

# Generalized one-electron spin functions and self-similarity measures

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A simple method for construction of eigenfunctions of one-electron spin angular momentum operators from products of the primitive one-electron spin functions is presented. Properties of these functions and their applications to the evaluation of some integrals met in theory of quantum similarity are briefly discussed.

**KEY WORDS:** quantum similarity measures, one-electron spin functions, coupling of angular momenta, spin density

## 1. Introduction

Some of the similarity measures appearing in the theory of quantum similarity may be expressed in terms of integrals involving products of  $N$ -electron density functions [1,2]:

$$Q[\rho_k^a, \rho_\ell^b] = \int_{\Omega_{ab}} \rho_k^a \rho_\ell^b d\tau. \quad (1)$$

In equation (1)  $\rho_k^a$  and  $\rho_\ell^b$  denote the densities corresponding, respectively, to states  $\Psi_k^a$  and  $\Psi_\ell^b$  of two quantum systems labeled as a and b. If  $a = b$  then equation (1) defines a measure of similarity between two states of the same quantum system. Furthermore, if  $k = \ell$ , the integral (1) defines a quantum self-similarity measure. Usually the densities depend upon both coordinates and spins of the electrons. The integration range  $\Omega_{ab}$  covers the area over which the similarity index has been defined and, in most cases, it is the entire space of electron coordinates and spins.

The evaluation of the coordinate-dependent part of integral (1), from a technical point of view, does not present any particular difficulty – it usually may be reduced to some specific overlap-like integrals or to some other well known quantum-mechanical quantities [2]. Technical novelties may appear in connection with the integrals over spin variables. The aim of this note is to present an algorithm for the evaluation of the integrals

$$Q^\sigma[\Xi_k, \Xi_\ell] = \langle \Xi_k(\sigma) | \Xi_\ell(\sigma) \rangle \quad (2)$$

over spin variables  $\sigma$  associated with the similarity index  $Q[\rho_k^a, \rho_\ell^b]$ .

## 2. Basic definitions

Let  $\Theta(j, m)$  be a one-electron eigenfunction of the square of the angular momentum operator,  $\hat{J}^2$ , and of its projection  $\hat{J}_z$ . Then, we have

$$\hat{J}^2\Theta(j, m) = j(j+1)\Theta(j, m), \quad \hat{J}_z\Theta(j, m) = m\Theta(j, m), \quad (3)$$

and

$$\langle \Theta(j, m) | \Theta(j', m') \rangle = \delta_{jj'} \delta_{mm'}. \quad (4)$$

The functions corresponding to  $j = \frac{1}{2}$  and  $m = \frac{1}{2}, -\frac{1}{2}$  are denoted  $\alpha$  and  $\beta$ :

$$\alpha \equiv \Theta\left(\frac{1}{2}, \frac{1}{2}\right), \quad \beta \equiv \Theta\left(\frac{1}{2}, -\frac{1}{2}\right). \quad (5)$$

The ladder operators

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y \quad \text{and} \quad \hat{J}_- = \hat{J}_x - i\hat{J}_y$$

act on  $\Theta(j, m)$  in the well-known manner:

$$\hat{J}_+\Theta(j, m) = \sqrt{j(j+1) - m(m+1)} \Theta(j, m+1), \quad (6)$$

$$\hat{J}_-\Theta(j, m) = \sqrt{j(j+1) - m(m-1)} \Theta(j, m-1). \quad (7)$$

For the purpose of this paper it is convenient to represent  $\hat{J}_+$  and  $\hat{J}_-$  as differential operators acting in the spin space [3]:

$$\hat{J}_+ = \alpha \frac{\partial}{\partial \beta}, \quad \hat{J}_- = \beta \frac{\partial}{\partial \alpha}. \quad (8)$$

The spin integrals appearing in evaluation of  $Q[\rho_k^a, \rho_\ell^b]$  defined in equation (1) are, in general, reducible to

$$Q^\sigma[\Xi, \Xi'] = \prod_{j=1}^N \langle \Xi_{p_j q_j}(j) | \Xi_{p'_j q'_j}(j) \rangle, \quad (9)$$

where

$$\Xi_{p_j q_j}(j) = \alpha^{p_j}(j) \beta^{q_j}(j), \quad (10)$$

$\alpha$  and  $\beta$  are the primitive one-electron spin functions and the index  $j$  refers to the  $j$ th electron.

Functions composed of products of  $p + q > 1$  of the primitive one-electron spin functions will be referred to hereafter as the *generalized spin functions*. In order to evaluate integrals involving the generalized spin functions we express them in terms of the normalized eigenfunctions of the one-electron spin operators. For simplicity, these operators are denoted hereafter  $\hat{J}^2$  and  $\hat{J}_z$  and their eigenfunctions are  $\Theta(j, m)$ .

### 3. Generalized one-electron spin functions

If we assume that

$$\Theta\left(\frac{n}{2}, \frac{n}{2}\right) = f(j)\alpha^n\beta^0, \quad (11)$$

then, after acting on the right-hand-side of equation (11) with operator  $\hat{J}_-$  defined in equation (8) and transforming the left-hand-side according to equation (7), we get

$$\begin{aligned} \sqrt{n \cdot 1} \Theta\left(\frac{n}{2}, \frac{n}{2} - 1\right) &= f(j)n\alpha^{n-1}\beta^1, \\ \sqrt{n(n-1) \cdot 1 \cdot 2} \Theta\left(\frac{n}{2}, \frac{n}{2} - 2\right) &= f(j)n(n-1)\alpha^{n-2}\beta^2, \\ \sqrt{n(n-1)(n-2) \cdot 1 \cdot 2 \cdot 3} \Theta\left(\frac{n}{2}, \frac{n}{2} - 3\right) &= f(j)n(n-1)(n-2)\alpha^{n-3}\beta^3, \\ &\vdots \end{aligned}$$

Hence, in general,

$$\Theta(j, m) = f(j)\sqrt{\frac{(2j)!}{(j+m)!(j-m)!}}\alpha^{j+m}\beta^{j-m}, \quad (12)$$

with  $m = -j, -j+1, \dots, j$  and  $f(j)$  selected so that  $\langle \Theta(j, m) | \Theta(j, m) \rangle = 1$ .

The Clebsh–Gordan expansion for the spin functions  $\Theta(j, m)$  may be written as [4]

$$\Theta(j, m) = \sqrt{\frac{j+m}{2j}} \Theta\left(j - \frac{1}{2}, m - \frac{1}{2}\right)\alpha + \sqrt{\frac{j-m}{2j}} \Theta\left(j - \frac{1}{2}, m + \frac{1}{2}\right)\beta. \quad (13)$$

By substitution of equation (12) to (13), after some simple algebra, we get

$$f(j)\sqrt{\frac{2j}{(j+m)(j-m)}} = f\left(j - \frac{1}{2}\right) \left[ \sqrt{\frac{j+m}{2j(j-m)}} + \sqrt{\frac{j-m}{2j(j+m)}} \right]$$

and from here

$$f(j) = f\left(j - \frac{1}{2}\right). \quad (14)$$

Taking  $j = \frac{1}{2}$ , i.e.,  $m = \pm\frac{1}{2}$ , equation (12) becomes

$$\Theta\left(\frac{1}{2}, \frac{1}{2}\right) = f\left(\frac{1}{2}\right)\alpha, \quad \Theta\left(\frac{1}{2}, -\frac{1}{2}\right) = f\left(\frac{1}{2}\right)\beta.$$

Then, due to equation (5),  $f\left(\frac{1}{2}\right) = 1$ . Consequently, by recursively using equation (14) we get  $f(j) = 1$ .

Equation (13) may be used for the genealogical construction of the one-electron spin functions  $\Theta(j, m)$  from  $\Theta\left(j - \frac{1}{2}, m'\right)$ . However, as we know from the general theory of coupling angular momenta, the angular momentum eigenstate  $\Theta(j, m)$  may

also be obtained by coupling  $\Theta(j + \frac{1}{2}, m \pm \frac{1}{2})$  with  $\Theta(\frac{1}{2}, \mp \frac{1}{2})$ . The resulting equation reads

$$\Theta(j, m) = -\sqrt{\frac{j-m+1}{2j+2}} \Theta(j + \frac{1}{2}, m - \frac{1}{2})\alpha + \sqrt{\frac{j+m+1}{2j+2}} \Theta(j + \frac{1}{2}, m + \frac{1}{2})\beta. \quad (15)$$

As one can easily check by substitution of equation (12) in the right-hand-side of equation (15), in this case  $\Theta(j, m) = 0$ . This result is in agreement with equation (12): there is only one genealogical path of construction of a generalized spin function, defined by equation (13). If  $\Theta(j, m)$  is multiplied by a primitive spin function then the value of  $j$  in the resulting generalized spin function always increases.

#### 4. Integrals

Since all products of the primitive one-electron spin functions may be expressed in terms of  $\Theta(j, m)$ , all integrals involving these products may be evaluated by using the orthogonality relation given by equation (4). In order to illustrate the approach we elaborate in detail the case of  $N = 2$ .

Let us assume that  $\Psi_k^a$  is associated with a two-electron spin function  $X_m^a(\sigma_1, \sigma_2)$  and  $\Psi_\ell^b$  with  $X_{m'}^b(\sigma_1, \sigma_2)$ , where  $\{X_m^a, X_{m'}^b\} = \{S_0, T_{-1}, T_0, T_1\}$ ,  $\sigma_1, \sigma_2$  are spin coordinates of the electrons and

$$\begin{aligned} S_0(\sigma_1, \sigma_2) &\equiv \frac{1}{\sqrt{2}}[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)], \\ T_{-1}(\sigma_1, \sigma_2) &\equiv \beta(\sigma_1)\beta(\sigma_2), \\ T_0(\sigma_1, \sigma_2) &\equiv \frac{1}{\sqrt{2}}[\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)], \\ T_1(\sigma_1, \sigma_2) &\equiv \alpha(\sigma_1)\alpha(\sigma_2). \end{aligned}$$

According to equation (12), there are three generalized one-electron spin functions which may be constructed from products of two primitive one-electron spin functions:

$$\begin{aligned} T_{-1}(\sigma_1) &\equiv \Theta(1, -1) = \alpha^2, \\ T_0(\sigma_1) &\equiv \Theta(1, 0) = \sqrt{2} \alpha\beta, \\ T_1(\sigma_1) &\equiv \Theta(1, 1) = \beta^2. \end{aligned}$$

Let us note that

$$T_m(\sigma_1) = \lim_{\sigma_2 \rightarrow \sigma_1} T_m(\sigma_1, \sigma_2). \quad (16)$$

Due to equations (13) and (15) the analogous rule also applies in the general case.

After some simple algebra we get

$$\begin{aligned} |S_0(\sigma_1, \sigma_2)|^2 &= \frac{1}{2} [T_1(\sigma_1)T_{-1}(\sigma_2) - T_0(\sigma_1)T_0(\sigma_2) + T_1(\sigma_1)T_{-1}(\sigma_2)], \\ |T_{-1}(\sigma_1, \sigma_2)|^2 &= T_{-1}(\sigma_1)T_{-1}(\sigma_2), \end{aligned}$$

$$\begin{aligned} |T_0(\sigma_1, \sigma_2)|^2 &= \frac{1}{2} [T_1(\sigma_1)T_{-1}(\sigma_2) + T_0(\sigma_1)T_0(\sigma_2) + T_1(\sigma_1)T_{-1}(\sigma_2)], \\ |T_1(\sigma_1, \sigma_2)|^2 &= T_1(\sigma_1)T_1(\sigma_2). \end{aligned} \quad (17)$$

Consequently,

$$Q^\sigma [ |X_m(\sigma_1, \sigma_2)|^2, |X'_{m'}(\sigma_1, \sigma_2)|^2 ] = \frac{3 + |m|}{4} \delta_{XX'} \delta_{mm'}, \quad (18)$$

where  $\{X, X'\} = \{S, T\}$  and  $Q^\sigma [X_m, X'_{m'}]$  is defined in equation (2).

A generalization of this procedure to a many-electron case is straightforward, though specific implementations may be tedious if  $N$  is sufficiently large. Using equation (12) we can transform an arbitrary product of the primitive one-electron spin functions  $\alpha$  and  $\beta$  of a given electron to a normalized function  $\Theta(j, m)$ . Then, applying equation (4) one can perform all the integrations involved.

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### References

- [1] R. Carbó-Dorca and E. Besalú, Extended Sobolev and Hilbert spaces and approximate stationary solutions for electronic systems with the non-linear Schrödinger equation, Institute of Computational Chemistry, Technical report IT-IQC-00-25.
- [2] R. Carbó-Dorca, Ll. Amat, E. Besalú, X. Gironés and D. Robert, *J. Mol. Structure (Theochem)* 504 (2000) 181.
- [3] R.N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (Wiley, New York, 1988).
- [4] A. Messiah, *Mécanique Quantique*, Vol. 2 (Dunod, Paris, 1960).