4.4.3 Addition of Angular Momenta

Suppose now that we have two spin-1/2 particles—for example, the electron and the proton in the ground state of hydrogen. Each can have spin up or spin down, so there are four possibilities in all: 

\[ \mathbf{\uparrow}\uparrow, \ \mathbf{\uparrow}\downarrow, \ \mathbf{\downarrow}\uparrow, \ \mathbf{\downarrow}\downarrow. \]  

where the first arrow refers to the electron and the second to the proton. **Question:** What is the total angular momentum of the atom? Let 

\[ S \equiv S^{(1)} + S^{(2)}. \]  

Each of the four composite states is an eigenstate of \[ S_z \]—the \( z \)-components simply add 

\[ S_z(x_1 x_2) = (S^{(1)}_z + S^{(2)}_z) x_1 x_2 = (S^{(1)}_z x_1) x_2 + x_1 (S^{(2)}_z x_2) = (\hbar m_1 x_1) x_2 + x_1 (\hbar m_2 x_2) = \hbar (m_1 + m_2) x_2. \]

[Note that \( S^{(1)} \) acts only on \( x_1 \), and \( S^{(2)} \) acts only on \( x_2 \).] So \( m \) (the quantum number for the composite system) is just \( m_1 + m_2 \):

\[ \begin{align*}
\mathbf{\uparrow}\uparrow: & \ m = 1; \\
\mathbf{\uparrow}\downarrow: & \ m = 0; \\
\mathbf{\downarrow}\uparrow: & \ m = 0; \\
\mathbf{\downarrow}\downarrow: & \ m = -1.
\end{align*} \]

\[ \uparrow\uparrow = \left\{ \begin{array}{c}
\uparrow \\
\downarrow
\end{array} \right\} = \left\{ \begin{array}{c}
\uparrow \\
\downarrow
\end{array} \right\}, \quad m = 1 \quad \text{(triplet)}.
\]  

(If you apply the raising or lowering operator to this state, you'll get zero. See Problem 4.35.)

I claim, then, that the combination of two spin-1/2 particles can carry a total spin of \( 0 \) or \( 1 \), depending on whether they occupy the triplet or the singlet configuration. To confirm this, I need to prove that the triplet states are eigenvectors of \( S^2 \) with eigenvalue \( 2\hbar^2 \) and the singlet is an eigenvector of \( S^2 \) with eigenvalue \( 0 \). Now 

\[ S^2 = (S^{(1)} + S^{(2)})^2 = (S^{(1)}_z + S^{(2)}_z)^2 = (S^{(1)}_z)^2 + (S^{(2)}_z)^2 + 2S^{(1)}_z S^{(2)}_z. \]  

Using Equations 4.142 and 4.146, we have 

\[ S^{(1)}_z = \frac{\hbar}{2} \left( \begin{array}{c}
\mathbf{\uparrow} \\
\mathbf{\downarrow}
\end{array} \right) \quad \text{and} \quad S^{(2)}_z = \frac{\hbar}{2} \left( \begin{array}{c}
\mathbf{\uparrow} \\
\mathbf{\downarrow}
\end{array} \right). \]  

\[ \begin{align*}
S^{(1)}_z S^{(1)}_z (\mathbf{\uparrow}\downarrow) &= \left( \frac{\hbar}{2} \right)^2 + \left( \frac{\hbar}{2} \right)^2 = \frac{\hbar^2}{4} \left( \begin{array}{cc}
\mathbf{\uparrow} & \mathbf{\downarrow}
\end{array} \right) + \left( \begin{array}{cc}
\mathbf{\uparrow} & \mathbf{\downarrow}
\end{array} \right) = \frac{\hbar^2}{4} \left( \begin{array}{cc}
\mathbf{\uparrow} & \mathbf{\downarrow}
\end{array} \right) + \frac{\hbar^2}{4} \left( \begin{array}{cc}
\mathbf{\uparrow} & \mathbf{\downarrow}
\end{array} \right) = \frac{\hbar^2}{4} (2 \uparrow\downarrow - \uparrow\downarrow). 
\end{align*} \]

Similarly, 

\[ S^{(2)}_z (\mathbf{\uparrow}\downarrow) = \frac{\hbar^2}{4} (2 \mathbf{\uparrow}\downarrow - \mathbf{\uparrow}\downarrow). \]

It follows that 

\[ S_{z_1} S_{z_2} (\mathbf{\uparrow}\downarrow) = \frac{\hbar^2}{4} (2 \mathbf{\uparrow}\downarrow - \uparrow\downarrow) = \frac{\hbar^2}{4} |10\rangle. \]

and 

\[ S_{z_1} S_{z_2} (\mathbf{\uparrow}\downarrow) = \frac{\hbar^2}{4} (2 \mathbf{\uparrow}\downarrow - \uparrow\downarrow) = -\frac{\hbar^2}{4} |00\rangle. \]

Returning to Equation 4.179 (and again using Equation 4.142), we conclude that 

\[ S^2 |10\rangle = \left( \frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + \frac{2\hbar^2}{4} \right) |10\rangle = 2\hbar^2 |10\rangle, \]

so \( |10\rangle \) is indeed an eigenvector of \( S^2 \) with eigenvalue \( 2\hbar^2 \); and 

\[ S^2 |00\rangle = \left( \frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - \frac{2\hbar^2}{4} \right) |00\rangle = 0, \]

so \( |00\rangle \) is an eigenstate of \( S^2 \) with eigenvalue \( 0 \). (I will leave it for you to confirm that \( |11\rangle \) and \( |\bar{1}\bar{1}\rangle \) are eigenvectors of \( S^2 \), with the appropriate eigenvalues—see Problem 4.35.)

What we have just done (combining spin 1/2 with spin 1/2 to get spin 1 and spin 0) is the simplest example of a larger problem: If you combine spin \( 1 \) with spin \( 2 \), what total spin \( s \) can you get? The answer is that you get every spin from \( s = (s_1 + s_2) \) down to \( (s_1 - s_2) \)—or \((s_1 - s_2), \), if \( s_2 > s_1 \)—in integer steps:

\[ s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \ldots, |s_1 - s_2|. \]

(Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another, and the lowest occurs when they are antiparallel.)

As a check, try applying the lowering operator to \( |10\rangle \); what should you get? See Problem 4.35. This is called the triplet combination, for the obvious reason. Meanwhile, the orthogonal state with \( m = 0 \) carries \( s = 0 \):

\[ \left\{ \begin{array}{c}
0 \downarrow \\
0 \uparrow
\end{array} \right\} = \left\{ \begin{array}{c}
0 \downarrow \\
0 \uparrow
\end{array} \right\}, \quad m = 0 \quad \text{(singlet)}.
\]
CHAPTER XI. ADDITION OF ANGULAR MOMENTA

These results appear clearly in the matrix which represents $S_z$ in the
\[ \{ | e_1, e_2 \rangle \} \] basis. Choosing the basis vectors in the order indicated in (B-1), that
matrix can be written:

\[
(S_z) = \hbar \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix}
\]

\( S_z = S_{z1} + S_{z2} \)

3. Diagonalization of $S^2$

All that remains to be done is to find and then diagonalize the matrix which
represents $S^2$ in the \( \{ | e_1, e_2 \rangle \} \) basis. We know in advance that it is not diagonal,
since $S^2$ does not commute with $S_{z1}$ and $S_{z2}$:

\[ S^2 = (S_{z1} + S_{z2})^2 \]

a. Calculation of the Matrix Representing $S^1$

We are going to apply $S^2$ to each of the basis vectors. To do this, we shall use
formulas (B-5) and (B-6):

\[ S^1 = S_1^1 + S_1^2 + 2S_1S_2 + S_1^1S_2 + S_1^2S_2 + S_1S_2^1 + S_1S_2^2 \]

(B-16)

The four vectors $| e_1, e_2 \rangle$ are eigenvectors of $S_1^1$, $S_1^2$, $S_{1z}$ and $S_{2z}$ [formulas (B-2)],
and the action of the operators $S_{1z}$ and $S_{2z}$ can be derived from formulas (B-7) of
chapter IX. We therefore find:

\[ S^2 | +, + \rangle = \left( \frac{3}{4} \hbar^2 + \frac{3}{4} \hbar^2 \right) | +, + \rangle + \frac{1}{2} \hbar^2 | +, + \rangle = 2\hbar^2 | +, + \rangle \]

(B-17-a)

\[ S^2 | +, - \rangle = \left( \frac{3}{4} \hbar^2 + \frac{3}{4} \hbar^2 \right) | +, - \rangle - \frac{1}{2} \hbar^2 | +, - \rangle + \hbar^2 | -, + \rangle = \hbar^2 [ | +, - \rangle + | -, + \rangle ] \]

(B-17-b)

\[ S^2 | -, + \rangle = \left( \frac{3}{4} \hbar^2 + \frac{3}{4} \hbar^2 \right) | -, + \rangle - \frac{1}{2} \hbar^2 | -, + \rangle + \hbar^2 | +, - \rangle = \hbar^2 [ | -, + \rangle + | +, - \rangle ] \]

(B-17-c)

\[ S^2 | -, - \rangle = \left( \frac{3}{4} \hbar^2 + \frac{3}{4} \hbar^2 \right) | -, - \rangle + \frac{1}{2} \hbar^2 | -, - \rangle = 2\hbar^2 | -, - \rangle \]

(B-17-d)
The matrix representing $S^2$ in the basis of the four vectors $| e_1, e_2 >$, arranged in the order given in (B-1), is therefore:

\[
(S^2) = \hbar^2 \begin{pmatrix}
2 & 0 & 0 & 0 \\
0 & 1 & 1 & 0 \\
0 & 1 & 1 & 0 \\
0 & 0 & 0 & 2
\end{pmatrix}
\]  

\hspace{1cm} (B-18)

**COMMENT:**

The zeros appearing in this matrix were to be expected. $S^2$ commutes with $S_z$, and therefore has non-zero matrix elements only between eigenvectors of $S_z$ associated with the same eigenvalue. According to the results of §2, the only non-diagonal elements of $S^2$ which could be different from zero are those which relate $| +, + >$ to $| -, + >$.

**b. EIGENVALUES AND EIGENVECTORS OF S^2**

Matrix (B-18) can be broken down into three submatrices (as shown by the dotted lines). Two of them are one-dimensional: the vectors $| +, + >$ and $| -, - >$ are eigenvectors of $S^2$, as is also shown by relations (B-17-a) and (B-17-d). The associated eigenvalues are both equal to $2\hbar^2$.

We must now diagonalize the $2 \times 2$ submatrix:

\[
(S^2)_0 = \hbar^2 \begin{pmatrix}
1 & 1 \\
1 & 1
\end{pmatrix}
\]  

\hspace{1cm} (B-19)

which represents $S^2$ inside the two-dimensional subspace spanned by $| +, - >$ and $| -, + >$, that is, the eigensubspace of $S_z$ corresponding to $M = 0$. The eigenvalues $\lambda \hbar^2$ of matrix (B-19) can be obtained by solving the characteristic equation:

\[
(1 - \lambda)^2 - 1 = 0
\]  

\hspace{1cm} (B-20)

The roots of this equation are $\lambda = 0$ and $\lambda = 2$. This yields the last two eigenvalues of $S^2$: 0 and $2\hbar^2$. An elementary calculation yields the corresponding eigenvectors:

\[
\frac{1}{\sqrt{2}} [ | +, - > + | -, + > ] \]  

for the eigenvalue $2\hbar^2$  

\hspace{1cm} (B-21-a)

\[
\frac{1}{\sqrt{2}} [ | +, - > - | -, + > ] \]  

for the eigenvalue 0  

\hspace{1cm} (B-21-b)

(of course, they are defined only to within a global phase factor; the coefficients $1/\sqrt{2}$ insure their normalization).

The operator $S^2$ therefore possesses two distinct eigenvalues: 0 and $2\hbar^2$. The first one is non-degenerate and corresponds to vector (B-21-b). The second one is three-fold degenerate, and the vectors $| +, + >$, $| -, - >$ and (B-21-a) form an orthonormal basis in the associated eigensubspace.
4. Results: triplet and singlet

Thus we have obtained the eigenvalues of $S^2$ and $S_z$, as well as a system of eigenvectors common to these two observables. We shall summarize these results by expressing them in the notation of equations (B-12).

The quantum number $S$ of (B-12-b) can take on two values: 0 and 1. The first one is associated with a single vector, (B-21-b), which is also an eigenvector of $S_z$ with the eigenvalue 0, since it is a linear combination of $|+, +\rangle$ and $|-, +\rangle$; we shall therefore denote this vector by $|0, 0\rangle$:

$$|0, 0\rangle = \frac{1}{\sqrt{2}} [ | +, + \rangle - | -, + \rangle] \quad (B-22)$$

Three vectors which differ by their values of $M$ are associated with the value $S = 1$:

$$\begin{align*}
|1, 1\rangle & = |+, +\rangle \\
|1, 0\rangle & = \frac{1}{\sqrt{2}} [ | +, - \rangle + | -, + \rangle] \\
|1, -1\rangle & = | -, - \rangle
\end{align*} \quad (B-23)$$

It can easily be shown that the four vectors $|S, M\rangle$ given in (B-22) and (B-23) form an orthonormal basis. Specification of $S$ and $M$ suffices to define uniquely a vector of this basis. From this, it can be shown that $S^2$ and $S_z$ constitute a C.S.C.O. (which could include $S^2_1$ and $S^2_2$, although it is not necessary here).

Therefore, when two spin 1/2's ($s_1 = s_2 = 1/2$) are added, the number $S$ which characterizes the eigenvalues $S(S+1)\hbar^2$ of the observable $S^2$ can be equal either to 1 or to 0. With each of these two values of $S$ is associated a family of $(2S+1)$ orthogonal vectors (three for $S = 1$, one for $S = 0$) corresponding to the $(2S+1)$ values of $M$ which are compatible with $S$.

Comments:

(i) The family (B-23) of the three vectors $|1, M\rangle$ $(M = 1, 0, -1)$ constitutes what is called a triplet; the vector $|0, 0\rangle$ is called a singlet state.

(ii) The triplet states are symmetric with respect to an exchange of two spins, whereas the singlet state is antisymmetric. This means that if each vector $|\epsilon_1, \epsilon_2\rangle$ is replaced by the vector $|\epsilon_2, \epsilon_1\rangle$, expressions (B-23) remain invariant, while (B-22) changes sign. We shall see in chapter XIV the importance of this property when the two particles whose spins are added are identical. Furthermore, it enables us to find the right linear combination of $|+, +\rangle$ and $|-, +\rangle$ which must be associated with $|+, +\rangle$ and $|-, -\rangle$ (clearly symmetric) in order to complete the triplet. The singlet state, on the other hand, is the antisymmetric linear combination of $|+, -\rangle$ and $|-, +\rangle$, which is orthogonal to the preceding one.