Week 11

PHY 303 Quantum Mechanics
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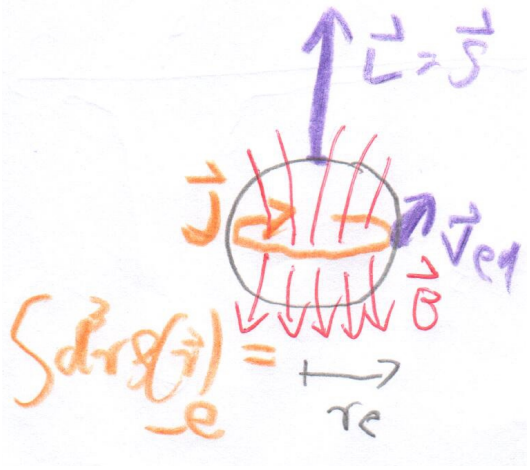
4.7 Spin

The angular momentum that we have discussed in section 4.1.2 and section 4.3 was orbital angular momentum. It arises through motion of a particle in space relative to a point, such as the electron orbiting the proton, see section 4.6. It turns out that there is also another type of angular momentum in nature, which is intrinsic to fundamental particles (and hence not related to any spatial motion as per present understanding). This is called spin, essentially for historic reasons and for an intuitive but wrong (see example 37) picture of it involving the fundamental particle spinning about its body axis.

Example 36, Experimental requirement for spin: We had learnt in PHY106 that the lines in Hydrogen spectra are due to photons of frequency ω carrying the energy that matches the difference $\hbar\omega_{nm} = (E_n - E_m)$ between two energy levels as in Eq. (4.90). It turns out that Eq. (4.90) only describes experimental observations correctly when looking on large energy scales. When zooming in onto a given spectral lines, these typically split up into multiple lines even for an isolated atom. This is called e.g. fine-structure (PHY304/402) and is not described by Eq. (4.90). One also observes that lines split into more lines when the atom is placed into a magnetic field. This is called Zeeman effect (PHY304/402). Again the splittings can usually not be explained by the states $\phi_{n\ell m}$ in Eq. (4.91). So what is going on?

Example 37, Electron as a spinning charged sphere (classical picture): Goudsmit and Uhlenbeck proposed that the electron carries an intrinsic angular momentum and magnetic moment.



left: Both could be the case if the electron was e.g. a uniformly charged sphere that is spinning about its own axis, as shown on the left. The circulating charge represents a current loop as shown, which creates a magnetic field using the right hand rule.

Example continued: You can calculate using PHY305 that the angular momentum of a sphere of mass m_e and radius r_e spinning with angular frequency ω is $S = I\omega$, with moment of inertia $I = \frac{2}{5} m_e r_e^2$. Experiments deduced that the intrinsic angular momentum of the electron has magnitude $S = \hbar\sqrt{s(s+1)}$ (compare Eq. (4.52)) with $s = \frac{1}{2}$, i.e. $S = \sqrt{3}\hbar/2$. Using $v_{eq} = \omega r_e$, with equatorial velocity v_{eq}, we find

$$v_{eq} = \frac{5\sqrt{3}}{4} \frac{\hbar}{m_e r_e}. \tag{4.99}$$

Inserting $m_e = 9.109 \times 10^{-31}$ kg and the present upper limit on the electron radius $r_e \approx 10^{-22}$ m (https://en.wikipedia.org/wiki/Electron), we find $v_{eq} \approx 8 \times 10^9 c$, for speed of light c. Clearly that cannot be right.

- The value given above is the present upper limit on r_e, however the theory presently takes the electron as a point-particle. Instead of the picture above, we thus accept the experimental evidence that it carries an intrinsic angular momentum (spin) of fixed magnitude $s = 1/2$ which we call $\hat{\mathbf{S}}$. Associated with that is an intrinsic magnetic moment $\hat{\mu} = -g\mu_B \hat{\mathbf{S}}$, where $\mu_B = e\hbar/(2m_e) = 9.27 \times 10^{-24}\ J/T$ is called the Bohr magneton, and $g \approx 2$ is called the electron g-factor.

- We know that the intrinsic quantity must be an angular momentum, because it behaves in every way like one, e.g. in conservation of angular momentum during photon emission of an atom.

- Some of you might learn later, in courses on relativistic quantum mechanics or quantum-field theory, that in order to construct a relativistic (that means Lorentz invariant) quantum theory of a charged particle like the electron, it needs to have a spin degree of freedom (its wavefunction must be a vector, not a scalar, see section 4.7.2).

4.7.1 Spin operators and states

Since we know that spin behaves just like an angular momentum, we can apply most of what we learnt earlier about orbital angular momentum (henceforth we call a non-spin angular momentum such as $\hat{\mathbf{L}}$ "orbital angular momentum", to emphasize the difference). We define the

Spin operator

$$\hat{\mathbf{S}} = [\hat{S}_x, \hat{S}_y, \hat{S}_z]^T, \tag{4.100}$$

and assume that the components of this vector operator fulfill the usual commutation relations for angular momentum, as in Eq. (4.23):

$$\left[\hat{S}_n, \hat{S}_m\right] = i\hbar \sum_\ell \epsilon_{nm\ell} \hat{S}_\ell. \tag{4.101}$$

In exact analogy to orbital angular momentum, we then also have additional

Spin commutation relations

$$\begin{aligned}
\left[\hat{S}_n, \hat{S}_m\right] &= i\hbar \sum_\ell \epsilon_{nm\ell} \hat{S}_\ell, \\
\left[\hat{\mathbf{S}}^2, \hat{S}_m\right] &= 0, \\
\left[\hat{S}_z, \hat{S}_\pm\right] &= \pm\hbar \hat{S}_\pm, \\
\left[\hat{\mathbf{S}}^2, \hat{S}_\pm\right] &= 0,
\end{aligned} \tag{4.102}$$

where we have used the spin ladder operators

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y, \tag{4.103}$$

again completely analogous to Eq. (4.57).

Since the algebraic construction of angular momentum states of section 4.4 was solely based on the angular momentum commutators, it fully applies here too. We just will replace $\ell \to s$ and $m \to m_s$, to indicate that we are dealing with spin. We also can never write a position space representation for spin states, so what earlier was $Y_\ell^m(\theta, \varphi)$ becomes $|\, s\, m_s \,\rangle$ now when dealing with spin. Hence we have the following

Spin quantum states $|\, s\, m_s \,\rangle$ (and their properties)

$$\hat{\mathbf{S}}^2|\, s\, m_s \,\rangle = \hbar^2 s(s+1)|\, s\, m_s \,\rangle, \tag{4.104}$$

$$\hat{S}_z|\, s\, m_s \,\rangle = \hbar m_s|\, s\, m_s \,\rangle, \tag{4.105}$$

$$\hat{S}_\pm|\, s\, m_s \,\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}|\, s\, (m_s \pm 1) \,\rangle, \tag{4.106}$$

with ranges $s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$ and $-s \le m_s \le s$ in integer steps.

- Recall that the discussion in section 4.4 gave us that m_s (earlier m) must range from some $-s$ to s (earlier ℓ) in integer steps. This is only possible if ℓ itself is an integer or half-integer. Hence the spin-quantum number s can take the values listed above.
- In contrast, for orbital angular momentum half-integer ℓ are excluded because these also give rise to half-integer values of m and then the $e^{im\varphi}$ part of the position representation of the angular wavefunction would not be single valued. For spin that constraint does not arise.
- It turns out that fundamental particles of a certain kind, always carry a fixed value of the spin (electrons $s = 1/2$, photons $s = 1$ (with $m_s = 0$ forbidden), quarks $s = 1/2$).

4.7.2 Spin 1/2

The list above already shows why $s = 1/2$ is the most important (and luckily simplest) case. In that case there are only two possible m_s states which we write as $|\, s = \frac{1}{2}\, m_s = \pm\frac{1}{2} \,\rangle$ or shorter $|\, \frac{1}{2}\ \pm\frac{1}{2} \,\rangle$ or even shorter $|\uparrow\rangle = |\, \frac{1}{2}\ +\frac{1}{2} \,\rangle$ (called "spin-up") and $|\downarrow\rangle = |\, \frac{1}{2}\ -\frac{1}{2} \,\rangle$ (called "spin-down"). The Hilbertspace (see section 1.5.4) of (only the) spin of a spin-1/2 particle is thus two dimensional, spanned by the two basis states $|\uparrow\rangle$ and $|\downarrow\rangle$. This makes it particularly convenient to handle everything using matrix-representations (see section 3.3), for both, operators and states.

Since our vector space is just 2D, we can use basis vectors

$$\boldsymbol{\chi}_\uparrow = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \boldsymbol{\chi}_\downarrow = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{4.107}$$

The most general quantum state for a spin-1/2 is

$$|\, \Psi \,\rangle = c_\uparrow|\uparrow\rangle + c_\downarrow|\downarrow\rangle \tag{4.108}$$

with $|c_\uparrow|^2 + |c_\downarrow|^2 = 1$. In the matrix representation we can write this as

$$\boldsymbol{\chi} = \begin{bmatrix} c_\uparrow \\ c_\downarrow \end{bmatrix} = c_\uparrow\boldsymbol{\chi}_\uparrow + c_\downarrow\boldsymbol{\chi}_\downarrow. \tag{4.109}$$

This representation of the spin wavefunction is called a spinor.

We can invert the relations (4.106) to find

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-), \qquad \hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-), \tag{4.110}$$

and then evaluate all possible matrix elements $\langle\, sm_s\,|\hat{O}|\,sm_{s'}\,\rangle$ for $s = 1/2$ and $m_s, m_{s'} \in \{1/2, -1/2\}$ for all spin operators $\hat{O}$ of interest, as we have done below. (There is only four matrix elements to evaluate for each).

Matrix representation of spin-operators

$$\underline{\underline{S_x}} = \frac{\hbar}{2}\underline{\underline{\sigma_x}}, \quad \underline{\underline{S_y}} = \frac{\hbar}{2}\underline{\underline{\sigma_y}}, \quad \underline{\underline{S_z}} = \frac{\hbar}{2}\underline{\underline{\sigma_z}}, \quad \underline{\underline{S_+}} = \hbar\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \quad \underline{\underline{S_-}} = \hbar\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \tag{4.111}$$

where we have used the Pauli matrices

$$\underline{\underline{\sigma_x}} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \underline{\underline{\sigma_y}} = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \underline{\underline{\sigma_z}} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{4.112}$$

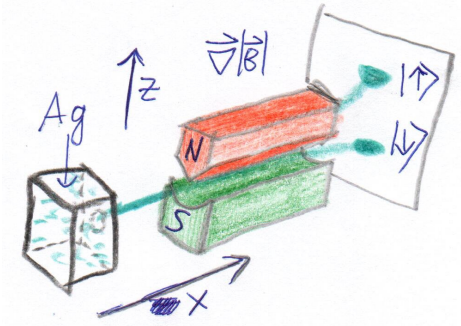
- The matrices for spin components are Hermitian as they should be, while those for ladder operator are not.
- The Pauli matrices together with the unit matrix $\mathbb{1}$ form a basis of the space of 2×2 matrices. This means we can write every operator in a 2D Hilbertspace as a sum of these matrices (operators), see also section 4.7.3.
- The eigenstates of $\hat{S}_z$ are $|\uparrow\rangle$ and $|\downarrow\rangle$ by definition.
- The matrix representations above make it easy to also find the eigenvectors for the other components, e.g. $\hat{S}_x$. In terms of eigenvectors of the matrix, these are

$$\boldsymbol{\chi}_{\leftarrow} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad \boldsymbol{\chi}_{\rightarrow} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}. \tag{4.113}$$

  with $\underline{\underline{S_x}}\boldsymbol{\chi}_{\leftarrow} = +\frac{\hbar}{2}\boldsymbol{\chi}_{\leftarrow}$ and $\underline{\underline{S_x}}\boldsymbol{\chi}_{\rightarrow} = -\frac{\hbar}{2}\boldsymbol{\chi}_{\rightarrow}$. Converted again into bra-ket notation, this means

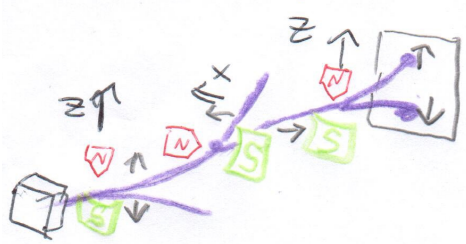
$$|\leftarrow\rangle = (|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}, \quad |\rightarrow\rangle = (|\uparrow\rangle - |\downarrow\rangle)/\sqrt{2}. \tag{4.114}$$

Example 38, Stern-Gerlach experiment: undertaken in 1922 to explore the quantization of angular momentum, see figure below. The Ag atom angular momentum is just given by the valence electron spin, hence $s = 1/2$. The magnetic moment of the atom due to the electron is $\hat{\boldsymbol{\mu}} = -g_s\mu_B\hat{\mathbf{S}}/\hbar$, in an inhomogeneous magnetic field this yields a Force $\hat{\mathbf{F}} = -\boldsymbol{\nabla}[-\hat{\boldsymbol{\mu}}\cdot\mathbf{B}]$. With magnetic field and inhomogeneity along z we reach, all up: $F_z = -g_s\mu_B\hat{S}_z\frac{\partial}{\partial z}B_z$.



left: A beam of silver atoms is directed through a region of inhomogeneous magnetic field. The resultant different forces experienced by $|\uparrow\rangle$ and $|\downarrow\rangle$ atoms split the beam up into only two discrete spots. The device has thus demonstrated quantisation of $\hat{S}_z$ *and* measured the value of $\hat{S}_z$ for each atom (depending on whether it ended up in the top spot or bottom spot).

Example 39, Repeated spin measurements: Spin states are often the simplest example to discuss the weirdness of quantum mechanics.



left: Consider a sequence of Stern-Gerlach apparatuses, as shown on the left, but with different directions for the magnetic field inhomogeneity (pointing from S to Nz). Thus in the first magnet the force depends on $\hat{S}_z$ in the second on $\hat{S}_x$ and in the third again on $\hat{S}_z$.

For an atom that ended up in the top spot after magnet 1, we know the spin state was $|\uparrow\rangle$. If we now would immediately measure $\hat{S}_z$ again, the probability to find $-\hbar/2$ would be zero. What happens in the second magnet?

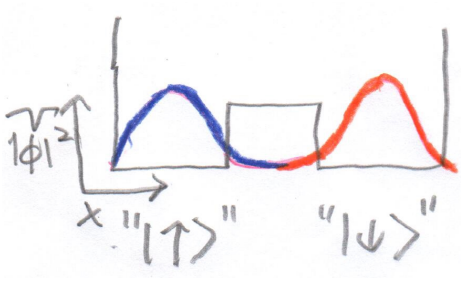
Example continued: We can use Eq. (4.114) to write $|\uparrow\rangle = (|\leftarrow\rangle + |\rightarrow\rangle)/\sqrt{2}$. Using postulate III in section 3.6 we thus know that the second magnet will measure $\hat{S}_x \simeq +\hbar/2$ (left spot) with probability 1/2 and $\hat{S}_x \simeq= -\hbar/2$ (right spot) also with probability 1/2. Now lets use the third Stern-Gerlach magnet on the left spot, where atoms were in $|\leftarrow\rangle = (|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}$. Applying postulate III in section 3.6 again, we deduce a 50-50 probability for either spin up or spin down, even though after the first magnet the probability for down was zero!!! Apparently the in between measurement of x has messed things up. It did that because $\left[\hat{S}_x, \hat{S}_x\right] \neq 0$.

The scenario in section 39 is really similar to the sequence discussed in example 24, but since the Hilbert-space for spin-1/2 is only two dimensional, the spin-example is much neater.

4.7.3 Pseudospin

Regardless of what the actual states are, any quantum mechanical system that has only two-states could be described with a vector representation of the form (4.109) and all operators on these states can be written in terms of Pauli matrices (4.112). When using this approach, one talks of a "pseudo-spin" system. That means the degree of freedom might actually not be a spin, but the math can all be handled by "thinking of" a spin system. The approach is most common for $s = 1/2$ and two-state systems, but also works for more states and higher spins.

Example 40, Coupled quantum dots: Consider two coupled quantum dots as seen in the Assignment.



left: For a more gentler design than in that assignment, we can realize a scenario where the particle is only ever in the ground-state of the left well $\phi_{1L}(x)$, or the ground state of the right well $\phi_{1R}(x)$. We can then write the wavefunction as $\Psi(x) = c_L\phi_{1L}(x) + c_R\phi_{1R}(x)$. If we simply label $\phi_{1L}(x) \simeq |\uparrow\rangle$ and $\phi_{1R}(x) \simeq |\downarrow\rangle$.

Example 41, Q-Bits: Quantum computers are based on a Q-bit, which is any quantum state with only two basis states

$$|\,\Psi\,\rangle = c_0|\,0\,\rangle + c_1|\,1\,\rangle. \tag{4.115}$$

A Q-bit is more powerful than a classical bit, since it can carry not only the information 0 versus 1 but c_0 and c_1 (i.e. complex numbers). We know from (4.108) that this could be the actual spin 1/2 of a particle, but more often one uses (meta-)stable internal states of atoms and ions, or even current quantum states of superconducting circuits.

4.8 Addition of Angular momenta

We just learnt that the electron carries intrinsic angular momentum, called spin, and learnt earlier in week 8=10 that it may also carry orbital angular momentum. Angular momentum is conserved only "alltogether", so we need to be able to add quantum mechanical angular momenta.

We assume there are two particles, labelled 1 and 2, having spin s_1 and s_2 respectively. The first one has a spin state $|\,s_1, m_{s1}\,\rangle$ and the second $|\,s_2, m_{s2}\,\rangle$. We had seen in section 4.1.3 briefly, that a state describing the position of two particles get one position variable for each. Similarly a state describing the spin of two particles, now gets the full set of spin quantum numbers for each.

We write a

Two particle spin state

$$|\,s_1, m_{s1}; s_2, m_{s2}\,\rangle = |\,s_1, m_{s1}\,\rangle \otimes |\,s_2, m_{s2}\,\rangle, \tag{4.116}$$

where $\otimes$ is the tensor product.

- We now have two spin operators, $\hat{\mathbf{S}}_1$ for particle 1 and $\hat{\mathbf{S}}_2$ for particle 2. The simplest way to understand the above state (without having to worry about the technicality "tensor

product"), is to define the state through the (hopefully logical) action of those spin operators:

$$\begin{aligned}
\hat{\mathbf{S}}_1^2|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle &= \hbar^2 s_1(s_1+1)|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle, \\
\hat{S}_{z1}|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle &= \hbar m_{s1}|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle, \\
\hat{\mathbf{S}}_2^2|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle &= \hbar^2 s_2(s_2+1)|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle, \\
\hat{S}_{z2}|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle &= \hbar m_{s2}|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle.
\end{aligned} \tag{4.117}$$

Tensor product (bonus): (simplified version). Given an arbitrary vector $\mathbf{v} \in \mathcal{V}$ in an N-dimensional vector space $\mathcal{V}$, with components v_n, and another vector $\mathbf{w} \in \mathcal{W}$ in an M-dimensional vector space $\mathcal{W}$, you can think of the tensor product $\otimes$ of these vectors as an $N \times M$ matrix

$$\mathbf{v} \otimes \mathbf{w} = \begin{bmatrix} v_1 w_1 & v_1 w_2 & \cdots & v_1 w_M \\ v_2 w_1 & v_2 w_2 & \cdots & v_2 w_M \\ \vdots & \vdots & \ddots & \vdots \\ v_N w_1 & v_N w_2 & \cdots & v_n w_M \end{bmatrix} \tag{4.118}$$

The space of all these matrices is itself a vector-space again, written $\mathcal{V} \otimes \mathcal{W}$, and called the tensor product of $\mathcal{V}$ and $\mathcal{W}$. We can repeat the operation to add a third "dimension" to the matrix (making it a cube of numbers, rather than a square) etc., thus generating even higher dimensional objects than Matrices (ND arrays).
After forming (4.118) we can turn $\mathbf{v} \otimes \mathbf{w}$ again into a vector (in a $N \times M$ dimensional space), by reshaping:

$$\mathbf{v} \otimes \mathbf{w} = \begin{bmatrix} v_1 w_1 & v_1 w_2 & \cdots & v_1 w_M & v_2 w_1 & v_2 w_2 & \cdots & v_n w_{M-1} & v_n w_M \end{bmatrix}^T. \tag{4.119}$$

- For a more rigorous mathematical definition, see math courses.
- For the present course, knowing the dotpoints above the yellow box should be sufficient.

From the two single spin operators, we can define

Total spin operators

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2. \tag{4.120}$$

From this we find $\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$ and

$$\hat{S}^{\pm} = \hat{S}_1^{\pm} + \hat{S}_2^{\pm}. \tag{4.121}$$

- Here $\hat{\mathbf{S}}$ describes the total spin of the two particles, and hence $\hat{S}_z$ the total z-component.

- Using the definition (4.106) to find ladder operators for the total spin, we can see that these decompose into ladder operators for the sub-spins.

Now we want to find what the action of the total spin operators (4.120) onto basis states such as (4.116) is, in order to re-label those with some quantum numbers that pertain to the total spin, instead of the individual spins. For the z-component, this is easy:

$$\hat{S}_z|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle = (\hat{S}_{z1}+\hat{S}_{z2})|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle \overset{Eq.\ (4.117)}{=} \hbar \underbrace{(m_{s1}+m_{s2})}_{\equiv m_s} |\, s_1, m_{s1}; s_2, m_{s2}\,\rangle. \tag{4.122}$$

Apparently the state is an eigenstate of $\hat{S}_z$ with eigenvalue $\hbar m_s$ where $m_s = m_{s1} + m_{s2}$ is the quantum number for the total z-component. Unfortunately $\hat{\mathbf{S}}^2$ turns out a little more complicated. We follow Griffith and sort this with the example of

Example 42, Addition of two spin 1/2: We can use the notation of section 4.7.2. The advantage of $s_1 = s_2 = 1/2$ is that it is easy to list all the possible spin states of the kind (4.116), and their resultant total m_s:

$$\begin{aligned}
|\, s_1 = \frac{1}{2}, m_{s1} = \frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = \frac{1}{2}\,\rangle &= |\uparrow\uparrow\rangle, \quad m_s = 1,\\
|\, s_1 = \frac{1}{2}, m_{s1} = \frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = -\frac{1}{2}\,\rangle &= |\uparrow\downarrow\rangle, \quad m_s = 0,\\
|\, s_1 = \frac{1}{2}, m_{s1} = -\frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = \frac{1}{2}\,\rangle &= |\downarrow\uparrow\rangle, \quad m_s = 0,\\
|\, s_1 = \frac{1}{2}, m_{s1} = -\frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = -\frac{1}{2}\,\rangle &= |\downarrow\downarrow\rangle, \quad m_s = -1.
\end{aligned} \tag{4.123}$$

Given that the total z-component ranges over $m_s = -1, 0, 1$ and considering our earlier rules $-\ell \le m \le \ell$, we might suspect that a total angular momentum (spin) of $s = 1$ is in the picture. But we have one state too many.
To figure out why, let us successively apply the total lowering operator $\hat{S}^-$ from (4.121) to the state $|\uparrow\uparrow\rangle$. In the first step we find

$$\hat{S}^-|\uparrow\uparrow\rangle \overset{Eq.\ (4.121)}{=} \left(\hat{S}_1^-|\uparrow\rangle\right)|\uparrow\rangle + |\uparrow\rangle\left(\hat{S}_2^-|\uparrow\rangle\right) \overset{Eq.\ (4.106)}{=} (\hbar|\downarrow\rangle)|\uparrow\rangle + |\uparrow\rangle(\hbar|\downarrow\rangle). \tag{4.124}$$

Fixing the normalisation again[a], we write the resultant state as $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$. Applying $\hat{S}^-$ one more time gets us into $|\downarrow\downarrow\rangle$ and any further time gives 0 (exercise). What happened to the fourth state from (4.123)? We can form one more linear combination out of the middle ones: $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$. Here, applying either $\hat{S}^-$ or $\hat{S}^+$ gives zero (exercise). This looks suspiciously like angular momentum zero: $s = 0$, for which the only allowed m_s would be zero.

[a] The rule for many-body states is: whenever the quantum numbers are different for any of the constituents, the states are orthogonal. E.g. $\langle\uparrow\uparrow|\uparrow\downarrow\rangle = 0$

Example continued: You can indeed show (Griffith), that $\hat{\mathbf{S}}^2|\uparrow\uparrow\rangle = \hbar^2 s(s+1)|\uparrow\uparrow\rangle$ with $s = 1$ and similarly for the other two states we obtained above by applying the lowering operator, while $\hat{\mathbf{S}}^2(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2} = 0$. We call the former three triplet states and the last one singlet state, and can now re-relabel them as originally planned with quantum numbers s and m_s for the combined spin state:

$$\begin{aligned} |\, s = 1, m_s = 1 \,\rangle &= |\uparrow\uparrow\rangle, \\ |\, s = 1, m_s = 0 \,\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \\ |\, s = 1, m_s = -1 \,\rangle &= |\downarrow\downarrow\rangle, \\ |\, s = 0, m_s = 0 \,\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \end{aligned} \tag{4.125}$$

Effectively switching between $|\, s m_s \,\rangle$ and $|\, s_1, m_{s1}; s_2, m_{s2} \,\rangle$ is just a basis change from an individual spin basis to a combined spin basis.

Without doing the proof for that, we now state the result for any other values of s_1 and s_2:

General addition of spins When describing two spins s_1 and s_2 with a combined basis, the total spin quantum number s can vary over the entire range:

$$s = s_1 + s_2, s_1 + s_2 - 1, \cdots, |s_1 - s_2|, \tag{4.126}$$

in integer steps. For a given s, the z-component quantum number m_s takes the usual range $-s \leq m_s \leq s$.
We can always write the combined basis states as a sum of the individual basis states:

$$|\, s\, m_s \,\rangle = \sum_{m_1, m_2; m_1 + m_2 = m} C^{(s_1 s_2; s)}_{(m_1, m_2; m)} |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle \tag{4.127}$$

where the coefficients $C^{(s_1 s_2; s)}_{(m_1, m_2; m)}$ are called Clebsch-Gordon coefficients.

- While we wrote "addition of spins" in the above, the same scheme works for the addition of orbital angular momenta $\hat{\mathbf{L}}_1$ and $\hat{\mathbf{L}}_2$ or the addition of an orbital angular momentum $\hat{\mathbf{L}}$ and a spin $\hat{\mathbf{S}}$.
- You can find algorithms on how to calculate any Clebsch-Gordon coefficients in the more advanced books. Or you might nowadays just want to use an online calculator for them, such as e.g. https://www.volya.net/index.php?id=vc .
- You can visualise the range (4.126) somewhat through the addition of 3D vectors: The magnitude of $\mathbf{v} = \mathbf{w}_1 + \mathbf{w}_2$ is largest when the two constituent vectors are parallel, in which case $|\mathbf{v}| = |\mathbf{w}_1| + |\mathbf{w}_2|$. It is smallest when they are antiparallel, in which case $|\mathbf{v}| = |\mathbf{w}_1| - |\mathbf{w}_2|$ if $|\mathbf{w}_1| > |\mathbf{w}_2|$. You can find diagrams carrying this visualisation further in many books.