

# Kekulé-based Valence Bond Model.

## I. The Ground-state Properties of Conjugated $\pi$ -Systems<sup>†</sup>

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The Kekulé-based valence bond (VB) method, in which the VB model is solved using covalent Kekulé structures as basis functions, is justified in the present work. This method is demonstrated to provide satisfactory descriptions for resonance energies and bond lengths of benzenoid hydrocarbons, being in good agreement with SCF-MO and experimental results. In addition, an alternative way of discussing characters of localized substructures within a polycyclic benzenoid system is suggested based upon such simplified VB calculations. Finally, the symmetries of VB ground states for nonalternant conjugated systems are also illustrated to be obtainable through these calculations, presenting very useful information for understanding the chemical behaviors of some nonalternant conjugated molecules.

**Keywords** valence bond model, Kekulé structures, benzenoid hydrocarbons, nonalternant conjugated molecules

### Introduction

It has been acknowledged that both the Hückel molecular orbital (HMO) and valence bond (VB) methods are valid starting points for describing the chemical behaviors of alternant conjugated systems without degenerate ground states (for example, cyclobutadiene is excluded).<sup>1</sup> Recently, we<sup>2</sup> and others<sup>3</sup> have shown that the exact results of the VB model can also account well for aromaticities, bond lengths and reactivities of benzenoid hydrocarbons, which had been thought to be the particular realm of the HMO theory.<sup>4,5</sup> Even for some conjugated systems with four-membered rings, the VB model is also verified to give reasonable predictions as well if a correc-

tion term is appropriately added.<sup>6,7</sup> Nevertheless, it is also apparent for some of nonalternant systems that both methods give irreconcilable results. In the early 1950s, Craig<sup>8</sup> pointed out that some unsaturated molecules, with totally symmetrical HMO ground states, would have VB ground states not belonging to the most symmetrical irreducible representation of the molecular point group. Following Craig's ideas, Lee further demonstrated that in these systems neither the HMO nor the VB model is sufficient to provide a satisfactory picture of the molecule.<sup>1</sup> Instead we should resort to the Hubbard<sup>9</sup> or Pariser-Parr-Pople (PPP) model<sup>10</sup> for conjugated nonalternant  $\pi$ -systems which lie intermediate between the Hückel and VB antipodes.<sup>11,12</sup> Summarizing above brief discussion, we think that these two theories are actually complementary to each other, both conducive to the understanding of the chemical behaviors of conjugated systems.

It is well known that with increasing the size of the chemical system, the dimension of the VB Hamiltonian-space increases exponentially, making the rigorous treatments formidable for larger molecules of interest. Although efficient computational techniques are employed, the exact solution of the VB model has been limited to those conjugated molecules with no more than 24  $\pi$ -centers.<sup>2,3</sup> Therefore, schemes of obtaining the approximate VB solution are crucial in extending applications of this model to larger systems. In fact, Pauling and Wheland<sup>13</sup> first suggested in their resonance theory that the small limited set of covalent Kekulé structures can be used as

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basis functions to approximately solve the VB model. As a further simplification, they assumed that each Kekulé structure has the same contribution to the ground state of the chemical system. With the resonance theory, they successfully explained a number of experimental facts at the qualitative level.<sup>13</sup> Following Pauling and Wheland's resonance-theoretic ideas, Herndon and Randić independently developed parameterized "structure-resonance theory"<sup>14</sup> and "conjugated-circuit theory"<sup>15</sup> respectively, both based on Kekulé structures and the equal-weight assumption. These two theories have been used to give valuable predictions in reasonably good agreement with experiments.<sup>16,17</sup>

Different from treatments of these authors, in this work we abandon the assumption that each Kekulé function plays the same role, instead we solve the VB model numerically on assuming that the wave functions of a given system can be expressed as a linear combination of its covalent Kekulé structures (we term this method as the Kekulé-based VB throughout this work). This simplification greatly facilitates our investigation on very large conjugated systems (> 24  $\pi$  centers) from the VB viewpoints because the number of Kekulé functions is drastically less than the dimension of the complete VB space for a large molecule. It should be addressed that although this approximation has long been adopted, its justification is not available because exact VB calculations for a series of molecules with up to 24  $\pi$ -electrons can be routinely handled only in recent years.<sup>2,3</sup> In this paper, by comparing the results of Kekulé-based VB calculations with those exact VB values, we will demonstrate that this approximate scheme is nearly size-consistent and can give valuable predictions for most of systems investigated as the exact VB calculations do. Following its justification, this method is applied to systematically discuss resonance energies, bond lengths, and local properties for benzenoid hydrocarbons up to 54  $\pi$ -electrons. Moreover, we extend the application of this simple VB scheme to nonalternant  $\pi$ -systems, with emphasis on determining the symmetrical properties of the VB ground-state wave functions because most of nonalternant species with nontotally symmetrical VB ground states are suggested to exhibit less aromatic or even antiaromatic characters.<sup>4,8</sup> Our calculations manifest that the present VB approach is superior to the previous empirical Craig's rule<sup>8</sup> which may yield ambiguous predictions for some species,<sup>4</sup> as well as Lee's rule<sup>1</sup> which is not easy to handle for large systems.

## The valence bond model and its Kekulé-based approximation

For conjugated  $\pi$ -networks, the traditionally used VB Hamiltonian can be formulated as follows,<sup>18</sup>

$$H = J \sum_{i-j} (2S_i \cdot S_j - \frac{1}{2}) \quad (1)$$

where  $S_i$  denotes the spin operator for site  $i$ ,  $J$  is an (positive) exchange parameter, and  $i-j$  stands for the nearest-neighbor pair. We easily recognize that this model is intrinsically topological owing to the fact that all sites and bonds in a molecule are implicitly assumed to be identical. It has been shown that this model is the simplest form of the effective Hamiltonian derived from the Hubbard model when the correlation between electrons is very strong.<sup>6,19</sup> This model is exemplified to work very well for benzenoid systems,<sup>2,3</sup> and reasonably for other species without four-membered rings.<sup>6</sup> As is well known, this Hamiltonian operates solely on the space of covalent VB structures, which increases drastically in size with the number of atoms of molecules. Therefore approximate schemes for solving this model are desired when extending the VB treatments to larger molecules.<sup>18</sup> As has been addressed above, an approach which is closely related to the chemical intuition is to represent the wave function of a molecule as a linear combination of its Kekulé structure functions,<sup>13</sup> *i. e.*,

$$\Psi = \sum_i C_i K_i \quad (2)$$

here  $K_i$  signifies the basis function corresponding to the  $i$ th Kekulé structure, and  $C_i$  is the coefficient associated with  $K_i$  to be determined variationally. Obviously, the wave functions as in Eq. (2) only represent those of singlet states, being of current interest in this work. After selecting basis functions, the coefficients and eigenvalues can be evaluated by solving Eq. (3),

$$(H - ES)C = 0 \quad (3)$$

where  $H$  is the Hamiltonian matrix and  $S$  is the overlap matrix. The matrix elements  $H_{ij}(\langle K_i | H | K_j \rangle)$ ,  $S_{ij}(\langle K_i | K_j \rangle)$  between the Kekulé structures  $K_i$  and  $K_j$  can be computed easily in terms of Pauling's diagrammatic

rules.<sup>13a</sup> According to his rules, we obtain superposition diagrams by superimposing two arbitrary Kekulé structures, say  $K_i$  and  $K_j$ , then we have

$$S_{ij} = (-1)^{n_i} 2^{n_i - N/2} \quad (4a)$$

$$\langle K_i | 2S_i \cdot S_j - \frac{1}{2} | K_j \rangle = \begin{cases} -2S_{ij} & \text{if } i \text{ and } j \text{ are in the same island;} \\ -\frac{1}{2} S_{ij} & \text{otherwise.} \end{cases} \quad (4b)$$

where  $n_i$ ,  $n_j$ , and  $N$  stand for the number of resulting islands which are closed diagrams, reversals needed for forming the standard islands, and atoms in a molecule, respectively. In addition, in actual calculations we must generate all Kekulé structures for a given system at first. We have written a FORTRAN program based on the adjacency matrix of a molecule for this purpose.

On the basis of the above arguments, we can now routinely carry out Kekulé-based VB calculations for larger  $\pi$ -systems with no more than 5000 Kekulé structures. This greatly enlarges the scope of VB treatments, and makes it possible to account for some chemical properties for large quantities of conjugated molecules from VB viewpoints. In the next section, we first compare the results of Kekulé-based VB calculations with those exact VB values available to demonstrate the applicability of this approximate scheme. Then applications of this method to benzenoid and nonalternant systems are discussed systematically.

## Results and discussion

### *The justification of the Kekulé-based VB method*

Within the classical VB model, the importance of Kekulé structures has ever been emphasized by pioneering workers in this field.<sup>13</sup> However, the theoretical justification of the Kekulé-based VB method becomes possible until the exact VB solutions of a series of conjugated systems have been attained in recent years.<sup>2,3</sup> Here, we intend to justify this simple VB approach by comparing its ground-state energies and wave functions with those exact VB values available.

Nearly three dozens of  $\pi$ -systems as shown in Fig. 1 are selected for our purpose of comparison. Most of these

systems are benzenoids in which the topological VB model proves to be most successful.<sup>2,3</sup> Some nonalternant species are also included considering that the VB theory can also give valuable information for these systems. First, ground-state energies of these species are collected in Table 1 to test the effectiveness of this Kekulé-based VB scheme. To visualize the comparison clearly, in Fig. 2 we display the correlation between the approximate and exact VB values. As expected, we can find from Table 1 that for each species most of its ground-state energy is obtainable in this simple VB scheme although only Kekulé-structure functions are employed here to construct basis functions. Especially, 12 isomers (14–25) of 22  $\pi$ -electrons provide a critical test to this simple model. One can see that this method correctly predicts the relative order of thermodynamic stabilities among these isomeric species except some isomers with the equal Kekulé structure counts. In fact, those “similar” species, which are hardly differentiated from each other by the simple model, do have little difference in their ground-state energies as exemplified by the exact calculations. In another aspect, we encouragingly notice from Fig. 2 that a linear relationship holds very well between the approximate and exact ground-state energies for all considered compounds (correlation coefficient, 0.999). This implies that the Kekulé-based VB scheme is nearly of size-consistency, indicating that it can be applied to different size of molecules. It is worth pointing out that although this simple VB scheme works well as a whole, the results listed in Table 1 also bring its certain limitations to light. For the polyacene series in which the number of Kekulé structures increases only linearly with chain length, it can be found that the ratio of the approximate and exact ground-state energies decreases slightly with increasing the size of systems, and so does in some nonalternant systems. In the following, we will show that for these species their ground-state wave functions obtained from Kekulé-based VB calculations are also relatively less reliable to allow satisfactory descriptions of their ground-state properties.

Now let us investigate the quality of approximate ground-state wave functions. In previous reports<sup>2</sup> we have shown that within the VB framework some local indices derived from ground-state wave functions correlate well with certain molecular ground-state properties. This reminds us of that we may assess the quality of the approximate wave functions by directly comparing these local indices calculated from both approximate and exact VB

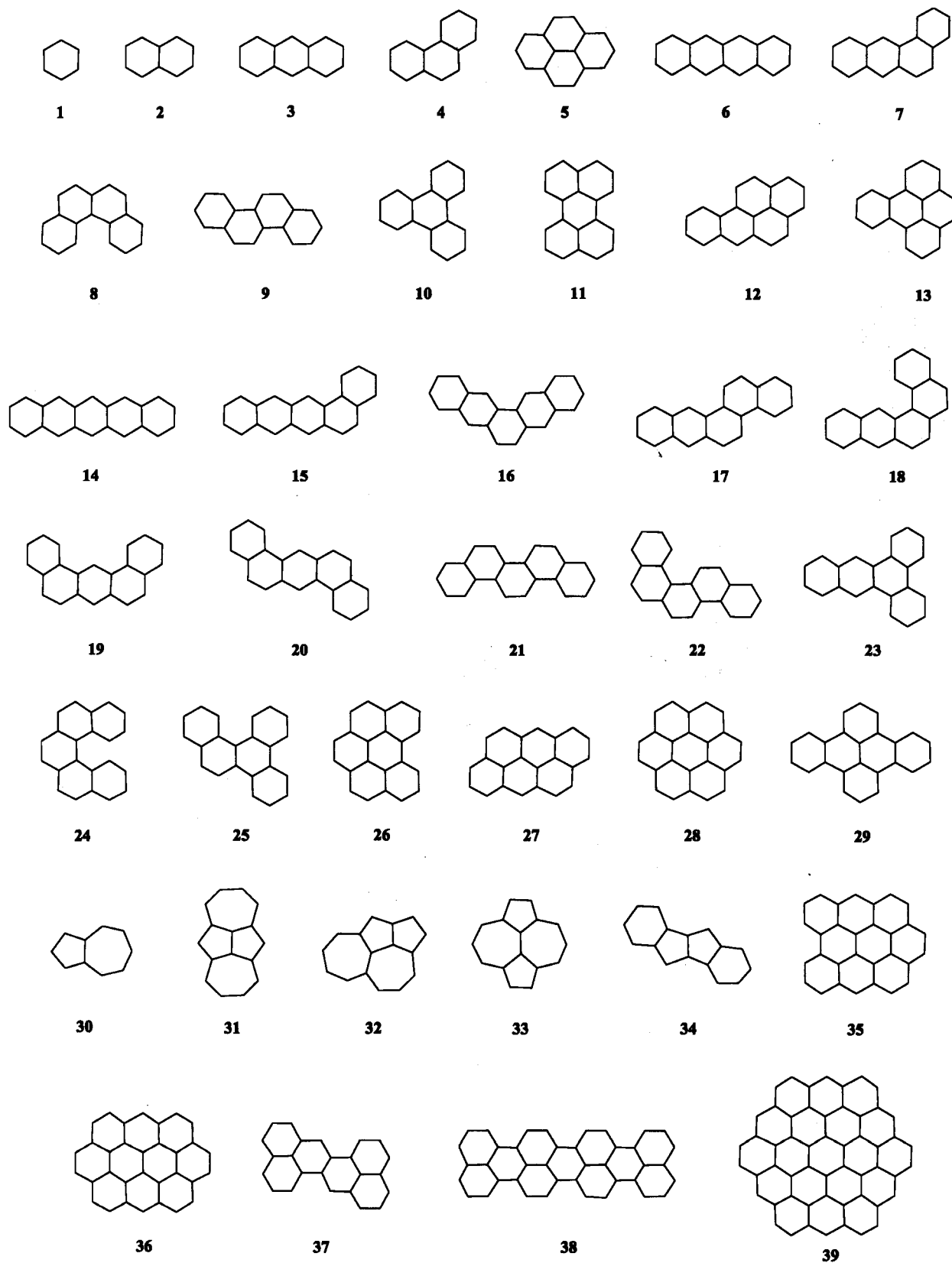
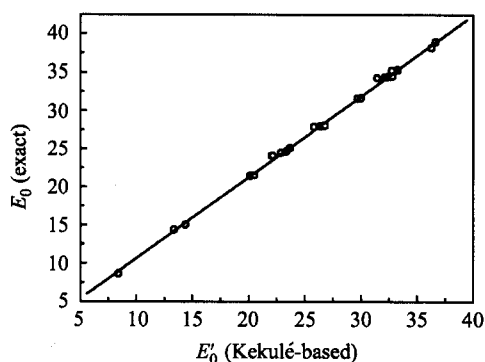


Fig. 1 Selected conjugated systems.

**Table 1** Ground-state energies (in -J) of a series of conjugated systems calculated from the exact and Kekulé-based VB approaches<sup>a</sup>

Compd	$E_0'$ (Kekulé-based)	$E_0$ (exact)	Ratio ( $E_0'/E_0$ )	Compd	$E_0'$ (Kekulé-based)	$E_0$ (exact)	Ratio ( $E_0'/E_0$ )
1	8.4000	8.6055	0.976	18	32.4270	34.4131	0.942
2	14.3703	15.0400	0.955	19	32.5985	34.4345	0.947
3	20.1500	21.4505	0.939	20	32.5985	34.4348	0.947
4	20.5248	21.5225	0.954	21	32.7012	34.4708	0.949
5	23.6977	25.1326	0.943	22	32.7012	34.4691	0.949
6	25.8300	27.8582	0.927	23	32.7307	34.4684	0.950
7	26.3977	27.9444	0.945	24	32.7012	34.4681	0.949
8	26.5939	27.9931	0.950	25	32.8234	34.5028	0.951
9	26.5939	27.9949	0.950	26	33.2590	35.2847	0.943
10	26.8067	28.0394	0.956	27	32.7498	35.1934	0.931
11	29.7407	31.6032	0.941	28	36.6435	38.9510	0.941
12	29.6773	31.5920	0.939	29	36.3014	38.1688	0.951
13	30.0065	31.6513	0.948	30	13.3529	14.3881	0.928
14	31.4526	34.2665	0.918	31	22.0826	24.0431	0.918
15	32.1295	34.3550	0.935	32	22.1444	24.0895	0.919
16	32.3114	34.3697	0.940	33	22.8900	24.4907	0.935
17	32.4270	34.4151	0.942	34	23.3648	24.6506	0.948

<sup>a</sup>Values of species **28**, **29** are taken from Ref. 3. For other compounds, the Lanczos method introduced in Ref. 2 is employed to obtain their ground-state energies.



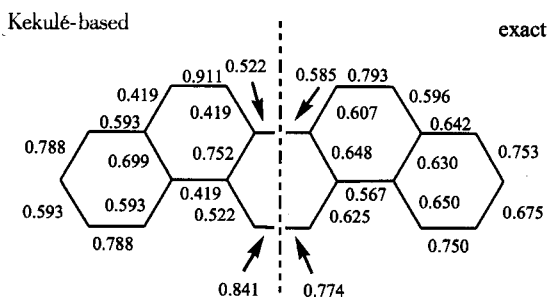
**Fig. 2** The correlation between the ground-state energies (in -J) calculated from the Kekulé-based and exact VB models.

ground-state wave functions. Remembering that the most important one among those indices is the ground-state singlet probability (SP), from which other indices can be deduced, we focus our comparison on this index. For convenience of our subsequent discussion, we cite the definition of SP as follows,<sup>2</sup>

$$P_{ij}^S = \langle \Psi | \frac{1}{2} (a_i^+ a_j^+ - a_j^+ a_i^+) (a_j a_i - a_i a_j) | \Psi \rangle \quad (5)$$

where  $\Psi$  represents the VB ground-state wave function, and  $P_{ij}^S$  means the probability of finding a singlet arrangement between atoms  $i$  and  $j$ . It has been shown that this quantity is actually analogous to the Coulson bond order in the HMO theory.<sup>2</sup> Since  $P_{ij}^S$  derived from exact VB wave functions is closely related to the  $i$ - $j$  bond length, it is interesting to compare this index obtained from the approximate and exact VB approaches. We take picene (21) as an example (Scheme 1).

**Scheme 1**



At first sight, one can observe that the approximate SPs are slightly higher than the exact ones for some

bonds, and become lower for other bonds, *i. e.*, the Kekulé-based SPs may be not sufficiently exact in absolute magnitude. However, a careful comparison still reveals that there exists a good linear correlation between the approximate and exact SPs, as displayed in Fig. 3. On this account, the Kekulé-based ground-state wave functions can be reasonably utilized to delineate some ground-state properties of conjugated systems, especially benzenoid hydrocarbons.

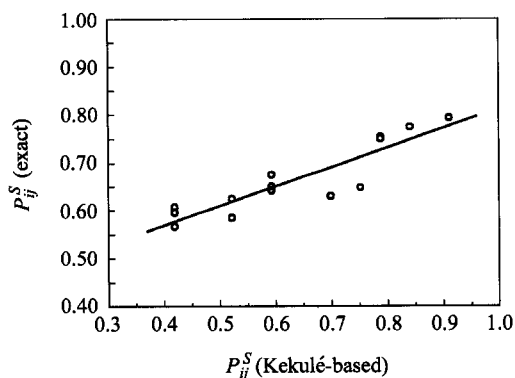


Fig. 3 The comparison of ground-state SPs computed by the Kekulé-based and exact VB models.

On the basis of above arguments, it seems likely that the Kekulé-based VB approach is a successful approximate scheme for solving the VB model. In the following sections, we will outline some applications of this method to benzenoid and nonalternant conjugated  $\pi$ -systems.

#### Benzenoid hydrocarbons

The electronic structures and ground-state properties of benzenoid systems have been well studied within the semiempirical HMO and PPP SCF-MO theories.<sup>4,5,20</sup> In the meanwhile, some attempts have also been made to understand chemical behaviors of this class of compounds from viewpoints of VB ideas.<sup>2,3,14,15,21,22</sup> For example, the famous Pauling bond orders defined in terms of Kekulé structures are shown to give fairly accurate predictions on carbon-carbon bond lengths,<sup>21</sup> and the relative weight of a given ring in a polycyclic system in the enumeration of Kekulé structures often correlates well with its local aromaticity.<sup>22</sup> Especially, one may be bewildered by the fact that even the parameterized resonance-theoretic versions<sup>14,15</sup> can give resonance energies congruent with Dewar-de Liano LCAO-SCF MO results.<sup>20a</sup> Obviously, al-

though experimental chemists usually employ these conceptually simple VB terminologies, theorists are circumspect in their words on these apparent success because rare quantitative quantum mechanic evidence has been given even within the classical VB framework. Encouragingly, recent exact VB calculations for a series of medium-sized  $\pi$ -systems have eliminated theorist's suspicion to a great degree.<sup>2,3</sup> Here, based on the Kekulé-based VB calculations, we again demonstrate that these chemically intuitive approaches are definitely supported.

#### A. Resonance energies

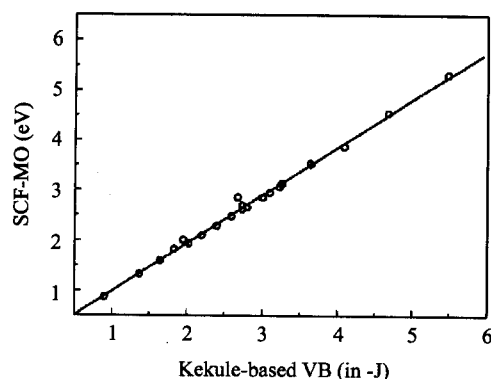
Resonance energies of 24 benzenoid systems calculated by the Kekulé-based VB approach are listed in Table 2. For comparison, Dewar-de Liano SCF-MO results are also cited.<sup>20a</sup> Paralleling to the definition of the reference structure in the SCF-MO method,<sup>20a</sup> the results of our resonance energies are also referred to a single localized Kekulé structure. Surprisingly, one can see from Table 2 that the present simple VB and the SCF-MO results correlate very well. This point is further reinforced by the remarkable linear relationship between these two drastically different theories as depicted in Fig. 4. Owing to this extremely close correlation, it can be expected that the present VB treatment can also give reasonable interpretations on the resonance stabilization of most of benzenoid  $\pi$ -systems as the SCF-MO method. For instance, the resonance energies of compounds **11**, **37** and **38** are rigorously equal to the sum of the resonance energies of 2, 2, and 4 naphthalene segments respectively, being consistent with the available chemical evidence and the SCF-MO predictions.<sup>20a</sup> In spite of this, there are also some dissimilarities of the two different methods in some special systems. The polyacene-like series are actually such a class of compounds in which resonance energies of the Kekulé-based VB method may deviate gradually from those of the SCF-MO theory with increasing the length of the polyacene chain, as indicated in the changeover of resonance energies from benzene (**1**), naphthalene (**2**), anthracene (**3**), naphthacene (**6**), and pentacene (**14**). The reason resulting in this limitation can also be attributed to the fact of their linearly increased numbers of Kekulé structures upon the increase in their sizes, which consequently lead to underestimates to some degree of their thermodynamic stabilities as mentioned above. On the other hand, these molecules with long polyacene com-

ponents are intrinsically less stable, being qualitatively consistent with our simple VB calculations.

**Table 2** Resonance energies of some benzenoid hydrocarbons

Compd	Kekulé-based VB (-J)	SCF-MO <sup>a</sup> (eV)
1	0.900	0.869
2	1.370	1.323
3	1.650	1.600
4	2.025	1.933
5	2.198	2.098
6	1.830	1.822
7	2.398	2.291
8	2.594	2.478
9	2.594	2.483
10	2.807	2.654
11	2.741	2.619
12	2.677	2.854
13	3.006	2.853
14	1.952	2.004
19	3.098	2.948
20	3.098	2.948
23	3.231	3.058
26	3.259	3.128
28	3.643	3.524
35	4.088	3.862
36	4.679	4.539
37	2.741	2.694
38	5.481	5.309
39	8.140	

<sup>a</sup> Values are from Ref. 20a.



**Fig. 4** The correlation between resonance energies of benzenoids calculated from the Kekulé-based VB and Dewar-de Llanos SCF-MO approaches.

## B. Bond lengths

In the previous section, we have verified that the local index  $P_{ij}^S$  computed from Kekulé-based VB wave functions may approximately reflect the strength of the  $i-j$  bond and interrelate with the  $i-j$  bond length. To demonstrate this point, we have calculated the Kekulé-based ground-state SPs on various bonds for several selected benzenoid systems. Our results are collected in Table 3. As ever done in the exact VB treatments,<sup>2</sup> two typical species, benzene and pyrene, are selected to deduce the empirical formula between the bond length and the corresponding ground-state SP. The least square fit for these two molecules results in a good linear formula below,

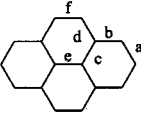
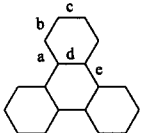
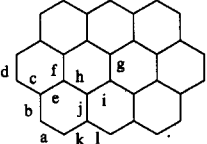
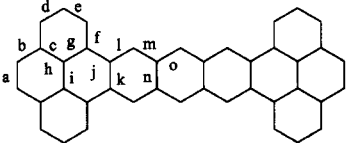
$$d_{ij} \text{ (nm)} = 14.87 - 1.23 P_{ij}^S \text{ (Kekulé-based VB)} \quad (6)$$

where  $d_{ij}$  designates the length of  $i-j$  bond. By using this relationship, we can obtain a theoretical estimate of an arbitrary carbon-carbon bond length from the corresponding ground-state SP. The results listed in Table 3 indicate that the average deviation of the calculated and experimental values is slightly smaller than that of the HMO theory if the Coulson bond order-bond length relationship is utilized,<sup>4</sup> and comparable to that derived from the empirical Pauling bond orders.<sup>21</sup> Therefore, now we can answer another question: why are the empirical Pauling bond orders, which are solely based on examinations of the Kekulé structures, successful in predicting the bond lengths of benzenoid hydrocarbons? The reason seems clear because there exists a close correspondence between the local ground-state SP and the corresponding Pauling bond order, as shown in Fig. 5 for tetrabenzo [de, no, st, c<sub>1</sub>, d<sub>1</sub>]heptacene. We notice that previous interpretations on this problem mainly concentrated on the superficial mathematical interrelation between the Pauling and Coulson bond order.<sup>23</sup> In reality, from above discussions we recognize that the Pauling bond order may be considered to approximately represent the VB bond order like the local ground-state SP.

## C. Characterization of molecular fragments

Experimental chemists have found increasing evidence that some of chemical properties of a polycyclic benzenoid system can be understood in terms of the fea-

Table 3 Bond lengths in some benzenoid hydrocarbons (nm)

Compound	Bond	Singlet probability	Bond lengths		
			calcd <sup>a</sup>	exptl <sup>b</sup>	
Benzene		0.700	14.00	13.97	
Pyrene 	a	0.690	14.02	13.95	
	b	0.690	14.02	14.06	
	c	0.637	14.09	14.25	
	d	0.356	14.43	14.38	
	e	0.460	14.30	14.30	
	f	0.948	13.70	13.67	
				± 0.06	± 0.04
Triphenylene 	a	0.659	14.06	14.10	
	b	0.735	13.97	13.81	
	c	0.659	14.06	13.97	
	d	0.708	14.00	14.13	
	e	0.311	14.49	14.58	
				± 0.10	± 0.06
Ovalene 	a	0.934	13.72	13.54	
	b	0.377	14.41	14.32	
	c	0.600	14.13	14.11	
	d	0.771	13.92	13.66	
	e	0.704	14.00	14.29	
	f	0.573	14.16	14.24	
	g	0.366	14.42	14.35	
	h	0.434	14.34	14.29	
	i	0.657	14.06	14.19	
	j	0.617	14.11	14.25	
	k	0.377	14.41	14.45	
	l	0.684	14.03	14.01	
				± 0.11	± 0.05
	Tetrabenzo [de, no, st, c <sub>1</sub> , d <sub>1</sub> ] heptacene <sup>c</sup> 	a	0.933	13.72	13.4
b		0.381	14.40	14.4	
c		0.624	14.10	14.2	
d		0.761	13.93	13.6	
e		0.624	14.10	14.0	
f		0.761	13.93	13.9	
g		0.619	14.11	14.2	
h		0.684	14.02	14.1	
i		0.396	14.38	14.3	
j		0.264	14.54	14.8	
k		0.436	14.33	14.6	
l		0.890	13.78	13.6	
m		0.441	14.33	14.2	
n		0.569	14.17	14.2	
o		0.619	14.03	13.8	
			± 0.15		

<sup>a</sup> The average deviation between calculated and experimental values is listed for each compound. <sup>b</sup> Values are from Ref. 21 and references therein except for tetrabenzo[de, no, st, c<sub>1</sub>, d<sub>1</sub>]heptacene. <sup>c</sup> Data come from Ref. 36.



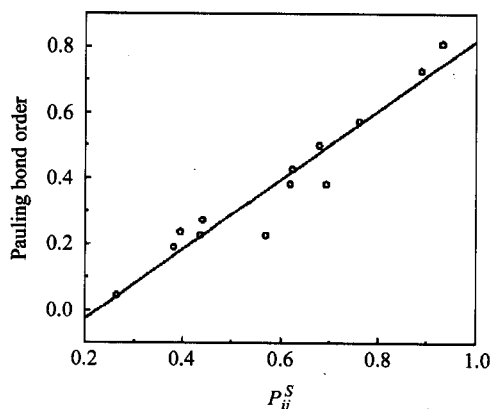


Fig. 5 The relationship between ground-state SPs from Kekulé-based VB calculations and Pauling bond orders for tetra-benzo[de, no, st, c<sub>1</sub>, d<sub>1</sub>]heptacene.



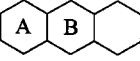
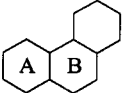

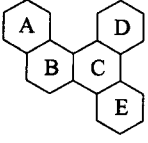
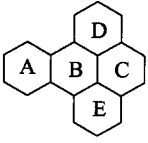
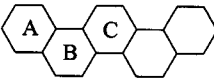
tures of its component fragments.<sup>24</sup> Theoretically, there are also some attempts toward this goal.<sup>2,22,25</sup> In our previous exact VB treatments,<sup>2</sup> we have defined the ratio of the local ring energy to the ground-state energy of benzene as a measure of the benzene-like character of individual rings. According to this definition, we can also evaluate the benzene-like index of a given ring by use of the present Kekulé-based VB ground-state wave functions. Similarly, when this definition is extended to larger molecular fragments, the naphthalene-like or phenanthrene-like character of the corresponding fragments is easily obtainable. In general, the local energy of a certain fragment in the ground state of its parent system can be estimated directly by<sup>2</sup>

$$E_q = -2J \sum_{i-j} P_{ij}^S \quad (7)$$

where the  $i-j$  denotes the bond belonging to the  $q$ th fragment. Based on this equation, we illustrate the analysis of molecular fragments for a few selected molecules in Table 4. As expected, the Kekulé-based VB results are in harmony with those of exact VB results in most of systems except in anthracene.<sup>2</sup> It has been emphasized above that the limitations of Kekulé-based VB calculations to such polyacene-like compounds are inevitable. Besides this, it is advantageous to comment on the data of other molecules. For perylene, our results show that it can be regarded as two naphthalene units connected through an "empty" ring.<sup>26</sup> Similarly, both benzo[e]pyrene and picene, to the first approximation, can be considered to be composed of phenanthrene and benzene subunits bridged by a nearly empty ring. Indeed, their similar

electronic absorption spectra support this analysis.<sup>27</sup> In addition, our calculations for the largest molecule, kekulene[12], are in accordance with experimental results that this molecule behaves like an assembly of phenanthrene fragments.<sup>28</sup>

Table 4 The characterization of molecular fragments within some benzenoid systems

Compound	Fragment <sup>a</sup>	<i>R</i> (Kekulé-based)	<i>R</i> (exact)
Benzene			
	A	1.000	1.000
Naphthalene			
	A	0.935	0.945
Anthracene			
	A	0.875	0.934
	B	0.925	0.902
Phenanthrene			
	A	0.973	0.956
	B	0.833	0.885
Perylene			
	A(B)	0.935	0.929
	B	0.622	0.814
	C	0.622	0.814
	A + B	1.000	0.981
Benz[g]chrysene			
	A	0.947	0.950
	B	0.913	0.905
	C	0.776	0.832
	D	0.983	0.960
	E	0.983	0.961
	A + B	0.992	0.978
Benzo[e]pyrene			
	A	0.992	0.962
	B	0.708	0.825
	C	0.821	0.888
	D(E)	0.969	0.934
	D + C + E	0.998	0.987
Picene			
	A	0.965	0.953
	B	0.861	0.893
	C	0.931	0.951
	A + B + C	0.987	0.982

Continued

Compound	Fragment <sup>a</sup>	<i>R</i> (Kekulé-based)	<i>R</i> (exact)
Kekulene[12]	A(C)	0.968	
	B(D)	0.780	
	A + B + C	0.985	
Ovalene	A	0.932	
	B	0.820	
	C	0.941	
	D	0.743	

<sup>a</sup>Values in individual rings are used to characterize their benzene-like features. Similarly, values for subsystems such as A + B, A + B + C are measurements of their naphthalene-like and phenanthrene-like characters respectively.

Finally, it is meaningful to compare the present Kekulé-based VB results with those of Randić's graph theoretical approach,<sup>22</sup> which is also based on the Kekulé structures. In the Randić's method, the relative weight of a given ring in the enumerations of Kekulé structures is taken as the index characterizing the benzene-like character. Surprisingly, these two indices are basically parallel in almost all compounds. Therefore, the applicability of Randić's index which is only based on the chemical intuition is validated in the present work.

#### Nonalternant systems

As has been addressed previously, the VB model actually works well in those systems where the electron-electron correlation is very strong, whereas in reality the electron correlation in conjugated systems is intermediate. Owing to this reason, the success of the VB theory in interpreting many ground-state properties of benzenoid systems as demonstrated above is undoubtedly surprising. This may be attributed to the fact that the symmetry of the ground state is invariant with increasing the magnitude of the electron correlation from the uncorrelated HMO to the strongly correlated VB limit.<sup>1</sup> Therefore both the simple HMO (or SCF-MO) and the VB models can give congruent predictions provided that some indices are appropriate-

ly defined within the respective model.<sup>2-5,13</sup> However, works<sup>1,29</sup> have indicated that the electron correlation has a significant influence on the chemical behaviors of some nonalternant species, especially in the cases when their HMO and VB ground-state wave functions do not belong to the same irreducible representation of the molecular symmetry group. For these compounds, both the HMO and VB models may be inappropriate as the zero-order Hamiltonian, instead the Hubbard or more elaborate SCF-MO model should be used. Although these compounds may generally have relatively narrow energy gaps between the ground and first excited states, it is still hard to judge whether such a compound is aromatic or pseudoaromatic, and may undergo the symmetry distortion without deliberate Hubbard or more elaborate SCF-MO calculations. Despite this, it is still valuable to know whether the VB ground-state wave function of a given nonalternant compound is totally symmetric or not, since this information can at least serve as useful adjunct to SCF-MO calculations.

In fact, Craig has ever proposed an empirical rule for this problem,<sup>8</sup> but his rule can be applied only to conjugated hydrocarbons in which at least two  $\pi$ -centers lie on a symmetry axis. Moreover, it has been pointed out that application of his rule to some systems may yield ambiguous results.<sup>1,4</sup> Recently, Lee has suggested a perturbation method,<sup>1</sup> but his method is not easy to carry out for larger species. Here we illustrate that the present Kekulé-based VB calculations can generally give a correct assignment of the symmetry of the VB ground-state wave function for a given nonalternant compound.

Our results for several selected nonalternant systems are displayed in Fig. 6. Clearly, Craig's rule fails in most of these compounds except for **40** and **44**, in which it agrees with the present calculations. Among these compounds, species **40**, **41**, **42**, **44**, **47** and **48** are predicted to possess nontotally symmetric VB ground states. These results can be related to some interesting experimental facts. The hexaphenyl derivative of **40**,<sup>30</sup> dimethyl derivative of **42**,<sup>31</sup> and alkyl derivative of **44**<sup>32</sup> have been prepared, but they were found to have the character of bond alternation. Species **41** is experimentally proven to be very reactive and have actually a triplet ground state.<sup>33</sup> Compound **47** is still unknown. Although the species **48** has been obtained, it shows an unusual long wave absorption spectrum.<sup>34</sup> In contrast, for remaining compounds **43**, **45**, **46** and **49** with totally symmetric VB ground

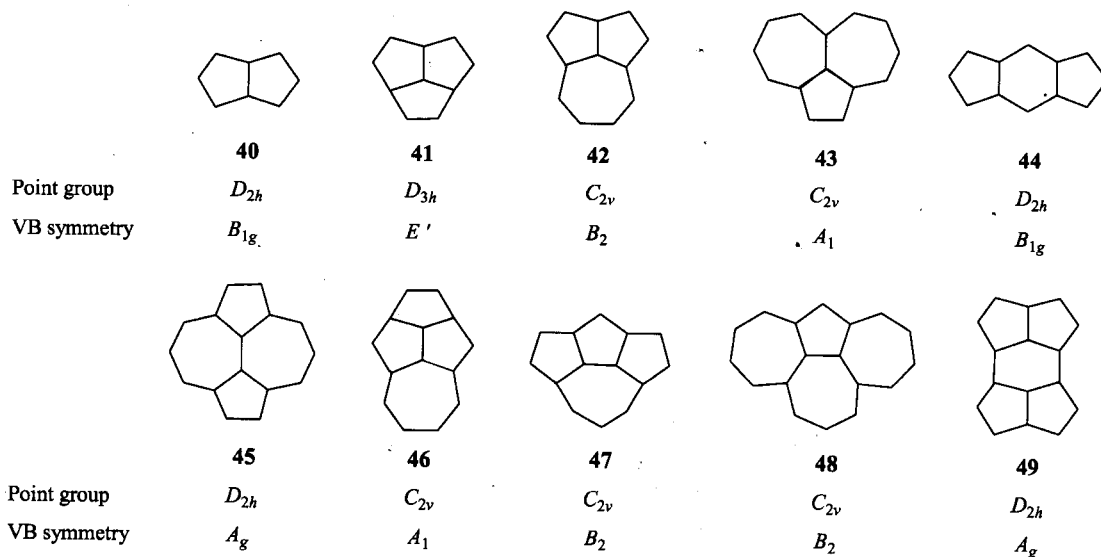


Fig. 6 Selected nonalternant systems.

states, the dimethyl and tetramethyl derivatives of 43 have been prepared, and exhibit symmetrical planar structures.<sup>34</sup> The species 45 has been known for many years and proven to behave as an aromatic compound.<sup>35</sup> The compounds 46 and 49, though still unknown, may be expected to be thermally more stable than the corresponding 41 and 40. According to the above results, we find that those compounds with nontotally symmetric VB ground states indeed exhibit some unusual chemical and physical properties. Encouragingly, the Kekulé-based VB calculations are demonstrated to be capable of determining the symmetries of the VB ground states for nonalternant systems.

## Conclusions

In this paper, we present a systematical investigation on the Kekulé-based VB method. First, by comparing with the exact VB results, the applicability and limitations of this method are elucidated. Then applications of this method to benzenoid and nonalternant systems are emphatically outlined. Our calculations indicate that the Kekulé-based VB approach can provide satisfactory descriptions for resonance energies and bond lengths of benzenoid hydrocarbons, being in good agreement with SCF-MO and experimental results. In addition, we show that the characterization of localized substructures within a large benzenoid system can be easily performed by use of the present VB calculations. In the meanwhile, some extensively used topo-

logical indices based on Kekulé structures, such as the Pauling bond order and the Randić's benzene-like index, are verified to be basically valid within the Kekulé-based VB framework. Beside these, when applied to nonalternant systems, the present VB method generally settles the problem of predicting the VB ground-state symmetry of a given compound. Therefore, the present VB results are also useful in understanding certain chemical behaviors of some nonalternant conjugated hydrocarbons, playing a complementary role to complex SCF-MO calculations. Finally, it is worth pointing out that the Kekulé-based VB method can also find its applications in describing the reactivities and electronic absorption spectra of benzenoid hydrocarbons, which will appear in other publications in the near future.

Concludingly, we believe that the Kekulé-based VB theory is of considerable use in not only contributing many qualitative chemical concepts but also providing semiquantitative descriptions for some of physical and chemical properties of conjugated  $\pi$ -systems.

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