Theoret. Chim. Acta (Berl.) 36, 289—296 (1975)


# The Synthetic Construction of Spin Eigenfunctions in Second Quantization Representation

Paul J. A. Ruttink

Theoretical Chemistry Group, Rijksuniversiteit Utrecht, The Netherlands

Received July 5, 1974

The second quantization method is used to derive a recursion formula for the construction of spin eigenfunctions in the branching diagram method which simplifies the application of this method considerably. By application of this recursion formula the branching diagram functions are expressed as linear combinations of spin-paired functions. A one-to-one correspondence is established between the set of branching diagram paths and the set of spin-paired functions used to construct the branching diagram functions. This leads to a simple method for the construction of independent sets of spin-paired functions for arbitrary multiplicities.

*Key words:* Genealogical construction – Spin-pairing method – Independent spin eigenfunctions

## 1. Introduction

The methods currently used for the construction of (anti-symmetrical) spin eigenfunctions may be divided into three types: synthetic [1–4], analytic [3–7], and numerical [8]. It is our purpose to show how the second quantization technique may be used to simplify and to relate two different types of the synthetic approach, viz. the genealogical construction [2, 3] and the spin-pairing method [4, 9].

In the genealogical construction an orthonormal basis of branching diagram functions is generated by a recursive procedure, which leads to expansions in terms of simple spin products. The number of steps in this procedure increases rapidly with the number of electrons, which makes this method cumbersome for configurations with a large number of singly occupied orbitals.

The spin-pairing method, on the other hand, is easy to apply to functions for an arbitrary number of electrons, but it has the disadvantage that it leads to a basis set which is dependent. For singlet states this difficulty may be removed by selecting those functions which correspond to canonical Rumer diagrams [9]. However, for $S > 0$, this method fails, because the number of Rumer diagrams not containing crossed arrows exceeds the number of independent spin eigenfunctions.

In the following it will be shown that branching diagram paths may be used instead of Rumer diagrams as an aid in the construction of an independent (but non-orthogonal) set of spin-paired functions for arbitrary values of $S$. This may be done by some simple rules, as will be explained in detail in Section 4.

The orthogonalization of the spin-paired functions generated in this way may then be effected by a linear transformation, leading to a set of branch-diagram

functions. The elements of the transformation matrix may be calculated by a recursive procedure, which relates branching-diagram functions corresponding to closely related paths. As a result, the number of steps in the recursive procedure is decreased by a factor of 2, compared to the usual [2, 3] method. Moreover, by using a suitable normalization of the branching-diagram functions, the transformation coefficients may be tabulated as positive integers. This procedure will be outlined in Section 3.

Some definitions and conventions to be used later are given in Section 2.

## 2. Second Quantization Representation of the Genealogical Construction and the Spin-Pairing Method

The functions with which we are dealing may be completely characterized by $\boldsymbol{n}$, $S$, $M$, and $\boldsymbol{t}$, defined as follows. $\boldsymbol{n}$ symbolizes a set of occupation numbers $n_i$, i.e. the space weight of the function [10]. $S$ and $M$ correspond to the eigenvalues of $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$ respectively, and $M$ is also the spin weight $(n_\alpha, n_\beta)$, $M = \frac{1}{2}(n_\alpha - n_\beta)$. $\boldsymbol{t}$ is equivalent to the Yamanouchi-symbol, corresponding to a certain path in the branching diagram [1, 3].

The recursion formulas used in the genealogical construction involve the addition of an $\alpha$- or $\beta$-spin function to an $N$-electron spin eigenfunction. In the second quantization formalism this is symbolized by *creation* operators, and the formulas may therefore be reformulated in second quantization representation in the following way. We define the fermion operators $\boldsymbol{c}_j^\dagger$, $\boldsymbol{c}_j$, $\bar{\boldsymbol{c}}_j^\dagger$, and $\bar{\boldsymbol{c}}_j$ [11], where $\boldsymbol{c}_j^\dagger$ and $\bar{\boldsymbol{c}}_j^\dagger$ are creation operators for orbital $j$ with $\alpha$ and $\beta$ spin, respectively, and $\boldsymbol{c}_j$ and $\bar{\boldsymbol{c}}_j$ are the associated annihilation operators. These operators satisfy the usual anticommutation relations [11].

In the following the index $i$ will be taken for an orbital which is occupied in a function on which an annihilation operator acts, whereas the index $r$ corresponds to an orbital which is not occupied in a function to which a creation operator is applied. Arbitrary orbitals are indicated by indices $j$, $l$ or $k$.

For the case $M = S$ the recursion formulas [2, 3] then take the following form:

$$|\boldsymbol{n}', S+\tfrac{1}{2}, \boldsymbol{t}'\rangle = \boldsymbol{c}_r^\dagger |\boldsymbol{n}, S, \boldsymbol{t}\rangle \equiv \boldsymbol{C}_r(1)|\boldsymbol{n}, S, \boldsymbol{t}\rangle\,, \tag{1a}$$

$$|\boldsymbol{n}', S-\tfrac{1}{2}, \boldsymbol{t}''\rangle = (2S(2S+1))^{-\frac{1}{2}}(-\boldsymbol{c}_r^\dagger \boldsymbol{S}_- + 2S\bar{\boldsymbol{c}}_r^\dagger)|\boldsymbol{n}, S, \boldsymbol{t}\rangle \equiv \boldsymbol{C}_r(S,-1)|\boldsymbol{n}, S, \boldsymbol{t}\rangle\,. \tag{1b}$$

These are also the defining equations for the shift operators $\boldsymbol{C}_r(1)$ and $\boldsymbol{C}_r(S,-1)$, which change the eigenvalue of $\boldsymbol{S}^2$ from $S$ to $S+\frac{1}{2}$ and $S-\frac{1}{2}$ respectively. $\boldsymbol{C}_r(1)$ is a step-up operator, which does not depend on the spin eigenvalue of the function to which it is applied. The step-down operator, however, does depend on $S$, and this is indicated by rendering it in the form $\boldsymbol{C}_r(S,-1)$. Both operators are also shift operators with respect to the space weight $n$.

We will also need expressions for shift operators in terms of the *annihilation* operators. In order to obtain these we need the following result. The usual definition of a shift operator $\boldsymbol{B}$ with respect to $\boldsymbol{A}$ is equivalent to

$$\boldsymbol{AB} - \boldsymbol{BA} \equiv (\boldsymbol{A}, \boldsymbol{B}) = k\boldsymbol{B}\,.$$

This follows from

$$\boldsymbol{A}(\boldsymbol{B}|a\rangle) = \{(\boldsymbol{A}, \boldsymbol{B}) + \boldsymbol{B}\boldsymbol{A}\}|a\rangle = (k + a)(\boldsymbol{B}|a\rangle)$$

where an eigenfunction of $\boldsymbol{A}$ with eigenvalue $a$ is designated by $|a\rangle$. Moreover, if $\boldsymbol{C}$ commutes with $\boldsymbol{A}$, then $\boldsymbol{D} = (\boldsymbol{B}, \boldsymbol{C})$ is also a shift operator with respect to $A$, for

$$(\boldsymbol{A}, \boldsymbol{D}) = (\boldsymbol{A}, (\boldsymbol{B}, \boldsymbol{C})) = ((\boldsymbol{A}, \boldsymbol{B}), \boldsymbol{C}) - ((\boldsymbol{A}, \boldsymbol{C}), \boldsymbol{B}) = k(\boldsymbol{B}, \boldsymbol{C}) = k\boldsymbol{D}\,.$$

Now, it may be verified from the anticommutation relations and the second quantization expressions for the spin operators [6, 10], that the operator $\boldsymbol{c}_j\bar{\boldsymbol{c}}_j$ commutes with $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$. Therefore the commutators $\boldsymbol{A}_j(1) \equiv (\boldsymbol{C}_j(1), \boldsymbol{c}_j\bar{\boldsymbol{c}}_j)$ and $\boldsymbol{A}_j(S, -1) \equiv (\boldsymbol{C}_j(S, -1), \boldsymbol{c}_j\bar{\boldsymbol{c}}_j)$ are again shift operators with respect to $\boldsymbol{S}^2$. Expansion of these commutators yields the desired shift operators in terms of annihilation operators:

$$\boldsymbol{A}_i(1) = \bar{\boldsymbol{c}}_i\,, \tag{2a}$$

$$\boldsymbol{A}_i(S, -1) = -(2S(2S+1))^{-\frac{1}{2}}(\bar{\boldsymbol{c}}_i\boldsymbol{S}_- + 2S\boldsymbol{c}_i)\,, \tag{2b}$$

with

$$|\boldsymbol{n}', S + \tfrac{1}{2}, \boldsymbol{t}'\rangle = \boldsymbol{A}_i(1)\,|\boldsymbol{n}, S, \boldsymbol{t}\rangle$$
$$|\boldsymbol{n}', S - \tfrac{1}{2}, \boldsymbol{t}''\rangle = \boldsymbol{A}_i(S, -1)\,|\boldsymbol{n}, S, \boldsymbol{t}\rangle\,.$$

Equations (1) and (2) may be summarized by

$$|\boldsymbol{n}', S \pm \tfrac{1}{2}, \boldsymbol{t}'\rangle = \boldsymbol{B}_j(S, t_j)\,|\boldsymbol{n}, S, \boldsymbol{t}\rangle\,.$$

The explicit form of $\boldsymbol{B}_j(S, t_j)$ is given by Eq. (2) if orbital $j$ is occupied in $|\boldsymbol{n}, S, \boldsymbol{t}\rangle$ and by Eq. (1) if orbital $j$ is not occupied in $|\boldsymbol{n}, S, \boldsymbol{t}\rangle$. $t_j = \pm 1$, corresponding to a step up or drown in the branching diagram, and $t_j$ is added to the set $\boldsymbol{t}$ by operating with $\boldsymbol{B}_j(S, t_j)$ on $|\boldsymbol{n}, S, \boldsymbol{t}\rangle$, i.e. $\boldsymbol{t}' = \{t, t_j\}$. The set $\boldsymbol{t} = \{t_k\}$ corresponds to the Yamanouchi-symbol $\{r_k\}$, with $r_k = 1$ if $t_k = 1$ and $r_k = 2$ if $t_k = -1$.

Any spin eigenfunction pertaining to the genealogical construction may now be generated by repeated application of Eq. (3):

$$|\boldsymbol{n}, S, \boldsymbol{t}\rangle = \prod_{l=1}^{n_s} \boldsymbol{B}_{j_l}(S_l, t_l)\,|0\rangle \tag{4}$$

with

$$S = S_{n_s+1}$$
$$S_l = \tfrac{1}{2}\sum_{p=1}^{l-1} t_p \geqq 0$$
$$S_1 = 0$$
$$t_1 = 0\,.$$

$n_s$ = number of singly occupied orbitals in $|n, S, t\rangle$.

$|0\rangle$ is a reference state to be described below.

Functions $|\boldsymbol{n}, S, \boldsymbol{t}\rangle$ corresponding to different branching diagram paths are obtained by varying $t_l$ in Eq. (4) and the basis may be made complete by taking all possibilities for $t_l$ with the restriction

$$\sum_{p=1}^{l} t_p \geqq 0\,.$$

The functions with a fixed sequence of orbital indices form a basis (complete or overcomplete) spanning the associated subspace with fixed space weight, i.e. for an orbital configuration. Since the dimension of this subspace depends only on the number of singly occupied orbitals, these functions only constitute a complete orthonormal basis if the orbital indices $j_l$ in Eq. (4) are all different [12]. This may be assumed without loss of generality because the reference state $|0\rangle$ may always be chosen such that this condition is fulfilled, e.g. by choosing for the reference state a closed-shell state such that the number of shift operators involved in the transition from this state to the configuration at hand equals the number of singly occupied orbitals in this configuration. Moreover, if $|\boldsymbol{n}, S, \boldsymbol{t}\rangle$ is an $N$-electron state and if $|0\rangle$ is an $N_0$-electron state, it will be assumed that the following relation holds:

$$N_0 = \begin{cases} N \text{ for } N = \text{even} \\ N-1 \text{ for } N = \text{odd}. \end{cases}$$

This implies that for $N = \text{even}$ the number of creation operators $n_c$ in Eq. (4) equals the number of annihilation operators $n_a$, whereas for $N = \text{odd}$ we have $n_c = n_a + 1$.

We now turn to the alternative method for the construction of spin eigenfunctions, viz. the spin-pairing method. In order to obtain a second quantization representation for this method we start by defining transition operators as follows [13]:

$$\boldsymbol{C}_{k\to l} \equiv \boldsymbol{C}_l(\tfrac{1}{2}, -1)\,\boldsymbol{A}_k(1) = 2^{-\frac{1}{2}}(\boldsymbol{c}_l^\dagger \boldsymbol{c}_k + \bar{\boldsymbol{c}}_l^\dagger \bar{\boldsymbol{c}}_k)\,. \tag{5}$$

If the spin eigenfunctions are generated from the reference state $|0\rangle$ described above, only those transition operators are needed, for which $k \in \{i\}$ and $l \in \{r\}$. The transition operators commute with $\boldsymbol{S}^2$, and therefore $S$ is not changed if these operators are applied to a spin eigenfunction. Spin eigenfunctions with the same value of $S$ as the reference state, but with different space weights may be generated by repeated application of transition operators:

$$|\boldsymbol{n}, 0, \boldsymbol{p}_0\rangle = \prod_{k=1}^{m} \boldsymbol{C}_{i_k \to r_k} |0\rangle \tag{6}$$

where $p$ indicates that the resulting functions belong to a spin eigenfunction basis of spin-paired functions and $|\boldsymbol{n}, S, \boldsymbol{p}_0\rangle$ is the first member of this basis.

A spin eigenfunction with an arbitrary value of $S$ may be obtained by adding a certain number of step-up operators $B_j(1)$:

$$|\boldsymbol{n}, S, \boldsymbol{p}_0\rangle = \prod_{l=1}^{2S} B_{j_l}(1)\,|\boldsymbol{n}', 0, \boldsymbol{p}_0\rangle = \prod_{l=1}^{2S} B_{j_l}(1) \prod_{k=1}^{m} \boldsymbol{C}_{i_k \to r_k} |0\rangle \tag{7}$$

with $m = \frac{1}{2}(n_s - 2s)$.

It will again be assumed that all orbital indices are different, in which case may be shown from the anticommutation relations for the fermion operators, that

$$(\boldsymbol{C}_{i\to r}, \boldsymbol{C}_{j\to s}) = (\boldsymbol{C}_{i\to r}, \boldsymbol{B}_j(1)) = (\boldsymbol{B}_j(1), \boldsymbol{B}_k(1)) = 0\,. \tag{8}$$

In this case the basis is made complete by choosing a number of permutations of orbital indices, such that an independent set of functions results. How this may be done will be explained in Section 4.

Equation (7) is the second quantization equivalent of the spin-pairing method [4]. This may be shown as follows. If a transition operator acts on the reference state, a singlet function with two singly occupied orbitals is generated and consequently each factor $\boldsymbol{C}_{i\to r}$ in Eq. (7) corresponds to a factor $(\alpha\beta-\beta\alpha)$ in the spin-pairing method. Moreover, from Eqs. (1 a) and (2 a) it follows that the step-up operators $\boldsymbol{B}_j(1)$ correspond to factors $\alpha$ in $|\boldsymbol{n}, S, 1\rangle$, and thus Eq. (7) corresponds to a spin function constructed from factors $(\alpha\beta-\beta\alpha)$ and $\alpha$, as in the spin-pairing method.

## 3. Recursion Formulas

The function of Eq. (7) may be expressed in terms of shift operators by using Eqs. (1), (2), and (5):

$$|\boldsymbol{n}, S, \boldsymbol{p}_0\rangle = \prod_{l}^{2S} \boldsymbol{B}_{j_l}(1) \prod_{k}^{m} (\boldsymbol{C}_{r_k}(\tfrac{1}{2}, -1)\, \boldsymbol{A}_{i_k}(1))\, |0\rangle = |\boldsymbol{n}, S, \boldsymbol{t}_0\rangle\,. \tag{9}$$

This function is identical with the branching diagram function corresponding to the lowest path (indicated by $\boldsymbol{t}_0$).

In order to proceed, we need the commutation relations of $\boldsymbol{S}_-$ with $\boldsymbol{c}_r^\dagger$ and $\bar{\boldsymbol{c}}_i$. These relations follow directly from the second quantization expression for $\boldsymbol{S}_-$ and the anticommutation relations for the fermion operators and are found to be

$$(\boldsymbol{S}_-, \boldsymbol{c}_r^\dagger) = \bar{\boldsymbol{c}}_r^\dagger$$
$$(\boldsymbol{S}_-, \bar{\boldsymbol{c}}_i) = -\boldsymbol{c}_i\,.$$

All functions corresponding to higher paths may now be generated from the function of Eq. (9) by a recursion formula, which may be derived using this result and Eqs. (1)–(3) and (5). The result is

$$\boldsymbol{B}_j(S+\tfrac{1}{2}, -1)\, \boldsymbol{B}_l(1) = (S+1)^{-\frac{1}{2}} (S^{\frac{1}{2}} \boldsymbol{B}_j(1)\ \boldsymbol{B}_l(S, -1) + (2S+1)^{\frac{1}{2}}\, \boldsymbol{C}_{i\to r})\,. \tag{10}$$

The branching-diagram functions may be ordered via the sets $\boldsymbol{t} = \{t_j\}$ in exactly the same way as for the space weight $\boldsymbol{n}$ [10]. With this ordering one has the relation $\boldsymbol{t} > \boldsymbol{t}'$, if the sequence $\boldsymbol{B}_j(S+\frac{1}{2}, -1)\, \boldsymbol{B}_l(1)$ when applied to the function $|\boldsymbol{n}', S, \boldsymbol{t}''\rangle$, produces the function $|\boldsymbol{n}, S, \boldsymbol{t}\rangle$, while the function $|\boldsymbol{n}, S, \boldsymbol{t}'\rangle$ is generated from the same function by the sequence $\boldsymbol{B}_j(1)\, \boldsymbol{B}_l(S, -1)$.

Repeated application of Eq. (10) leads to functions of the form

$$|\boldsymbol{n}, S, \boldsymbol{t}\rangle = \sum_{p}^{g} c_{pt} \boldsymbol{P}_p |\boldsymbol{n}, S, \boldsymbol{p}_0\rangle \tag{11}$$

with $g = f(n_s, S) =$ the dimension of the subspace with fixed space weight and containing $n_s$ singly occupied orbitals and $\boldsymbol{P}_p$ is a permutation operating on the orbital indices $i_l$ and $r_l$.

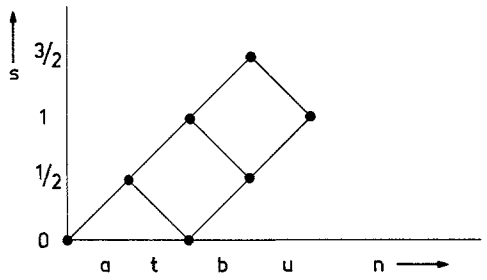


Fig. 1. Spin eigenfunctions with $S=1$, $n_s=4$

This may be illustrated by an example (see Fig. 1), where Eq. (8) is used in order to move the transition operators to the right in the spin-paired functions:

$$\begin{aligned}|\boldsymbol{n}, S, \boldsymbol{t}\rangle &= \boldsymbol{C}_u(\tfrac{3}{2}, -1)\,\boldsymbol{A}_b(1)\,\boldsymbol{C}_t(1)\,\boldsymbol{A}_a(1)\,|0\rangle \\ &= 2^{-\frac{1}{2}}(\boldsymbol{C}_u(1)\,\boldsymbol{A}_b(l, -1) + 3^{\frac{1}{2}}\boldsymbol{C}_{b\to u})\,\boldsymbol{C}_t(1)\,\boldsymbol{A}_a(1)\,|0\rangle \\ &= \{(\tfrac{3}{2})^{\frac{1}{2}}\boldsymbol{C}_{b\to u}\boldsymbol{C}_t(1)\,\boldsymbol{A}_a(1) + 2^{-\frac{1}{2}}(\tfrac{3}{2})^{-\frac{1}{2}}\boldsymbol{C}_u(1)((\tfrac{1}{2})^{\frac{1}{2}}\boldsymbol{A}_b(1)\boldsymbol{C}_t(\tfrac{1}{2}, -1) + 2^{\frac{1}{2}}\boldsymbol{C}_{b\to t})\boldsymbol{A}_a(1)\}\,|0\rangle \\ &= 6^{-\frac{1}{2}}(3\boldsymbol{C}_t(1)\,\boldsymbol{A}_a(1)\,\boldsymbol{C}_{b\to u} + 2\boldsymbol{C}_u(1)\,\boldsymbol{A}_a(1)\,\boldsymbol{C}_{b\to t} + \boldsymbol{C}_u(1)\,\boldsymbol{A}_b(1)\,\boldsymbol{C}_{a\to t})\,|0\rangle\,.\end{aligned}$$

If, as in the above example, the function $|\boldsymbol{n}, S, \boldsymbol{t}\rangle$ expressed in the form of Eq. (4) contains only one step-down operator $\boldsymbol{C}_j(S, -1)$ followed by an arbitrary (odd) number ($2m-1$, say) of step-up operators $\boldsymbol{B}_j(1)$, then the coefficients $c_{pt}$ of Eq. (11) may be calculated explicitly. Repeated application of Eqs. (8) and (10) then yields

$$\begin{aligned}&\boldsymbol{C}_{r_m}(m-\tfrac{1}{2}, -1)\,\boldsymbol{A}_{i_m}(1)\prod_{k=1}^{m-1}(\boldsymbol{C}_{r_k}(1)\,\boldsymbol{A}_{i_k}(1))\,|\boldsymbol{n}, 0, \boldsymbol{t}_0\rangle \\ &= N(m)\sum_{p=l}^{2m-1} c_p \boldsymbol{P}_p\left\{\boldsymbol{C}_{i_m\to r_m}\prod_{k=1}^{m-1}(\boldsymbol{C}_{r_k}(1)\,\boldsymbol{A}_{i_k}(1))\right\}\,|\boldsymbol{n}, 0, \boldsymbol{t}_0\rangle\end{aligned} \tag{12a}$$

with

$$\begin{aligned}c_p &= 2m-p\,, \\ \boldsymbol{P}_l &= 1\end{aligned} \tag{12b}$$

$$\boldsymbol{P}_p = \begin{cases}\boldsymbol{P}(i_l, i_{l+1})\,\boldsymbol{P}_{p-1}, & l = m-(p+1)/2 \quad \text{for} \quad p=\text{odd} \\ \boldsymbol{P}(r_l, r_{l+1})\,\boldsymbol{P}_{p-1}, & l = m-p/2 \quad \text{for} \quad p=\text{even}\,,\end{cases} \tag{12c}$$

$$N(m) = \Big(\sum_p c_p\Big)^{-\frac{1}{2}} = (m(2m-1))^{-\frac{1}{2}}\,. \tag{12d}$$

An analogous formula holds for the case where the sequence starts with $\boldsymbol{A}_i(S, -1)$ rather than $\boldsymbol{C}_r(S, -1)$, the only difference being that Eqs. (12b) and (12d) are replaced by

$$c_p = 2m-p-1\,; \tag{12e}$$

$$N(m) = ((2m-2)\,(2m-1))^{-\frac{1}{2}}\,. \tag{12f}$$

From Eqs. (12b) and (12e) it is clear that with a suitably chosen normalization the coefficients $c_p$ have a simple form. Moreover, the normalization constant

$N(m)$ may be calculated directly even though the spin-paired functions are not orthogonal.

These results also hold for the general case Eq. (11), and the coefficients may thus be tabulated as positive integers. By repeated application of Eqs. (12) it may be verified that the normalization constant may always be calculated directly from the coefficients by

$$N(t) = \left(\sum_p c_p\right)^{-\frac{1}{2}}.$$

However, in this case it is not possible to derive an explicit formula for the coefficients $c_p$. Equation (12) then has to be applied a number of times. For this number $n_r$ the following relation holds

$$n_r \leqq \tfrac{1}{2} n_s - S$$

whereas in the conventional method $n_s$ steps are needed. The number of terms in the expansion (11) is also smaller than in an expansion involving Slater determinants as basis functions, because each spinpaired function contains a number of determinants. This especially applies to low values of $S$.

## 4. Independent Spin-paired Functions

In Eq. (10) the left-hand side and the first term in the righthand side correspond to orthogonal branching-diagram functions. If the latter function contains $p$ independent spin-paired functions Eq. (10) implies that the second term in the right-hand side must correspond to a function containing at least one spin-paired function which is independent of the $p$ functions contained in the first term. This function may be extracted from the branching-diagram function by repeated application of Eq. (10) to the reference state $|\boldsymbol{n}, S, \boldsymbol{t}_0\rangle$. Each time the first term in the right hand side of Eq. (10) is discarded. The number of singly occupied orbitals in the branching diagram part of the second term decreases by two and by moving the transition operators to the right (using Eq. (8)), this eventually leads to a spin-paired function of the form

$$|\boldsymbol{n}, S, \boldsymbol{p}\rangle = \boldsymbol{P}_p |\boldsymbol{n}, S, \boldsymbol{p}_0\rangle \tag{13}$$

with $|\boldsymbol{n}, S, \boldsymbol{p}_0\rangle$ given by Eq. (7). Since the transition operators commute with each other and with the step-up operators, this function is uniquely determined by the form of the branching diagram path. Consequently each time a new branching diagram function is generated by applying Eq. (10), a new permutation $\boldsymbol{P}_p$ (corresponding to a unique independent spin-paired function $|\boldsymbol{n}, S, \boldsymbol{p}\rangle$) is generated. Therefore a one-to-one correspondence exists between the set of branching diagram paths and the basis of spin-paired functions generated by our method.

The construction of an independent set of spin-paired functions may also be realized by the following procedure, which must be applied for each branching-diagram path in turn.

Find two orbital indices $k$ and $l$ ($k < l$), such that the associated shift operators $\boldsymbol{B}_k(1)$ and $\boldsymbol{B}_l(S, -1)$ are neighbours in the branching diagram function, Eq. (4).

Replace $\boldsymbol{B}_k(1)\,\boldsymbol{B}_l(S,-1)$ by a transition operator ($\boldsymbol{C}_{k\to l}$ or $\boldsymbol{C}_{l\to k}$), and remove the steps corresponding to $k$ and $l$ from the branching diagram path. The operators $\boldsymbol{B}_{k-1}$ and $\boldsymbol{B}_{l+1}$ thus become neighbours in the function associated with the remaining part of the branching diagram path. This procedure is repeated until all operators $\boldsymbol{B}_k(S,-1)$ are removed and the result is a function of the form of Eq. (13).

This method is a generalization of the Rumer diagram method [9] to arbitrary values of $S$. In the latter method one selects all diagrams which contain only non-crossing arrows, but this restriction is only sufficient for $S=0$. For $S>0$ the number of canonical Rumer diagrams is larger than the number of independent spin-paired functions. The present method corresponds to a selection of those canonical Rumer diagrams which may be associated with an independent set of spin-paired functions. This may easily be shown by the following argument. Replacing the operators $\boldsymbol{B}_k(1)\,\boldsymbol{B}_l(S,-1)$ by a transition operator in a branching diagram function corresponds to drawing an arrow connecting $k$ and $l$ in a Rumer diagram. Since $k$ and $l$ always correspond to neighbour positions in the branching diagram path, the arrows in the Rumer diagram cannot cross. Therefore the Rumer diagram corresponding to a spin-paired function constructed by the present method will be one of the canonical diagrams.

## References

1. Yamanouchi, T.: Proc. Phys. Math. Soc. (Japan) **19**, 436 (1937)
   Rutherford, D. F.: Substitutional analysis. Cambridge, England: University Press 1948
   McIntosh, H. V.: J. Math. Phys. **1**, 453 (1960)
   Coleman, A. J.: Advan. Quantum Chem. **4**, 83 (1968)
2. Kotani, M., Amemiya, A., Ishiguro, E., Kimura, T.: Tables of molecular integrals. Tokyo: Maruzen 1963
3. Pauncz, R.: Alternant molecular orbital method. London: Saunders 1967
4. McWeeny, R., Sutcliffe, B. T.: Methods of molecular quantum mechanics. London: Academic Press 1969
5. Löwdin, P.-O.: Phys. Rev. **97**, 1509 (1955); Rev. Mod. Phys. **34**, 520 (1962); Rev. Mod. Phys. **36**, 966 (1964)
6. Kouba, J., Öhrn, Y.: Intern. J. Quantum Chem. **3**, 513 (1969)
7. Smith, V. H., Harris, F. E.: J. Math. Phys. **10**, 771 (1969)
8. Schaefer III, H. F.: J. Comp. Phys. **6**, 142 (1970);
   Kuprievich, V. A., Kruglyak, Y. A., Mozdor, E. V.: Croat. Chem. Acta **43**, 1 (1971)
9. Rumer, G.: Göttinger Nachr. **1932**, 377
   Eyring, H., Walter, J., Kimball, G. E.: Quantum chemistry. New York: Wiley 1944
10. Moshinsky, M.: In: Moshinsky, M., Brody, T. A., Jacob, G. (Eds.): Many-body problems and other selected topics in theoretical physics, Vol. I. New York: Gordon and Breach 1966
    Moshinsky, M.: J. Math. Phys. **4**, 1128 (1963)
11. Merzbacher, E.: Quantum mechanics, 2nd Ed., Chapters 20 and 21. New York: Wiley 1970
12. Harris, F. E.: Advan. Quantum Chem. **3**, 61 (1967)
13. Simons, J.: J. Chem. Phys. **55**, 1218 (1971)

Dr. P. J. A. Ruttink
Theoretical Chemistry Group
Rijksuniversiteit Utrecht
Padualaan 8
Utrecht, The Netherlands