Spin Eigenfunctions and Two Electron Systems

Virtually all wavefunctions are written as linear combinations of Slater determinants so we will consider the effect of the spin operators on these functions.

First consider the two-electron Slater Determinants that can be formed from two orthogonal spatial orbitals a & b. Since either orbital may have an α or β spin

$$\hat{\mathbf{A}}\, a\left\{\frac{\alpha}{\beta}\right\} b\left\{\frac{\alpha}{\beta}\right\}$$

we may form the following $2^2 = 4$ determinants

$$\varphi_1 = \hat{\mathcal{A}} a\alpha b\alpha\ ,\ \varphi_2 = \hat{\mathcal{A}} a\alpha b\beta\ ,\ \varphi_3 = \hat{\mathcal{A}} a\beta b\alpha \text{ and } \varphi_4 = \hat{\mathcal{A}} a\beta b\beta$$

First consider the effect of $\hat{S}_z$ on $\varphi_1(1,2)$. Clearly since $\hat{S}_z$ is symmetric in the two coordinates it commutes with $\hat{\mathcal{A}}$ and we may write

$$\hat{S}_z\varphi_1(1,2) = \hat{S}_z\hat{\mathcal{A}} a\alpha b\alpha = \hat{\mathcal{A}}\hat{S}_z a\alpha b\alpha \equiv \hat{\mathcal{A}}\hat{S}_z a(1)\alpha(1)b(2)\alpha(2)$$

Since the spin operators operate only on the spin variables so we need only consider

$$\hat{S}_z\alpha(1)\alpha(2) = \left(\hat{s}_z(1) + \hat{s}_z(2)\right)\alpha(1)\alpha(2) = \hat{s}_z(1)\alpha(1)\alpha(2) + \hat{s}_z(2)\alpha(1)\alpha(2) = \alpha(1)\alpha(2)$$

and so $\varphi_1(1,2)$ is an eigenfunction of $\hat{S}_z$ with an eigenvalue of 1.

$$\hat{S}_z\varphi_1(1,2) = \varphi_1(1,2)$$

Now consider the effect of $\hat{S}_z$ on $\varphi_2(1,2)$.

$$\hat{S}_z\varphi_2(1,2) = \hat{S}_z\hat{\mathcal{A}} a\alpha b\beta = \hat{\mathcal{A}}\hat{S}_z a\alpha b\beta \equiv \hat{\mathcal{A}}\hat{S}_z a(1)\alpha(1)b(2)\beta(2)$$

As before we need only consider the effect of $\hat{S}_z$ on the spin variables.

$$\hat{S}_z\alpha(1)\beta(2) = \left(\hat{s}_z(1) + \hat{s}_z(2)\right)\alpha(1)\beta(2) = \hat{s}_z(1)\alpha(1)\beta(2) + \hat{s}_z(2)\alpha(1)\beta(2) = 0$$

so $\varphi_2(1,2)$ is an eigenfunction of $\hat{S}_z$ with an eigenvalue of 0.

$$\hat{S}_z\varphi_2(1,2) = 0$$

In a similar way we find that $\varphi_3(1,2)$ and $\varphi_4(1,2)$ are eigenfunctions of $\hat{S}_z$ with eigenvalues of 0 and -1 respectively. Note that the eigenvalue of $\hat{S}_z$ is simply $\frac{1}{2}\left(N_\alpha - N_\beta\right)$ where N_α & N_β are the number of α & β spin functions.

What about $\hat{S}^2$? As with $\hat{S}_z$ this is a symmetric operator that commutes with $\hat{H}$ and so

$$\hat{S}^2\varphi_2(1,2) = \hat{S}^2\hat{\boldsymbol{\mathcal{A}}}a\alpha b\beta = \hat{\boldsymbol{\mathcal{A}}}\hat{S}^2 a\alpha b\beta \equiv \hat{\boldsymbol{\mathcal{A}}}\hat{S}^2 a(1)\alpha(1)b(2)\beta(2)$$

We need only consider

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

Where we made use of $\hat{S}_z\alpha(1)\beta(2) = 0$. Continuing we first have the effect of $\hat{S}_-$

$$\hat{S}_-\alpha(1)\beta(2) = \hat{s}_-(1)\alpha(1)\beta(2) + \hat{s}_-(2)\alpha(1)\beta(2) = \beta(1)\beta(2)$$

and then operate with $\hat{S}_+$ on these results

$$\hat{S}_+\beta(1)\beta(2) = \hat{s}_+(1)\beta(1)\beta(2) + \hat{s}_+(2)\beta(1)\beta(2) = \alpha(1)\beta(2) + \beta(1)\alpha(2)$$

So the effect of $\hat{S}^2$ on $\varphi_2(1,2)$ is

$$\hat{S}^2\varphi_2(1,2) = \hat{\boldsymbol{\mathcal{A}}}a(1)b(2)(\alpha(1)\beta(2) + \beta(1)\alpha(2)) = \hat{\boldsymbol{\mathcal{A}}}a(1)b(2)\alpha(1)\beta(2) + \hat{\boldsymbol{\mathcal{A}}}a(1)b(2)\beta(1)\alpha(2)$$

and with our convention for labeling the electrons

$$\hat{S}^2\varphi_2(1,2) = \hat{\boldsymbol{\mathcal{A}}}a\alpha b\beta + \hat{\boldsymbol{\mathcal{A}}}a\beta b\alpha = \varphi_2(1,2) + \varphi_3(1,2)$$

and we see that $\varphi_2(1,2)$ is ***not*** an eigenfunction of $\hat{S}^2$. Note however that if we operate on $\varphi_3(1,2)$ we have

$$\hat{S}^2\varphi_3(1,2) = \hat{\boldsymbol{\mathcal{A}}}a\alpha b\beta + \hat{\boldsymbol{\mathcal{A}}}a\beta b\alpha = \varphi_2(1,2) + \varphi_3(1,2)$$

and so the sum and difference of $\varphi_2(1,2)$ and $\varphi_3(1,2)$ are eigenfunctions of $\hat{S}^2$, the sum being a triplet corresponding to $S = 1$

$$\hat{S}^2\left(\varphi_2(1,2)+\varphi_3(1,2)\right)=2\left(\varphi_2(1,2)+\varphi_3(1,2)\right)$$

and the difference being a singlet, $S=0$.

$$\hat{S}^2\left(\varphi_2(1,2)-\varphi_3(1,2)\right)=0\left(\varphi_2(1,2)-\varphi_3(1,2)\right)=0$$

Operating on $\varphi_1(1,2)$ and $\varphi_4(1,2)$ we find that they are both eigenfunctions of $\hat{S}^2$ with eigenvalue 2 or triplets with a spin quantum number S=1. In summary for the two electron system we have the three components of a triplet and a singlet.

Function	S	M
$\varphi_1(1,2)$	1	1
$\frac{1}{\sqrt{2}}\left(\varphi_2(1,2)+\varphi_3(1,2)\right)$	1	0
$\frac{1}{\sqrt{2}}\left(\varphi_2(1,2)-\varphi_3(1,2)\right)$	0	0
$\varphi_4(1,2)$	1	-1

Where the functions have been normalized.

Note however if $a=b$ all of the triplet functions vanish and the function

$\varphi(1,2)=\hat{\mathcal{A}}a\alpha a\beta$ is a singlet.