Moderne Theoretische Physik I
Grundlagen der Quantenmechanik

Summer Semester 2024
Exercise Sheet 9

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Due date: 28. 06. 2024.

The problems whose solutions you need to upload are designated with stars.

⋆ Problem 1 ⋆ Particle in an electromagnetic field

In the presence of an external classical electromagnetic field, the Hamiltonian describing a charged particle is

$$\hat{H}(t) = \frac{[\hat{\boldsymbol{p}} - q\boldsymbol{A}(\boldsymbol{r},t)]^2}{2m} + q\varphi(\boldsymbol{r},t) + V(\boldsymbol{r}), \tag{1}$$

where $\hat{\boldsymbol{p}} = -\mathrm{i}\hbar\boldsymbol{\nabla}$, q is the charge, and φ and $\boldsymbol{A}$ are the scalar and vector potentials. We're in 3D and we shall use the position representation and SI units. Because we are treating the electromagnetic field classically, φ and $\boldsymbol{A}$ are real numbers, rather than operators, and their space and time-dependence is imposed externally.

1. If you are given a solution of the Schrödinger equation

$$\mathrm{i}\hbar\partial_t\Psi(\boldsymbol{r},t) = \hat{H}\Psi(\boldsymbol{r},t), \tag{2}$$

what Schrödinger equation does the wavefunction $\Psi'(\boldsymbol{r},t) = \mathrm{e}^{-\mathrm{i}q\lambda(\boldsymbol{r},t)/\hbar}\Psi(\boldsymbol{r},t)$ satisfy? Absorb the changes into redefinitions of $\boldsymbol{A}$ and φ. What does this transformation from $(\Psi, \boldsymbol{A}, \varphi)$ to $(\Psi', \boldsymbol{A}', \varphi')$ represent physically?

2. Find the charge current $\boldsymbol{j}(\boldsymbol{r},t)$ that enters the charge conservation law

$$\partial_t\rho(\boldsymbol{r},t) + \boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0, \tag{3}$$

where $\rho(\boldsymbol{r},t) = q\,|\Psi(\boldsymbol{r},t)|^2$.

3. How do $\rho(\boldsymbol{r},t)$ and $\boldsymbol{j}(\boldsymbol{r},t)$ transform under the transformation of part 1 of this problem?

Solution 1

1. Let us rewrite the Schrödinger equation in the following form

$$\left\{[-\mathrm{i}\hbar\partial_t + q\varphi(\boldsymbol{r},t)] + \frac{[-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A}(\boldsymbol{r},t)]^2}{2m} + V(\boldsymbol{r})\right\}\Psi(\boldsymbol{r},t) = 0.$$

The key identity is:

$$\mathrm{e}^{-\mathrm{i}f(\boldsymbol{r},t)/\hbar}(-\mathrm{i}\hbar\partial_\mu)\mathrm{e}^{\mathrm{i}f(\boldsymbol{r},t)/\hbar} = -\mathrm{i}\hbar\partial_\mu + [\partial_\mu f(\boldsymbol{r},t)].$$

Hence once we multiply the initial Schrödinger equation with $\mathrm{e}^{-\mathrm{i}q\lambda(\boldsymbol{r},t)/\hbar}$ from the left

$$\mathrm{e}^{-\mathrm{i}q\lambda(\boldsymbol{r},t)/\hbar}\left\{[-\mathrm{i}\hbar\partial_t + q\varphi(\boldsymbol{r},t)] + \frac{[-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A}(\boldsymbol{r},t)]^2}{2m} + V(\boldsymbol{r})\right\}\mathrm{e}^{\mathrm{i}q\lambda(\boldsymbol{r},t)/\hbar}\Psi'(\boldsymbol{r},t) = 0$$

it becomes

$$\left\{[-\mathrm{i}\hbar\partial_t + q\varphi'(\boldsymbol{r},t)] + \frac{[-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A}'(\boldsymbol{r},t)]^2}{2m} + V(\boldsymbol{r})\right\}\Psi'(\boldsymbol{r},t) = 0$$

with

$$\begin{aligned}
\Psi'(\boldsymbol{r},t) &= \mathrm{e}^{-\mathrm{i}q\lambda(\boldsymbol{r},t)/\hbar}\Psi(\boldsymbol{r},t),\\
\varphi'(\boldsymbol{r},t) &= \varphi(\boldsymbol{r},t) + \partial_t\lambda(\boldsymbol{r},t),\\
\boldsymbol{A}'(\boldsymbol{r},t) &= \boldsymbol{A}(\boldsymbol{r},t) - \boldsymbol{\nabla}\lambda(\boldsymbol{r},t).
\end{aligned}$$

Physically, this is a gauge transformation. Thus in quantum mechanics, gauge transforming the scalar and vector potentials needs to be accompanied with a change in the phase of the wavefunction.

2. The charge conservation law is derived in the same way as in the neutral case. We take the Schrödinger equation for Ψ and its adjoint

$$\left\{\left[-\mathrm{i}\hbar\overrightarrow{\partial}_t + q\varphi(\boldsymbol{r},t)\right] + \frac{\left[-\mathrm{i}\hbar\overrightarrow{\boldsymbol{\nabla}} - q\boldsymbol{A}(\boldsymbol{r},t)\right]^2}{2m} + V(\boldsymbol{r})\right\}\Psi(\boldsymbol{r},t) = 0,$$

$$\Psi^\dagger(\boldsymbol{r},t)\left\{\left[+\mathrm{i}\hbar\overleftarrow{\partial}_t + q\varphi(\boldsymbol{r},t)\right] + \frac{\left[+\mathrm{i}\hbar\overleftarrow{\boldsymbol{\nabla}} - q\boldsymbol{A}(\boldsymbol{r},t)\right]^2}{2m} + V(\boldsymbol{r})\right\} = 0,$$

contract them with $\Psi^\dagger$ and Ψ, respectively,

$$\Psi^\dagger(\boldsymbol{r},t)\left\{\left[-\mathrm{i}\hbar\overrightarrow{\partial}_t + q\varphi(\boldsymbol{r},t)\right] + \frac{\left[-\mathrm{i}\hbar\overrightarrow{\boldsymbol{\nabla}} - q\boldsymbol{A}(\boldsymbol{r},t)\right]^2}{2m} + V(\boldsymbol{r})\right\}\Psi(\boldsymbol{r},t) = 0,$$

$$\Psi^\dagger(\boldsymbol{r},t)\left\{\left[+\mathrm{i}\hbar\overleftarrow{\partial}_t + q\varphi(\boldsymbol{r},t)\right] + \frac{\left[+\mathrm{i}\hbar\overleftarrow{\boldsymbol{\nabla}} - q\boldsymbol{A}(\boldsymbol{r},t)\right]^2}{2m} + V(\boldsymbol{r})\right\}\Psi(\boldsymbol{r},t) = 0,$$

and subtract to get:

$$\begin{aligned}
&\Psi^\dagger(\boldsymbol{r},t)\left\{\left[-\mathrm{i}\hbar\overrightarrow{\partial}_t + q\varphi(\boldsymbol{r},t)\right] - \left[+\mathrm{i}\hbar\overleftarrow{\partial}_t + q\varphi(\boldsymbol{r},t)\right]\right.\\
&\left.+\frac{\left[-\mathrm{i}\hbar\overrightarrow{\boldsymbol{\nabla}} - q\boldsymbol{A}(\boldsymbol{r},t)\right]^2}{2m} + V(\boldsymbol{r}) - \frac{\left[+\mathrm{i}\hbar\overleftarrow{\boldsymbol{\nabla}} - q\boldsymbol{A}(\boldsymbol{r},t)\right]^2}{2m} - V(\boldsymbol{r})\right\}\Psi(\boldsymbol{r},t) = 0.
\end{aligned}$$

The φ and V terms cancel, as do some of the additional terms that have $\boldsymbol{A}$ after writing out the latter terms. The final result is

$$-\mathrm{i}\frac{\hbar}{q}\partial_t\rho(\boldsymbol{r},t) - \mathrm{i}\frac{\hbar}{q}\boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0,$$

that is

$$\partial_t\rho(\boldsymbol{r},t) + \boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0$$

with

$$\rho(\boldsymbol{r},t) = q\,|\Psi(\boldsymbol{r},t)|^2\,,$$
$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{q}{m}\Psi^\dagger(\boldsymbol{r},t)\Big[-\mathrm{i}\hbar\tfrac{1}{2}(\overrightarrow{\boldsymbol{\nabla}} - \overleftarrow{\boldsymbol{\nabla}}) - q\boldsymbol{A}(\boldsymbol{r},t)\Big]\Psi(\boldsymbol{r},t).$$

3. ρ is obviously invariant because the absolute values does not change under phase rotations. For $\boldsymbol{j}$ we use the same trick from before to show that

$$\begin{aligned}\boldsymbol{j}(\boldsymbol{r},t) &= \frac{1}{m}\Psi^\dagger(\boldsymbol{r},t)\Big[-\mathrm{i}\hbar\tfrac{1}{2}(\overrightarrow{\boldsymbol{\nabla}} - \overleftarrow{\boldsymbol{\nabla}}) - q\boldsymbol{A}(\boldsymbol{r},t)\Big]\Psi(\boldsymbol{r},t)\\ &= \frac{1}{m}\Psi'^\dagger(\boldsymbol{r},t)\Big[-\mathrm{i}\hbar\tfrac{1}{2}(\overrightarrow{\boldsymbol{\nabla}} - \overleftarrow{\boldsymbol{\nabla}}) - q\boldsymbol{A}'(\boldsymbol{r},t)\Big]\Psi'(\boldsymbol{r},t)\end{aligned}$$

with $\Psi'(\boldsymbol{r},t) = \mathrm{e}^{-\mathrm{i}q\lambda(\boldsymbol{r},t)/\hbar}\Psi(\boldsymbol{r},t)$ and $\boldsymbol{A}'(\boldsymbol{r},t) = \boldsymbol{A}(\boldsymbol{r},t) - \boldsymbol{\nabla}\lambda(\boldsymbol{r},t)$, is also invariant. Thus ρ and $\boldsymbol{j}$ are gauge invariant, as they must be since they are physically measurable quantities just like, e.g., the electric field.

⋆ Problem 2 ⋆ Spin precession

Consider a spin-$\frac{1}{2}$ particle coupled to the magnetic field:

$$\hat{H} = -\hat{\boldsymbol{\mu}}\cdot\boldsymbol{B} = -(\hat{\mu}_x B_x + \hat{\mu}_y B_y + \hat{\mu}_z B_z), \tag{4}$$

where $\hat{\boldsymbol{\mu}} = -\gamma\hat{\boldsymbol{S}}$ is the magnetic dipole moment, γ is the gyromagnetic ratio, $\hat{\boldsymbol{S}} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}$ is a vector of spin operators, and $\boldsymbol{B}$ is the magnetic field. (Note that $\hat{\boldsymbol{\sigma}} = (\sigma_x,\sigma_y,\sigma_z) \equiv \hat{\boldsymbol{x}}\sigma_x + \hat{\boldsymbol{y}}\sigma_y + \hat{\boldsymbol{z}}\sigma_z$ is a convenient shorthand for a vector whose components are operators, in this case 2×2 Pauli matrices, similarly to how the momentum $\hat{\boldsymbol{p}} = (\hat{p}_x,\hat{p}_y,\hat{p}_z) \equiv \hat{\boldsymbol{x}}\hat{p}_x + \hat{\boldsymbol{y}}\hat{p}_y + \hat{\boldsymbol{z}}\hat{p}_z$ is vector composed of differentiation operators.)

1. Diagonalize this Hamiltonian for an arbitrary magnetic field $\boldsymbol{B} = B_0\hat{\boldsymbol{n}}$, where $\hat{\boldsymbol{n}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ is a unit vector whose direction is oriented along an arbitrary direction.
2. Write down the Ehrenfest equation for the spin expectation value $\left\langle\hat{\boldsymbol{S}}(t)\right\rangle$.
3. If $\boldsymbol{B} = B_0\hat{\boldsymbol{z}}$ points along z, and $\left\langle\hat{\boldsymbol{S}}(t=0)\right\rangle = \frac{\hbar}{2}\hat{\boldsymbol{x}}$, find $\left\langle\hat{\boldsymbol{S}}(t)\right\rangle$ by solving the Ehrenfest equation.
4. Now assume that $\boldsymbol{B} = B_0\hat{\boldsymbol{z}}$ and that the wavefunction initially equals $|\Psi(t=0)\rangle = \frac{1}{\sqrt{2}}(|{\uparrow}\rangle + |{\downarrow}\rangle)$. Calculate $|\Psi(t)\rangle$ by solving the Schrödinger equations and then calculate $\left\langle\Psi(t)\middle|\hat{\boldsymbol{S}}\middle|\Psi(t)\right\rangle$. Compare with the previous part of this problem.

Solution 2

1. The Hamiltonian equals

$$\hat{H} = \frac{\gamma\hbar B_0}{2}\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{\sigma}} = \frac{\gamma\hbar B_0}{2}\begin{pmatrix}\cos\theta & \sin\theta\mathrm{e}^{-\mathrm{i}\phi}\\ \sin\theta\mathrm{e}^{\mathrm{i}\phi} & -\cos\theta\end{pmatrix},$$

and it is diagonalized in the usual way to obtain:

$$|\hat{\boldsymbol{n}},+\rangle = \begin{pmatrix}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}\mathrm{e}^{\mathrm{i}\phi}\end{pmatrix}, \qquad E_+ = +\frac{\gamma\hbar B_0}{2},$$
$$|\hat{\boldsymbol{n}},-\rangle = \begin{pmatrix}\sin\frac{\theta}{2}\\ -\cos\frac{\theta}{2}\mathrm{e}^{\mathrm{i}\phi}\end{pmatrix}, \qquad E_- = -\frac{\gamma\hbar B_0}{2}.$$

2. Since $[\hat{S}_i, \hat{S}_j] = \mathrm{i}\hbar \sum_k \epsilon_{ijk} \hat{S}_k$, it follows that

$$\begin{aligned}
\mathrm{i}\hbar\partial_t \left\langle \hat{S}_i \right\rangle &= \left\langle [\hat{S}_i, \hat{H}] \right\rangle = \sum_j \gamma B_j \left\langle [\hat{S}_i, \hat{S}_j] \right\rangle \\
&= \sum_{jk} \gamma B_j \mathrm{i}\hbar \epsilon_{ijk} \left\langle \hat{S}_k \right\rangle, \\
\partial_t \left\langle \hat{S}_i \right\rangle &= \gamma \sum_{jk} \epsilon_{ijk} B_j \left\langle \hat{S}_k \right\rangle,
\end{aligned}$$

or more compactly in vector notation

$$\partial_t \left\langle \hat{\boldsymbol{S}} \right\rangle = \gamma \boldsymbol{B} \times \left\langle \hat{\boldsymbol{S}} \right\rangle.$$

3. The Ehrenfest equation we wrote down is nothing but the equation for the precession of a vector rotating with the angular frequency $\boldsymbol{\omega} = \gamma \boldsymbol{B}$, known as the Larmor frequency. The solution to this problem is known from classical mechanics. In the particular case of the problem:

$$\left\langle \hat{\boldsymbol{S}}(t) \right\rangle = \frac{\hbar}{2}(\hat{\boldsymbol{x}} \cos \Omega t + \hat{\boldsymbol{y}} \sin \Omega t),$$

where $\Omega = \gamma B_0$.

4. Since we have diagonalized the Hamiltonian, we know that the general solution of the Schrödinger equation is

$$|\Psi(t)\rangle = c_+ \mathrm{e}^{-\mathrm{i}E_+ t/\hbar} |\hat{\boldsymbol{n}}, +\rangle + c_- \mathrm{e}^{-\mathrm{i}E_- t/\hbar} |\hat{\boldsymbol{n}}, -\rangle .$$

For $\boldsymbol{B} = B_0 \hat{\boldsymbol{z}}$ and $|\Psi(t=0)\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$, this means

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}} \mathrm{e}^{-\mathrm{i}\Omega t/2} |\uparrow\rangle + \frac{1}{\sqrt{2}} \mathrm{e}^{\mathrm{i}\Omega t/2} |\downarrow\rangle$$

where $\Omega = \gamma B_0$. Hence

$$\begin{aligned}
\left\langle \Psi(t) \middle| \hat{S}_x \middle| \Psi(t) \right\rangle &= \frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{e}^{\mathrm{i}\Omega t/2} & \mathrm{e}^{-\mathrm{i}\Omega t/2} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{e}^{-\mathrm{i}\Omega t/2} \\ \mathrm{e}^{\mathrm{i}\Omega t/2} \end{pmatrix} = \frac{\hbar}{2} \cos \Omega t, \\
\left\langle \Psi(t) \middle| \hat{S}_y \middle| \Psi(t) \right\rangle &= \frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{e}^{\mathrm{i}\Omega t/2} & \mathrm{e}^{-\mathrm{i}\Omega t/2} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{e}^{-\mathrm{i}\Omega t/2} \\ \mathrm{e}^{\mathrm{i}\Omega t/2} \end{pmatrix} = \frac{\hbar}{2} \sin \Omega t, \\
\left\langle \Psi(t) \middle| \hat{S}_z \middle| \Psi(t) \right\rangle &= \frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{e}^{\mathrm{i}\Omega t/2} & \mathrm{e}^{-\mathrm{i}\Omega t/2} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{e}^{-\mathrm{i}\Omega t/2} \\ \mathrm{e}^{\mathrm{i}\Omega t/2} \end{pmatrix} = 0,
\end{aligned}$$

which agrees with what we found by solving the Ehrenfest equation.

Problem 3 Singlet and triplet states

Consider two spin-$\frac{1}{2}$ particles.

Formally, the total Hilbert space describing two particles is given by the *tensor product* of the Hilbert spaces describing the particles individually. In this case, the individual Hilbert spaces are $\mathbb{C}^2$ and $\mathbb{C}^2$, and their tensor product is $\mathbb{C}^2 \otimes \mathbb{C}^2 = \mathbb{C}^{2\times 2} = \mathbb{C}^4$. The tensor product of two 2-component vectors

$$v = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}, \qquad u = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \tag{5}$$

is the 4-component vector

$$v \otimes u = \begin{pmatrix} v_1 u_1 \\ v_1 u_2 \\ v_2 u_1 \\ v_2 u_2 \end{pmatrix}. \tag{6}$$

The tensor product of two 2×2 matrices

$$A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}, \qquad B = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \tag{7}$$

is defined as the 4×4 matrix

$$A \otimes B = \left(\begin{array}{cc|cc} A_{11}B_{11} & A_{11}B_{12} & A_{12}B_{11} & A_{12}B_{12} \\ A_{11}B_{21} & A_{11}B_{22} & A_{12}B_{21} & A_{12}B_{22} \\ \hline A_{21}B_{11} & A_{21}B_{12} & A_{22}B_{11} & A_{22}B_{12} \\ A_{21}B_{21} & A_{21}B_{22} & A_{22}B_{21} & A_{22}B_{22} \end{array}\right), \tag{8}$$

where the horizontal and vertical lines were added for readability only. Notice how the tensor product is linear in both of its arguments and how it is not commutative, $A \otimes B \neq B \otimes A$.

If the spin operator of an individual particle is given by $\hat{\boldsymbol{S}} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}$, where $\hat{\boldsymbol{\sigma}} = (\sigma_x, \sigma_y, \sigma_z)$ are Pauli matrices, then the spin operators of the first and second particles are $\hat{\boldsymbol{S}}_1 = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}} \otimes \mathbb{1}$ and $\hat{\boldsymbol{S}}_2 = \frac{\hbar}{2}\mathbb{1} \otimes \hat{\boldsymbol{\sigma}}$ in the basis $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$ of the total Hilbert space; here $\mathbb{1}$ is the 2×2 identity matrix.

1. Write down the matrices for $\hat{S}_{1,x}$ and $\hat{S}_{2,y}$ in the $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$ basis.
2. Show that $[\hat{S}_{1,i}, \hat{S}_{2,j}] = 0$. (Hint: do this abstractly using $(A \otimes B)(C \otimes D) = (AB) \otimes (CD)$.)
3. Introduce $\hat{\boldsymbol{\Sigma}} = \hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2$. Calculate $[\hat{\Sigma}_i, \hat{\Sigma}_j]$ and find the matrices for $\hat{\boldsymbol{\Sigma}}^2$ and $\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2$.
4. Diagonalize the total spin $\hat{\boldsymbol{\Sigma}}^2$ simultaneously with the total spin along z $\hat{\Sigma}_z$. Make sure that the phases of the different eigenvectors are properly related through raising and lower operations $\hat{\Sigma}_\pm$. What spin values do you find?

Solution 3

1. They are

$$\hat{S}_{1,x} = \frac{\hbar}{2}\begin{pmatrix} & & 1 & \\ & & & 1 \\ 1 & & & \\ & 1 & & \end{pmatrix}, \qquad \hat{S}_{2,y} = \frac{\hbar}{2}\begin{pmatrix} & -\mathrm{i} & & \\ \mathrm{i} & & & \\ & & & -\mathrm{i} \\ & & \mathrm{i} & \end{pmatrix}.$$

2. This follows from

$$\begin{aligned} [\hat{S}_{1,i}, \hat{S}_{2,j}] &= (\hat{S}_i \otimes \mathbb{1})(\mathbb{1} \otimes \hat{S}_j) - (\mathbb{1} \otimes \hat{S}_j)(\hat{S}_i \otimes \mathbb{1}) \\ &= (\hat{S}_i\mathbb{1}) \otimes (\mathbb{1}\hat{S}_j) - (\mathbb{1}\hat{S}_i) \otimes (\hat{S}_j\mathbb{1}) \\ &= \hat{S}_i \otimes \hat{S}_j - \hat{S}_i \otimes \hat{S}_j = 0. \end{aligned}$$

3. We have:

$$\begin{aligned} [\hat{\Sigma}_i, \hat{\Sigma}_j] &= [\hat{S}_{1,i} + \hat{S}_{2,i}, \hat{S}_{1,j} + \hat{S}_{2,j}] = [\hat{S}_{1,i}, \hat{S}_{1,j}] + [\hat{S}_{2,i}, \hat{S}_{2,j}] \\ &= \mathrm{i}\hbar\sum_k(\hat{S}_{1,k} + \hat{S}_{2,k}) = \mathrm{i}\hbar\sum_k \hat{\Sigma}_k. \end{aligned}$$

   Moreover

$$\begin{aligned} \hat{\boldsymbol{\Sigma}}^2 &= (\hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2)^2 = \hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 + \hat{\boldsymbol{S}}_2 \cdot \hat{\boldsymbol{S}}_1 \\ &= \frac{\hbar^2}{4}\sum_i \sigma_i^2 \otimes \mathbb{1} + \frac{\hbar^2}{4}\sum_i \sigma_i^2 \otimes \mathbb{1} + 2\frac{\hbar^2}{4}\sum_i \sigma_i \otimes \sigma_i \\ &= \frac{3\hbar^2}{2}\mathbb{1} \otimes \mathbb{1} + \frac{\hbar^2}{2}\sum_i \sigma_i \otimes \sigma_i, \\ \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 &= \frac{\hbar^2}{4}\sum_i \sigma_i \otimes \sigma_i. \end{aligned}$$

where

$$\sum_i \sigma_i \otimes \sigma_i = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$
$$= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Hence

$$\hat{\boldsymbol{\Sigma}}^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix},$$
$$\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

4. Since

$$\hat{S}_z = \hbar \begin{pmatrix} 1 & & & \\ & 0 & & \\ & & 0 & \\ & & & -1 \end{pmatrix},$$

the singlet state is

$$|s=0, m=0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}},$$

and the triplet states are

$$|s=1, m=1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = |\uparrow\uparrow\rangle\,,$$
$$|s=1, m=0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} = \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}},$$
$$|s=1, m=-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = |\downarrow\downarrow\rangle\,.$$

Note that $\hat{\Sigma}_- \, |s=1, m=1\rangle = \hbar\sqrt{2}\, |s=1, m=0\rangle$, where

$$\hat{\Sigma}_- = \hbar \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \end{pmatrix}.$$

The possible spins are $s = 0$ and $s = 1$, as follows from $\hat{\boldsymbol{\Sigma}}^2 \, |s, m\rangle = \hbar^2 s(s+1) \, |s, m\rangle$.