The Valence Bond Calculations on Conjugated Hydrocarbons of Medium to Infinite Sizes

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In the past decade, we devoted time to the valence bond (VB) study of huge conjugated hydrocarbons by employing the Heisenberg model. Due to the dimension of the covalent space exponentially increasing with the size of molecule, the exact solution of the VB model for large molecules encounters a fundamental difficulty. Before 1990, Alexander and Schmalz published ground-state energy results on a set of benzenoids of up to 24 π-electrons using the graphical unitary group approach. Around 1995, we employed Lanczos technique to diagonalize the VB Hamiltonian and presented the low-lying state energies and wave functions of benzenoids with up to 22 π-centers. In terms of wave functions, the physical and chemical behaviors of these conjugated species have been discussed in detail. In succession, we generalized the VB calculation to larger systems by proposing an algorithm in coding all Slater determinants of the covalent space with conserved spin quantum number. The exact solutions of the VB model have been obtained for conjugated species with up to 30 π-electrons. Recently, we broke through this limitation by extending the density-matrix renormalization group (DMRG) method of White to the quasi-one-dimensional system. The VB energies of the ground states for two series of polycyclic aromatic hydrocarbons, polyacene and polyphenanthrene, of arbitrary lengths defined by the number of constituent hexagons have been obtained. The effective conjugated length for these infinite long-chain polymers could be estimated.

Keywords: Valence bond model; Density-matrix renormalization group method; Conjugated hydrocarbons.

1. INTRODUCTION

The valence bond (VB) theory originates from the Heitler-London treatment of the hydrogen molecule in 1927 and relates the chemical bond to the spin pairing of the shared electrons localized around the linking atoms (or atomic cores).[1,2] In the VB theory, the exchange of atomic spins and the resonance of covalent VB structures result in energy lowering and the formation of molecules. In contrast, the molecular orbital (MO) theory accounts for bonding in terms of a delocalized picture in which electrons move around all nuclei of the molecule. Thus, the VB model is more closely related to the chemist's idea of molecules as consisting of atoms held together by localized bonds than is the MO method.[3-5]

Over the past decades, however, the MO theory has been developing due to the computational advantage that the basis sets are orthogonal. Various semi-empirical and ab initio SCF schemes as well as some MO-based correlation methods are available to explore the physical and chemical behaviors of conjugated molecules.[6-8] In contrast, the development of the VB theory has been seriously hindered by the non-orthogonal atomic wave functions and the exponentially increased configuration space for many-electron molecules. In the early days of VB theory, in order to make energy calculations possible, Pauling and his contemporaries assumed that the orbitals could be considered orthogonal to each other.[3,4] This assumption resulted in a dramatic simplification for VB calculations and the resultant form of VB theory is now termed the classical VB theory. But the number of covalent VB structures still rapidly increases with the number of valence electrons, and the exact solutions of the classical VB model for the medium-sized many-electron molecules were prohibited. Even though, there are still several threads of development concerning the VB model in understanding many physical and chemical properties of conjugated molecules.[9-20] For example, with the advent of powerful computers, use of the graphical unitary-group technique has led to the exact VB ground-state energies for benzenoid hydrocar-

bons (BHs) up to N = 24 sites.[14] Around 1995, our group employed the Lanczos technique to diagonalize the VB Hamiltonian and presented the low-lying state energies and wave functions of benzenoids with up to 22 π-centers.[15] In terms of wave functions, the physical and chemical behaviors of these conjugated species have been discussed in detail.[15] To extend calculations to even larger species, efficient strategies are desirable. Recently, our group has obtained the exact energies and wave functions of the ground and lowest excited states for a large number of conjugated systems with up to 28 π-electrons by reducing the size of the Hamiltonian matrix on the basis of molecular point group and spin symmetry, efficiently coding the Slater determinants, and diagonalizing the matrix with the powerful Lanczos method.[20] The exact solutions offer the possibility for the reinterpretation of various molecular behaviors and the validation of approximate methods.[21,22] Based on the exact energies and wave functions, we have successfully interpreted the bond lengths, reactivities, aromaticities of a large number of benzenoid hydrocarbons within the VB model, which have been collected in a book.[23]

In order to further study the size dependence of the properties of large or even infinite conjugated systems, we must resort to approximate calculation methods for obtaining approximate solutions as accurately as possible. One of the most powerful techniques for studying strongly correlated electron systems, the density-matrix renormalization group (DMRG) method introduced by White, has been shown to be extremely successful in solving the many-electron models for one-dimensional systems,[24] especially the Heisenberg model[24-28] and the Hubbard model.[29-31] Within the VB model we recently introduced a scheme for treating the cata-condensed aromatic systems and carried out DMRG calculations on energies of the ground and the first triplet states for polyacene (Pac) and polyphenanthrene (Pph) of arbitrary lengths.[28] In comparison with the exact results, numerical errors of the DMRG energies per site are less than 10^{-5} J.[28] The saturation of some interesting properties, such as the local aromaticity of constituent hexagons, upon the propagation of Pac and Pph series has been investigated,[28] giving interesting information on understanding the transition from molecules to solids with the VB model.

In this article, we briefly describe the VB model for the π-conjugated systems. Then the efficient computational methods of reducing the size of the Hamiltonian matrix on the basis of molecular point group and spin symmetry, coding the Slater determinants, and diagonalizing the matrix with the powerful Lanczos method for exactly solving the VB model for medium-sized conjugated systems and the DMRG method for obtaining approximate solutions of the VB model

for large benzenoids are introduced. The applications of the VB model to Pac and Pph series are briefly reviewed. Finally, the outlook for extending the VB models to new regimes is addressed.

2. THE VB MODEL FOR π-CONJUGATED MOLECULES

It is well known that the properties of conjugated molecules are principally determined by their π-electrons. Furthermore, planar conjugated molecules are prototypical in that their π-electrons could be separately treated from the remaining σ-electrons. Hence, semi-empirical theoretical models developed mainly for conjugated molecules treated only the π-electrons explicitly but incorporated the effects of the σ-electrons and the nuclei into some adjustable parameters featuring these models. The VB model could be such a model, which may be simplified as in Eq. (1).

$$\hat{H}_{VB} = J\sum_{i \sim j}(2\hat{S}_i \cdot \hat{S}_j - 1/2) \tag{1}$$

where J is a positive exchange parameter, implicitly assuming that the exchange integral has the same value for the two $2p_\pi$ orbitals of any two carbon atoms bonded to each other.

We would like to point out that the VB model (Eq. (1)) has also proven to be the second-order effective Hamiltonian of the many-electron Hubbard model in the strongly correlated limit via degenerate perturbation theory[32] and other methods.[33,34] These methods can lead to systematic procedures for improving the VB model by introducing higher order corrections.[11] On the other side, a geometry-dependent VB model,[12] analogous to the model Hamiltonian (Eq. (1)), has also been proposed, in which the σ and π energy dependence to the bond length and bond twisting are incorporated into the parameters. Despite that these variants of the VB model can usually provide slightly better descriptions for a certain conjugated molecule,[11,12,16-19] the VB model (Eq. (1)) is appropriate for studying a group of conjugated molecules to probe structure-property relationships, and consequently will be employed as our working VB model in subsequent sections.

Then a question is raised: how the VB model can be solved for a given conjugated system. In fact, the model Hamiltonian (Eq. (1)) actually acts on the space of pure spin functions, either of the Weyl-Rumer (WR) form[35] or the simple product of one-electron spin functions. The matrix element between any two WR functions can be obtained by using Pauling's graphical rules,[4] while the matrix element be-

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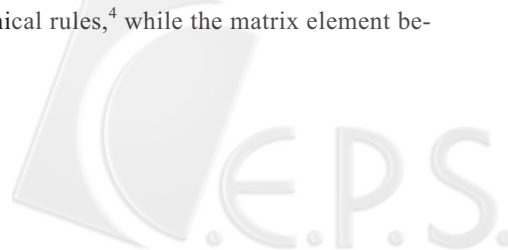
tween two simple spin products is easily available using the following expression

$$2\hat{S}_i \cdot \hat{S}_j = \hat{S}_{i+}\hat{S}_{j-} + \hat{S}_{i-}\hat{S}_{j+} + 2\hat{S}_{iz}\hat{S}_{jz} \quad (2)$$

Expanding the "wave function" in a linear combination of pure spin functions could yield the correct secular equations and thus correct eigenvalues. However, such spin-only "wave functions" could not be considered complete since complete wave functions must describe both the spatial and spin motions of electrons and must be antisymmetric under exchange of any two electrons. It would be better to rewrite the VB model (1) in the second quantization form as given in Eq. (2), in which its eigenstates can be taken as a linear combination of Slater determinants or neutral VB structures. Then

$$\hat{H}_{VB} = \hat{H}_D + \hat{H}_I \quad (3)$$

where

$$\hat{H}_D = -J\sum_{i-j}(a_{\bar{i}}^+ a_j^+ a_j a_{\bar{i}} + a_i^+ a_{\bar{j}}^+ a_{\bar{j}} a_i) \quad (4a)$$

$$\hat{H}_I = J\sum_{i-j}(a_{\bar{i}}^+ a_j^+ a_{\bar{j}} a_i + a_i^+ a_{\bar{j}}^+ a_j a_{\bar{i}}) \quad (4b)$$

Here $a_{\bar{i}}^+$ and a_i are the creation operator of the spin-down electron and the annihilation operator of the spin-up at site i, respectively. In the derivation, we have employed the relationships such as $\hat{S}_{j+} = a_j^+ a_{\bar{j}}$, $\hat{S}_{j-} = a_{\bar{j}}^+ a_j$, $\hat{S}_{jz} = 1/2(a_j^+ a_j - a_{\bar{j}}^+ a_{\bar{j}})$, and so on, which are easily confirmed by testing the effect of each side of these expressions on the two spin orbitals $\phi_j(r_j)\alpha(s_j)$ and $\phi_j(r_j)\beta(s_j)$, $\phi_j(r_j)$ being the $2p_\pi$ orbital of the jth carbon atom.

The model Hamiltonian (Eq. (3)) can be solved in various spin spaces in which S or its z-component M is conserved. For a given conjugated molecule with N π-electrons, the number of linearly independent covalent VB structures in a certain S subspace is known to be $f_S^N = (2S+1)N!/(N/2+S+1)!(N/2-S)!$,[35] while the number of neutral Slater determinants with quantum number M, n(M), equals the binomial coefficient $n(M) = C_{N/2-M}^N$. It is clear that in either case the dimension of the Hamiltonian matrix is exponentially proportional to the size of the system. In this chapter, the Slater determinants are chosen to be the N-electron basis functions, in which the VB model (Eq. (3)) is solved for various S_z spaces respectively.

For the medium-sized conjugated molecules, the solution of the VB model needs efficient computational techniques, which will be described in the next subsection.

3. COMPUTATIONAL METHODS

3.1. Coding of the Slater determinants

As introduced above, for a conjugated molecule with N π-electrons (or carbon atoms), the VB wave function spans the subspace characterized by quantum number M with dimension $n(M)$ equal to a binomial coefficient $n(M) = C_{N/2-M}^N$. This implies that the dimension for the subspace of M increases exponentially with the size of the system. For example, we have n(0) = 184,765, n(1) = 167,960 for N = 20, which increase sharply to n(0) = 40,116,600, n(1) = 37,442,160 when N = 28. Obviously, the storage of such an enormous number of determinants is important for the efficient implementation of VB calculations. For this purpose, we introduce an algorithm of coding the Slater determinants for minimizing the searching time and saving the storing space in the central memory of the computer.[20]

Each Slater determinant is defined by a unique array of site numbers 1, 2, …, N with specific spin distribution. Apparently, one can extract the sequence of spin-up (or spin-down) sites to specify a determinant. For example, when N is even and M = 0, this spin-up site sequence consists of N/2 numbers, $\{\alpha_1, \alpha_2, K, \alpha_{N/2}\}$ where α_i $(i = 1, 2, …, N/2)$ satisfies $\alpha_1 < \alpha_2 < ... < \alpha_{N/2}$ and $i \le \alpha_i \le N/2+i$. For illustration, we list the twenty Slater determinants and their spin-up sequences, $\{\alpha_1, \alpha_2, \alpha_3\}$ for N = 6 and M = 0 in Table 1. Let us demonstrate the coding of Slater determinants. We have arranged them one by one in sequential entries: we put $\{\beta_1, \beta_2, \beta_3\}$ ahead of $\{\gamma_1, \gamma_2, \gamma_3\}$, if $\beta_1 < \gamma_1$ or $\beta_1 = \gamma_1$, but $\beta_2 < \gamma_2$, or if $\beta_1 = \gamma_1$, $\beta_2 = \gamma_2$, but $\beta_3 < \gamma_3$. Thus, for the whole set of determinants we can define ordinal numbers from 1 to 20 shown in the third column of Table 1. There is a one-to-one correspondence between the spin-up site sequence and the ordinal number, and in fact we can derive an analytical formula to connect them. The ordinal number, δ, of the sequence $\{\alpha_1\alpha_2\alpha_3\}$ can be analytically written as

$$\delta\{\alpha_1\alpha_2\alpha_3\} = \sum_{j=1}^{\alpha_1-1}C_{3-1}^{6-j} + \sum_{j=1}^{\alpha_2-\alpha_1-1}C_{3-2}^{6-\alpha_1-j} + \sum_{j=1}^{\alpha_3-\alpha_2-1}C_{3-3}^{6-\alpha_2-1} + 1 \quad (5)$$

For example, one of the determinants, $|1\bar{2}3\bar{4}5\bar{6}\rangle$, with the spin-up sequence {246} corresponds to the ordinal number 15, i.e.,

$$\delta\{246\} = C_{3-1}^{6-1} + C_{3-2}^{6-2-1} + C_{3-3}^{6-4-1} + 1$$
$$= C_2^5 + C_1^3 + 1 + 1 = 10 + 3 + 1 + 1 = 15 \quad (6)$$

This coding procedure can be extended to systems having N π-electrons. The spin-up site sequence $\{\alpha_1, \alpha_2, …, \alpha_i, …, \alpha_{N/2-M}\}$ with $\alpha_1 < \alpha_2 < … < \alpha_{N/2-M}$ is extracted from the

Table 1. The Coding of Slater Determinants for M=0 and N=6

Slater determinant	$\alpha_1\alpha_2\alpha_3$	Coset	Ordinal number	Slater determinant	$\alpha_1\alpha_2\alpha_3$	Coset	Ordinal number
$|1\,2\,3\,\bar4\,\bar5\,\bar6|$	123	E	1	$|\bar1\,2\,3\,4\,\bar5\,\bar6|$	234	A	11
$|1\,2\,\bar3\,4\,\bar5\,\bar6|$	124	C	2	$|\bar1\,2\,3\,\bar4\,5\,\bar6|$	235	C	12
$|1\,2\,\bar3\,\bar4\,5\,\bar6|$	125	C	3	$|\bar1\,2\,3\,\bar4\,\bar5\,6|$	236	C	13
$|1\,2\,\bar3\,\bar4\,\bar5\,6|$	126	A	4	$|\bar1\,2\,\bar3\,4\,5\,\bar6|$	245	D	14
$|1\,\bar2\,3\,4\,\bar5\,\bar6|$	134	C	5	$|\bar1\,2\,\bar3\,4\,\bar5\,6|$	246	B	15
$|1\,\bar2\,3\,\bar4\,5\,\bar6|$	135	A	6	$|\bar1\,2\,\bar3\,\bar4\,5\,6|$	256	D	16
$|1\,\bar2\,3\,\bar4\,\bar5\,6|$	136	C	7	$|\bar1\,\bar2\,3\,4\,5\,\bar6|$	345	B	17
$|1\,\bar2\,\bar3\,4\,5\,\bar6|$	145	D	8	$|\bar1\,\bar2\,3\,4\,\bar5\,6|$	346	D	18
$|1\,\bar2\,\bar3\,4\,\bar5\,6|$	146	D	9	$|\bar1\,\bar2\,3\,\bar4\,5\,6|$	356	D	19
$|1\,\bar2\,\bar3\,\bar4\,5\,6|$	156	B	10	$|\bar1\,\bar2\,\bar3\,4\,5\,6|$	456	E	20

Slater determinant of quantum number M. No matter how huge the dimension of the subspace is, an ordinal number can be defined uniquely for every determinant to maintain the one-to-one correspondence with the spin-up sequence. The general formula is as follows

$$\delta\{\alpha_1,\alpha_2,...,\alpha_i,...,\alpha_{N/2-M}\} = \sum_{i=1}^{N/2-M}\sum_{j} C_{N/2-M-i}^{N-\alpha_{i-1}-j} +1 \qquad (7)$$

where $1 \leq j \leq \alpha_i - \alpha_{i-1} -1$ and $\alpha_0 \equiv 0$. Obviously, Eq. (7) generates natural numbers from 1 to n(M), mapping one-to-one to the Slater determinants of conserved M, as displayed in Table 1 for N = 6.

In summary, we can use natural numbers obtained using Eq. (7) instead of the spin-up sequences to store the n(M) Slater determinants in the central memory of the computer. As a result, the time consumed in searching the determinants and the space needed to store the determinants are minimized.

3.2. Symmetry adapted linear combinations (SALCs) of the determinants

The VB Hamiltonian matrix can be split into N+1 blocks characterized by M = 0, ±1, ±2, …, ±N/2 for even N. Each block of dimension n(M) can be reduced again by utilizing the molecular point symmetry. Eigenvalues of each eigenlevel are found in the M = 0 block, in which the spin-inversion symmetry can be employed for further simplification.

One can deal with the reduction by constructing SALCs of the Slater determinants via the projection operator approach. In other words, we factorize n(M) Slater determinants into disjoint invariant subspaces under the point group of the molecule. An invariant subspace includes a subset of determinants generated by operating on an arbitrary determinant with all symmetry elements of the molecular point group G. Because a single determinant generating one of these invariant subspaces S may be invariant under a subgroup H of G, the basis determinants of S correspond to cosets of H in G. Often coset representatives of H in G may be themselves chosen to form a group, called the factor group. For illustration, the 20 determinants of M = 0 for trimethylene-cyclopropane have been partitioned into six invariant subspaces under the point group D_{3h}, symbolized by A, B, C, D, E, and F in Table 1. The factor groups for A (B), C (D) and E (F) are C_3, C_{3v} and identity group, respectively. The sum of the orders of factor group equals the dimension of M = 0 block, n(0), i.e., 20 = 3+3+6+6 +1+1.

After the factorization, one can derive SALCs within each invariant subspace via the action of the projection operator. The projection operator for irreducible representation j is defined as

$$\hat{P}^j = (N)^{-1/2}\sum_{R}\sigma(R)\chi^j(R)R \qquad (8)$$

where N is the normalizing factor, the summation runs over all symmetry operations of the factor group, $\chi^j(R)$ is the character of the jth irreducible representation and $\sigma(R)$ is a phase factor equal to +1 or −1 depending on whether R refers to an

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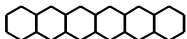*J. Chin. Chem. Soc., Vol. 50, No. 3B, 2003* **721**

even or odd permutation of atom sites. For the computation of low-lying states, we can limit our attention to one-dimensional irreducible representations. Consider trimethylenecyclopropane as an example. It is easy to derive six SALCs of A'_1 by using the operator (Eq. (8)) on each of the six invariant subspaces and two SALCs of A'_2 from C and D displayed in Table 1 under point group D_{3h}. Thus, we simplify the calculation by reducing the original 20×20 matrix to smaller matrices, 6×6 and 2×2, provided we deal with the lowest singlet and triplet states only.
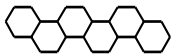
For medium-sized molecules such as hexacene of 26 π-electrons, n(0) is equal to 10,400,600. By means of symmetry, the ground state is solved from the block of A_g under point group D_{2h} with a dimension of 2,600,612. Thus the Hamiltonian matrix can be considerably reduced for those molecules with higher symmetry. For hexacene and two other benzenoids, the dimensions of one-dimensional irreducible representations in subspaces of M = 0, 1, and 2 are listed in Table 2.

In addition, the spin-inversion symmetry is available for M = 0. The operator $\hat{O}$ is defined when it acts on a Slater determinant, transforming all spin-up sites to spin-down sites and vice versa. Thus the space of M = 0 is invariant under the group $[I, \hat{O}]$ which consists of identity and spin-inversion operations. Let us discuss the 20 determinants of M = 0 for trimethylene-cyclopropane, the spin-inversion operator transforms A to B, C to D, and E to F, or vice versa, respectively. Under the compounded group $D_{3h} \otimes [I, \hat{O}]$, a pair of Slater determinants that are transformable via the spin-inversion operation should combine, as represented by A $\pm$ B, C $\pm$ D and E $\pm$

Table 2. Dimensions of Each Irreducible Representation in the Various S_Z Spaces

D_{2h}	A_g $(A_g{}^+)^a$	B_{1g} $(B_{1g}{}^+)$	B_{2u} $(B_{2u}{}^+)$	B_u $(B_u{}^+)$	Total dimensions in S_Z space
$S_Z = 0$	2,600,612 (1,302,354)	2,599,688 (1,309,756)	2,599,688 (1,309,756)	2,600,612 (1,314,514)	10,400,600
$S_Z = 1$	2,415,712	2,413,996	2,413,996	2,413,996	9,657,700
$S_Z = 2$	1,931,936	1,931,144	1,931,144	1,931,936	7,726,160

C_{2h}	A_g $(A_g{}^+)$	B_u $(B_u{}^+)$	Total dimensions in S_Z space
$S_Z = 0$	5,200,300 (2,602,198)	5,200,300 (2,606,294)	10,400,600
$S_Z = 1$	4,827,992	4,829,708	9,657,700
$S_Z = 2$	3,863,080	3,863,080	7,726,160

D_{2h}	A_g $(A_g{}^+)$	B_{1g} $(B_{1g}{}^+)$	B_{2u} $(B_{2u}{}^+)$	B_u $(B_u{}^+)$	Total dimensions in S_Z space
$S_Z = 0$	10,032,648 (5,020,420)	10,027,368 (5,013,684)	10,027,368 (5,013,684)	10,029,216 (5,010,512)	40,116,600
$S_Z = 1$	9,362,256	9,358,824	9,358,824	9,362,256	37,442,160
$S_Z = 2$	7,608,483	7,603,896	7,603,896	7,605,480	30,421,755

a The values in brackets are the dimensions of the totally symmetric irreducible representation, according to the point group plus spin-inversion symmetry $G \otimes \hat{o}$.

F respectively. Thus blocks A_1' and A_2' are further reduced to two 3×3 and two 1×1 blocks belonging to irreducible representations $A_1'^+$, $A_1'^-$ and $A_2'^+$, $A_2'^-$ of group $D_{3h} \otimes [I, \hat{O}]$.

The combination of Slater determinants in different invariant subspaces to simplify the secular equation has been called the "half-projected Hartree-Fock" method.[36,37] In general, under the compounded group of point group and spin-inversion, all irreducible subspaces have smaller dimensions: nearly half of those in the point group alone. These are illustrated in Table 2 for three molecules. After the SALCs of the Slater determinants have been obtained, the Lanczos method[38] is employed for diagonalization.

3.3. Lanczos method

The central idea of the Lanczos method[38] is to transform a general quantum model to a chain model or, in matrix language, to convert a general symmetric matrix into a tridiagonal matrix via an orthogonal transformation. By recursion, the eigenvalue can be effectively computed from a well-behaved initial state, ψ_0. If ψ_0 (normalized to 1) has a nonzero projection over the true ground state, ψ, the recursion can give a good approximation to the ground state as accurately as possible. Otherwise, it will converge to an excited state. Since the larger the number of spin-alternations in a determinant, the lower its energy will be, the classical Néel state is usually chosen as an initial state to determine the ground state. For low-lying excited states, the same procedure can be implemented in other subspaces of different M. Comparing the energies of these states, the first excited and other low-lying excited states can be picked out.[18]

Let's describe this recursion process. By operating with $\hat{H}$ on ψ_0, we define a state ψ_1 as follows

$$\psi_1 = (\hat{H}\psi_0 - a_o\psi_0)/b_1 \tag{9}$$

where

$$a_0 = \left\langle \psi_0 \left| \hat{H} \right| \psi_0 \right\rangle \tag{10}$$

$$b_1^2 = \left\langle (\hat{H}\psi_0 - a_0\psi_0) \middle| (\hat{H}\psi_0 - a_0\psi_0) \right\rangle \tag{11}$$

It is obvious that ψ_1 is normalized and orthogonal to ψ_0.

Once we have obtained ψ_0 and ψ_1, we can construct a set of orthonormal states $\{\psi_2, \psi_3, K, \psi_n\}$ in succession defined by the following relation

$$\psi_n = (\hat{H}\psi_{n-1} - a_{n-1}\psi_{n-1} - b_{n-1}\psi_{n-2})/b_n \tag{12}$$

where

$$a_{n-1} = \left\langle \psi_{n-1} \left| \hat{H} \right| \psi_{n-1} \right\rangle \tag{13}$$

$$b_n^2 = \left\langle (\hat{H}\psi_{n-1} - a_{n-1}\psi_{n-1} - b_{n-1}\psi_{n-2}) \middle| (\hat{H}\psi_{n-1} - a_{n-1}\psi_{n-1} - b_{n-1}\psi_{n-2}) \right\rangle \tag{14}$$

Obviously, all ψ_i ($i \leq n$) span a tridiagonal symmetric matrix of $\hat{H}$ with diagonal entries $\{a_0, a_1, ..., a_{n-1}\}$ and their nearest-neighbor off-diagonal entries $\{b_1, b_2, ..., b_n\}$ represented by a chain graph. Then the secular equation for the chain model is solved for the eigenvalues instead of the original Hamiltonian matrix.

For a tridiagonal matrix, less entries, $3n$, rather than $n \times n$, have to be stored. If we limit ourselves to the ground state and a few excited states, the recursive calculation can terminate at some early stage under recursions much less than n, giving the eigenvalues steadily converging toward exact results. The tridiagonal Hamiltonian matrix facilitates the computation for the corresponding eigenvectors in terms of the transformed basis set expressed by Eqs. (9) and (12). In order to obtain the eigenvectors in the original Hilbert space, we must repeat the recursion procedure accumulating the basis vectors with their corresponding weights. Then the resultant wave functions can be employed for evaluating various quantities of interest, with the purpose of gaining the structure-property relationships for conjugated molecules.

3.4. DMRG method

As mentioned before, the VB exact calculation is limited to the medium-sized benzenoid hydrocarbons up to 28 π-electrons nowadays, due to the exponential increase in the number of states with the system size. Our physical intuition suggests that not all of those numerous states contribute significantly to the low-lying states. There are several schemes proposed for efficiently truncating the configuration space. For example, within the MO framework the truncated configuration interaction (CI) method, which considers a subspace with the Hartree-Fock state plus some excited configurations relative to the Hartree-Fock state, is one of such methods.[7] But for the strongly correlated systems, the truncated CI method can hardly describe the low-lying states properly.

Wilson developed another truncation technique, named the "numerical renormalization group" for solving the Kondo impurity problem.[39] His renormalization group procedure was soon applied to a number of quantum lattice models such as the Hubbard and VB models. Unfortunately, this approach was less reliable than other numerical approaches (e.g., Monte Carlo method). In 1992, White developed a more reliable and accurate method, the density matrix renormalization

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group (DMRG), for one-dimensional lattice systems.[24] Different from the numerical renormalization group algorithm, the density matrix concept is introduced in DMRG and is used to tell us which states are the most important.[24,40,41]

We begin the DMRG scheme by dividing the system of a given size, referred to as the superblock, into two parts, i.e., the system block and the environment block. We diagonalize the superblock and focus on a particular eigenstate of the system. Then we define the reduced probability density matrix ρ as follows, and apply the density matrix to choose which states we wish to keep.

If ψ is a state of the superblock,

$$|\psi\rangle = \sum_{ij} C_{ij} |i\rangle |j\rangle \qquad (15)$$

where $|i\rangle$ labels the states of the system block, and $|j\rangle$ labels the states of the environment block, and C_{ij} is the expansion coefficient of the compound state $|i\rangle |j\rangle$. For the system block, its reduced density matrix ρ is defined by

$$\rho_{ii'} = \sum_{j} C_{ij} C_{i'j} \qquad (16)$$

The diagonalization of ρ leads to a set of eigenvalues ω_α and eigenvectors u^α. According to the definition of the density matrix, the states corresponding to larger eigenvalues of density matrix ρ are the more probable configurations of the system block. In other words, the optimal states to be kept are the most probable eigenstates of the block density matrix. Therefore, we may discard those smaller eigenvalues and associated eigenvectors. Accordingly, the matrix representation of a given operator (such as H) is transformed into $H' = OHO^+$ of dimension m, producing a new system block. O is rectangular, specified by the m highest eigenvectors u^α ($\alpha = 1, 2, \ldots,$ m) of ρ as columns, and O^+ is the transfer of O.

To proceed, one adds a block to the starting block to form a superblock of larger size. Repeating the above treatment recursively, we can obtain the targeted eigenvalues and eigenvectors for conjugated systems of various sizes. Because the width of the system significantly influences the numerical accuracy, we must keep the number of adding states as small as possible in comparison with the retaining states at each step in calculations.

Take Polyacene (Pac) as an illustration.[28] We begin with anthracene. In the first step, we calculate the ground state of anthracene using the Lanczos method. Then we break the anthracene into two parts, L (left) and R (right), as shown in Chart 1.
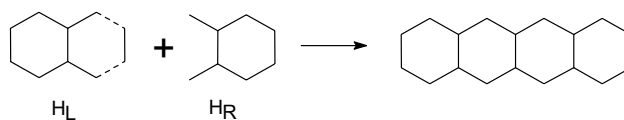
Then we form the density matrix of the left block, which is diagonalized for choosing m eigenvectors with the

Chart 1
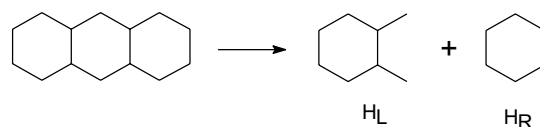
largest eigenvalues to induce a new system block, $H_L' = OH_LO^+$. In the next step, we form a larger superblock as shown in Chart 2 using H_L', an extra ethylene (added block), and H_R', which is the reflection of the left block H_L.

Chart 2

Then we diagonalize the combined blocks displayed above and obtain the ground state of naphthacene. Repeating similar steps as described above, we can locate the ground states of higher members of polyacenes one by one. A similar treatment can be done for other conjugated systems, for example, polyphenanthrenes (Pph).

4. APPLICATIONS OF VB MODEL TO Pac AND Pph SERIES

Using the effective computational methods introduced above, the VB energies and wave functions of the ground and the lowest excited states have been calculated for Pac and Pph with up to 26 π-electrons (Fig. 1). Here, we will demonstrate that these results can be used to account for some physical and chemical properties such as the local and global aromaticities of conjugated systems.

The concept of aromaticity has been rooted in the thought of chemists for a long time. Aromaticity, which is associated with high thermodynamic stability and low reactivity, is helpful in unearthing structure-activity relations and designing novel molecular systems.[42,43] For the polycyclic benzenoids, it is necessary to further subdivide the concept of aromaticity into local and global aromaticities. For a certain hexagon within a polycyclic compound, its local aromaticity could be understood as to what extent it chemically behaves like benzene.[42] Global aromaticity, or conventionally termed aromaticity in short, is usually assumed to reflect the thermodynamic stability and kinetic reactivity of a species as a

whole.[44]

Although measures to quantify local and global aromaticities have been principally calculated by means of MO theory, we demonstrate in this section that with the exact VB results for Pac and Pph we obtained it is now plausible to discuss local and global aromaticities for these BHs from a strict VB model.

4.1. Local aromaticity

Local aromaticity has been studied for many years; several indices based on either approximate VB[22,45] or simple MO calculations[46,47] have been put forward to account for local aromaticity. Similar to Herndon-Ellzey's definition of local aromaticity,[22b] we define the relative local hexagon energy (RLHE) as the ratio of the local hexagon energy to the ground-state energy of benzene to measure the local aromaticity of individual rings.[15] Due to the additivity of singlet probabilities, $p_{ij}^s = \langle \Psi | \frac{1}{2}(a_i^+ a_j^+ - a_i^+ a_j^+)(a_j^- a_i^- - a_j^- a_i^-) | \Psi \rangle$ on various bonds as indicated in Eq. (17),

$$E_\pi = \left\langle \Psi \left| J\sum_{i-j}(2\hat{S}_i \cdot \hat{S}_j - \frac{1}{2}) \right| \Psi \right\rangle = \langle \Psi | H_D + H_I | \Psi \rangle$$
$$= -2J\sum_{i-j} P_{ij}^s \qquad (17)$$

the local energy of each hexagon in the ground state of a given BH can be directly calculated by

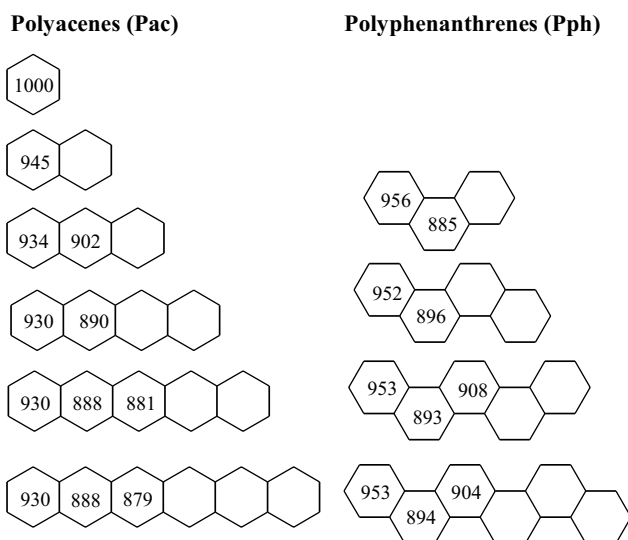$$E_r = -2J \sum_{i-j}^{rth-ring} P_{ij}^s \qquad (18)$$

Polyacenes (Pac)   **Polyphenanthrenes (Pph)**

Fig. 1. RLHE values of Pac and Pph series. Values are given as 1000 RLHE.

where the summation goes over the bonds in the rth hexagon.

The calculated RLHE values of Pacs and Pph series have been given in Fig. 1. For the polyacene series, the local aromaticity of each hexagon reflected by its corresponding RLHE monotonously decreases from the terminal toward the central, verifying the idea of the "aromatic dilution" of Clar's sextet concepts.[42] Along this series, the local aromaticity of the end hexagons becomes weaker gradually and finally arrives at a constant value with the increasing number of rings, while the decrease in the local aromaticity of the middle rings is more noticeable. Thus, the ease on addition reaction occurring across the para positions in the central rings of long chain polyacenes could be anticipated, in accord with the observed increasing reactivity upon the annelation of hexagons.[48] While in the Pph series, the local aromaticity does not decrease monotonously from the terminal hexagons toward the center, showing a trend in consistence with sextet concepts.[42] In addition, the central rings of long chain Pph are predicted to bear larger stability than those in a long Pac series due to the larger RLHE values for the middle rings in Pph.

It has been shown that a linear relationship between the present RLHEs and the $\bar{r}_L^P$ values (normalized benzene character in PPP-MO theory[46]) holds very well. Very recently, Suresh and Gadre[48] suggested a new local aromaticity index based on the molecular electrostatic potential topography (MESP) of the π regions of BHs, which is obtainable from ab initio MO calculations. This index was also found to bear linear correlation with our RLHE values. As a result, one can see that VB and MO models give consistent interpretations on the local aromaticity of BHs. Moreover, it is encouraging that the RLHE index avoids the limitations of those VB indices[22b,45] based solely on the enumeration of the Kekulé structures, which provide unsatisfactory predictions of local aromaticity for individual rings within some BHs such as the polyacene series.

4.2. Global aromaticity

Quantitative descriptions of global aromaticity usually start from consideration of the thermodynamic stability of aromatic compounds relative to reference acyclic olefins. Traditionally, resonance energy (RE) per π electron (REPE)[49] has been extensively employed as a quantitative measure of global aromaticity. Resonance energy is defined as the difference between the total π-electron energy of a given conjugated molecule and that of its corresponding hypothetical reference structure. Several strategies for determining the reference structure and its energy have been reported,[49-53] and resultant REPE values correlate reasonably well with each other, giving predictions consistent with chemical facts.

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As is done in MO theory, REPE values can be computed within the VB model if an appropriate reference structure and its energy are determined.[20] Then

$$REPE = RE/N \qquad (19)$$

where

$$RE = E_\pi - E_\pi (ref) \qquad (20)$$

and E_π is the VB ground state energy of the studied molecule, and $E_\pi(ref)$ is the VB ground state energy of the acyclic π-conjugated reference system.

The scheme for determining the energy of the reference structure proposed by Jiang, Tang, and Hoffmann (JTH hereafter)[53] is unique in parameterizing and independent of Kekulé structures and consequently will be employed here. The details of evaluation of the π-electron energy of the acyclic reference system have been introduced in Refs. 20 and 23, which will not be repeated here.

According to the JTH scheme,[23,53] the RE and REPE values for Pac and Pph series are calculated. Our VB RE values bear an excellent linear correlation with the delocalization energies obtained by Wiberg[55] at the B3LYP/6-311G** level (the correlation coefficient = 0.994) for the first four members of polyacene and polyphenanthrene series, respectively. Thus it appears that the VB RE is a good measure of the thermodynamic stability for isomeric BHs. However, for comparing the global aromaticity of BHs of different sizes, REPE values are needed. For the polyacene and polyphenanthrene series, the variation of their REPE values with the number of hexagons is displayed in Fig. 2.

One can notice that polyacenes exhibit a descending trend of the global aromaticity with the increase in the number of hexagons, in good accord with corresponding experimental facts and MO-based REPE values.[49-53] Nevertheless, VB REPEs of [n]phenanthrenes remain constant with variation of n, while corresponding REPE scales within the simple MO theory show a slight decrease in the global aromaticity along the series, at least for the members we studied.[49-53]

The inconsistency between predictions made by MO REPEs and VB REPEs may be attributed to the different natures of simple MO and VB theories, i.e., the simple MO theory is a one-electron model, free of electron correlation, but VB theory is a many-electron, correlation model. This difference may result in the different topological dependence of π-conjugation in MO and VB models, as illustrated by the

[n]phenanthrene series.

Besides the REPE index, absolute hardness and relative hardness,[44] indices that could simultaneously cover stability and reactivity, have been shown to be good measures of global aromaticity. Interestingly, it was demonstrated that absolute hardness (or relative hardness) correlates with REPE in general, thus yielding similar predictions in most cases.[44]

4.3. Pac and Pph series toward the infinite size

To extend the applications of the VB model to conjugated systems with medium or even infinite size, the DMRG method described in section 3.4 is a powerful tool for obtaining very accurate low-lying states. Recently, we have shown that the DMRG scheme gives very accurate ground state energies and properties for quasi-one-dimensional systems Pac and Pph of arbitrary lengths defined by the number of constituent hexagons n (or carbon atoms $N = 4n + 2$) in reference to the available exact values.[28] The strategy of choosing the suitable blocks in the DMRG algorithm for these two cata-condensed aromatic systems were introduced in section 3.4.

In comparison with those from the exact diagonalization method, extensive validations of our DMRG scheme on the ground states of Pac and Pph from $n = 3$ to $n = 6$ and under the truncation with $m = 128, 256$ and 512 states in each iteration have been done.[28] Obviously, the more states are retained in the truncation, the better the numerical precision is. For the least m of 128 states, the maximum numerical error between DMRG and exact values is $3 \times 10^{-5} J$ for the ground state. When the retained states are increased to 512, the maximum
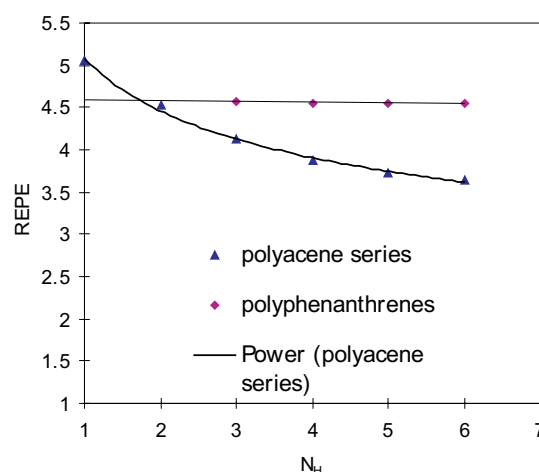

Fig. 2. The REPE values (given as 0.01 REPE and in units of J) vs. the number of hexagons (N_H) for polyacene and polyphenanthrene series.

numerical deviation decreases to 10^{-5} *J* for the ground states. These results are much better than those obtained from other approximate schemes.[56] Considering that in most chemical problems the energy calculation with an error of less than 10^{-3} *J* will be satisfactory, *m* = 256 states is employed for longer Pac and Pph for the balance of efficiency and accuracy.[28]

The energies of the ground states for Pac and Pph with n up to 10 calculated by the DMRG (*m* = 256) method are given elsewhere.[28,54] The average ground-state energy per π electron of Pac and Pph against the number of hexagons in these two series are plotted in Fig. 3 to show the convergence trend. It is clear that the energy curve of Pph always falls below that of Pac, being consistent with the well-known fact of the higher thermal stability of Pph relative to Pac.[57] The convergence of these two series with the chain length can also be analyzed by using the increment of energy between two neighboring members for the homologous series $\Delta E_s = E_s(n)$-$E_s(n\text{-}1)$. For both series ΔE_s varies negligibly when *n* exceeds 8. The simple formulae for evaluating the ground state energies (in units of *J*) of these two series are derived as follows.

$$E_s = -53.4953 - 6.4102n \quad \text{(Pac)} \tag{21}$$
$$E_s = -53.8968 - 6.4754n \quad \text{(Pph)} \tag{22}$$

From the above formulae, we can deduce that the ground state energies per electron of Pac and Pph at infinite chain length are -1.6025 *J* and -1.6189 *J*, respectively. Therefore, these numerical data provide valuable information for the transition from oligomers to polymers.

Previous studies in section 4.1 have shown that for medium-sized Pac and Pph, RLHE values decrease from the terminal ring to the central.[15] Naturally, one will ask whether the
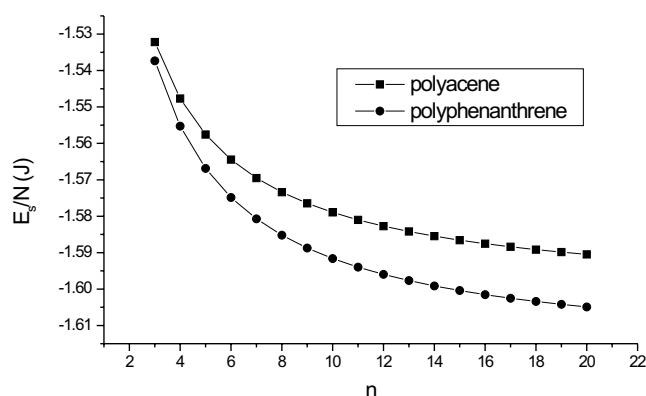

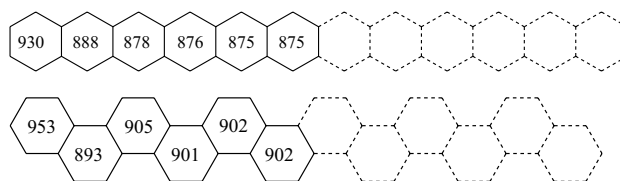Fig. 3. The average ground energy per π-electron versus chain length.

Fig. 4. Convergence of 1000*RLHE values in long-chain Pac and Pph.

value of RLHE approaches to a limit as Pac or Pph is elongated. Here we show the values of 1000*RLHE for Pac and Pph with *n* = 12 in Fig. 4. One can see that the RLHE of the central hexagon converges to a constant value when the chain length of Pac and Pph reaches 12. Thus, based on the local aromaticity index, the effective conjugated length is predicted to be 12 for both Pac and Pph from our DMRG calculations.

5. CONCLUDING REMARKS

In this article, we have reviewed the VB model and its applications to Pac and Pph series. Effective computational techniques, the Lanczos method and the DMRG method, for exactly and approximately solving VB models, respectively, are also briefly reviewed.

Exemplified by the first four members of two series of polycyclic hydrocarbons, Pac and Pph, up to 26 π-sites, our study demonstrated that with exact VB results we obtained it is feasible to discuss local and global aromaticities for conjugated systems. To extend the applications of the VB model to large benzenoid systems, the DMRG method has been employed to solve the VB model for Pac and Pph. Using the DMRG results, we investigated the convergence of the ground-state energy and the local aromaticity of individual hexagons with the chain length for these two series. Therefore, the powerful DMRG method makes the VB models to become computationally accessible for larger oligomers, which will enable the transition from oligomers to polymers to be studied. More applications of the VB models to conjugated systems could be expected in the near future.

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for their collaborations.

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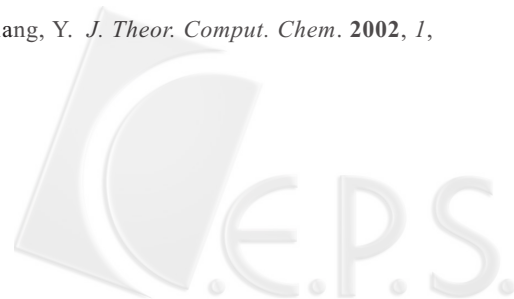
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