUSSION

A point crucial in achieving size-consistincy here is that all the unlinked terms with disjoint cycles have cancelled. For instance, the operator sum $\Lambda(6,6)$ for a large (graphitic) system admitting M π-bonds should generally involve $\sim M^2$ pairs of disjoint 6-cycles and so give rise to expectation values scaling $\sim M^2$, although size-extensive energies scale $\sim M$. Also for a system with noninteracting subsystems, this operator sum $\Lambda(6,6)$ would generally give a nonadditive expectation value, unlike the energy. Thus such a cancellation of unlinked terms in H should be anticipated, for a "proper" theoretical development. Indeed for a so-called "multiplicative" quantity such as $\underline{S}$ the "properness" of the present type of expansion (and consequent results) is argued elsewhere (ref. 25). Our results of sections 6 and 7 evidently achieve the desired size consistency.

There have been several other researchers who have addressed the problem of the derivation of the conjugated-circuits model within a quantum chemical framework. Gomes (ref. 26) starts from the VB model of Pauling and Wheland restricted to the space of Kekulé structures, much as we have in section 2. Then he proposes to discard all superposition diagrams in $\underline{H}$ and $\underline{S}$ with more than one big island. This does not give size-extensive corrections. But evidently Gomes also intends to discard all terms in $\underline{S}$ with any (even one) big island. Thence he proceeds to much the same functional form as suggested by Randić (ref. 7), and then he parameterizes this form against resonance energies for a free-electron model. Another researcher Gründler (ref. 27) starts from a bond-orbital approach apparently akin to that of Živković (ref. 22) and finds that computations lead to resonance energies comparing well with the logarithm of the count of Kekulé structures and with the average number of conjugated 6-circuits per Kekulé structure.

There are advantages in our present approach. It is more nearly analytical and is developed in such a way as to reproduce energies of the antecedent model up through a given overlap order. The approach of applying the inverse square-root overlap matrix is a standard numerical procedure in quantum chemistry, but its application in the present type of context to develop model Hamiltonians seems to have been less utilized. Clearly it should also be of use in connection with spaces other than of Kekulé structures. For instance, the whole space of covalent valence-bond structures might be so treated to obtain an orthogonalized Pauling-Wheland model which then via quasi-degenerate perturbation theory might be block-diagonalized on the subspace of Kekulé structures. Evidently then a refined Simpson-Herndon model should be obtained simulating the full covalent-space valence-bond model. We surmise that the leading terms should involve the same operators we have already found in section 6, but with different values for their coefficients. As noted in section 7 additional features (e.g., terms) have already been found not occurring in the earlier work of Simpson, Herndon and Randić. Any physical consequences of these differences remain yet to be clarified. A point of note is that because of phases (i.e., signs) on matrix elements for the case of nonalternants it is not so clear how derivations would proceed or whether they would so readily lead to anything like the currently used conjugated-circuits models.

In conclusion, a systematic size-consistent derivational procedure for Simpson-Herndon Hamiltonians and conjugated-circuit models has been illustrated. In addition to some novel terms arising, extensions to other circumstances, seen possible. Aid in these derivations is found in our development of the fundamental Kekulé-space algebra, which should also have many other applications, as in solving models defined on the space of Kekulé structures.

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