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New algorithm for nonorthogonal ab initio valence bond calculations. II: Subgraph-driven method

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The "permanent" method for nonorthogonal VB calculations is extensively developed, and the so-called "subgraph-driven" procedure is proposed. To achieve high efficiency, the summation of a huge number of permanents is treated as a whole system, and the intermediate quantities, the "contracted-cofactors" of various orders, are introduced for the systematic summation. These intermediate quantities can be characterized by pairing graphs of $2n$ elements ($n = 1, 2, \ldots \frac{1}{2}N - 2$). Some test calculations for systems of up to 20 electrons are performed. The practice shows that this method is highly efficient, and the CPU time increases in a quite moderate way with the increasing number of electrons.

1. Introduction

Recently there has been a considerable increase of interest in the valence bond method [1]. A significant role in the resurgence of VB theory is played by nonorthogonal valence bond calculation of electronic structures [2–5]. To get a meaningful VB description of electronic structures of many electron systems, the use of overlap-enhanced (usually energy-optimized) AO-like orbitals are necessary [2–7]. A number of successful nonorthogonal VB calculations have been reported recently [2,5,7]. As the VB theory is very closely related to the well established concepts of chemistry such as valence [8], hybridization and resonance [9], it is likely that nonorthogonal VB calculation will provide some "simple patterns of understanding" of chemical phenomena at a basic level. However, the nonorthogonal difficulty remains the major obstacle of such kind of VB calculation. Therefore there is a strong need for a much more powerful algorithm for nonorthogonal VB calculation. The Slater-determinant method is probably the most efficient method which

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is currently used by a number of authors such as Cooper, Gerratt and Raimondi [2–4] and van Lenthe's group [5,10], and the cofactor method of Löwdin [11] is used to deal with determinants of nonorthogonal orbitals. The difficulty of this method lies in the exponential length of Slater-determinant expansion of a VB function and the evaluation of cofactors. Some sophisticated computational techniques have been developed by a number of authors [3,4,10] to reduce the computational effort, and two practical VB programs based on the spin-coupled valence bond (SCVB) method [3] and self-consistent-field valence bond (SCFVB) method [12], respectively, are well developed and have been applied to a wide range of chemical systems [2–5]. Another mathematically beautiful method for VB calculation is the group theoretical approach as used recently by McWeeny [13], and Zhang and Li [14]. In this approach, the spin-free form of VB wave functions is used. Generally, the wave function can be expressed as a linear combination of VB functions of several resonance structures, and we can evaluate the VB matrix elements by the following expressions:

$$\langle \psi_{\mathrm{VB}} | \psi'_{\mathrm{VB}} \rangle = \sum_{P \in S_N} D_{11}^{[\lambda]}(P) \langle \Omega | P | \Omega' \rangle \,, \tag{1a}$$

$$\langle \psi_{\mathrm{VB}} | H | \psi'_{\mathrm{VB}} \rangle = \sum_{P \in S_N} D_{11}^{[\lambda]}(P) \langle \Omega | PH | \Omega' \rangle \,. \tag{1b}$$

Here $\Omega(\Omega')$ is a product of N orbitals, and $D_{11}^{[\lambda]}(P)$ are matrix elements of the irreducible representation $[\lambda] = [2^{\frac{1}{2}N-S}, 1^{2S}]$. In this paper we follow the convention that the permutations are defined to act on the indexes of the orbitals in the bra, i.e.

$$\begin{aligned} \langle \Omega | P &\equiv \langle \phi_1(1)\phi_2(2) \ldots \phi_N(N) | P \\ &= \langle \phi_{p_1}(1)\phi_{p_2}(2) \ldots \phi_{p_N}(N) | \,, \end{aligned} \tag{2}$$

where

$$P = \begin{pmatrix} 1 & 2 & \ldots & N \\ p_1 & p_2 & \ldots & p_N \end{pmatrix} . \tag{3}$$

As both expressions involve the summation over $N!$ permutations, a direct application of this formalism is impracticable. Although this method is believed to be less effective than the Slater-determinant method, we have a strong feeling that it seems more reasonable to seek a powerful algorithm in the group theoretical approach [15], because the VB wave function is very closely related to the symmetric group S_N, and the $N!$ problem results from the $N!$ permutations involved in the antisymmetrizer. We note the fact that both $\langle \Omega | P | \Omega' \rangle$ and $\langle \Omega | PH | \Omega' \rangle$ can be expressed as a product of several factors, for example, $\langle \Omega | P | \Omega' \rangle$ is a product of N factors. Therefore as the permutation goes smoothly, i.e. form one permutation to another, only a small part of the elements change their positions, only part of the factors change from term to term; thus the key to the efficiency of calculation is to avoid repeated

computations by using this fact. In our previous paper [15] we represented a primitive formalism for such a purpose based on left-coset decomposition of the symmetric group. It was found that the summation over each left coset turns into a "permanent" of order $N/2$. It is much more efficient to sum up permanents than to sum $N!$ terms separately. Moreover, each left-coset can be characterized by a pairing pattern of N elements, thus as the pairing pattern changes smoothly, the corresponding matrix of the permanent will also change smoothly in a parallel way. That means, some kind of intermediate quantities appear frequently in the whole computation. Therefore it should be possible to achieve even higher computational efficiency by using such a fact. The questions are: (a) what is the proper way for the systematic summation of a huge number of permanents; and (b) what kind of intermediate quantities should be used. In this paper, the "subgraph-driven" method is proposed for the systematic summation, and the "contracted cofactors" of various orders are introduced as the frequently re-used intermediate quantities. Each contracted cofactor is a sum of a set of subpermanents multiplied by proper group theoretical factors. The contracted cofactors of order n can be characterized by subgraphs of pairing patterns of $2n$ elements, and the higher order contracted cofactors can be evaluated form the lower ones, therefore the sum of a large number of permanents can be finally obtained by a recurrence procedure. Similar recurrence relations were introduced by Gerratt [16] and used by Pyper and Gerratt [17]. A new VB program using the subgraph-driven procedure has been developed. A universal file, which depends only on the irreducible representation of the symmetric group S_N, is used in the program. This file represents the knowledge of the unique subgraphs and the group theoretical factors. The practice shows that the new algorithm is much more powerful than the simple "permanent" method.

2. "Permanent" method

The permanent method, which was referred to as the "positive determinant" method in ref. [15], is the starting point of this work. For the sake of convenience, the basic formulas of this method will be briefly represented here, and we restrict our consideration to the case of spin = 0. The spin-free form of VB wave functions of N electrons can be expressed as following:

$$\psi_{\mathrm{VB}} = e_{11}^{[\lambda]}\Omega\,, \tag{4}$$

where

$$e_{11}^{[\lambda]} = \left(\frac{f_\lambda}{N!}\right)^{\frac{1}{2}} \sum_{P\in S_N} D_{11}^{[\lambda]}(P)P \tag{5}$$

and

$$\Omega = \phi_1(1)\phi_2(2)\ldots\phi_N(N)\,, \tag{6}$$

where $\phi_i (i = 1, 2, \ldots, N)$ are one-electron orbitals, which can be expanded as a linear combination of atomic orbitals. By choosing different products, say $\Omega' (= \prod \phi_i')$, we can obtain VB wave functions corresponding to different VB structures. This form of VB wave functions leads to eqs. (1a) and (1b) for overlap and Hamiltonian matrix elements, respectively. A better way to evaluate overlap and Hamiltonian matrix elements is to classify the permutations of S_N into a number of subsets according to the left-coset decomposition of the group S_N:

$$S_N = \bigcup_i q_i Q , \tag{7}$$

where Q is a properly defined subgroup of S_N with $2^{\frac{1}{2}N}(\frac{1}{2}N)!$ permutations [18], and q_i are the left-coset generators (representatives). An important property of the left coset is that all permutations belonging to the same left coset have the same D_{11}-value. Thus we obtain the new expressions of eqs. (1a) and (1b) as

$$\langle \psi_{\mathrm{VB}} | \psi_{\mathrm{VB}}' \rangle = \sum_i D_{11}^{[\lambda]}(q_i) \sum_{Q_j \in Q} \langle \Omega | q_i Q_j | \Omega' \rangle , \tag{8a}$$

$$\langle \psi_{\mathrm{VB}} | H | \psi_{\mathrm{VB}}' \rangle = \sum_i D_{11}^{[\lambda]}(q_i) \sum_{Q_j \in Q} \langle \Omega | q_i Q_j H | \Omega' \rangle . \tag{8b}$$

It is shown that the second factor in eq. (8a) corresponds to a permanent of order $N/2$, or a few permanents for eq. (8b). The permanent of an $n \times n$ matrix $A = (a_{ij}, 1 \leqslant i < j \leqslant n)$, written $per(A)$, is defined by [19]

$$per(A) = \sum_{P \in S_n} \prod_{i=1}^{n} a_{ip_i} . \tag{9}$$

As shown in a previous paper [15], there is a one to one correspondence between the left cosets and the pairing patterns of N elements $1, 2, \ldots, N$. If we have a coset with a representative q_i as following:

$$q_i = \begin{pmatrix} 1 & 2 & 3 & 4 & \ldots & N-1 & N \\ a_1 & a_2 & b_1 & b_2 & \ldots & d_1 & d_2 \end{pmatrix} , \tag{10}$$

then this coset can be characterized by the following pairing pattern: $(a_1\ a_2)$, $(b_1\ b_2)$, $\ldots$, $(d_1\ d_2)$. It is known that all the permutations of the coset have the same pairing pattern.

Now let us consider the expressions for overlap and Hamiltonian matrix elements.

Overlap matrix element $\langle \Psi_{\mathrm{VB}} | \Psi_{\mathrm{VB}}' \rangle$

For each pairing pattern(graph) G_N^i we can construct a matrix $M(G_N^i)$ in the following way:

$$G_N^i = \begin{matrix} (a_1\ a_2) \\ (b_1\ b_2) \\ \cdots \\ (c_1\ c_2) \\ \cdots \\ (d_1\ d_2) \end{matrix}, \quad M(G_N^i) = \begin{bmatrix} A_1 & A_2 & \ldots & A_{\frac{N}{2}} \\ B_1 & B_2 & \ldots & B_{\frac{N}{2}} \\ \ldots & \ldots & \ldots & \ldots \\ C_1 & C_2 & \ldots & C_{\frac{N}{2}} \\ \ldots & \ldots & \ldots & \ldots \\ D_1 & D_2 & \ldots & D_{\frac{N}{2}} \end{bmatrix}, \tag{11}$$

where the matrix elements can be obtained by

$$\begin{aligned} A_1 &= \langle\phi_{a_1}|\phi'_1\rangle\langle\phi_{a_2}|\phi'_2\rangle + \langle\phi_{a_1}|\phi'_2\rangle\langle\phi_{a_2}|\phi'_1\rangle \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ C_k &= \langle\phi_{c_1}|\phi'_{2k-1}\rangle\langle\phi_{c_2}|\phi'_{2k}\rangle + \langle\phi_{c_2}|\phi'_{2k-1}\rangle\langle\phi_{c_1}|\phi'_{2k}\rangle \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned} \tag{12}$$

Obviously, each pair in G_N^i corresponds to a row of the elements of the matrix. Thus the elements change in a parallel way as the pairs in G_N^i.

The overlap matrix element is then obtained by

$$\langle\psi_{\mathrm{VB}}|\psi'_{\mathrm{VB}}\rangle = \sum_{i=1}^{M_N} D_{11}^{[\lambda]}(G_N^i)\, per(G_N^i)\,, \tag{13}$$

where M_N is the number of the pairing patterns of N elements, and $per(G_N^i)$ denotes the permanent of the matrix $M(G_N^i)$.

Hamiltonian matrix element $\langle\Psi_{\mathrm{VB}}|H|\Psi'_{\mathrm{VB}}\rangle$

(a) Contribution from one-body operators

Let G_A denote a pair of two elements $(a_1\ a_2)$, $(1 \leqslant a_1 < a_2 \leqslant N)$, and G_i^A denote one of the subgraphs of $N-2$ elements (1, 2, ..., N, without a_1 and a_2). For each combination of G_A and G_i^A (it forms a graph of N elements), we can construct a matrix $M(F_A, G_i^A)$ as follows:

$$(G_A, G_i^A) = \begin{matrix} (a_1\ a_2) \\ (b_1\ b_2) \\ \cdots \\ (c_1\ c_2) \\ \cdots \\ (d_1\ d_2) \end{matrix}, \quad M(F_A, G_i^A) = \begin{bmatrix} F_1 & F_2 & \ldots & F_{\frac{N}{2}} \\ B_1 & B_2 & \ldots & B_{\frac{N}{2}} \\ \ldots & \ldots & \ldots & \ldots \\ C_1 & C_2 & \ldots & C_{\frac{N}{2}} \\ \ldots & \ldots & \ldots & \ldots \\ D_1 & D_2 & \ldots & D_{\frac{N}{2}} \end{bmatrix}, \tag{14}$$

where the first row of the elements, which corresponds to the subgraph G_A, is associated with one-electron operators. They can be evaluated by

$$
\begin{aligned}
F_1 = &\langle\phi_{a_1}|f(1)|\phi'_1\rangle\langle\phi_{a_2}|\phi'_2\rangle + \langle\phi_{a_1}|f(1)|\phi'_2\rangle\langle\phi_{a_2}|\phi'_1\rangle \\
&+ \langle\phi_{a_1}|\phi'_1\rangle\langle\phi_{a_2}|f(1)|\phi'_2\rangle + \langle\phi_{a_1}|\phi'_2\rangle\langle\phi_{a_2}|f(1)|\phi'_1\rangle \\
&+ \langle\phi_{a_1}\phi_{a_2}|g(1,2)|\phi'_1\phi'_2\rangle + \langle\phi_{a_1}\phi_{a_2}|g(1,2)|\phi'_2\phi'_1\rangle \\
&\cdots\cdots\cdots\cdots
\end{aligned} \tag{15}
$$

$$
\begin{aligned}
F_k = &\langle\phi_{a_1}|f(1)|\phi'_{2k-1}\rangle\langle\phi_{a_2}|\phi'_{2k}\rangle + \langle\phi_{a_1}|f(1)|\phi'_{2k}\rangle\langle\phi_{a_2}|\phi'_{2k-1}\rangle \\
&+ \langle\phi_{a_1}|\phi'_{2k-1}\rangle\langle\phi_{a_2}|f(1)|\phi'_{2k}\rangle + \langle\phi_{a_1}|\phi'_{2k}\rangle\langle\phi_{a_2}|f(1)|\phi'_{2k-1}\rangle \\
&+ \langle\phi_{a_1}\phi_{a_2}|g(1,2)|\phi'_{2k-1}\phi'_{2k}\rangle + \langle\phi_{a_1}\phi_{a_2}|g(1,2)|\phi'_{2k}\phi'_{2k-1}\rangle\,.
\end{aligned} \tag{16}
$$

The other matrix elements are obtained in the same way as shown in eq. (12) for overlap. One should note that the partial contribution from two-electron operators is included in the above expression, as it can be treated in exactly the same way as one-electron operators.

The total contribution of one-electron operators and partial contribution of two-electron operators is obtained by

$$
H_1 = \sum_{a_1<a_2}^{N} \sum_{i=1}^{M_{N-2}} D_{11}^{[\lambda]}(G_A, G_i^A)\, per(F_A, G_i^A)\,, \tag{17}
$$

where $per(F_A, G_i^A)$ denotes the permanent of the matrix $M(F_A, G_i^A)$. The first summation runs over all possible pairs $(a_1\ \ a_2)(1 \leqslant a_1 < a_2 \leqslant N)$, and the second summation runs over the subgraphs of $N-2$ elements $(1, 2, \ldots, N$, without a_1 and $a_2)$, and $D_{11}^{[\lambda]}(G_A, G_i^A)$ is the D_{11}-value of the pairing graph which consists of the pair G_A and the subgraph G_i^A.

(b) The remaining contribution of two-electron operators can be obtained in the following way:

Let G_{AB} denote a subgraph of four elements a, b, c and $d(1 \leqslant a < b < c < d \leqslant N)$; it consists of two pairs $A(a_1\ \ a_2)$ and $B(b_1\ \ b_2)$, where $(a_1, a_2, b_1, b_2) \in (a, b, c, d)$, and G_i^{AB} denotes one of the subgraphs of $N-4$ elements $(1, 2, \ldots, N$, without a, b, c and $d)$. Obviously, any combination of (G_{AB}, G_i^{AB}) forms a pairing graph of N elements. Suppose this pairing graph and the corresponding matrix take the following forms:

$$
(G_{AB}, G_i^{AB}) = \begin{matrix} (a_1\ \ a_2) \\ (b_1\ \ b_2) \\ \cdots \\ (c_1\ \ c_2) \\ \cdots \\ (d_1\ \ d_2) \end{matrix}, \quad
M(G_{AB}, G_i^{AB}) = \begin{bmatrix} A_1 & A_2 & \ldots & A_{\frac{N}{2}} \\ B_1 & B_2 & \ldots & B_{\frac{N}{2}} \\ \cdots & \cdots & \cdots & \cdots \\ C_1 & C_2 & \ldots & C_{\frac{N}{2}} \\ \cdots & \cdots & \cdots & \cdots \\ D_1 & D_2 & \ldots & D_{\frac{N}{2}} \end{bmatrix}, \tag{18}
$$

where the matrix elements are evaluated by eq. (12). The permanent of the matrix $M(G_{AB}, G_i^{AB})$ can be obtained by Laplace expansion in the following way:

$$per(G_{AB}, G_i^{AB}) = \sum_{k<l} M_{kl}^{AB} L_{kl}^{AB} , \tag{19}$$

where M_{kl}^{AB} are subpermanents of the first two rows which correspond to pairs A and B, i.e. $M_{kl}^{AB} = A_k B_l + A_l B_k$, and L_{kl}^{AB} are the corresponding cofactors, i.e. the subpermanents corresponding to the subgraph G_i^{AB} without kth and lth columns. To evaluate the two-electron contribution of this graph which has two pairs A, B associated with two-electron operators, we have a similar expression:

$$per(g_{AB}, G_i^{AB}) = \sum_{k<l} g_{kl}^{AB} L_{kl}^{AB} , \tag{20}$$

where g_{kl}^{AB} are factors of two-body operators related to the first two pairs A, B. The explicit expression of g_{kl}^{AB} is shown below:

$$g_{kl}^{AB} = \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{r=2k-1}^{2k} \sum_{s=2l-1}^{2l} (g_{ijrs} S_{i'r'} S_{j's'} + g_{ijsr} S_{i's'} S_{j'r'}) , \tag{21}$$

where

$$g_{ijrs} = \langle \phi_{a_i}(1) \phi_{b_j}(2) | g(1,2) | \phi'_r(1) \phi'_s(2) \rangle , \tag{22}$$

$$S_{ir} = \langle \phi_{a_i} | \phi'_r \rangle , \quad S_{js} = \langle \phi_{b_j} | \phi'_s \rangle , \tag{23}$$

and

$$i + i' = 3 , \quad j + j' = 3 , \quad r + r' = 4k - 1 , \quad s + s' = 4l - 1 . \tag{24}$$

Obviously, g_{kl}^{AB} contains 32 terms, and they always appear as a compact unit. Therefore the computational effort is reduced greatly.

The total contribution is obtained by

$$H_2 = \sum_{a<b<c<d}^{N} \sum_{G_{AB}} \sum_{i=1}^{M_{N-4}} D_{11}^{[\lambda]}(G_{AB}, G_i^{AB}) \, per(g_{AB}, G_i^{AB}) . \tag{25}$$

From eqs. (17) and (25), we can obtain the total Hamiltonian.

3. Evaluation of permanents by successive Laplace expansion

The definition of permanents is quite similar to that of determinants. However, the permanents fail to inherit two key properties of determinants, the multiplicative properties and the invariance under elementary operations on matrices; therefore it is more difficult to evaluate a permanent. The evaluation of the permanent of an $n \times n$ matrix by direct use of the definition requires $(n-1)n!$ multiplications, thus

this method is impracticable for large N. A complete account of the theory of permanents, applications and methods for the evaluation of permanents is given in ref. [19]. For general matrices, three methods are available, together with some variants of them: the Jurkat–Ryser method [19b], the Binet–Minc method [19a], and the Ryser method [19c]. The numbers of multiplications required by the three methods are 4^n, $(n/2)^{n/2}$ and $(n-1)(2^n-1)$, respectively. Obviously, the Ryser method is the most efficient. This method begins with the product of the row sums of the matrix, and then discards the superfluous terms in the product. A modified variant of this method [19d] reduces the number of multiplications by a factor 2. In the previous paper [15], a simple method was introduced. In this method, the subpermanents of higher order are computed by using the subpermanents of lower order, and the permanents are finally obtained by the successive use of the Laplace expansion of permanents. The efficiency of this method is very close to that of the improved Ryser method [19d]. For example, the evaluation of a permanent of order 12 requires 2.4×10^4 multiplications by the successive Laplace expansion method [15], and the improved Ryser method requires 2.3×10^4 multiplications for the evaluation of the same permanent. The advantage of the Laplace expansion method is that this method can be easily complemented in a computer program, and is quite suitable for the systematic summation of a huge number of permanents. In the following sections, it will be discussed how the successive Laplace expansion is used in the new algorithm.

4. Basic idea of the new algorithm

The motivation of this work comes from the following consideration: in the permanent method of VB calculations, we always deal with the sum of permanents of a huge number of matrices, and from one matrix to another, there might be only a small part of the matrix elements of them are different, therefore one should concentrate on the development of a global, overall efficient, algorithm by using such a fact. Similar "global strategy" in the Slater-determinant expansion of VB calculations is well developed by Raimondi and Gianinetti [20], Rettrup and Thorsteinsson [21] and Cooper et al. [4]. As a simple example to explain the idea of systematic summation of a set of permanents, let us consider the summation of the permanents of the following 9 pairing graphs:

G_{AB}	(1 2)	(1 2)	(1 2)	(1 3)	(1 3)	(1 3)	(1 4)	(1 4)	(1 4)
	(3 4)	(3 4)	(3 4)	(2 4)	(2 4)	(2 4)	(2 3)	(2 3)	(2 3)
G_{CD}	(5 6)	(5 7)	(5 8)	(5 6)	(5 7)	(5 8)	(5 6)	(5 7)	(5 8)
	(7 8)	(6 8)	(6 7)	(7 8)	(6 8)	(6 7)	(7 8)	(6 8)	(6 7)
$D_{11}(G_{ABCD})$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$

Obviously, each pairing graph consists of two parts, G_{AB} and G_{CD}, and each part has 3 possible patterns (subgraphs G^i_{AB}, G^i_{CD}, $i = 1, 2, 3$) as following:

$$\begin{array}{cccccc} (1\ 2) & (1\ 3) & (1\ 4) & (5\ 6) & (5\ 7) & (5\ 8) \\ (3\ 4) & (2\ 4) & (2\ 3) & (7\ 8) & (6\ 8) & (6\ 7) \\ G^1_{AB} & G^2_{AB} & G^3_{AB} & G^1_{CD} & G^2_{CD} & G^3_{CD} \end{array}$$

and the 3×3 combinations result in the 9 pairing patterns shown above.

There are two ways to perform the summation. The first way is to evaluate the 9 permanents separately, and then sum the contributions from each of them. For example, let us consider the permanent of the pairing graph (G^1_{AB}, G^1_{CD}):

pairing graph		matrix	subpermanents
G^1_{AB}	(1 2), (3 4)	$\begin{bmatrix} A^1_1 & A^1_2 & A^1_3 & A^1_4 \\ B^1_1 & B^1_2 & B^1_3 & B^1_4 \\ C^1_1 & C^1_2 & C^1_3 & C^1_4 \\ D^1_1 & D^1_2 & D^1_3 & D^1_4 \end{bmatrix}$	$AB^1_{12}, AB^1_{13}, AB^1_{14}, AB^1_{23}, AB^{13}_{24}, AB^1_{34}$
G^1_{CD}	(5 6), (7 8)		$CD^1_{12}, CD^1_{13}, CD^1_{14}, CD^1_{23}, CD^1_{24}, CD^1_{34}$

where

$$\begin{aligned} AB^1_{kl} &= A^1_k B^1_l + A^1_l B^1_k \\ CD^1_{kl} &= C^1_k D^1_l + C^1_l D^1_k \end{aligned} \qquad (1 \le k < l \le 4)\,. \tag{26}$$

The permanent of the matrix shown above can be obtained by Laplace expansion:

$$\begin{aligned} per(G^1_{AB}, G^1_{CD}) = {} & AB^1_{12}CD^1_{34} + AB^1_{13}CD^1_{24} + AB^1_{14}CD^1_{23} + AB^1_{23}CD^1_{14} \\ & + AB^1_{24}CD^1_{13} + AB^1_{34}CD^1_{12}\,. \end{aligned} \tag{27}$$

For other different subgraphs, we can also get the corresponding sets of subpermanents:

$$G^2_{AB}\colon \{AB^2_{kl}\};\quad G^3_{AB}\colon \{AB^3_{kl}\};\quad G^2_{CD}\colon \{CD^2_{kl}\};\quad G^3_{CD}\colon \{CD^3_{kl}\}\quad (1 \le k < l \le 4)\,.$$

Thus the first way of summation can be represented by the following expression:

$$\begin{aligned} SUM &= \sum_{i=1}^{3}\sum_{j=1}^{3} D^{[\lambda]}_{11}(G^i_{AB}, G^j_{CD})\, per(G^i_{AB}, G^j_{CD}) \\ &= \sum_{i=1}^{3}\sum_{j=1}^{3} D^{[\lambda]}_{11}(G^i_{AB}, G^j_{CD})(AB^i_{12}CD^j_{34} + AB^i_{13}CD^j_{24} + AB^i_{14}CD^j_{23} \\ &\quad + AB^i_{23}CD^j_{14} + AB^i_{24}CD^j_{13} + AB^i_{34}CD^j_{12})\,. \end{aligned} \tag{28}$$

The numbers of multiplications, additions and subtractions involved in the above procedure are 60, 49 and 4, respectively.

In the second way, we treat the summation of the 9 permanents as a whole. As mentioned above, the 9 pairing graphs $\{G_{ABCD}(i,j)\}$ consist of two subgraphs G^i_{AB} and G^j_{CD} $(i,j = 1, 2, 3)$. Moreover, if we assign values to these subgraphs in the following way:

$$d(G^1_{AB}) = 1, \quad d(G^2_{AB}) = -\tfrac{1}{2}; \quad d(G^3_{AB}) = -\tfrac{1}{2}; \quad d(G^1_{CD}) = 1;$$

$$d(G^2_{CD}) = -\tfrac{1}{2}; \quad d(G^3_{CD}) = -\tfrac{1}{2},$$

then we have

$$D^{[\lambda]}_{11}(G^i_{AB}, G^j_{CD}) = d(G^i_{AB}) \cdot d(G^j_{CD}). \tag{29}$$

With this relation, we can rewrite eq. (28) in the following form:

$$SUM = \left[\sum_{i=1}^{3} d(G^i_{AB}) AB^i_{12}\right]\left[\sum_{i=1}^{3} d(G^i_{CD}) CD^i_{34}\right] + \ldots \left[\sum_{i=1}^{3} d(G^i_{AB}) AB^i_{34}\right]\left[\sum_{i=1}^{3} d(G^i_{CD}) CD^i_{12}\right]. \tag{30}$$

That means, instead of performing the summation of the 9 permanents separately, we can first sum over the subgraphs $\{G^i_{AB}\}$ and $\{G^j_{CD}\}$, and obtain the two sets of "contracted subpermanents" $\{AB_{kl}\}$ and $\{CD_{kl}\}$ as written below:

$$AB_{kl} = \sum_{i=1}^{3} d(G^{AB}_i) \cdot AB^i_{kl} = AB^1_{kl} - \tfrac{1}{2}(AB^2_{kl} + AB^3_{kl}), \tag{31}$$

$$CD_{kl} = \sum_{i=1}^{3} d(G^i_{CD}) \cdot CD^i_{kl} = D^1_{kl} - \tfrac{1}{2}(CD^2_{kl} + CD^3_{kl}). \tag{32}$$

Then we can obtain the full sum of the 9 permanents by the following expression:

$$SUM = AB_{12} \cdot CD_{34} + AB_{13} \cdot CD_{24} + AB_{14} \cdot CD_{23} + AB_{23} \cdot CD_{14} + AB_{34} \cdot CD_{12}. \tag{33}$$

The numbers of various operations in this procedure are shown as following:

multiplications: 18; additions: 17; subtractions: 12.

Obviously, the second way is much more economical than the first one. This simple example shows us that from the starting point of the permanent method we can go

much further to achieve higher efficiency of nonorthogonal VB calculations. To deal with the general cases, we need a systematic method. Besides, as the summation involves both the left cosets (pairing graphs) and their D_{11}-values, we need sufficient knowledge about the mathematics of left cosets and properties of D_{11}-values. In the following section, some results concerning the properties of D_{11}-values of cosets are discussed.

5. Properties of D_{11}-values of left-cosets

As mentioned above, each left coset can be characterized by a pairing graph of N elements, and there is a one-to-one correspondence between the pairing graphs and the left cosets. Thus it is more convenient to use graphic language in the following discussion. It can be known that the number of pairing graphs of N (even number) elements M_N takes the following value:

$$M_N = \prod_{k=1}^{N/2} (2k-1)\,. \tag{34}$$

Obviously, M_N is a rapidly increasing number. For example, $M_{20} = 6.5 \times 10^8$. It would be a very difficult task to accumulate the contributions of a huge number of permanents in a direct way. However, one should note that this large number comes from the combination of a quite limited number of pairs, thus it is always possible to classify the graphs into a number of subsets, and in each subset all the pairing graphs have a subgraph, say g_1, in common, and the differences among them come from the subgraphs g_2, the remaining parts of the graphs. To obtain the sum of all the permanents corresponding to one subset of the graphs, one can first run the summation over all subgraphs g_2 and obtain a set of intermediate quantities. The subpermanents corresponding to the subgraph g_1 need to be computed only once. After that the sum of all the permanents can be easily obtained by Laplace expansion using the subpermanents and the intermediate quantities.

The following properties of D_{11}-values of pairing graphs make it possible to do the summation of permanents in a more systematic way. Suppose we have a subset of pairing graphs in which all the members have a subgraph g_{2n} of n pairs in common, while the subgraphs g^i_{N-2n} (of the remaining $N/2-n$ pairs) are all different, then it can be known that the number of the graphs of this subset is exactly the same as the number of the pairing graphs of $N-2n$ elements, and the D_{11}-values of the pairing graphs in the subset changes in a parallel way as the D_{11}-values of the left cosets of S_{N-2n} as

$$D_{11}^{[\lambda_N]}(g_{2n}, g^i_{N-2n}) = F(g_{2n}) \cdot D_{11}^{[\lambda_{N-2n}]}(G^i_{N-2n})\,, \tag{35}$$

where $F(g_{2n})$ is a constant, which depends on g_{2n}, $[\lambda_{2n}] = [2^{N/2}, 1^0]$, $[\lambda_{N-2n}] = [2^{N/2-n}, 1^0]$, and G^i_{N-2n} are the pairing graphs of the left cosets of S_{N-2n}. The

details about the constant factor $F(g_{2n})$ and one-to-one correspondence of g^i_{N-2n} and G^i_{N-2n} are given in Appendix for the case $n = 1$ and 2.

6. A new procedure for evaluating Hamiltonian matrix elements

(a) Subgraph-representatives and the contracted cofactors

In VB calculations we need to evaluate both overlap and Hamiltonian matrix elements of VB wavefunctions. The most time consuming step is to evaluate Hamiltonian matrix elements, especially the two-electron terms. In the permanent formalism the most time consuming step is that given by eq. (25). In this section we concentrate on this step. The evaluation of the overlap matrix elements and the one-electron contribution becomes quite easy after this step, because all the required intermediate quantities are available after that.

From eq. (20) we can rewrite eq. (25) in the following form:

$$H_2 = \sum_{a<b<c<d}^{N} \sum_{G_{AB}} \sum_{i=1}^{M_{N-4}} D^{[\lambda]}_{11}(G_{AB}, G^{AB}_i) \cdot \sum_{k<l} g^{AB}_{kl} L^{AB}_{kl}(i) , \tag{36}$$

where G_{AB} is a subgraph of 4 elements a, b, c and d, and G^{AB}_i are subgraphs of $N-4$ elements (1, 2, ..., N, without a, b, c and d), g^{AB}_{kl} are the two-electron factors associated with two pairs A, B, i.e. the subgraph G_{AB}, and $L^{AB}_{kl}(i)$ are the corresponding cofactors, i.e. the subpermanents without the rows A, B, and columns k, l, index i means that the subpermanents correspond to subgraph G^{AB}_i. In the summation, the group theoretical factors, the D_{11}-values are involved. As shown in the previous section and Appendix, we have

$$D_{11}(G_{AB}, G^{AB}_i) = F_{AB} D_{11}(G^i_{N-4}) \quad (i = 1, 2, \ldots M_{N-4}) , \tag{37}$$

where

$$G^i_{N-4} = \hat{R}_{AB} G^{AB}_i . \tag{38}$$

F_{AB} is a factor which depends on the two pairs A and B, and $D_{11}(G^i_{N-4})$ (the superscripts $[\lambda]$ are henceforth dropped for clarity) are the D_{11}-values of the left cosets of S_{N-4} characterized by graphs G^i_{N-4}. $\hat{R}_{AB}$ is an operator which changes subgraphs G^{AB}_i into G^i_{N-4}. Thus we can assign values to the subgraphs G^{AB}_i and subgraph G_{AB} in the following way:

$$\begin{aligned} d(G^{AB}_i) &= D_{11}(G^i_{N-4}) \\ &= D_{11}(\hat{R}_{AB} G^{AB}_i) , \end{aligned} \tag{39}$$

$$d(G_{AB}) = F_{AB} . \tag{40}$$

In the set of subgraphs (G^{AB}_i, $i = 1, 2, \ldots, M_{N-4}$), there is one and only one sub-

graph, say G_m^{AB}, which has the maximal d-value, i.e. $d(G_m^{AB}) = 1$. Suppose the subgraph G_m^{AB} takes the following pairing pattern:

$$(e_1\ e_2)$$
$$(f_1\ f_2)$$
$$\cdots$$
$$(g_1\ g_2)$$

then the operator $\hat{R}_{AB}$ can be expressed as follow:

$$\hat{R}_{AB} = \begin{pmatrix} e_1 & e_2 & f_1 & f_2 & \cdots & g_1 & g_2 \\ 1 & 2 & 3 & 4 & \cdots & N-5 & N-4 \end{pmatrix}. \tag{41}$$

Details about how to find the operator $\hat{R}_{AB}$ and consequently the subgraph G_m^{AB} were given in Appendix. From this special subgraph, we can find the other members of the set $(G_i^{AB}, i = 1, 2, \ldots, M_{N-4})$ and obtain their d-values by eq. (39). Therefore we can choose G_m^{AB} as the representative of the set of subgraphs $\{G_i^{AB}\}$. It not only characterizes a set of M_{N-4} subgraphs, but also their d-values.

From the expression of the two-electron factors, eq. (21), one can see that it requires considerable efforts to compute these factors $\{g_{kl}^{AB}\}$. Fortunately, it is not necessary to evaluate them each time at the summation over the subgraphs, as the two-electron factors $\{g_{kl}^{AB}\}$ are independent of the subgraphs G_i^{AB}. Therefore it is appropriate to execute the summation of the cofactors $L_{kl}^{AB}(i)$ over these subgraphs as

$$H_2 = \sum_{a<b<c<d}^{N} \sum_{G_{AB}} F_{AB} \sum_{k<l} g_{kl}^{AB} \sum_{i=1}^{M_{N-4}} d(G_i^{AB}) L_{kl}^{AB}(i) \tag{42}$$

$$= \sum_{a<b<c<d}^{N} \sum_{G_{AB}} F_{AB} \sum_{k<l} g_{kl}^{AB} L_{kl}^{AB}, \tag{43}$$

where

$$L_{kl}^{AB} = \sum_{i=1}^{M_{N-4}} d(G_i^{AB}) L_{kl}^{AB}(i) \tag{44}$$

and we call $\{L_{kl}^{AB}\}(1 \leqslant k < l \leqslant N/2)$ the "contracted cofactors" which correspond to the set of subgraphs $\{G_i^{AB}\}$. In the program we use G_m^{AB}, the subgraph-representative of this set, to characterize these contracted cofactors. Thus for each subgraph-representative, there is a set of contracted cofactors.

After the contracted cofactors have been obtained, the summation is greatly reduced as shown by eq. (43). Thus the next step is to find an efficient way to obtain all the contracted cofactors. In eq. (43), the first two summations go through all possible ways of choosing two pairs A, B out of N elements. The number of the first two summations can be given as

$$M_{AB} = N(N-1)(N-2)(N-3)/8\,. \tag{45}$$

While it is known that the number of unique subgraph-representatives involved in eq. (43), $N_G(N,4)$, is given by

$$N_G(N,4) = N(N-2)(N^2-8N+17)/8\,. \tag{46}$$

Obviously $N_G(N,4)$ is less than M_{AB}. This leads to the reduction of the computation in a certain depth. Now the major problem is how to compute the contracted cofactors of all the unique subgraph-representatives in a systematic and efficient way. Let us consider how to execute the summation over the subgraphs $\{G_i^{AB}\}$ in eq. (44). Suppose the subgraph G_i^{AB} and the corresponding submatrix $M_{kl}^{AB}(i)$ take the following form:

$$G_i^{AB} = \begin{matrix} (c_1 \;\; c_2) \\ (d_1 \;\; d_2) \\ \cdots \\ (h_1 \;\; h_2) \end{matrix},$$

$$M_{kl}^{AB}(i) = \begin{bmatrix} C_1 & \cdots & C_{k-1} & C_{k+1} & \cdots & C_{l-1} & C_{l+1} & \cdots & C_{\frac{N}{2}} \\ D_1 & \cdots & D_{k-1} & D_{k+1} & \cdots & D_{l-1} & D_{l+1} & \cdots & D_{\frac{N}{2}} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ H_1 & \cdots & H_{k-1} & H_{k+1} & \cdots & H_{l-1} & H_{l+1} & \cdots & H_{\frac{N}{2}} \end{bmatrix}. \tag{47}$$

We can evaluate the permanent of the matrix $M_{kl}^{AB}(i)$, $L_{kl}^{AB}(i)$, by Laplace expansion:

$$L_{kl}^{AB}(i) = \sum_{m\neq k,l} C_m(i) L_{klm}^{ABC}(i)\,, \tag{48}$$

where $C_m(i)$ are the elements of the first row, which corresponds to the first pair $(c_1 \;\; c_2)$ of G_i^{AB}, and $L_{klm}^{ABC}(i)$ are the corresponding cofactors. Thus eq. (44) becomes

$$L_{kl}^{AB} = \sum_{i=1}^{M_{N-4}} d(G_i^{AB}) \sum_{m\neq k,l} C_m(i) L_{klm}^{ABC}(i)\,. \tag{49}$$

The first summation runs over all possible subgraphs of $N-4$ elements $(1, 2, \ldots, N$, without a, b, c and $d)$. Let "e" be one of the elements, then it is always possible to choose a pair containing element "e", say $(e\ f)$, as the first pair G_C of the subgraph G_i^{AB}. Let G_j^{ABC} denote the subgraphs of the remaining $N-6$ elements $(1, 2, \ldots, N$, without a, b, c, d, e and $f)$. The combination of (G_C, G_j^{ABC}) provides part of the sub-

graphs $\{G_i^{AB}\}$. If one replaces the element f by other elements and performs the same procedure, one obtains all subgraphs $\{G_i^{AB}\}$. Thus we can rewrite eq. (49) as

$$L_{kl}^{AB} = \sum_{G_C} \sum_{j=1}^{M_{N-6}} d(G_C, G_j^{ABC}) \sum_{m \neq k,l} C_m L_{klm}^{ABC}(j) , \tag{50}$$

where C_m are elements of the first row corresponding to G_C. The first summation runs over $N-5$ possible pairs G_C which have a fixed element "e". Usually we choose the smallest element as the fixed element in G_C. The second summation runs over M_{N-6} subgraphs of the remaining $N-6$ elements. Moreover, as it can be known from the above discussion, the d-values of subgraphs $\{G_i^{AB}\}$ can be represented by the D_{11}-values of the pairing graphs of S_{N-4}:

$$d(G_i^{AB}) = D_{11}(G_{N-4}^i) , \tag{51}$$

where

$$G_{N-4}^i = \hat{R}_{AB} G_i^{AB} .$$

Therefore we can factorize the d-values of G_i^{AB} in a similar way as for the D_{11}-values of G_{N-4}^i:

$$\begin{aligned} d(G_C, G_j^{ABC}) &= D_{11}(\hat{R}_{AB} G_C, \hat{R}_{AB} G_j^{ABC}) \\ &= F_C \cdot D_{11}(\hat{R}_{ABC} G_j^{ABC}) \\ &= F_C \cdot D_{11}(G_{N-6}^j) , \end{aligned} \tag{52}$$

where $\hat{R}_{ABC}$ is an operator to renumber the elements of subgraph G_j^{ABC}. Details about how to construct this operator are shown in Appendix. The constant F_C can be simply determined in the following way: suppose the pair $G_C = (e\ f)$, then

$$F_C = \begin{cases} 1 , & \text{if } PA(\hat{R}_{AB} e) = \hat{R}_{AB} f , \\ -\frac{1}{2} , & \text{otherwise} , \end{cases} \tag{53}$$

where $PA(n)$ is an integer function defined in Appendix. Thus we can assign to the pair G_C and to the subgraphs G_j^{ABC} the following values:

$$d(G_c) = F_c ,$$

$$d(G_j^{ABC}) = D_{11}(\hat{R}_{ABC} G_j^{ABC}) . \tag{55}$$

Similarly, we can define the subgraph-representative of the set of subgraphs $\{G_j^{ABC}\}$ as one that has the largest d-value. If we denote this subgraph as G_m^{ABC}, we have $d(G_m^{ABC}) = 1$.

As the elements C_m depend only on the pair G_C, one can compute the contracted cofactors L_{kl}^{AB} by the Laplace expansion method shown in eq. (50). Therefore it is appropriate to sum over the subgraphs $\{G_j^{ABC}\}$ first:

$$L_{kl}^{AB} = \sum_{G_C} F_C \sum_{m\neq k,l} C_m \sum_{j=1}^{M^{N-6}} L_{klm}^{ABC}(j) d(G_j^{ABC})$$
$$= \sum_{G_C} F_C \sum_{m\neq k,l} C_m L_{klm}^{ABC}, \tag{56}$$

where

$$L_{klm}^{ABC} = \sum_{j=1}^{M_{N-6}} L_{klm}^{ABC}(j) \cdot d(G_j^{ABC}) \tag{57}$$

and we call L_{klm}^{ABC} $(1 \leqslant k < l < m \leqslant N/2)$ the contracted cofactor of order $\frac{1}{2}N - 3$. Such a set of contracted cofactors can be characterized by the subgraph G_m^{ABC}. An important advantage of using contracted cofactors is that it is not necessary to evaluate all the involved terms $\{L_{klm}^{ABC}\}(m \neq k, l)$ for each term L_{kl}^{AB}, while the evaluation of the contracted cofactors $\{L_{klm}^{ABC}\}$ is the most time consuming step for obtaining the higher order contracted cofactors $\{L_{kl}^{AB}\}$. In fact, to evaluate a set of $C(\frac{1}{2}N : 2)$ contracted cofactors $\{L_{kl}^{AB}\}$ of a subgraph-representative of $N - 4$ elements, $N - 5$ subgraph-representatives of $N - 6$ elements are involved, and each of them has a set of $C(\frac{1}{2}N : 3)$ contracted cofactors $\{L_{klm}^{ABC}\}$, where $C(m : n) = m!/[n!(m - n)!]$. To evaluate each term L_{kl}^{AB}, the $\frac{1}{2}N - 2$ contracted cofactors of each lower subgraph-representative are used, the contracted cofactors of lower order are therefore repeatedly used for evaluating all terms $\{L_{kl}^{AB}\}$ of the same subgraph-representative, because $C(\frac{1}{2}N : 2)(\frac{1}{2}N - 2) > C(\frac{1}{2}N : 3)$. It means that by using lower contracted cofactors $\{L_{klm}^{ABC}\}$, the computational effort for evaluating $\{L_{kl}^{AB}\}$ is reduced by a factor

$$R_A = C(\tfrac{1}{2}N : 2)(\tfrac{1}{2}N - 2)/C(\tfrac{1}{2}N : 3)$$
$$= 3. \tag{58}$$

Generally, in the step to evaluate the contracted cofactors of order n, the most time consuming part is to evaluate contracted cofactors of order $n - 1$, while the above procedure leads to a reduction of computation by a factor of $(\frac{1}{2}N - n - 1)$.

A further significant reduction of computation effort comes from the following fact: the lower contracted cofactors are not only repeatedly used for the contracted cofactors of one higher subgraph-representative, but also might be repeatedly used for the contracted cofactors of other different subgraph-representatives. Let $N_G(N, 2n)$ denote the number of unique subgraph-representatives of $N - 2n$ elements. To evaluate the contracted cofactors of each subgraph-representative of $N - 2n$ elements, the contracted cofactors of $N - 2n - 1$ lower subgraph-representatives will be involved. Thus to evaluate the contracted cofactors of all $N_G(N, 2n)$ subgraph-representatives of $N - 2n$ elements, in principle $N_G(N, 2n)(N - 2n - 1)$ lower subgraph-representatives have to be determined. However, the number of

Table 1a
The numbers of unique subgraph-representatives in the subgraph-driven method for nonorthogonal VB calculations of the N-electron system.

		Number of unique subgraph-representatives						
		Number of elements in subgraphs:						
		4	6	8	10	12	14	16
N	8	102						
	10	222	370					
	12	370	1390	975				
	14	650	2780	5415	2121			
	16	975	7220	12635	15771	4060		
	18	1515	12635	51555	42056	37996	7092	
	20	2121	26285	103110	244216	113988	80172	11565

unique lower subgraph-representatives, $N_G(N, 2n+2)$, is usually much smaller. Thus to evaluate the contracted cofactors of a subgraph-representative, it is not necessary to evaluate the contracted cofactors of all lower subgraph-representatives involved. This leads to an essential reduction of computation by a factor

$$R_B = N_G(N, 2n)(N - 2n - 1)/N_G(N, 2n+2)\,. \tag{59}$$

Obviously, the above strategy can be continued until we get all the unique subgraph-representatives of 4 elements. In each step we can achieve a reduction of computation by a factor $R_A \times R_B$, therefore the whole computation of nonorthogonal VB calculations is greatly reduced. The numbers of unique subgraph-representatives of various orders are obtained by a graph-analysis programm. The results are shown in table 1a. The reduction factors for each step are shown in table 1b. It can be seen that the numbers of unique subgraph representatives increase in a quite moderate fashion with the increasing number of electrons N. Moreover, the

Table 1b
The reduction factors by using contracted cofactors of various orders.

		Reduction factors						
		Order of contracted cofactors:						
		2	3	4	5	6	7	8
N	8	6.2						
	10	33.3	5.1					
	12	94.0	19.6	4.6				
	14	128	68.2	14.1	4.2			
	16	259	73.5	56.2	11.3	4.0		
	18	334	200	44.9	50.0	9.7	3.9	
	20	558	220	149.2	30.8	45.7	8.7	3.8

new algorithm is quite suitable for vectorization and parallelization on large computers.

(b) Subgraph-driven procedure

The contracted cofactors of the highest order can be contructed systematicly by recurrence starting from the contracted cofactors of order 2, which correspond to subgraph-representatives of 4 elements. Suppose one subgraph-representative G_4 and its other two members and the corresponding matrices take the following form:

$$\begin{matrix}(e_1\ e_2)\\(f_1\ f_2)\end{matrix}\ ,\quad \begin{bmatrix} E_1 & E_2 & \dots & E_{\frac{N}{2}} \\ F_1 & F_2 & \dots & F_{\frac{N}{2}} \end{bmatrix},$$

$$d(G_4) = 1\,, \tag{60}$$

$$\begin{matrix}(e_1\ f_1)\\(e_2\ f_2)\end{matrix}\ ,\quad \begin{bmatrix} E'_1 & E'_2 & \dots & E'_{\frac{N}{2}} \\ F'_1 & F'_2 & \dots & F'_{\frac{N}{2}} \end{bmatrix},$$

$$d(G'_4) = -\tfrac{1}{2}\,,$$

$$\begin{matrix}(e_1\ f_2)\\(e_2\ f_1)\end{matrix}\ ,\quad \begin{bmatrix} E''_1 & E''_2 & \dots & E''_{\frac{N}{2}} \\ F''_1 & F''_2 & \dots & F''_{\frac{N}{2}} \end{bmatrix},$$

$$d(G''_4) = -\tfrac{1}{2}\,,$$

where the matrix elements are evaluated by eq. (12) according to the pairing patterns. The contracted cofactors corresponding to the subgraph-representative G_4 can be evaluated by the following formula:

$$EF_{kl} = (E_kF_l + E_lF_k) - \tfrac{1}{2}(E'_kF'_l + E'_lF'_k + E''_kF''_l + E''_lF''_k)\,.$$

In the program, these quantities are stored in a two-dimensional array, in which each column is a set of contracted cofactors of a subgraph-representative. Generally, after obtaining all the contracted cofactors of order n, the quantities of lower order can be discarded. One can evaluate the contracted cofactors of order $n+1$ by using only the contacted cofactors of order n as shown below:

$$L^{AB\dots C}_{kl\dots m} = \sum_{G_D} F_D \sum_{r\neq k,l,\dots m} D_r L^{AB\dots CD}_{kl\dots mr}\,, \tag{61}$$

where $L^{AB\dots C}$ are contracted cofactors of order $n+1$, and $L^{AB\dots CD}$ are contracted cofactors of order n, D_r are matrix elements corresponding to the pair G_D (i.e. a subgraph of 2 elements), and the F_D is the group theoretical factor associated with the pair G_D. To evaluate the contracted cofactor of order $n+1$, the lower contracted cofactors of $2n+1$ subgraph-representatives are involved. The first summation in eq. (61) goes over $2n+1$ combinations of a pair G_D and a subgraph representative

of $2n$ elements. The second summation comes from the Laplace expansion. Thus for each subgraph-representation of $2n+2$ elements, we need $2n+1$ terms to describe the $2n+1$ combinations, and each term gives the following information: the pair D, the factor F_D, and the index of the subgraph representative. As all these group theoretical quantities are independent of the chemical system under consideration, it is more convenient to store all these quantities in a universal file, and they can be used forever. The whole computational process is controlled by such a universal file, which represents the knowledge of all unique subgraph-representatives. Thus this procedure is called "subgraph-driven" method. After evaluating the two-electron term of the Hamiltonian, all the required contracted cofactors of order $\frac{1}{2}N-2$ are available for evaluating the one-electron part and the overlap. In fact, both of them are computed during the calculation of the two-electron term.

(c) Comparison with other methods

In connection with this work, it might be interesting to mention the works of quite a few other authors [4,16,17,21]. Similar recurrence relations of left coset decompositions are described by Gerratt [16] and were used by Pyper and Gerratt [17] to construct density matrices of various order $D^{(n)}$. However, the explicit evaluation of the group representation matrix elements of permutations is avoided in this work. The use of graph theory in the Slater-determinant expansion of VB calculations was represented recently by Rettrup and Thorsteinsson [21], and was applied by Cooper et al. [4] in the spin-coupled VB theory. The essential idea in this work is similar to the strategy in the "super-cofactor" method [4], that is to avoid repeated computation by introducing some kind of intermediate quantities which will be frequently used in the overall computation. Therefore this strategy reduces significantly the computational effort in the group theoretical approaches. Although this paper is concentrated on the efficiency of evaluating one individual VB matrix element, it is possible to follow the same global strategy in the calculations of the multistructure VB wave functions. A detailed discussion on this is beyond the scope of this paper.

7. Programming and the efficiency of the new algorithm

A new version of the program AMOY-VB has been developed according to the formalism shown above, To run the program, a universal file which is related only to the symmetric group S_N is used. This file can be created by the graph-analysis program, and the size depends on N, the number of electrons of the system. Usually, the CPU time for creating this file is comparable with that for the VB calculations, thus it is better to prepare this file separately, and store it in a permanent file for repeated use. In addition to the capability of performing multistructure VB calculations, the program can also be used for the orbital optimization. The super-CI method [22] and the DIIS [23] technique have been implemented in the

program. To evaluate all the VB matrix elements in an efficient way, the program also follows a global strategy. Details of the algorithm for the efficient evaluation of the super-CI matrix elements will be reported elsewhere.

To check the program, some testing calculations of simple systems were performed. As there are no data of nonorthogonal VB calculations for more than 12 electrons available, we have chosen some special hypothetical systems consisting of hydrogen atoms:

$$\begin{array}{l} H{-}{-}H{-}{-}H\ldots H \\ R\,|\quad\ |\quad\ |\quad\ | \\ H{-}{-}H{-}{-}H\ldots H \\ \quad R \end{array}$$

where R is the distance between two hydrogen atoms. The reason we have chosen these system is that we can make predictions even without VB calculations, and therefore it is able to make comparison with the explicit VB calculations.

(a) A well-known advantage of VB theory is that it can give the correct results for the dissociation limit. Thus the first test calculation is done for H_{16} with distance $R = 10$ Å. In this case, the VB energy should be very close to the UHF energy. This is exactly the case (no difference within the machine accuracy).

$$E(\mathrm{UHF}) = -7.46530960615 \text{ a.u. (STO-3G)},$$

$$E(\mathrm{VB}) = -7.46530960615 \text{ a.u.}$$

(b) VB calculation of doubly occupied system: H_8^{8-} with $R = 1.0$ Å. As the minimal basis set is used, all the 8 linear independent orbitals are doubly occupied by the 16 electrons, and any kind of many body wave functions have the exactly the same energy. Our VB program also gives the same value:

$$E(\mathrm{RHF}) = 12.0093959554 \text{ a.u. (STO-3G)},$$

$$E(\mathrm{VB}) = 12.0093959554 \text{ a.u.}$$

(c) H_{2n} ($n = 1, 2, \ldots, 10$), with distance $R = 1.0$ Å. We can expect for H_{2n} that: (1) As a H_2 unit is added to the chain, the increment of the total energy of H_{2n} should converge to a definite value quickly. (2) The overlap of the VB function should change in an exponential way, i.e. $S^n = S^{n-1} \cdot S^0$, where $S^n = \langle \Psi_{\mathrm{VB}}^n | \Psi_{\mathrm{VB}}^n \rangle$ and S^0 converges to a constant quickly. This is the case as shown in table 2.

(d) CH_4, with $R_{\mathrm{C-H}} = 1.082$ (optimized geometry with 6-31G/RHF). The self-consistent-field valence bond (SCFVB) calculation and the spin-coupled VB (SCVB) [4] calculation were performed for this molecule using 6-31G basis set. In the SCFVB calculation, 8 orbitals for constructing the four C–H bonds were optimized using the super-CI method [22] and DIIS technique [23]. It turns out that 4 optimized orbitals have strong parentage of the four coresponding sp^3 hybridized

Table 2
The total energy (a.u.) and overlap of H_{2n}. The STO-3G basis set is used.

$2n$	E(VB)	$\Delta E = E_n - E_{n-1}$	S^n	$S^0 = S^n/S^{n-1}$
2	−1.076241	−1.076241	1.246497	1.246497
4	−1.850558	−0.774317	0.965155	0.774294
6	−2.633248	−0.782690	0.744548	0.771429
8	−3.415835	−0.782587	0.573915	0.770823
10	−4.197545	−0.781710	0.442283	0.770642
12	−4.979258	−0.781713	0.340847	0.770654
14	−5.760944	−0.781686	0.262675	0.770654
16	−6.542619	−0.781675	0.202431	0.770652
18	−7.324290	−0.781671	0.156004	0.770653
20	−8.105959	−0.781669	0.120225	0.770653

orbtials of the carbon atom, and the other 4 orbitals have obvious parentage of the corresponding s-orbitals of hydrogen atoms. The energies of SCFVB and SCVB wave functions, respectively, are given as following:

$$E(\text{SCFVB}) = -40.24281587 \text{ a.u.},$$

$$E(\text{SCVB}) = -40.24678847 \text{ a.u.},$$

$$E(\text{RHF}) = -40.18055416 \text{ a.u.},$$

where E(RHF) is the energy of the Hartree–Fock wave function. The optimized orbitals from the SCFVB calculation were used for the construction of the SCVB wave function without further optimization. The 14 independent VB structures are all included in the SCVB calculation. It is found that the SCFVB wave function has a very large overlap (0.997) with the SCVB wave function (both wave functions are normalized). This also means that the SCVB calculation does not change much the wave function in the case of methane molecule.

The above test calculations make us certain that the new algorithm is both theoretically and technically correct. Moreover, the practice shows that the new program is very efficient, and the CPU time increases in a quite moderate way with increasing N. Table 3 shows the CPU time and the approximate estimation of the number of multiplications for a single VB calculation.

Table 3
The CPU-time T (s) of nonorthogonal VB calculations of N electrons on HITAC/S820 and the approximate estimation of the number (M) of multiplications.

N	$\leqslant 10$	12	14	16	18	20
T	< 0.1	0.5	2.0	7.5	35	227
M		2.3×10^6	8.6×10^6	8.8×10^7	6.9×10^8	5.9×10^9
$N!$		4.8×10^8	8.7×10^{10}	2.1×10^{13}	6.4×10^{15}	2.4×10^{18}

8. Summary

In this paper, a highly efficient algorithm for nonorthogonal VB calculations is proposed in the group theoretical formalism. The efficiency of the new algorithm comes from two aspects: (a) The contracted cofactors are introduced as the intermediate quantities, which are repeatedly used in the systematic summation over all permanents. These quantities can be characterized by some pairing graphs of $2n$ elements ($n = 1, 2, \ldots$), and each pairing graph of $2n$ elements corresponds a set of $C(\frac{1}{2}N : n)$ contracted cofactors. (b) The numbers of pairing graphs of various order in the "subgraph-driven" procedure increase in a quite moderate way with the increasing number of electrons. Repeated computation is efficiently avoided in the new algorithm. Further improvement of the program will be on technical aspects, e.g. vectorization and parallelization on large computers, and installation of some new supporting codes.

The present work shows that it is possible to find a powerful algorithm in the spin-free formalism of VB wave functions and gives us strong confidence in the group theoretical approach. In principle, the same strategy can be used for the case of spin $S > 0$. Actually, the case of spin $S = \frac{1}{2}$ can be treated in exactly the same way as the case of $S = 0$.

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Appendix

It can be shown that among all the pairing graphs of N elements, there is one and only one graph which has the maximal absolute D_{11}-value, and we denote this graph as G_N^1. It has the following pairing pattern:

$$
\begin{array}{c}
(1 \quad 2) \\
(3 \quad 4) \\
\cdots \\
(2k-1 \quad 2k) \\
\cdots \\
(N-1 \quad N)
\end{array}
$$

Before further discussion, let us define an integer function $PA(n)$:

$$
\begin{aligned}
&PA(2k-1) = 2k \\
&PA(2k) = 2k-1
\end{aligned}
\qquad (k = 1, 2, \ldots). \tag{62}
$$

Obviously function $PA(n)$ is an operator to find the partner of number n in the pairing graph G_N^1.

Now, let us consider a subset of pairing graphs of N elements. In this subset, every graph has a pair $A(=(a_1 \quad a_2), a_1 < a_2)$ in common. Obviously, each pairing graph of this subset can be partitioned into two subgraphs G_A and G_i^A, where the subgraph G_A consists of the pair A, and the other subgraph G_i^A is one of the pairing graphs of $N-2$ elements (1, 2, ..., N, without a_1, and a_2). There are two cases.

Case I: $PA(a_1) = a_2$, that means if a_1 is an odd number, say $2k-1$, then a_2 is the consecutive even number $2k$.

In this case we have the following results:

(a) There is one and only one graph G_1^A in this subset which has the maximal absolute D_{11}-value, and it has the same pattern as G_N^1, except one pair $(2k-1 \quad 2k)$ is taken away. This subgraph G_1^A is

$$
\begin{array}{cc}
\begin{array}{c}
(1 \quad 2) \\
(3 \quad 4) \\
\cdots \\
(2k-3 \quad 2k-2) \\
(2k+1 \quad 2k+2) \\
\cdots \\
(N-1 \quad N) \\
G_1^A
\end{array}
&
\begin{array}{c}
\\
\\
\\
\overset{\hat{R}}{\Rightarrow} \\
\\
\\
\\
\\
\end{array}
\qquad
\begin{array}{c}
(1 \quad 2) \\
(3 \quad 4) \\
\cdots \\
(2k-3 \quad 2k-2) \\
(2k-1 \quad 2k) \\
\cdots \\
(N-3 \quad N-2) \\
G_{N-2}^1
\end{array}
\end{array}
$$

(b) Let $\hat{R}$ be a operator which renumber the elements in subgraphs G_1^A in such a way that it changes G_1^A, as shown above, into G_{N-2}^1. For example, one can choose such an operator $\hat{R}$ as

$$\hat{R} = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & 2k-3 & 2k-2 & 2k+1 & 2k+2 & \dots & N-1 & N \\ 1 & 2 & 3 & 4 & \dots & 2k-3 & 2k-2 & 2k-1 & 2k & \dots & N-3 & N-2 \end{pmatrix} \tag{63}$$

Then we have

$$D_{11}(G_A, G_i^A) = D_{11}(G_{N-2}^i), \tag{64}$$

where

$$G_{N-2}^i = \hat{R} G_i^A \tag{65}$$

and $D_{11}(G_{N-2}^i)$ is the D_{11}-value of the pairing graph of the symmetric group S_{N-2}.

Case II: $PA(a_1) \neq a_2$. Suppose $a_1 \in (2k-1, 2k)$, and $a_2 \in (2l-1, 2l)$, $k < l$.

In this case, G_1^A has the same pattern as G_N^1, except two pairs $(a_1 \;\; PA(a_1))$ and $(a_2 \;\; PA(a_2))$ are replaced by one new pair $(PA(a_1) \;\; PA(a_2))$. Let R be an operator to change G_1^A into G_{N-2}^i; for example,

$$\hat{R} = \begin{pmatrix} 1 & \dots & 2k-2 & PA(a_1) & PA(a_2) & 2k+1 & \dots & 2l-2 & 2l+1 & 2l+2 & \dots & N \\ 1 & \dots & 2k-2 & 2k-1 & 2k & 2k+1 & \dots & 2l-2 & 2l-1 & 2l & \dots & N-2 \end{pmatrix} \tag{66}$$

then we have the similar expression:

$$D_{11}(G_A, G_i^A) = -\tfrac{1}{2} D_{11}(G_{N-2}^i), \tag{67}$$

where

$$G_{N-2}^i = \hat{R} G_i^A .$$

The above expressions show us a way to evaluate the D_{11}-values of the left cosets of S_N from the D_{11}-values of the lower symmetric group S_{N-2}. Obviously, similar relation exists between S_{N-2} and S_{N-4}. Therefor the above relationship gives the complete knowledge about D_{11}-values of cosets. Actually, we do not evaluate D_{11}-values explicitly, while the above recurrence relations are used in the calculations. Comparing eq. (64) and eq. (67), they differ from each other only by a factor $-\frac{1}{2}$. Therefore we can assign a value to subgraph G_A, i.e. the pair A, in the following way: in case I, the subgraph G_A has a factor 1, and in case II G_A has a factor $-\frac{1}{2}$.

Since the two-electron factors g_{kl}^{AB} in eq. (21) are associated with a subgraph of two pairs, let us consider such a subset of pairing graphs: each of them consists of subgraph G_{AB}^i and G_j^{AB}, where G_{AB}^i is one of the subgraphs of 4 elements (a, b, c, d) (without lose of generality, we can assume that $a < b < c < d$), and G_j^{AB} is one of the subgraphs of the remaining $N-4$ elements $(1, 2, \dots, N$, without a, b, c and $d)$. There are 3 cases:

Case I: $PA(a) = b$ and $PA(c) = d$.

Case II: One pair of elements from $(a\,b\,c\,d)$, say a' and b', satisfy $PA(a') = b'$. There are three subcases: (1) $PA(a) = b$, $PA(c) \neq d$; (2) $PA(b) = d$, $PA(a) \neq c$; (3) $PA(a) \neq b$, $PA(c) = d$.

Case III: $PA(a) \neq b$, $PA(b) \neq c$ and $PA(c) \neq d$.

In case I we can assume $a = 2k-1, b = 2k, c = 2l-1, d = 2l$, and we have

$$D_{11}(G^i_{AB}, G^{AB}_j) = d(G^i_{AB}) \cdot d(G^{AB}_j) \quad (i = 1,2,3;\ j = 1,2,\ldots M_{N-4}), \tag{68}$$

where $d(G^i_{AB})$ take the following values:

$$\begin{array}{lccc} G^i_{AB} & (a\ b) & (a\ c) & (a\ d) \\ & (c\ d) & (b\ d) & (b\ c) \\ d(G^i_{AB}) & 1 & -\frac{1}{2} & -\frac{1}{2} \end{array} \tag{69}$$

and $d(G^{AB}_j)$ changes in a parallel way as the D_{11}-values of the left cosets of S_{N-4}:

$$d(G^{AB}_j) = D_{11}(G^j_{N-4}). \tag{70}$$

The correspondence between G^{AB}_j and G^j_{N-4} is set up by the following operation:

$$G^j_{N-4} = \hat{R} G^{AB}_j, \tag{71}$$

where the operator $\hat{R}$ renumbers the elements of G^{AB}_j in the following way:

$$\hat{R} = \begin{pmatrix} 1 & \ldots & 2k-2 & 2k+1 & 2k+2 & \ldots & 2l-2 & 2l+1 & 2l+2 & \ldots & N \\ 1 & \ldots & 2k-2 & 2k-1 & 2k & \ldots & 2l-4 & 2l-3 & 2l-2 & \ldots & N-4 \end{pmatrix}. \tag{72}$$

For case II, it is enough to show the result for the subcase $PA(a) = b$. In this case we can assume $a = 2k-1$, and $b = 2k$, and we have

$$D_{11}(G^i_{AB}, G^{AB}_j) = -\tfrac{1}{2} d(G^i_{AB}) \cdot d(G^{AB}_j) \quad (i = 1,2,3;\ j = 1,2,\ldots M_{N-4}), \tag{73}$$

where $d(G^i_{AB})$ take the same values as shown in eq. (69) and

$$d(G^{AB}_j) = D_{11}(G^j_{N-4}), \tag{74}$$

where

$$G^j_{N-4} = \hat{R} G^{AB}_j \tag{75}$$

and the operator $\hat{R}$ is as shown below:

$$\hat{R} = \begin{pmatrix} 1 & \ldots & 2k-2 & 2k+1 & 2k+2 & PA(c) & PA(d) & \ldots & N-1 & N \\ 1 & \ldots & 2k-2 & 2k-1 & 2k & 2k+1 & 2k+2 & \ldots & N-5 & N-4 \end{pmatrix}. \tag{76}$$

For case III, we have

$$D_{11}(G^i_{AB}, G^{AB}_j) = \tfrac{1}{4} D_{11}(G^{ij}_{N-4}), \tag{77}$$

where

$$G^{ij}_{N-4} = \hat{R}_i G^{AB}_j \quad (i = 1,2,3;\ j = 1,2,\ldots M_{N-4}) \tag{78}$$

and the operator $\hat{R}_i$ depends on the subgraph G^i_{AB}. Suppose the subgraph G^i_{AB} has two pairs as follows:

$$G^i_{AB} = \begin{matrix}(a' & b')\\ (c' & d')\end{matrix}, \quad \text{where } (a',b',c',d') \in (a,b,c,d)\,, \tag{79}$$

then the operator $\hat{R}_i$ can be chosen as following:

$$\hat{R}_i = \begin{pmatrix} 2k-1 & 2k & 2l-1 & 2l & \ldots & PA(a') & PA(b') & PA(c') & PA(d') \\ 1 & 2 & 3 & 4 & \ldots & N-7 & N-6 & N-5 & N-4 \end{pmatrix}. \tag{80}$$

Generally, if G_{2n} is a subgraph of $2n$ elements, and G^{N-2n}_i is one of the subgraphs of the remaining $N-2n$ elements, then we have

$$D_{11}(G_{2n}, G^{N-2n}_i) = F(G_{2n}) \cdot D_{11}(G^i_{N-2n}) \quad (i = 1,2,\ldots M_{N-2n})\,, \tag{81}$$

where

$$G^i_{N-2n} = \hat{R} G^{N-2n}_i\,.$$

Here $F(G_{2n})$ is a factor which only depends on the subgraph G_{2n}, and it can be obtained from the recurrence relations shown above. $\hat{R}$ is an operator to renumber the elements of the subgraphs, and $D_{11}(G^i_{N-2n})$ are the D_{11}-values of S_{N-2n}.

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