Theor Chim Acta (1994) 89: 105–121

**Theoretica Chimica Acta**



# New algorithm for nonorthogonal *ab initio* valence-bond calculations

## I. New strategy and basic expressions

**Jiabo Li**[1,2], **Wei Wu**[1]

[1] Department of Chemistry, Xiamen University, 361005, P.R. of China
[2] Theoretical Chemistry, Friedrich-Alexander University Erlangen Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany

Received December 6, 1993/Accepted April 1, 1994

**Summary.** A new algorithm for nonorthogonal *ab initio* valence bond calculation has been deduced based on the left-coset decomposition of the symmetric group $S_N$. The strategy in the new approach is that, instead of performing the summation over $N!$ permutations of group $S_N$, we sum the left cosets, and each coset corresponds to a "positive determinant" of order $N/2$ for the evaluation of overlap, or a few positive determinants for Hamiltonian. Therefore, the computation turns into accumulating positive determinants. The expressions for evaluating both overlap and Hamiltonian matrix elements of VB functions are given in detail. Our practice shows that such a positive determinant method is quite attractive and it provides an excellent starting point for developing an even much more efficient algorithm of nonorthogonal VB calculation.

**Key words:** Valence–bond method – Nonorthogonal problem – Group theoretical approach

## 1 Introduction

Electron correlation plays a central role in many chemical phenomena. To deal with this problem, various theoretical methods have been used. Among them, the MO-theory based CI method is the mostly used one. The other is the valence–bond (VB) method [1]. One striking advantage of VB theory is that it is closely related to the well established chemical concepts such as valence [2], hybridization and resonance [3]. The VB function constructed from nonorthogonal orbitals incorporates considerable correlation in a very physical and highly visual way [4, 5], thus can reveal new insights into some fundamental phenomena. However, the practical calculation based on nonorthogonal orbitals is still a great challenge due to the nonorthogonal difficulty (or sometimes referred to as $N!$ problem). Probably, the most practical approach is to expand the VB wave function as a linear combination of $2^{\frac{1}{2}N-S}$ Slater-determinants and consequently evaluate the contributions of each pair of Slater determinants by using Löwdin's rules [6] for determinants of nonorthogonal orbitals. This method was used long ago by Matsen [7], Raimondi [8], Barlint-Kurti and Karplus [9], and recently by Cooper et al. [4] and Sironi et al. [5], and van Lenthe's group [10–12]. The difficulty of this method

resides on the exponentially increasing length of expansion and the need for repeated evaluation of determinant cofactors. To avoid the nonorthogonal difficulty while keep some advantages of nonorthogonal VB theory, the so-called GVB method was proposed [13], and it was successfully applied to a wide range of systems. Recently, some technical approaches to this problem have been extensively investigated [10, 11, 14]. Another mathematically beautiful method is the group theoretical approach [15–23]. In this formalism, the spin-free form of the VB function is used [22]. Such a form of VB wave function can be obtained by $\Psi_{VB} = e_{11}^{[\lambda]}\Omega$, where $e_{11}^{[\lambda]}$ is a standard projection operator associated with the first Young–Yamanouchi basis of irrep $[\lambda] = [2^{\frac{1}{2}N-S}, 1^{2S}]$, and $\Omega$ is a simple product of single particle orbitals, i.e. $\Omega = \prod_i \phi_i(i)$. This form of VB wave function leads to the expressions involving $N!$ (permutations) terms for both overlap and Hamiltonian. Such a formalism is used by McWeeny in the "permutation-driven" procedure [22]. As the computationl effort increases in an alarming rate with increasing $N$, this approach seems to be workable only for quite small systems. Although the mathematics of VB wave function has been extensively investigated [15–25], the development on the technical aspects of the group theoretical approach have not been so well developed as for the Slater-determinant method [4, 5, 10–12, 14].

In modern chemistry, it is more acceptable to seek some "primitive patterns of understanding", therefore much attention has been turned back to the VB theory [1], and there is a considerable resurgence on *ab initio* VB calculations [4, 5, 10–12, 14, 22]. Thus there is a strong need for a powerful method for nonorthogonal VB calculations. To find even a partial solution to the $N!$ problem, the fundamental research together with highly efficient algorithm and computer techniques are required. As the VB wave function is closely related to the symmetric group $S_N$, it seems more reasonable to seek a powerful algorithm in the group theoretical approach. In this paper we present a new algorithm in spin-free formalism. In this algorithm, the positive determinants are introduced for evaluating overlap and Hamiltonian matrix elements of VB functions. The practice shows that this method is quite promising, and it provides a starting point for a more sophisticated treatment.

## 2 Spin-free form of the VB wave function and the nonorthogonal difficulty

The general form of valence bond wave function, called HLSP function [26, 27], is the extension of Heitler–London function [28]. It can be obtained by antisymmetrizing a product of a spin eigenfunction and a spatial function as $\Psi_{VB} = \hat{A}\Omega\Theta$, where $\hat{A}$ is the antisymmetrizer $\hat{A} = \sum_P \delta(P)P$, ($\delta(P) = \pm 1$ according to the parity of the permutation $P$), $\Omega = \prod_i \phi_i(i)$, and $\Theta$ is an eigenfunction of spin, $S$:

$$\Theta = \prod_{i=1}^{N/2-S} 2^{-1/2}[\alpha(2i-1)\beta(2i) - \beta(2i-1)\alpha(2i)] \prod_{j=N-2S-1}^{N} \alpha(j). \tag{1}$$

Such a VB wave function describes the chemical bonding of the following orbital pairs: $\phi_1$–$\phi_2$, $\phi_3$–$\phi_4$, ..., $\phi_{\frac{1}{2}N-S-1}$–$\phi_{\frac{1}{2}N-S}$. Obviously, it is a linear combination of $2^{\frac{1}{2}N-S}$ Slater determinants.

Over the past several decades, the mathematical form of VB theory has been extensively studied and many excellent relations were revealed. For example, if the Hamiltonian is free of spin operators, then the many electron wave function can be expressed in spin-free form [15, 22–25]. The symmetry-adapted spin-free VB

function can be obtained by projecting a simple orbital product with a standard projection operator $e_{11}^{[\lambda]}$ [22–25], i.e.

$$\Psi_{\mathrm{VB}} = e_{11}^{[\lambda]}\Omega, \tag{2}$$

where

$$e_{11}^{[\lambda]} = \left(\frac{f_\lambda}{N!}\right)^{\frac{1}{2}} \sum_{P\in S_N} D_{11}^{[\lambda]}(P)P \tag{3}$$

and

$$\Omega = \phi_1(1)\phi_2(2)\ldots\phi_N(N), \tag{4}$$

$f_\lambda$ is the dimension of the irrep $[\lambda] = [2^{\frac{1}{2}N-S}, 1^{2S}]$, and $D_{11}^{[\lambda]}(P)$ are the irreducible-representation-matrix-elements associated with the first Young–Yamanouchi basis. $D_{11}^{[\lambda]}(P)$ can be evaluated either by Rumer–Pauling algorithm [29] or by a simpler algorithm proposed by Zhang [30]. For the case $S = 0$, the procedure is even simpler: first we draw lines between every two elements in the following way: 1–2, 3–4, ..., $(2k-1)$–$2k$, ..., $(N-1)$–$N$. Suppose a permutation $P$ takes the following form:

$$P = \begin{pmatrix} 1 & 2 & 3 & 4 & \cdots & N-1 & N \\ P_1 & P_2 & P_3 & P_4 & \cdots & P_{N-1} & P_N \end{pmatrix}, \tag{5}$$

then we draw lines between every two elements in another way as below: $P_1$–$P_2$, $P_3$–$P_4$, ..., $P_{2k-1}$–$P_{2k}$, ..., $P_{N-1}$–$P_N$, thus we get a graph of $N$ elements linked by $N$ lines. These lines form some topological loops. Suppose the number of loops is $L$, then we have

$$D_{11}^{[\lambda]}(P) = \left(-\frac{1}{2}\right)^{N/2-L}. \tag{6}$$

Such a form of VB function leads to the following expression for the evaluation of the overlap and Hamiltonian matrix elements of VB functions:

$$\langle\psi_{\mathrm{VB}}|\psi_{\mathrm{VB}}\rangle = \sum_{P\in S_N} D_{11}^{[\lambda]}(P)\langle\Omega|P\Omega\rangle, \tag{7a}$$

$$\langle\psi_{\mathrm{VB}}|H|\psi_{\mathrm{VB}}\rangle = \sum_{P\in S_N} D_{11}^{[\lambda]}(P)\langle\Omega|H|P\Omega\rangle. \tag{7b}$$

These are the basic expressions for the group theoretical approach. Although extensive investigations on VB wave functions have been made, less progress has been achieved on the technical aspects of computation in the group theoretical approach. In both expressions, the summation runs over $N!$ permutations. If the orbitals are orthogonal, then most of the terms are zero, however if the orbitals are nonorthogonal, most of the terms are not zero (in the case of $S = 0, \frac{1}{2}$ no term is null), and one has to evaluate all these terms explicitly. In the above expressions, each term is a product of two factors, one is the group theoretical factor $D_{11}^{[\lambda]}(P)$ and the other is the physical factor. Thus to evaluate each term one needs to evaluate both factors. Although there are some simple rules to evaluate $D_{11}^{[\lambda]}(P)$ quite easily, it does not seem to help much for solving the $N!$ problem. It is not practicable to apply the above expression for nonorthogonal VB calculations when the number of electrons is large.

## 3 The new idea for nonorthogonal VB calculations

To explain the idea in a simple way, we restrict our consideration to the case of spin $S = 0$ in the following discussion. The new idea of nonorthogonal VB calculation using group theoretical method comes from the following consideration. As mentioned above, each term in Eqs. (7a) and (7b) is a product of a group theoretical factor $D_{11}^{[\lambda]}(P)$ and a physical factor $\langle\Omega|P\Omega\rangle$ (or $\langle\Omega|H|P\Omega\rangle$). The group theoretical factor is independent of the system, and it has some simple values as expressed by Eq. (6). As a result, it seems much better to classify the permutations of $S_N$ in some way according to their $D_{11}$-values, thus we need not evaluate them explicitly. This idea was used long ago by Klein to deal with projection operations of the symmetric group [18, 19]. Moreover, the physical factor is also a product of several factors, for example:

$$\langle\Omega|P\Omega\rangle = S_{1p_1}S_{2p_2} \ldots S_{ip_i} \ldots S_{Np_N}, \tag{8}$$

where $P$ is a permutation as shown by Eq. (5), and

$$S_{1p_1} = \langle\phi_1|\phi_{1p_1}\rangle, \ \ldots, \ S_{ip_i} = \langle\phi_i|\phi_{ip_i}\rangle, \ \ldots, \ S_{Np_N} = \langle\phi_N|\phi_{p_N}\rangle.$$

In the following discussion, the permutations are defined to act on the indexes of orbitals. For example, if the permutation $P$ is shown in Eq. (5), then we have

$$P\phi_1(1)\phi_2(2) \ldots \phi_N(N) = \phi_{p_1}(1)\phi_{p_2}(2) \ldots \phi_{p_N}(N). \tag{9}$$

As the permutation $P$ changes smoothly, i.e. from one permutation to another, only a small number of elements $\{P_i\}$ in Eq. (5) change their positions, then only the same number of these factors $\{S_{ip}\}$ change. Therefore the basic idea of reducing computational effort is to find a systematic way to make use of this fact. However without a powerful mathematic formalism we do not know how to do it exactly. The key to this problem is the left-coset decomposition of the symmetric group $S_N$. This idea is stimulated by the early work of Gallup [17], Klein and Junker [18, 19] and also by the recent work of Wu and Zhang [26]. We found that the left-coset decomposition of $S_N$ provides a proper way to classify the $N!$ permutations of $S_N$ for the above purpose, and the summation going over each left-coset corresponds to a positive determinant. Moreover, this positive determinant method seems to be an excellent starting point for a more powerful group theoretical approach. In this paper, the details of this new method are given.

*Definition of subgroup Q.* The definition of subgroup $Q$ comes from the properties of the first Young–Yamanouchi basis $|[\lambda]\rangle$ (and VB wave function have the same properties) upon permutations:

$$Q_j|[\lambda]\rangle = |[\lambda]\rangle \quad (Q_j \in Q) \tag{10}$$

and $Q$ can be expressed as a product of two subgroups $G_1$ and $G_2$: $Q = G_1 \times G_2$. Let us give the explicit expression of $G_1$ and $G_2$. Suppose we assign indexes $1, 2, \ldots, N$ in the two-column boxes of the Young diagram $[\lambda] = [2^{\frac{1}{2}N}, 1^0]$ from

left to right and from top to bottom as follow:

| | |
|---|---|
| 1 | 2 |
| 3 | 4 |
| ⋮ | ⋮ |
| $2i-1$ | $2i$ |
| ⋮ | ⋮ |
| $N-1$ | $N$ |

(a)

Let $T_i$ be the symmetric group of the indices in the $i$th row, i.e. $T_i = [e, (2i-1\ 2i)]$, then $G_1$ is the direct product of all $T_i$, i.e. $G_1 = [e, (1\ 2)] \otimes [e, (3\ 4)] \otimes \ldots \otimes [e, (2i-1\ 2i)] \otimes \ldots \otimes [e, (N-1\ N)]$, and subgroup $G_2 = \{P_1 P_2\}$, where $P_1$ are permutations of indices in the first column, i.e. the odd numbers, while $P_2$ are the corresponding permutations of even number indices $2i$ ($i = 1, 2, \ldots, N/2$).

It is easier to understand the subgroup $Q$ in the following way: suppose we represent a permutation $P$ of Eq. (5) in a two-column-box form as following:

| | |
|---|---|
| $p_1$ | $p_2$ |
| $p_3$ | $p_4$ |
| ⋮ | ⋮ |
| $p_{2i-1}$ | $p_{2i}$ |
| ⋮ | ⋮ |
| $p_{N-1}$ | $p_N$ |

(b)

thus the elementary permutation can be show as (a). Now we have $N/2$ pairs 1–2, 3–4, ..., $(2i-1)$–$2i$, $(N-1)$–$N$, and each pair occupies a row, and each element of the pair occupies one of the two boxes in the row. Obviously, there are $2^{\frac{1}{2}N}(\frac{1}{2}N)!$ ways to occupy the two-column boxes, and each way corresponds to a permutation of subgroup $Q$. Thus subgroup $Q$ has $2^{\frac{1}{2}N}(\frac{1}{2}N)!$ permutations. It is easy to know that subgroup $G_1$ represents the intra-row exchange (there are $2^{\frac{1}{2}N}$ ways), while $G_2$ represents the order of the $N/2$ pairs (there are $(\frac{1}{2}N)!$ arrangements of $N/2$ pairs. For example, the symmetric group $S_4$ has a subgroup $Q$ of 8 permutations, which can be shown in the two-column-box form as following:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 1 | 2 | 2 | 1 | 2 | 1 |
| 3 | 4 | 4 | 3 | 3 | 4 | 4 | 3 |
| , | | , | | , | | , | |
| 3 | 4 | 3 | 4 | 4 | 3 | 4 | 3 |
| 1 | 2 | 2 | 1 | 1 | 2 | 2 | 1 |
| , | | , | | , | | . | |

*The left-coset-decomposition of the symmetric group* $S_N$. The $N!$ permutations of $S_N$ group can be classified according to the following left-coset decomposition of $S_N$:

$$S_N = \bigcup_i q_i Q. \tag{11}$$

This means, the $N!$ permutations are divided into a number of left cosets, and each left coset $q_iQ$ has the same number of permutations as the subgroup $Q$. $q_i$ is the left-coset generator (representative) of the left coset $q_iQ$. Actually, any permutation of the coset can be chosen as the representative of the coset. For example, $S_4$ can be partitioned into three left cosets in the following way:

$q_1Q =$ $\begin{array}{|c|c|}\hline 1&2\\\hline 3&4\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 1&2\\\hline 4&3\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 2&1\\\hline 3&4\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 2&1\\\hline 4&3\\\hline\end{array}$,

$\begin{array}{|c|c|}\hline 3&4\\\hline 1&2\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 3&4\\\hline 2&1\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 4&3\\\hline 1&2\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 4&3\\\hline 2&1\\\hline\end{array}$,

$q_2Q =$ $\begin{array}{|c|c|}\hline 1&3\\\hline 2&4\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 1&3\\\hline 4&2\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 3&1\\\hline 2&4\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 3&1\\\hline 4&2\\\hline\end{array}$,

$\begin{array}{|c|c|}\hline 2&4\\\hline 1&3\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 2&4\\\hline 3&1\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 4&2\\\hline 1&3\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 4&3\\\hline 2&1\\\hline\end{array}$,

$q_3Q =$ $\begin{array}{|c|c|}\hline 1&4\\\hline 3&2\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 1&4\\\hline 2&3\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 4&1\\\hline 3&2\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 4&1\\\hline 2&3\\\hline\end{array}$,

$\begin{array}{|c|c|}\hline 3&2\\\hline 1&4\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 3&2\\\hline 4&1\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 2&3\\\hline 1&4\\\hline\end{array}$, $\begin{array}{|c|c|}\hline 2&3\\\hline 4&1\\\hline\end{array}$,

The meaning of the left coset $q_iQ$ can be easily understood. Suppose the coset generator $q_i$ in the two column-box form is as following:

$$\begin{array}{|c|c|}\hline a_1&a_2\\\hline b_1&b_2\\\hline \vdots&\vdots\\\hline d_1&d_2\\\hline\end{array}$$

Thus we have $N/2$ pairs $a_1$–$a_2$, $b_1$–$b_2$, ..., $d_1$–$d_2$, and let each pair occupy one row of the above two-column boxes, and each element of the pair occupies one of the box in the row. All the possible ways to occupy the two-column boxes by these $N/2$ pairs $a_1$–$a_2$, $b_1$–$b_2$, ..., $d_1$–$d_2$ correspond to the permutations of the coset $q_iQ$.

A crucial important property of the coset decomposition is that all permutations belonging to the same left coset have the same $D_{11}$-value. Therefore we need

not evaluate the $D_{11}$-value for each permutation, and we get a new expression of Eqs. (7a) and (7b):

$$\langle \psi_{VB} | \psi_{VB} \rangle = \sum_{q_i} D_{11}^{[\lambda]}(q_i) \sum_{Q_j \in Q} \langle \Omega | q_i Q_j \Omega \rangle , \tag{12}$$

$$\langle \psi_{VB} | H | \psi_{VB} \rangle = \sum_{q_i} D_{11}^{[\lambda]}(q_i) \sum_{Q_j \in Q} \langle \Omega | H | q_i Q_j \Omega \rangle . \tag{13}$$

As will be shown in the next section, the second summation corresponds to a positive determinant.

*Graphic characteristic of left cosets.* As shown above, the left coset $q_i Q$ can be regarded as all possible ways to occupy the two column-boxes for a certain pairing patterns of $N$ elements 1, 2, ..., $N$. Therefore for each left coset generator $q_i$, where

$$q_1 = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & N-1 & N \\ a_1 & a_2 & b_1 & b_2 & \dots & d_1 & d_2 \end{pmatrix} \tag{14}$$

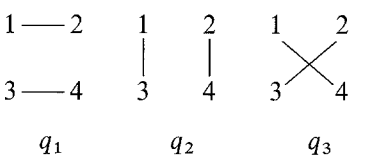
can be characterized by a graph of pairing pattern of $N$ elements:

$$\begin{array}{c} a_1 - a_2 \\ b_1 - b_2 \\ \vdots \\ d_1 - d_2 \end{array}$$

Therefore, the number of pairing patterns of $N$ (even number) elements can be given as

$$M_N = (N-1)(N-3) \dots 3 \times 1 \tag{15}$$

For example, there are 3 coset generators of $S_4$ which correspond to the following 3 pairing patterns of 4 elements:




The $D_{11}$-values of the cosets are as following: $D_{11}^{[\lambda]}(q_1) = 1$, $D_{11}^{[\lambda]}(q_2) = D_{11}^{[\lambda]}(q_3) = -\frac{1}{2}$.

## 4 Overlap matrix elements of VB wave functions

In Eqs. (12) and (13), the $N!$ permutations are divided into a number of left cosets. Let us consider the summation going over a left coset in Eq. (12):

$$\sum_{Q_j \in Q} \langle \Omega | q_i Q_j \Omega \rangle \tag{16}$$

and the generator $q_i$ shown in two-column-box form is as following:

$$q_i = \begin{array}{|c|c|l} \hline a_1 & a_2 & 1 \\ \hline b_1 & b_2 & 2 \\ \hline \vdots & \vdots & \\ \hline c_1 & c_2 & k \\ \hline \vdots & \vdots & \\ \hline d_1 & d_2 & \frac{1}{2}N \\ \hline \end{array} \tag{17}$$

From the above discussion we know that for a left coset $q_iQ$ ( $= q_iG_1 \times G_2$), the subgroup $G_1$ represents the permutations of elements within the pairs $a_1$–$a_2$, $b_1$–$b_2$, ..., $d_1$–$d_2$, and $G_2$ represents the order of these pairs. Thus to run the summation over the left coset we can fix the permutation of $G_2$ and run the summation over $G_1$, that means we keep all the pairs in certain order, say $a, b, \ldots, d$ (here we use $a$ to denote a pair $a_1$–$a_2$, and $b$ denote the pair $b_1$–$b_2$, ...), and accumulate the contribution by exchanging the positions of elements of each pair within the row:

$$\sum_{g_1 \in G_1} \sum_{g_2 \in G_2} \langle \Omega | q_i g_1 g_2 \Omega \rangle . \tag{18}$$

Obviously,

$$q_i\Omega = \phi_{a_1}(1)\phi_{a_2}(2)\phi_{b_1}(3)\phi_{b_2}(4) \ldots \phi_{c_1}(2k-1)\phi_{c_2}(2k) \ldots \phi_{d_1}(N-1)\phi_{d_2}(N) \tag{19}$$

and

$$q_i(1\ 2)\Omega = \phi_{a_2}(1)\phi_{a_1}(2)\phi_{b_1}(3)\phi_{b_2}(4) \ldots \phi_{c_1}(2k-1)\phi_{c_2}(2k) \ldots \phi_{d_1}(N-1)\phi_{d_2}(N), \tag{20}$$

thus

$$\begin{aligned} \sum_{g_1 \in [e,(1\ 2)]} \langle \Omega | q_i g_1 | \Omega \rangle &= (\langle \phi_1 | \phi_{a_1} \rangle \langle \phi_2 | \phi_{a_2} \rangle + \langle \phi_1 | \phi_{a_2} \rangle \langle \phi_2 | \phi_{a_1} \rangle) \cdot \\ &\quad \langle \phi_3 | \phi_{b_1} \rangle \langle \phi_4 | \phi_{b_2} \rangle \ldots \langle \phi_{N-1} | \phi_{d_1} \rangle \langle \phi_N | \phi_{d_2} \rangle \\ &= (S_{1a_1}S_{2a_2} + S_{1a_2}S_{2a_1})S_{3b_1}S_{4b_2} \ldots S_{2k-1c_1}S_{2kc_2} \ldots S_{N-1d_1}S_{Nd_2}, \end{aligned} \tag{21}$$

where

$$S_{1a_1} = \langle \phi_1 | \phi_{a_1} \rangle, \; S_{2a_2} = \langle \phi_2 | \phi_{a_2} \rangle, \; \ldots, \; S_{2k-1c_1} = \langle \phi_{2k-1} | \phi_{c_1} \rangle, \; \ldots \cdot \tag{22}$$

From the same reasoning, the summation over $[e, (1\ 2)] \otimes [e, (3\ 4)]$ leads to the following expression:

$$\begin{aligned} \sum_{g_1 \in [e,(1\ 2)] \otimes [e,(3\ 4)]} \langle \Omega | q_i g_1 | \Omega \rangle &= (S_{1a_1}S_{2a_2} + S_{1a_2}S_{2a_1})(S_{3b_1}S_{4b_2} + S_{3b_2}S_{4b_1}) \\ &\quad \ldots S_{2k-1c_1}S_{2kc_2} \ldots S_{N-1d_1}S_{Nd_2} . \end{aligned} \tag{23}$$

This procedure can go for totally $N/2$ times and finally we have

$$\sum_{g_1 \in G_1} \langle \Omega | q_i g_1 | \Omega \rangle = (S_{1a_1} S_{2a_2} + S_{1a_2} S_{2a_1})(S_{3b_1} S_{4b_2} + S_{3b_2} S_{4b_1}) \ldots (S_{2k-1c_1} S_{2kc_2} + S_{2k-1c_2} S_{2kc_1}) \ldots (S_{N-1d_1} S_{Nd_2} + S_{N-1d_2} S_{Nd_1}), \tag{24}$$

let

$$A_1 = (S_{1a_1} S_{2a_2} + S_{1a_2} S_{2a_1}), \qquad B_2 = (S_{3b_1} S_{4b_2} + S_{3b_2} S_{4b_1}), \ldots$$
$$C_k = (S_{2k-1c_1} S_{2kc_2} + S_{2k-1c_1} S_{2kc_1}), \ldots \qquad D_{N/2} = (S_{N-1d_1} S_{Nd_2} + S_{N-1d_2} S_{Nd_1}), \tag{25}$$

then we get a more compact form of above expression, i.e.

$$\sum_{g_1 \in G_1} \langle \Omega | q_i g_1 | \Omega \rangle = A_1 B_2 \ldots C_k \ldots D_{N/2}. \tag{26}$$

This means that the summation going over $2^{\frac{1}{2}N}$ permutations of subgroup $G_1$ turns to be just one term which is a product of $N/2$ factors, and each factor can be obtained by Eq. (25) very easily. Now let us consider the case that $g_2$ is different from the elementary permutation.

Suppose

$q_i g_2 =$

| | |
|---|---|
| $a'_1$ | $a'_2$ |
| $b'_1$ | $b'_2$ |
| $\vdots$ | $\vdots$ |
| $c'_1$ | $c'_2$ |
| $\vdots$ | $\vdots$ |
| $d'_1$ | $d'_2$ |

(27)

From the definition of $G_2$ it can be known that the $N/2$ pairs $a'_1$–$a'_2$, $b'_1$–$b'_2$, ..., $d'_1$–$d'_2$ is a new order of the pairs $a_1$–$a_2$, $b_1$–$b_2$, ..., $d_1$–$d_2$. If we fix $g_2$ and the subset $q_i G_1 g_2$ is resulted by exchanging the elements within the rows of above diagram, while keep the order of these pairs unchanged. From the same reasoning as above we know that the summation running over the subset $q_i G_1 g_2$ let similar expression:

$$\sum_{g_1 \in G_1} \langle \Omega | q_i g_1 g_2 | \Omega \rangle = A'_1 B'_2 \ldots C'_k \ldots D'_{N/2}. \tag{28}$$

where

$$A'_1 = (S_{1a'_1} S_{2a'_2} + S_{1a'_2} S_{2a'_1}), \qquad B_2 = (S_{3b'_1} S_{4b'_2} + S_{3b'_2} S_{4b'_1}), \ldots$$
$$C'_k = (S_{2k-1c'_1} S_{2kc'_2} + S_{2k-1c'_2} S_{2kc'_1}), \ldots \qquad D'_{N/2} = (S_{N-1d'_1} S_{Nd'_2} + S_{N-1d'_2} S_{Nd'_1}), \tag{29}$$

Therefore the summation over the $(\frac{1}{2}N)!$ permutations of $G_2$ leads to the following "positive determinant" $\det(q_i)$ of order $N/2$,

$$\det(q_i) = \begin{vmatrix} A_1 & A_2 & A_3 & \ldots\ldots & A_{N/2} \\ B_1 & B_2 & B_3 & \ldots\ldots & B_{N/2} \\ \multicolumn{5}{c}{\ldots\ldots\ldots\ldots\ldots\ldots} \\ C_1 & C_2 & C_3 & \ldots\ldots & C_{N/2} \\ \multicolumn{5}{c}{\ldots\ldots\ldots\ldots\ldots\ldots} \\ D_1 & D_2 & D_3 & \ldots\ldots & D_{N/2} \end{vmatrix} \tag{30}$$

i.e. $\det(q_i) = \sum_j \langle \Omega | q_i Q_j | \Omega \rangle$. A positive determinant is different from the usual determinant just by omitting the parity factor ( $\pm 1$) of each term. For example

$$\begin{vmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{vmatrix} = A_1B_2C_3 + A_1C_2B_3 + C_1A_2B_3 + B_1A_2C_3 + B_1C_2A_3 + C_1B_2A_3 \tag{31}$$

(normal determinant $= A_1B_2C_3 - A_1C_2B_3 + C_1A_2B_3 - B_1A_2C_3 + B_1C_2A_3 - C_1B_2A_3$).

As shown above, every $2^{\frac{1}{2}N}$ terms in the permutation-driven procedure turns to be just one term of a positive determinant. Finally, we get a new expression of overlap of VB wave function as following:

$$\langle \psi_{\mathrm{VB}} | \psi_{\mathrm{VB}} \rangle = \sum_{q_i} D_{11}^{[\lambda]}(q_i) \det(q_i), \tag{32}$$

where the summation goes over all left coset generators. Thus in the new procedure, only the coset generators (or the pairing patterns of $N$ elements) and their $D_{11}$-values are involved, and we need not go through $N!$ permutations of $S_N$.

## 5 Hamiltonian matrix elements

Similar procedure can be applied to the evaluation of Hamiltonian of VB wave function. As both one- and two-electron operators are involved in Hamiltonian operator, the expression of Hamiltonian is much more complicated. Generally, the Hamiltonian operator can be expressed as the sum of one- and two- operators:

$$H = F + G = \sum_{i=1}^{N} f(i) + \sum_{i<j}^{N} g(i,j). \tag{33}$$

Let us consider the contributions from one-electron operators first. In spin-free formalism, we have

$$\langle \psi_{\mathrm{VB}} | F | \psi_{\mathrm{VB}} \rangle = \sum_{P \in S_N} D_{11}^{[\lambda]}(P) \sum_{m=1}^{N} \langle \Omega | f(m) | P\Omega \rangle \tag{34}$$

and the left-coset decomposition of $S_N$ leads to the new expression:

$$\langle \psi_{\mathrm{VB}} | F | \psi_{\mathrm{VB}} \rangle = \sum_i D_{11}^{[\lambda]}(q_i) \sum_{m=1}^{N} \sum_{Q_j \in Q} \langle \Omega | f(m) | q_i Q_j \Omega \rangle . \tag{35}$$

Let us consider the summation over a coset $q_i Q$ and the operators $f(1)$ and $f(2)$, where $q_i$ is shown in Eq. (17). From the same reasoning as shown above, we have

$$\sum_{g_1 \in G_1} \langle \Omega | f(1) + f(2) | q_i g_1 \Omega \rangle = F_1^A B_2 \ldots D_{N/2} , \tag{36}$$

where

$$F_1^A = F_{1a_1} S_{2a_2} + F_{1a_2} S_{2a_1} + S_{1a_1} F_{2a_2} + S_{1a_2} F_{2a_1} , \tag{37}$$

and

$$F_{1a_1} = \langle \phi_1 | f | \phi_{a_1} \rangle , \qquad F_{2a_2} = \langle \phi_2 | f | \phi_{a_2} \rangle , \ldots \tag{38}$$

$B_2, \ldots, D_{\frac{1}{2}N}$ are defined in the same way as above. Therefore the summation going over the left coset $q_i Q$ leads to the following positive determinant:

$$\sum_{Q_j \in Q} \langle \Omega | f(1) + f(2) | q_i Q_j \Omega \rangle = \det(F_1, q_i) , \tag{39}$$

where

$$\det(F_1, q_i) = \begin{vmatrix} F_1^A & A_2 & A_3 & \ldots\ldots & A_{N/2} \\ F_1^B & B_2 & B_3 & \ldots\ldots & B_{N/2} \\ & \ldots\ldots\ldots\ldots & & & \\ F_1^C & C_2 & C_3 & \ldots\ldots & C_{N/2} \\ & \ldots\ldots\ldots\ldots & & & \\ F_1^D & D_2 & D_3 & \ldots\ldots & D_{N/2} \end{vmatrix} \tag{40}$$

From the same reasoning, we have

$$\sum_{Q_j \in Q} \langle \Omega | f(2k-1) + f(2k) | q_i Q_j \Omega \rangle = \det(F_k, q_i) , \tag{41}$$

where

$$\det(F_k, q_i) = \begin{vmatrix} A_1 & A_2 & \ldots & F_k^A & \ldots & A_{N/2} \\ B_1 & B_2 & \ldots & F_k^B & \ldots & B_{N/2} \\ & \ldots\ldots\ldots\ldots & & & & \\ C_1 & C_2 & \ldots & F_k^C & \ldots & C_{N/2} \\ & \ldots\ldots\ldots\ldots & & & & \\ D_1 & D_2 & \ldots & F_k^D & \ldots & D_{N/2} \end{vmatrix} \tag{42}$$

Finally we get the expression for the contribution of one-electron operators to Hamiltonian as following:

$$\langle \psi_{\mathrm{VB}} | F | \psi_{\mathrm{VB}} \rangle = \sum_{k=1}^{N/2} \sum_i D_{11}^{[\lambda]}(q_i) \det(F_k, q_i) . \tag{43}$$

Now let us consider the expression for two-electron operators:

The two-electron operators $g(k,l)$ can be divided into two groups. Group I, $g(2k-1,2k)$ $(k=1,2,\ldots,N/2)$; group II: $g(k,l)$, where $k\in(2m-1,2m)$, $1\in(2n-1,2n)$ and $m\neq n$. Let us consider the contribution from $g(1,2)$, $g(3,4)$, $\ldots$, $g(N-1,N)$ first. One can find that

$$\sum_{g_1\in G_1}\langle\Omega|g(2k-1,2k)q_ig_1|\Omega\rangle = A_1B_2\ldots G_k^C\ldots D_{N/2}, \tag{44}$$

where

$$\begin{aligned} G_k^C = &\langle\phi_{2k-1}(1)\phi_{2k}(2)|g(1,2)|\phi_{c_1}(1)\phi_{c_2}(2)\rangle \\ &+\langle\phi_{2k-1}(1)\phi_{2k}(2)|g(1,2)|\phi_{c_2}(1)\phi_{c_1}(2)\rangle \end{aligned} \tag{45}$$

and similarly, we can get

$$\sum_{g_1\in G_1}\langle\Omega|g(2k-1,2k)q_ig_1g_2|\Omega\rangle = A_1'B_2'\ldots G_k^{C'}\ldots D_{N/2}', \tag{46}$$

where

$$q_ig_2 = \begin{array}{|c|c|}\hline a_1' & a_2' \\ \hline b_1' & b_2' \\ \hline \vdots & \vdots \\ \hline c_1' & c_2' \\ \hline \vdots & \vdots \\ \hline d_1' & d_2' \\ \hline \end{array} \tag{47}$$

and

$$\begin{aligned} G_k^{C'} = &\langle\phi_{2k-1}(1)\phi_{2k}(2)|g(1,2)|\phi_{c_1'}(1)\phi_{c_2'}(2)\rangle \\ &+\langle\phi_{2k-1}(1)\phi_{2k}(2)|g(1,2)|\phi_{c_2'}(1)\phi_{c_1'}(2)\rangle. \end{aligned} \tag{48}$$

Thus the summation going over both $G_1$ and $G_2$ (i.e. the left coset $q_iQ$ leads to the following positive determinant:

$$\sum_{Q_j\in Q}\langle\Omega|g(2k-1,2k)|q_iQ_j|\Omega\rangle = \det(G_k,q_i), \tag{49}$$

where

$$\det(G_k,q_i) = \begin{vmatrix} A_1 & A_2 & \ldots & G_k^A & \ldots & A_{N/2} \\ B_1 & B_2 & \ldots & G_k^B & \ldots & B_{N/2} \\ & \ldots\ldots & & \ldots\ldots & & \\ C_1 & C_2 & \ldots & G_k^C & \ldots & C_{N/2} \\ & \ldots\ldots & & \ldots\ldots & & \\ D_1 & D_2 & \ldots & G_k^D & \ldots & D_{N/2} \end{vmatrix} \tag{50}$$

We can see that Eqs. (42) and (50) have the same form, thus it is better to combine them into one, i.e.

$$\sum_{Q_j\in Q}\langle\Omega|f(2k-1)+f(2k)+g(2k-1,2k)|q_iQ_j|\Omega\rangle = \det(H_k,q_i), \tag{51}$$

where

$$\det(H_k, q_i) = \begin{vmatrix} A_1 & A_2 & \dots & H_k^A & \dots & A_{N/2} \\ B_1 & B_2 & \dots & H_k^B & \dots & B_{N/2} \\ & \dots\dots\dots\dots\dots\dots & & & & \\ C_1 & C_2 & \dots & H_k^C & \dots & C_{N/2} \\ & \dots\dots\dots\dots\dots\dots & & & & \\ D_1 & D_2 & \dots & H_k^D & \dots & D_{N/2} \end{vmatrix} \tag{52}$$

and

$$H_k^A = F_k^A + G_k^A,\ H_k^B = F_k^B + G_k^B,\ \dots,\ H_k^D = F_k^D + G_k^D,$$

Finally, let us consider the operators $g(k, l)$, $k \in (2m-1, 2m)$, $j \in (2n-1, 2n)$ and $m \neq n$. Thus for each pair $(m, n)$, there are 4 operators $g(2m-1, 2n-1)$, $g(2m-1, 2n)$, $g(2m, 2n-1)$ and $g(2m, 2n)$. Although we cannot get an exact positive determinant for the contribution of these two-electron operators, the expression takes the same form as Laplace expansion of a positive determinant.

Suppose

$$\det(q_i) = \begin{vmatrix} A_1 & A_2 & A_3 & \dots\ \dots & A_{N/2} \\ B_1 & B_2 & B_3 & \dots\ \dots & B_{N/2} \\ & \dots\dots\dots\dots\dots\dots & & & \\ C_1 & C_2 & C_3 & \dots\ \dots & C_{N/2} \\ & \dots\dots\dots\dots\dots\dots & & & \\ D_1 & D_2 & D_3 & \dots\ \dots & D_{N/2} \end{vmatrix} \tag{53}$$

$$= \sum_{k<l} M_{mn}^{kl} L_{mn}^{kl}, \tag{54}$$

where $M_{mn}^{kl}$ are positive subdeterminants of $k, l$th rows and $m, n$th columns, and $L_{mn}^{kl}$ are the corresponding cofactors, i.e. the positive subdeterminants of above matrix without the $k, l$th rows and $m, n$th columns. Then we have

$$\sum_{r=2m-1}^{2m} \sum_{s=2n-1}^{2n} \sum_{Q_j \in Q} \langle \Omega | g(r, s) | q_i Q_j \Omega \rangle = \sum_{k<l} G_{mn}^{kl} L_{mn}^{kl} = \det(G_{mn}, q_i), \tag{55}$$

where

$$G_{mn}^{kl} = \sum_{i=2m-1}^{2m} \sum_{j=2n-1}^{2n} \sum_{r=2k-1}^{2k} \sum_{s=2l-1}^{2l} [g_{ijrs} S_{i'r'} S_{j's'} + g_{ijsr} S_{i's'} S_{j'r'}], \tag{56}$$

$$g_{ijrs} = \langle \phi_i(1) \phi_j(2) | g(1, 2) | \phi_{P_r}(1) \phi_{P_s}(2) \rangle, \tag{57}$$

$$i + i' = 4m - 1,\quad j + j' = 4n - 1,\quad r + r' = 4k - 1,\quad s + s' = 4l - 1, \tag{58}$$

and

$$S_{ir} = \langle \phi_i | \phi_{P_r} \rangle \tag{59}$$

$$q_i = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & N \\ P_1 & P_2 & P_3 & P_4 & \dots & P_N \end{pmatrix}. \tag{60}$$

Obviously, $G_{mn}^{kl}$ is a sum of 32 terms, and these 32 terms always appear as a compact unit repeatedly. This reduces computational effort greatly.

Finally, we get the completed expression of Hamiltonian of VB wave function:

$$\langle \psi_{\mathrm{VB}} | \psi_{\mathrm{VB}} \rangle = \sum_i D_{11}^{[\lambda]}(q_i) \left[ \sum_{j=1}^{N/2} \det(H_j, q_i) + \sum_{m<n}^{N/2} \det(G_{mn}, q_i) \right], \tag{61}$$

In practice, it seems more convenient to use a slightly different expression:

$$\langle \psi_{\mathrm{VB}} | \psi_{\mathrm{VB}} \rangle = \sum_i D_{11}^{[\lambda]}(q_i) \left[ \sum_{j=1}^{N/2} \det(H'_j, q_i) + \sum_{m<n}^{N/2} \det(G'_{mn}, q_i) \right], \tag{62}$$

where $\det(H_j, q_i)$ and $\det(G_{mn}, q_i)$ are defined as following:

$$\det(H'_k, q_i) = \begin{vmatrix} A_1 & A_2 & A_3 & \dots\dots & A_{N/2} \\ B_1 & B_2 & B_3 & \dots\dots & B_{N/2} \\ \dots\dots & \dots\dots & \dots\dots & \dots\dots & \dots\dots \\ H_1^C & H_2^C & H_3^C & \dots\dots & H_{N/2}^C \\ \dots\dots & \dots\dots & \dots\dots & \dots\dots & \dots\dots \\ D_1 & D_2 & D_3 & \dots\dots & D_{N/2} \end{vmatrix}, \tag{63}$$

$$\det(G'_{mn}, q_i) = \sum_{k<l} G_{kl}^{mn} L_{kl}^{mn}. \tag{64}$$

The matrix elements and the positive subdeterminants are defined in the same way as in Eq. (51) and Eq. (55), respectively. It can be easily shown that

$$\sum_{j=1}^{N/2} \det(H_j, q_i) = \sum_{j=1}^{N/2} \det(H'_j, q_i) \tag{65}$$

and

$$\sum_{m<n}^{N/2} \det(G_{mn}, q_i) = \sum_{m<n}^{N/2} \det(G'_{mn}, q_i). \tag{66}$$

## 6 Implementation of the new method and the efficiency

*Evaluation of positive determinants by Laplace expansion.* An $n \times n$ positive determinant consists of $n!$ terms, and each term is a product of $n$ factors. If the $n!$ terms are treated separately, then it requires $(n-1)n!$ operations of multiplication.

However, the computational effort can be reduced significantly by using Laplace expansion method. Let us consider an $n \times n$ positive determinant as shown below.

$$\begin{vmatrix} A_1 & A_2 & A_3 & \ldots\ \ldots & A_n \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & & & & \\ B_1 & B_2 & B_3 & \ldots\ \ldots & B_n \\ C_1 & C_2 & C_3 & \ldots\ \ldots & C_n \\ D_1 & D_2 & D_3 & \ldots\ \ldots & D_n \end{vmatrix} \tag{67}$$

The first step is to evaluate the $2 \times 2$ sub-positive determinants corresponding to the last two rows $\{C_i\}, \{D_i\}$. There are $n(n-1)/2$ terms, and each term requires two multiplications:

$$(CD)_{ij} = C_i D_j + C_j D_i . \tag{68}$$

The next step is to evaluate the sub-positive determinants of higher order by using the sub-positive determinants of lower order, i.e. the $3 \times 3$ positive determinants of the last three rows can be evaluated by

$$(BCD)_{ijk} = B_i(CD)_{jk} + B_j(CD)_{ik} + B_k(CD)_{ij} . \tag{69}$$

Obviously, there are $n(n-1)(n-2)/3!$ sub-positive determinants of order 3, and each one requires 3 multiplications. This procedure can be continued for totally $n-1$ times. The number of multiplication operations for each step are shown as following:

*Step* 1: $2 \times n(n-1)/2$

*Step* 2: $3 \times n(n-1)(n-2)/3!$

*Step k*: $(k+1)n(n-1) \ldots (n-k)/(k+1)!$

The total number of multiplication operations for the evaluation of one $n \times n$ positive determinant is given in Table 1.

**Table 1.** The number ($M$) of multiplication operations for the evaluation of one $n \times n$ positive determinant by Laplace expansion method

| $n$ | $M$ | $(n-1)n!$ |
|---|---|---|
| 2 | 2 | 2 |
| 3 | 9 | 9 |
| 4 | 28 | 72 |
| 5 | 75 | 480 |
| 6 | 186 | 3600 |
| 7 | 441 | 30240 |
| 8 | 1016 | 282240 |
| 9 | 2295 | 2903040 |
| 10 | 5110 | 32659200 |
| 11 | 11253 | 399168000 |
| 12 | 24564 | 9740503040 |

From Table 1 one can see that the computational effort increases approximately with $2^n$, which is much slower than $(n-1)n!$. For $N = 20$, the corresponding positive determinants are of order 10, and each one requires only 5110 operations.

*Efficiency of the new method.* The above theoretical formalism has been implemented into an *ab initio* valence bond program AMOY-VB at Xiamen (Amoy) University. As the summation is performed over the left cosets, rather than the $N!$ permutations, the computation is largely reduced. This has been confirmed in our practice. Using the full valence bond calculation of π-electron system of benzene as an example, the evaluation of all the VB elements of a $175 \times 175$ matrix requires 55 min on M-340/FACOM by permutation-driven method, while the new method requires only 41 s, which is 80 times faster. Moreover, the graphic pattern of the left cosets will change gradually from one left coset to another, thus the corresponding matrix of the positive determinant will change gradually too. This fact can be used to get further reduction of the computation for larger systems. The techniques based on this fact and the concerning theoretical problems are discussed in detail elsewhere [31]. The calculation of one VB structure of a 16-electron system requi res about 1 min on a workstation using the updated version of our VB program, while it is very difficult to perform the same calculation using the permutation-driven method.

## 7 Summary of the new method

In this paper, we have proposed a new algorithm for nonorthogonal valence bond calculation based on the left coset decomposition of $S_N$. The new expressions for evaluating the overlap and Hamiltonian matrix elements of spin-free VB wave functions are given in detail. The efficiency of the new algorithm comes from two aspects. First, it is not necessary to obtain either permutations or their $D_{11}$-values individually. Second, instead of accumulating the contribution of each permutation separately, the new procedure treats the contribution of all $2^{\frac{1}{2}N}(\frac{1}{2}N)!$ permutations of each left coset as a basic unit, and this basic unit turns out to be a positive determinant of order $N/2$ for overlap- or a few positive determinants for Hamiltonian matrix elements.

In principle, the same strategy can be applied to the case of spin $S > 0$. Actually, we can introduce a subgroup $Q$ which has $2^{\frac{1}{2}N-S}(\frac{1}{2}N - S)!(2S)!$ permutations. For the evaluation of overlap matrix elements, we have a product of two determinants for each left coset, one is a positive determinant of order $\frac{1}{2}N - S$, and the other is a usual determinant of order $2S$. Moreover, in the case of $S \geq 1$, the $D_{11}^{[\lambda]}$-values of some cosets are zero, thus these cosets have no contribution to the matrix elements of VB wave function. The case of $S = \frac{1}{2}, 1$ can be treated in a much similar way as the case of $S = 0$, and little change in the program is required.

*Acknowledgements.* One of us (J. Li) is very grateful to the Alexander-von-Humboldt Foundation for the award to a Fellowship that makes his stay at the Chair for Theoretical Chemistry at the University Erlangen-Nürnberg possible. He is deeply indebted to Professor Janos Ladik for numerous valuable suggestions and for his careful reading and improvement of this manuscript. We wish to express our sincere thanks to Professor J. Gerratt and Dr. D.L. Cooper for sending us some of their publications, and to Dr. J. Verkeek for his Ph.D thesis during the preparation of this paper. We thank Dr. Y. Mo for his interest and valuable discussion. This work was partially supported by the National Science Foundation of China.

## References


1. For a recent review on VB theory, see the special issues of J Mol Struct (THEOCHEM), (1991) 229; (1992) 259; (1992) 260; (1992) 261
2. Coulson CA (1961) Valence. Oxford University Press, London
3. Pauling L (1960) The Nature of the Chemical Bond. Cornell University Press, Ithaca, NY
4. Cooper DL, Gerratt J, Raimondi D (1991) Chem Rev 91:929
5. Sironi M, Cooper DL, Gerratt J, Raimondi M (1990) J Am Chem Soc 112:5054; Sironi M, Raimondi M, Cooper DL, Gerratt J (1991) J Phys Chem 95:10617
6. Löwdin PO (1955) Phys Rev 97:1474
7. Miller J, Friedman R, Hurst R, Matsen FA (1957) J Chem Phys 27:1386
8. Raimondi M, Simonetta M, Tantardim GF (1972) J Chem Phys 56:5091
9. Balint-Kurti GG, Karplus M (1968) J Chem Phys 50:478
10. Verbeek J, van Lenthe JH (1991) J Mol Struc (THEOCHEM) 229:115
11. Verbeek J (1990) Nonorthogonal orbitals in ab initio many-electron wave functions. PhD thesis, University of Utrecht
12. Langenberg JH, Ruttink PJA (1993) Theor Chim Acta 85:285
13. Goddard III WA (1967) Phys Rev 157:81; (1968) 167:120; (1968) J Chem Phys 48:1008; 48:5337
14. Cooper DL, Gerratt J, Raimondi M, Sironi M, Thorsteinsson T (1993) Theor Chim Acta 85:261
15. Matsen FA (1964) Adv Quantum Chem 1:50
16. Matsen FA, Cantu AA (1969) J Phys Chem 73:2488
17. Gallup GA (1969) J Chem Phys 50:1206
18. Klein DJ, Junker BR (1971) J Chem Phys 54:4294
19. Junker BR, Klein DJ (1971) J Chem Phys 55:5532
20. Dinesha KV, Sarma CR, Rettrup S (1981) Adv Quantum Chem 14:125
21. Gallup GA, Vance RL, Collins JR, Norbeck JM (1982) Adv Quantum Chem 16:229
22. McWeeny R (1988) J Mol Struct (THEOCHEM) 168:459; (1991) 229:29; (1990) Int J Quantum Chem (QCS) 24:733
23. Zhang Q, Li X (1989) J Mol Struct (THEOCHEM) 198:413
24. Li X, Zhang Q (1989) Int J Quantum Chem 36:599
25. Li X, Paldus J (1991) J Mol Struct (THEOCHEM) 229:249
26. Slater JC (1931) Phys Rev 38:1109
27. Pauling L (1933) J Chem Phys 1:280
28. Heitler W, London F (1927) Z Phys 44:455
29. Cooper IL, McWeeny R (1966) J Chem Phys 45:226; (1968) 49:3323
30. Wu W, Zhang Q (1991) J Mol Sci (Beijing) 7:54
31. Li J, J Math Chem (submitted)