Addition of Angular Momenta

What we have so far considered to be an 'exact' solution for the many electron problem, should really be called 'exact non-relativistic' solution. A relativistic treatment is needed to properly introduce spin and a relativistic term in the Hamiltonian then also appears, the so-called spin-orbit coupling. While this is a rather small correction for most atoms, especially the smaller ones, it is important to be aware of this. Most importantly, it means that the total orbital angular momentum and the total spin are no longer constants of the motion, i.e. conserved quantities that can be used to characterize the system. This is an example of the problem of 'adding angular momenta' in quantum mechanics.

Constants of the Motion

It is particularly valuable to know any property of the system that does not change with time. Such properties are called 'constants of the motion'. One example is the total energy. For a closed system, the total energy is a constant. The angular momentum of a rotating, classical object is another example. In a system of two or more interacting objects, it is the total angular momentum that is conserved. As mentioned above, for an electron in an atoms, one needs to add the angular momentum due to the motion of the electron around the nucleus of the atom and the angular momentum due to the spin of the electron to get the total angular momentum, which is conserved. Identifying such constants of the motion is important whether one is dealing with classical mechanics or quantum mechanics. In quantum mechanics it is, furthermore, useful to work with eigenfunctions of operators that correspond to constants of the motion. Such operators commute with the Hamiltonian as can be seen from the following calculation.

The expectation value of an arbitrary operator Ω has time dependence:

$$\frac{d}{dt} < \psi|\Omega|\psi > = \frac{d < \psi|}{dt}\ \Omega|\psi > + < \psi|\frac{d\Omega}{dt}|\psi > + < \psi|\Omega\ \frac{d|\psi >}{dt}$$

$$\text{where}\quad \frac{d|\psi >}{dt} = \frac{1}{i\hbar}H|\psi >$$

$$\text{and}\quad \frac{d < \psi|}{dt} = \frac{1}{-i\hbar} < \psi|H.$$

When the operator, Ω, itself is not explicitly time dependent, the middle term vanishes, $d\Omega/dt = 0$. Then

$$\frac{d}{dt} < \psi|\Omega|\psi >= \frac{i}{\hbar} < \psi|H\Omega - \Omega H|\psi > .$$

The observable $< \psi|\Omega|\psi >$ is, therefore, a constant of the motion if $[H, \Omega] = 0$.

As an example, the orbital angular momentum $\vec{L}$ of an electron in a spherically symmetric potential (such as an electron interacting with a heavy nucleus) satisfies $[H, \vec{L}] = 0$ and, therefore, is a constant of the motion. It is natural to use the eigenfunctions of $\vec{L}$, the spherical harmonics $Y_\ell^m(\theta, \phi)$, to represent the (θ, ϕ) dependence. The r dependence separates and we are left with solving a one-dimensional problem. Recall the discussion of the hydrogen-like atoms.

When two angular momenta are present and when there is an interaction between them, then each one separately will not be a constant of the motion. It is then advantageous to define a new vector, the total angular momentum, which in the absence of external perturbations, is a constant of the motion. Following is a discussion of two simple but important examples that illustrate this.

Example 1: Two particles interacting via spherically symmetric potential (for example the two electrons in a He atom).

The Hamiltonian is

$$H = H_1 + H_2 + v$$

where

$$H_1 = -\frac{\hbar^2}{2m}\nabla_1^2 + V(r_1)$$
$$H_2 = -\frac{\hbar^2}{2m}\nabla_2^2 + V(r_2)$$
$$v = v(r_{12}) = v(|\vec{r}_2 - \vec{r}_1|).$$

We are assuming that each particle is in a force field with spherical symmetry,

$$V(r_1) = V(|\vec{r}_1|) \text{ and } V(r_2) = V(|\vec{r}_2|).$$

Therefore, the orbital angular momentum and the Hamiltonian for each particle commute

$$[L_1, H_1] = [L_2, H_2] = 0.$$

We also have

$$[L_1, H_2] = [L_2, H_1] = 0$$

(L_1 and H_2 act on different variables, and similarly L_2 and H_1). Therefore, the individual angular momenta L_1 and L_2 would be constants of the motion, i.e. $[L_1, H] = [L_2, H] = 0$, if the interaction $v(r_{12})$ were absent.

Even when the interaction, v, is present, a combination of $\vec{L}_1$ and $\vec{L}_2$ can be found that is a constant of the motion as long as v only depends on the scalar distance between the particles

$$r_{12} = |\vec{r}_1 - \vec{r}_2| = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}\ .$$

Find: $[L_{1z}, H]$:

Using the definition of L_{1z}

$$L_{1z} = \frac{\hbar}{i}(x_1\frac{\partial}{\partial y_1} - y_1\frac{\partial}{\partial x_1})$$

and the product rule for differentiation gives

$$\begin{aligned}
[L_{1z}, H]\ \psi(\vec{r}_1, \vec{r}_2) &= [L_{1z}, v]\ \psi = L_{1z}v\psi - vL_{1z}\psi \\
&= \frac{\hbar}{i}\left(x_1\frac{\partial(v\psi)}{\partial y_1} - y_1\frac{\partial(v\psi)}{\partial x_1}\right) - v\frac{\hbar}{i}\left(x_1\frac{\partial\psi}{\partial y_1} - y_1\frac{\partial\psi}{\partial x_1}\right) \\
&= \frac{\hbar}{i}\left(x_1\frac{\partial v}{\partial y_1}\psi + x_1 v\frac{\partial\psi}{\partial y_1} - y_1\frac{\partial v}{\partial x_1}\psi - y_1 v\frac{\partial\psi}{\partial x_1} - x_1 v\frac{\partial\psi}{\partial y_1} + y_1 v\frac{\partial\psi}{\partial x_1}\right) \\
&= \frac{\hbar}{i}\left(x_1\frac{\partial v}{\partial y_1} - y_1\frac{\partial v}{\partial x_1}\right)\ \psi(\vec{r}_1, \vec{r}_2) \\
&= \frac{\hbar}{i}\left(x_1\frac{y_1 - y_2}{r_{12}}v'(r_{12}) - y_1\frac{x_1 - x_2}{r_{12}}v'(r_{12})\right)\ \psi(\vec{r}_1, \vec{r}_2) \\
&= \frac{\hbar}{i}\left(y_1x_2 - x_1y_2\right)\frac{v'(r_{12})}{r_{12}}\ \psi(\vec{r}_1, \vec{r}_2).
\end{aligned}$$

The derivatives of v can be found using the chain rule

$$\frac{\partial v(r_{12})}{\partial y_1} = \frac{\partial r_{12}}{\partial y_1}\frac{\partial v(r_{12})}{\partial r_{12}} = \frac{y_1 - y_2}{r_{12}}\ v'(r_{12})$$

with v' denoting the derivative of the potential function $v(\alpha)$ with respect to the argument α. Therefore, in operator form,

$$\begin{aligned}
\big[L_{1z}, H\big] &= \frac{\hbar}{i}\left(Y_1X_2 - X_1Y_2\right)\frac{v'(r_{12})}{r_{12}} \\
&\neq 0.
\end{aligned}$$

When the interaction $v(r_{12})$ is present, L_{1z} is no longer a constant of the motion. Similarly,

$$\big[L_{2z}, H\big] = \frac{\hbar}{i}\left(Y_2X_1 - X_2Y_1\right)\frac{v'(r_{12})}{r_{12}}.$$

However, if the two results are added together to obtain a commutator for $L_{1z} + L_{2z}$

$$\begin{aligned}
\big[L_{1z} + L_{2z}, H\big] &= \frac{\hbar}{i}\frac{v(r_{12})}{r_{12}}\left(Y_1X_2 - X_1Y_2 + Y_2X_1 - X_2Y_1\right) \\
&= 0.
\end{aligned}$$

The sum $L_{1z} + L_{2z}$ is a constant of the motion. Similarly we could show that $L_{1y} + L_{2y}$ and $L_{1x} + L_{2x}$ are also constants of the motion. Therefore, we can define a new vector $\vec{L} \equiv \vec{L}_1 + \vec{L}_2$ which is a constant of the motion. The commutation relations for the

components of this new vector are

$$\begin{aligned}
[L_x, L_y] &= [L_{1x} + L_{2x}, L_{1y} + L_{2y}] \\
&= [L_{1x}, L_{1y}] + [L_{1x}, L_{2y}] + [L_{2x}, L_{1y}] + [L_{2x}, L_{2y}] \\
&= i\hbar\ L_{1z} + i\hbar\ L_{2z} \\
&= i\hbar\ L_z
\end{aligned}$$

and, similarly,

$$[L_y, L_z] = i\hbar\ L_x$$

and

$$[L_z, L_x] = i\hbar\ L_y.$$

So, by definition, $\vec{L}$ is an angular momentum. It is the *total* angular momentum. If the two particles start out in an eigenstate of $\vec{L}$, they will remain in that state unless the system is perturbed. The problem of 'adding angular momenta' involves finding those states in terms of the eigenstates of $\vec{L}_1$ and $\vec{L}_2$.

In classical mechanics the situation is analogous. Total angular momentum of two interacting particles is constant but not the angular momentum of each particle separately if the two interact. But, we usually do not have the problem of basis set transformations in classical mechanics.

Example 2: A particle with spin moving in a central potential $v(r)$ in the presence of spin-orbit coupling.

First of all, if the Hamiltonian is simply

$$H = -\frac{\hbar^2}{2m}\nabla^2 + v(r)$$

then $[\vec{L}, H] = 0$ and $[\vec{S}, H] = 0$. That is, the two angular momenta are separately constants of the motion if the Hamiltonian does not couple $\vec{L}$ and $\vec{S}$.

But in relativistic quantum mechanics the spin and orbital angular momenta turn out to be interacting, or, equivalently, they are coupled together. The interaction is called *spin-orbit coupling* and has the form

$$\vec{L} \cdot \vec{S} = L_x S_x + L_y S_y + L_z S_z.$$

In the electronic states of atoms, this leads to the various *terms* and *term symbols* which are a more rigorous description of the state of the atom than electron configuration. The electron configuration does not take into account spin-orbit coupling. It turns out that the coupling strength is a function of the distance to the origin, $\zeta(r)$. Thus, the full Hamiltonian including spin-orbit coupling can be written as

$$H = -\frac{\hbar^2}{2m}\nabla^2 + v(r) + \zeta(r)\vec{L} \cdot \vec{S}.$$

Due to the spin-orbit coupling the orbital angular momentum $\vec{L}$ is no longer a constant of the motion. The commutator for the z component, for example, is

$$\begin{aligned}
[L_z, H] &= \zeta\ [L_z, L_x S_x + L_y S_y + L_z S_z] \\
&= \zeta\ (S_x[L_z, L_x] + S_y[L_z, L_y] + S_z[L_z, L_z]) \\
&= \zeta\ (S_x i\hbar L_y + S_y(-i\hbar L_x)) \\
&= \zeta\ i\hbar(S_x L_y - S_y L_x) \\
&\neq 0
\end{aligned}$$

Similarly, the spin $\vec{S}$ is no longer a constant of the motion.

$$\begin{aligned}
[S_z, H] &= \zeta\ i\hbar(L_x S_y - L_y S_x) \\
&\neq 0.
\end{aligned}$$

However, the z-component of the sum of the two angular momentum vectors, $\vec{L}_z + \vec{S}_z$, is a constant of the motion as can be seen by adding the two commutators above,

$$[L_z + S_z, H] = 0.$$

Similar calculation can be done for the x and y components. Therefore, the total angular momentum $\vec{J} \equiv \vec{L} + \vec{S}$ is a constant of the motion. Again, we can easily show that $\vec{J}$ satisfies the commutation relations that define an angular momentum vector

$$[J_x, J_y] = i\hbar J_z, \quad \text{etc.}$$

The Hamiltonians in examples 1 and 2 are common. Working with the eigenstates of the total angular momentum rather than the eigenstates of the individual angular momenta greatly simplifies calculations is such cases. The problem of 'addition of angular momenta' therefore involves more than just addition of two vectors, we need to find the eigenstates of the total angular momentum and express them in terms of the already known eigenstates of the individual angular momenta.

Definition of Clebsch-Gordan coefficients:

The general problem can be stated in the following way: Given two angular momenta $\vec{L}$ and $\vec{S}$ (not necessarily orbital and spin angular momenta, here $\vec{L}$ and $\vec{S}$ are used as general symbols for any two angular momenta) and their eigenkets $|\ell m_\ell>$ and $|s m_s>$, a complete set of eigenkets for the combined system can be constructed by direct multiplication

$$|\ell s m_\ell m_s> \equiv |\ell m_\ell> \otimes |s m_s> .$$

This is a complete set and forms a basis but these kets do not correspond to a constant of the motion. Instead, one would like to transform to a new set of kets $|jm>$ that

correspond to eigenstates of J^2, J_z, L^2 and S^2 where the total angular momentum is defined as $\vec{J} \equiv \vec{L} + \vec{S}$. That is, the new kets should satisfy

$$J^2|jm>= j(j+1)\hbar^2|jm>$$

$$J_z|jm>= m\hbar|jm>$$

$$L^2|jm>= \ell(\ell+1)\hbar^2|jm>$$

and

$$S^2|jm>= s(s+1)\hbar^2|jm> .$$

The new vectors can be constructed from the direct product basis

$$|jm>= \sum_{m_\ell=-\ell}^{\ell} \sum_{m_s=-s}^{s} a_{\ell s m_\ell m_s;jm}|\ell s m_\ell m_s>$$

and the problem reduces to finding the linear combination coefficients $a_{\ell s m_\ell m_s;jm} =< \ell s m_\ell m_s \; |jm>$ which are called *Clebsch-Gordan* coefficients. They have been tabulated in may books and are also preprogrammed in various mathematical software packages.

Solution for Two Spin 1/2 Particles:

The general method for finding eigenstates of the total angular momentum is a bit involved and it is worthwhile to illustrate the essence of the problem in the simple but important case of two spin $\frac{1}{2}$ angular momenta. Here a straight forward application of linear algebra will do the job. Later, this same problem will be solved using the general method, and finally the general solution will be presented.

The total spin angular momentum is $\vec{S} \equiv \vec{S}_1 + \vec{S}_2$. We want to find a set of states $|sm>$ such that $\vec{S}^2|sm>= s(s+1)\hbar^2|sm>$ and $S_z|sm>= m\hbar|sm>$. We will express them as linear combinations of the direct products of eigenstates of $\vec{S}_1$ and eigenstates of $\vec{S}_2$:

$$|sm>= a\;|++>\; + b\;|+->\; + c\;|-+>\; + d\;|-->\; .$$

The direct product states satisfy

$$S_{1z}|++> = \frac{\hbar}{2}|++>$$

$$S_{1z}|+->= \frac{\hbar}{2}|+->$$

$$S_{1z}|-+> = -\frac{\hbar}{2}|-+>$$

$$S_{1z}|--> = -\frac{\hbar}{2}|-->$$

and similar relationships for S_{2z}. The length of the two spin vectors is necessarily the same

$$S_1^2|\pm\pm> = S_2^2|\pm\pm> = \frac{3\hbar^2}{4}|\pm\pm> .$$

Using the direct product states as basis (in the same order as above), the state $|sm>$ can be expressed in vector notation as

$$|sm>= \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} .$$

First, we will find 4x4 matrices representing the operators S^2 and S_z and then by diagonalizing, get the eigenvectors $|sm>$.

Matrix for S_z:

We need to evaluate all the matrix elements of S_z in this basis.

$$S_z = \begin{pmatrix} <++|S_z|++> & <++|S_z|+-> & <++|S_z|-+> & <++|S_z|--> \\ <+-|S_z|++> & <+-|S_z|+-> & \cdots & \cdots \\ <-+|S_z|++> & \cdots & \cdots & \cdots \\ <--|S_z|++> & \cdots & \cdots & <--|S_z|--> \end{pmatrix} .$$

First, applying the operator to $|++>$

$$S_z|++>= S_{1z}|++> +S_{2z}|++>= \left(\frac{\hbar}{2}+\frac{\hbar}{2}\right)|++>= \hbar|++>$$

the first column is

$$\begin{aligned} <++|S_z|++> &= \hbar \\ <+-|S_z|++> &= 0 \\ <-+|S_z|++> &= 0 \\ <--|S_z|++> &= 0. \end{aligned}$$

The second and third columns only have zeros because

$$S_z|+->= \left(\frac{\hbar}{2}-\frac{\hbar}{2}\right)\ |+->= 0$$

and

$$S_z|-+>= \left(-\frac{\hbar}{2}+\frac{\hbar}{2}\right)\ |-+>= 0.$$

The fourth column has one non-zero element just like the first column,

$$S_z|-->= \left(-\frac{\hbar}{2}-\frac{\hbar}{2}\right)\ |-->= -\hbar\ |--> .$$

The full matrix is

$$S_z = \begin{pmatrix} \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar \end{pmatrix} .$$

This is already diagonal, i.e., the basis vectors $|\pm\pm>$ are eigenvectors of S_z. Any linear combination that only mixes the $|+->$ and $|-+>$ vectors will also be an eigenvector.

Matrix for S^2:

By definition of the total angular momentum, we have

$$S^2 = \vec{S}\cdot\vec{S} = (\vec{S}_1 + \vec{S}_2)\cdot(\vec{S}_1 + \vec{S}_2) = S_1^2 + S_2^2 + 2\vec{S}_1\cdot\vec{S}_2.$$

The action of the S_1^2 and S_2^2 operators can be readily evaluated but we need a convenient expression for $\vec{S}_1\cdot\vec{S}_2$ so that the action of this operator on the direct basis functions can be evaluated. Written in terms of the Cartesian components

$$\vec{S}_1\cdot\vec{S}_2 \;=\; S_{1x}S_{2x} \;+\; S_{1y}S_{2y} \;+\; S_{1z}S_{2z}$$

The action of the last term, $S_{1z}S_{2z}$, on the direct product states can easily be evaluated, but the first two terms involving the x and y components are not as straight forward because the direct product states are not eigenstates of those operators. Since we have chosen to know the projection of the spin on the z-axis, the projection onto the $y-$ and $x-$axes is not known. It is convenient here to make use of the raising and lowering operators for angular momentum to rewrite S_{1x} and S_{1y} as

$$S_{1x} = \frac{1}{2}\left(S_{1+} + S_{1-}\right)$$

$$S_{1y} = \frac{1}{2i}\left(S_{1+} - S_{1-}\right)$$

and similarly for the S_{2x} and S_{2y} operators. Using this, the $\vec{S}_1\cdot\vec{S}_2$ operator can be written as

$$\vec{S}_1\cdot\vec{S}_2 \;== \frac{1}{2}\left(S_{1+}S_{2-} + S_{1-}S_{2+}\right) + S_{1z}S_{2z}.$$

First find the matrix representation for the $S_{1z}S_{2z}$ part:

$$S_{1z}S_{2z}|++> = \left(\frac{\hbar}{2}\right)\left(\frac{\hbar}{2}\right)|++> = \left(\frac{\hbar}{2}\right)^2|++>$$

$$S_{1z}S_{2z}|+-> = \left(\frac{\hbar}{2}\right)\left(-\frac{\hbar}{2}\right)|+-> = -\left(\frac{\hbar}{2}\right)^2|+->$$

$$S_{1z}S_{2z}|-+> = \left(-\frac{\hbar}{2}\right)\left(\frac{\hbar}{2}\right)|-+> = -\left(\frac{\hbar}{2}\right)^2|-+>$$

$$S_{1z}S_{2z}|--> = \left(-\frac{\hbar}{2}\right)\left(-\frac{\hbar}{2}\right)|--> = \left(\frac{\hbar}{2}\right)^2|--> .$$

Left multiplying with each of the basis vectors gives a diagonal matrix

$$S_{1z}S_{2z} = \left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} .$$

Then, find the matrix representation of the $(S_{1+}S_{2-} + S_{1-}S_{2+})$ part: The first column only has zeros, since

$$\begin{aligned} (S_{1+}S_{2-} + S_{1-}S_{2+}) \mid ++> &= S_{1+}S_{2-} \mid ++> + S_{1-}S_{2+} \mid ++> \\ &= \hbar S_{1+} \mid +-> + 0 \\ &= 0 \ . \end{aligned}$$

Similarly, the fourth column only has zeros,

$$(S_{1+}S_{2-} + S_{1-}S_{2+}) \mid --> = 0 \ .$$

However the second and third column have one non-zero element

$$\begin{aligned} (S_{1+}S_{2-} + S_{1-}S_{2+}) \mid +-> &= S_{1+}S_{2-} \mid +-> + S_{1-}S_{2+} \mid +-> \\ &= 0 + \hbar S_{1-} \mid ++> \\ &= \hbar^2 \mid -+> \end{aligned}$$

and

$$\begin{aligned} (S_{1+}S_{2-} + S_{1-}S_{2+}) \mid -+> &= S_{1+}S_{2-} \mid -+> + S_{1-}S_{2+} \mid -+> \\ &= \hbar S_{1+} \mid --> + 0 \\ &= \hbar^2 \mid +-> . \end{aligned}$$

Left multiplying with each of the basis vectors gives the matrix

$$S_{1+}S_{2-} + S_{1-}S_{2+} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar^2 & 0 \\ 0 & \hbar^2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

The S_1^2 and S_2^2 matrices are simple:

$$S_1^2 = S_2^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} .$$

Adding the various contributions finally gives:

$$S^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} .$$

We need to find linear combinations of the $|\pm\pm>$ that make both the S_z and the S^2 matrices diagonal. We will diagonalize the S^2 matrix and find that the eigenvectors heppen to be also eigenvectors of S_z. Let $|sm>$ denote the eigenvectors and define $\lambda \equiv s(s+1)$. Then $S^2|sm> -\lambda\hbar^2|sm>= 0$, or in matrix form

$$\hbar^2 \begin{pmatrix} 2-\lambda & 0 & 0 & 0 \\ 0 & 1-\lambda & 1 & 0 \\ 0 & 1 & 1-\lambda & 0 \\ 0 & 0 & 0 & 2-\lambda \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = 0 \ .$$

This has non-trivial solutions (i.e. $(abcd) \neq 0$) when

$$det \begin{pmatrix} 2-\lambda & 0 & 0 & 0 \\ 0 & 1-\lambda & 1 & 0 \\ 0 & 1 & 1-\lambda & 0 \\ 0 & 0 & 0 & 2-\lambda \end{pmatrix} = 0.$$

Expanding the determinant gives

$$(2-\lambda)^2 \ det \begin{pmatrix} 1-\lambda & 1 \\ 1 & 1-\lambda \end{pmatrix} = 0$$

$$(2-\lambda)^2((1-\lambda)^2 - 1) = 0.$$

This is a fourth order equation for λ, with four roots. From the first factor we get twice the solution $\lambda = 2$ which gives $s = 1$. From the second factor we get $1 - 2\lambda + \lambda^2 - 1 = 0$, i.e., $\lambda = 0$ meaning $s = 0$ and $\lambda = 2$ meaning $s = 1$ once more. So s has two possible values: 0 which is non-degenerate, and 1 which is threefold degenerate.

Find the corresponding eigenvectors:
For $\underline{s = 0:}$ $(\lambda = 0)$

$$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = 0.$$

This gives $a = 0, d = 0$ and $b + c = 0$, i.e., $b = -c$.

Normalized, the eigenvector is

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \ (|+->\ -\ |-+>).$$

Since only the $|+->$ and $|-+>$ states get mixed here, this new vector remains an eigenvector of S_z. This nondegenerate eigenstate is called the *singlet*.

For $\underline{s = 1:}$ $(\lambda = 2)$

$$\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & (2-2) \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = 0.$$

This gives $b - c = 0$.

Since this is a threefold degenerate eigenvalue, we need three linearly independent eigenvectors. Given that there is no constraint on a, we can easily generate one normalized eigenvector by taking $a = 1$ and $b = c = d = 0$. This is simply the $|++>$ state. Similarly, we can take $d = 1$ and $a = d = c = 0$. This is the $|-->$ state. For the third eigenvector, we must have $a = 0$ and $b = 0$ since it must be linearly independent of the first two. We are then left with the condition $b = c$, and the normalized vector is $\frac{1}{\sqrt{2}}$ $(|+->+|-+>)$. Again, since only the $|+->$ and $|-+>$ states get mixed here, this is vector is also an eigenvector of S_z. This triply degenerate eigenvalue is called the *triplet*.

Summary:

The solutions are the states $|sm>$ with the following values for the quantum numbers and expansions in the direct product basis vectors:

The singlet state, $s = 0$ has $m = 0$ and is $|00>= \frac{1}{\sqrt{2}}$ $(|+->-|-+>)$.

The triplet state, $s = 1$ has

$$\begin{aligned} m = 1 \quad & |11> = |++> \\ m = 0 \quad & |10> = \frac{1}{\sqrt{2}} \, (|+-> + |-+>) \\ m = -1 \quad & |1-1> = |--> . \end{aligned}$$

These four vectors form a basis and are simultaneously eigenvectors of both S^2 and S_z (as well as S_1^2 and S_2^2).

Time Evolution of Coupled Spin 1/2 Particles: (CDL F_X)

To illustrate the significance of the preceding result, consider two spin $\frac{1}{2}$ particles that are coupled by the interaction $a\vec{S}_1 \cdot \vec{S}_2$, i.e., the Hamiltonian is:

$$H = H_1 + H_2 + a\vec{S}_1 \cdot \vec{S}_2.$$

The direct product states $|\pm\pm>$ are eigenstates of the independent particle Hamiltonian $H_0 = H_1 + H_2$. However, when the interaction W is turned on, those are no longer eigenstates. Therefore, even if the state of the system is, for example, as $|+->$ at time $t = 0$, the orientations of the spins will have reversed some time later and the system can be described as $|-+>$. This can be illustrated with a simple calculation.

The time independent, stationary states are the eigenstates of the total angular momentum $|sm>= |00>, |11>, |10>$ and $|1-1>$. In order to express the time evolution of

an arbitrary state, we need the energies of the stationary states. We need to evaluate the coupling term which can be rewritten as

$$W = a\vec{S}_1 \cdot \vec{S}_2 = \frac{a}{2}\left[S^2 - S_1^2 - S_2^2\right] = \frac{a}{2}\left[S^2 - \frac{3}{2}\hbar^2\right]$$

Since there are two possible values for s, $s = 0$ and $s = 1$, there are two distinct energy levels:

$$W|00>= \frac{a}{2}\ \left[0 - \frac{3}{2}\hbar^2\right]\ |00>= -\frac{3a}{4}\hbar^2\ |00>\equiv E_-\ |00>$$

and

$$W|1m>= \frac{a}{2}\ \left[2\hbar^2 - \frac{3}{2}\hbar^2\right] = \frac{a}{4}\hbar^2\ |1m>\equiv E_+\ |1m>\ .$$

The higher energy level, $E_+ = a\hbar^2/4$, is threefold degenerate while the lower level $E_- = -3a\hbar^2/4$, is non-degenerate.

Lets assume that initially, at $t = 0$, the state is

$$|\psi>_{(0)}= |\ +-> \ .$$

From the previous result, we can see that this can be rewritten in terms of the stationary states as

$$\frac{1}{\sqrt{2}}\ (|10>\ +\ |00>)\ .$$

At a later time t the state is

$$|\psi>_{(t)} = \frac{1}{\sqrt{2}}\ \left[e^{-ia\hbar t/4}\ |10>\ + e^{i3a\hbar t/4}\ |00>\right].$$

In particular, at time $t = \pi/a\hbar$ we have

$$\begin{aligned} |\psi>_{(\pi/a\hbar)} &= \left[e^{-i\pi/4}\ |10> \ + e^{i3\pi/4}\ |00>\right] \\ &= \frac{1}{\sqrt{2}}\ e^{-i\pi/4}\ [|10> + e^{i\pi}|00>] \\ &= \frac{1}{\sqrt{2}}\ e^{-i\pi/4}\ [|10> - |00>] \\ &= e^{-i\pi/4}\ |-+> \end{aligned}$$

i.e., the spins have reversed their orientation from the initial state at $t = 0$.

General Method:

The direct diagonalization used above to solve the problem involving two spin $\frac{1}{2}$ particles does not lend itself well to generalizations. The solution for adding any two angular momentum vectors can be expressed more explicitly by using another, somewhat more involved procedure. This procedure makes use of the fact that the total angular momentum satisfies the general properties of angular momenta, in particular the restrictions on the possible values of the quantum numbers s and m. It is most simply illustrated by solving again the addition of two angular momenta with $s_1 = s_2 = \frac{1}{2}$.

Example: Again, do two spin $\frac{1}{2}$ particles.

As we saw in the previous solution to this problem, the vectors $|++>, |+->, |-+>$ and $|-->$ (the direct product vectors) are already eigenstates of S_z. The eigenvalues are $m = m_1 + m_2$. Here m can be $-1, 0$ and 1, with 0 being twofold degenerate.

In forming the linear combinations

$$|sm> = a\ |++> \ + b\ |+-> \ + c\ |-+> \ + d\ |-->$$

we must not mix states with unequal m, otherwise the resulting vector will not be eigenvector of S_z. This means we can only mix $|+->$ and $|-+>$. The possible values of m

are therefore the same as the values of $m_1 + m_2$. Letting m_1 and m_2 run over all possible values, the value of $m_1 + m_2$ is 1 once, -1 once and 0 twice.

No value of m is larger than 1. Since we know that m will take any value in the range $-s \leq m \leq s$, this means we cannot have s larger than 1. The value $m_1 + m_2 = 1$ does appear once, so we must have one total angular momentum state with $m = 1$. This means states with $s = 1$ exist with $|11>$ being one of them. The expansion of this state in the direct product basis is easy to find since only one of those has $m_1 + m_2 = 1$, $a = 1,\ b = c = d = 0$. Therefore, $|11> = |++>$. Again, using the fact that m will take all values in the range $-s \leq m \leq s$, we must have two other states corresponding to $s = 1$, namely $|10>$ and $|1\,-1>$. We can obtain both of these by applying the lowering operator S_- to $|11>$. From the general properties of angular momenta we get:

$$S_-|11> = \hbar\sqrt{1(1+1) - 1(1-1)}\ |10> = \hbar\sqrt{2}\ |10> .$$

Equivalently, applying the lowering operator in the direct product representation gives

$$S_-|11> = (S_{1-} + S_{2-}\ |++> = \hbar\ (|-+>\ +\ |+->).$$

Subtracting the two equations gives the $m = 0$ state

$$|10> = \frac{1}{\sqrt{2}}\ (|-+>\ +\ |+->).$$

Applying S_- again gives the $m = -1$ state:

$$S_-|10> = \hbar\sqrt{1(1+1) - 0(0-1)}\ |1-1> = \hbar\sqrt{2}\ |1-1>$$

Equivalently, using the direct product basis

$$\begin{aligned} S_-|10> &= (S_{1-} + S_{2-})\ \frac{1}{\sqrt{2}}\ (|-+>\ +\ |+->) \\ &= \frac{\hbar}{\sqrt{2}}\ (|-->\ +\ |-->) = \hbar\sqrt{2}\ |--> . \end{aligned}$$

Subtracting the two equations, we have

$$|1-1> =\ |--> .$$

There is only one more state to be found (the total must be four) and the only one of the possible values of m not accounted for is the second occurance of $m_1 + m_2 = 0 = m$. This state must have $s = 0$ and is therefore the $|00>$ state. Expressed in terms of the direct product basis, only the $m = 0$ states, namely $|+->$ and $|-+>$, can be involved. Say

$$|00> =\ \alpha\ |+->\ +\beta\ |-+> .$$

Choosing $|00>$ to be normalized $<00|00>=1=|\alpha|^2+|\beta|^2$. Furthermore, this state must be orthogonal to the other states $|11>, |10>$, and $|1-1>$. In particular, $|00>$ must be orthogonal to the other $m=0$ state

$$\begin{aligned} <00|10> &= 0 \\ &= \frac{1}{\sqrt{2}}\ (\alpha^*\ \beta^*)\ \begin{pmatrix} 1 \\ 1 \end{pmatrix} \end{aligned}$$

Therefore $\alpha = -\beta$ and

$$|00>= \frac{1}{\sqrt{2}}\ (|+->\ -|-+>).$$

The General Solution: $\vec{J} \equiv \vec{L} + \vec{S}$

Given the direct product basis $|\ell s m_\ell m_s>$, the task is to find eigenvectors of J^2,J_z,L^2 and S^2 denoted $|jm>$ as linear combinations:

$$|jm>= \sum_{m_\ell} \sum_{m_s} a_{\ell s m_\ell m_s; jm} |\ell s m_\ell m_s> .$$

Since the new states are eigenvectors of L^2 and S^2 with given eigenvalues ℓ and s, the linear compbination can only involve direct product vectors with those values of ℓ and s. The total number of states is $(2\ell+1)(2s+1)$. The direct product states $|\ell s m_\ell m_s>$ are already eigenvectors of J_z with eigenvalues $m = m_\ell + m_s$ where $-\ell \le m_\ell \le \ell$ and $-s \le m_s \le s$. Therefore, m can take the values $(\ell+s), (\ell+s-1), \ldots, -(\ell+s)$.

Example: $\ell = 2$ and $s = 1$

No value of m is larger than $\ell + s$. Therefore, we cannot have j larger than $\ell + s$. We have one state with $m = \ell + s$ and since we can only mix states with equal m, that state must be

$$j = \ell + s\ ,\quad m = \ell + s :$$

$$|\underbrace{\ell+s}_{j}\ \underbrace{\ell+s}_{m}>=|\ell\ s\underbrace{\ell}_{m_\ell}\underbrace{s}_{m_s}> .$$

The choice of phase is arbitrary here. This choice, taking the Clebsch-Gordan coefficient to be real and positive, will ensure that all the coefficients are real.

By applying the lowering operator we can generate $2(\ell+s)+1$ states with $j=\ell+s$,

$$|\ell+s\ \ell+s-1>=\ J_-\ |\ell\ s\ \ell\ s> .$$

By repeated application of J_- we finally get to the $m=-(\ell+s)$ state.

Since the total number of states is $(2\ell+1)(2s+1)$, we still have to find $(2\ell+1)(2s+1)-(2(\ell+s)+1)$ more. The states that are left have a maximum m value of $m=\ell+s-1$ (since the $m=\ell+s$ state has already been determined). Therefore, we must have states with $j=\ell+s-1$. We can find the $j=\ell+s-1$, $m=\ell+s-1$ state by taking a linear combination of the two direct product states that have $m=\ell+s-1$. Choosing this state to be normalized and orthogonal to the $j=\ell+s$, $m=\ell+s-1$ state determines the expansion coefficients. Then we can apply J_- repeatedly to generate the full set of $2(\ell+s-1)+1$ states corresponding to $j=\ell+s-1$, and so on.

What is the smallest value of j? Just counting the number of states, which must be the same in the direct product basis as in the total angular momentum basis, gives an equation that can be solved to give the minimum j value, denoted here as j_0

$$\sum_{j=j_0}^{\ell+s}(2j+1)=(2\ell+1)(2s+1)$$

$$(\ell+s)(\ell+s+1)-(j_0-1)j_0+\ell+s-(j_0-1)=4\ell s+2\ell+2s+1$$

$$j_0^2=\ell^2-2\ell s+s^2=(\ell-s)^2.$$

Therefore the minimum value for j is $j_0=|\ell-s|$.

The final result is that j can take the values $(\ell+s),(\ell+s-1),\ldots,|\ell-s|$. This means that j must be such that a triangle can be formed with sides l,s,j. Therefore, this limitation on the range of j is called the 'triangle rule'. Tables of the expansion coefficients, the Clebsch-Gordan coefficients, $a_{\ell s m_\ell m_s;jm}$ can be found in books on angular momentum (Edmonds, or Rose, or Condon & Shortley). Several computer programs provide the values of the the Clebsch-Gordan coefficients, for example Mathematica. Recursion and orthogonality relations can be derived for the Clebsch-Gordan coefficients, see CLD B_X.