

Consider two spin $\frac{1}{2}$ particles, whose spins are described by the Pauli operators σ_1 and σ_2 . Let $\mathbf{e}$ be the unit vector connecting the two particles and define the operator

$$S_{12} = 3(\sigma_1 \cdot \hat{\mathbf{e}})(\sigma_2 \cdot \hat{\mathbf{e}}) - \sigma_1 \cdot \sigma_2$$

Show that if the two particles are in an $S=0$ state (singlet) then

$$S_{12}X_{\text{singlet}} = 0$$

Show that for a triplet state

$$(S_{12}-2)(S_{12}+4)X_{\text{singlet}} = 0$$

(Hint: Choose $\mathbf{e}$ along the z-axis)

We will solve the problem in $S_{1z} - S_{2z}$ (non-interacting) representation.

Choose $\hat{\mathbf{e}}$ along the z-axis.

Solution:

$$\sigma_1 \cdot \hat{\mathbf{e}} = \sigma_{1z} \text{ and } \sigma_2 \cdot \hat{\mathbf{e}} = \sigma_{2z}$$

$$\begin{aligned} S_{12} &= 3(\sigma_1 \cdot \hat{\mathbf{e}})(\sigma_2 \cdot \hat{\mathbf{e}}) - \sigma_1 \cdot \sigma_2 \\ &= 3\sigma_{1z}\sigma_{2z} - (\sigma_{1x}\sigma_{2x} + \sigma_{1y}\sigma_{2y} + \sigma_{1z}\sigma_{2z}) \\ &= 2\sigma_{1z}\sigma_{2z} - \sigma_{1x} \cdot \sigma_{2x} - \sigma_{1y} \cdot \sigma_{2y} \\ &= 2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_2 - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_2 - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_1 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_2 \end{aligned}$$

Note that you cannot multiply the two matrices together, because they belong to two different particles.

In $S_{1z} - S_{2z}$ (non-interacting) representation,

$$X_{\text{singlet}} = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) = \frac{1}{\sqrt{2}} \left[\begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \right]$$

$$S_{12}X_{\text{singlet}} = \left[2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_2 - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_2 - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_1 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_2 \right] \frac{1}{\sqrt{2}} \left[\begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \right]$$

$$\therefore S_{12} X_{\text{singlet}}$$

$$\begin{aligned}
&= \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \right] \\
&\quad - \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \right] \\
&= \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ -1 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ i \end{pmatrix}_1 \begin{pmatrix} -i \\ 0 \end{pmatrix}_2 \right] - \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 0 \\ -1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} -i \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ i \end{pmatrix}_2 \right] \\
&= \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ -1 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - i \cdot i \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} -1 \\ 0 \end{pmatrix}_2 \right] - \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 0 \\ -1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - i \cdot i \begin{pmatrix} -1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \right] \\
&= \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ -1 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 + \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} -1 \\ 0 \end{pmatrix}_2 \right] - \frac{1}{\sqrt{2}} \left[2 \begin{pmatrix} 0 \\ -1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 + \begin{pmatrix} -1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \right] \\
&= \frac{1}{\sqrt{2}} \left[-2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \right] - \frac{1}{\sqrt{2}} \left[-2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \right] \\
&= \frac{1}{\sqrt{2}} \left[-2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 + 2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 + \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 + \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \right] \\
&= \underline{\underline{0}}
\end{aligned}$$

We can use the above “mechanical method” to prove $(S_{12}-2)(S_{12}+4) X_{\text{singlet}} = 0$. Note that there are three triplet states:

$$X_{\text{triplet } 1} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2$$

$$X_{\text{triplet } 2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2$$

$$X_{\text{triplet } 3} = \frac{1}{\sqrt{2}} \left[\begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 + \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \right]$$

And you have to prove each case independently. Since we have demonstrated the mechanical method already, we will prove this by a more efficient approach:

In $S_{1z} - S_{2z}$ (non - interacting) representation.

We first note that

$$(\bar{S}_1 + \bar{S}_2)^2 = \frac{\hbar^2}{4}(\bar{\sigma}_1 + \bar{\sigma}_2)^2 = \frac{\hbar^2}{4}(\bar{\sigma}_1^2 + \bar{\sigma}_2^2 + 2\bar{\sigma}_1 \cdot \bar{\sigma}_2)$$

$$\bar{\sigma}^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 3 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\therefore (\bar{S}_1 + \bar{S}_2)^2 = \frac{\hbar^2}{4}(\bar{\sigma}_1^2 + \bar{\sigma}_2^2 + 2\bar{\sigma}_1 \cdot \bar{\sigma}_2) = \frac{\hbar^2}{4}(6I + 2\bar{\sigma}_1 \cdot \bar{\sigma}_2)$$

$$2\bar{\sigma}_1 \cdot \bar{\sigma}_2 = \frac{4}{\hbar^2}(\bar{S}_1 + \bar{S}_2)^2 - 6I$$

$$\Rightarrow \bar{\sigma}_1 \cdot \bar{\sigma}_2 = \frac{2}{\hbar^2}(\bar{S}_1 + \bar{S}_2)^2 - 3I$$

$$S_{12} = 3(\sigma_1 \cdot \hat{e})(\sigma_2 \cdot \hat{e}) - \sigma_1 \cdot \sigma_2 = 3\sigma_{1z}\sigma_{2z} - \bar{\sigma}_1 \cdot \bar{\sigma}_2$$

$$= 3\sigma_{1z}\sigma_{2z} - \left(\frac{2}{\hbar^2}(\bar{S}_1 + \bar{S}_2)^2 - 3I \right)$$

$$\text{For triplet state, } S = 1. \therefore (\bar{S}_1 + \bar{S}_2)^2 = 1(1+1)\hbar^2 = 2\hbar^2$$

$$S_{12} = 3\sigma_{1z}\sigma_{2z} - \left(\frac{2}{\hbar^2}(\bar{S}_1 + \bar{S}_2)^2 - 3I \right) = 3\sigma_{1z}\sigma_{2z} - \left(\frac{2}{\hbar^2} \cdot 2\hbar^2 - 3I \right)$$

$$= 3\sigma_{1z}\sigma_{2z} - I$$

Case1.

$$X_{\text{triplet } 1} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2$$

$$S_{12}X_{\text{triplet } 1} = (3\sigma_{1z}\sigma_{2z} - I) \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 = (3-1) \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 = 2X_{\text{triplet } 1}$$

$$\therefore (S_{12} - 2)X_{\text{triplet } 1} = 0$$

Case 2.

$$X_{\text{triplet } 2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2$$

$$S_{12}X_{\text{triplet } 2} = (3\sigma_{1z}\sigma_{2z} - I) \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 = [3(-1 \cdot -1) - 1] \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 = 2X_{\text{triplet } 2}$$

$$\therefore (S_{12} - 2)X_{\text{triplet } 2} = 0$$

Case1.

$$X_{\text{triplet } 1} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2$$

$$S_{12} X_{\text{triplet } 1} = (3\sigma_{1z} \sigma_{2z} - I) \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 = (3-1) \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 = 2X_{\text{triplet } 1}$$

$$\therefore (S_{12} - 2)X_{\text{triplet } 1} = 0$$

Case 2.

$$X_{\text{triplet } 2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2$$

$$S_{12} X_{\text{triplet } 2} = (3\sigma_{1z} \sigma_{2z} - I) \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 = [3(-1 \cdot -1) - 1] \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 = 2X_{\text{triplet } 2}$$

$$\therefore (S_{12} - 2)X_{\text{triplet } 2} = 0$$

Case 3.

$$\begin{aligned} X_{\text{triplet } 3} &= (3\sigma_{1z} \sigma_{2z} - I) \frac{1}{\sqrt{2}} \left[\begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 + \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \right] \\ &= [3(1 \cdot -1) - 1] \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 + [3(-1 \cdot 1) - 1] \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \\ &= -4 \cdot \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 + (-4) \cdot \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \\ &= -4 \frac{1}{\sqrt{2}} \left[\begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 + \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \right] \\ &= -4X_{\text{triplet } 3} \end{aligned}$$

$$\therefore (S_{12} + 4)X_{\text{triplet } 3} = 0$$

To include all three cases, we have

$$(S_{12} - 2)(S_{12} + 4)X_{\text{triplet } 3} = 0$$