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Spin-Adapted Wave Functions of the Serber Type and Time Reversal

Jan Vojtík

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 12138 Prague, Czechoslovakia

Jiří Fišer

Department of Physical Chemistry, Charles University, 12840 Prague, Czechoslovakia

A procedure is proposed for generating Serber-type spin eigenfunctions with $M_s=0$. The procedure uses the time-reversal invariance of these functions to increase the efficiency and to reduce the storage requirements. Simplifications in calculating the matrix elements of an observable operator which follow from the use of the time-reversal symmetry are briefly discussed.

Key words: Spin-adapted functions of the Serber type – Time reversal

1. Introduction

In quantum chemistry, one usually uses the spin-free Hamiltonian. As a consequence, the total spin operators $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$ are constants of motion and it is therefore advantageous to work with wave functions which are eigenfunctions of the total spin operators $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$. When extensive CI-type calculations are performed, the computing time involved depends on the way in which the eigenfunctions of the operators $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$ are constructed. A method which is perhaps most suited for calculations of this type is that based on the Serber-type spin eigenfunctions [1, 2]. These functions, besides being eigenfunctions of the operators $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$, are also eigenfunctions of the geminal spin operators $\bar{\boldsymbol{S}}_\mu^2$, $\mu=1, 2, \ldots, n$. For even numbers of electrons $N=2n$, these operators are defined as follows

$$\bar{\boldsymbol{S}}_\mu^2=(\boldsymbol{S}_{2\mu-1}+\boldsymbol{S}_{2\mu})^2\,; \quad \mu=1,\ldots,n \tag{1}$$

where $\boldsymbol{S}_\nu$, $\nu\in(1, N)$, is the vector spin operator for the ν'th electron. N-electron basis wave functions are taken as antisymmetrized space-spin functions

$$\Phi_\alpha(N, S, M_s)=c\mathcal{A}[\Phi(N)\Theta_\alpha(N, S, M_s)]. \tag{2}$$

Here $\Phi(N)=\prod_{i=1}^{N}\varphi_{k_i}(i)$ is a space product function, Θ_α is a Serber-type spin

function and c is a normalization constant. Basis functions (2) are of course *spin adapted.* The advantage in using the functions of the type (2) lies in that the evaluation of the matrix elements is not too much more complicated than that between two *Slater determinants* [2, 3].

In our recent paper we have examined the time-reversal (TR) invariance of the usual spin-independent Hamiltonian of a molecular system. We have shown that the TR symmetry can be used with advantage when states with $M_s=0$ are treated [4]. The purpose of this communication is to elaborate the exploitation of the TR in the construction and the use of wave functions with Serber-type spin part. We choose a computer-oriented approach in which the spin eigenfunctions are obtained by diagonalization.

2. Bases for Construction of Serber-Type Spin Functions and Splitting of Spin Spaces

As was already mentioned in the introduction, the Serber-type spin functions are also eigenfunctions of the geminal spin operators $\bar{\boldsymbol{S}}_\mu^2$. The simplest basis for a $2n$-electron system is formed by the geminal spin products

$$W(2n, M_s, ., \bar{s}_\mu, .; ., \overline{m}_\mu, .) = \prod_{\mu=1}^{n} w_\mu(\bar{s}_\mu, \overline{m}_\mu) \tag{3}$$

where $w_\mu(\bar{s}_\mu, \overline{m}_\mu)$ is a normalized spin eigenfunction of the operators $\bar{\boldsymbol{S}}_\mu^2$ and $\bar{\boldsymbol{S}}_{z\mu}$ with eigenvalues $\bar{s}_\mu(\bar{s}_\mu+1)$ and $\overline{m}_\mu$, respectively. For example $w_\mu(1, 0)=2^{-1/2}[\alpha(2\mu-1)\beta(2\mu)+\beta(2\mu-1)\alpha(2\mu)]$. $M_s=\sum_\mu \overline{m}_\mu$ is the value of the z-component of the total spin.

It can be noted that the choice of the basis (3) leads to the splitting of a spin space $\mathscr{S}(N, M_s)$, adapted with respect to $\boldsymbol{S}_z$, into subspaces $\mathscr{S}(N, M_s, ., \bar{s}_\mu, .)$ differing in $\bar{s}_\mu$ [6]. Since geminal spins $\bar{s}_\mu$ take on the values 0 and 1, there are 2^n of these subspaces. Of course, these subspaces are not interacting with respect to $\boldsymbol{S}^2$.

Now let us turn our attention to a space $\mathscr{S}(2n, 0, ., \bar{s}_\mu, .)$. Consider first the action of the TR operator on a geminal spin eigenfunction $w_\mu(\bar{s}_\mu, \overline{m}_\mu)$. Starting from the definition of the TR operator [5] it can be easily shown that

$$\mathscr{K} w_\mu(\bar{s}_\mu, \overline{m}_\mu) = (-1)^{\bar{s}_\mu - \overline{m}_\mu} w_\mu(\bar{s}_\mu, -\overline{m}_\mu). \tag{4}$$

Further, we obtain

$$\mathscr{K} W(2n, 0, ., \bar{s}_\mu, .; ., \overline{m}_\mu, .) = (-1)^{\sum_\mu(\bar{s}_\mu - \overline{m}_\mu)} W(2n, 0, ., \bar{s}_\mu, .; ., -\overline{m}_\mu, .). \tag{5}$$

We can therefore conclude that besides the spin space $\mathscr{S}(2n, 0)$ the subspaces $\mathscr{S}(2n, 0, ., \bar{s}_\mu, .)$ are also invariant under TR. As a consequence, a subspace $\mathscr{S}(2n, 0, ., \bar{s}_\mu, .)$ can generally be split into two eigenspaces of the TR operator $\mathscr{S}_{+1}(2n, 0, ., \bar{s}_\mu, .)$ and $\mathscr{S}_{-1}(2n, 0, ., \bar{s}_\mu, .)$, corresponding to eigenvalues $+1$ and -1, respectively. These subspaces can be characterized by a set of even spins $(+1)$ or odd spins (-1) [4]. Thus, spin states with a given S can be obtained by diagonalizing the $\boldsymbol{S}^2$ matrix representatives in the subspaces $\mathscr{S}_{(-1)^S}(2n, 0, ., \bar{s}_\mu, .)$ only. The basis

which enables this simplification can be constructed with the help of the TR projection operators [4]

$$\mathscr{P}_{\pm 1}=\tfrac{1}{2}(I\pm\mathscr{K}) \tag{6}$$

where I is the unit operator. The operators $\mathscr{P}_{\pm 1}$ satisfy the operator equation $\mathscr{K}\mathscr{P}_{\pm 1}=\pm 1\mathscr{P}_{\pm 1}$. The TR adapted orthonormal basis functions for generating Serber-type spin eigenfunctions with $M_s=0$ then can be taken as follows

$$W_{\pm 1}(2n, 0, ., \bar{s}_\mu, .; ., \overline{m}_\mu, .)=C\mathscr{P}_{\pm 1}W(2n, 0, ., \bar{s}_\mu, .; ., \overline{m}_\mu, .). \tag{7}$$

$C=1$ for $\overline{m}_\mu=0$, $\mu\in\{1, ., n\}$, and $C=2^{1/2}$ otherwise. It should be noted that the spin functions $W(2n, 0, ., \bar{s}_\mu, .; ., 0, .)$ are TR-adapted and contain one of the components W_{+1}, W_{-1} only (cf. Eq. (5)).

In applications of the direct diagonalization method for constructing spin eigenfunctions, the limiting factor are the dimensions of the matrices to be diagonalized. On the other hand, these dimensions characterize the size of the expansions of the resulting spin eigenfunctions and thus determine the complexity of the CI calculations with these functions. It seems therefore appropriate to turn attention to the dimensions of the spin subspaces in the splitting

$$\mathscr{S}(2n, 0)=\sum_{\bar{s}_1, ., \bar{s}_\mu}\mathscr{S}(2n, 0, ., \bar{s}_\mu, .)=\sum_{\bar{s}_1, ., \bar{s}_\mu}[\mathscr{S}_{+1}(2n, 0, ., \bar{s}_\mu, .)+ +\mathscr{S}_{-1}(2n, 0, ., \bar{s}_\mu, .)]. \tag{8}$$

The additional splitting in (8) is due to TR. Subspaces with a given $\sum_{\mu=1}^{n}\bar{s}_\mu=q$ can be related to each other by appropriate permutational operations. The number of these subspaces is $\binom{n}{q}$ and for their dimension we obtain

$$d_q=\sum_{k=0}^{p}\binom{q}{k}\binom{q-k}{k} \tag{9}$$

where $p=q/2$ for q even and $p=(q-1)/2$ for q odd. Let us denote a space with a given q as $\mathscr{S}(2n, 0; q)$. The dimensions of the two subspaces $\mathscr{S}_{\pm 1}(2n, 0; q)$ are given by

$$d_q^{\pm 1}=\mathrm{Tr}(\mathscr{P}_{\pm 1}) \tag{10}$$

where the trace is taken over a space $\mathscr{S}(2n, 0; q)$. It is easy to see from Eqs. (5) and (6) that

$$d_q^{\pm 1}=\frac{d_q\pm(-1)^q}{2}. \tag{11}$$

The dimensions of individual subspaces $\mathscr{S}(2n, 0; q)$ and $\mathscr{S}_{\pm 1}(2n, 0; q)$ for $n=1, ., 6$, together with the numbers of resulting spin states (see Sect. 3) are listed in Table 1. We can conclude that on exploiting the TR in generating Serber-type spin eigenfunctions with a given S by the direct diagonalization, the number of subproblems to be diagonalized does not change. The dimension of an individual subspace depends on S and is roughly one half of the dimension of the primary subspace.

Table 1. Splitting of spin space $\mathscr{S}(2n, 0)$ according to Eq. (8) for $2n$ electrons; $n=1,..., 6$[a]

$q=\sum_{\mu=1}^{n} \bar{s}_\mu$	Dimension of $\mathscr{S}(2n, 0; q)$ d_q	d_q^{+1}	Number of spin states in each subspace				d_q^{-1}	Number of spin states in each subspace		
			$S=0$	$S=2$	$S=4$	$S=6$		$S=1$	$S=3$	$S=5$
0	1	1	1	0	0	0	0	0	0	0
1	1	0	0	0	0	0	1	1	0	0
2	3	2	1	1	0	0	1	1	0	0
3	7	3	1	2	0	0	4	3	1	0
4	19	10	3	6	1	0	9	6	3	0
5	51	25	6	15	4	0	26	15	10	1
6	141	71	15	40	15	1	70	36	29	5

[a] For a $2n$-electron problem only subspaces $\mathscr{S}(2n, 0; q)$ with $q \leqslant n$ occur. Their number is given by binomial coefficient $\binom{n}{q}$

3. Construction of Serber-Type Spin Eigenfunctions

After having chosen an orthonormal TR-adapted basis, it is necessary to calculate the matrix elements of the $\boldsymbol{S}^2$ operator, i.e. the following expressions

$$\langle \boldsymbol{S}^2 \rangle_{ij}^{\pm} \equiv C_i C_j \langle \mathscr{P}_{\pm 1} W_i | \boldsymbol{S}^2 | \mathscr{P}_{\pm 1} W_j \rangle \tag{12}$$

where we have omitted the "arguments" of the functions W_i. On using Eq. (6), the commutation relation $[\mathscr{K}, \boldsymbol{S}^2]_- = 0$, the antiunitary property of the TR operator and the equation $\mathscr{K}^2 = (-1)^N$ we obtain

$$\langle \boldsymbol{S}^2 \rangle_{ij}^{\pm} = \frac{C_i C_j}{2} \{ \langle W_i | \boldsymbol{S}^2 | W_j \rangle \pm \langle W_i | \boldsymbol{S}^2 \mathscr{K} | W_j \rangle \}. \tag{13}$$

The first contribution can be evaluated by means of the formulas given by Salmon *et al.* [6].

There are two ways of evaluating the second term in Eq. (13). One can either calculate $\mathscr{K} W_j$ by means of Eq. (5) and then use the formulas by Salmon *et al.*, or to derive rules for evaluation of the matrix elements or the operator $\boldsymbol{S}^2 \mathscr{K}$ between geminal spin products and then use them.

A program has been written for exploiting TR to construct Serber-type spin eigenfunctions with $M_s = 0$ for a given total spin S. It handles cases up to 12 electrons. The program (1) chooses the product functions W_i corresponding to the spin subspaces $\mathscr{S}_{(-1)^S}(2n, 0; q)$, $q=2,.., n$, (2) calculates the matrix elements (13), (3) diagonalizes the individual $\boldsymbol{S}^2$ matrices, (4) selects and stores the eigenvectors with a given S. In fact, one representative of the $\binom{n}{q}$ subspaces $\mathscr{S}_{(-1)^S}(2n, 0; q)$ has been treated in this way; the other Serber-type spin eigenfunctions have been obtained by making use of the (permutational) relations between these subspaces.

The numbers of spin states obtained in individual runs of the program are given in Table 1. The only really noteworthy running times have been those for $N=12$ and $N=10$, mainly due to the diagonalization of the S^2 matrices in subspaces $\mathscr{S}_{(-1)^S}(N, 0; 6)$ and/or $\mathscr{S}_{(-1)^S}(N, 0; 5)$. The way in which the second term in Eq. (13) has been evaluated has had practically no effect on the running times. It can be noted that with our use of Jacobi algorithm, the time necessary for generating the corresponding spin eigenfunctions has been reduced to roughly 1/7–1/8 of the time which would be required for generating these spin eigenfunctions without the use of the time reversal.

4. Calculation of Matrix Elements of Observable Operators

We shall discuss the most common case when the space product functions $\Phi(2n)$ in Eq. (2) are constructed from the orthonormal orbitals φ_{k_i}. In this case the rules for the evaluation of a matrix element of an observable operator

$$\langle \Phi_\alpha(2n, S, 0) \,|\, \Omega \,|\, \Phi_\beta(2n, S, 0)\rangle \tag{14}$$

differ from the Slater-Condon rules by factors standing at individual one- and two-electron integrals. A factor is essentially the matrix element of a specific permutational operator $\boldsymbol{P}$ between corresponding spin functions [2, 3]

$$P_{\alpha\beta}=\langle \Theta_\alpha \,|\, \boldsymbol{P} \,|\, \Theta_\beta\rangle. \tag{15}$$

On using the expansion

$$\Theta_\alpha(2n, S, 0)=\sum_{k=1}^{d_{q,\alpha}^{(-1)^S}} C_{\alpha k}\mathscr{P}_{(-1)^S} W_k \tag{16}$$

we arrive at the following expression

$$P_{\alpha\beta}=\frac{1}{4}\sum_{k=1}^{d_{q,\alpha}^{(-1)^S}}\sum_{l=1}^{d_{q,\beta}^{(-1)^S}} C_{\alpha k}C_{\beta l}\{\langle W_k \,|\, \boldsymbol{P} \,|\, W_l\rangle \tag{17}$$

$$+\langle \mathscr{K} W_k \,|\, \boldsymbol{P} \,|\, \mathscr{K} W_l\rangle+(-1)^S\langle \mathscr{K} W_k \,|\, \boldsymbol{P} \,|\, W_l\rangle+(-1)^S\langle W_k \,|\, \boldsymbol{P} \,|\, \mathscr{K} W_l\rangle\}.$$

With the help of the relation $\mathscr{K}^2=(-1)^N$, the antiunitary property of the TR operator, and the relation $[\mathscr{K}, \boldsymbol{P}]_-=0$, the expression in curled brackets can be reduced to

$$2(\langle W_k \,|\, \boldsymbol{P} \,|\, W_l\rangle+(-1)^S\langle \mathscr{K} W_k \,|\, \boldsymbol{P} \,|\, W_l\rangle). \tag{18}$$

An alternative expression reads

$$2(\langle \boldsymbol{P}^{-1} W_k \,|\, W_l\rangle+(-1)^S\langle \boldsymbol{P}^{-1} W_k \,|\, \mathscr{K} W_l\rangle). \tag{18a}$$

Now, the action of the TR operator on a product spin function W_k is quite simple (cf. Eq. (5)) and the action of a permutational operator $\boldsymbol{P}$ is more complicated. It is

therefore advisable to use alternatively Eq. (18) or (18a) depending on whether $d_{q,\alpha}^{(-1)^S} \geqslant d_{q,\beta}^{(-1)^S}$ or not, respectively. On comparing Eqs. (15), (17) and (9), (11) we see that, with the above recommendation, the work involved in evaluating a matrix element $P_{\alpha\beta}$ is, in using TR invariance, generally reduced to roughly one half.

5. Discussion

Simplifications ensuing from the use of the time reversal operator in generating and using the Serber-type spin functions with $M_s=0$ stem from the use of the TR-adapted basis. With this basis, only independent coefficients in expansions of individual spin eigenstates are needed. As has been shown, the size of expansions of the Serber-type spin functions is reduced to roughly one half. In the computer-oriented procedure, this circumstance leads to the reduction of storage requirements and of the computing time necessary for diagonalization of the individual S^2 matrices. These facts, in turn, make the procedure practicable for greater numbers of electrons.

On the other hand, the TR-adapted basis functions are more complex than the primary ones having, in general, the form $C'\{W(2n, 0, ., \bar{s}_\mu, . ; ., \bar{m}_\mu, .) + (-1)^S W(2n, 0, ., \bar{s}_\mu, . ; ., -\bar{m}_\mu, .)\}$. One might be led to conclude from this expression that no gain can ensue from the exploitation of the TR-symmetry in evaluation of the matrix elements of an operator between Serber-type spin eigenfunctions with $M_s=0$. Eqs. (13, 17, 18, 18a) show that even in this case the "spin" part of the work is reduced to roughly one half.

It should be stressed that the above argument refers to the spin eigenfunctions with $M_s=0$. With the singlet spin states the active exploitation of the TR-symmetry is therefore without any reservation profitable. With the $2n$-electron states of higher multiplicity the situation is different: In the conventional approach, these states are known to be handled in the best way in the subspace $|M_s|=S$.

In concluding this communication we wish to compare the above procedure with the most suitable conventional one for higher spin multiplets. In the $S=|M_s|=1$ case, the number of spin subspaces $\mathscr{S}(2n, 1; q)$, $1 \leqslant q \leqslant n$ is equal to that of spaces $\mathscr{S}(2n, 0; q)$, i.e., $\binom{n}{q}$. For $q=1, 2, .., 6$, the dimensions of the spaces $\mathscr{S}(2n, 1; q)$ are equal to 1, 2, 6, 16, 45 and 126, respectively. On comparing these values with the corresponding values d_q^{-1} of Table 1, we see that from the point of view of construction of spin functions and storage requirements, states with $M_s=0$ are more advisable to work with. As far as the use of these spin functions is concerned, no definite general conclusion can be made. The choice between spin functions with $M_s=0$ and $M_s=1$ should be made upon taking into account number of electrons, type of spin functions included in CI calculations etc.

An analogous consideration for higher multiplicities reveals that functions with $|M_s|=S$ are to be preferred to those with $M_s=0$.

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