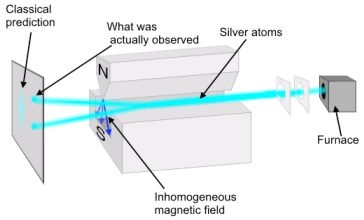
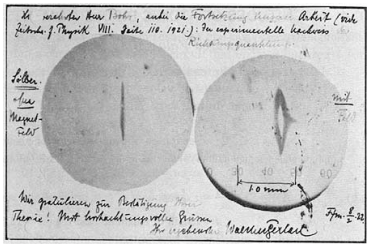
Chapter 6

Spin

Until we have focussed on the quantum mechanics of particles which are "featureless", carrying no internal degrees of freedom. However, a relativistic formulation of quantum mechanics shows that particles can exhibit an intrinsic angular momentum component known as spin. However, the discovery of the spin degree of freedom marginally predates the development of relativistic quantum mechanics by Dirac and was acheived in a ground-breaking experiement by Stern and Gerlach (1922). In their experiment, they passed a well-collimated beam of silver atoms through a region of inhomogeneous field before allowing the particles to impact on a photographic plate (see figure). The magnetic field was directed perpendicular to the beam, and has a strong gradient, $\partial_z B_z \neq 0$ so that a beam comprised of atoms with a magnetic moment would be bent towards the z or -z axis. As the magnetic moment will be proportional to the total angular momentum, such an experiment can be thought of as a measurement of its projection along z.

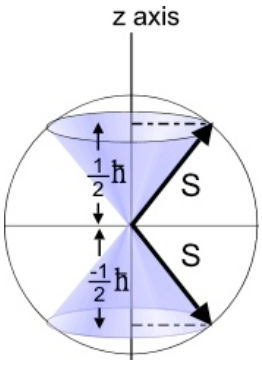




Gerlach's postcard, dated 8th February 1922, to Niels Bohr. It shows a photograph of the beam splitting, with the message, in translation: "Attached [is] the experimental proof of directional quantization. We congratulate [you] on the confirmation of your theory." (Physics Today December 2003)

At the time of the experiment, there was an expectation that the magnetic moment of the atom was generated in its entirety by the orbital angular momentum. As such, one would expect that there would be a minimum of three possible values of the z-component of angular momentum: the lowest non-zero orbital angular momentum is $\ell = 1$, with allowed values of the z-component $m\hbar$, $m = 1, 0, -1$. Curiously, Stern and Gerlach's experiment (right) showed that the beam of silver atoms split into *two*! This discovery, which caused great discussion and surprise presented a puzzle.

However, in our derivation of allowed angular momentum eigenvalues we found that, although for any system the allowed values of m form a ladder with spacing $\hbar$, we could not rule out half-integral values of m. The lowest such case, $\ell = 1/2$, would in fact have just two allowed m values: $m = \pm 1/2$. However, such an ℓ value could not translate to an orbital angular momentum because the z-component of the orbital wavefunction, ψ has a factor $e^{\pm i\phi}$, and therefore acquires a factor -1 on rotating through 2π! This would imply that ψ is not single-valued, which doesn't make sense for a Schrödinger-type wavefunction.



Yet the experimental result was irrefutable. Therefore, this must be a new kind of non-orbital angular momentum – spin. Conceptually, just as the Earth has orbital angular momentum in its yearly circle around the sun, and also spin angular momentum from its daily turning, the electron has an analogous spin. But this analogy has obvious limitations: the Earth's spin is after all made up of material orbiting around the axis through the poles. The electron spin cannot be imagined as arising from a rotating body, since orbital angular momenta always come in integral multiples of $\hbar$. Fortunately, this lack of a simple quasi-mechanical picture underlying electron spin doesn't

prevent us from using the general angular momentum machinery developed ealier, which followed just from analyzing the effect of spatial rotation on a quantum mechanical system.

6.1 Spinors, spin pperators, Pauli matrices

The Hilbert space of angular momentum states for spin 1/2 is two-dimensional. Various notations are used: $|\ell, m\rangle$ becomes $|s, m\rangle$ or, more graphically,

$$\boxed{|1/2, 1/2\rangle = |\uparrow\rangle, \qquad |1/2, -1/2\rangle = |\downarrow\rangle\,.}$$

A general state of spin can be written as the lienar combination,

$$\alpha|\uparrow\rangle + \beta|\downarrow\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

with the normalisation condition, $|\alpha|^2 + |\beta|^2 = 1$, and this two-dimensional ket is called a **spinor**. Operators acting on spinors are necessarily of the form of 2×2 matrices. We shall adopt the usual practice of denoting the angular momentum components L_i by S_i for spins. (Once again, for clarity, we also drop the hats on the angular momentum operators!)

Wolfgang Pauli and Niels Bohr demonstrating 'tippe top' toy at the inauguration of the new Institute of Physics at Lund, Sweden 1954.

From our definition of the spinor, it is evident that the z-component of the spin can be represented as the matrix,

$$S_z = \frac{\hbar}{2}\sigma_z, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

From the general formulae (4.5) for raising and lowering operators $S_\pm = S_x \pm iS_y$, with $s = 1/2$, we have $S_+|1/2, -1/2\rangle = \hbar|1/2, 1/2\rangle$, $S_-|1/2, 1/2\rangle = \hbar|1/2, -1/2\rangle$, or, in matrix form,

$$S_x + iS_y = S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad S_x - iS_y = S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

It therefore follows that an appropriate matrix representation for spin 1/2 is ggiven by the **Pauli spin matrices**, $\mathbf{S} = \frac{\hbar}{2}\sigma$ where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6.1}$$

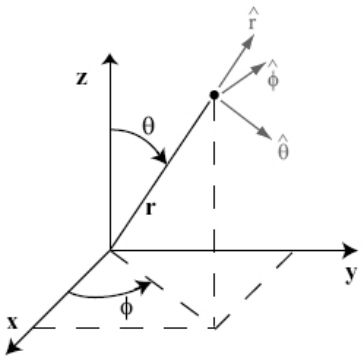
These matrices are Hermitian, traceless, and obey the relations $\sigma_i^2 = \mathbb{I}$, $\sigma_i\sigma_j = -\sigma_j\sigma_i$, and $\sigma_i\sigma_j = i\sigma_k$ for (i, j, k) a cyclic permutation of $(1, 2, 3)$. These relations can be summarised by the identity,

$$\boxed{\sigma_i\sigma_j = \mathbb{I}\delta_{ij} + i\epsilon_{ijk}\sigma_k\,.}$$

The total spin $\mathbf{S}^2 = \frac{\hbar^2}{4}\sigma^2 = \frac{3}{4}\hbar^2$, i.e. $s(s+1)\hbar^2$ for $s = 1/2$.

▷ Exercise. Explain why any 2×2 matrix can be written in the form $\alpha_0\mathbb{I} + \sum_i \alpha_i\sigma_i$. Use your results to show that (a) $(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})^2 = \mathbb{I}$ for any unit vector $\hat{\mathbf{n}}$, and (b) $(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B}) = (\mathbf{A}\cdot\mathbf{B})\mathbb{I} + \boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B})$.

6.2 Relating the spinor to the spin direction



For a general state $\alpha|\uparrow\rangle + \beta|\downarrow\rangle$, how do α, β relate to which way the spin is pointing? To find out, let us assume that it is pointing up along the unit vector $\hat{\mathbf{n}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, i.e. in the direction (θ, ϕ). In other words, the spin is an eigenstate of the operator $\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}$ having eigenvalue unity:

$$\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} .$$

From this expression, we find that $\alpha/\beta = (n_x - in_y)/(1 - n_z) = e^{-i\phi}\cot(\theta/2)$ (exercise). Then, making use of the normalisation, $|\alpha|^2 + |\beta|^2 = 1$, we obtain (up to an arbitrary phase)

$$\boxed{\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\phi/2}\cos(\theta/2) \\ e^{i\phi/2}\sin(\theta/2) \end{pmatrix} .}$$

Since $e^{-i\phi}\cot(\theta/2)$ can be used to specify any complex number with $0 \le \theta \le \pi$, $0 \le \phi < 2\pi$, so for any possible spinor, there is an associated direction along which the spin points up.

▷ INFO. **The spin rotation operator:** In general, the rotation operator for rotation through an angle θ about an axis in the direction of the unit vector $\hat{\mathbf{n}}$ is given by $e^{i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}$ where $\mathbf{J}$ denotes the angular momentum operator. For spin, $\mathbf{J} = \mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$, and the rotation operator takes the form[1] $e^{i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar} = e^{i(\theta/2)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})}$. Expanding the exponential, and making use of the Pauli matrix identities ($(\mathbf{n}\cdot\boldsymbol{\sigma})^2 = \mathbb{I}$), one can show that (exercise)

$$e^{i(\theta/2)(\mathbf{n}\cdot\boldsymbol{\sigma})} = \mathbb{I}\cos(\theta/2) + i\mathbf{n}\cdot\boldsymbol{\sigma}\sin(\theta/2) .$$

The rotation operator is a 2×2 matrix operating on the ket space. The 2×2 rotation matrices are unitary and form a group known as SU(2); the 2 refers to the dimensionality, the U to their being unitary, and the S signifying determinant $+1$. Note that for rotation about the z-axis, $\hat{\mathbf{n}} = (0, 0, 1)$, it is more natural to replace θ with ϕ, and the rotation operator takes the form,

$$e^{i(\theta/2)(\mathbf{n}\cdot\boldsymbol{\sigma})} = \begin{pmatrix} e^{-i\phi/2} & 0 \\ 0 & e^{i\phi/2} \end{pmatrix} .$$

In particular, the wavefunction is multiplied by -1 for a rotation of 2π. Since this is true for any initial wave function, it is clearly also true for rotation through 2π about any axis.

▷ EXERCISE. Construct the infinitesimal version of the rotation operator $e^{i\delta\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}$ for spin 1/2, and prove that $e^{i\delta\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\boldsymbol{\sigma}e^{-i\delta\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar} = \boldsymbol{\sigma} + \delta\theta\hat{\mathbf{n}}\times\boldsymbol{\sigma}$, i.e. $\boldsymbol{\sigma}$ is rotated in the same way as an ordinary three-vector - note particularly that the change depends on the angle rotated through (as opposed to the half-angle) so, reassuringly, there is no -1 for a complete rotation (as there cannot be - the direction of the spin is a physical observable, and cannot be changed on rotating the measuring frame through 2π).

[1] Warning: do not confuse θ – the rotation angle - with the spherical polar angle used to parameterise $\hat{\mathbf{n}}$.

6.3 Spin precession in a magnetic field

Consider a magnetized classical object spinning about it's centre of mass, with angular momentum $\mathbf{L}$ and parallel magnetic moment $\boldsymbol{\mu}$, $\boldsymbol{\mu} = \gamma\mathbf{L}$. The constant γ is called the gyromagnetic ratio. Now suppose that we impose a magnetic field $\mathbf{B}$ along, say, the z-direction. This will exert a torque $\mathbf{T} = \boldsymbol{\mu} \times \mathbf{B} = \gamma\mathbf{L} \times \mathbf{B} = \frac{d\mathbf{L}}{dt}$. This equation is easily solved and shows that the angular momentum vector $\mathbf{L}$ precesses about the magnetic field direction with angular velocity of precession $\boldsymbol{\omega}_0 = -\gamma\mathbf{B}$.[2]

In the following, we will show that precisely the same result appears in the study of the quantum mechanics of an electron spin in a magnetic field. The electron has magnetic dipole moment $\boldsymbol{\mu} = \gamma\mathbf{S}$, where $\gamma = g\frac{-e}{2m_e}$ and the gyromagnetic ratio, g, is very close to 2.[3] The Hamiltonian for the interaction of the electron's dipole moment with the magnetic field is given by $\hat{H} = -\boldsymbol{\mu} \cdot \mathbf{B} = -\gamma\mathbf{S} \cdot \mathbf{B}$. Hence the time development is specified by the equation $|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$, with the time-evolution operator (or propagator), $\hat{U}(t) = e^{-i\hat{H}t/\hbar} = e^{i\gamma\sigma\cdot\mathbf{B}t/2}$. However, this is nothing but the rotation operator (as shown earlier) through an angle $-\gamma Bt$ about the direction of $\mathbf{B}$!

For an arbitrary initial spin orientation

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\phi/2}\cos(\theta/2) \\ e^{i\phi/2}\sin(\theta/2) \end{pmatrix},$$

the propagator for a magnetic field in the z-direction is given by

$$U(t) = e^{i\gamma\sigma\cdot\mathbf{B}t/2} = \begin{pmatrix} e^{-i\omega_0 t/2} & 0 \\ 0 & e^{i\omega_0 t/2} \end{pmatrix},$$

so the time-dependent spinor is set by

$$\begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} = \begin{pmatrix} e^{-i(\phi+\omega_0 t)/2}\cos(\theta/2) \\ e^{i(\phi+\omega_0 t)/2}\sin(\theta/2) \end{pmatrix}.$$

The angle θ between the spin and the field stays constant while the azimuthal angle around the field increases as $\phi = \phi_0 + \omega_0 t$, exactly as in the classical case. The frequency $\omega_0 = g\omega_c$, where $\omega_c = \frac{|e|B}{2m_e}$ denotes the cyclotron frequency. For a magnetic field of 1 T, $\omega_c \simeq 10^{11}$ rads/s.

▷ Exercise. For a spin initially pointing along the x-axis, prove that $\langle S_x(t)\rangle = (\hbar/2)\cos(\omega_0 t)$.

6.3.1 Paramagnetic Resonance

The analysis above shows that the spin precession frequency is independent of the angle of the spin with respect to the field direction. Consider then how this looks in a frame of reference which is itself rotating with angular velocity ω about the z-axis. Let us specify the magnetic field $\mathbf{B}_0 = B_0\hat{\mathbf{z}}$, since we'll soon be adding another component. In the rotating frame, the observed precession frequency is $\boldsymbol{\omega}_r = -\gamma(\mathbf{B}_0 + \boldsymbol{\omega}/\gamma)$, so there is a different effective

[2] Proof: From the equation of motion, with $L_+ = L_x + iL_y$, $\frac{dL_+}{dt} = -i\gamma BL_+$, $L_+ = L_+^0 e^{-i\gamma Bt}$. Of course, $\frac{dL_z}{dt} = 0$, since $\frac{d\mathbf{L}}{dt} = \gamma\mathbf{L} \times \mathbf{B}$ is perpendicular to $\mathbf{B}$, which is in the z-direction.

[3] This g-factor terminology is used more widely: the magnetic moment of an atom is written $\mu = g\mu_B$, where $\mu_B = \frac{e\hbar}{2m_e}$ is the known as the **Bohr magneton**, and g depends on the total orbital angular momentum and total spin of the particular atom.

field ($\mathbf{B}_0 + \boldsymbol{\omega}/\gamma$) in the rotating frame. Obviously, if the frame rotates exactly at the precession frequency, $\boldsymbol{\omega} = \boldsymbol{\omega}_0 = -\gamma\mathbf{B}_0$, spins pointing in any direction will remain at rest in that frame – there is no effective field at all.

Suppose we now add a small rotating magnetic field with angular frequency $\boldsymbol{\omega}$ in the xy plane, so the total magnetic field,

$$\mathbf{B} = B_0\hat{\mathbf{z}} + B_1(\hat{\mathbf{e}}_x\cos(\omega t) - \hat{\mathbf{e}}_y\sin(\omega t))\,.$$

The effective magnetic field in the frame rotating with the same frequency ω as the small added field is then given by

$$\mathbf{B}_r = (B_0 + \omega/\gamma)\hat{\mathbf{z}} + B_1\hat{\mathbf{e}}_x\,.$$

Now, if we tune the angular frequency of the small rotating field so that it exactly matches the precession frequency in the original static magnetic field, $\boldsymbol{\omega} = \boldsymbol{\omega}_0 = -\gamma\mathbf{B}_0$, all the magnetic moment will see in the rotating frame is the small field in the x-direction! It will therefore precess about the x-direction at the slow angular speed γB_1. This matching of the small field rotation frequency with the large field spin precession frequency is the "resonance".

If the spins are lined up preferentially in the z-direction by the static field, and the small resonant oscillating field is switched on for a time such that $\gamma B_1 t = \pi/2$, the spins will be preferentially in the y-direction in the rotating frame, so in the lab they will be rotating in the xy plane, and a coil will pick up an a.c. signal from the induced e.m.f.

▷ INFO. **Nuclear magnetic resonance** is an important tool in chemical analysis. As the name implies, the method uses the spin magnetic moments of nuclei (particularly hydrogen) and resonant excitation. **Magnetic resonance imaging** uses the same basic principle to get an image (of the inside of a body for example). In basic NMR, a strong static B field is applied. A spin 1/2 proton in a hydrogen nucleus then has two energy eigenstates. After some time, most of the protons fall into the lower of the two states. We now use an electromagnetic wave (RF pulse) to excite some of the protons back into the higher energy state. The proton's magnetic moment interacts with the oscillating B field of the EM wave through the Hamiltonian,

$$\hat{H} = -\boldsymbol{\mu}\cdot\mathbf{B} = \frac{g_p e}{2m_p c}\mathbf{S}\cdot\mathbf{B} = \frac{g_p e\hbar}{4m_p c}\boldsymbol{\sigma}\cdot\mathbf{B} = \frac{g_p}{2}\mu_N\boldsymbol{\sigma}\cdot\mathbf{B}\,,$$

where the gyromagnetic ratio of the proton is about +5.6. The magnetic moment is $2.79\mu_N$ (nuclear magnetons). Different nuclei will have different gyromagnetic ratios giving more degrees of freedom with which to work. The strong static B field is chosen to lie in the z direction and the polarization of the oscillating EM wave is chosen so that the B field points in the x direction. The EM wave has (angular) frequency ω,

$$\hat{H} = \frac{g_p}{2}\mu_N B_z\sigma_z + B_x\cos(\omega t)\sigma_x = \frac{g_p}{2}\mu_N\begin{pmatrix} B_z & B_x\cos(\omega t) \\ B_x\cos(\omega t) & -B_z\end{pmatrix}.$$

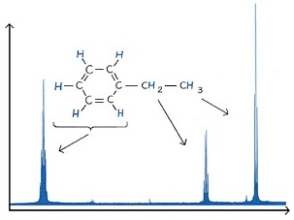
If we now apply the time-dependent Schrödinger equation, $i\hbar\partial_t\boldsymbol{\chi} = \hat{H}\boldsymbol{\chi}$, i.e.

$$\begin{pmatrix}\dot{a}\\ \dot{b}\end{pmatrix} = -i\begin{pmatrix}\omega_0 & \omega_I\cos(\omega t)\\ \omega_I\cos(\omega t) & -\omega_0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix},$$

where $\omega_0 = g_p\mu_N B_z/2\hbar$ and $\omega_I = g_p\mu_N B_x/2\hbar$, we obtain,

$$\partial_t(be^{-i\omega_0 t}) = -\frac{\omega_I}{2}\left(e^{i(\omega-2\omega_0)t} + e^{-i(\omega+2\omega_0)t}\right).$$

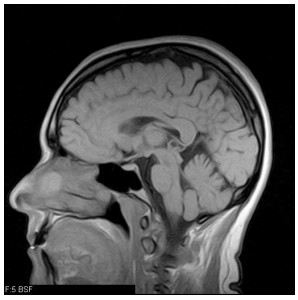
The second term oscillates rapidly and can be neglected. The first term will only result in significant transitions if $\omega \approx 2\omega_0$. Note that this is exactly the condition that ensures that the energy of the photons in the EM field $E = \hbar\omega$ is equal to the energy difference between the two spin states $\Delta E = 2\hbar\omega_0$. The conservation of energy



A proton NMR spectrum of a solution containing a simple organic compound, ethyl benzene. Each group of signals corresponds to protons in a different part of the molecule.

condition must be satisfied well enough to get a significant transition rate. In NMR, we observe the transitions back to the lower energy state. These emit EM radiation at the same frequency and we can detect it after the stronger input pulse ends (or by more complex methods).

NMR is a powerful tool in chemical analysis because the molecular field adds to the external B field so that the resonant frequency depends on the molecule as well as the nucleus. We can learn about molecular fields or just use NMR to see what molecules are present in a sample. In MRI, we typically concentrate on the one nucleus like hydrogen. We can put a gradient in B_z so that only a thin slice of the material has ω tuned to the resonant frequency. Therefore we can excite transitions to the higher energy state in only a slice of the sample. If we vary (in the orthogonal direction!) the B field during the decay, we can recover 3d images.



High resolution MRI scan of a brain!

6.4 Addition of angular momenta

In subsequent chapters, it will be necessary to add angular momentum, be it the addition of orbital and spin angular momenta, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \mathbf{S}$, as with the study of spin-orbit coupling in atoms, or the addition of general angular momenta, $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ as occurs in the consideration of multi-electron atoms. In the following section, we will explore three problems: The addition of two spin 1/2 degrees of freedom; the addition of a general orbital angular momentum and spin; and the addition of spin $J = 1$ angular momenta. However, before addressing these examples in turn, let us first make some general remarks.

Without specifying any particular application, let us consider the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ where $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ correspond to distinct degrees of freedom, $[\hat{\mathbf{J}}_1, \hat{\mathbf{J}}_2] = 0$, and the individual operators obey angular momentum commutation relations. As a result, the total angular momentum also obeys angular momentum commutation relations,

$$[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k \, .$$

For each angular momentum component, the states $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ where $m_i = -j_i, \cdots j_i$, provide a basis of states of the total angular momentum operator, $\hat{\mathbf{J}}_i^2$ and the projection $\hat{J}_{iz}$. Together, they form a complete basis which can be used to span the states of the coupled spins,[4]

$$|j_1, m_1, j_2, m_2\rangle \equiv |j_1, m_1\rangle \otimes |j_2, m_2\rangle \, .$$

These product states are also eigenstates of $\hat{J}_z$ with eigenvalue $\hbar(m_1 + m_2)$, but not of $\hat{\mathbf{J}}^2$.

▷ Exercise. Show that $[\hat{\mathbf{J}}^2, \hat{J}_{iz}] \neq 0$.

However, for practical application, we require a basis in which the total angular momentum operator $\hat{\mathbf{J}}^2$ is also diagonal. That is, we must find eigenstates $|j, m_j, j_1, j_2\rangle$ of the four mutually commuting operators $\hat{\mathbf{J}}^2$, $\hat{J}_z$, $\hat{\mathbf{J}}_1^2$, and $\hat{\mathbf{J}}_2^2$.

In general, the relation between the two basis can be expressed as

$$|j, m_j, j_1, j_2\rangle = \sum_{m_1, m_2} |j_1, m_1, j_2, m_2\rangle\langle j_1, m_1, j_2, m_2 | j, m_j, j_1, j_2\rangle \, ,$$

[4]Here $\otimes$ denotes the "direct product" and shows that the two constituent spin states access their own independent Hilbert space.

where the matrix elements are known as **Clebsch-Gordon coefficients**. In general, the determination of these coefficients from first principles is a somewhat soul destroying exercise and one that we do not intend to pursue in great detail.[5] In any case, for practical purposes, such coefficients have been tabulated in the literature and can be readily obtained. However, in some simple cases, these matrix elements can be determined straightforwardly. Moreover, the algorithmic programme by which they are deduced offer some new conceptual insights.

Operationally, the mechanism for finding the basis states of the total angular momentum operator follow the strategy:

1. As a unique entry, the basis state with maximal $J_{\max}$ and $m_j = J_{\max}$ is easy to deduce from the original basis states since it involves the product of states of **highest weight**,

$$|J_{\max}, m_j = J_{\max}, j_1, j_2\rangle = |j_1, m_1 = j_1\rangle \otimes |j_2, m_2 = j_2\rangle \,,$$

   where $J_{\max} = j_1 + j_2$.

2. From this state, we can use of the total spin lowering operator $\hat{J}_-$ to find all states with $J = J_{\max}$ and $m_j = -J_{\max} \cdots J_{\max}$.

3. From the state with $J = J_{\max}$ and $m_j = J_{\max} - 1$, one can then obtain the state with $J = J_{\max} - 1$ and $m_j = J_{\max} - 1$ by orthogonality.[6] Now one can return to the second step of the programme and repeat until $J = |j_1 - j_2|$ when all $(2j_1 + 1)(2j_2 + 1)$ basis states have been obtained.

6.4.1 Addition of two spin $1/2$ degrees of freedom

For two spin 1/2 degrees of freedom, we could simply construct and diagonalize the complete 4×4 matrix elements of the total spin. However, to gain some intuition for the general case, let us consider the programme above. Firstly, the maximal total spin state is given by

$$|S = 1, m_S = 1, s_1 = 1/2, s_2 = 1/2\rangle = |s_1 = 1/2, m_{s_1} = 1/2\rangle \otimes |s_2 = 1/2, m_{s_2} = 1/2\rangle \,.$$

Now, since $s_1 = 1/2$ and $s = 1/2$ is implicit, we can rewrite this equation in a more colloquial form as

$$|S = 1, m_S = 1\rangle = |\uparrow_1\rangle \otimes |\uparrow_2\rangle \,.$$

We now follow step 2 of the programme and subject the maximal spin state to the total spin lowering operator, $\hat{S}_- = \hat{S}_1^- + \hat{S}_1^+$. In doing so, making use of Eq. (4.5), we find

$$\hat{S}_-|S = 1, m_S = 1\rangle = \sqrt{2}\hbar|S = 1, m_S = 0\rangle = \hbar\left(|\downarrow_1\rangle \otimes |\uparrow_2\rangle + |\uparrow_1\rangle \otimes |\downarrow_2\rangle\right) \,,$$

[5] In fact, one may show that the general matrix element is given by

$$\langle j_1, m_1, j_2, m_2|j, m_j, j_1, j_2\rangle = \delta_{m_j, m_1+m_2}\sqrt{\frac{(j_1 + j_2 - j)!(j + j_1 - j_2)!(j + j_2 - j_1)!(2j+1)}{(j + j_1 + j_2 + 1)!}}$$
$$\times \sum_k \frac{(-1)^k\sqrt{(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!(j + m)!(j - m)!}}{k!(j_1 + j_2 - j - k)!(j_1 - m_1 - k)!(j_2 + m_2 - k)!(j - j_2 + m_1 + k)!(j - j_1 - m_2 + k)!} \,.$$

[6] Alternatively, as a maximal spin state, $|J = J_{\max} - 1, m_j = J_{\max} - 1, j_1, j_2\rangle$ can be identified by the "killing" action of the raising operator, $\hat{J}_+$.

i.e. $|S=1,m_S=0\rangle = \frac{1}{\sqrt{2}}(|\downarrow_1\rangle\otimes|\uparrow_2\rangle + |\uparrow_1\rangle\otimes|\downarrow_2\rangle)$. Similarly,

$$\hat{S}_-|S=1,m_S=0\rangle = \sqrt{2}\hbar|S=1,m_S=-1\rangle = \sqrt{2}\hbar|\downarrow_1\rangle\otimes|\downarrow_2\rangle\,,$$

i.e. $|S=1,m_S=-1\rangle = |\downarrow_1\rangle\otimes|\downarrow_2\rangle$. This completes the construction of the manifold of spin $S=1$ states – the **spin triplet** states. Following the programme, we must now consider the lower spin state.

In this case, the next multiplet is the unique total **spin singlet** state $|S=0,m_S=0\rangle$. The latter must be orthogonal to the spin triplet state $|S=1,m_S=0\rangle$. As a result, we can deduce that

$$|S=0,m_S=0\rangle = \frac{1}{\sqrt{2}}\left(|\downarrow_1\rangle\otimes|\uparrow_2\rangle - |\uparrow_1\rangle\otimes|\downarrow_2\rangle\right)\,.$$

6.4.2 Addition of angular momentum and spin

We now turn to the problem of the addition of angular momentum and spin, $\hat{\mathbf{J}}=\hat{\mathbf{L}}+\hat{\mathbf{S}}$. In the original basis, for a given angular momentum ℓ, one can identify $2\times(2\ell+1)$ product states $|\ell,m_\ell\rangle\otimes|\uparrow\rangle$ and $|\ell,m_\ell\rangle\otimes|\downarrow\rangle$, with $m_\ell=-\ell,\cdots\ell$, involving eigenstates of $\hat{\mathbf{L}}^2$, $\hat{L}_z$, $\hat{\mathbf{S}}^2$ and $\hat{S}_z$, but not $\hat{\mathbf{J}}^2$. From these basis states, we are looking for eigenstates of $\hat{\mathbf{J}}^2$, $\hat{J}_z$, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$. To undertake this programme, it is helpful to recall the action of the angular momentum raising and lower operators,

$$\hat{L}_\pm|\ell,m_\ell\rangle = ((\ell\pm m_\ell+1)(\ell\mp m_\ell))^{1/2}\hbar|\ell,m_\ell\pm1\rangle\,,$$

as well as the identity

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2+\hat{\mathbf{S}}^2+\overbrace{2\hat{L}_z\hat{S}_z+\hat{L}_+\hat{S}_-+\hat{S}_+\hat{L}_-}^{2\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}}\,.$$

For the eigenstates of $\hat{\mathbf{J}}^2$, $\hat{J}_z$, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ we will adopt the notation $|j,m_j,\ell\rangle$ leaving the spin $S=1/2$ implicit. The maximal spin state is given by[7]

$$|\ell+1/2,\ell+1/2,\ell\rangle = |\ell,\ell\rangle\otimes|\uparrow\rangle\,.$$

To obtain the remaining states in the multiplet, $|j=\ell+1/2,m_{j=\ell+1/2},\ell\rangle$, we may simply apply the total spin lowering operator $\hat{J}_-$,

$$\hat{J}_-|\ell,\ell\rangle\otimes|\uparrow\rangle = \hbar(2\ell)^{1/2}|\ell,\ell-1\rangle\otimes|\uparrow\rangle + \hbar|\ell,\ell\rangle\otimes|\downarrow\rangle\,.$$

Normalising the right-hand side of this expression, one obtains the spin state,

$$|\ell+1/2,\ell-1/2,\ell\rangle = \sqrt{\frac{2\ell}{2\ell+1}}|\ell,\ell-1\rangle\otimes|\uparrow\rangle + \sqrt{\frac{1}{2\ell+1}}|\ell,\ell\rangle\otimes|\downarrow\rangle\,.$$

[7] The proof runs as follows:

$$\hat{J}_z|\ell,\ell\rangle\otimes|\uparrow\rangle = (\hat{L}_z+\hat{S}_z)|\ell,\ell\rangle\otimes|\uparrow\rangle = (\ell+1/2)\hbar|\ell,\ell\rangle\otimes|\uparrow\rangle\,,$$

and

$$\begin{aligned}\hat{\mathbf{J}}^2|\ell,\ell\rangle\otimes|\uparrow\rangle &= \hbar^2(\ell(\ell+1)+1/2(1/2+1)+2\ell\frac{1}{2})|\ell,\ell\rangle\otimes|\uparrow\rangle\\ &= \hbar^2(\ell+1/2)(\ell+3/2)|\ell,\ell\rangle\otimes|\uparrow\rangle\,.\end{aligned}$$

By repeating this programme, one can develop an expression for the full set of basis states,

$$|j=\ell+1/2,m_j,\ell\rangle=\sqrt{\frac{\ell+m_j+1/2}{2\ell+1}}|\ell,m_j-1/2\rangle\otimes|\uparrow\rangle \\ +\sqrt{\frac{\ell-m_j+1/2}{2\ell+1}}|\ell,m_j+1/2\rangle\otimes|\downarrow\rangle\,,$$

with $m_j=\ell+1/2,\cdots,-(\ell+1/2)$. In order to obtain the remaining states with $j=\ell-1/2$, we may look for states with $m_j=\ell-1/2,\cdots,-(\ell-1/2)$ which are orthogonal to $|\ell+1/2,m_j,\ell\rangle$. Doing so, we obtain

$$|\ell-1/2,m_j,\ell\rangle=-\sqrt{\frac{\ell-m_j+1/2}{2\ell+1}}|\ell,m_j-1/2\rangle\otimes|\uparrow\rangle \\ +\sqrt{\frac{\ell+m_j+1/2}{2\ell+1}}|\ell,m_j+1/2\rangle\otimes|\downarrow\rangle\,.$$

Finally, these states can be cast in a compact form by setting

$$\boxed{|j=\ell\pm1/2,m_j,\ell\rangle=\alpha_\pm|\ell,m_j-1/2\rangle\otimes|\uparrow\rangle+\beta_\pm|\ell,m_j+1/2\rangle\otimes|\downarrow\rangle\,,} \quad (6.2)$$

where $\alpha_\pm=\pm\sqrt{\frac{\ell\pm m_j+1/2}{2\ell+1}}=\pm\beta_\mp$.

6.4.3 Addition of two angular momenta $J=1$

As mentioned above, for the general case the programme is algebraically technical and unrewarding. However, for completeness, we consider here the explicit example of the addition of two spin 1 degrees of freedom. Once again, the maximal spin state is given by

$$|J=2,m_J=2,j_1=1,j_2=1\rangle=|j_1=1,m_1=1\rangle\otimes|j_2=1,m_2=1\rangle\,,$$

or, more concisely, $|2,2\rangle=|1\rangle\otimes|1\rangle$, where we leave j_1 and j_2 implicit. Once again, making use of Eq. (4.5) and an ecomony of notation, we find (exercise)

$$\begin{cases} |2,2\rangle=|1\rangle\otimes|1\rangle \\ |2,1\rangle=\frac{1}{\sqrt{2}}\left(|0\rangle\otimes|1\rangle+|1\rangle\otimes|0\rangle\right) \\ |2,0\rangle=\frac{1}{\sqrt{6}}\left(|-1\rangle\otimes|1\rangle+2|0\rangle\otimes|0\rangle+|1\rangle\otimes|-1\rangle\right) \\ |2,-1\rangle=\frac{1}{\sqrt{2}}\left(|0\rangle\otimes|-1\rangle+|-1\rangle\otimes|0\rangle\right) \\ |2,2\rangle=|-1\rangle\otimes|-1\rangle \end{cases}.$$

Then, from the expression for $|2,1\rangle$, we can construct the next maximal spin state $|1,1\rangle=\frac{1}{\sqrt{2}}(|0\rangle\otimes|1\rangle-|1\rangle\otimes|0\rangle)$, from the orthogonality condition. Once again, acting on this state with the total spin lowering operator, we obtain the remaining members of the multiplet,

$$\begin{cases} |1,1\rangle=\frac{1}{\sqrt{2}}\left(|0\rangle\otimes|1\rangle-|1\rangle\otimes|0\rangle\right) \\ |1,0\rangle=\frac{1}{\sqrt{2}}\left(|-1\rangle\otimes|1\rangle-|1\rangle\otimes|-1\rangle\right) \\ |1,-1\rangle=\frac{1}{\sqrt{2}}\left(|-1\rangle\otimes|0\rangle-|0\rangle\otimes|-1\rangle\right) \end{cases}.$$

Finally, finding the state orthogonal to $|1,0\rangle$ and $|2,0\rangle$, we obtain the final state,

$$|0,0\rangle=\frac{1}{\sqrt{3}}\left(|-1\rangle\otimes|1\rangle-|0\rangle\otimes|0\rangle+|1\rangle\otimes|-1\rangle\right).$$