APPENDIX Q

Singlet and Triplet States for Two Electrons

An angular momentum is a vector, which also pertains to spin angular momenta (see Chapter 1). The spin angular momentum of a certain number of elementary particles is a sum of their spin vectors. To obtain the total spin vector, therefore, we have to add the x-, y-, and z-components of the spins of the particles, and to construct from them the total vector. Then we might be interested in the corresponding spin operators. These operators will be created using the Pauli matrices.[1]

Using them, we immediately find that for a single particle, the following identity holds:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hat{S}_z^2 + \hat{S}_+\hat{S}_- - \hbar\hat{S}_z, \tag{Q.1}$$

where $\hat{S}_+$ and $\hat{S}_-$ are the *lowering* and *raising* operators, respectively:

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \tag{Q.2}$$

$$\hat{S}_- = \hat{S}_x - i\hat{S}_y, \tag{Q.3}$$

that satisfy the useful relations justifying their names:

$$\hat{S}_+\alpha = 0,$$
$$\hat{S}_+\beta = \hbar\alpha,$$
$$\hat{S}_-\alpha = \hbar\beta,$$
$$\hat{S}_-\beta = 0.$$

For any stationary state, the wave function is an eigenfunction of the square of the total spin operator and of the z-component of the total spin operator. The one- and two-electron cases are the only ones for which the total wave function is a *product* of a space and of a spin parts.

The maximum projection of the electron spin on the z-axis is equal to $\frac{1}{2}$ a.u. Hence, the maximum projection for the total spin of two electrons is equal to 1. This means that in this case, only two spin states are possible: the *singlet state*, corresponding to $S = 0$, and the *triplet state*, with $S = 1$ (see Postulate V). In the singlet state, the two electronic spins are opposite ("*pairing of electrons*"), while in the triplet state, the spin vectors are "*parallel*" (cf., Fig. 1.11

[1] See Postulate VI in Chapter 1.

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in Chapter 1). As always, the possible projection of the total spin takes one of the values: $M_S = -S, -S+1, \ldots, +S$; i.e., $M_S = 0$ for the singlet state and $M_S = -1, 0, +1$ for the triplet state.

Now it will be shown that the two-electron spin function $\alpha(1)\beta(2) - \alpha(2)\beta(1)$ ensures the singlet state. First, let us construct the square of the total spin of the two electrons:

$$\boldsymbol{S}^2 = (\boldsymbol{s}_1 + \boldsymbol{s}_2)^2 = \boldsymbol{s}_1^2 + \boldsymbol{s}_2^2 + 2\boldsymbol{s}_1\boldsymbol{s}_2.$$

Thus, to create the operator $\hat{\boldsymbol{S}}^2$, we need the operators $\hat{s}_1^2$ and $\hat{s}_2^2$, which will be expressed by the lowering and raising operators according to Eq. (Q.1), and the scalar product $\hat{\boldsymbol{s}}_1\hat{\boldsymbol{s}}_2$ expressed as a sum of products of the corresponding components x, y and z (we know, how they act, see Postulate V in Chapter 1). If $\hat{S}^2$ acts on $\alpha(1)\beta(2)$, then after five lines of derivation, we obtain

$$\hat{S}^2\left[\alpha(1)\beta(2)\right] = \hbar^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)];$$

similarly,

$$\hat{S}^2\left[\alpha(2)\beta(1)\right] = \hbar^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)].$$

Now we will use this result to calculate $\hat{S}^2[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ and $\hat{S}^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$. We have

$$\hat{S}^2[\alpha(1)\beta(2) - \alpha(2)\beta(1)] = 0 \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \equiv S(S+1)\hbar^2[\alpha(1)\beta(2) - \alpha(2)\beta(1)],$$

where $S = 0$ (singlet); and

$$\hat{S}^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)] = 2$$
$$\hbar^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \equiv S(S+1)\hbar^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)],$$

where $S = 1$ (triplet).

If the operator $\hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$ acts on $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$, then we obtain $0 \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$. This means that in the singlet state, the projection of the spin on the z axis is equal to 0. This is what we expect from a singlet state function.

On the other hand, if $\hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$ acts on $[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$, then we have $0 \times [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$; i.e., the function $[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$ is such a triplet function, which corresponds to the zero projection of the total spin. A similarly simple calculation for the spin functions $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ gives the eigenvalue $S_z = \hbar$ and $S_z = -\hbar$, respectively. Therefore, after normalization,[2]

$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]$ is a singlet function, while $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)]$, $\alpha(1)\alpha(2)$, and $\beta(1)\beta(2)$ represent three triplet functions.

[2] For example, let us check the normalization of the singlet function $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$:

$$\begin{aligned}
&\sum_{\sigma_1}\sum_{\sigma_2}\left\{\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]\right\}^2 \\
&\quad = \sum_{\sigma_1}\sum_{\sigma_2}\frac{1}{2}\{[\alpha(1)]^2[\beta(2)]^2 + [\alpha(2)]^2[\beta(1)]^2 - 2[\alpha(2)\beta(2)][\alpha(1)\beta(1)]\} \\
&\quad = \frac{1}{2}\left\{\sum_{\sigma_1}[\alpha(1)]^2\sum_{\sigma_2}[\beta(2)]^2 + \sum_{\sigma_2}[\alpha(2)]^2\sum_{\sigma_1}[\beta(1)]^2 - 2\sum_{\sigma_2}[\alpha(2)\beta(2)]\sum_{\sigma_1}[\alpha(1)\beta(1)]\right\} \\
&\quad = \frac{1}{2}\{1\cdot 1 + 1\cdot 1 - 2\cdot 0\cdot 0\} = 1.
\end{aligned}$$