Many Electron Spin Eigenfunctions

An arbitrary Slater determinant for N electrons can be written as

$$\hat{\mathcal{A}}\Phi(1,2,\cdots,N)\chi_M(1,2,\cdots,N)$$

Where $\Phi\left(1,2,\cdots,N\right)=a(1)b(2)\cdots c(N)$ is a product of N orthonormal spatial functions and $\chi_M\left(1,2,\cdots,N\right)$ is a product of N_α α spin functions and N_β β spin functions and therefore has an eigenvalue of $\hat{S}_z$ equal to $M=\frac{1}{2}\left(N_\alpha-N_\beta\right)$. Note that we do not consider double occupied spatial orbital when investigating the spin characteristics of a Slater Determinant. To determine the effect of $\hat{S}^2$ on the Slater determinant we need only investigate $\hat{S}^2\chi_M\left(1,2,\cdots,N\right)$. Accordingly if we want a Slater determinant to be an eigenfunction of $\hat{S}^2$ with an eigenvalue $S\left(S+1\right)$ we need only to write

$$\hat{\mathcal{A}}\Phi(1,2,\cdots,N)\chi_{SM}(1,2,\cdots,N)$$

Where $\hat{S}^2\chi_{SM}(1,2,\cdots,N)=S\left(S+1\right)\chi_{SM}(1,2,\cdots,N)$. The problem is how to find $\chi_{SM}(1,2,\cdots,N)$ and there are several general approaches. Consider for example a three- electron system. We may form $2^3=8$ spin functions and we list them below labeled by the M quantum number. We assume the electron order is 1, 2, 3, so $\alpha\beta\alpha=\alpha(1)\beta(2)\alpha(3)$

Number	Function	M
1	$\alpha\alpha\alpha$	3/2
2	$\alpha\alpha\beta$	1/2
3	$\alpha\beta\alpha$	1/2
4	$\beta\alpha\alpha$	1/2
5	$\beta\beta\alpha$	-1/2
6	$\beta\alpha\beta$	-1/2
7	$\alpha\beta\beta$	-1/2
8	$\beta\beta\beta$	-3/2

Note that $\alpha\alpha\alpha$ & $\beta\beta\beta$ must be eigenfunctions of $\hat{S}^2$ with S=3/2 and $M=\pm 3/2$. Functions 2, 3 and 4 must span the space containing one quartet (S=3/2) and two doublets (S=1/2) all with M=1/2 while functions 5, 6, and 7 lie in the $M=-1/2$ subspace of the eigenfunctions of $\hat{S}^2$. So for the M=1/2 subspace we may write

$$\varphi_1 = \left| S = 3/2, M = 1/2 \right\rangle = a_1\alpha\alpha\beta + a_2\alpha\beta\alpha + a_3\beta\alpha\alpha$$
$$\varphi_2 = \left| S = 1/2, M = 1/2 \right\rangle = b_1\alpha\alpha\beta + b_2\alpha\beta\alpha + b_3\beta\alpha\alpha$$
$$\varphi_3 = \left| S = 1/2, M = 1/2 \right\rangle = c_1\alpha\alpha\beta + c_2\alpha\beta\alpha + c_3\beta\alpha\alpha$$

Or in matrix form

$$\begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \varphi_3 \end{pmatrix} = \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{pmatrix} \begin{pmatrix} \alpha\alpha\beta \\ \alpha\beta\alpha \\ \beta\alpha\alpha \end{pmatrix}$$

We may invert the matrix and write

$$\begin{pmatrix} \alpha\alpha\beta \\ \alpha\beta\alpha \\ \beta\alpha\alpha \end{pmatrix} = \begin{pmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \varphi_3 \end{pmatrix}$$

Where

$$\begin{pmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{pmatrix} = \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{pmatrix}^{-1}$$

The spin function $\alpha\alpha\beta$ is a linear combination of the quartet, φ_1 and the two doublets, $\varphi_2 \,\&\, \varphi_3$

$$\alpha\alpha\beta = A_1\varphi_1 + A_2\varphi_2 + A_3\varphi_3$$

To determine φ_1 we will operate on $\alpha\alpha\beta$ with a projection operator that will annihilate $\varphi_2 \,\&\, \varphi_3$

$$\left(\hat{S}^2 - \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)\right)\alpha\alpha\beta = A_1\left(\tfrac{3}{2}\left(\tfrac{3}{2}+1\right) - \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)\right)\varphi_1 = 3A_1\varphi_1$$

And since

$$\hat{S}^2\alpha\alpha\beta = \left(\hat{S}_+\hat{S}_- - S_z + S_z^2\right)\alpha\alpha\beta = \left(\hat{S}_+\hat{S}_- - 1/4\right)\alpha\alpha\beta$$

And

$$\hat{S}_+\hat{S}_-\alpha\alpha\beta = \hat{S}_+\left(\beta\alpha\beta + \alpha\beta\beta\right) = 2\alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha$$

So we have

$$\hat{S}^2 \alpha\alpha\beta = 7/4\, \alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha$$

And therefore

$$\left(\hat{S}^2 - 3/4\right)\alpha\alpha\beta = \alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha = 3A_1\varphi_1$$

After normalization we have

$$\varphi_1 = \left|S = 3/2, M = 1/2\right\rangle = \frac{1}{\sqrt{3}}\left(\alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha\right)$$

To find the doublets we annihilate the quartet.

$$\left(\hat{S}^2 - \tfrac{3}{2}\left(\tfrac{3}{2}+1\right)\right)\alpha\alpha\beta = \left(\tfrac{1}{2}\left(\tfrac{1}{2}+1\right) - \tfrac{3}{2}\left(\tfrac{3}{2}+1\right)\right)\left(A_2\varphi_2 + A_3\varphi_3\right)$$

Note that since $\varphi_2\ \&\ \varphi_3$ are both doublets any linear combination is a doublet so

$$\left(\hat{S}^2 - \tfrac{3}{2}\left(\tfrac{3}{2}+1\right)\right)\alpha\alpha\beta = -2\alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha$$

is a doublet. The other linearly independent doublet is found by projecting the quartet out of one of the remaining functions, either $\alpha\beta\alpha \text{ or } \beta\alpha\alpha$.

$$\left(\hat{S}^2 - \tfrac{3}{2}\left(\tfrac{3}{2}+1\right)\right)\alpha\beta\alpha = -2\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta$$
$$\left(\hat{S}^2 - \tfrac{3}{2}\left(\tfrac{3}{2}+1\right)\right)\alpha\alpha\beta = -2\alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha$$

We then have three normalized doublet spin functions

$$\frac{1}{\sqrt{6}}\left(-2\alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha\right)$$
$$\frac{1}{\sqrt{6}}\left(-2\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta\right)$$
$$\frac{1}{\sqrt{6}}\left(-2\beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta\right)$$

Note that these three doublets can not be linearly independent because there are only two in the space. We can form two orthonormal functions by taking

$$\frac{1}{\sqrt{6}}\left(-2\alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha\right)$$

as one doublet and forming the second by subtracting

$$\frac{1}{\sqrt{6}}\left(-2\alpha\beta\alpha+\beta\alpha\alpha+\alpha\alpha\beta\right) \textit{ from } \frac{1}{\sqrt{6}}\left(-2\beta\alpha\alpha+\alpha\beta\alpha+\alpha\alpha\beta\right)$$

We have, after normalization the second doublet.

$$\frac{1}{\sqrt{2}}\left(\alpha\beta\alpha-\beta\alpha\alpha\right).$$

We can form the remaining $M=-1/2$ functions by the same projection operator technique but it instructive to use the raising and lowering operators.
Recall that for any angular momentum eigenfunction $\left|J,M\right\rangle$ operating with $\hat{J}_{\pm}$ keeps J the same and changes M to $M\pm1$

$$\hat{J}_{\pm}\left|J,M\right\rangle = A(J,M)\left|J,M\pm1\right\rangle$$

Given $\left|S=3/2,M=1/2\right\rangle$ we may form $\left|S=3/2,M=-1/2\right\rangle$ by operating with $\hat{S}_{-}$ so

$$\left|S=3/2,M=-1/2\right\rangle \approx \hat{S}_{-}\left(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha\right)=2\left(\alpha\beta\beta+\beta\alpha\beta+\beta\beta\alpha\right)$$

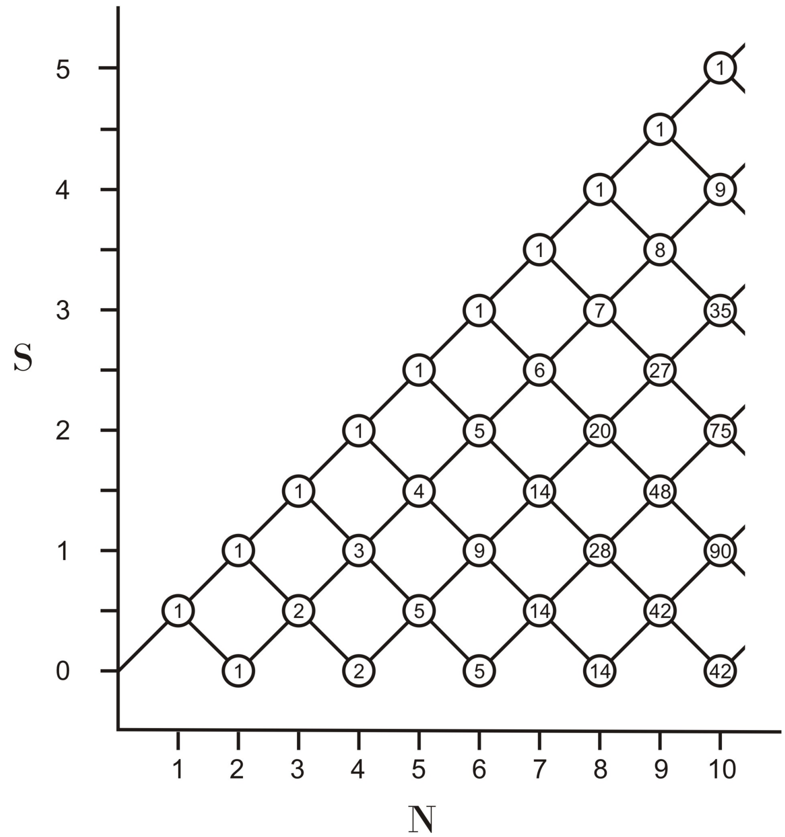
and after normalization we have

$$\left|S=3/2,M=-1/2\right\rangle = \frac{1}{\sqrt{3}}\left(\alpha\beta\beta+\beta\alpha\beta+\beta\beta\alpha\right)$$

Exercise
Show that the effect of the lowering operator $\hat{S}_{-}$ on $\alpha\alpha\alpha$ is the same function $\left|S=3/2,M=1/2\right\rangle$ obtained by using the projection operator on $\alpha\alpha\beta$.

Branching Diagram

A very convenient way of keeping track of the number of spin eigenfunctions of a given multiplicity for an N electron system is the branching diagram shown below



The diagram is constructed as follows. A two-electron system is constructed from a one electron system by coupling the additional spin $1/2$ and the original spin $1/2$ into either a singlet (down) or a triplet (up). To form the spin eigenfunctions for a three electron system we couple the two electron triplet into a quartet (up) and a doublet (down). Additionally the singlet may be coupled (up) into a doublet. We then have 1 quartet and two doublets. To form the 4 electron system we couple the quartet into a quintet (up) and into a triplet (down). The two doublets couple up to form two additional triplets and down to form two singlets. The four electron system then can form 1 quintet $(S=2)$, 3 triplets $(S=1)$and 2 singlets $(S=0)$ for a total of 16 states. This is of course the required 2^4. Note the rapid increase in the number of low spin eiegenfunctions as the number of unpaired electrons increases. For *N=10* we have *42* singlets, *90* triplets, *75* quintets, *35* septets, *9* nonets and *1* bigtet.

We gather below a few explicit spin eigenfunction for *N=1 to 5* and specifically for the case $M=S$. Lower values of M for a particular S may be generated using the lowering operator $\hat{S}_-$. These are from the Sanibel notes of Frank E Harris. Note that the functions have been factored where possible to highlight the physical couplings. For example the N=4 singlet, $(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)/2$ obtains from the singlet coupling of electron pairs 1&2 and 3&4 while the N=5 doublet, $(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\alpha/2$ also obtains from the singlet coupling of electron pairs

1&2 and 3&4 with the doublet spin angular momentum being carried by the α spin of electron 5.

Orthonormal Spin Functions for N spins with total spin S through N=5

N	S	χ_{SS}
1	1/2	α
2	1	$(\alpha\beta+\beta\alpha)/\sqrt{2}$
2	0	$(\alpha\beta-\beta\alpha)/\sqrt{2}$
3	3/2	$\alpha\alpha\alpha$
3	1/2	$(\alpha\beta-\beta\alpha)\alpha/\sqrt{2}$
3	1/2	$(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$
4	2	$\alpha\alpha\alpha\alpha$
4	1	$(\alpha\beta-\beta\alpha)\alpha\alpha/\sqrt{2}$
4	1	$(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)\alpha/\sqrt{6}$
4	1	$(\beta\alpha\alpha\alpha+\alpha\beta\alpha\alpha+\alpha\alpha\beta\alpha-3\alpha\alpha\alpha\beta)/\sqrt{12}$
4	0	$(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)/2$
4	0	$(2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha-\alpha\beta\alpha\beta-\beta\alpha\beta\alpha-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)/\sqrt{12}$
5	5/2	$\alpha\alpha\alpha\alpha\alpha$
5	3/2	$(\alpha\beta-\beta\alpha)\alpha\alpha\alpha/\sqrt{2}$
5	3/2	$(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)\alpha\alpha/\sqrt{6}$
5	3/2	$(\beta\alpha\alpha\alpha+\alpha\beta\alpha\alpha+\alpha\alpha\beta\alpha-3\alpha\alpha\alpha\beta)\alpha/\sqrt{12}$
5	3/2	$(\beta\alpha\alpha\alpha\alpha+\alpha\beta\alpha\alpha\alpha+\alpha\alpha\beta\alpha\alpha+\alpha\alpha\alpha\beta\alpha-4\alpha\alpha\alpha\alpha\beta)/\sqrt{20}$
5	1/2	$(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\alpha/2$
5	1/2	$(2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha-\alpha\beta\alpha\beta-\beta\alpha\beta\alpha-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)\alpha/\sqrt{12}$
5	1/2	$(\alpha\beta-\beta\alpha)(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{12}$
5	1/2	$(\alpha\alpha\alpha\beta\beta+\alpha\alpha\beta\alpha\beta+\beta\beta\alpha\alpha\alpha-\alpha\beta\alpha\alpha\beta-\beta\alpha\alpha\alpha\beta-\alpha\alpha\beta\beta\alpha)/\sqrt{6}$
5	1/2	$(2\alpha\alpha\beta\alpha\beta-2\alpha\alpha\alpha\beta\beta+\alpha\beta\alpha\beta\alpha+\beta\alpha\alpha\beta\alpha-\alpha\beta\beta\alpha\alpha-\beta\alpha\beta\alpha\alpha)/\sqrt{12}$