A Second Quantized Formulation of Valence Bond Theory

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Valence bond theory is formulated in terms of second quantized operators and is related to the theory of the unitary group of spin-free orbital transformations. The construction of Weyl basis states, the evaluation of matrix elements, and the application to a linked-diagram valence bond perturbation theory are all discussed.

Key words: Valence bond theory, second quantization formulation of $\sim$

1. Introduction

To compute with high accuracy the energies and other properties of molecules with light nuclei a spin-free Hamiltonian is diagonalized in a large, suitably chosen vector space. This formulation can be tedious and difficult and lack a simple physical interpretation. Both the Hartree-Fock and the valence bond (VB) theories simplify molecular calculations by particular truncations of the vector space and at the same time they supply simple physical interpretations: the orbital concept in the first case and the classical chemical bond structure concept in the second.

Second quantization techniques have been extensively applied with much success to Hartree-Fock and molecular orbital based theories. However, general valence bond treatments do not seem to have previously been so formulated, although such a formulation has been proposed [1]. This paper carries out such a development, in the course of which we exploit the well-known connection [2] between second quantized problems and the unitary group. Particularly we demonstrate how the computation of matrix elements in this formulation becomes a simple problem in the theory of the unitary group of (spin-free) orbital transformations. We thus find an alternative to the classical Rumer basis [3], and also to the diagrammatic Pauling number method [4] or to Löwdin's determinantal method [5] for evaluating matrix elements.

In Section 2 we review the relevant relations between the unitary group and second quantized operators. In Section 3 we present the second quantized Weyl basis [6, 7] for the unitary group, and show that it leads to a new formulation of the usual space-spin [3, 4] and spin-free [8] VB theories. In Section 4 the evaluation of the matrix elements is described for the orthogonal case. Using a second-quantized theory [9] of nonorthogonal orbitals, we obtain similar results for this more general case in Section 5. Finally in Section 6 we indicate how the techniques of Sections 4 and 5 are applicable to a linked-diagram perturbation theory [10] based on the valence-bond states as zero-order.

2. Second Quantization and the Unitary Group

In the second quantized formulation we employ Fermion creation and annihilation operators, $a_{m\sigma}^+$ and $a_{m\sigma}$,

$$\{a_{m\sigma}, a_{n\tau}\} = \{a_{m\sigma}^+, a_{n\tau}^+\} = 0 \qquad \{a_{m\sigma}^+, a_{n\tau}\} = \delta_{mn}\delta_{\sigma\tau} \tag{2.1}$$

where m, n label spin-free orbitals and σ, $\tau = \alpha$, β label spins. As is well-known the Schroedinger Hamiltonian, involving 1- and 2-electron operators $\hbar$ and v, may be represented as

$$H = \sum_{m\sigma} \sum_{n\tau} \langle m\sigma|\hbar|n\tau \rangle a_{m\sigma}^+ a_{n\tau}$$
$$+ \tfrac{1}{2} \sum_{m\sigma m'\sigma'} \sum_{n\tau n'\tau'} \langle m\sigma \otimes n\tau|v|m'\sigma' \otimes n'\tau' \rangle a_{m\sigma}^+ a_{n\tau}^+ a_{n'\tau'} a_{m'\sigma'} . \tag{2.2}$$

Defining [2]

$$C_{m\sigma}^{n\tau} \equiv a_{m\sigma}^+ a_{n\tau} \tag{2.3}$$

we note that [as follows from the anticommutation relations of (2.1)],

$$[C_{m\sigma}^{n\tau}, C_{m'\sigma'}^{n'\tau'}] = \delta_{nm'}\delta_{\tau\sigma'} C_{m\sigma}^{n'\tau'} - \delta_{n'm}\delta_{\tau'\sigma} C_{m'\sigma'}^{n\tau} \qquad (C_{m\sigma}^{n\tau})^+ = C_{n\tau}^{m\sigma} . \tag{2.4}$$

These commutation relations are known to identify the $C_{n\tau}^{m\sigma}$ as generators of the Lie algebra of the unitary group $U(2\varrho)$, where ϱ is the number of spin-free orbitals. The Hamiltonian (2.2) may be seen to be expressable entirely as an element of this Lie algebra of $U(2\varrho)$,

$$H = \sum_{m\sigma} \sum_{n\tau} \langle m\sigma|\hbar|n\tau \rangle C_{m\sigma}^{n\tau}$$
$$+ \tfrac{1}{2} \sum_{m\sigma m'\sigma'} \sum_{n\tau n'\tau'} \langle m\sigma \otimes n\tau|v|m'\sigma' \otimes n'\tau' \rangle \cdot (C_{m\sigma}^{m'\sigma'} C_{n\tau}^{n'\tau'} - \delta_{nm'}\delta_{\tau\sigma'} C_{m\sigma}^{n'\tau'}) . \tag{2.5}$$

We assume that the interactions are spin-independent,

$$\langle m\sigma|\hbar|n\tau \rangle = \delta_{\sigma\tau}\langle m|\hbar|n \rangle \qquad \langle m\sigma \otimes n\tau|v|m'\sigma' \otimes n'\tau' \rangle = \delta_{\sigma\sigma'}\delta_{\tau\tau'}\langle m \otimes n|v|m' \otimes n' \rangle . \tag{2.6}$$

In this case we may recast [2] the problem in a form supressing the spin labels. We define

$$\mathscr{C}_m^n \equiv \sum_\sigma C_{m\sigma}^{n\sigma} \qquad C_\sigma^\tau \equiv \sum_m C_{m\sigma}^{m\tau} . \tag{2.7}$$

These new operators obey the commutation rules

$$[\mathscr{C}_m^n, \mathscr{C}_{m'}^{n'}] = \delta_{nm'}\mathscr{C}_m^{n'} - \delta_{n'm}\mathscr{C}_{m'}^n \qquad [C_\sigma^\tau, C_{\sigma'}^{\tau'}] = \delta_{\tau\sigma'}C_\sigma^{\tau'} - \delta_{\tau'\sigma}C_{\sigma'}^\tau \qquad [\mathscr{C}_m^n, C_\sigma^\tau] = 0$$

(2.8)

Hence the C_m^n are the generators for the Lie algebra of the unitary group $\mathscr{U}(\varrho)$ acting on the space of spin-free orbitals. The C_σ^τ are generators of the familiar unitary group $U(2)$ for the total electron spin. Further the elements of $\mathscr{U}(\varrho)$ and $U(2)$ commute so that they may be represented as acting on separate spaces. Since H is spin-free, we obtain

$$H = \sum_{mn} \langle m|\hbar|n \rangle \, \mathscr{C}_m^n$$
$$+ \tfrac{1}{2} \sum_{mn} \sum_{m'n'} \langle m \otimes n|v|m' \otimes n' \rangle (\mathscr{C}_m^{m'} \mathscr{C}_n^{n'} - \delta_{nm'}\mathscr{C}_m^{n'}).$$

(2.9)

Hence H is an element of the Lie algebra of $\mathscr{U}(\varrho)$, and will be diagonalized within the irreducible spaces for $\mathscr{U}(\varrho)$. The eigenkets to H will be homogeneous polynomials in the creation operators acting on the vacuum. The degree of these polynomials is given by the number N of electrons. In addition we see that these polynomials form a basis for the $\langle 1^N, 0, ..., 0 \rangle$ irreducible representation of $U(2\varrho)$. Since every element of $U(2)$ commutes with H, we also see that these eigenkets are symmetry adapted to $U(2)$ and also $\mathscr{U}(\varrho)$. Thus we sequence-adapt to the chain

$$U(2\varrho) \supset \mathscr{U}(\varrho) \otimes U(2).$$

(2.10)

Since the irreducible representations of $U(2)$ correspond to (1- or) 2-rowed Young diagrams, those of $\mathscr{U}(\varrho)$ must correspond to the conjugate (1- or) 2-columned Young diagrams.

3. The Weyl or VB Basis

Many treatments of the unitary group employ the orthonormal Gelfand states [2] as a basis for the irreducible representations. Here, however, we shall use the nonorthogonal Weyl states [6] because of their correspondence to valence bond states and the consequent physical interpretation. The set of states we are interested in is obtained by acting on the vacuum ket with polynomials of creation operators constructed as follows:

1. Draw the spin-free Young pattern corresponding to the irreducible representation of interest.

2. Fill the diagram with one creation operator in each box such that the spin indices $\sigma = \alpha$ and β are in the first and second columns, respectively.

3. Write the product of these creation operators symmetrized with respect to the orbital indices that occur in each row.

The generalized Young tableaux obtained in this way are called [7] index diagrams. We may formally indicate the implementation of these rules if we let $i_1, ..., i_{N-p}$ and $j_1, ..., j_p$ be the spinfree orbital labels proceeding down the first and second columns of the index diagram. Then letting $\hat{P}$ denote the row

symmetrizer of the diagram, the state constructed via the above rules is

$$
\begin{aligned}
|\{i_1, \ldots, i_{N-p}\}\{j_1, \ldots, j_p\}\rangle &= (-1)^{(N-2p)p}\hat{\boldsymbol{P}} \cdot \{a_{i,\alpha}^+ \ldots a_{i_{N-p}\alpha}^+\}\{a_{i_1 j_1 \beta}^+ \ldots a_{j_p \beta}^+\}|0\rangle \\
&= \varDelta_{i_1 j_1}^{\alpha\beta} \ldots \varDelta_{i_p j_p}^{\alpha\beta} \cdot a_{i_{p+1}\alpha}^+ \ldots a_{i_{N-p}\alpha}^+|0\rangle .
\end{aligned}
\tag{3.1}
$$

Here we have defined

$$
\varDelta_{ij}^{\alpha\beta} \equiv a_{i\alpha}^+ a_{j\beta}^+ + a_{j\alpha}^+ a_{i\beta}^+ .
\tag{3.2}
$$

The ket of (3.1) is then the Weyl state associated with the indicated index diagram.

Since the symmetrization of orbital indices is equivalent to antisymmetrization of spin indices, we have

$$
\varDelta_{ij}^{\alpha\beta} = a_{i\alpha}^+ a_{j\beta}^+ - a_{i\beta}^+ a_{j\alpha}^+ .
\tag{3.3}
$$

Therefore each $\varDelta$ gives a spin of zero, and the pair of orbitals in the same row of the index diagram are coupled to spin zero. The remaining $N-2p$ creation operators in (3.1), which are not involved in $\varDelta$'s, are all of α-spin and hence couple to a spin of

$$
S = \frac{N}{2} - p .
\tag{3.4}
$$

This then is the overall spin of the ket in (3.1). The identity with the usual VB *ansatz* is established by writing (3.1) in the conventional orbital notation

$$
\begin{aligned}
|\{i_1, \ldots, i_{N-p}\}\{j_1, \ldots, j_p\}\rangle &= (-1)^{(N-2p)p}\mathscr{A}\hat{\boldsymbol{P}}\{\varphi_{i_1}(1)\alpha(1) \ldots \varphi_{i_{N-p}}(N-p)\alpha(N-p)\} \\
&\quad \cdot \{\varphi_{j_1}(N-p+1)\beta(N-p+1) \ldots \varphi_{j_p}(N)\beta(N)\} \\
&= \mathscr{A} \cdot \varphi_{i_1}(1)\varphi_{j_1}(2)\varphi_{i_2}(3) \ldots \varphi_{j_p}(2p) \\
&\quad \cdot \varphi_{i_{p+1}}(2p+1) \ldots \varphi_{i_{N-p}}(N) \\
&\quad \cdot \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \ldots \{\alpha(2p-1)\beta(2p) \\
&\quad - \beta(2p-1)\alpha(2p)\} \cdot \alpha(2p+1) \ldots \alpha(N) .
\end{aligned}
\tag{3.5}
$$

This last form is that typically [3] found. It is also readily seen to be equivalent to the spin-free bond function [8]

$$
\begin{aligned}
|\{i_1, \ldots, i_{N-p}\}\{j_1, \ldots, j_p\}\rangle &\backsimeq \boldsymbol{NP} \cdot \varphi_{i_1}(1)\varphi_{j_1}(2)\varphi_{i_2}(3) \ldots \varphi_{j_p}(2p) \\
&\quad \cdot \varphi_{i_{p+1}}(2p+1) \ldots \varphi_{i_{N-p}}(N) \\
&\backsimeq \boldsymbol{N} \cdot \{\varphi_{i_1}(1)\varphi_{j_1}(2) + \varphi_{j_1}(1)\varphi_{i_1}(2)\} \\
&\quad \ldots \{\varphi_{i_p}(2p-1)\varphi_{j_p}(2p) + \varphi_{j_p}(2p-1)\varphi_{i_p}(2p)\} \\
&\quad \cdot \varphi_{i_{p+1}}(2p+1) \ldots \varphi_{i_{N-p}}(N)
\end{aligned}
\tag{3.6}
$$

where $\boldsymbol{P}$ and $\boldsymbol{N}$ are symmetric and antisymmetric sums of permutations along rows and columns of the spin-free Young tableau associated with the index diagram by replacing the orbital labels with the corresponding particle labels.

We proceed in the second-quantized notation to indicate some additional conventions. From the identities (which follow from (2.1) and (3.2))

$$\Delta_{lm}^{\alpha\beta}\Delta_{ln}^{\alpha\beta} = -\tfrac{1}{2}\Delta_{ll}^{\alpha\beta}\Delta_{mn}^{\alpha\beta}$$

$$\Delta_{lm}^{\alpha\beta}a_{l\alpha}^{+} = -\tfrac{1}{2}\Delta_{ll}^{\alpha\beta}a_{m\alpha}^{+}$$

(3.7)

we see that every state with two equal (spin-free) orbital indices is proportional to a state where these two orbital indices stand in the same row. Other trivial linear dependencies arise if the pair of orbital labels in a row are interchanged or if two rows of equal length are bodily interchanged. Thus presuming an ordering for the orbitals we add the following conventions to our earlier stated rules for constructing the Weyl (or VB) states:

4. Doubly-occupied orbitals occur in the same row of the index diagram; further these rows are located at the top of the diagram in decreasing order from top to bottom.

5. Singly-occupied but paired orbitals are inserted in the remaining rows of length two in the index diagram such that they decrease on proceeding from left to right and, at least in the first column, from top to bottom.

6. Singly-occupied and unpaired orbitals are inserted in the tail of the index diagram with their order decreasing from top to bottom.

We shall henceforth denote these Weyl states, satisfying conditions 1 to 6 by $|\Psi^J\rangle$ with J labelling the particular index diagram from which it is constructed.

Although the conditions 1–6 yield a set of Weyl states in which no two are simply proportional, linear dependence still occurs. There are several different manners by which a basis may be chosen from this overcomplete set. One such choice is obtained on replacing conditions 5 and 6 above by the stricter condition:

5–6: All singly-occupied orbitals are inserted in the Young pattern such that they decrease on proceeding from left to right along rows and from top to bottom down columns. That conditions 1, 2, 3, 4, and 5–6 designate a basis for the irreducible representation defined by the Young pattern involved, may be seen as follows: the doubly-occupied orbitals in the first rows necessarily couple as singlets to the remaining portion of the diagram in only a single way; hence this doubly occupied portion of the diagrams may be neglected in further symmetry considerations, whence it is seen that standard index diagrams remain; but these diagrams are known [7] as a tool to construct a Weyl basis for irreducible tensors, and [6] this method then directly extends to the construction of the present basis functions via creation operators.

An alternative manner by which to choose a basis from this overcomplete set is the generalized Rumer method [3], wherein singly-occupied orbitals located on the boundary of a circle are bonded in pairs to one another or to a pole also on the circle boundary such that no bonds cross. Obviously these Rumer diagrams yield index diagrams satisfying conditions 1 through 6, and hence another Weyl basis may be constructed on applying the corresponding polynomials to the vacuum ket.

4. Evaluation of Matrix Elements

A particular advantage to using such second-quantized Weyl states is found in the rather simple approach to evaluating matrix elements. The application of a generator $\mathscr{C}_m^{m'}$ of $\mathscr{U}(\varrho)$ to a Weyl state is discussed in Ref. 1. We easily see that

$$[\mathscr{C}_m^{m'}, \Delta_{nn'}^{\alpha\beta}] = \delta_{nm'}\Delta_{mn'}^{\alpha\beta} + \delta_{n'm'}\Delta_{nm}^{\alpha\beta}$$

$$[\mathscr{C}_m^{m'}, a_{n\alpha}^+] = \delta_{m'n}a_{m\alpha}^+ \tag{4.1}$$

$$\mathscr{C}_m^{m'}|0\rangle = 0 .$$

In using these relations we simply apply $\mathscr{C}_m^{m'}$ to a Weyl state and move $\mathscr{C}_m^{m'}$ to the right through the polynomial of creation operators; terms without $\mathscr{C}_m^{m'}$ may arise from commutators during this process and the final term in which $\mathscr{C}_m^{m'}$ is brought all the way through the polynomial to be applied to the vacuum ket gives zero. Any other term arising from the commutators in (4.1) is first to be simplified using (3.7) to obtain a state satisfying conditions 1 to 6 except possibly for the order of the factors in the resulting creation operator polynomial. Finally full satisfaction of conditions 1 to 6 is obtained along with a phase of ± 1 simply by reordering factors.

As an example we consider the application of $\mathscr{C}_m^{m'}$ to the Weyl state

$$\left| \begin{array}{|c|c|} \hline a & b \\ \hline c \\ \cline{1-1} d \\ \cline{1-1} \end{array} \right\rangle = + \Delta_{ab}^{\alpha\beta}a_{c\alpha}^+a_{d\alpha}^+\left|0\right\rangle . \tag{4.2}$$

Thus

$$\mathscr{C}_d^b\left| \begin{array}{|c|c|} \hline a & b \\ \hline c \\ \cline{1-1} d \\ \cline{1-1} \end{array} \right\rangle = + [\mathscr{C}_d^b, \Delta_{ab}^{\alpha\beta}]\, a_{c\alpha}^+a_{d\alpha}^+\left|0\right\rangle$$

$$= + \Delta_{ad}^{\alpha\beta}a_{c\alpha}^+a_{d\alpha}^+\left|0\right\rangle \tag{4.3}$$

$$= -\tfrac{1}{2} \Delta_{dd}^{\alpha\beta}a_{c\alpha}^+a_{a\alpha}^+\left|0\right\rangle .$$

We see that $\Delta_{ab}^{\alpha\beta}$ and $a_{d\alpha}^+$ have merely been replaced by $-\tfrac{1}{2}\Delta_{dd}^{\alpha\beta}$ and $a_{a\alpha}^+$, respectively, and we denote this replacement

$$\Delta_{ab}^{\alpha\beta}a_{d\alpha}^+ \rightarrow -\tfrac{1}{2}\Delta_{dd}^{\alpha\beta}a_{a\alpha}^+ . \tag{4.4}$$

Finally by reordering the creation operators corresponding to the unpaired electrons we obtain a Weyl state satisfying conditions 1, 2, 3, 4, and 5–6,

$$\mathscr{C}_d^b\left| \begin{array}{|c|c|} \hline a & b \\ \hline c \\ \cline{1-1} d \\ \cline{1-1} \end{array} \right\rangle = \tfrac{1}{2}\Delta_{dd}^{\alpha\beta}a_{a\alpha}^+a_{c\alpha}^+\left|0\right\rangle = \tfrac{1}{2}\left| \begin{array}{|c|c|} \hline d & d \\ \hline a \\ \cline{1-1} c \\ \cline{1-1} \end{array} \right\rangle \tag{4.5}$$

Table 1. Replacements appearing on applying $\mathscr{C}_m^{m'}$ to a Weyl state

$m \diagdown m'$	unoccupied	singly occupied paired	singly occupied unpaired	doubly occupied
unoccupied	0	$\Delta_{m'n'}^{\alpha\beta} \to \Delta_{mn'}^{\alpha\beta}$	$a_{m'\alpha}^+ \to a_{m\alpha}^+$	$\Delta_{m'm'}^{\alpha\beta} \to 2\Delta_{m'm}^{\alpha\beta}$
singly occupied paired	0	$\Delta_{m'n'}^{\alpha\beta}\Delta_{mn}^{\alpha\beta} \to -\frac{1}{2}\Delta_{nn'}^{\alpha\beta}\Delta_{mm}^{\alpha\beta}$ or $\Delta_{mm'}^{\alpha\beta} \to \Delta_{mm}^{\alpha\beta}$	$\Delta_{mn}^{\alpha\beta} a_{m'\alpha}^+ \to -\frac{1}{2}\Delta_{mm}^{\alpha\beta} a_{n\alpha}^+$	$\Delta_{mn}^{\alpha\beta}\Delta_{m'm'}^{\alpha\beta} \to -\Delta_{mm}^{\alpha\beta}\Delta_{m'n}^{\alpha\beta}$
singly occupied unpaired	0	$\Delta_{m'n'}^{\alpha\beta} a_{m\alpha}^+ \to -\frac{1}{2}\Delta_{m'm}^{\alpha\beta} a_{n'\alpha}^+$	$a_{m\alpha}^+ a_{m'\alpha}^+ \to 0$	$\Delta_{m'm'}^{\alpha\beta} a_{m\alpha}^+ \to -\Delta_{mm}^{\alpha\beta} a_{m'\alpha}^+$
doubly occupied	0	0	0	0

In Table 1 we indicate the replacements, analogous to Eqs. (4.3) and (4.4) of the example, for all possible cases. Following the replacements of Table 1, the phase for the appropriate Weyl state is simply -1 raised to a power; this power is nonzero only for positions (1, 3), (2, 3), (3, 2), and (3, 4) of the table, and in these cases the power simply is the number of positions which the replaced singly-occupied orbital must be moved to achieve standard ordering of the creation operators. (We note no phase arises from reordering the Δ's since they all commute.) We thus obtain

$$\mathscr{C}_m^{m'}|\Psi^J\rangle = \gamma(m, m', J)|\Psi^{J'(m,m',J)}\rangle \qquad (4.6)$$

and the matrix element $\langle\Psi^J|\mathscr{C}_m^{m'}|\Psi^J\rangle$ is evaluated as $\gamma(m, m', J)$ times the overlap $\langle\Psi^I|\Psi^{J'}\rangle$. Two-electron matrix elements are similarly obtained as a product of two γ-coefficients times a single overlap, plus a term of the one-electron type.

5. The Case of Nonorthogonal Orbitals

If as is often the case the VB (or Weyl) states are to be constructed from nonorthogonal orbitals, we need to generalize the method of section 4. The nonorthogonal orbitals case is distinguished from the orthogonal orbital case via the modified anticommutation relations

$$\{a_{m\sigma}, a_{n\tau}\} = \{a_{m\sigma}^+, a_{n\tau}^+\} = 0$$
$$\{a_{m\sigma}^+, a_{n\tau}\} = \delta_{\sigma\tau}\langle n|m\rangle \qquad (5.1)$$

where $\langle n|m\rangle$ is the overlap integral between orbitals n and m. In developing the ensuing second-quantized theory we initially follow an earlier treatment [9].

However, we ultimately differ from this earlier work in dealing with Weyl states rather than the Gelfand states, which are equivalent to the usual Young-Yamanouchi basis with successively coupled spins.

We let M denote the orbital overlap matrix with $(m, n)th$ element $\langle m|n \rangle$. Assuming the orbitals are linearly independent, we see that M has an inverse M^{-1} whose $(m, n)th$ element we denote by $\langle \hat{m}|\hat{n} \rangle$. The orbital $|\hat{m}\rangle$ dual to $|m\rangle$ then is defined to be

$$|\hat{m}\rangle \equiv \sum_n |n\rangle \langle \hat{n}|\hat{m} \rangle . \tag{5.2}$$

Clearly the elements of M^{-1} are the overlaps of these dual orbitals, and

$$|m\rangle = \sum_n |\hat{n}\rangle \langle n|m \rangle \langle \hat{n}|m \rangle = \langle n|\hat{m} \rangle = \delta_{nm} . \tag{5.3}$$

Associated with the dual orbitals we have dual annihilation operators

$$\hat{a}_{m\sigma} = \sum_n a_{n\sigma} \langle \hat{n}|\hat{m} \rangle \tag{5.4}$$

(as well as, dual creation operators, which we however do not explicitly require). From (5.1) and (5.4) we have

$$\{\hat{a}_{m\sigma}, \hat{a}_{n\sigma}\} = \{a_{m\sigma}^+, a_{n\sigma}^+\} = 0$$
$$\{a_{m\sigma}^+, \hat{a}_{n\sigma}\} = \delta_{mn} \delta_{\sigma\tau} . \tag{5.5}$$

The Hamiltonian of Eq. (2.2) may [9] be written as

$$H = \sum_{m\sigma} \sum_{n\tau} \langle m\sigma|\hat{h}|\hat{n}\tau \rangle\, a_{m\sigma}^+ \hat{a}_{n\tau}$$
$$+ \tfrac{1}{2} \sum_{mom'\sigma'} \sum_{n\tau n'\tau'} \langle m\sigma \otimes n\tau|v|\hat{m}'\sigma \otimes \hat{n}'\tau \rangle \cdot a_{m\sigma}^+ a_{n\tau}^+ \hat{a}_{n'\tau'} \hat{a}_{m'\sigma'} \tag{5.6}$$

where the one- and two-body matrix elements are defined between regular bras and dual kets. As the anticommutation relations (5.5) are similar to those of Eq. (2.1), the operators

$$\hat{C}_{m\sigma}^{n\tau} \equiv a_{m\sigma}^+ \hat{a}_{n\tau} \tag{5.7}$$

have the same commutation relations as the $C_{m\sigma}^{n\tau}$ evince in (2.4). However, the hermitian property no longer holds, as

$$(\hat{C}_{m\sigma}^{n\tau})^+ \neq \hat{C}_{n\tau}^{m\sigma} . \tag{5.8}$$

Therefore the group generated by the $\hat{C}_{m\sigma}^{n\tau}$ must be considered as $GL\,(2\varrho)$ rather than $U(2\varrho)$. Again we could write the Hamiltonian in terms of the generators of (5.7), similar to Eq. (2.5), and we may define the contracted operators

$$\hat{\mathscr{C}}_m^n \equiv \sum_\sigma \hat{C}_{m\sigma}^{n\sigma}$$
$$C_\sigma^\tau \equiv \sum_m \hat{C}_{m\sigma}^{n\tau} . \tag{5.9}$$

Here $\hat{\mathscr{C}}_m^n$ generates a group $\mathscr{GL}(\varrho)$ while C_σ^τ still generates the $U(2)$ group related to total spin because $(C_\sigma^\tau)^+ = C_\tau^\sigma$. Therefore we write the latter generators

without a caret. A spin-independent Hamiltonian may then be written as

$$H = \sum_{mn} \langle m|\hat{h}|\hat{n}\rangle \, \mathscr{C}_m^n + \tfrac{1}{2}\sum_{mn}\sum_{m'n'} \langle m\otimes n|v|\hat{m}'\otimes\hat{n}'\rangle \, (\mathscr{C}_m^{m'}\mathscr{C}_n^{n'} - \delta_{nn'}\mathscr{C}_m^{n'}). \tag{5.10}$$

Now we may deal with Weyl states constructed from nonorthogonal orbitals in complete analogy with Sections 3 and 4. The VB states may again be constructed as Weyl states using only the $a_{m\alpha}^+$ creation operators as described in Section 3. In order to evaluate matrix elements we note that for nonorthogonal orbitals Eq. (4.1) is replaced by

$$[\mathscr{C}_m^{m'}, \varDelta_{nn'}^{\alpha\beta}] = \delta_{nm'}\varDelta_{mn'}^{\alpha\beta} + \delta_{n'm'}\varDelta_{nm}^{\alpha\beta}$$

$$[\mathscr{C}_m^{m'}, a_{n\alpha}^+] = \delta_{nm'}a_{m\alpha}^+$$

$$\mathscr{C}_m^{m'}|0\rangle = 0. \tag{5.11}$$

We therefore obtain immediately, similar to (4.6), that

$$\mathscr{C}_m^{m'}|\Psi^J\rangle = \gamma(m, m', J)\,|\Psi^{J'(m,m',J)}\rangle \tag{5.12}$$

where $\gamma(m, m', J)$ and $J'(m, m', J)$ are obtained exactly as in the orthogonal case. The only difference is thus that the overlaps $\langle\Psi^J|\Psi^{J'}\rangle$ are more complicated in this case. They can again be calculated, for instance, by expanding in Slater determinants and evaluating [5] the matrix element between two Slater determinants as the determinant of the orbital overlap matrix between the orbitals of the two Slater determinants. The present method of matrix element evaluation clearly avoids first- and second-order adjugate matrix manipulations, as found in Löwdin's method [5]. Clearly also the diagrams and island untwisting and counting of Pauling's method [4] are avoided too.

Finally it is of significance to note that matrix elements between a dual Weyl state (defined to be constructed from dual orbitals) and an ordinary Weyl state is evaluated particularly easily. Equation (5.12) still applies, but we finally wish to evaluate overlaps as $\langle\hat{\Psi}^J|\Psi^J\rangle$, where $|\hat{\Psi}^I\rangle$ is a dual Weyl state. If these are expanded out in terms of overlaps between dual and ordinary Slater determinants, then each of these Slater determinant overlaps is simply either ± 1 or 0, depending on whether or not exactly corresponding dual and ordinary orbitals appear in the two Slater determinants. This use of dual Weyl states results in a nonhermitian matrix representation of H, but even more importantly will only be of interest if all the Weyl states corresponding to a given (spin-free) orbital occupation scheme are to be used in the calculation. (This last result is seen since a subspace of Weyl states and the corresponding dual subspace spanned by the corresponding Weyl states are not in general identical.) Such matrix elements between dual and ordinary Weyl states arise naturally in the next section.

6. Perturbation Theory

The present second-quantized formulation of the electronic interaction problem lends itself to the development of a perturbation formalism based upon a zero-order VB picture. A zero-order VB wave function is considered

to be a linear combination of Weyl states constrained only to involve the same spin-free orbitals in each term. Our zero-order VB Hamiltonian thus does not mix configurations with different spin-free orbitals,

$$
H^0 = \sum_m \langle m|\hat{h}|\hat{m}\rangle \,\hat{\mathscr{C}}^m_m + \tfrac{1}{2}\sum_{mn}\{\langle m\otimes n|v|\hat{m}\otimes\hat{n}\rangle \,(\hat{\mathscr{C}}^m_m\hat{\mathscr{C}}^n_n - \delta_{mn}\hat{\mathscr{C}}^m_m)
$$
$$
+ \langle m\otimes n|v|\hat{n}\otimes\hat{m}\rangle \,(\hat{\mathscr{C}}^n_m\hat{\mathscr{C}}^m_n - \hat{\mathscr{C}}^m_m)\} \,.
$$
(6.1)

Here the use of the nonorthogonal orbitals and their duals generally yields a nonhermitian H^0, which however still leads [11] to a consistent perturbation theory. The perturbation consists of all remaining terms in H.

We can briefly compare the zero-order VB picture of (6.1) with the usual single-determinant zero-order pictures such as arise in SCF or Hartree-Fock theories. These more common zero-order pictures constrain the zero-order Hamiltonian not to mix terms with different spin-orbitals (in contrast to our VB prescription in terms of spin-free orbitals). The single-determinant zero-order Hamiltonian is then like that of (6.1) except that part of the $\langle m\otimes n|v|\hat{n}\otimes\hat{m}\rangle$ exchange term of (6.1) is omitted. This occurs since

$$
\hat{\mathscr{C}}^n_m\hat{\mathscr{C}}^m_n - \hat{\mathscr{C}}^m_m = \sum_{\sigma\tau} a^+_{m\sigma}a^+_{n\tau}\hat{a}_{m\tau}\hat{a}_{n\sigma}
$$
$$
= \sum_\sigma a^+_{m\sigma}a^+_{n\sigma}\hat{a}_{m\sigma}\hat{a}_{n\sigma} + \sum_\sigma a^+_{m\sigma}a^+_{n\bar{\sigma}}\hat{a}_{m\bar{\sigma}}\hat{a}_{n\sigma}
$$
(6.2)

and the second term here does not conserve spin-orbitals. In both single determinant and VB approaches the spin-free orbitals might be optimized [12]. However, this optimized VB approach then necessarily yields energetic results of equal or greater accuracy, since the VB result includes some configuration interaction among single determinants. Thus we expect the VB type of zero-order Hamiltonian in (6.1) to be more accurate than the corresponding zero-order single-determinant Hamiltonian, which deletes part of the $\langle m\otimes n|v|\hat{n}\otimes\hat{m}\rangle$ term.

The various terms of the Hamiltonian are conveniently expressed in a diagrammatic form. We consider a set of horizontal positions each identified with an orbital. Then arrows between these points indicate how a given term transfers electrons among the orbitals

$$
n\longrightarrow m \equiv \langle m|h|\hat{n}\rangle \,\hat{\mathscr{C}}^n_m
$$

$$
l\xrightarrow{\ k\ \ }_{\widetilde{n}}\longrightarrow m \equiv \langle m\otimes k|v|\hat{n}\otimes\hat{l}\rangle \,(\hat{\mathscr{C}}^n_m\hat{\mathscr{C}}^l_k - \delta_{nk}\hat{\mathscr{C}}^l_m)
$$
(6.3)

$$
= \langle k\otimes m|v|\hat{l}\otimes\hat{n}\rangle \,(\hat{\mathscr{C}}^l_k\hat{\mathscr{C}}^n_m - \delta_{lm}\hat{\mathscr{C}}^n_k) \,.
$$

If some of the orbitals are identical in (6.3), arrows may loop or two may diverge and/or converge on the same point. A squiggly line connecting two arrows merely emphasizes they both arise from the same interaction. The presence of one or two arrows indicates one- or two-electron interactions. These diagrams naturally indicate the possible coordinate-space motions of electrons from one localized spin-free orbital to another, and thus they compliment the more common Feynman diagrams which most naturally indicate the possible momentum-space scatterings of electrons from one delocalized spin-

orbital to another. Physically the present diagrammatic representation is more natural because of the typical localization of VB-orbitals.

An unlabelled diagram (i.e., without orbital labels) is defined to be a sum over all possible labellings with orbitals for distinct positions in the unlabelled diagram remaining distinct. Then the zero-order Hamiltonian and perturbation may be written

$$H^0 = \text{⊙} + \text{⊙⊙} + \text{⊙⌇⊙} + \text{⊙}$$
$$V = V^{(1)} + V^{(2)} \tag{6.4}$$
$$V^{(1)} \equiv \longrightarrow + \text{⊙}\rightarrow + \text{⊙}\text{⌇}\rightarrow + \text{⊙}\leftarrow + \rightarrow\rightarrow$$
$$V^{(2)} \equiv \text{⊙} + \rightarrow\!\!\leftarrow + \leftrightarrow + \rightarrow\text{⌇}\rightarrow .$$

Here the perturbation has been divided into first- and second-order portions which yield single and double excitations with regard to changes in spin-free orbital occupation number.

Products of operators may be diagrammatically indicated by stacking the composite diagrams up with the usual convention that the higher the vertical position of a portion of the diagram the further the corresponding operator is to the left in the product. Horizontal bars can also be introduced in diagrams to represent zero-order resolvents

$$\mathscr{R}^0 \equiv \frac{1}{E^0 - H^0} \equiv {\sum_k}' \frac{1}{E^0 - E_k^0} |\Psi_k^0\rangle \langle \hat{\Psi}_k^0| \tag{6.5}$$

Here $|\hat{\Psi}_k^0\rangle$ is the state dual to the zero-order state $|\Psi_k^0\rangle$,

$$H^0 |\Psi_k^0\rangle = E_k^0 |\Psi_k^0\rangle \tag{6.6}$$

and the zero-order level E^0 to be perturbed will be assumed to be nondegenerate, although generalizations to degenerate cases are [10] possible. It is important to note the simplicity of constructing the dual states $|\hat{\Psi}_k^0\rangle$ invoked in (6.5). We have, in correspondence with (5.11),

$$[(\hat{A}_{nn'}^{\alpha\beta})^+, \hat{\mathscr{C}}_{m'}^m] = \delta_{nm'}(\hat{A}_{mn'}^{\alpha\beta})^+ + \delta_{n'm'}(\hat{A}_{nm}^{\alpha\beta})^+$$

$$[\hat{a}_{n\alpha}, \hat{\mathscr{C}}_{m'}^m] = \delta_{nm'}\hat{a}_{m\alpha} \tag{6.7}$$

$$\langle 0|\hat{\mathscr{C}}_{m'}^m = 0 .$$

Thus if we choose $|\hat{\Psi}_k^0\rangle$ to be the ket composed from linear combinations of products of dual creation operators applied to the vacuum ket $|0\rangle$ in the same manner as $|\Psi_k^0\rangle$ is composed from ordinary creation operators applied to $|0\rangle$, then

$$\langle \hat{\Psi}_k^0|H^0 = E_k^0 \langle \hat{\Psi}_k^0| \qquad \langle \hat{\Psi}_k^0|\Psi_{k'}^0\rangle \sim \delta_{kk'} . \tag{6.8}$$

Equality is obtained in the last equation using the proper normalization. Clearly these $|\hat{\Psi}_k^0\rangle$ are the desired dual states, and are easily constructed only from the spin-free orbital overlap matrix (which is significantly simpler to deal with than the configuration overlap matrix).

Perturbation theory for the nonhermitian case develops [11] similarly to that for the hermitian case, where now one merely uses the dual states in bra-positions. The first-, second- and third-order energies are

$$E^{(1)} = \langle \hat{\Psi}^0 | V^{(1)} | \Psi^0 \rangle = 0$$

$$E^{(2)} = \langle \hat{\Psi}^0 | \{ V^{(1)} \mathcal{R}^0 V^{(1)} + V^{(2)} \} | \Psi^0 \rangle = \langle \hat{\Psi}^0 | V^{(1)} \mathcal{R}^0 V^{(1)} | \Psi^0 \rangle \qquad (6.9)$$

$$E^{(3)} = \langle \hat{\Psi}^0 | \{ V^{(1)} \mathcal{R}^0 (V^{(1)} - E^{(1)}) \mathcal{R}^0 V^{(1)} + V^{(1)} \mathcal{R}^0 V^{(2)} + V^{(2)} \mathcal{R}^0 V^{(1)} \} | \Psi^0 \rangle = 0 .$$

We note that since each additional perturbation order is associated with a change of one spin-free orbital occupation number by one, all odd-order perturbation energies are, in fact, zero.

The various terms in the second-order perturbation energy of (6.9) are depicted in a diagramatic form in Fig. 1. Clearly to obtain a nonzero contribution any occupation number changes obtained in applying the $V^{(1)}$ to the right of $\mathcal{R}^0$ to the ket must be balanced by the same occupation number changes arising from the second $V^{(1)}$ to the left of $\mathcal{R}^0$. Hence we require (in any order) the same number of arrows coming into an orbital position as leave it. To evaluate the perturbation energies the various diagram expectation values are expanded, as, for instance,

$$\langle \hat{\Psi}^0 | \overset{\longrightarrow}{\underset{\longleftarrow}{\rule{1.5cm}{0pt}}} | \Psi^0 \rangle = \sum_{mn} \langle m | \hbar | \hat{n} \rangle \, \langle n | \hbar | \hat{m} \rangle$$

$$\cdot \sum_k^{m \to n} \cdot \frac{1}{E^0 - E_k^0} \langle \hat{\Psi}^0 | \hat{\mathscr{C}}_m^n | \Psi_k^0 \rangle \, \langle \hat{\Psi}_k^0 | \hat{\mathscr{C}}_n^m | \Psi^0 \rangle \qquad (6.10)$$
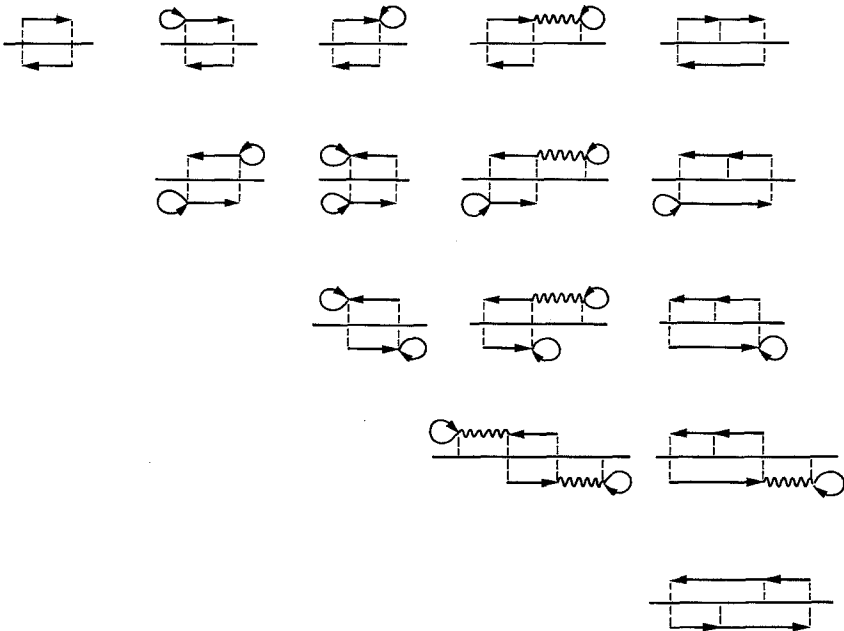

Fig. 1. Diagrams contributing to the second-order energy. If the diagrams above the diagonal are flipped upside-down all the remaining unlisted second-order diagrams are obtained

where the k-sum over excited zero-order states extends only over those states involving a single excitation from orbital m to n. The matrix elements $\langle \hat{\Psi}_k^0 | \hat{\mathscr{C}}_{m'}^m | \Psi_{k'}^0 \rangle$ may be evaluated using the transformation properties of the $\mathscr{C}_{m'}^m$ as described in Section 5.

7. Conclusion

We have thus indicated a second quantized formulation of valence bond theory. The relation of the formulation to the theory of the unitary group is exploited in evaluating matrix elements. Indeed this utility of the unitary group along with the Weyl (or VB) basis is not surprising, particularly in view of previous uses of the unitary group in evaluating matrix elements on the Gelfand basis, not only in nuclear physics [2] but recently also [13] in quantum chemistry. It is noteworthy that in many applications the Weyl basis yields simpler matrix element formulas and also is expected to be more directly physically interpretable in terms of chemical bond concepts. The resulting manipulative techniques can then be expected to enable development and application of new approximations for either semiempirical or *ab initio* computations. Even in the general case of nonorthogonal orbitals the current techniques are found to be applicable. Further linked-diagram perturbation theories were found to apply, in a manner reminescent of the more familiar MO approaches.

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