Chapter 8
Spin and Addition of Angular Momentum Type Operators

We have seen in Section 7.4 that representations of the angular momentum Lie algebra (7.21) are labelled by a quantum number ℓ which can take half-integer or integer values. However, we have also seen in Section 7.5 that ℓ is limited to integer values when the operators $\boldsymbol{M}$ actually refer to angular momentum, because the wave functions[1] $\langle\boldsymbol{x}|n,\ell,m_\ell\rangle$ or $\langle\boldsymbol{x}|k,\ell,m_\ell\rangle$ for angular momentum eigenstates must be single valued. It was therefore very surprising when Stern, Gerlach, Goudsmit, Uhlenbeck and Pauli in the 1920s discovered that half-integer values of ℓ are also realized in nature, although in that case ℓ cannot be related to an angular momentum any more. Half-integer values of ℓ arise in nature because leptons and quarks carry a representation of the "covering group" SU(2) of the proper rotation group SO(3), where SU(2) stands for the group which can be represented by special unitary 2×2 matrices[2]. The designation "special" refers to the fact that the matrices are also required to have determinant 1. The generators of the groups SU(2) and SO(3) satisfy the same Lie algebra (7.21), but for every rotation matrix $\underline{R}(\boldsymbol{\varphi}) = \underline{R}(\boldsymbol{\varphi} + 2\pi\hat{\boldsymbol{\varphi}})$ there are two unitary 2×2 matrices $\underline{U}(\boldsymbol{\varphi}) = -\underline{U}(\boldsymbol{\varphi} + 2\pi\hat{\boldsymbol{\varphi}})$. In that sense SU(2) provides a double cover of SO(3).

We will use the notations $\boldsymbol{l}$ and $\boldsymbol{M}$ for angular momenta, and $\boldsymbol{s}$ or $\boldsymbol{S}$ for spins.

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[1] We denote the magnetic quantum number with m_ℓ in this chapter because m will denote the mass of a particle.

[2] Ultimately, all particles carry representations of the covering group SL(2,$\mathbb{C}$) of the group SO(1,3) of proper orthochronous Lorentz transformations, see Appendices B and H.

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8.1 Spin and magnetic dipole interactions

A particle of charge q and mass m which moves with angular momentum $\boldsymbol{l}$ through a constant magnetic field $\boldsymbol{B}$ has its energy levels shifted through a Zeeman term in the Hamiltonian,

$$H_Z = -\frac{q}{2m}\boldsymbol{l}\cdot\boldsymbol{B}. \tag{8.1}$$

We will explore the origin of this term in Chapter 15, see Problem 15.2, but for now we can think of it as a magnetic dipole term with a dipole moment

$$\boldsymbol{\mu}_l = \frac{q}{2m}\boldsymbol{l}.$$

The relation between $\boldsymbol{\mu}_l$ and $\boldsymbol{l}$ can be motivated from electrodynamics, but is actually a consequence of the coupling to magnetic vector potentials in the Schrödinger equation.

The quantization $\langle \ell, m_\ell | l_z | \ell, m_\ell \rangle = \hbar m_\ell$ for angular momentum components in a fixed direction yields a Zeeman shift

$$\Delta E = -\frac{q\hbar}{2m} B m_\ell, \quad -\ell \leq m_\ell \leq \ell,$$

of the energy levels of a charged particle in a magnetic field. For orbital momentum the resulting number $2\ell + 1$ of energy levels is odd. However, the observation of motion of Ag atoms through an inhomogeneous field by Stern and Gerlach in 1921 revealed a split of energy levels of these atoms into two levels in a magnetic field. This complies with a split into $2s + 1$ levels only if the angular momentum like quantum number s is $1/2$. This additional angular momentum type quantum number is denoted as spin. Spin behaves in many respects similar to angular momentum, but it cannot be an orbital angular momentum because that would exclude half-integer values for s. Another major difference to angular momentum concerns the fact that the spectroscopically observed splitting of energy levels due to spin complies with a magnetic dipole type interaction only if the corresponding Zeeman type term is increased by a factor g_s,

$$H = -\boldsymbol{\mu}_s\cdot\boldsymbol{B}, \quad \boldsymbol{\mu}_s = g_s\frac{q}{2m}\boldsymbol{s}.$$

This "anomalous g factor" is in very good approximation $g_s \simeq 2$. The relation between $\boldsymbol{\mu}_s$ and $\boldsymbol{s}$ is a consequence of relativistic quantum mechanics and will be explained in Section 21.5.

The important observation for now is that there exist operators which satisfy the angular momentum Lie algebra (7.21),

$$[S_i, S_j] = \mathrm{i}\hbar\epsilon_{ijk}S_k,$$

and therefore have representations of the form (7.26–7.31),

$$
\begin{aligned}
S_z|s,m_s\rangle &= \hbar m_s|s,m_s\rangle, &(8.2)\\
S_\pm|s,m_s\rangle &= \hbar\sqrt{s(s+1)-m_s(m_s\pm 1)}\,|s,m_s\pm 1\rangle, &(8.3)\\
\boldsymbol{S}^2|s,m_s\rangle &= \hbar^2 s(s+1)|s,m_s\rangle.
\end{aligned}
$$

However, these operators are not related to orbital angular momentum and therefore can have half-integer values of the quantum number s in their representations.

Our previous calculations of matrix representations of the rotation group in Section 7.4 imply that spin is related to transformation properties of particle wave functions under rotations. However, before we can elaborate on this, we have to take a closer look at the representations with $s = 1/2$.

In the following mapping between matrices we use an index mapping for the magnetic quantum numbers $m_s = \pm 1/2$ to indices

$$a(m_s) = (3/2) - m_s, \tag{8.4}$$

i.e. $m_s = 1/2 \to a(m_s) = 1, m_s = -1/2 \to a(m_s) = 2$.

Substitution of $s = 1/2$ in equations (8.2, 8.3) yields

$$\langle 1/2, m_s'|S_3|1/2, m_s\rangle = \hbar m_s \delta_{m_s',m_s} = \frac{\hbar}{2}(\sigma_3)_{a(m_s'),a(m_s)}, \tag{8.5}$$

$$\langle 1/2, m_s'|S_1|1/2, m_s\rangle = \frac{\hbar}{2}\left(\delta_{m_s',m_s+1} + \delta_{m_s',m_s-1}\right) = \frac{\hbar}{2}(\sigma_1)_{a(m_s'),a(m_s)}, \tag{8.6}$$

and

$$\langle 1/2, m_s'|S_2|1/2, m_s\rangle = \frac{\hbar}{2\mathrm{i}}\left(\delta_{m_s',m_s+1} - \delta_{m_s',m_s-1}\right) = \frac{\hbar}{2}(\sigma_2)_{a(m_s'),a(m_s)}, \tag{8.7}$$

with the Pauli matrices

$$\underline{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \underline{\sigma}_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \underline{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{8.8}$$

The Pauli matrices provide a basis for hermitian traceless 2 × 2 matrices and satisfy the relation

$$\underline{\sigma}_i \cdot \underline{\sigma}_j = \delta_{ij}\underline{1} + \mathrm{i}\epsilon_{ijk}\underline{\sigma}_k. \tag{8.9}$$

The index mapping $m_s \to a(m_s)$ is employed in the notation of spin states as $|1/2, m_s\rangle \to |a(m_s)\rangle$ such that a general $s = 1/2$ state is

$$|\psi\rangle = \sum_{m_s=1/2}^{-1/2} |1/2, m_s\rangle\langle 1/2, m_s|\psi\rangle = \sum_{a=1}^{2} |a\rangle\langle a|\psi\rangle \tag{8.10}$$

Knowledge of a spin 1/2 state $|\psi\rangle$ is equivalent to the knowledge of its two components $\langle 1/2, 1/2|\psi\rangle \equiv \langle 1|\psi\rangle \equiv \psi_1$, $\langle 1/2, -1/2|\psi\rangle \equiv \langle 2|\psi\rangle \equiv \psi_2$. In column notation this corresponds to the *2-spinor* ψ

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \tag{8.11}$$

such that application of a spin operator S_i

$$\langle 1/2, m_s|\psi'\rangle = \langle 1/2, m_s|S_i|\psi\rangle = \sum_{m'_s=1/2}^{-1/2} \langle 1/2, m_s|S_i|1/2, m'_s\rangle\langle 1/2, m'_s|\psi\rangle$$

corresponds to the matrix multiplication

$$\psi' = \frac{\hbar}{2}\underline{\sigma}_i \cdot \psi. \tag{8.12}$$

For example, a general electron state $|\psi\rangle$ corresponds to a superposition of spin orientations $\pm 1/2$ and a superposition of $\boldsymbol{x}$ eigenstates,

$$|\psi\rangle = \int d^3\boldsymbol{x} \sum_{m_s=1/2}^{-1/2} |\boldsymbol{x}; m_s\rangle\langle \boldsymbol{x}; m_s|\psi\rangle \equiv \int d^3\boldsymbol{x} \sum_{m_s=1/2}^{-1/2} |\boldsymbol{x}; m_s\rangle \psi_{a(m_s)}(\boldsymbol{x}),$$

and is given in 2-spinor notation (listing all common index conventions) as

$$\psi(\boldsymbol{x}) = \begin{pmatrix} \psi_1(\boldsymbol{x}) \\ \psi_2(\boldsymbol{x}) \end{pmatrix} \equiv \begin{pmatrix} \psi_{1/2}(\boldsymbol{x}) \\ \psi_{-1/2}(\boldsymbol{x}) \end{pmatrix} \equiv \begin{pmatrix} \psi_+(\boldsymbol{x}) \\ \psi_-(\boldsymbol{x}) \end{pmatrix} \equiv \begin{pmatrix} \psi_\uparrow(\boldsymbol{x}) \\ \psi_\downarrow(\boldsymbol{x}) \end{pmatrix}. \tag{8.13}$$

The normalization is

$$\int d^3\boldsymbol{x} \left(|\psi_1(\boldsymbol{x})|^2 + |\psi_2(\boldsymbol{x})|^2\right) = 1.$$

The probability densities for finding the electron with spin up or down in the location $\boldsymbol{x}$ are $|\psi_1(\boldsymbol{x})|^2$ and $|\psi_2(\boldsymbol{x})|^2$, respectively, while the probability density to find the electron in the location $\boldsymbol{x}$ in any spin orientation is $|\psi_1(\boldsymbol{x})|^2 + |\psi_2(\boldsymbol{x})|^2$. Note that these three probability densities can have maxima in three different locations, which reminds us how questionable the concept of a particle is in quantum mechanics.

8.2 Transformation of scalar, spinor, and vector wave functions under rotations

The commutation relations between angular momentum $\boldsymbol{M} = \mathbf{x} \times \mathbf{p}$ and $\mathbf{x}$,

$$[M_i, \mathrm{x}_j] = \mathrm{i}\hbar\epsilon_{ijk}\mathrm{x}_k$$

imply with the rotation generators $(L_i)_{jk} = \epsilon_{ijk}$ and the rotation matrices from Section 7.4

$$\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right)\mathbf{x}\exp\left(-\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right) = \exp(-\boldsymbol{\varphi}\cdot\boldsymbol{L})\,\cdot\mathbf{x} = \underline{R}(-\boldsymbol{\varphi})\cdot\mathbf{x},$$

and therefore

$$\langle\boldsymbol{x}|\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right) = \langle\underline{R}(-\boldsymbol{\varphi})\cdot\boldsymbol{x}|.$$

Rotation of a state

$$|\psi(t)\rangle \to |\psi'(t)\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right)|\psi(t)\rangle$$

therefore implies for the rotated wave function

$$\langle\boldsymbol{x}'|\psi'(t)\rangle = \langle\underline{R}(\boldsymbol{\varphi})\cdot\boldsymbol{x}|\psi'(t)\rangle = \langle\boldsymbol{x}|\psi(t)\rangle, \tag{8.14}$$

where

$$\boldsymbol{x}' = \underline{R}(\boldsymbol{\varphi})\cdot\boldsymbol{x}$$

is the rotated coordinate vector.

A transformation behavior like (8.14) tells us that the transformed wave function at the transformed set of coordinates is the same as the original wave function at the original set of coordinates. Such a transformation behavior is denoted as a *scalar* transformation law, and the corresponding wave functions are scalar functions.

On the other hand, spinor wave functions have two components which denote probability amplitudes for spin orientation along a given spatial axis, conventionally chosen as the z axis. The z' axis of the rotated frame will generically have a direction which is different from the z axis, and the probability amplitudes for spin along the z' direction will be different from the probability amplitudes along the z direction.

The rotated 2-spinor state

$$|\psi(t)\rangle \to |\psi'(t)\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\,(\boldsymbol{M}+\boldsymbol{S})\right)|\psi(t)\rangle \tag{8.15}$$

has components

$$\begin{aligned}\langle\boldsymbol{x}',a|\psi'(t)\rangle \equiv \psi'_a(\boldsymbol{x}',t) &= \langle\underline{R}(\boldsymbol{\varphi})\cdot\boldsymbol{x},a|\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\,(\boldsymbol{M}+\boldsymbol{S})\right)|\psi(t)\rangle \\ &= \langle\boldsymbol{x},a|\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{S}\right)|\psi(t)\rangle = \left[\exp\left(\frac{\mathrm{i}}{2}\boldsymbol{\varphi}\cdot\underline{\boldsymbol{\sigma}}\right)\right]_{ab}\langle\boldsymbol{x},b|\psi(t)\rangle\end{aligned}$$

or in terms of the column 2-spinor (8.13),

$$\psi'(\boldsymbol{x}',t) = \exp\left(\frac{\mathrm{i}}{2}\boldsymbol{\varphi}\cdot\underline{\boldsymbol{\sigma}}\right)\cdot\psi(\boldsymbol{x},t). \tag{8.16}$$

For comparison, we also give the result if we use the representation (8.2, 8.3) with $s = 1$ for the spin operators $\boldsymbol{S}$ on wave functions. In that case the matrix correspondence

$$\langle s = 1/2, m_s'|\boldsymbol{S}|s = 1/2, m_s\rangle = \hbar\boldsymbol{\sigma}_{a(m_s'),a(m_s)}/2$$

is replaced in a first step by

$$\langle s = 1, m_s'|\boldsymbol{S}|s = 1, m_s\rangle = \hbar\boldsymbol{\Sigma}_{j(m_s'),j(m_s)}$$

with $j(m_s) = 2 - m_s$,

$$\underline{\Sigma}_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \underline{\Sigma}_2 = \frac{\mathrm{i}}{\sqrt{2}}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$\underline{\Sigma}_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{8.17}$$

However, this is still not the standard matrix representation for spin $s = 1$. The connection with the conventional representation (7.18) of vector rotation operators is achieved through the similarity transformation

$$\underline{\boldsymbol{L}} = \frac{\mathrm{i}}{\hbar}\underline{\boldsymbol{M}} = \mathrm{i}\underline{A}\cdot\underline{\boldsymbol{\Sigma}}\cdot\underline{A}^{-1} \tag{8.18}$$

with the unitary matrix

$$\underline{A} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & 0 & 1 \\ -\mathrm{i} & 0 & -\mathrm{i} \\ 0 & \sqrt{2} & 0 \end{pmatrix}, \quad \underline{A}^{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & \mathrm{i} & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & \mathrm{i} & 0 \end{pmatrix}.$$

The transformation law for *vector wave functions* $\langle\boldsymbol{x}, i|A(t)\rangle \equiv A_i(\boldsymbol{x},t)$ under rotations is then given in terms of the same rotation matrices $\underline{R}(\boldsymbol{\varphi}) = \exp(\boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}})$ which effect rotations of the vector $\boldsymbol{x}$,

$$\boldsymbol{x}' = \exp(\boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}})\cdot\boldsymbol{x}, \quad \boldsymbol{A}'(\boldsymbol{x}',t) = \exp(\boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}})\cdot\boldsymbol{A}(\boldsymbol{x},t). \tag{8.19}$$

We will see in Chapter 18 that photons are described by vector wave functions.

8.3 Addition of angular momentum like quantities

In classical mechanics, angular momentum is an additive vector quantity which is conserved in rotationally symmetric systems. Furthermore, the transformation equation (8.15) for spinor states involved addition of two different operators which both satisfy the angular momentum Lie algebra (7.21). However, before immersing ourselves into the technicalities of how angular momentum type operators are combined in quantum mechanics, it is worthwhile to point out that interactions in atoms and materials provide another direct physical motivation for addition of angular momentum like quantities.

We have seen in Section 7.1 that relative motion of two interacting particles with an interaction potential $V(\boldsymbol{x}_1 - \boldsymbol{x}_2)$ can be described in terms of effective single particle motion of a (quasi)particle with location $\boldsymbol{r}(t) = \boldsymbol{x}_1(t) - \boldsymbol{x}_2(t)$, mass $m = m_1 m_2/(m_1+m_2)$, momentum $\boldsymbol{p} = (m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2)/(m_1+m_2)$ and angular momentum $\boldsymbol{l} = \boldsymbol{r}\times\boldsymbol{p}$.

Furthermore, if $m_2 \gg m_1$, but the charge q_2 is not much larger than q_1 and the spin $|\boldsymbol{s}_2|$ is not much larger than $|\boldsymbol{s}_1|$, then we can assign a charge[3] $q = q_1$ and a spin $\boldsymbol{s} = \boldsymbol{s}_1$ to the quasiparticle with mass $m \simeq m_1$.

A particle of charge $-e$ and mass m with angular momentum operators $\boldsymbol{l}$ and spin $\boldsymbol{s}$ experiences a contribution to its energy levels from an interaction term

$$H_{l\cdot s} = \frac{\mu_0 e^2}{8\pi m^2 r^3}\boldsymbol{l}\cdot\boldsymbol{s} \tag{8.20}$$

in its Hamiltonian, if it is moving in the electric field $\boldsymbol{E} = \hat{\boldsymbol{r}}e/(4\pi\epsilon_0 r^2)$ of a much heavier particle of charge e. One can think of $H_{l\cdot s}$ as a magnetic dipole-dipole interaction $(\mu_0/4\pi r^3)\boldsymbol{\mu}_l\cdot\boldsymbol{\mu}_s$, but finally it arises as a consequence of a relativistic generalization of the Schrödinger equation. We will see this in Chapter 21, in particular equation (21.117). However, for the moment we simply accept the existence of terms like (8.20) as an experimental fact. These terms contribute to the fine structure of spectral lines. The term (8.20) is known as a *spin-orbit coupling* term or *ls* coupling term, and applies in this particular form to the energy levels of the quasiparticle which describes relative motion in a two-particle system. However, if there are many charged particles like in a many-electron atom, then there will also be interaction terms between angular momenta and spins of different particles in the system, i.e. we will have terms of the form

$$H_{j_1\cdot j_2} = f(r_{12})\boldsymbol{j}_1\cdot\boldsymbol{j}_2, \tag{8.21}$$

where $\boldsymbol{j}_i$ are angular momentum like operators. We will superficially denote all these operators (including spin) simply as angular momentum operators in the following.

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[3] We will return to the question of assignment of charge and spin to the quasiparticle for relative motion in Section 18.4.

Diagonalization of Hamiltonians like (8.20) or (8.21) requires us to combine two operators to a new operator according to $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$ or $\boldsymbol{j} = \boldsymbol{j}_1 + \boldsymbol{j}_1$, respectively. From the perspective of spectroscopy, terms like (8.20) or (8.21) are the very reason why we have to know how to combine two angular momentum type operators in quantum mechanics. Diagonalization of (8.20) and (8.21) is important for understanding the spectra of atoms and molecules, and spin-orbit coupling also affects energy levels in materials. Furthermore, Hamiltonians of the form $-2J\boldsymbol{s}_1 \cdot \boldsymbol{s}_2$ provide an effective description of interactions in magnetic materials, see Section 17.7, and they are important for spin entanglement and spintronics. The advantage of introducing the combined angular momentum operator $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$ is that it also satisfies angular momentum commutation rules (7.21) $[j_a, j_b] = \mathrm{i}\hbar\epsilon_{abc}j_c$ and therefore should have eigenstates $|j, m_j\rangle$,

$$\boldsymbol{j}^2|j, m_j\rangle = \hbar^2 j(j+1)|j, m_j\rangle, \quad j_z|j, m_j\rangle = \hbar m_j|j, m_j\rangle. \tag{8.22}$$

However, $\boldsymbol{j}$ commutes with $\boldsymbol{l}^2$ and $\boldsymbol{s}^2$, $[j_a, \boldsymbol{l}^2] = [j_a, \boldsymbol{s}^2] = 0$, and therefore we can try to construct the states in (8.22) such that they also satisfy the properties

$$\boldsymbol{l}^2|j, m_j, \ell, s\rangle = \hbar^2 \ell(\ell+1)|j, m_j, \ell, s\rangle,$$
$$\boldsymbol{s}^2|j, m_j, \ell, s\rangle = \hbar^2 s(s+1)|j, m_j, \ell, s\rangle.$$

The advantage of these states is that they are eigenstates of the coupling operator (8.20),

$$\begin{aligned}\boldsymbol{l}\cdot\boldsymbol{s}|j, m_j, \ell, s\rangle &= \frac{\boldsymbol{j}^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2}{2}|j, m_j, \ell, s\rangle \\ &= \hbar^2\frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2}|j, m_j, \ell, s\rangle,\end{aligned} \tag{8.23}$$

and therefore the energy shifts from spin-orbit coupling in these states are

$$\Delta E = \frac{\mu_0 e^2\hbar^2}{16\pi m^2}\langle r^{-3}\rangle\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]. \tag{8.24}$$

The states that we know for the operators $\boldsymbol{l}$ and $\boldsymbol{s}$ are the eigenstates $|\ell, m_\ell\rangle$ for $\boldsymbol{l}^2$ and l_z, and $|s, m_s\rangle$ for $\boldsymbol{s}^2$ and s_z, respectively. We can combine these states into states

$$|\ell, m_\ell\rangle \otimes |s, m_s\rangle \equiv |\ell, m_\ell; s, m_s\rangle \tag{8.25}$$

which will be denoted as a tensor product basis of angular momentum states. The understanding in the tensor product notation is that $\boldsymbol{l}$ only acts on the first factor and $\boldsymbol{s}$ only on the second factor. Strictly speaking the combined angular momentum operator should be written as

$$\boldsymbol{j} = \boldsymbol{l} \otimes 1 + 1 \otimes \boldsymbol{s},$$

which automatically ensures the correct rule

$$\boldsymbol{j}(|\ell, m_\ell\rangle \otimes |s, m_s\rangle) = \boldsymbol{l}|\ell, m_\ell\rangle \otimes |s, m_s\rangle + |\ell, m_\ell\rangle \otimes \boldsymbol{s}|s, m_s\rangle,$$

but we will continue with the standard physics notation $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$.

The main problem for combination of angular momenta is how to construct the eigenstates $|j, m_j, \ell, s\rangle$ for total angular momentum from the tensor products (8.25) of eigenstates of the initial angular momenta,

$$|j, m_j, \ell, s\rangle = \sum_{m_\ell, m_s} |\ell, m_\ell; s, m_s\rangle\langle\ell, m_\ell; s, m_s|j, m_j, \ell, s\rangle. \tag{8.26}$$

We will denote the states $|j, m_j, \ell, s\rangle$ as the combined angular momentum states.

There is no summation over indices $\ell' \neq \ell$ or $s' \neq s$ on the right hand side because all states involved are eigenstates of $\boldsymbol{l}^2$ and $\boldsymbol{s}^2$ with the same eigenvalues $\hbar^2\ell(\ell+1)$ or $\hbar^2 s(s+1)$, respectively.

The components $\langle\ell, m_\ell; s, m_s|j, m_j, \ell, s\rangle$ of the transformation matrix from the initial angular momenta states to the combined angular momentum states are known as *Clebsch-Gordan coefficients* or *vector addition coefficients*. The notation $\langle\ell, m_\ell; s, m_s|j, m_j, \ell, s\rangle$ is logically satisfactory by explicitly showing that the Clebsch-Gordan coefficients can also be thought of as the representation of the combined angular momentum states $|j, m_j, \ell, s\rangle$ in the basis of tensor product states $|\ell, m_\ell; s, m_s\rangle$. However, the notation is also redundant in terms of the quantum numbers ℓ and s, and a little clumsy. It is therefore convenient to abbreviate the notation by setting

$$\langle\ell, m_\ell; s, m_s|j, m_j, \ell, s\rangle \equiv \langle\ell, m_\ell; s, m_s|j, m_j\rangle.$$

The new angular momentum eigenstates must also be normalizable and orthogonal for different eigenvalues, i.e. the transformation matrix must be unitary,

$$\sum_{m_\ell, m_s} \langle j, m_j|\ell, m_\ell; s, m_s\rangle\langle\ell, m_\ell; s, m_s|j', m_j'\rangle = \delta_{j,j'}\delta_{m_j,m_j'}, \tag{8.27}$$

$$\sum_{j,m_j} \langle\ell, m_\ell; s, m_s|j, m_j\rangle\langle j, m_j|\ell, m_\ell'; s, m_s'\rangle = \delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'}. \tag{8.28}$$

The hermiticity properties

$$j_z = (l_z + s_z)^+, \quad j_\pm = (l_\mp + s_\mp)^+$$

imply with the definition (4.31) of adjoint operators the relations

$$m_j\langle\ell, m_\ell; s, m_s|j, m_j\rangle = (m_\ell + m_s)\,\langle\ell, m_\ell; s, m_s|j, m_j\rangle \tag{8.29}$$

and

$$\begin{aligned}&\sqrt{j(j+1)-m_j(m_j\pm 1)}\langle\ell,m_\ell;s,m_s|j,m_j\pm 1\rangle\\&=\sqrt{\ell(\ell+1)-m_\ell(m_\ell\mp 1)}\langle\ell,m_\ell\mp 1;s,m_s|j,m_j\rangle\\&\quad+\sqrt{s(s+1)-m_s(m_s\mp 1)}\langle\ell,m_\ell;s,m_s\mp 1|j,m_j\rangle.\end{aligned}\tag{8.30}$$

Equation (8.29) yields

$$\langle\ell,m_\ell;s,m_s|j,m_j\rangle=\delta_{m_\ell+m_s,m_j}\langle\ell,m_\ell;s,m_s|j,m_\ell+m_s\rangle.$$

The highest occurring value of m_j which is also the highest occurring value for j is therefore $\ell+s$, and there is only one such state. This determines the state $|\ell+s,\ell+s,\ell,s\rangle$ up to a phase factor to

$$|\ell+s,\ell+s,\ell,s\rangle=|\ell,\ell;s,s\rangle,\tag{8.31}$$

i.e. we choose the phase factor as

$$\langle\ell,\ell;s,s|\ell+s,\ell+s\rangle=1.$$

Repeated application of $j_-=l_-+s_-$ on the state (8.31) then yields all the remaining states of the form $|\ell+s,m_j,\ell,s\rangle$ or equivalently the remaining Clebsch-Gordan coefficients of the form $\langle\ell,m_\ell;s,m_s|\ell+s,m_j=m_\ell+m_s\rangle$ with $-\ell-s\le m_j<\ell+s$. For example, the next two lower states with $j=\ell+s$ are given by

$$\begin{aligned}j_-|\ell+s,\ell+s,\ell,s\rangle&=\sqrt{2(\ell+s)}|\ell+s,\ell+s-1,\ell,s\rangle\\&=\sqrt{2\ell}|\ell,\ell-1;s,s\rangle+\sqrt{2s}|\ell,\ell;s,s-1\rangle\end{aligned}$$

and

$$\begin{aligned}j_-^2|\ell+s,\ell+s,\ell,s\rangle&=2\sqrt{\ell+s}\sqrt{2(\ell+s)-1}|\ell+s,\ell+s-2,\ell,s\rangle\\&=2\sqrt{\ell(2\ell-1)}|\ell,\ell-2;s,s\rangle+4\sqrt{\ell s}|\ell,\ell-1;s,s-1\rangle\\&\quad+2\sqrt{s(2s-1)}|\ell,\ell;s,s-2\rangle.\end{aligned}\tag{8.32}$$

However, we have two states in the $|\ell,m_\ell;s,m_s\rangle$ basis with total magnetic quantum number $\ell+s-1$, but so far discovered only one state in the $|j,m_j,\ell,s\rangle$ basis with this magnetic quantum number. We can therefore construct a second state with $m_j=\ell+s-1$, which is orthogonal to the state $|\ell+s,\ell+s-1,\ell,s\rangle$,

$$|\ell+s-1,\ell+s-1,\ell,s\rangle=\sqrt{\frac{s}{\ell+s}}|\ell,\ell-1;s,s\rangle-\sqrt{\frac{\ell}{\ell+s}}|\ell,\ell;s,s-1\rangle.\tag{8.33}$$

Application of $\boldsymbol{j}^2$ would show that this state has $j = \ell + s - 1$, which was already anticipated in the notation. Repeated application of the lowering operator j_- on this state would then yield all remaining states of the form $|\ell + s - 1, m_j, \ell, s\rangle$ with $1 - \ell - s \leq m_j < \ell + s - 1$, e.g.

$$\begin{aligned}\sqrt{\ell+s-1}|\ell+s-1,\ell+s-2,\ell,s\rangle &= \sqrt{s\frac{2\ell-1}{\ell+s}}|\ell,\ell-2;s,s\rangle \\ &- \sqrt{\ell\frac{2s-1}{\ell+s}}|\ell,\ell;s,s-2\rangle + \frac{s-\ell}{\sqrt{\ell+s}}|\ell,\ell-1;s-1,s\rangle. \end{aligned} \tag{8.34}$$

We have three states with $m_j = \ell + s - 2$ in the direct product basis, *viz.* $|\ell, \ell - 2; s, s\rangle$, $|\ell, \ell; s, s - 2\rangle$ and $|\ell, \ell - 1; s - 1, s\rangle$, but so far we have only constructed two states in the combined angular momentum basis with $m_j = \ell + s - 2$, *viz.* $|\ell + s, \ell + s - 2, \ell, s\rangle$ and $|\ell + s - 1, \ell + s - 2, \ell, s\rangle$. We can therefore construct a third state in the combined angular momentum basis which is orthogonal to the other two states,

$$\begin{aligned}|\ell+s-2,\ell+s-2,\ell,s\rangle &\propto |\ell,\ell-1;s-1,s\rangle \\ &- |\ell+s,\ell+s-2,\ell,s\rangle\langle\ell+s,\ell+s-2,\ell,s|\ell,\ell-1;s-1,s\rangle \\ &- |\ell+s-1,\ell+s-2,\ell,s\rangle\langle\ell+s-1,\ell+s-2,\ell,s|\ell,\ell-1;s-1,s\rangle.\end{aligned}$$

Substitution of the states and Clebsch-Gordan coefficients from (8.32) and (8.34) and normalization yields

$$\begin{aligned}|\ell+s-2,\ell+s-2,\ell,s\rangle &= \sqrt{\frac{(2\ell-1)(2s-1)}{(2\ell+2s-1)(\ell+s-1)}}|\ell,\ell-1;s-1,s\rangle \\ &+ \frac{\sqrt{\ell(2\ell-1)}|\ell,\ell;s,s-2\rangle - \sqrt{s(2s-1)}|\ell,\ell-2;s,s\rangle}{\sqrt{(2\ell+2s-1)(\ell+s-1)}}.\end{aligned} \tag{8.35}$$

Application of j_- then yields the remaining states of the form $|\ell + s - 2, m_j, \ell, s\rangle$. This process of repeated applications of j_- and forming new states with lower j through orthogonalization to the higher j states terminates when j reaches a minimal value $j = |\ell - s|$, when all $(2\ell + 1)(2s + 1)$ states $|\ell, m_\ell; s, m_s\rangle$ have been converted into the same number of states of the form $|j, m_j, \ell, s\rangle$. In particular, we observe that there are $2 \times \min(\ell, s) + 1$ allowed values for j,

$$j \in \{|\ell - s|, |\ell - s| + 1, \ldots, \ell + s - 1, \ell + s\}. \tag{8.36}$$

The procedure to reduce the state space in terms of total angular momentum eigenstates $|j, m_j, \ell, s\rangle$ through repeated applications of j_- and orthogonalizations is lengthy when the number of states $(2\ell + 1)(2s + 1)$ is large, and the reader will certainly appreciate that Wigner [42] and Racah[4] have derived expressions for general Clebsch-Gordan coefficients. Racah derived in particular the following expression (see also [9, 34])

$$\begin{aligned}\langle \ell, m_\ell; s, m_s | j, m_j \rangle &= \delta_{m_\ell + m_s, m_j}\\ &\times \sum_{\nu=\nu_1}^{\nu_2} (-)^\nu \left(\frac{\sqrt{(2j+1)\cdot(\ell+s-j)!\cdot(j+\ell-s)!\cdot(j+s-\ell)!}}{\sqrt{(j+\ell+s+1)!}\cdot\nu!\cdot(\ell-m_\ell-\nu)!\cdot(s+m_s-\nu)!}\right.\\ &\times \left.\frac{\sqrt{(\ell+m_\ell)!\cdot(\ell-m_\ell)!\cdot(s+m_s)!\cdot(s-m_s)!\cdot(j+m_j)!\cdot(j-m_j)!}}{(j-s+m_\ell+\nu)!\cdot(j-\ell-m_s+\nu)!\cdot(\ell+s-j-\nu)!}\right).\end{aligned} \tag{8.37}$$

The boundaries of the summation are determined by the requirements

$$\max[0, s-m_\ell-j, \ell+m_s-j] \le \nu \le \min[\ell+s-j, \ell-m_\ell, s+m_s].$$

Even if we decide to follow the standard convention of using real Clebsch-Gordan coefficients, there are still sign ambiguities for every particular value of j in $|\ell - s| \le j \le \ell + s$. This arises from the ambiguity of constructing the next orthogonal state when going from completed sets of states $|j', m_{j'}, \ell, s\rangle$, $j < j' \le \ell + s$ to the next lower level j, because a sign ambiguity arises in the construction of the next orthogonal state $|j, j, \ell, s\rangle$. For example, Racah's formula (8.37) would give us the state $|\ell + s - 2, \ell + s - 2, \ell, s\rangle$ constructed before in equation (8.35), but with an overall minus sign.

Tables of Clebsch-Gordan coefficients had been compiled in the olden days, but nowadays these coefficients are implemented in commercial mathematical software programs for numerical and symbolic calculation, and there are also free online applets for the calculation of Clebsch-Gordan coefficients.

8.4 Problems

8.1. Calculate the spinor rotation matrix

$$\underline{U}(\boldsymbol{\varphi}) = \exp\left(\frac{\mathrm{i}}{2}\boldsymbol{\varphi}\cdot\underline{\boldsymbol{\sigma}}\right).$$

Hint: Use the expansion of the exponential function and consider odd and even powers of the exponent separately.

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[4] G. Racah, Phys. Rev. 62, 438 (1942).

Verify the property

$$\underline{U}(\boldsymbol{\varphi}) = -\underline{U}(\boldsymbol{\varphi} + 2\pi\hat{\boldsymbol{\varphi}}).$$

8.2. We perform a rotation of the reference frame by an angle φ around the x-axis. How does this change the coordinates of the vector $\boldsymbol{x}$? Suppose we have a spinor which has only a spin up component in the old reference frame. How large are the spin up and spin down components of the spinor with respect to the rotated z axis?

8.3. The Cartesian coordinates $\{x, y, z\}$ transform under rotations according to

$$\boldsymbol{x} \to \boldsymbol{x}' = \exp\left(\boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}}\right) \cdot \boldsymbol{x}.$$

Construct coordinates $\{X, Y, Z\}$ which transform with the matrices (8.17) under rotations,

$$\boldsymbol{X} \to \boldsymbol{X}' = \exp\left(\mathrm{i}\boldsymbol{\varphi} \cdot \underline{\boldsymbol{\Sigma}}\right) \cdot \boldsymbol{X}.$$

8.4. Construct the matrices $\langle s, m_s'|\boldsymbol{S}|s, m_s\rangle = \hbar\boldsymbol{\Sigma}_{j(m_s'),j(m_s)}$ for $s = 3/2$. Choose the index mapping $m_s \to j(m_s)$ such that

$$\underline{\Sigma}_3 = \frac{1}{2}\begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}.$$

Suppose we have an excited Lithium atom in a spin $s = 3/2$ state, which is described by the 4-component wave function $\Psi_j(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3)$, $1 \leq j \leq 4$. How does this wave function transform under a rotation around the x axis by an angle $\varphi = \pi/2$?

8.5. Construct all the states $|j, m_j, \ell = 1, s = 1/2\rangle$ as linear combinations of the tensor product states $|\ell = 1, m_\ell; s = 1/2, m_s\rangle$, using either the recursive construction from the state $|j = 3/2, m_j = 3/2, \ell = 1, s = 1/2\rangle = |\ell = 1, m_\ell = 1; s = 1/2, m_s = 1/2\rangle$ or Racah's formula (8.37). Compare with the results from a symbolic computation program or an online applet for the calculation of Clebsch-Gordan coefficients.