Note

Normalization of projected spin eigenfunctions

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Received 11 July 1997

We find the normalization integral for projected spin eigenfunctions, defined by means of character projection operators of the symmetric group. We also obtain a reduced expression for these spin eigenfunctions.

1. Introduction and definitions

Compact expressions have recently been presented [4] for evaluating electronic matrix elements between wavefunctions based on projected spin eigenfunctions. Projected spin eigenfunctions were first introduced by Löwdin [10] and have been developed further by various authors [13]. Such N-electron spin eigenfunctions of $\widehat{S}^2$ and $\widehat{S}_z$, with quantum numbers S and M, respectively, are neither orthogonal nor normalized, and one obstacle to their further use, including the formulation presented in [4], is the lack of an explicit expression for the normalization integral. The main purpose of the present note is to obtain such an expression.

For the high-spin case ($M = S$) Kramer [8] has shown that Löwdin's projection operator [10] is equivalent to the character projection operator

$$\widehat{\mathcal{X}}^{[\lambda]} = \frac{f_S^N}{N!} \sum_{P \in \mathcal{S}_N} \mathcal{X}^{[\lambda]}(P)\widehat{P}, \tag{1}$$

in which $[\lambda] = [N/2 + S, N/2 - S] \equiv [n_\alpha, n_\beta]$ labels an irreducible representation of the symmetric group $\mathcal{S}_N$. $\mathcal{X}^{[\lambda]}(P)$ is the character of the permutation P in the representation, and (for any value of M) f_S^N is the dimension of the spin space for

* Financed by Faculty of Natural Sciences at Copenhagen University.
** Financial support from the Danish National Science Research Council is gratefully acknowledged.

the given values of N and S:

$$f_S^N = \frac{(2S+1)N!}{(N/2+S+1)!(N/2-S)!}. \tag{2}$$

The question of what set of primitive eigenfunctions of $\widehat{S}_z$ to start from, in order to obtain a complete set of f_S^N N-electron spin eigenfunctions, was first addressed by Löwdin [11]. He suggested that all simple spin products that can be associated with a standard Young tableau lead to a complete linearly independent set, as was subsequently proved by Gershgorn [6] and Pauncz [12]. Let the first primitive spin function θ_1 be

$$\theta_1 = \alpha(1)\alpha(2)\cdots\alpha(n_\alpha)\beta(n_\alpha+1)\cdots\beta(n_\alpha+n_\beta), \tag{3}$$

which can be associated with the tableau

$$T_1 = \begin{array}{|c|c|c|c|}\hline 1 & 2 & \cdots\cdots & n_\alpha \\ \hline n_\alpha+1 & \cdots & n_\alpha+n_\beta & \\ \hline \end{array}\ . \tag{4}$$

When the standard Young tableaux associated with spin eigenfunctions are ordered in last letter sequence (see, for example, [15]), $\widehat{P}_k$ is defined as the permutation operator that converts the first tableau T_1 into the kth tableau T_k:

$$\widehat{P}_k T_1 = T_k. \tag{5}$$

In the following, we call these permutations standard Young tableaux permutations. It means that we can write the kth simple spin product as

$$\theta_k = \widehat{P}_k \theta_1. \tag{6}$$

A complete linearly independent set of projected spin eigenfunctions is therefore

$$\Theta_k = \widehat{\mathcal{X}}^{[\lambda]}\widehat{P}_k\theta_1 = \widehat{P}_k\widehat{\mathcal{X}}^{[\lambda]}\theta_1, \quad k = 1, 2, \ldots, f_S^N. \tag{7}$$

The character operator $\widehat{\mathcal{X}}^{[\lambda]}$ commutes with any $\widehat{P}_k$ since it belongs to the centrum of the group algebra [14].

2. Normalization of the spin eigenfunctions

In order to determine the normalization constant for the character projected spin eigenfunctions we evaluate $\langle\Theta_k|\Theta_k\rangle$ by inserting the expression in equation (7) and moving all operators in the bra over to the ket

$$\langle\Theta_k|\Theta_k\rangle = \big\langle\theta_1\big|\big(\widehat{\mathcal{X}}^{[\lambda]}\big)^\dagger\big(\widehat{P}_k\big)^\dagger\widehat{P}_k\widehat{\mathcal{X}}^{[\lambda]}\theta_1\big\rangle. \tag{8}$$

Utilizing that $(\widehat{\mathcal{X}}^{[\lambda]})^\dagger = \widehat{\mathcal{X}}^{[\lambda]}$ and $(\widehat{P}_k)^\dagger = \widehat{P}_k^{-1}$ we obtain

$$\langle\Theta_k|\Theta_k\rangle = \big\langle\theta_1\big|\big(\widehat{\mathcal{X}}^{[\lambda]}\big)^2\theta_1\big\rangle. \tag{9}$$

The character operator is idempotent, and so

$$\langle\Theta_k|\Theta_k\rangle = \frac{f_S^N}{N!}\sum_{P\in\mathcal{S}_N}\mathcal{X}^{[\lambda]}(P)\big\langle\theta_1\big|\widehat{P}\theta_1\big\rangle. \tag{10}$$

We note that the spin strings in the bra and ket must have matching α and β functions in order for the integral to be non-zero. In the following, $\mathcal{S}_{n_\alpha}$ denotes the symmetric group which permutes the numbers $1, 2, \ldots, n_\alpha$, and $\mathcal{S}_{n_\beta}$ the group acting on the numbers $n_\alpha + 1, \ldots, n_\alpha + n_\beta$. Application of a permutation from the direct product group [7], $\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}$, to the first spin string θ_1 in equation (3) leaves the spin string unchanged:

$$\widehat{P}\theta_1 = \theta_1, \quad \text{for } P \in \mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}. \tag{11}$$

Accordingly, we get

$$\langle\Theta_k|\Theta_k\rangle = \frac{f_S^N}{N!}\sum_{P\in\mathcal{S}_{n_\alpha}\otimes\mathcal{S}_{n_\beta}}\mathcal{X}^{[\lambda]}(P). \tag{12}$$

In order to evaluate the sum over irreducible characters of $[\lambda]$ we look at the irreducible representation $[\lambda]$ restricted to $\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}$. The subduced representation $[\lambda]{\downarrow}(\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta})$ will in general be reducible. Let us express it as a sum over all irreducible representations of $\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}$:

$$[\lambda]{\downarrow}(\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}) = \sum_{[\mu]} a_\mu[\mu], \tag{13}$$

where $[\mu]$ is of the form $[\lambda_\alpha] \otimes [\lambda_\beta]$ and $[\lambda_\alpha]$ is an irreducible representation of $\mathcal{S}_{n_\alpha}$ and $[\lambda_\beta]$ is an irreducible representation of $\mathcal{S}_{n_\beta}$ (see, for example, [3]). When the individual representations are irreducible, the product must be as well. The irreducible product character $\mathcal{X}^{[\mu]}$ can be expressed in terms of the individual characters:

$$\mathcal{X}^{[\mu]}(P) = \mathcal{X}^{[\lambda_\alpha]}(P_\alpha)\mathcal{X}^{[\lambda_\beta]}(P_\beta), \tag{14}$$

where $P_\alpha \in \mathcal{S}_{n_\alpha}$, $P_\beta \in \mathcal{S}_{n_\beta}$ and $P = P_\alpha P_\beta$. The subduced character $\mathcal{X}^{[\lambda]\downarrow}$ is therefore

$$\sum_{P\in\mathcal{S}_{n_\alpha}\otimes\mathcal{S}_{n_\beta}}\mathcal{X}^{[\lambda]\downarrow}(P) = \sum_{[\lambda_\alpha],[\lambda_\beta]} a_{\lambda_\alpha\lambda_\beta}\Bigg(\sum_{P_\alpha\in\mathcal{S}_{n_\alpha}}\mathcal{X}^{[\lambda_\alpha]}(P_\alpha)\Bigg) \times \Bigg(\sum_{P_\beta\in\mathcal{S}_{n_\beta}}\mathcal{X}^{[\lambda_\beta]}(P_\beta)\Bigg). \tag{15}$$

Let us multiply each term in the $\mathcal{S}_{n_\alpha}$ summation by $\mathcal{X}^{[n_\alpha]}(P_\alpha) = 1$ so that we obtain

$$\sum_{P_\alpha\in\mathcal{S}_{n_\alpha}}\mathcal{X}^{[\lambda_\alpha]}(P_\alpha)\mathcal{X}^{[n_\alpha]}(P_\alpha) = \delta_{[\lambda_\alpha],[n_\alpha]}n_\alpha!, \tag{16}$$

in which we have used the orthogonality of the irreducible characters of $\mathcal{S}_{n_\alpha}$ (see, for example, [1]). Utilizing the same procedure for $\mathcal{S}_{n_\beta}$, we obtain

$$\sum_{P\in \mathcal{S}_{n_\alpha}\otimes\mathcal{S}_{n_\beta}} \mathcal{X}^{[\lambda]\downarrow}(P) = a_{n_\alpha n_\beta} n_\alpha! n_\beta!. \tag{17}$$

In order to determine the coefficient $a_{n_\alpha n_\beta}$ we use the Frobenius reciprocity theorem [2,5], which was originally expressed in terms of characters of representations, although later formulations also concern representations. Since $\mathcal{S}_N$ is a group with an irreducible representation $[\lambda] = [n_\alpha, n_\beta]$ and $\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}$ is a subgroup of $\mathcal{S}_N$ with an irreducible representation $[n_\alpha] \otimes [n_\beta]$, we have:

> The frequency of $[\lambda]$ in the induced representation $([n_\alpha] \otimes [n_\beta])\uparrow\mathcal{S}_N$ is equal to the frequency of $[n_\alpha] \otimes [n_\beta]$ in the subduced representation $[\lambda]\downarrow(\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta})$.

The outer product $[n_\alpha] \otimes [n_\beta]$ can be resolved into irreducible representations of $\mathcal{S}_N$ as [7,9]

$$[n_\alpha] \otimes [n_\beta] = [n_\alpha + n_\beta] + [n_\alpha + n_\beta - 1, 1] + \cdots + [n_\alpha, n_\beta], \tag{18}$$

which implies that $a_{n_\alpha n_\beta} = 1$. As a consequence, we find that the normalization in equation (12) becomes

$$\langle\Theta_k|\Theta_k\rangle = \frac{f_S^N}{N!} n_\alpha! n_\beta! = \frac{2S+1}{n_\alpha+1}. \tag{19}$$

Thus, we obtain the character projected spin eigenfunctions normalized to unity as

$$\Theta_k = \sqrt{\frac{n_\alpha+1}{2S+1}} \widehat{P}_k \widehat{\mathcal{X}}^{[\lambda]} \theta_1. \tag{20}$$

3. Reduced expression for the spin eigenfunctions

We observe from equation (1) that the spin eigenfunctions Θ_k in equation (20) contain $N!$ terms. However, there exist only

$$N_\alpha \equiv \binom{N}{n_\alpha} = \frac{N!}{n_\alpha! n_\beta!} \tag{21}$$

different simple spin products with the given values of n_α and n_β. This implies that a reduced form of Θ_k can be found.

Let $\mathcal{S}_N$ be expressed in terms of left cosets of the direct product group $\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}$,

$$\mathcal{S}_N = Q_1(\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}) \oplus Q_2(\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}) \oplus \cdots \oplus Q_{N_\alpha}(\mathcal{S}_{n_\alpha} \otimes \mathcal{S}_{n_\beta}). \tag{22}$$

The sum over the symmetric group elements in $\widehat{\mathcal{X}}^{[\lambda]}$ can then be divided into two summations as

$$\widehat{\mathcal{X}}^{[\lambda]} = \frac{f_S^N}{N!}\sum_{i=1}^{N_\alpha}\left(\sum_{P\in\mathcal{S}_{n_\alpha}\otimes\mathcal{S}_{n_\beta}}\mathcal{X}^{[\lambda]}(Q_iP)\widehat{Q}_i\widehat{P}\right). \tag{23}$$

Utilizing equations (11) and (23) we are able to rewrite the spin eigenfunction Θ_k as

$$\Theta_k = \sqrt{\frac{n_\alpha+1}{2S+1}}\frac{f_S^N}{N!}\sum_{i=1}^{N_\alpha}\left(\sum_{P\in\mathcal{S}_{n_\alpha}\otimes\mathcal{S}_{n_\beta}}\mathcal{X}^{[\lambda]}(Q_iP)\right)\widehat{P}_k\widehat{Q}_i\theta_1. \tag{24}$$

The set of primitive spin functions $\{\widehat{Q}_i\theta_1\colon\ i = 1,2,\ldots,N_\alpha\}$ is complete, so that it must remain unaltered under the action of the standard Young tableau permutation, $\widehat{P}_k$:

$$\widehat{P}_k\{\widehat{Q}_i\theta_1\} = \{\widehat{Q}_i\theta_1\}. \tag{25}$$

The individual spin products, however, are permuted according to $\widehat{P}_k$. An alternative expression for Θ_k is therefore

$$\Theta_k = \sqrt{\frac{n_\alpha+1}{2S+1}}\frac{f_S^N}{N!}\sum_{i=1}^{N_\alpha}\left(\sum_{P\in\mathcal{S}_{n_\alpha}\otimes\mathcal{S}_{n_\beta}}\mathcal{X}^{[\lambda]}\bigl(P_k^{-1}Q_iP\bigr)\right)\widehat{Q}_i\theta_1. \tag{26}$$

The inner summation is actually just an integer, so let us define the constant b_{ki} as

$$b_{ki} = \sqrt{\frac{n_\alpha+1}{2S+1}}\frac{f_S^N}{N!}\sum_{P\in\mathcal{S}_{n_\alpha}\otimes\mathcal{S}_{n_\beta}}\mathcal{X}^{[\lambda]}\bigl(P_k^{-1}Q_iP\bigr), \tag{27}$$

so that we have the following reduced form of Θ_k:

$$\Theta_k = \sum_{i=1}^{N_\alpha} b_{ki}\widehat{Q}_i\theta_1. \tag{28}$$

Acknowledgements

The authors wish to thank Prof. Ruben Pauncz and Prof. Brian Sutcliffe for their interest in this work.

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