Chapter 7

Spin and Spin–Addition

7.1 Stern-Gerlach Experiment – Electron Spin

In 1922, at a time, the hydrogen atom was thought to be understood completely in terms of Bohr's atom model, two assistants at the University of Frankfurt, Otto Stern and Walther Gerlach, performed an experiment which showed that the electrons carry some intrinsic angular momentum, the spin, which is quantized in two distinct levels. This was one of the most important experiments done in the twentieth century, as its consequences allowed for many interesting experimental and theoretical applications.

7.1.1 Electron in a Magnetic Field

To fully understand the concept of spin, we start by reviewing the some properties of a classical charged particle rotating about its own symmetry axis. The angular momentum due to this rotation, let us call it $\vec{S}$, will create a magnetic dipole moment $\vec{\mu}$, proportional to the angular momentum

$$\vec{\mu} \,=\, \gamma\, \vec{S} \,=\, g\, \frac{q}{2\, m\, c}\, \vec{S}\,, \tag{7.1}$$

where γ is the *gyromagnetic ratio* and g is just called *g-factor*. For the electron we have

$$\vec{\mu} \,=\, \gamma_{\mathrm{e}}\, \vec{S} \,=\, -\, g_{\mathrm{e}}\, \frac{e}{2\, m_{\mathrm{e}}\, c}\, \vec{S} \,=\, -\, g_{\mathrm{e}}\, \frac{\mu_{\mathrm{B}}}{\hbar}\, \vec{S}\,. \tag{7.2}$$

The g-factor of the electron equals two, $g_{\mathrm{e}} = 2$, although for a classical angular momentum, it should be equal to 1. The fact, that the spin of the electron contributes twice as strong to the magnetic moment as its orbital angular momentum, is called the *anomalous magnetic moment* of the electron. The constant μ_{B} is known as *Bohr's magneton*[1].

If such a magnetic dipole is subject to an external (homogeneous) magnetic field $\vec{B}$ it starts to precess, due to the torque $\vec{\Gamma}$, known as the *Larmor torque*, exerted by the magnetic field

$$\vec{\Gamma} \,=\, \vec{\mu} \,\times\, \vec{B} \,=\, \gamma\, \vec{S} \,\times\, \vec{B}\,, \tag{7.3}$$

[1]Bohr's magneton is here given in Gaussian CGS units. In SI-units it looks the same, but the speed of light is removed, $\mu_{\mathrm{B}} = \frac{e\hbar}{2m_{\mathrm{e}}}$.

The potential energy corresponding to this torque is given by

$$H \;=\; -\,\vec{\mu}\,\vec{B}\,. \tag{7.4}$$

Thus the Hamiltonian for a particle with spin in an exterior magnetic field of strength $\vec{B}$ is of the form

$$H \;=\; -\,\gamma\,\vec{S}\,\vec{B}\,. \tag{7.5}$$

7.1.2 Stern-Gerlach Experiment

In the Stern-Gerlach experiment silver atoms, carrying no orbital angular momentum but with a single electron opening up a new s-orbital[2] ($l = 0$), were sent through a special magnet which generates an inhomogeneous magnetic field, see Fig. 7.1. The properties

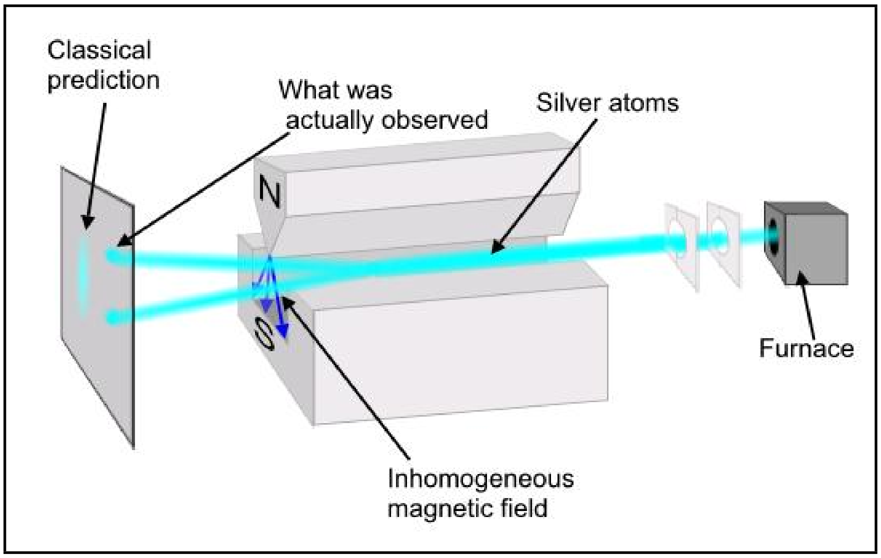

Figure 7.1: Stern-Gerlach Experiment: The inhomogeneous magnetic field exerts a force on the silver atoms, depending on the spin z-component. Classically a continuous distribution is expected, but the experiment reveals only two values of the spin z-component. Figure from: http://en.wikipedia.org/wiki/Image:Stern-Gerlach_experiment.PNG

of the silver atom in this state are such that the atom takes over the intrinsic angular momentum, i.e. spin, of this outermost single electron.

The inhomogenity of the magnetic field causes a force $\vec{F}$ acting on the magnetic dipole in addition to the torque

$$\vec{F} \;=\; -\,\vec{\nabla}\,V \;=\; \vec{\nabla}\,(\vec{\mu}\,\vec{B})\,, \tag{7.6}$$

[2]This notation is often used in spectroscopy, where one labels the states of different angular momenta by s ("sharp", $l = 0$), p ("principal", $l = 1$), d ("diffuse", $l = 2$), f ("fundamental", $l = 3$) and alphabetically from there on, i.e. g,h,i,...; Every azimuthal quantum number is degenerate in the sense that it allows for $2 \cdot (2l + 1)$ bound electrons, which together are called an orbital.

where $V = H$ if the particle is at rest. Since the force depends on the value of the spin, it can be used to separate different spins. Classically, the prediction would be a continuous distribution, bounded by two values, representing spins parallel and antiparallel to the direction of the magnetic field. All the spins which are not perfectly (anti-)aligned with the magnetic field would be expected to have components in that direction that lie in between these maximal and minimal values. We can write the magnetic field as a homogeneous and an inhomogeneous part, such that it is oriented parallel to the z-axis, i.e. $B_{\text{x}} = B_{\text{y}=0}$,

$$\vec{B} \,=\, B_{\text{z}}\,\vec{e}_{\text{z}} \,=\, (B_{\text{hom}} \,+\, \alpha\, z)\,\vec{e}_{\text{z}}\,. \tag{7.7}$$

The force can then be expressed via the z-component of the spin $\vec{S}$, which in the quantum mechanical formalism will be an operator

$$F_{\text{z}} \,=\, \alpha\,\gamma\,S_{\text{z}}\,. \tag{7.8}$$

The separation of the particles with different spin then reveals experimentally the eigenvalues of this operator.

The result of the experiment shows that the particles are equally distributed among two possible values of the spin z-component, half of the particles end up at the upper spot ("spin up"), the other half at the lower spot ("spin down"). Spin is a angular momentum observable, where the degeneracy of a given eigenvalue l is $(2l+1)$. Since we observe two possible eigenvalues for the spin z-component (or any other direction chosen), see Fig. 7.2, we conclude the following value for s

$$2\,s \,+\, 1 \,=\, 2 \quad \Rightarrow \quad s \,=\, \frac{1}{2}\,. \tag{7.9}$$

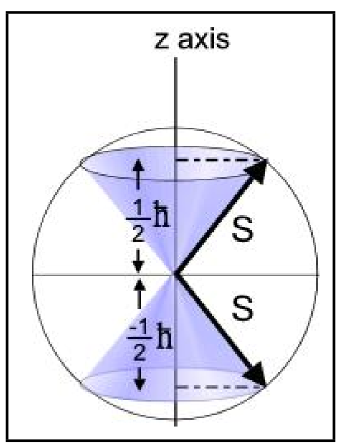

Figure 7.2: Spin $\frac{1}{2}$: The spin component in a given direction, usually the z-direction, of a spin $\frac{1}{2}$ particle is always found in either the eigenstate "$\uparrow$" with eigenvalue $+\frac{1}{2}$ or "$\downarrow$" with eigenvalue $-\frac{1}{2}$. Figure from: http://en.wikipedia.org/wiki/Image:Quantum_projection_of_S_onto_z_for_spin_half_particles.PNG

Result: Two additional quantum numbers are needed to characterize the nature of the electron, the *spin quantum number* s and the *magnetic spin quantum number* $m_s = -s, \cdots, +s$. We conclude: ***spin is quantized*** and the eigenvalues of the corresponding observables are given by

$$S_z \rightarrow \hbar\, m_s \,=\, \pm\frac{\hbar}{2} \quad , \quad \vec{S}^2 \,\rightarrow\, \hbar^2\, s\,(s\,+\,1) \,=\, \frac{3}{4}\,\hbar^2 \,. \tag{7.10}$$

The spin measurement is an example often used to describe a typical quantum mechanical measurement. Let us therefore elaborate this example in more detail. Consider a source emitting spin $\frac{1}{2}$ particles in an unknown spin state. The particles propagate along the y-axis and pass through a spin measurement apparatus, realized by a Stern-Gerlach magnet as described in Fig. 7.1, which is oriented along the z-axis, see Fig. 7.3.

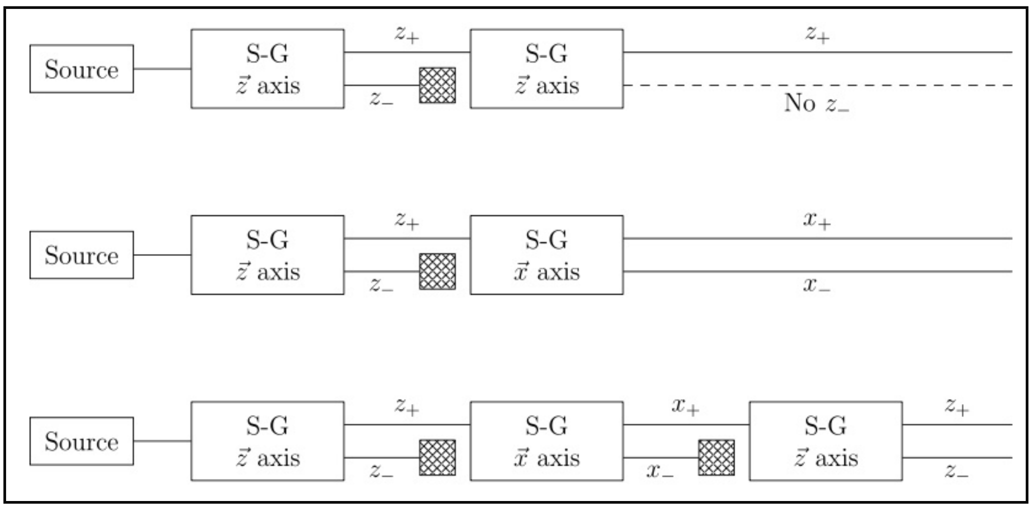

Figure 7.3: Spin $\frac{1}{2}$ measurement: Spin measurements change the state of the particles, if they are not in an eigenstate of the corresponding operator. Therefore subsequent measurements along perpendicular directions produce random results. Figure from: http://en.wikipedia.org/wiki/Image:Sg-seq.svg

All particles leaving the Stern-Gerlach apparatus are then in an eigenstate of the S_z operator, i.e., their spin is either "up" or "down" with respect to the z-direction. Let's now concentrate on the "spin up" particles (in z-direction), that means we block up the "spin down" in some way, and perform another spin measurement on this part of the beam. If the second measurement is also aligned along the z-direction then all particles will provide the result "spin up", since they are all already in an eigenstate of S_z (see the upper part of Fig. 7.3). The measurement of a particle being in an eigenstate of the corresponding operator leaves the state unchanged, therefore no particle will "flip" its spin.

If, however, we perform the spin measurement along a direction perpendicular to the z-axis, let's choose the x-axis, then the results will be equally distributed among "spin up" or "spin down" in x-direction (see the middle part of Fig. 7.3). Thus, even though we knew the state of the particles beforehand, in this case the measurement resulted in a random spin flip in either of the measurement directions. Mathematically, this property is expressed by the nonvanishing of the commutator of the spin operators

$$[\, S_{\mathrm{z}} \, , \, S_{\mathrm{x}} \,] \neq 0 \, . \tag{7.11}$$

If we finally repeat the measurement along the z-direction the result will be random again (see the lower part of Fig. 7.3). We do not obtain precise information about the spin in different directions at the same time, due to the nonvanishing of the commutator (7.11) there holds an uncertainty relation for the spin observables.

Of course, we could also choose an orientation of the Stern-Gerlach magnet along some arbitrary direction. Let us assume we rotate the measurement apparatus by an angle θ (in the $z - x$ plane), then the probability P_+ to find the particle with "spin up" and P_- to find the particle with "spin down" (along this new direction) is given by

$$P_+ \, = \, \cos^2 \frac{\theta}{2} \quad \text{and} \quad P_- \, = \, \sin^2 \frac{\theta}{2} \, , \quad \text{such that} \quad P_+ \, + \, P_- \, = \, 1 \, . \tag{7.12}$$

7.2 Mathematical Formulation of Spin

Now we turn to the theoretical formulation of spin. We will describe spin by an operator, more specifically by a 2×2 matrix, since it has two degrees of freedom and we choose convenient matrices which are named after Wolfgang Pauli.

7.2.1 The Pauli–Matrices

The *spin observable* $\vec{S}$ is mathematically expressed by a vector whose components are matrices

$$\vec{S} \, = \, \frac{\hbar}{2} \, \vec{\sigma} \, , \tag{7.13}$$

where the vector $\vec{\sigma}$ contains the so-called ***Pauli matrices*** $\sigma_{\mathrm{x}}, \sigma_{\mathrm{y}}, \sigma_{\mathrm{z}}$:

$$\vec{\sigma} \, = \, \begin{pmatrix} \sigma_{\mathrm{x}} \\ \sigma_{\mathrm{y}} \\ \sigma_{\mathrm{z}} \end{pmatrix} \, , \; \sigma_{\mathrm{x}} \, = \, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \, , \; \sigma_{\mathrm{y}} \, = \, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \, , \; \sigma_{\mathrm{z}} \, = \, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \, . \tag{7.14}$$

Then the spin vector $\vec{S}$ (or the Pauli vector $\vec{\sigma}$) can be interpreted as the generator of rotations (remember Theorem 6.1) in the sense that there is a unitary operator $U(\theta)$

$$U(\theta) \, = \, e^{\frac{i}{\hbar} \vec{\theta} \vec{S}} \, = \, \mathbb{1} \, \cos \frac{\theta}{2} \, + \, i \, \hat{n} \, \vec{\sigma} \, \sin \frac{\theta}{2} \, , \tag{7.15}$$

generating rotations around the $\vec{\theta}$-axis by an angle $|\vec{\theta}|$ of the state vectors in Hilbert space. The scalar product $\vec{\theta} \vec{\sigma}$ is to be understood as a matrix

$$\vec{\theta} \vec{\sigma} \, = \, \theta_{\mathrm{x}} \, \sigma_{\mathrm{x}} \, + \, \theta_{\mathrm{y}} \, \sigma_{\mathrm{y}} \, + \, \theta_{\mathrm{z}} \, \sigma_{\mathrm{z}} \, . \tag{7.16}$$

What's very interesting to note here is the fact that a spin $\frac{1}{2}$ particle has to be rotated by $2 \times 2\pi = 4\pi$ (!) in order to become the same state, very much in contrast to our classical expectation. It is due to the factor $\frac{1}{2}$ in the exponent. This very interesting quantum feature has been experimentally verified by the group of Helmut Rauch [16] using neutron interferometry.

7.2.2 Spin Algebra

Since spin is some kind of angular momentum we just use again the Lie algebra [3], which we found for the angular momentum observables, and replace the operator $\vec{L}$ by $\vec{S}$

$$[\, S_i \, , \, S_j \,] \; = \; i\hbar \, \epsilon_{ijk} \, S_k \; . \tag{7.17}$$

The spin observable squared also commutes with all the spin components, as in Eq. (6.19)

$$\left[\vec{S}^{\,2} \, , \, S_i \right] \; = \; 0 \; . \tag{7.18}$$

Still in total analogy with Definition 6.1 we can construct ladder operators $S_\pm$

$$S_\pm \; := \; S_\mathrm{x} \, \pm \, i \, S_\mathrm{y} \, , \tag{7.19}$$

which satisfy the analogous commutation relations as before (see Eqs. (6.21) and (6.23))

$$[\, S_\mathrm{z} \, , \, S_\pm \,] \;\; = \;\; \pm \, \hbar \, S_\pm \tag{7.20}$$

$$[\, S_+ \, , \, S_- \,] \;\; = \;\; 2 \, \hbar \, S_\mathrm{z} \; . \tag{7.21}$$

The operators now act on the space of (2 component) spinor states, a two–dimensional Hilbert space which is equipped with a basis of eigenstates $|\, s \, , \, m_\mathrm{s} \,\rangle$, labeled by their eigenvalues s and m_s of $\vec{S}^{\,2}$ and S_z respectively

$$\left|\, \tfrac{1}{2} \, , \, \tfrac{1}{2} \,\right\rangle \equiv |\!\uparrow\rangle \quad , \quad \left|\, \tfrac{1}{2} \, , \, -\tfrac{1}{2} \,\right\rangle \equiv |\!\downarrow\rangle \; . \tag{7.22}$$

These two states, we call them "up" and "down", are eigenstates of the σ_z Pauli matrix, which we can interpret as the spin observable in z-direction, with eigenvalues $+1$ and -1

$$\sigma_\mathrm{z} \, |\!\uparrow\rangle \;\; = \;\; + \, |\!\uparrow\rangle \tag{7.23}$$

$$\sigma_\mathrm{z} \, |\!\downarrow\rangle \;\; = \;\; - \, |\!\downarrow\rangle \; . \tag{7.24}$$

[3] Remark for experts: The Lie algebra we studied earlier was that of the three–dimensional rotation group $SO(3)$, the group of orthogonal (hence the "O") 3×3 matrices with determinant 1 (which is indicated by "S" for "special"), while we here are studying the group $SU(2)$, the group of unitary 2×2 matrices with determinant 1. The fact that these two Lie algebras look identical is not a mere coincidence, but is due to the fact that $SU(2)$ is the so called universal covering group of $SO(3)$ relating those groups in a very close way.

The eigenstates are orthogonal and normalized, i.e.

$$\langle \uparrow | \downarrow \rangle = 0 \quad , \quad \langle \uparrow | \uparrow \rangle = \langle \downarrow | \downarrow \rangle = 1 \, . \tag{7.25}$$

Let's now gather the established facts to find a representation of the operators on the aforesaid 2–dimensional Hilbert space by noting that we are looking for a hermitian 2×2 matrix with eigenvalues ± 1, which is trivially satisfied by choosing

$$\sigma_{\rm z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \tag{7.26}$$

The eigenstates take the form

$$| \uparrow \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad | \downarrow \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \tag{7.27}$$

We then construct ladder operators from the Pauli matrices, i.e.

$$\sigma_{\pm} = \sigma_{\rm x} \pm i \, \sigma_{\rm y} \, , \tag{7.28}$$

which satisfy the spin algebra (recall Eq. (7.17) or Eq. (7.20))

$$[\, \sigma_{\rm z} \, , \, \sigma_{\pm} \,] = \pm 2 \, \sigma_{\pm} \, . \tag{7.29}$$

Since the following relations hold true for the ladder operators

$$\sigma_- \, | \uparrow \rangle = 2 \, | \downarrow \rangle \tag{7.30}$$

$$\sigma_+ \, | \downarrow \rangle = 2 \, | \uparrow \rangle \tag{7.31}$$

$$\sigma_- \, | \downarrow \rangle = \sigma_+ \, | \uparrow \rangle = 0 \, , \tag{7.32}$$

we can represent them as

$$\sigma_+ = 2 \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad , \quad \sigma_- = 2 \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} . \tag{7.33}$$

We then easily get the representation of $\sigma_{\rm x}$ and $\sigma_{\rm y}$ from Eq. (7.28)

$$\sigma_{\rm x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \sigma_{\rm y} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} . \tag{7.34}$$

Properties of the Pauli matrices:

The Pauli matrices satisfy a Lie algebra

$$[\, \sigma_{\rm i} \, , \, \sigma_{\rm j} \,] = 2 \, i \, \epsilon_{\rm ijk} \, \sigma_{\rm k} \; , \tag{7.35}$$

their square is the identity (in two dimensions) and they are traceless

$$\sigma_i^2 = \mathbb{1} \quad , \quad \mathrm{Tr}\,\sigma_i = 0 \,. \tag{7.36}$$

Furthermore, an interesting property arises if one considers not only the square of the Pauli matrices, but the following object

$$(\vec{\sigma}\,\vec{A})\,(\vec{\sigma}\,\vec{B}) = \vec{A}\,\vec{B} + i\,\vec{\sigma}\,(\vec{A} \times \vec{B}) \,. \tag{7.37}$$

If we e.g. set $\vec{A} = \vec{B} = \vec{P}$ in Eq. (7.37) the cross product on the right side vanishes and we can express the kinetic energy as

$$\frac{\vec{p}^{\,2}}{2m} = \frac{(\vec{\sigma}\vec{p})^2}{2m} \,. \tag{7.38}$$

It turns out to be actually the correct way to include spin into the kinetic part of the Schrödinger equation.

7.2.3 Spin Measurements

Let us now verify on the theoretical side the conclusions about the spin measurements which we presented in Fig. 7.3. So we assume to have already performed a measurement in the z-direction and thus obtained a particle in the "up" state $|\uparrow\rangle$. If we again perform a measurement in the same direction, which means we apply the operator σ_z on the state $|\uparrow\rangle$, we always get the result +1

$$\langle\uparrow|\underbrace{\sigma_z\,|\uparrow\rangle}_{+1\,|\uparrow\rangle} = \langle\uparrow|\uparrow\rangle = 1 \,. \tag{7.39}$$

It is easily verified that we will always get the result −1 if we perform the same measurement in the state $|\downarrow\rangle$.

Let us now consider a spin measurement in x-direction on that "up" state

$$\langle\uparrow|\underbrace{\sigma_x\,|\uparrow\rangle}_{|\downarrow\rangle} = \langle\uparrow|\downarrow\rangle = 0 \,. \tag{7.40}$$

What we find is that, though individual results give ±1, on average we find a zero result. The reason is that each individual result +1 or −1 occurs exactly to 50% of the total outcome. That the individual measurements give ±1 is obvious since these are the eigenvalues of σ_x. The corresponding eigenfunctions are given by

$$|+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \quad , \quad |-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} \,. \tag{7.41}$$

7.3 Two Particles with Spin $\frac{1}{2}$

In this section we show how to describe a system of two particles with spin, how to combine the two spins. The addition of the two spins of the constituent particles works in the same way as the addition of any other angular momenta. To describe the states of the combined spin we need the ***tensor product*** operation "$\otimes$", which expresses a product between elements of different (Hilbert) spaces, e.g. $\mathcal{H}^{\mathrm{A}}$, $\mathcal{H}^{\mathrm{B}}$. These tensor products form an element of a larger (Hilbert) space $\mathcal{H}^{\mathrm{AB}}$, where

$$\mathcal{H}^{\mathrm{AB}} = \mathcal{H}^{\mathrm{A}} \otimes \mathcal{H}^{\mathrm{B}} . \tag{7.42}$$

To give this a little more substance, let us consider two spin $\frac{1}{2}$ particles that each can be in either of the states $\uparrow$ or $\downarrow$. Then we conclude that there are 4 different ways to combine these states: $\uparrow\uparrow$, $\uparrow\downarrow$, $\downarrow\uparrow$, and $\downarrow\downarrow$, which we construct by using the tensor product operation (in the notation the tensor product $\otimes$ is often omitted for brevity)

$$|\uparrow\rangle \otimes |\uparrow\rangle = |\uparrow\rangle\,|\uparrow\rangle = |\uparrow\uparrow\rangle \tag{7.43}$$

$$|\uparrow\rangle \otimes |\downarrow\rangle = |\uparrow\rangle\,|\downarrow\rangle = |\uparrow\downarrow\rangle \tag{7.44}$$

$$|\downarrow\rangle \otimes |\uparrow\rangle = |\downarrow\rangle\,|\uparrow\rangle = |\downarrow\uparrow\rangle \tag{7.45}$$

$$|\downarrow\rangle \otimes |\downarrow\rangle = |\downarrow\rangle\,|\downarrow\rangle = |\downarrow\downarrow\rangle \,. \tag{7.46}$$

Let us now try to define the spin operators for the composite system by looking at the tensor product structure of the Hilbert space (see Eq. (7.42)). Since we know the individual spin operators $\vec{S}^{\,(\mathrm{A})}$ and $\vec{S}^{\,(\mathrm{B})}$ acting in $\mathcal{H}^{\mathrm{A}}$ or $\mathcal{H}^{\mathrm{B}}$ respectively, we construct the composite spin operator such that the individual operators are acting in their respective subspace, i.e. we set

$$\vec{S}^{\,(\mathrm{AB})} = \vec{S}^{\,(\mathrm{A})} \otimes \mathbb{1}^{\,(\mathrm{B})} + \mathbb{1}^{\,(\mathrm{A})} \otimes \vec{S}^{\,(\mathrm{B})} = \vec{S}^{\,(\mathrm{A})} + \vec{S}^{\,(\mathrm{B})} \,. \tag{7.47}$$

In total analogy we construct the operator for the spin component in z-direction as

$$S_{\mathrm{z}}^{(\mathrm{AB})} = S_{\mathrm{z}}^{(\mathrm{A})} \otimes \mathbb{1}^{\,(\mathrm{B})} + \mathbb{1}^{\,(\mathrm{A})} \otimes S_{\mathrm{z}}^{(\mathrm{B})} = S_{\mathrm{z}}^{(\mathrm{A})} + S_{\mathrm{z}}^{(\mathrm{B})} \,. \tag{7.48}$$

Next we calculate the spin z-component of the vector $\uparrow\uparrow$ (Eq. (7.43)) by using the relations discussed above, in particular Eqs. (7.23), (7.24) and Eq. (7.13)

$$\begin{aligned} S_{\mathrm{z}}^{(\mathrm{AB})}\,|\uparrow\uparrow\rangle &= \big(S_{\mathrm{z}}^{(\mathrm{A})} + S_{\mathrm{z}}^{(\mathrm{B})}\big)\,|\uparrow\rangle \otimes |\uparrow\rangle = \\ &= (S_{\mathrm{z}}^{(\mathrm{A})}\,|\uparrow\rangle) \otimes |\uparrow\rangle + |\uparrow\rangle \otimes (S_{\mathrm{z}}^{(\mathrm{B})}\,|\uparrow\rangle) = \\ &= (\frac{\hbar}{2}\,|\uparrow\rangle) \otimes |\uparrow\rangle + |\uparrow\rangle \otimes (\frac{\hbar}{2}\,|\uparrow\rangle) = \\ &= (\frac{\hbar}{2} + \frac{\hbar}{2})\,|\uparrow\rangle \otimes |\uparrow\rangle = \hbar\,|\uparrow\uparrow\rangle \,. \end{aligned} \tag{7.49}$$

Using the same methods, for the other combinations (Eqs. (7.44) - (7.46)), we find

$$S_{\mathrm{z}}\,|\downarrow\downarrow\rangle = -\hbar\,|\downarrow\downarrow\rangle \tag{7.50}$$

$$S_{\mathrm{z}}\,|\uparrow\downarrow\rangle = S_{\mathrm{z}}\,|\downarrow\uparrow\rangle = 0 \,, \tag{7.51}$$

where we dropped the label AB for ease of notation. If not indicated otherwise the operators now always act on the total space, analogously to Eqs. (7.47) and (7.48). Unluckily, these naive combinations of two spins, although eigenstates of the S_z operator, are not all of them simultaneous eigenstates of the squared spin operator $\vec{S}^{\,2}$. The operator $\vec{S}^{\,2}$ we now express in terms of tensor products

$$\begin{aligned} \vec{S}^{\,2} &= (\vec{S}^{\,(AB)})^2 = \left(\vec{S}^{\,(A)} \otimes \mathbb{1}^{(B)} + \mathbb{1}^{(A)} \otimes \vec{S}^{\,(B)}\right)^2 = \\ &= (\vec{S}^{\,(A)})^2 \otimes \mathbb{1}^{(B)} + 2\,\vec{S}^{\,(A)} \otimes \vec{S}^{\,(B)} + \mathbb{1}^{(A)} \otimes (\vec{S}^{\,(B)})^2 \,. \end{aligned} \tag{7.52}$$

We calculate $(\vec{S}^{\,(A)})^2$ by using a property of the Pauli matrices Eq. (7.36)

$$(\vec{S}^{\,(A)})^2 = \frac{\hbar^2}{4}\left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right) = \frac{\hbar^2}{4}\,3\,\mathbb{1} = \frac{3}{4}\,\hbar^2 \,. \tag{7.53}$$

Using this result we rewrite Eq. (7.52)

$$\begin{aligned} \vec{S}^{\,2} &= \frac{3}{4}\hbar^2\,\mathbb{1}^{(A)} \otimes \mathbb{1}^{(B)} + 2\,\vec{S}^{\,(A)} \otimes \vec{S}^{\,(B)} + \frac{3}{4}\hbar^2\,\mathbb{1}^{(A)} \otimes \mathbb{1}^{(B)} = \\ &= \frac{\hbar^2}{4}\left[\,6\,\mathbb{1} \otimes \mathbb{1} + 2\,(\sigma_x \otimes \sigma_x + \sigma_y \otimes \sigma_y + \sigma_z \otimes \sigma_z)\right] \,. \end{aligned} \tag{7.54}$$

Computing the action of $\vec{S}^{\,2}$ on our spin states (Eqs. (7.43) - (7.46)) we find that, though $\uparrow\uparrow$ and $\downarrow\downarrow$ are indeed also eigenstates of $\vec{S}^{\,2}$ corresponding to a quantum number $s = 1$

$$\begin{aligned} \vec{S}^{\,2}\,|\!\uparrow\uparrow\rangle &= \frac{\hbar^2}{4}\left[\,6\,\mathbb{1} \otimes \mathbb{1} + 2\,(\sigma_x \otimes \sigma_x + \sigma_y \otimes \sigma_y + \sigma_z \otimes \sigma_z)\right]|\!\uparrow\rangle \otimes |\!\uparrow\rangle = \\ &= \frac{\hbar^2}{4}\left[\,6\,|\!\uparrow\uparrow\rangle + 2\,|\!\downarrow\downarrow\rangle + 2\,(i)^2\,|\!\downarrow\downarrow\rangle + 2\,|\!\uparrow\uparrow\rangle\right] = \\ &= \frac{\hbar^2}{4}\,8\,|\!\uparrow\uparrow\rangle = 2\,\hbar^2\,|\!\uparrow\uparrow\rangle = \hbar^2\,1\,(1 + 1)\,|\!\uparrow\uparrow\rangle \,, \end{aligned} \tag{7.55}$$

$$\vec{S}^{\,2}\,|\!\downarrow\downarrow\rangle = 2\,\hbar^2\,|\!\downarrow\downarrow\rangle \,, \tag{7.56}$$

the states $\uparrow\downarrow$ and $\downarrow\uparrow$ are no eigenstates[4] of the squared spin operator

$$\vec{S}^{\,2}\,|\!\uparrow\downarrow\rangle = \vec{S}^{\,2}\,|\!\downarrow\uparrow\rangle = \hbar^2\,(|\!\uparrow\downarrow\rangle + |\!\downarrow\uparrow\rangle) \,. \tag{7.57}$$

However, we can form linear combinations of the states $\uparrow\downarrow$ and $\downarrow\uparrow$, where we choose the appropriate weights[5] $\frac{1}{\sqrt{2}}$ for normalization, which are eigenstates to the quantum numbers $s = 1$ and $s = 0$

$$\vec{S}^{\,2}\,\tfrac{1}{\sqrt{2}}\,(|\!\uparrow\downarrow\rangle + |\!\downarrow\uparrow\rangle) = 2\,\hbar^2\,\tfrac{1}{\sqrt{2}}\,(|\!\uparrow\downarrow\rangle + |\!\downarrow\uparrow\rangle) \tag{7.58}$$

[4] Generally, naively forming tensor products of simultaneous eigenstates of squared angular momentum and angular momentum z-component operators does not give an eigenstate of the corresponding operators on the tensor product space. There is, however, a simple way of finding these eigenstates, by calculating the so called Clebsch-Gordon coefficients, which though mathematically simple can be a quite tiresome procedure.

[5] They are the Clebsch-Gordon coefficients for the addition of two spin $\frac{1}{2}$'s.

$$\vec{S}^2 \, \tfrac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle \, - \, |\downarrow\uparrow\rangle \right) \; = \; 0 \, . \tag{7.59}$$

So we find a ***triplet*** of states $|\, s, \, m_{\rm s} \,\rangle$, belonging to the spin quantum number $s = 1$, with magnetic spin quantum numbers $m_{\rm s} = -1, 0, 1$,

$$|\, 1, \, -1 \,\rangle \;\; = \;\; |\downarrow\downarrow\rangle \tag{7.60}$$

$$|\, 1, \, 0 \,\rangle \;\; = \;\; \tfrac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle \, + \, |\downarrow\uparrow\rangle \right) \tag{7.61}$$

$$|\, 1, \, +1 \,\rangle \;\; = \;\; |\uparrow\uparrow\rangle \tag{7.62}$$

and a ***singlet*** with quantum numbers $s = 0$ and $m_{\rm s} = 0$

$$|\, 0, \, 0 \,\rangle \; = \; \tfrac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle \, - \, |\downarrow\uparrow\rangle \right) \, . \tag{7.63}$$

Remark I: Of course, we could have also calculated the state (7.61) by applying the lowering operator S_- (see Eq. (7.19)) to the $|\uparrow\uparrow\rangle$ state

$$S_- \, |\uparrow\uparrow\rangle \, = \, \left(S_-^{\rm A} \, + \, S_-^{\rm B} \right) \, |\uparrow\uparrow\rangle \, = \, \hbar \, \left(|\uparrow\downarrow\rangle \, + \, |\downarrow\uparrow\rangle \right) \, . \tag{7.64}$$

Remark II: Statistics. We divide particles into two groups, those of integer spin values, called ***bosons***, and those of half-integer spin values, called ***fermions***. One can then conclude, that wave functions describing bosons must always be even/symmetric functions, while the ones, describing fermions must be odd/antisymmetric functions. This causes for both types of particles to be subjected to different statistical behavior, fermions are governed by the ***Fermi–Dirac statistics*** while bosons follow the ***Bose–Einstein statistics***.

One very important conclusion from this spin–statistic relation is the so called *Pauli exclusion principle.*

> **Proposition 7.3.1 (Pauli exclusion principle)** *No two or more fermions may occupy the same quantum state simultaneously.*

Therefore, if we describe two (or more) electrons in the same spin state (symmetric spin states), they can not be located at the same position, since this would also be a symmetric state and thus the total wave function would be symmetric, which is impossible for fermions.