

VI. SPIN-ADAPTED CONFIGURATIONS

A. Preliminary Considerations

We have described the spin of a single electron by the two spin functions $\alpha(\omega) \equiv \alpha$ and $\beta(\omega) \equiv \beta$. In this Sect. we will discuss spin in more detail and consider the spin states of many-electron systems. We will describe *restricted* Slater determinants that are formed from spinorbitals whose spatial parts are restricted to be the same for α and β spins (i.e., $\{\phi_i\} = \{\psi_i\alpha, \psi_i\beta\}$). Restricted determinants, except in special cases, are not eigenfunctions of the total electron spin operator. However, by taking appropriate linear combinations of such determinants we can form *spin-adapted configurations*, which are proper eigenfunctions. Finally, we will describe *unrestricted* determinants, which are formed from spinorbitals that have different spatial parts for different spins (i.e., $\{\phi_i\} = \{\psi_i^\alpha\alpha, \psi_i^\beta\beta\}$).

In the usual nonrelativistic treatment, such as considered here, the Hamiltonian does not contain any spin coordinates and hence both S^2 and S_z commute with the Hamiltonian

$$[\mathbf{H}, S^2] = 0 = [\mathbf{H}, S_z] \quad (6.1)$$

Consequently, the exact eigenfunctions of the Hamiltonian are also eigenfunctions of the two spin operators

$$S^2 |\Phi\rangle = S(S+1) |\Phi\rangle \quad (6.2)$$

$$S_z |\Phi\rangle = M_S |\Phi\rangle \quad (6.3)$$

where S and M_S are the spin quantum numbers describing the total spin and its z component of an N -electron $|\Phi\rangle$. States with $S = 0, 1/2, 1, 3/2, \dots$ have multiplicity $2S + 1 = 1, 2, 3, 4, \dots$ and are called singlets, doublets, triplets, quartets, etc. Approximate solutions of the Schrödinger equation are not necessarily pure spin states. However, it is often convenient to constrain approximate wavefunctions to be pure singlets, doublets, triplets, etc.

Any single determinant is an eigenfunction of S_z . In particular

$$\begin{aligned} S_z |\phi_i \phi_j \cdots \phi_k\rangle &= \frac{1}{2} (N_\alpha - N_\beta) |\phi_i \phi_j \cdots \phi_k\rangle \\ &= M_S |\phi_i \phi_j \cdots \phi_k\rangle \end{aligned} \quad (6.4)$$

where N_α is the number of spinorbitals with α spin and N_β is the number of spinorbitals with β spin. However, single determinants are not necessarily eigenfunctions of S^2 . As we

will discuss in the next Subsection, by combining a small number of single determinants it is possible to form spin-adapted configurations that are correct eigenfunctions of \mathbf{S}^2 .

B. Restricted Determinants and Spin-Adapted Configurations

As we have seen, given a set of K orthonormal spatial orbitals $\{\psi_i | i = 1, 2, \dots, K\}$ we can form a set of $2K$ spinorbitals $\{\phi_i | i = 1, 2, \dots, 2K\}$ by multiplying each spatial orbital by either the α or β spin function

$$\phi_{2i-1}(\mathbf{x}) = \psi_i(\mathbf{r}) \alpha(\omega)$$

$$i = 1, 2, \dots, K$$

$$\phi_{2i}(\mathbf{x}) = \psi_i(\mathbf{r}) \beta(\omega)$$

Such spinorbitals are called *restricted* spinorbitals and determinants formed from them are restricted determinants. In such a determinant a given spatial orbital ψ_i can be occupied either by a single electron (spin up or down) or by two electrons (one with up and the other with spin down). It is convenient to classify types of restricted determinants according to the number of spatial orbitals that are singly occupied. A determinant in which each spatial orbital is doubly occupied is called a *closed-shell* determinant (see Fig. VI.1). An *open shell* refers to a spatial orbital that contains a single electron. One refers to determinants by the number of open shells they contain.

$$\begin{array}{r}
\vdots \\
\vdots \\
\cdots \cdots \cdots \psi_6 \\
\cdots \cdots \cdots \psi_5 \\
\cdots \uparrow \downarrow \cdots \psi_4 \\
\cdots \cdots \cdots \psi_3 \\
\cdots \uparrow \downarrow \cdots \psi_2 \\
\cdots \uparrow \downarrow \cdots \psi_1 \\
|{}^1\Phi\rangle = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \phi_4 \bar{\phi}_4\rangle
\end{array}$$

Fig.VI.1 A singlet closed – shell determinant

All the electron spins are paired in a closed-shell determinant, and it is not surprising that a closed-shell determinant is a pure singlet. That is, it is an eigenfunction of S^2 with eigenvalue zero,

$$S^2 |\phi_i \bar{\phi}_i \phi_j \bar{\phi}_j \cdots\rangle = 0(0+1) |\phi_i \bar{\phi}_i \phi_j \bar{\phi}_j \cdots\rangle = 0 \quad (6.5)$$

Let us consider the construction of a wavefunction of a two-electron system in which the two spinorbitals in the Hartree product are to be fabricated from two different space orbitals ψ_1 and ψ_2 which are assumed to be separately normalized and mutually orthogonal; for example, in the case of a two-electron atom, ψ_1 and ψ_2 may be two different hydrogenlike atomic orbitals. Since we have two possible spin functions, α and β , we can form the four different spinorbitals $\psi_1\alpha$, $\psi_1\beta$, $\psi_2\alpha$, and $\psi_2\beta$. In general, when one has $2N$ spinorbitals to be used n at a time ($n \leq 2N$), the total number of different combinations is given by

$$\eta = \binom{2N}{n} = \frac{(2N)!}{n!(2N-n)!} \quad (6.6)$$

In the two-electron function we have four spinorbitals to be used two at a time, so that we can obtain six different simple products, namely,

$$\begin{array}{r}
\Phi_{12}^{HP\alpha\alpha} = \psi_1(1)\alpha(1)\psi_2(2)\alpha(2) \quad 1 \\
\Phi_{12}^{HP\beta\beta} = \psi_1(1)\beta(1)\psi_2(2)\beta(2) \quad -1
\end{array}$$

$$\begin{aligned}
\Phi_{12}^{HP\alpha\beta} &= \psi_1(1) \alpha(1) \psi_2(2) \beta(2) & 0 \\
\Phi_{12}^{HP\beta\alpha} &= \psi_1(1) \beta(1) \psi_2(2) \alpha(2) & 0 \\
\Phi_{11}^{HP\alpha\beta} &= \psi_1(1) \alpha(1) \psi_1(2) \beta(2) & 0 \\
\Phi_{22}^{HP\alpha\beta} &= \psi_2(1) \alpha(1) \psi_2(2) \beta(2) & 0
\end{aligned} \tag{6.7}$$

Products such as $\Phi_{11}^{HP\alpha\alpha}$ are excluded on the basis of the exclusion principle. The numbers to the right of each product function signify the S_z eigenvalues, i.e., M_S . These eigenvalues are readily verified by the direct application of S_z to a particular function using the appropriate relations, for example

$$\begin{aligned}
S_z \Phi_{12}^{HP\alpha\alpha} &= (S_{z1} + S_{z2}) \psi_1(1) \alpha(1) \psi_2(2) \alpha(2) \\
&= \psi_1(1) [S_{z1} \alpha(1)] \psi_2(2) \alpha(2) + \psi_1(1) \alpha(1) \psi_2(2) [S_{z2} \alpha(2)] \\
&= \frac{1}{2} \psi_1(1) \alpha(1) \psi_2(2) \alpha(2) + \frac{1}{2} \psi_1(1) \alpha(1) \psi_2(2) \alpha(2) = \Phi_{12}^{HP\alpha\alpha}
\end{aligned} \tag{6.8}$$

i.e., the eigenvalue M_S of $\Phi_{12}^{HP\alpha\alpha}$ is 1. In general, the M_S eigenvalue of a product wavefunction (antisymmetrized or not) is given by the simple expression

$$M_S = \frac{1}{2} (N_\alpha - N_\beta) \tag{6.9}$$

The product functions (6.7), as they now stand, are not antisymmetric as required by the Pauli principle. For example, we could just as well represent the first function in (6.7) by

$$\Phi_{21}^{HP\alpha\alpha} = \psi_2(1) \alpha(1) \psi_1(2) \alpha(2) \tag{6.10}$$

where the coordinates of the two electrons have been interchanged. Now consider the function obtained by taking the difference of $\Phi_{12}^{HP\alpha\alpha}$ and $\Phi_{21}^{HP\alpha\alpha}$, namely,

$$\begin{aligned}
2^{-1/2} (\Phi_{12}^{HP\alpha\alpha} - \Phi_{21}^{HP\alpha\alpha}) &= 2^{-1/2} [\psi_1(1)\alpha(1)\psi_2(2)\alpha(2) - \psi_2(1)\alpha(1)\psi_1(2)\alpha(2)] \\
&= 2^{-1/2} [\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)]\alpha(1)\alpha(2) \\
&= -2^{-1/2} (\Phi_{21}^{HP\alpha\alpha} - \Phi_{12}^{HP\alpha\alpha})
\end{aligned} \tag{6.11}$$

where $2^{-1/2}$ is the normalization factor. It is evident that the function (6.11) is antisymmetric, as a result, in this case, of the spatial functions. It is readily verified that the antisymmetric function (6.11) is also representable by the determinant

$$\Phi_{12}^{\alpha\alpha} = \frac{1}{2!^{1/2}} \text{Det} \begin{pmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\alpha(1) \\ \psi_1(2)\alpha(2) & \psi_2(2)\alpha(2) \end{pmatrix} \tag{6.12}$$

in which $\Phi_{12}^{HP\alpha\alpha}$ itself is the product of the diagonal elements and $\Phi_{21}^{HP\alpha\alpha}$ is the product of the remaining elements. It is often convenient to adopt a simplified notation for determinantal wavefunctions and to write (6.12) as

$$\Phi_{12}^{\alpha\alpha} = 2^{-1/2} (\psi_1\psi_2 - \psi_2\psi_1)\alpha\alpha \tag{6.13}$$

where it is understood that electrons 1 and 2 are associated with each product in the natural order 1, 2 from left to right. An even simpler notation, which we shall use quite frequently, is

$$\Phi_{12}^{\alpha\alpha} = |\phi_1\phi_2| \tag{6.14}$$

where the vertical bars imply a determinant (including the normalization factor) and ϕ_1 and ϕ_2 imply spinorbitals formed from the spatial orbitals ψ_1 and ψ_2 along with spin functions. For spinorbitals formed with β spin functions, one would write

$$\Phi_{12}^{\beta\beta} = 2^{-1/2} (\psi_1\psi_2 - \psi_2\psi_1)\beta\beta = |\bar{\phi}_1\bar{\phi}_2| \tag{6.15}$$

The horizontal bar over a spatial orbital indicates that a β spin function is to be associated with that spatial orbital in forming the spinorbital.

Exactly the same trick suffices to antisymmetrize each of the remaining product functions of Eq. (6.7). We thus obtain

$$\begin{aligned}
\Phi_{12}^{\alpha\beta} &= 2^{-1/2} (\psi_1\psi_2\alpha\beta - \psi_2\psi_1\beta\alpha) = |\phi_1\bar{\phi}_2| \\
\Phi_{12}^{\beta\alpha} &= 2^{-1/2} (\psi_1\psi_2\beta\alpha - \psi_2\psi_1\alpha\beta) = |\bar{\phi}_1\phi_2| \\
\Phi_{11}^{\alpha\beta} &= 2^{-1/2} \psi_1\psi_1(\alpha\beta - \beta\alpha) = |\phi_1\bar{\phi}_1| \\
\Phi_{22}^{\alpha\beta} &= 2^{-1/2} \psi_2\psi_2(\alpha\beta - \beta\alpha) = |\phi_2\bar{\phi}_2|
\end{aligned} \tag{6.16}$$

These determinantal forms arise from the special choice of representing approximate wavefunctions as antisymmetrized products of orbitals.

Examination of an expanded determinantal wavefunction reveals that it is not possible, in general, to speak of an electron as occupying a definite orbital, since the antisymmetrization has the formal effect of distributing each electron over more than one space orbital.

By use of the relations of spin operators we can investigate the behavior of the six antisymmetrized functions given by Eqs. (6.14) to (6.16) with respect to the operator S^2 . It is found (after some rather tedious algebra) that all except $|\phi_1 \bar{\phi}_2|$ and $|\bar{\phi}_1 \phi_2|$ are eigenfunctions of S^2 . However, if we form the linear combinations

$$2^{-1/2} (|\phi_1 \bar{\phi}_2| \pm |\bar{\phi}_1 \phi_2|) = 2^{-1} (\psi_1 \psi_2 \mp \psi_2 \psi_1) (\alpha \beta \pm \beta \alpha) \quad (6.17)$$

we obtain two different eigenfunctions of S^2 . The determinantal wavefunctions formed from the products (6.7) along with their S_z and S^2 eigenvalues are given by

<i>Eigenfunctions</i>	M_S	$S(S+1)$
$ \phi_1 \phi_2 $	1	2
$ \bar{\phi}_1 \bar{\phi}_2 $	-1	2
$2^{-1/2} (\phi_1 \bar{\phi}_2 + \bar{\phi}_1 \phi_2)$	0	2
$2^{-1/2} (\phi_1 \bar{\phi}_2 - \bar{\phi}_1 \phi_2)$	0	0
$ \phi_1 \bar{\phi}_1 $	0	0
$ \phi_2 \bar{\phi}_2 $	0	0

In the simple two-electron case considered here, the final wavefunctions all factor into a spatial wavefunction and a spin wavefunction. This behavior does not carry over into wavefunctions involving more than two electrons.

The first three functions have the same spatial function, that is, $\psi_1 \psi_2 - \psi_2 \psi_1$, but each has a different spin function. Since each of these has the same value of $S(S+1)$, we say that these functions form the three components of a triplet state, i.e., a state which has threefold spin degeneracy. This degeneracy follows from the fact that the energy associated with a wavefunction depends only upon the spatial functions. The remaining functions all have $S(S+1)$ values of zero, and since they have different spatial portions, they represent three different nondegenerate states, called *singlet states*. It should be noted that the triplet-state

spatial function is antisymmetric with symmetric spin functions and that the singlet-state spatial functions are all symmetric with antisymmetric spin functions.

Either of the last two functions can be used to describe the ground state of a two-electron system. Thus if ϕ_1 (or ϕ_2) is ϕ_{1s} (a hydrogenlike 1s orbital), we obtain the familiar ground-state wavefunction for the helium atom, namely,

$$\xi = |\phi_{1s} \bar{\phi}_{1s}| = 2^{-1/2} \phi_{1s}(1) \phi_{1s}(2) (\alpha \beta - \beta \alpha) \quad (6.18)$$

except that there is now a spin wavefunction present. It is easy to demonstrate that this spin wavefunction is immaterial as far as expectation values of spin-free operators are concerned. If \mathbf{G} is a spin-free operator, its expectation value for a system described by the wavefunction (6.18) is

$$\begin{aligned} \langle \mathbf{G} \rangle &= \langle \xi | \mathbf{G} | \xi \rangle = \int \int |\phi_{1s} \bar{\phi}_{1s}| \mathbf{G} |\phi_{1s} \bar{\phi}_{1s}| d\mathbf{r} d\sigma \\ &= \int \phi_{1s}^*(1) \phi_{1s}^*(2) \mathbf{G} \phi_{1s}(1) \phi_{1s}(2) d\mathbf{r} \int \frac{|\alpha \beta - \beta \alpha|^2}{2} d\sigma \end{aligned} \quad (6.19)$$

By use of Eq. (4.16) we see that the right-hand integral becomes

$$\begin{aligned} \frac{1}{2} \int |\alpha \beta - \beta \alpha|^2 d\sigma &= \frac{1}{2} \left(\int \alpha^* \alpha d\sigma_1 \int \beta^* \beta d\sigma_2 \right. \\ &\quad \left. - 2 \int \alpha^* \beta d\sigma_1 \int \beta^* \alpha d\sigma_2 + \int \beta^* \beta d\sigma_1 \int \alpha^* \alpha d\sigma_2 \right) = \frac{1}{2} (1 - 0 + 1) = 1 \end{aligned} \quad (6.20)$$

Thus, the spin functions integrate out to unity, and the expectation value of \mathbf{G} is simply

$$\langle \mathbf{G} \rangle = \langle \phi_{1s}(1) \phi_{1s}(2) | \mathbf{G} | \phi_{1s}(1) \phi_{1s}(2) \rangle \quad (6.21)$$

In the case of systems with more than two electrons, it turns out that the spin functions also integrate to unity even though one cannot factor the total electronic wavefunction into a spatial part and a spin part. In such a case it is necessary to take the spin functions into account in setting up the total wavefunction in order to obtain a spatial wavefunction of the correct symmetry. Once this is done, it is always possible to set up an expression for $\langle \mathbf{G} \rangle$ which does not involve the spin functions (see Sect. V.B).

C. The Excited States of the Helium Atom

The lowest excited state of the helium atom is represented to zeroth order by the configuration 1s2s. In Sect. VI.B we saw that this configuration leads to singlet and triplet

states. The zeroth-order approximation to the singlet-state wavefunction is

$${}^1\xi = 2^{-1/2} (|1s\bar{2}s\rangle - |\bar{1}s2s\rangle)$$

where we let $1s$ and $2s$ represent normalized hydrogenlike atomic orbitals. The zeroth-order approximation to the triplet-state wavefunctions is given by one of the functions

$${}^3\xi = \begin{pmatrix} 2^{-1/2} (|1s\bar{2}s\rangle + |\bar{1}s2s\rangle) \\ |1s2s\rangle \\ |\bar{1}s\bar{2}s\rangle \end{pmatrix}$$

We recall that the singlet function has the spatial portion $\psi_{1s}\psi_{2s} + \psi_{2s}\psi_{1s}$ with an antisymmetric spin function, whereas the triplet function has the spatial portion $\psi_{1s}\psi_{2s} - \psi_{2s}\psi_{1s}$ with one of three symmetric spin functions. The symmetric and antisymmetric spatial functions may be said to arise as a result of the double degeneracy of the unperturbed state (the independent-particle model); i.e., the two electrons are indistinguishable. The antisymmetrization is irrelevant to the unperturbed state (since the zeroth-order Hamiltonian is a sum of two one-electronic operators) but is required for the perturbed state since the complete Hamiltonian contains the two-electron term $1/r_{12}$. The lowest singlet and triplet states are usually designated by 2^1S_0 and 2^3S_1 , the number preceding the term symbol representing an effective principal quantum number. This effective principal quantum number arises from the Rydberg series of the atomic spectrum.

The first-order perturbation energies of helium in the $1s2s$ configuration (and in the absence of spin-orbit interaction) is given by the roots of the determinant

$$\text{Det} \begin{pmatrix} \mathbf{H}_{11}^{(1)} - \epsilon & \mathbf{H}_{12}^{(1)} \\ \mathbf{H}_{21}^{(1)} & \mathbf{H}_{22}^{(1)} - \epsilon \end{pmatrix} = 0$$

where

$$\mathbf{H}_{11}^{(1)} = \left\langle {}^1\xi \left| \frac{1}{r_{12}} \right| {}^1\xi \right\rangle$$

$$\mathbf{H}_{22}^{(1)} = \left\langle {}^3\xi \left| \frac{1}{r_{12}} \right| {}^3\xi \right\rangle$$

$$\mathbf{H}_{12}^{(1)} = \mathbf{H}_{21}^{(1)} = \left\langle {}^3\xi \left| \frac{1}{r_{12}} \right| {}^1\xi \right\rangle$$

Since S^2 commutes with $1/r_{12}$ and ${}^3\xi$ and ${}^1\xi$ have different S^2 eigenvalues, the off-diagonal matrix elements \mathbf{H}_{12} and \mathbf{H}_{21} vanish. The energies of the singlet and triplet states to first order then are

$${}^1E = \epsilon_{1s}^{(0)} + \epsilon_{2s}^{(0)} + \mathbf{H}_{11}^{(1)} \qquad {}^3E = \epsilon_{1s}^{(0)} + \epsilon_{2s}^{(0)} + \mathbf{H}_{22}^{(1)}$$

where the zeroth-order energy is given by $(\epsilon_i^{(0)} = -Z^2/2n^2$ in a.u.)

$$\epsilon_{1s}^{(0)} + \epsilon_{2s}^{(0)} = -\frac{4}{2} - \frac{4}{8} = -\frac{5}{2} \text{ a.u.}$$

Since two-electron wavefunctions (in the orbital approximation) factor into space and spin function, the matrix elements $\mathbf{H}_{11}^{(1)}$ and $\mathbf{H}_{22}^{(1)}$ can be evaluated from the spatial portions of ${}^1\xi$ and ${}^3\xi$, respectively; i.e., the spin integrates out to unit. One obtains, with the notation

$$1s \equiv \phi_{1s} = \psi_{1s}\alpha, \quad 2s \equiv \phi_{2s} = \psi_{2s}\alpha, \quad \overline{1s} \equiv \overline{\phi}_{1s} = \psi_{1s}\beta, \quad \overline{2s} \equiv \overline{\phi}_{2s} = \psi_{2s}\beta,$$

$$\begin{aligned} \mathbf{H}_{11}^{(1)} &= \frac{1}{2} \left\langle \left| \phi_{1s} \overline{\phi}_{2s} \right| - \left| \overline{\phi}_{1s} \phi_{2s} \right| \left| \frac{1}{r_{12}} \right| \left| \phi_{1s} \overline{\phi}_{2s} \right| - \left| \overline{\phi}_{1s} \phi_{2s} \right| \right\rangle \\ &= \left\langle \psi_{1s} \psi_{2s} \left| \frac{1}{r_{12}} \right| \psi_{1s} \psi_{2s} \right\rangle + \left\langle \psi_{1s} \psi_{2s} \left| \frac{1}{r_{12}} \right| \psi_{2s} \psi_{1s} \right\rangle = J_{12} + K_{12} \end{aligned}$$

$$\begin{aligned} \mathbf{H}_{22}^{(1)} &= \frac{1}{2} \left\langle \left| \phi_{1s} \overline{\phi}_{2s} \right| + \left| \overline{\phi}_{1s} \phi_{2s} \right| \left| \frac{1}{r_{12}} \right| \left| \phi_{1s} \overline{\phi}_{2s} \right| + \left| \overline{\phi}_{1s} \phi_{2s} \right| \right\rangle \\ &= \left\langle \psi_{1s} \psi_{2s} \left| \frac{1}{r_{12}} \right| \psi_{1s} \psi_{2s} \right\rangle - \left\langle \psi_{1s} \psi_{2s} \left| \frac{1}{r_{12}} \right| \psi_{2s} \psi_{1s} \right\rangle = J_{12} - K_{12} \end{aligned}$$

Thus, the energies of the 2^1S_0 and 2^3S_1 states are

$${}^1E = -\frac{5}{2} + J_{12} + K_{12} \qquad {}^3E = -\frac{5}{2} + J_{12} - K_{12}$$

The energy difference between the singlet and triplet states is

$${}^1E - {}^3E = 2K_{12}$$

From Sect. V.C we recall that $K_{12} > 0$, so that the triplet state is the lower in energy. This is in accord with Hund's rule of maximum multiplicity.

It is important to note that if one had used a simple product wavefunction $\phi_{1s}\phi_{2s}$, the singlet and triplet states would have the same energy, namely, $-\frac{5}{2} + J_{12}$. It is clear that the antisymmetry principle accounts for the separation of different spin states. *The spin functions, although not affecting the total energy directly, nevertheless influence the total energy by determining the form of the spatial portion of the wavefunction.*

The values of the coulombic and exchange integrals are 0.419 and 0.044 a.u., respectively. The singlet- and triplet-state energies then are

$${}^1E = -2.037 \text{ a.u.} \quad (\text{exp. } -2.147 \text{ a.u.})$$

$${}^3E = -2.125 \text{ a.u.} \quad (\text{exp. } -2.176 \text{ a.u.})$$

The singlet state is in error by 0.110 a.u., and the triplet state is in error by 0.051 a.u. The fact that the triplet-state error is lower is due largely to the fact that the screening effect is not so important for electrons with parallel spins as for electrons with antiparallel spins. This, in turn, is due to the fact that the antisymmetry principle tends to keep electrons with the same spin farther apart. On the other hand, the antisymmetry principle implies that electrons with different spins come closer together than is actually the case.

The tendency for electrons with like spins to avoid each other is often referred to as a *spin correlation* or *exchange correlation* effect. Such an effect is in addition to the radial and angular correlation. In general, the use of single-configurational antisymmetrized wavefunctions accounts for correlation effects in triplet states much better than in singlet states.

D. Construction of Determinantal Eigenfunctions of S^2

As mentioned in Subsection VI.A, wavefunctions which are eigenfunctions of S^2 are said to describe pure spin states, i.e., states which are characterized by a definite relative alignment of electron spins. Since one is almost always concerned with atoms and molecules which are in pure spin states, and since determinantal wavefunctions are generally not automatically eigenfunctions of S^2 , it is convenient to describe a systematic procedure for constructing wavefunctions for pure spin states.

Consider the eigenvalue equation

$$S_z \omega = M_S \omega \tag{6.22}$$

where ω is an N -electron function containing spin coordinates. For $N = 3$ we have

$$M_S = m_{s1} + m_{s2} + m_{s3} = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$M_S = m_{s1} + m_{s2} + m_{s3} = \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = \frac{1}{2}$$

$$M_S = m_{s1} + m_{s2} + m_{s3} = \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = -\frac{1}{2}$$

$$M_S = m_{s1} + m_{s2} + m_{s3} = -\frac{1}{2} - \frac{1}{2} - \frac{1}{2} = -\frac{3}{2}$$

i.e., there are four different possible spin alignments. Below we show that there are $2^3 = 8$ different ways in which these four M_S values can arise. These eight possibilities can be grouped as follows: the group $-\frac{3}{2} \leq M_S \leq \frac{3}{2}$, which corresponds to $S = \frac{3}{2}$ and thus represents a state with multiplicity $2S + 1 = 4$, and two groups $-\frac{1}{2} \leq M_S \leq \frac{1}{2}$, which corresponds to $S = \frac{1}{2}$ and thus represent states of multiplicity $2S + 1 = 2$. This means that an atom or molecule having three electrons outside a closed shell may exist in a quadruplet state or in one of two different doublet states.

Possible values of the S_z eigenvalues for a three – electron system

m_{s1}	m_{s2}	m_{s3}	M_S	Φ_i
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$ \phi_1 \phi_2 \phi_3 $
$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$ \phi_1 \phi_2 \bar{\phi}_3 $
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$ \phi_1 \bar{\phi}_2 \bar{\phi}_3 $
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$ \bar{\phi}_1 \bar{\phi}_2 \bar{\phi}_3 $
$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$ \bar{\phi}_1 \bar{\phi}_2 \phi_3 $
$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$ \bar{\phi}_1 \phi_2 \phi_3 $
$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$ \bar{\phi}_1 \phi_2 \bar{\phi}_3 $
$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$ \phi_1 \bar{\phi}_2 \phi_3 $

For $N > 3$ the above procedure is rather tedious to carry out, since there will be 2^N different spin couplings to write down. Thus a systematic procedure is required.

We now develop general methods which enable us to obtain:

(i) the number of independent spin states characterized by the quantum number S which exists for a system of N electrons when the space orbitals occupied by each electron are different. We denote this number $f(N, S)$.

Consider a many-electron spin function which is a simple product of N one-electron spin wavefunctions. Since each one-electron spin wavefunction is restricted to either α or β type, it follows that 2^N different many-electron spin wavefunctions may be generated. Each of these, of necessity, is a eigenfunction of S_z .

For a three-electron system, the possible values of S are $3/2$ and $1/2$. The values of $f(N, S)$ for this system are readily seen to be

$$f(3, 3/2) = \frac{3!}{3!0!} = 1 \tag{6.23}$$

$$f(3, 1/2) = \frac{3!}{2!1!} - 1 = 2 \tag{6.24}$$

In Eq. (6.23) we have in essence calculated the number of possible spin orientations which yield $M_S = 3/2$; the state $S = 3/2$ also contains three other spin components with $M_S = 1/2, -1/2,$ and $-3/2$. Thus, in Eq. (6.24) where we calculate the number of possible spin orientations with $M_S = 1/2$, before we associate the number 3 with the number of independent spin states $S = 1/2$ we must subtract out that one spin orientation with $M_S = 1/2$ belonging to $S = 3/2$ - hence Eq. (6.24). Thus, the three-electron system possesses one quartet spin wavefunction and two doublet spin wavefunctions. The total number of wavefunctions is $8 = 2^3 = 1 \times 4 + 2 \times 2$.

For a four-electron system, the values of S are 2, 1, and 0. The values of $f(N, S)$ are

$$f(4, 2) = \frac{4!}{4!0!} = 1 \quad \text{1 quintet} \tag{6.25}$$

$$f(4, 1) = \frac{4!}{3!1!} - 1 = 3 \quad \text{3 triplets} \tag{6.26}$$

$$f(4, 0) = \frac{4!}{2!2!} - 3 - 1 = 2 \quad \text{2 singlets} \tag{6.27}$$

The total number of wavefunctions is $16 = 2^4 = 1 \times 5 + 3 \times 3 + 2 \times 1$.

The results for the three- and four-electrons systems are now generalized in analogical fashion to yield

$$\begin{aligned} f(N, S) &= \frac{N!}{(N/2 - S)!(N/2 + S)!} - \frac{N!}{(N/2 - S - 1)!(N/2 + S + 1)!} \\ &= \frac{(2S + 1)N!}{(N/2 + S + 1)!(N/2 - S)!} \end{aligned} \quad (6.28)$$

Multiplication of this expression by $2S + 1$ and performing a summation over S gives the total number of wavefunctions

$$\sum_S (2S + 1) f(N, S) = 2^N \quad (6.29)$$

Thus, by insertion of the appropriate values of N and S into $f(N, S)$ we can evaluate the number of independent spin states of a given multiplicity available for an N -electron system. The results of such an evaluation are often presented in graphic form, in a construct such as Fig. VI.2 termed *branching diagram*, from which it is possible to carry out the analysis with very little labor. This diagram shows the number of states of different multiplicities obtainable for a given number of independent electrons. The diagram is very easy to construct beginning with a single electron and successively coupling other electron spins to it in all possible algebraic ways. In the diagram the number of states of a given multiplicity is indicated within a circle whose abscissa is the number of electrons and whose ordinate is the multiplicity. The diagram is constructed in such a way that each encircled number is the sum of the two adjacent encircled numbers to the left. We see that for four electrons one would have two singlet states ($M_S = 0$), three triplet states ($M_S = -1, 0$, and 1), and one quintet state ($M_S = -2, -1, 0, 1$, and 2). Thus for four electrons not in closed shells one could write down 16 linearly independent wavefunctions (not all of which would be automatically orthogonal) leading to six different energies.

(ii) A readily usable form of the operator S^2 . We may expand this operator as

$$S^2 = S_x^2 + S_y^2 + S_z^2 \tag{6.30}$$

If we now define

$$S_+ \equiv S_x + i S_y \qquad S_- \equiv S_x - i S_y \tag{6.31}$$

we obtain

$$\mathbf{S}_- \mathbf{S}_+ = \mathbf{S}_x^2 + \mathbf{S}_y^2 - \hbar \mathbf{S}_z \quad (6.32)$$

where the commutator relationship $[\mathbf{S}_x, \mathbf{S}_y] = i \hbar \mathbf{S}_z$ has been used. Insertion of Eq. (6.32) into (6.30) yields

$$\mathbf{S}^2 = \mathbf{S}_z^2 + \hbar \mathbf{S}_z + \mathbf{S}_- \mathbf{S}_+ \quad (6.33)$$

An equivalent form readily verifiable, is

$$\mathbf{S}^2 = \mathbf{S}_z^2 - \hbar \mathbf{S}_z + \mathbf{S}_+ \mathbf{S}_- \quad (6.34)$$

At this point we note that

$$\mathbf{S}_+ \equiv \sum_j \mathbf{s}_+(j) \quad \mathbf{S}_- \equiv \sum_j \mathbf{s}_-(j) \quad (6.35)$$

$$\mathbf{s}_+(j) \equiv \mathbf{s}_x(j) + i \mathbf{s}_y(j) \quad \mathbf{s}_-(j) \equiv \mathbf{s}_x(j) - i \mathbf{s}_y(j) \quad (6.36)$$

where j is an electron numbering index and \mathbf{s} is a one-electron operator. The effects of \mathbf{s}_+ and \mathbf{s}_- on the spin functions are

$$\mathbf{s}_-(j) \begin{pmatrix} \alpha(j) \\ \beta(j) \end{pmatrix} = \hbar \begin{pmatrix} \beta(j) \\ 0 \end{pmatrix} \quad \mathbf{s}_+(j) \begin{pmatrix} \alpha(j) \\ \beta(j) \end{pmatrix} = \hbar \begin{pmatrix} 0 \\ \alpha(j) \end{pmatrix} \quad (6.37)$$

The operator \mathbf{s}_- steps down α to β but annihilates β whereas \mathbf{s}_+ annihilates α but steps up β to α . If the operands of \mathbf{S}^2 are limited to Slater determinants or to simple products of spinorbitals (these will be always assumed to be the cases), the Eqs. (6.33) and (6.34) can be simplified further.

Consider the determinant

$$\Phi = |\psi_1 \alpha(1) \psi_2 \beta(2) \psi_3 \alpha(3) \cdots \psi_N \alpha(N)| \quad (6.38)$$

in which each electron is associated with a different space function. Since the spin operators do not affect the orbital parts and since no restriction need be placed on the spin function associated with a given space function (i.e., the spin function may be either α or β) it follows that the determinantal wavefunction of Eq. (6.38) may be abbreviated to

$$\Phi = |\alpha(1) \beta(2) \alpha(3) \cdots \alpha(N)| \quad (6.39)$$

Indeed, with no loss of information, we can use the condensation

$$\Phi = \alpha(1) \beta(2) \alpha(3) \cdots \equiv \alpha \beta \alpha \cdots \quad (6.40)$$

as long as we remember that all of these constitute a *short hand* for Eq. (6.38).

The results of operating on Φ of Eqs. (6.38), (6.39), or (6.40) with S_z and S_z^2 are

$$S_z \Phi = \frac{1}{2} (N_\alpha - N_\beta) \hbar \Phi \quad (6.41)$$

$$S_z^2 \Phi = \frac{1}{4} (N_\alpha - N_\beta)^2 \hbar^2 \Phi \quad (6.42)$$

We may rewrite $S_- S_+$ in the form

$$S_- S_+ = \sum_i^N s_-(i) s_+(i) + \sum_i^N \sum_{i \neq j}^N s_-(i) s_+(j) \quad (6.43)$$

and consider each of the parts on the right-hand side of this equation with respect to their effects on Φ . Consider first

$$\sum_i^N s_-(i) s_+(i) \Phi = \sum_i^N s_-(i) s_+(i) | \alpha(1) \beta(2) \cdots \alpha(N) | \quad (6.44)$$

By virtue of the one-electron nature of the $s_-(i) s_+(i)$ operator, Eq. (6.44) reduces to

$$\sum_i^N s_-(i) s_+(i) \Phi = N_\beta \hbar^2 \Phi \quad (6.45)$$

where the last equality follows from the noncommutativity of s_- and s_+ and from

$$s_-(i) s_+(i) \begin{pmatrix} \alpha(i) \\ \beta(i) \end{pmatrix} = \hbar^2 \begin{pmatrix} 0 \\ \beta(i) \end{pmatrix} \quad (6.46)$$

Consider next the two-electron operator part $\sum_i \sum_{i \neq j} s_-(i) s_+(j)$ and note that the result

$$s_-(i) s_+(j) \alpha(i) \beta(j) = \hbar^2 \beta(i) \alpha(j) \quad (6.47)$$

implies a formal identity of the operators

$$\sum_i \sum_{i \neq j} s_-(i) s_+(j) = \hbar^2 \sum_P P_{\alpha\beta} \quad (6.48)$$

where $P_{\alpha\beta}$ is an operator which exchanges α and β functions in the original determinant (i.e., $P_{\alpha\beta}$ is that subclass of all electron permutation operators which leads to an interchange of α and β spins), and where the sum is taken over all possible interchanges. For the two-electron

permutations, no terms survive. The effect of the operator $S_- S_+$ on Φ is then summarized in the expression

$$S_- S_+ \Phi = \left(N_\beta + \sum_{\mathbf{P}} P_{\alpha\beta} \right) \hbar^2 \Phi \quad (6.49)$$

If we now collect all the terms of Eqs. (6.41), (6.42), and (6.49) and insert them into Eq. (6.33), we obtain after a small amount of rearrangement

$$S^2 \Phi = \left[\sum_{\mathbf{P}} P_{\alpha\beta} + \frac{1}{4} [(N_\alpha - N_\beta)^2 + 2N] \right] \hbar^2 \Phi \quad (6.50)$$

where $N = N_\alpha + N_\beta$. Thus, given Φ as an eigenfunction of S^2 , it is a relatively simple matter to determine S .

(iii) A general method for construction of eigenfunctions with given S and M_S characteristics. For this purpose, we use projection operator techniques.

We now turn our attention to the generation of eigenfunctions of S^2 . Suppose we start with a trial wavefunction Φ_t which satisfies one condition - namely, that it be resolvable into a linear combination of eigenfunctions of S^2

$$\Phi_t = \sum_k c_{ik} \Phi(S_k) \quad (6.51)$$

where the summation runs over all possible values of S_k consistent with the specific number of electrons under consideration and where

$$S^2 \Phi(S_k) = S_k(S_k + 1) \hbar^2 \Phi(S_k) \quad (6.52)$$

The coefficients c_{ik} need not be known; all that is required is that Φ_t be a function in the domain spanned by the basis set $\Phi(S_k)$. It then follows that

$$[S^2 - S_i(S_i + 1) \hbar^2] \Phi_t = \sum_{k \neq i} d_k \Phi(S_k) \quad (6.53)$$

We may consider $[S^2 - S_i(S_i + 1)]$ to be an operator which eliminates any admixture of an S_i wavefunction from Φ_t . Successive application of such *annihilators* finally yields one pure spin state of specified multiplicity - if such a spin state exists in Φ_t . The required operator, with $\lambda_j = S_j(S_j + 1)\hbar^2$, can be written as

$$\mathcal{O}(S_k) = \prod_{i \neq k} \left(\frac{S^2 - \lambda_i}{\lambda_k - \lambda_i} \right) \quad (6.54)$$

This operator projects a wavefunction of the required spin quantum number (i.e., S_k) out of the general spin space; $\mathcal{O}(S_k)$ is a spin-projection operator.

E. Spin Eigenfunctions of a Three-Electron System: An Example Calculation

The eigenfunctions of S_z may be written immediately. In a simple short-hand form, using the condensate notation of Eq. (6.40) and from the results previously obtained for a three-electron system, they are

$$\begin{array}{ll}
 \alpha \alpha \alpha & M_S = \frac{3}{2} \\
 \alpha \alpha \beta & M_S = \frac{1}{2} \\
 \alpha \beta \alpha & M_S = \frac{1}{2} \\
 \beta \alpha \alpha & M_S = \frac{1}{2} \\
 \alpha \beta \beta & M_S = -\frac{1}{2} \\
 \beta \alpha \beta & M_S = -\frac{1}{2} \\
 \beta \beta \alpha & M_S = -\frac{1}{2} \\
 \beta \beta \beta & M_S = -\frac{3}{2}
 \end{array}$$

where, for example, $\alpha \beta \alpha$ denotes $|\psi_1 \alpha(1) \psi_2 \beta(2) \psi_3 \alpha(3)| \equiv |\phi_1 \bar{\phi}_2 \phi_3|$ with $\psi_1 \neq \psi_2 \neq \psi_3$. Inspection of the branching diagram of Fig. VI.2 indicates that we should obtain one quartet spin state ($S = \frac{3}{2}$) and two doublet spin states ($S = \frac{1}{2}$). The projection operators are

$$\mathcal{O}[3/2] = \frac{S^2 - 3/4}{15/4 - 3/4} \quad (6.55)$$

$$\mathcal{O}[1/2] = \frac{S^2 - 15/4}{3/4 - 15/4} \quad (6.56)$$

where, for brevity, we have eliminated the factor \hbar^2 from the operator S^2 . Since we have made no attempt to normalize the spin-projection operators, we fully expect that the spin-projected wavefunctions require normalization.

(a) Spin Eigenfunctions with $S = \frac{3}{2}$, $M_S = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

We first let $\mathcal{O}[3/2]$ operate on $\alpha \alpha \alpha$. The result is

$$\mathcal{O}[3/2] \alpha \alpha \alpha = \frac{[0 + \frac{1}{4}(3^2 + 2 \times 3)] \alpha \alpha \alpha - \frac{3}{4} \alpha \alpha \alpha}{15/4 - 3/4} = \alpha \alpha \alpha \quad (6.57)$$

Thus, it is clear that $\alpha\alpha\alpha$ is a satisfactory eigenfunction with $S = \frac{3}{2}$, $M_S = \frac{3}{2}$. Using the notation ${}^{2S+1}\Phi_{M_S}$ to denote the eigenfunctions of a given multiplicity and a given M_S we can write

$${}^4\Phi_{3/2} = \alpha\alpha\alpha \quad (6.58)$$

In order to exemplify the manner in which unwanted functions are eliminated, consider the result of $\mathcal{O}[1/2]$ operating on $\alpha\alpha\alpha$. The result is

$$\mathcal{O}[1/2]\alpha\alpha\alpha = \frac{[0 + \frac{1}{4}(3^2 + 2 \times 3)]\alpha\alpha\alpha - \frac{15}{4}\alpha\alpha\alpha}{3/4 - 15/4} = 0 \quad (6.59)$$

Thus, as evidenced by our inability to project a doublet spin eigenfunction out of $\alpha\alpha\alpha$, there is no doublet character in $\alpha\alpha\alpha$. This, of course, had to be the case - $\alpha\alpha\alpha$ is, after all, a quartet eigenfunction.

We next construct the spin wavefunction with $S = \frac{3}{2}$, $M_S = \frac{1}{2}$. Clearly, this eigenfunction may be a linear combination of $\alpha\alpha\beta$, $\alpha\beta\alpha$, and $\beta\alpha\alpha$ only. We start with $\alpha\alpha\beta$ to find

$$\begin{aligned} \mathcal{O}[3/2]\alpha\alpha\beta &= \frac{\left(\sum_{\mathbf{P}} \mathbf{P}_{\alpha\beta} + \frac{1}{4}[(N_{\alpha} - N_{\beta})^2 + 2N_{\alpha} + 2N_{\beta}]\right)\alpha\alpha\beta - \frac{3}{4}\alpha\alpha\beta}{15/4 - 3/4} \\ &= \frac{\alpha\beta\alpha + \beta\alpha\alpha + \frac{1}{4}[1^2 + 2 \times 2 + 2 \times 1]\alpha\alpha\beta - \frac{3}{4}\alpha\alpha\beta}{15/4 - 3/4} \\ &= \frac{1}{3}(\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta) \end{aligned} \quad (6.60)$$

Normalization yields

$${}^4\Phi_{1/2} = \frac{1}{3^{1/2}}(\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta) \quad (6.61)$$

The spin wavefunction with $S = \frac{3}{2}$, $M_S = -\frac{1}{2}$ is constructed in like manner from $\alpha\beta\beta$, $\beta\alpha\beta$, $\beta\beta\alpha$. It is found to be

$${}^4\Phi_{-1/2} = \frac{1}{3^{1/2}}(\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha) \quad (6.62)$$

The last of these four spin wavefunctions is

$${}^4\Phi_{-3/2} = \beta\beta\beta \quad (6.63)$$

(b) Spin Eigenfunctions with $S = \frac{1}{2}$, $M_S = \frac{1}{2}, -\frac{1}{2}$

There are two doublet spin wavefunctions. Those with $M_S = 1/2$ are constructed from $\alpha\alpha\beta$, $\alpha\beta\alpha$, and $\beta\alpha\alpha$. Letting $\mathcal{O}[1/2]$ operate on each of these in turn, we find

$$\begin{aligned}\mathcal{O}[1/2]\alpha\alpha\beta &= \frac{\left(\sum_{\mathbf{P}} \mathbf{P}_{\alpha\beta} + \frac{1}{4}[(N_{\alpha} - N_{\beta})^2 + 2N_{\alpha} + 2N_{\beta}]\right)\alpha\alpha\beta - \frac{15}{4}\alpha\alpha\beta}{3/4 - 15/4} \\ &= \frac{\alpha\beta\alpha + \beta\alpha\alpha + \frac{1}{4}[1^2 + 2 \times 2 + 2 \times 1]\alpha\alpha\beta - \frac{15}{4}\alpha\alpha\beta}{3/4 - 15/4} \\ &= -\frac{1}{3}(\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta)\end{aligned}\tag{6.64}$$

Analogously, it is found

$$\mathcal{O}[1/2]\alpha\beta\alpha = -\frac{1}{3}(\alpha\alpha\beta + \beta\alpha\alpha - 2\alpha\beta\alpha)\tag{6.65}$$

$$\mathcal{O}[1/2]\beta\alpha\alpha = -\frac{1}{3}(\alpha\beta\alpha + \alpha\alpha\beta - 2\beta\alpha\alpha)\tag{6.66}$$

Normalization of these three functions yields

$${}^2\Phi_{1/2} = (1/6)^{1/2}(\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta)$$

$${}^2\Phi_{1/2} = (1/6)^{1/2}(\alpha\alpha\beta + \beta\alpha\alpha - 2\alpha\beta\alpha)$$

$${}^2\Phi_{1/2} = (1/6)^{1/2}(\alpha\beta\alpha + \alpha\alpha\beta - 2\beta\alpha\alpha)$$

Thus three wavefunctions with $S = \frac{1}{2}$, $M_S = \frac{1}{2}$ have been constructed. However, one of them is linearly dependent on the other two and they are not orthogonal. Redundancy can be eliminated and orthogonality produced if we note the cyclic symmetry exhibited by these three wavefunctions and make maximum use of it. It is clear that these three wavefunctions can be represented as three in-plane vectors separated by 120° . Thus, the difference of any two functions is orthogonal to the remaining one. A possible set of orthonormal wavefunctions, then, is

$${}^2\Phi_{1/2} = (1/6)^{1/2}(\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta)\tag{6.67}$$

$${}^2\Phi_{1/2} = (1/2)^{1/2}(\beta\alpha\alpha - \alpha\beta\alpha)\tag{6.68}$$

The generation of the two wavefunctions ${}^2\Phi_{-1/2}$ proceeds in a similar way. One gets

$${}^2\Phi_{-1/2} = (1/6)^{1/2}(\beta\alpha\beta + \beta\beta\alpha - 2\alpha\beta\beta)\tag{6.69}$$

$${}^2\Phi_{-1/2} = (1/2)^{1/2} (\beta\beta\alpha - \beta\alpha\beta) \quad (6.70)$$

These results are summarized as follows:

S	M_S	<i>Spin Adapted Configuration</i>
3/2	+ 3/2	${}^4\Phi_{3/2} = \alpha\alpha\alpha$
3/2	+ 1/2	${}^4\Phi_{1/2} = 1/3^{1/2} (\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta)$
3/2	- 1/2	${}^4\Phi_{-1/2} = 1/3^{1/2} (\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha)$
3/2	- 3/2	${}^4\Phi_{-3/2} = \beta\beta\beta$
1/2	+ 1/2	${}^2\Phi_{1/2} = 1/6^{1/2} (\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta)$
1/2	+ 1/2	${}^2\Phi_{1/2} = 1/2^{1/2} (\beta\alpha\alpha - \alpha\beta\alpha)$
1/2	- 1/2	${}^2\Phi_{-1/2} = 1/6^{1/2} (\beta\alpha\beta + \beta\beta\alpha - 2\alpha\beta\beta)$
1/2	- 1/2	${}^2\Phi_{-1/2} = 1/2^{1/2} (\beta\beta\alpha - \beta\alpha\beta)$