

A partially projected wave function for radicals

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Received 6 October 1997

A partially projected wave function for odd electron systems with quantum number $M = 1/2$, containing μ spin functions α and ν spin functions β , with fractional spin component $S_z = 1/2$ and $3/2$ are derived from the totally projected wave function. To obtain these wave functions new symmetry relations between Sanibel coefficients for the odd electron case have been found, as well as the relations between primitive spin functions and their spin permutations. The wave function for the doublet state is shown not to contain contamination of the quadruplet state, and the wave function for the quadruplet does not have contamination of the duplet. Both wave functions exhibit equal forms except in the signs of their summation terms. The number of primitive spin functions depends on the number of electrons (n_s), it grows linearly as $n_s = (N + 3)/2$. It can be considered as a generalization of the half-projected Hartree–Fock wave function to the odd electron case. The HPHF wave function is defined for even electron systems and consists of only two Slater determinants, it has been shown to introduce some correlation effects and it has been successfully applied to calculate the low-lying excited states of molecules. Therefore, this investigation is the first step to propose a method to calculate the excited states of radicals when other methods are impracticable.

1. Introduction

The simple different orbitals for different spins (DODS) single Slater determinant wave functions of the UHF method permit us to take into account a part of the correlation energy since they give lower energies than the conventional (restricted) HF method using doubly filled orbitals. The use of the DODS wave functions has resulted, however, in the situation that the UHF wave functions fail to belong to a pure spin state; they are not eigenfunctions of the total spin operators \hat{S}^2 . Generally, the DODS Slater determinant can be considered as a sum of terms corresponding to all the multiplicities which are possible for the given number of electrons and given M eigenvalue of the resulting \hat{S}_z operator.

Löwdin [3] has proposed to select the component which corresponds to the desired multiplicity and to use the wave function obtained in this way as a trial wave function in the variational procedure. For this reason Löwdin introduced the spin projection

operator

$$\hat{\Theta}_S = \prod_{l \neq S} \frac{\hat{S}^2 - l(l+1)}{S(S+1) - l(l+1)}, \quad (1)$$

which annihilates all the components of any wave function except that component which has the desired spin multiplicity $2S+1$. The method consisting of the variational optimization of a spin-projected single DODS Slater determinant is called extended Hartree–Fock method (EHF) [3].

Since Löwdin's work in 1955 many authors have worked in this field using different approaches and techniques. We shall shortly discuss those works which are of most importance from the point of view of the present approach.

The EHF equations for the even electron [5,6] and odd electron [4] systems have been derived by Mayer, from the generalized Brillouin theorem using corresponding orbitals. Some applications of the EHF method to systems with even number of electrons, as butadiene, cyclobutadiene, and systems with odd number of electrons as benzyl radical, show that the EHF method introduces about 90% of the correlation energy in the firsts and more than 50% in the latter ones (comparing with what is known in the literature) [5,6].

In addition, the EHF resulting wave function has a very large overlap with the CI one. Therefore, the EHF wave function is very close to the CI one. By contrary, the UHF wave function has a much smaller overlap with the CI one, the UHF wave function may be considered much worse than the RHF one, even that it introduces some correlation in the energy.

More recently, Smeyers has worked out a simple variant of the partial annihilation, called half-projected HF (HPHF) [11,14]. The half-projected Hartree–Fock function was initially proposed in order to introduce some electronic correlation effects in the wave function for singlet ground states. In this model, the wave function is written as a linear combination of only two open-shell (DODS) Slater determinants [12]

$$\Psi^{\text{HPHF}} = \frac{1}{2} \{ |a_1 \bar{b}_1 a_2 \bar{b}_2 \dots a_n \bar{b}_n| + (-1)^{n+S} |b_1 \bar{a}_1 b_2 \bar{a}_2 \dots b_n \bar{a}_n| \}, \quad (2)$$

where the second Slater determinant is derived from the first by projection on the even spin momentum space.

It can be easily shown that this projector possesses the simple form [11,14]

$$\hat{A}(S) = \frac{1}{2} [1 + (-1)^{n+S} \hat{\rho}], \quad (3)$$

where n stands for the number of pairs of electrons and $\hat{\rho}$ is an operator which permutes all the a_i and b_i functions in the same shell.

It can be easily verified, also, that the $\hat{A}(S)$ is a projection operator which depends only on the parity of the spin number S :

$$\hat{A}(S) = [\hat{A}(S)]^2, \quad \hat{A}(0)\hat{A}(1) = 0, \quad (4)$$

that $\widehat{A}(0)$ projects on the spin space even; and $\widehat{A}(1)$ projects on the spin space odd.

Thus, the HPHF function is not a pure spin function. But the ground state wave function for singlet state will not contain triplet component which is usually the largest contaminant in a DODS function. Furthermore, it may be expected that the quintuplet contamination will be very small in a singlet ground state because of its higher energy.

The two-determinantal form of the HPHF function, however, suggested its use for the direct determination of the lowest singlet excited states. In this aim, a procedure similar to that for the ground state was developed and successfully applied to small molecular systems [2,9,15]. In these calculations, the HPHF model was shown to yield much better results than a single excitation CI calculation [2]. Also, this procedure has been described and successfully applied to the determination of the optimal geometry of relatively large systems as cyclobutanone and 3-cyclopenten-1-one, in their first singlet ($n \rightarrow \pi^*$) excited states [16], to which large CI calculations cannot be applied.

A similar wave function to the HPHF one would be desirable for odd electron systems. But the HPHF wave function cannot be directly extended to odd number of electrons because it has been derived from the fully projected wave function for even electron systems. Therefore, if one wants to write the analogous wave function with odd number of electrons, one has to go back to the fully projected one of the EHF method and to investigate whether there are relations between Sanibel coefficients as in the even electron case and if there are any relations between primitive spin functions and those obtained after a given permutation of spin.

2. Derivation of the wave function for odd electron systems

In general, in odd electron systems we have N spin 1/2 particles of which μ have z component up and $\nu = N - \mu \leq \mu$ have z component down. An eigenfunction of \widehat{S}^2 and \widehat{S}_z with eigenvalues $S(S+1)$ and M , respectively (the latter is satisfied with $(1/2)(\mu - \nu) = M \geq 0$), can be obtained by the use of the Löwdin projection operator $\widehat{\Theta}_S$ on the spin function $[\alpha^\mu][\beta^\nu]$, the product of the $\mu\alpha$'s and $\nu\beta$'s leads to the Löwdin expansion [3]

$$\widehat{\Theta}_{SM}[\alpha^\mu][\beta^\nu] = \sum_{q=1}^{\nu} C_q(S, M, n)[\alpha^{\mu-q}\beta^q][\alpha^q\beta^{\nu-q}], \quad (5)$$

where $[\alpha^p\beta^q]$ is the sum of all $\binom{p+q}{p}$ possible products of $p\alpha$ spin functions and $q\beta$ spin functions and $n = N/2$.

The coefficients in the case $M = S$ [7,8], called *principal case*, yield the expression

$$\Theta_{SS}[\alpha^\mu][\beta^\nu] = \frac{2S+1}{\mu+1} \sum_{q=0}^{\nu} (-1)^q \binom{\mu}{q}^{-1} [\alpha^{\mu-q}\beta^q][\alpha^q\beta^{\nu-q}]. \quad (6)$$

The Sanibel coefficients in the *principal case* can be given as

$$C_q = (-1)^q \frac{(2S+1)}{\mu+1} \binom{\mu}{q} \quad (7)$$

and

$$T_q = [\alpha^{\mu-q} \beta^q] [\alpha^q \beta^{\nu-q}]. \quad (8)$$

The case where $M = 0$ can be extracted from (6).

For the *general case* where $S > M$ the Sanibel coefficients have the form [17]

$$C_q(S, M, n) = \frac{2S+1}{1+n+S} \sum_{k=0}^{S-M} (-1)^{q+S-M-k} \binom{S-M}{k} \\ \times \binom{S+M}{S-M-k} \binom{n+S}{\mu-q+k}^{-1}. \quad (9)$$

We will use the Löwdin projection operators and the Sanibel coefficients in the next sections.

2.1. Symmetry relation between the Sanibel coefficients with odd number of electrons

The form of the Sanibel coefficients for the case $S = M$ having an odd number of electrons as has been shown above is

$$C_q = (-1)^q C_0 \binom{\mu}{q} \quad \text{with } C_0 = \frac{(2S+1)}{\mu+1}. \quad (10)$$

Let us substitute the index q by $\mu - q$ and we have

$$C_{\mu-q} = (-1)^{\mu-q} \binom{\mu}{\mu-q} C_0; \quad (11)$$

dividing expression (11) by expression (10),

$$\frac{C_{\mu-q}}{C_q} = \frac{(-1)^{\mu-q} \binom{\mu}{\mu-q}^{-1}}{(-1)^q \binom{\mu}{q}^{-1}} \quad (12)$$

for all q is then

$$\frac{C_{\mu-q}}{C_q} = \frac{(-1)^\mu}{(-1)^{2q}}, \quad (13)$$

by means of the identity between binomial coefficients:

$$\binom{n}{k} = \binom{n}{n-k}. \quad (14)$$

Finally, we have the symmetry relation

$$C_{\mu-q} = (-1)^{\mu} C_q, \quad q = 1, 2, \dots, \mu. \quad (15)$$

In the same way, for $C_{\nu-q}$ we find

$$\frac{C_{\nu-q}}{C_q} = \frac{(-1)^{\nu-q} \binom{\mu}{\nu-q}^{-1}}{(-1)^q \binom{\mu}{q}^{-1}} = (-1)^{\nu} \frac{(q+1)}{\mu-q} \quad (16)$$

and the symmetry relation¹

$$C_{\nu-q} = (-1)^{\nu} \frac{(q+1)}{\mu-q} C_q, \quad q = 0, 1, 2, \dots, \nu. \quad (17)$$

2.2. Relations among primitive spin functions and their spin permutations in the odd electron case

Let us define a new permutation operator $\widehat{P}_{\alpha\beta}^{\nu}$ of the spin functions, which interchanges simultaneously ν functions β for α and therefore ν functions α for β . We restrict here our study to those cases where $\mu = \nu + 1$, i.e., radicals, other cases with $\mu - \nu > 1$ will not be considered here. As there is one α function more than β functions, there is more than one possibility of interchanging the β functions by α , and the result is the sum of these possibilities. The number of terms of the sum then is given by $\binom{\mu}{\nu}$.

For example, taking a primitive function of 5 electrons,² $\widehat{P}_{\alpha\beta}^{\nu}$ acts as follows:

$$\widehat{P}_{\alpha\beta}^{\nu} \alpha\alpha\alpha\beta\beta = \beta\beta\alpha\alpha\alpha + \beta\alpha\beta\alpha\alpha + \alpha\beta\beta\alpha\alpha. \quad (18)$$

So, the action of the permutation operator on a primitive function yields a sum of primitive functions, belonging to the set of primitive functions obtained by application of the Löwdin projection operator, T_q , with $q = 0, 1, 2, \dots, \nu$. Following the case of 5 electrons, $\mu = 3$ and $\nu = 2$. The totally projected wave function is a sum of terms T_q , and, therefore, it is a sum of 10 primitive spin functions (permutations with repetition of 5 functions $P_5^{3,2} = 5!/(3!2!) = 10$):

$$\begin{aligned} T_0 &= [\alpha^3][\beta^2] = \alpha\alpha\alpha\beta\beta, \\ T_1 &= [\alpha^2\beta][\alpha\beta] = \alpha\alpha\beta\alpha\beta + \alpha\alpha\beta\beta\alpha + \alpha\beta\alpha\alpha\beta + \alpha\beta\alpha\beta\alpha \\ &\quad + \beta\alpha\alpha\alpha\beta + \beta\alpha\alpha\beta\alpha, \\ T_2 &= [\alpha\beta^2][\alpha^2\beta] = \alpha\beta\beta\alpha\alpha + \beta\alpha\beta\alpha\alpha + \beta\beta\alpha\alpha\alpha. \end{aligned} \quad (19)$$

¹ In the even electron case the symmetry relation is $C_{n-q} = (-1)^{n+S} C_q$.

² Using the following short notation $\alpha(1)\alpha(2)\beta(3) = \alpha\alpha\beta$.

Applying the permutation operator $\widehat{P}_{\alpha\beta}^{\nu}$ on every primitive function and collecting terms, we have in this example

$$\begin{aligned}\widehat{P}_{\alpha\beta}^{\nu}T_0 &= T_2, \\ \widehat{P}_{\alpha\beta}^{\nu}T_1 &= 2T_2 + 2T_1, \\ \widehat{P}_{\alpha\beta}^{\nu}T_2 &= 3T_2 + T_1.\end{aligned}\tag{20}$$

This result looks apparently arbitrary but investigating the action of $\widehat{P}_{\alpha\beta}^{\nu}$ on $T_0(\nu), T_1(\nu), T_2(\nu), T_3(\nu), T_4(\nu), T_5(\nu), \dots, T_{\nu}(\nu)$, ν being a given number of β electrons, one finds general expressions

$$\begin{aligned}\widehat{P}_{\alpha\beta}^{\nu}T_0(\nu) &= T_{\nu}(\nu), \\ \widehat{P}_{\alpha\beta}^{\nu}T_1(\nu) &= \nu T_{\nu}(\nu) + 2T_{\nu-1}(\nu), \\ \widehat{P}_{\alpha\beta}^{\nu}T_2(\nu) &= (\nu - 1)T_{\nu-1}(\nu) + 3T_{\nu-2}(\nu), \\ \widehat{P}_{\alpha\beta}^{\nu}T_3(\nu) &= (\nu - 2)T_{\nu-2}(\nu) + 4T_{\nu-3}(\nu), \\ \widehat{P}_{\alpha\beta}^{\nu}T_4(\nu) &= (\nu - 3)T_{\nu-3}(\nu) + 5T_{\nu-4}(\nu), \\ \widehat{P}_{\alpha\beta}^{\nu}T_5(\nu) &= (\nu - 4)T_{\nu-4}(\nu) + 6T_{\nu-5}(\nu), \\ &\vdots \\ \widehat{P}_{\alpha\beta}^{\nu}T_{\nu}(\nu) &= T_1(\nu) + \nu T_0(\nu).\end{aligned}\tag{21}$$

Now let us multiply from the left and the right side, respectively, all equations by their corresponding Sanibel coefficients C_0, C_1, \dots, C_{ν} :

$$\begin{aligned}C_0\widehat{P}_{\alpha\beta}^{\nu}T_0(\nu) &= C_0T_{\nu}(\nu), \\ C_1\widehat{P}_{\alpha\beta}^{\nu}T_1(\nu) &= \nu C_1T_{\nu}(\nu) + 2C_1T_{\nu-1}(\nu), \\ C_2\widehat{P}_{\alpha\beta}^{\nu}T_2(\nu) &= (\nu - 1)C_2T_{\nu-1}(\nu) + 3C_2T_{\nu-2}(\nu), \\ C_3\widehat{P}_{\alpha\beta}^{\nu}T_3(\nu) &= (\nu - 2)C_3T_{\nu-2}(\nu) + 4C_3T_{\nu-3}(\nu), \\ C_4\widehat{P}_{\alpha\beta}^{\nu}T_4(\nu) &= (\nu - 3)C_4T_{\nu-3}(\nu) + 5C_4T_{\nu-4}(\nu), \\ C_5\widehat{P}_{\alpha\beta}^{\nu}T_5(\nu) &= (\nu - 4)C_5T_{\nu-4}(\nu) + 6C_5T_{\nu-5}(\nu), \\ &\vdots \\ C_{\nu}\widehat{P}_{\alpha\beta}^{\nu}T_{\nu}(\nu) &= C_{\nu}T_1(\nu) + \nu C_{\nu}T_0(\nu).\end{aligned}\tag{22}$$

Performing the sum of all equations, we get a general expression³

$$\sum_{q=0}^{\nu} C_q \widehat{P}_{\alpha\beta}^{\nu} T_q = \sum_{q=0}^{\nu} (\mu - \nu + q) C_q T_{\nu-q} + \sum_{q=1}^{\nu} (\mu - q) C_q T_{\mu-q}. \quad (23)$$

This general formula will be used to prove that the Löwdin projection operator for the case $S = M$ ($M = 1/2$) acting on a function defined for $S = 3/2$ is zero, and, therefore, the function does not contain any spin contamination of a state $S = 1/2$ which is the next state in energy, and usual contamination in odd electron systems (see branching diagram [7]).

3. The partially projected wave function

We have investigated the symmetry relations between Sanibel coefficients and primitive spin functions and we have obtained the results shown in section 2. In this way we have found two wave functions that fulfill our requirements of spin, i.e., they do not contain any contamination of the energetically nearest state of spin. It would be desirable to show the derivation of such wave functions from the fully projected one, but until now no demonstration has been carried out. Nevertheless, we would like to investigate this aspect of the theory in further works. For this reason we propose the two wave functions as an ansatz, and we write at the moment only the spin part.

For duplet states, $S = 1/2$ (including normalization constant),

$$\Psi = \frac{1}{\sqrt{4 + \mu}} [2 + (-1)^{\nu} \widehat{P}_{\alpha\beta}^{\nu}] T_0, \quad (24)$$

where $\widehat{P}_{\alpha\beta}^{\nu}$ is defined in section 1 as the permutation operator which interchanges ν functions β for ν functions α simultaneously. This operator yields a sum, and ν is the number of β electrons. T_0 is the primitive function which is a product of μ functions α and ν functions β , in this order. So, considering the spin part, T_0 is the reference wave function.

For quadruplet states, $S = 3/2$ (including normalization constant),

$$\Psi = \frac{1}{\sqrt{1 + \mu}} [1 + (-1)^{\mu} \widehat{P}_{\alpha\beta}^{\nu}] T_0; \quad (25)$$

one may realize that the sign now depends on μ and the constant of the first term, which is always 2 for duplets, is now always 1 for quadruplets.

As for a given system $\mu = \nu + 1$ both wave functions have a different sign in the second part, and, of course, both wave functions are formed with the same primitive spin functions (see table 1).

³ This result cannot be expressed in an easier way because the indices must be such that there does not appear a term T_q which is not defined, i.e., T_{μ} . In the even electron case this is $\widehat{P}_{\alpha\beta}^{\nu} T_q = T_{n-q}$.

Table 1

Signs of the second part of the partially projected wave functions for $S = 1/2$ and $S = 3/2$ depending on the number of electrons, N (μ is the number of α spin functions and ν the number of β ones).

N	μ	ν	$(-1)^\nu$ in $\Psi(S = 1/2)$	$(-1)^\mu$ in $\Psi(S = 3/2)$
3	2	1	-	+
5	3	2	+	-
7	4	3	-	+
9	5	4	+	-
11	6	5	-	+

Let us investigate some examples, e.g., until 7 electrons. In the 3 electron case, the partially projected wave functions coincide with the exact eigenfunctions

$$\begin{aligned}\Psi(S = 1/2) &= 2\alpha\alpha\beta - (\beta\alpha\alpha + \alpha\beta\alpha), \\ \Psi(S = 3/2) &= \alpha\alpha\beta + (\beta\alpha\alpha + \alpha\beta\alpha).\end{aligned}\tag{26}$$

With 5 electrons,

$$\begin{aligned}\Psi(S = 1/2) &= 2\alpha\alpha\alpha\beta\beta + (\beta\beta\alpha\alpha\alpha + \beta\alpha\beta\alpha\alpha + \alpha\beta\beta\alpha\alpha), \\ \Psi(S = 3/2) &= \alpha\alpha\alpha\beta\beta - (\beta\beta\alpha\alpha\alpha + \beta\alpha\beta\alpha\alpha + \alpha\beta\beta\alpha\alpha).\end{aligned}\tag{27}$$

Finally, in the 7 electron case,

$$\begin{aligned}\Psi(S = 1/2) &= 2\alpha\alpha\alpha\alpha\beta\beta\beta - (\beta\beta\beta\alpha\alpha\alpha\alpha + \beta\beta\alpha\beta\alpha\alpha\alpha \\ &\quad + \beta\alpha\beta\beta\alpha\alpha\alpha + \alpha\beta\beta\beta\alpha\alpha\alpha), \\ \Psi(S = 3/2) &= \alpha\alpha\alpha\alpha\beta\beta\beta + (\beta\beta\beta\alpha\alpha\alpha\alpha + \beta\beta\alpha\beta\alpha\alpha\alpha \\ &\quad + \beta\alpha\beta\beta\alpha\alpha\alpha + \alpha\beta\beta\beta\alpha\alpha\alpha),\end{aligned}\tag{28}$$

all of them written out without normalization constants. The number of terms in the wave function grows with the number of electrons but very slowly.

Both wave functions can be written in a compact form, with S and N in the exponent and in the coefficient:

$$\Psi(S, N) = T_0 + \frac{(-1)^{N/2-S}}{5/2 - S} \hat{P}_{\alpha\beta}^\nu T_0;\tag{29}$$

this wave function is not valid for $S = 5/2$.

3.1. Demonstration: the partially projected wave function for the states $S = 3/2$ does not contain contamination of $S = 1/2$

Let us take the example $N = 5$ and let us see how the primitive spin functions cancel due to the coefficients. The Sanibel coefficients for the projector of the state

$S = 1/2$ are $C_0 = 1/2$, $C_1 = -1/6$ and $C_2 = 1/6$. T_0 , T_1 and T_2 are defined in equation (19).

Let us apply the projector $\widehat{\Theta}_{SS}(S = 1/2)$ on the wave function for the quadruplet state (27):

$$\widehat{\Theta}_{SS}(S = 1/2)\Psi(S = 3/2). \quad (30)$$

One has here to apply the projector on every primitive spin function. When the primitive spin function is different than T_0 one may realize that the Löwdin projection operator commutes with any arbitrary permutation of the spin functions, P_{ij} :⁴

$$\widehat{\Theta}_{SM}\widehat{P}_{ij} = \widehat{P}_{ij}\widehat{\Theta}_{SM}. \quad (31)$$

The Löwdin projection operator is linear, therefore it acts separately on every function

$$\widehat{\Theta}_{SS}\{\alpha\alpha\alpha\beta\beta - (\beta\beta\alpha\alpha\alpha + \beta\alpha\beta\alpha\alpha + \alpha\beta\beta\alpha\alpha)\} \quad (32)$$

and yields the sum

$$\begin{aligned} \widehat{\Theta}_{SS}\Psi = & \frac{1}{2}\alpha\alpha\alpha\beta\beta - \frac{1}{6}\alpha\alpha\beta\alpha\beta - \frac{1}{6}\alpha\alpha\beta\beta\alpha - \frac{1}{6}\alpha\beta\alpha\alpha\beta - \frac{1}{6}\alpha\beta\alpha\alpha\beta - \frac{1}{6}\alpha\eta\alpha\beta\alpha \\ & - \frac{1}{6}\beta\alpha\alpha\alpha\beta - \frac{1}{6}\beta\alpha\alpha\beta\alpha + \frac{1}{6}\alpha\beta\beta\alpha\alpha + \frac{1}{6}\beta\alpha\beta\alpha\alpha + \frac{1}{6}\beta\beta\alpha\alpha\alpha \\ & - \frac{1}{2}\beta\beta\alpha\alpha\alpha + \frac{1}{6}\alpha\beta\beta\alpha\alpha + \frac{1}{6}\beta\alpha\beta\alpha\alpha + \frac{1}{6}\alpha\beta\alpha\alpha\beta + \frac{1}{6}\beta\alpha\alpha\alpha\beta \\ & + \frac{1}{6}\alpha\beta\alpha\beta\alpha + \frac{1}{6}\beta\alpha\alpha\beta\alpha - \frac{1}{6}\alpha\alpha\beta\alpha\beta - \frac{1}{6}\alpha\alpha\beta\beta\alpha - \frac{1}{6}\alpha\alpha\alpha\beta\beta \\ & - \frac{1}{2}\beta\alpha\beta\alpha\alpha + \frac{1}{6}\alpha\alpha\beta\alpha\beta + \frac{1}{6}\beta\alpha\alpha\alpha\beta + \frac{1}{6}\alpha\beta\beta\alpha\alpha + \frac{1}{6}\beta\beta\alpha\alpha\alpha \\ & + \frac{1}{6}\alpha\alpha\beta\beta\alpha + \frac{1}{6}\beta\alpha\alpha\beta\alpha - \frac{1}{6}\alpha\beta\alpha\alpha\beta - \frac{1}{6}\alpha\alpha\alpha\beta\beta - \frac{1}{6}\alpha\beta\alpha\beta\alpha \\ & - \frac{1}{2}\alpha\beta\beta\alpha\alpha + \frac{1}{6}\alpha\alpha\beta\alpha\beta + \frac{1}{6}\alpha\beta\alpha\alpha\beta + \frac{1}{6}\alpha\alpha\beta\beta\alpha + \frac{1}{6}\alpha\beta\alpha\beta\alpha \\ & + \frac{1}{6}\beta\alpha\beta\alpha\alpha + \frac{1}{6}\beta\beta\alpha\alpha\alpha - \frac{1}{6}\alpha\alpha\alpha\beta\beta - \frac{1}{6}\beta\alpha\alpha\alpha\beta - \frac{1}{6}\beta\alpha\alpha\beta\alpha \\ & = 0. \end{aligned} \quad (33)$$

The result of the projection equal to zero means that the wave function has no component of spin $S = 1/2$ or, what is the same, it has no contamination of this state of spin. Since in the branching diagram one can see that with odd number of electrons the possible states of spin are all fractional numbers $S = 1/2, 3/2, 5/2, \dots$, the fact that the next state in energy is not present in the wave function, makes the wave function almost pure of spin contaminations. Other states as $5/2$, which may

⁴ For example, $\widehat{P}_{25}\alpha\alpha\alpha\beta\beta = \alpha\beta\alpha\beta\alpha$. With several spin permutations one can express any primitive spin function, belonging to the set of a projected wave function, in terms of the spin function $\alpha\alpha\alpha\beta\beta$.

be present, are expected to be very high in energy, at least with a few number of electrons.⁵

We have projected with $N = 7$, $N = 9$ and so on, and we have found the same result equal to zero. Therefore, a general demonstration is necessary.

The wave function for a N -electron system (odd) for a state $S = 3/2$ has been defined as

$$\Psi = T_0 + (-1)^\mu \widehat{P}_{\alpha\beta}^\nu T_0. \quad (34)$$

The Löwdin projection operator for the principal case yields a sum from every term of the wave function. Taking into account that the permutation spin operator commutes with the projection operator, one has

$$\widehat{\Theta}_{SS}\Psi = \sum_{q=0}^{\nu} C_q T_q + (-1)^\mu \widehat{P}_{\alpha\beta}^\nu \sum_{q=0}^{\nu} C_q T_q. \quad (35)$$

The permutation operator is linear and can act on every term of the sum

$$\sum_{q=0}^{\nu} C_q T_q + (-1)^\mu \sum_{q=0}^{\nu} C_q \widehat{P}_{\alpha\beta}^\nu T_q. \quad (36)$$

As we have derived the action of such a permutation operator on an arbitrary sum of terms T_q , but better, the sum of this actions in equation (23)⁶

$$\sum_{q=0}^{\nu} C_q T_q + (-1)^\mu \sum_{q=0}^{\nu} \{(\mu - q)C_q T_{\mu-q} + (\mu - \nu + q)C_q T_{\nu-q}\}. \quad (37)$$

The summation of the second term remains equal if we change the indices in the following way:

$$\sum_{q=0}^{\nu} C_q T_q + (-1)^\mu \sum_{q=0}^{\nu} \{qC_{\mu-q} T_q + (\mu - q)C_{\nu-q} T_q\}, \quad (38)$$

using the relation of symmetry of the Sanibel coefficients in the odd electron case, deduced in section 2.1:

$$\sum_{q=0}^{\nu} C_q T_q + (-1)^\mu \sum_{q=0}^{\nu} \left\{ q(-1)^\mu C_q T_q + (\mu - q) \frac{(q+1)}{\mu - q} (-1)^\nu C_q T_q \right\}. \quad (39)$$

⁵ For example, in the case $N = 5$, the branching diagram shows the degeneracy of the spin states, 5 duplets, 4 quadruplets and one sextuplet. This last one in a given spin configuration with $M = 1/2$ must be very high in energy, therefore the spin contamination is very small in the total wave function for the ground state.

⁶ It was necessary to multiply already with the Sanibel coefficients because the first terms T_0 has only one term and not two as the others.

Collecting terms we have

$$\sum_{q=0}^{\nu} C_q T_q + (-1)^{\mu} + \sum_{q=0}^{\nu} C_q T_q \{q(-1)^{\mu} + q(-1)^{\nu} + (-1)^{\nu}\}. \quad (40)$$

Finally, simplifying,

$$\sum_{q=0}^{\nu} C_q T_q \{1 + (-1)^{\mu}(-1)^{\nu}\} = 0, \quad \mu + \nu = N, \quad N \text{ is odd}; \quad (41)$$

N is the number of electrons defined as odd. We have demonstrated that

$$\widehat{\Theta}_{SS}(S = 1/2)\Psi(S = 3/2) = 0. \quad (42)$$

3.2. Demonstration: the partially projected wave function for the states $S = 1/2$ does not contain contamination of $S = 3/2$

As in section 3.1, we have a trial wave function for $S = 1/2$, for example, with $N = 5$ and we are going to show that it has no component of $S = 3/2$. Let us apply the projector $\widehat{\Theta}_{SS}(S = 3/2)$ on the wave function for the duplet state (27):

$$\widehat{\Theta}_{SM}\{2\alpha\alpha\alpha\beta\beta + (\beta\beta\alpha\alpha\alpha + \beta\alpha\beta\alpha\alpha + \alpha\beta\beta\alpha\alpha)\} \quad (43)$$

with $S = 3/2$ and $M = 1/2$, leading as a result a sum with equal terms but different coefficients. The Sanibel coefficients for the projector of the state $S = 3/2$ (9) are $C_0 = 2/5$, $C_1 = 1/15$ and $C_2 = -4/15$:

$$\begin{aligned} \widehat{\Theta}_{SM}\Psi &= \frac{4}{5}\alpha\alpha\alpha\beta\beta + \frac{2}{15}\alpha\alpha\beta\alpha\beta + \frac{2}{15}\alpha\alpha\beta\beta\alpha + \frac{2}{15}\alpha\beta\alpha\alpha\beta + \frac{2}{15}\alpha\beta\alpha\beta\alpha \\ &+ \frac{2}{15}\beta\alpha\alpha\alpha\beta + \frac{2}{15}\beta\alpha\alpha\beta\alpha - \frac{8}{15}\alpha\beta\beta\alpha\alpha - \frac{8}{15}\beta\alpha\beta\alpha\alpha - \frac{8}{15}\beta\beta\alpha\alpha\alpha \\ &+ \frac{2}{5}\beta\beta\alpha\alpha\alpha + \frac{1}{15}\alpha\beta\beta\alpha\alpha + \frac{1}{15}\beta\alpha\beta\alpha\alpha + \frac{1}{15}\alpha\beta\alpha\alpha\beta + \frac{1}{15}\beta\alpha\alpha\alpha\beta \\ &+ \frac{1}{15}\alpha\beta\alpha\beta\alpha + \frac{1}{15}\beta\alpha\alpha\beta\alpha - \frac{4}{15}\alpha\alpha\beta\alpha\beta - \frac{4}{15}\alpha\alpha\beta\beta\alpha - \frac{4}{15}\alpha\alpha\alpha\beta\beta \\ &+ \frac{2}{5}\beta\alpha\beta\alpha\alpha + \frac{1}{15}\alpha\alpha\beta\alpha\beta + \frac{1}{15}\beta\alpha\alpha\alpha\beta + \frac{1}{15}\alpha\beta\beta\alpha\alpha + \frac{1}{15}\beta\beta\alpha\alpha\alpha \\ &+ \frac{1}{15}\alpha\alpha\beta\beta\alpha + \frac{1}{15}\beta\alpha\alpha\beta\alpha - \frac{4}{15}\alpha\beta\alpha\alpha\beta - \frac{4}{15}\alpha\alpha\alpha\beta\beta - \frac{4}{15}\alpha\beta\alpha\beta\alpha \\ &+ \frac{2}{5}\alpha\beta\beta\alpha\alpha + \frac{1}{15}\alpha\alpha\beta\alpha\beta + \frac{1}{15}\alpha\beta\alpha\alpha\beta + \frac{1}{15}\alpha\alpha\beta\beta\alpha + \frac{1}{15}\alpha\beta\alpha\beta\alpha \\ &+ \frac{1}{15}\beta\alpha\beta\alpha\alpha + \frac{1}{15}\beta\beta\alpha\alpha\alpha - \frac{4}{15}\alpha\alpha\alpha\beta\beta - \frac{4}{15}\beta\alpha\alpha\alpha\beta - \frac{4}{15}\beta\alpha\alpha\beta\alpha \\ &= 0. \end{aligned} \quad (44)$$

The consequences of this result are analogous to section 3.1. We have projected with $N = 7$, $N = 9$ and so on, and we have found the same result equal to zero.

For the case $S = 3/2$ and $M = 1/2$, the equation of the Sanibel coefficients takes a simpler form,

$$C_q = \frac{2S+1}{1+n+S} \sum_{k=0}^1 (-1)^{q+1-k} \binom{1}{k} \binom{2}{1-k} \binom{\mu+1}{\mu-q+k}, \quad (45)$$

since for this case $n+1 = \mu+1$. We expand the summation and we put out of the sum the sign:

$$C_q = \frac{2S+1}{1+n+S} (-1)^q \left\{ \binom{\mu+1}{\mu-q+1}^{-1} - 2 \binom{\mu+1}{\mu-q}^{-1} \right\}. \quad (46)$$

Now let us calculate the binomial coefficients and perform the sum. A binomial coefficient can still be extracted and we get a simpler form of the coefficients for the particular case treated here:⁷

$$C_q = \frac{2S+1}{1+n+S} (-1)^q \frac{\mu-3q-1}{\mu+1} \binom{\mu}{q}^{-1}, \quad q = 0, 1, 2, \dots, \nu. \quad (47)$$

Using this formula to obtain $C_{\mu-q}$ and $C_{\nu-q}$ in a similar way as in section 2.1, one has

$$C_{\mu-q} = (-1)^\mu \frac{3q-2\mu-1}{\mu-3q-1} C_q, \quad q = 0, 1, 2, \dots, \nu, \quad (48)$$

$$C_{\nu-q} = (-1)^\nu \frac{(3q-2\nu)(q+1)}{(\mu-3q-1)(\mu-q)} C_q, \quad q = 0, 1, 2, \dots, \nu, \quad (49)$$

the symmetry relation of the Sanibel coefficients. They look now more complicated. Using them we perform a demonstration correspondingly as in section 3.1.

The wave function for odd electron systems for a state $S = 1/2$ has been defined as

$$\Psi = 2T_0 + (-1)^\nu \widehat{P}_{\alpha\beta}^\nu T_0. \quad (50)$$

The projection of the wave function on the space $S = 3/2$ yields

$$\widehat{\Theta}_{SM} \Psi = \sum_{q=0}^{\nu} C_q T_q + (-1)^\nu \sum_{q=0}^{\nu} C_q \widehat{P}_{\alpha\beta}^\nu T_q. \quad (51)$$

⁷ The factor $(2S+1)/(1+n+S)$ in the coefficients is different from C_0 , as in other cases of the Sanibel coefficients.

Since we know how the spin permutation operator acts on T_q (23),

$$\sum_{q=0}^{\nu} C_q T_q + (-1)^{\nu} \sum_{q=0}^{\nu} \{(\mu - q)C_q T_{\mu-q} + (\mu - \nu + q)C_q T_{\nu-q}\}. \quad (52)$$

The summation of the second term remains equal if we change the indices in the following way:

$$\sum_{q=0}^{\nu} C_q T_q + (-1)^{\nu} \sum_{q=0}^{\nu} \{q C_{\mu-q} T_q + (\mu - q)C_{\nu-q} T_q\}. \quad (53)$$

Using the relation of symmetry of the Sanibel coefficients in the odd electron case, deduced in this section,

$$\begin{aligned} \sum_{q=0}^{\nu} C_q T_q + (-1)^{\mu} \sum_{q=0}^{\nu} \left\{ q(-1)^{\mu} \frac{3q - 2\mu - 1}{\mu - 3q - 1} C_q T_q \right. \\ \left. + (\mu - q) \frac{(3q - 2\nu)(q + 1)}{(\mu - 3q - 1)(\mu - q)} (-1)^{\nu} C_q T_q \right\}; \end{aligned} \quad (54)$$

reorganizing the expression and remembering that $\mu = \nu + 1$ we have

$$\sum_{q=0}^{\nu} C_q T_q [2 + 2(-1)^{\mu}(-1)^{\nu}] = 0, \quad \mu + \nu = N, \quad N \text{ is odd}; \quad (55)$$

N is the number of electrons defined as odd. We have demonstrated that

$$\widehat{\Theta}_{SM}(S = 3/2)\Psi(S = 1/2) = 0. \quad (56)$$

4. General form of the partially projected wave function

As it is known, one can write the wave function as a product of spatial and spin part, with a spatial part as a Slater determinant:

$$\Psi = \widehat{A}\phi\varphi. \quad (57)$$

The Löwdin projection operator commutes with the antisymmetrization operator and with the spatial wave function, and in addition, with any permutation of the spin functions \widehat{P}_{ij} . Therefore, the spin projector acts on the spin function consisting of μ functions α followed of ν functions β , i.e., T_0 .

In the partially projected wave function we have then as many Slater determinants as primitive functions it contain:

$$\widehat{\Theta}_{SM}\Psi = \widehat{A}\phi\widehat{P}_{ij}\Theta_{SM}T_0. \quad (58)$$

Using the usual notation of a_i spatial orbitals for the α orbitals and b_i for the β ones, and ordering them as is usual in DODS determinants, we see the correspondence

$$\alpha\alpha\alpha\beta\beta \rightarrow a_1\bar{b}_1a_2\bar{b}_2a_3. \quad (59)$$

For example, in the case of 5 electrons the wave function looks

$$\Psi = |a_1\bar{b}_1a_2\bar{b}_2a_3| + \frac{1}{2}\{|a_1\bar{b}_1\bar{a}_2b_2a_3| + |\bar{a}_1b_1a_2b_2\bar{a}_3| + |a_1b_1\bar{a}_2b_2\bar{a}_3|\}. \quad (60)$$

We shall emphasize that the first Slater determinant is the reference one, and the determinants of the second part are Slater determinants where the α and β functions are interchanged, remaining one orbital a_i as α and this orbital is occupying all possible positions (there are so many Slater determinants as positions for the α orbitals inside of the a_i set). In general, the wave function is

$$\begin{aligned} \Psi = & |a_1\bar{b}_1a_2\bar{b}_2 \dots a_\nu\bar{b}_\nu a_\mu| + \frac{1}{2}\{|a_1\bar{b}_1\bar{a}_2 \dots \bar{a}_\nu b_\nu a_\mu| + |\bar{a}_1 b_1 \bar{a}_2 \dots \bar{a}_{\nu-1} b_{\nu-1} a_\nu b_\nu \bar{a}_\mu| \\ & + |\bar{a}_1 b_1 \bar{a}_2 \dots a_{\nu-1} b_{\nu-1} \bar{a}_\nu b_\nu a_\mu| + \dots + |a_1 b_1 \bar{a}_2 \dots \bar{a}_\nu b_\nu \bar{a}_\mu|\}. \end{aligned} \quad (61)$$

One can, finally redefine the permutation operator $\hat{P}_{\alpha\beta}^\nu$ as the operator which interchanges the α and β functions in the Slater determinant. The wave function consists then of one Slater determinant which is the reference one and a sum of Slater determinants which result from interchanging the spin functions in a shell and the odd electron, always α can occupy every shell not only the last one:

$$\begin{aligned} \Psi(S = 1/2) &= D_0 + \frac{(-1)^\nu}{2} \hat{P}_{\alpha\beta}^\nu D_0, \\ \Psi(S = 3/2) &= D_0 + (-1)^\mu \hat{P}_{\alpha\beta}^\nu D_0. \end{aligned} \quad (62)$$

5. Computational aspects

The partially projected wave function given in (62) is built up with two sets of orbitals a_i , $i = 1, 2, \dots, \nu + 1$, and b_j , $j = 1, 2, \dots, \nu$, which minimize the total energy. The orbitals of each set can be considered orthogonal among themselves since they are the eigenvectors of two symmetric Fock matrices:

$$\begin{aligned} \langle a_i | a_j \rangle &= \delta_{ij}, \quad i, j = 1, 2, \dots, \nu + 1, \\ \langle b_i | b_j \rangle &= \delta_{ij}, \quad i, j = 1, 2, \dots, \nu. \end{aligned} \quad (63)$$

Also, it is possible to perform two separate unitary transformations, so that the orbitals belonging to different shells are orthogonal. Such orbitals are known as corresponding orbitals [1]:

$$\langle a_i | b_j \rangle = \lambda_i \delta_{ij}, \quad i = 1, 2, \dots, \nu + 1, \quad j = 1, 2, \dots, \nu. \quad (64)$$

One may realize here that the overlap matrix \mathbf{S} has rectangular form, and that overlaps of the form $\langle b_i | a_{\nu+1} \rangle$ are zero by means of the corresponding orbitals.

In order to do this, Amos and Hall [1] proved that a rectangular matrix \mathbf{S} of order $\nu \times \mu$ ($\nu \leq \mu$) having a rank ν can be diagonalized by means of two unitary matrices⁸

$$\mathbf{U}^+ \mathbf{S} \mathbf{V} = \mathbf{T}. \quad (65)$$

One subjects the orbitals b_i and a_i to the unitary transformations \mathbf{U} and \mathbf{V} . The Hermitian matrix $\mathbf{S}^+ \mathbf{S}$ can be diagonalized by the unitary matrix \mathbf{V} of order $\mu \times \mu$. The unitary matrix \mathbf{U} of order $\nu \times \nu$ is obtained from the linearly independent eigenvectors of $\mathbf{S} \mathbf{V}$.

If the above orthogonality conditions are fulfilled, the Brillouin theorem also holds:⁹

$$\frac{\partial E}{\partial \varepsilon_{it}} = \langle \Psi | \hat{H} - E | \Psi_{it} \rangle = 0, \quad (66)$$

where Ψ_{it} is the partially projected wave function in which an a_i occupied orbital has been replaced for an a_t virtual one.

Introducing the wave function expression (62) into (66), the equations of the method can be obtained. Then it is necessary to evaluate the matrix elements according to the Slater–Condon rules [10]. From the equation of the method, a general Fock operator for determining the a_i orbitals of ground states of odd systems can be extracted and another one for the b_i orbitals. At this point one has 1) to develop an additional Fock operator for the non-paired electron [5,6], or 2) to find a common Fock operator, adding the Fock operators obtained for paired and non-paired electrons multiplied by the appropriate density matrices, as in the case of HPHF for excited states.

The procedure may be carried out by diagonalizing the \mathbf{H}^a and \mathbf{H}^b matrices alternatively as in the UHF procedure up to convergence.

In the calculation of the total energy, it is convenient to express this energy in parts, since the first matrix element corresponds to the UHF energy for the odd system, and the last ones can be considered as the correlation energy that introduces this partially projected wave function because it describes the delocalization of the non-paired electron.

Acknowledgements

The author is greatly indebted to Profs. Yves G. Smeyers, Peter Otto, István Mayer and Janos Ladik for fruitful discussions.

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⁸ The case $\nu \neq \mu$ occurs when the number of orbitals filled with spins α and β , respectively, is different.

⁹ The Brillouin theorem has been shown to hold in the case of the EHF and HPHF wave functions [5,6,13].

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