ELECTRON SPIN

We have seen that the electron has an orbital angular momentum associated to its motion around the nucleus. In addition, the electron has an **intrinsic angular momentum** called **spin angular momentum**. We have learned that each physical property has its corresponding operator in QM. For properties such as orbital angular momentum, we can construct the QM operator from the classical expression. **The spin of a microscopic particle has no analog in classical mechanics**, so we cannot use this method to construct operators for spin

ELECTRON SPIN

As the orbital angular-momentum, also the **spin angular-momentum is a vector**. So, we can talk about components S_x , S_y and S_z and hence a magnitude S. Analogously to the orbital angular-momentum operators $\hat{L}^2$, $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$, we have the spin angular-momentum operators $\hat{S}^2$, $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$.

$\hat{S}^2$ is the operator for the square of the magnitude of the total spin angular-momentum of a particle. $\hat{S}_z$ is the operator for the z component of the particle's spin angular momentum and so on

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

ELECTRON SPIN

We postulate that the spin angular-momentum operators obey the **same commutation relations as the orbital angular-momentum operators**. Therefore

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \qquad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x, \qquad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$$

$$[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y] = [\hat{S}^2, \hat{S}_z] = 0$$

These commutation rules imply the following eigenvalues for $\hat{S}^2$ and $\hat{S}_z$ for a set of common eigenfunctions. For an electron we have

$\hat{S}^2$ eigenvalues $\frac{3}{4}\hbar^2$ spin quantum number $s = 1/2$

$\hat{S}_z$ eigenvalues $\frac{1}{2}\hbar$ $-\frac{1}{2}\hbar$ $m_s = 1/2$ **spin up** $m_s = -1/2$ **spin down**

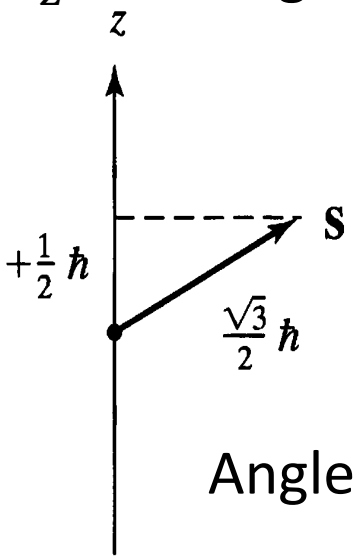
ELECTRON SPIN

The electron spin eigenfunctions that correspond to the $\hat{S}_z$ eigenvalues are denoted by α and β

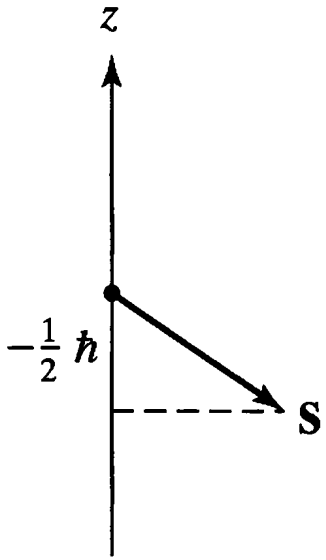
$$\hat{S}_z\alpha = +\tfrac{1}{2}\hbar\alpha \qquad \hat{S}_z\beta = -\tfrac{1}{2}\hbar\beta$$

Since $\hat{S}_z$ commutes with $\hat{S}^2$, we can take the eigenfunctions of $\hat{S}_z$ to be eigenfunctions of $\hat{S}^2$ also

$$\hat{S}^2\alpha = \tfrac{3}{4}\hbar^2\alpha, \qquad \hat{S}^2\beta = \tfrac{3}{4}\hbar^2\beta$$



Angle with z axis
- 54,7° for spin up
- 125,3° for spin down



ELECTRON SPIN

What is the variable for the spin eigenfunctions α and β?
One takes the possible spin quantum numbers m_s $(1/2 \text{ e } -1/2)$ as being values of the variable on which the spin eigenfunctions depend

$$\alpha(m) = \delta_{m,1/2} \qquad \beta(m) = \delta_{m,-1/2}$$

This guarantees the eigenfunctions be normalized and orthogonal

$$\sum_{m=-1/2}^{1/2} |\alpha(m)|^2 = 1 \quad \langle \alpha \,|\, \alpha \rangle = 1 \qquad \sum_{m=-1/2}^{1/2} |\beta(m)|^2 = 1 \quad \langle \beta \,|\, \beta \rangle = 1$$

Since the eigenfunctions α and β correspond to different eigenvalues of the operator $\hat{S}_z$, they are orthogonal

$$\sum_{m=-1/2}^{1/2} \alpha^*(m)\beta(m) = 0 \qquad \langle \alpha \,|\, \beta \rangle = 0$$

ELECTRON SPIN

When we consider the complete wave function for an electron including both space and spin variables, we shall normalize it according to

$$\sum_{m=-1/2}^{1/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi\,(x, y, z, m)|^2 \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 1$$

ELECTRON SPIN

The wave function specifying the state of an electron depends not only on the coordinates x, y, and z but also on the spin state of the electron. To a very good approximation, the Hamiltonian for a system of electrons does not involve the spin variables but is a function only of spatial coordinates and derivatives with respect to spatial coordinates. In the case of hydrogen-like atoms, we can separate the stationary-state wave function of the electron into a product of space and spin parts:

$$\psi(x, y, z)g(m)$$

where $g(m)$ can be either α or β (in general, a combination of them). Note that, if $\psi(x, y, z)$ is eigenfunction of the Hamiltonian, also $\psi(x, y, z)g(m)$ is eigenfunction of it

ELECTRON SPIN

We have an additional postulate of QM, which states that the **wave function of a system of electrons must be antisymmetric with respect to interchange of any two electrons.** This postulate is called the **Pauli principle**

Pauli showed that particles with half-integral spin ($s = 1/2, 3/2,$ and so on) require antisymmetric wave functions, while particles of integral spin ($s = 0, 1,$ and so on) require symmetric wave functions. Particles requiring antisymmetric wave functions, such as electrons, are called **fermions**, whereas particles requiring symmetric wave functions, such as photons, are called **bosons**

ELECTRON SPIN

The Pauli principle has an interesting consequence for a system of identical fermions. The antisymmetry requirement means that

$$\psi(q_1, q_2, \ldots, q_n) = -\psi(q_2, q_1, \ldots, q_n)$$

Consider the value of ψ when electrons 1 and 2 have the same coordinates, that is, when $x_1 = x_2$, $y_1 = y_2$, $z_1 = z_2$, and $m_{s1} = m_{s2}$. Putting $q_2 = q_1$, we have

$$\psi(q_1, q_1, \ldots, q_n) = -\psi(q_1, q_1, \ldots, q_n)$$

$$\psi(q_1, q_1, \ldots, q_n) = 0$$

Thus 2 electrons with the same spin have zero probability of being found at the same point in three-dimensional space

ELECTRON SPIN

Since ψ is a continuous function, the probability of finding two electrons with the same spin close to each other in space is quite small. Thus the Pauli antisymmetry principle forces electrons of like spin to keep apart from one another; to describe this, one often speaks of a **Pauli repulsion** between such electrons. This "repulsion" is not a real physical force, but a reflection of the fact that the electronic wave function must be antisymmetric with respect to electron exchange