# Physical Chemistry 2

*Lecture 10. Spin*

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paradichlorobenzene1724@gmail.com
kadryjh1724@snu.ac.kr

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서울대학교
SEOUL NATIONAL UNIVERSITY
Department of Chemistry

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Jiho Son

# Topics in Lecture 10

**What is spin?**

**Pauli exclusion principle (or antisymmetry principle)**

**Slater determinant**

**Orthohelium and parahelium**

**Angular momentum addition**

**Term symbols and Hund's rules**

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In Atkins' *Physical Chemistry* (11th ed.),

8B Many-electron atoms
8C Atomic spectra

# What is spin?

We cannot not describe *Stern-Gerlach experiment* (1922) to start this lecture.



Classical prediction

What was actually observed

Silver atoms

N

S

Inhomogeneous magnetic field

Furnace
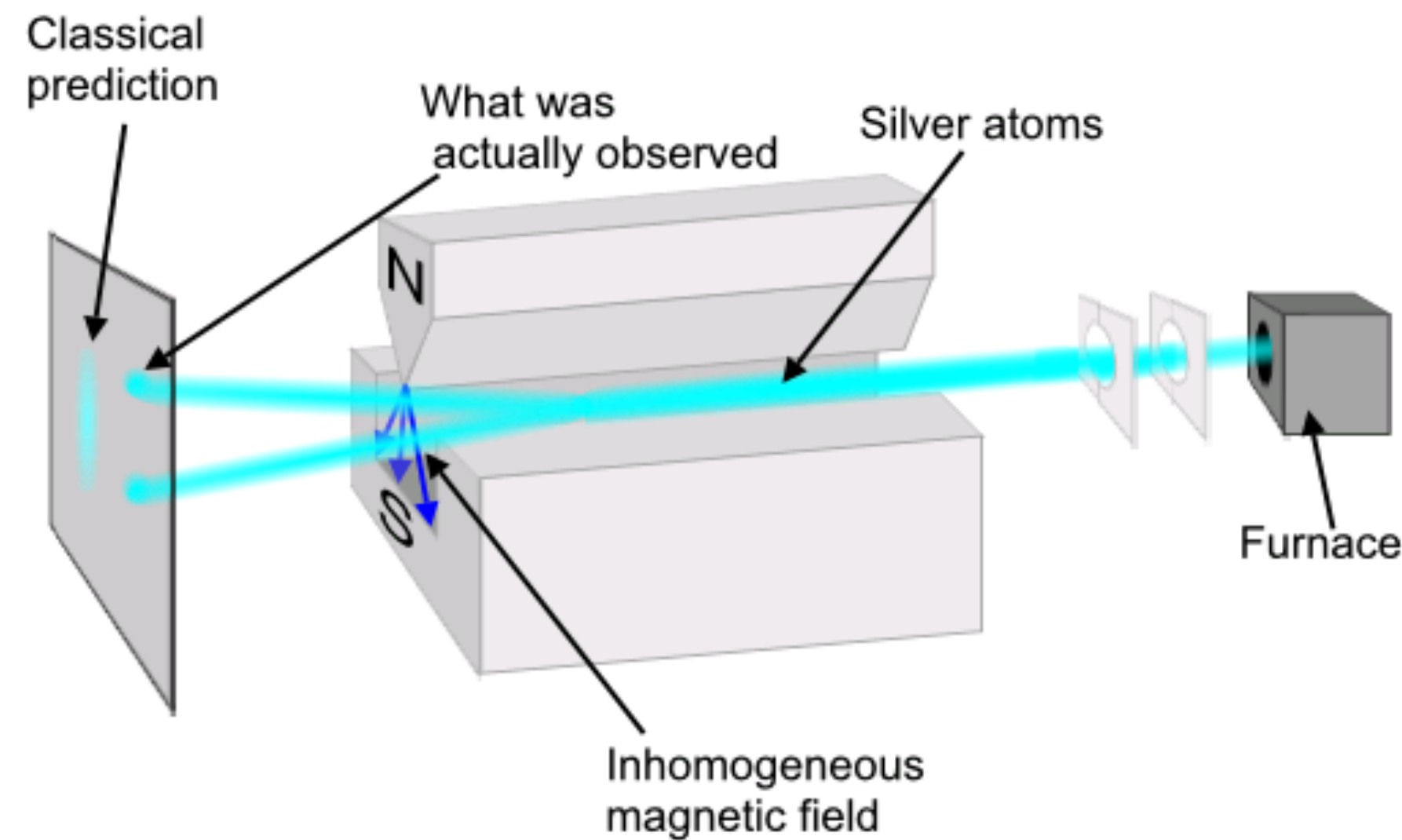
The silver atom (Ag) beam gets through the inhomogeneous magnetic field. Of course atoms are neutral. However, *splitting* observed on the screen.

This suggests some *internal degrees of freedom* that electron has.

One may compare spin degree of freedom with spinning top.

# Sequential Stern-Gerlach expt.
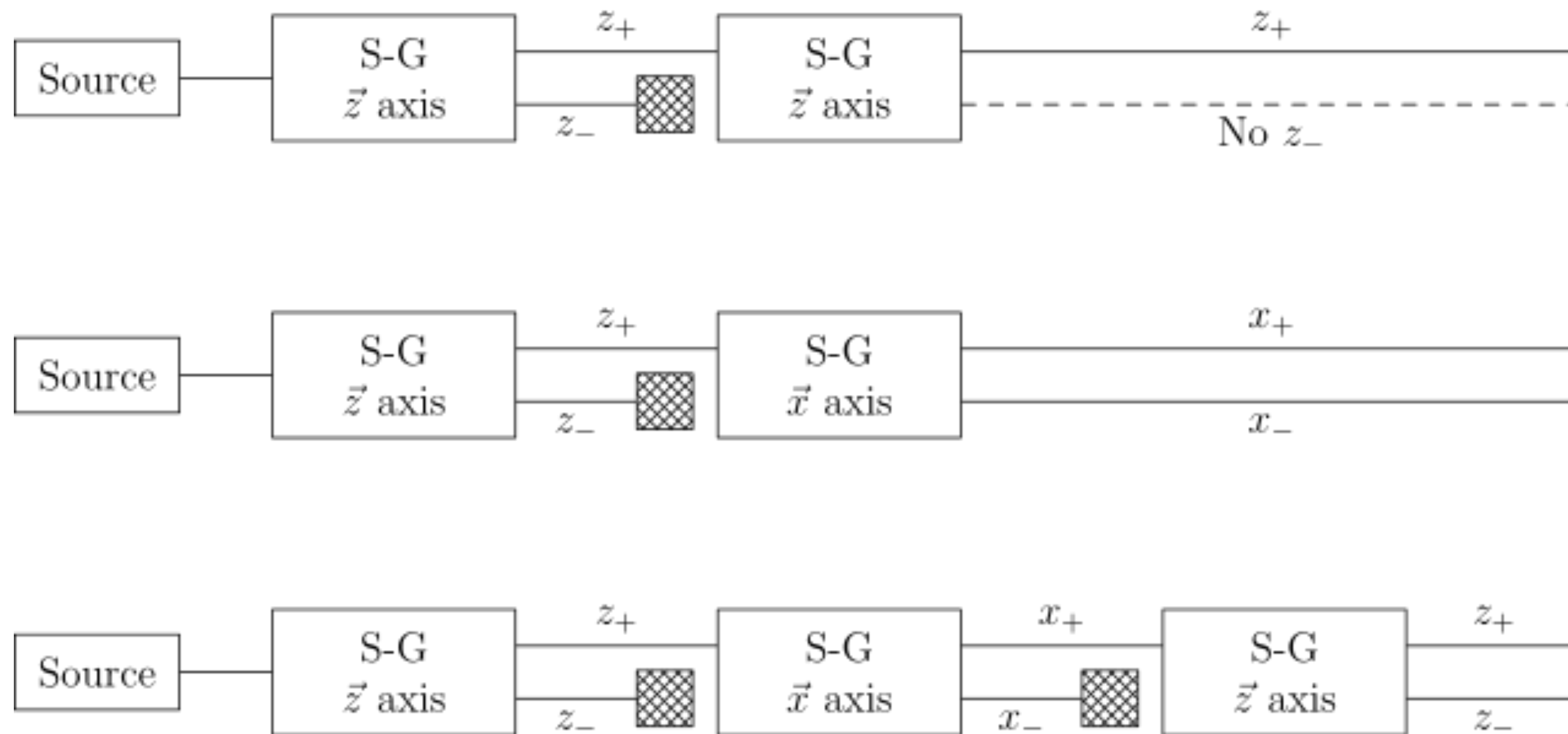
# What is spin?

We will introduce spin in *ad hoc* manner. Recall the eigenvalue equations for angular momentum.

$$\hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi), \quad \hat{L}_z Y_l^m(\theta, \phi) = \hbar m Y_l^m(\theta, \phi)$$

We *define* the spin operators and their eigenfunctions $\alpha$ and $\beta$ by the equations

$$\hat{S}^2 \alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha, \quad \hat{S}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\beta$$

$$\hat{S}_z\alpha = m_s\alpha = \frac{\hbar}{2}\alpha, \quad \hat{S}_z\beta = m_s\beta = -\frac{\hbar}{2}\beta$$

as if they corresponded to $l = 1/2$ case, which can have $m = -1/2$ and $m = +1/2$.

Note that we are not interested in specific form of $\alpha$ and $\beta$. They just came from the angular momentum analogy; they do not have to be specified any further.

# What is spin?

Similar with angular momentum, we can say that

$$L^2 = \hbar^2 l(l+1) \implies S^2 = \hbar^2 s(s+1)$$

Unlike $l$, $s$ can only have the value 1/2. **Spin is strictly a non-classical concept.**

Even if we do not know the explicit form of $\hat{S}^2$ and $\hat{S}_z$, we know that they are hermitian.
Therefore, spin eigenfunctions must be *orthonormal*.

$$\langle \alpha \,|\, \alpha \rangle = \langle \beta \,|\, \beta \rangle = 1, \quad \langle \alpha \,|\, \beta \rangle = \langle \beta \,|\, \alpha \rangle = 0$$

From now on, we should include the spin function with the *spatial* wave function.
If we know the spatial part $\psi(x, y, z)$, *spin orbitals* are

$$\Psi(x, y, z, \sigma) = \psi(x, y, z)\alpha(\sigma) \quad \text{or} \quad \Psi(x, y, z, \sigma) = \psi(x, y, z)\beta(\sigma)$$

# Pauli exclusion principle

In general chemistry, we learn Pauli exclusion principle: **no two electrons in an atom can have the same values of all four quantum numbers.**

Now we learn more fundamental statement of it, which is called *antisymmetry principle*.

**Postulate 6**

All electronic wave functions must be antisymmetric under the interchange of any two electrons.

(Example) If two electrons with same spin is in the same orbital, exchanging those two electrons does not change the sign of wavefunction: therefore it is prohibited.

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# Antisymmetry principle

**Example** Helium atom

$$\psi(1,2) = 1s\alpha(1) \cdot 1s\beta(2)$$

Electrons are *indistinguishable*, therefore, cannot be labelled. Thus, following wavefunction is equivalent with $\psi(1,2)$:

$$\psi(2,1) = 1s\alpha(2) \cdot 1s\beta(1)$$

Mathematically, indistinguishability requires that we take linear combinations involving all possible labelings of the electrons.

$$\Psi_1 = \psi(1,2) + \psi(2,1) = 1s\alpha(1)1s\beta(2) + 1s\alpha(2)1s\beta(1)$$

$$\Psi_2 = \psi(1,2) - \psi(2,1) = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$$

Both $\Psi_1$ and $\Psi_2$ seem to make sense, however $\Psi_2$ is the only choice since it satisfies antisymmetry.

$$\Psi_2(2,1) = \psi(2,1) - \psi(1,2) = -\Psi_2(1,2)$$

# Slater determinant

Note that appropriate wavefunction for the Helium ground state can be expressed as a *determinant*.

$$\Psi_2 = \psi(1,2) - \psi(2,1) = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

Surprisingly, determinantal wavefunctions satisfy all conditions that wavefunction should have.

Changing two electrons (changing two rows) changes the sign of the determinant.

Moreover, if we place both electrons in the same spin orbital (same column), determinant vanishes.
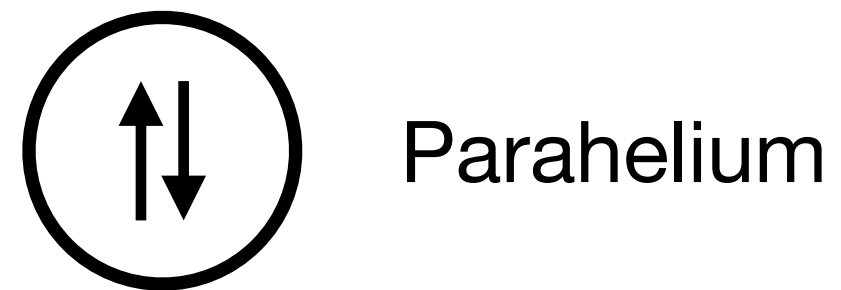
For *N* electrons, the *N*-electron determinantal wavefunction is called *Slater determinant*.

$$\Psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_N(1) \\ u_1(2) & u_2(2) & \cdots & u_N(2) \\ \vdots & \vdots & \vdots & \vdots \\ u_1(N) & u_2(N) & \cdots & u_N(N) \end{vmatrix}$$

# Helium

Note that Pauli exclusion principle requires antisymmetry of *total spin wavefunction*.

Consider ground state of He.

Parahelium

In this case, two electrons occupy 1s orbital. Therefore,

$$\psi_{\text{gs}} = \frac{1}{\sqrt{2}} \left[ 1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2) \right]$$

We call this a *singlet*. It has *symmetric* spatial part and *antisymmetric* spin part.

Orthohelium

Meanwhile, we can generate excited state with parallel spin. This is called a *triplet*.
The spin part is symmetric; therefore, its spatial part should be antisymmetric.

# Spin 1/2

There are two eigenstates. In $\left| s\, m_s \right\rangle$ notation,

$$\left| \frac{1}{2}\ \frac{1}{2} \right\rangle \textbf{ up spin, } \left| \uparrow \right\rangle \quad \textbf{and} \quad \left| \frac{1}{2}\ -\frac{1}{2} \right\rangle \textbf{ down spin, } \left| \downarrow \right\rangle$$

Using these as basis vectors, the general state of a spin-1/2 particle can be represented by a two-element column matrix, *spinor*.

$$\chi = \begin{bmatrix} a \\ b \end{bmatrix} = a\chi_+ + b\chi_- \quad \textbf{where} \quad \chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

With respect to this basis the spin operators become 2 by 2 matrices. Note that

$$\mathbf{S}^2\chi_+ = \frac{3}{4}\hbar^2\chi_+,\ \mathbf{S}^2\chi_- = \frac{3}{4}\hbar^2\chi_- \implies \mathbf{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

# Spin 1/2

Similarly,

$$\mathbf{S}_z \chi_+ = \frac{\hbar}{2} \chi_+, \ \mathbf{S}_z \chi_- = -\frac{\hbar}{2} \chi_- \implies \mathbf{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

We define *spin lowering and raising* operators: $\mathbf{S}_\pm = \mathbf{S}_x \pm i\mathbf{S}_y$. They satisfy

$$\mathbf{S}_+ \chi_- = \hbar \chi_+, \ \mathbf{S}_- \chi_+ = \hbar \chi_-, \ \mathbf{S}_+ \chi_+ = \mathbf{S}_- \chi_- = 0$$

So

$$\mathbf{S}_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \ \mathbf{S}_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \implies \mathbf{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \ \mathbf{S}_- = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

We define *Pauli spin matrices* here: $\vec{\mathbf{S}} = \frac{\hbar}{2} \vec{\sigma}$ where

$$\sigma_x \equiv \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \ \sigma_y \equiv \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \ \sigma_x \equiv \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

# Angular momentum addition

Suppose now we have two spin-1/2 particles. Both has $s = 1/2$, but $m_s$ can vary.

$$\hat{S}_1^2 \left| m_{s1} \, m_{s2} \right\rangle = \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \left| m_{s1} \, m_{s2} \right\rangle, \, \hat{S}_2^2 \left| m_{s1} \, m_{s2} \right\rangle = \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \left| m_{s1} \, m_{s2} \right\rangle$$

$$\hat{S}_{1z} \left| m_{s1} \, m_{s2} \right\rangle = m_{s1} \hbar \left| m_{s1} \, m_{s2} \right\rangle, \, \hat{S}_{2z} \left| m_{s1} \, m_{s2} \right\rangle = m_{s2} \hbar \left| m_{s1} \, m_{s2} \right\rangle$$

Just like angular momentum, spin itself is vector quantity. Therefore, it adds like vector.

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2, \, S_z = S_{1z} + S_{2z}$$

*z* component is simple:

$$\hat{S}_z \left| m_{s1} \, m_{s2} \right\rangle = \hat{S}_{z1} \left| m_{s1} \, m_{s2} \right\rangle + \hat{S}_{z2} \left| m_{s1} \, m_{s2} \right\rangle = (m_{s1} + m_{s2}) \hbar \left| m_{s1} \, m_{s2} \right\rangle$$

So we can write as

$$m_s = m_{s1} + m_{s2}$$

# Angular momentum addition

For two spin-1/2 particles, there are four possibilities:

$$\left| \frac{1}{2} \frac{1}{2} \right\rangle, m = 1$$

$$\left| \frac{1}{2} -\frac{1}{2} \right\rangle, m = 0$$

$$\left| -\frac{1}{2} \frac{1}{2} \right\rangle, m = 0 \qquad \longrightarrow \qquad s = 0 \text{ or } s = 1$$

$$\left| -\frac{1}{2} -\frac{1}{2} \right\rangle, m = -1$$
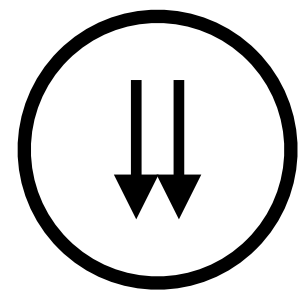
# Angular momentum addition

Calculate following operator.

$$\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_1 + \mathbf{S}_2) = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2$$
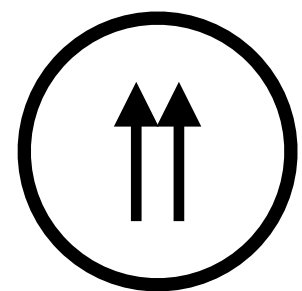
$\left| \dfrac{1}{2} \ \dfrac{1}{2} \right\rangle, \ m = 1$
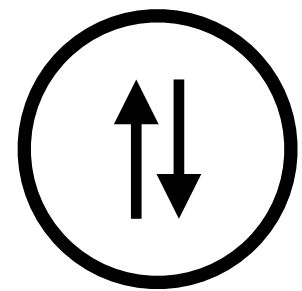
$\left| \dfrac{1}{2} \ -\dfrac{1}{2} \right\rangle, \ m = 0$
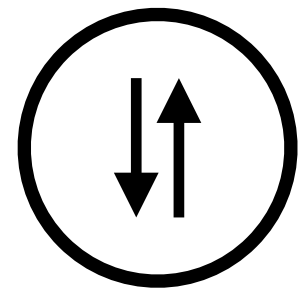
$\left| -\dfrac{1}{2} \ \dfrac{1}{2} \right\rangle, \ m = 0$

$\left| -\dfrac{1}{2} \ -\dfrac{1}{2} \right\rangle, \ m = -1$

Indeed eigenfunction

should check

# Angular momentum addition

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Check that |1/2 -1/2> state is not an eigenfunction of $\hat{S}^2$.

$$\mathbf{S}_1 \cdot \mathbf{S}_2 \,|\uparrow\downarrow\rangle = \mathbf{S}_{1x}\,|\uparrow\rangle\,\mathbf{S}_{2x}\,|\downarrow\rangle + \mathbf{S}_{1y}\,|\uparrow\rangle\,\mathbf{S}_{2y}\,|\downarrow\rangle + \mathbf{S}_{1z}\,|\uparrow\rangle\,\mathbf{S}_{2z}\,|\downarrow\rangle$$

$$= \frac{\hbar}{2}\,|\uparrow\rangle\,\frac{\hbar}{2}\,|\downarrow\rangle + \frac{i\hbar}{2}\,|\uparrow\rangle\,\frac{-i\hbar}{2}\,|\downarrow\rangle + \frac{\hbar}{2}\,|\uparrow\rangle\,\frac{-\hbar}{2}\,|\downarrow\rangle$$

$$= \frac{\hbar^2}{4}[2\,|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle]$$

Similarly, |-1/2 +1/2> state is not an eigenfunction of $\hat{S}^2$. Therefore, we need linear combination of them to yield eigenfunction of $\hat{S}^2$, not $\hat{S}_1^2$ and $\hat{S}_2^2$. The result is:

$$|1\,1\rangle = |\uparrow\uparrow\rangle$$

$$|1\,0\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle] \qquad\qquad |0\,0\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]$$

$$|1\,-1\rangle = |\downarrow\downarrow\rangle$$

Triplet ($s = 1$), symmetric          Singlet ($s = 0$), antisymmetric

# Angular momentum addition

For more general cases, the coefficients in front of the composite states are called *Clebsch-Gordan coefficients*, which is quite advanced topic in quantum mechanics.

$$\left|1\,1\right\rangle = \left|\uparrow\uparrow\right\rangle$$

$$\left|1\,0\right\rangle = \frac{1}{\sqrt{2}}[\left|\uparrow\downarrow\right\rangle + \left|\downarrow\uparrow\right\rangle] \qquad \left|0\,0\right\rangle = \frac{1}{\sqrt{2}}[\left|\uparrow\downarrow\right\rangle - \left|\downarrow\uparrow\right\rangle]$$

$$\left|1\,-1\right\rangle = \left|\downarrow\downarrow\right\rangle$$

Triplet ($s = 1$), symmetric          Singlet ($s = 0$), antisymmetric

From the antisymmetry principle, spatial wavefunction should be antisymmetric for triplet states and singlet state has symmetric spatial wavefunction.

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# Term symbols

First of all, we denote *total angular momentum* as sum of spin angular momentum and orbital angular momentum.

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

*Hund's rules* give us guidlines for electronic configuration in multielectron atom.

1. Maximize the total S.
2. Assign highest total angular momentum L.
3. For more than half-filled orbital, state with J=L+S is ground state. For less than half-filled, state with J=|L-S| is ground state.

The *term symbol* has following form: it denotes specific electronic configuration.

$$^{2S+1}L_J$$

$L = 0,1,2,3,\ldots$ are denoted as S, P, D, F, … .

Let's work with some examples.

# Term symbols

| | $1s$ | $2s$ | $2p\,(m=1)$ | $2p\,(m=0)$ | $2p\,(m=-1)$ | $S$ | $L$ | $J$ | symbol |
|---|---|---|---|---|---|---|---|---|---|
| $^1$H | ↑ | | | | | 1/2 | 0 | 1/2 | $^2S_{1/2}$ |
| $^2$He | ↑↓ | | | | | 0 | 0 | 0 | $^1S_0$ |
| $^3$Li | ↑↓ | ↑ | | | | 1/2 | 0 | 1/2 | $^2S_{1/2}$ |
| $^4$Be | ↑↓ | ↑↓ | | | | 0 | 0 | 0 | $^1S_0$ |
| $^5$B | ↑↓ | ↑↓ | ↑ | | | 1/2 | 1 | 1/2 | $^2P_{1/2}$ |
| $^6$C | ↑↓ | ↑↓ | ↑ | ↑ | | 1 | 1 | 0 | $^3P_0$ |
| $^7$N | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | 3/2 | 0 | 3/2 | $^4S_{3/2}$ |
| $^8$O | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | 1 | 1 | 2 | $^3P_2$ |
| $^9$F | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | 1/2 | 1 | 3/2 | $^2P_{3/2}$ |
| $^{10}$Ne | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | 0 | 0 | 0 | $^1S_0$ |