Chapter 11: Spin

What is Spin?

Real particles have "intrinsic" angular momentum. This degree of freedom is called spin. It is a fixed property of a particle that does not change. This is different than orbital angular momentum which does change, because for a given principal quantum number n, the orbital angular momentum quantum number can assume n different values of l. Classically, the angular momentum of a body orbiting another body, such as the earth orbiting the sun, would be described as orbital angular momentum, and the angular momentum of the earth revolving around its axis would be described as spin angular momentum. The quantum mechanical description is quite different. We cannot describe a classical orbital path for an electron in a hydrogen atom: we can describe only the probability density and the probability current. The quantum description of spin is also dramatically different than the classical description: quantum mechanically the electron is a point particle, and consequently it does not even have an axis about which it could spin....

The orbital angular momentum quantum number l identifies an eigenstate of the L^2 operator with eigenvalues $\sqrt{l(l+1)}\,\hbar$, so l is not the orbital angular momentum. Similarly, the instrinsic spin angular momentum is identified by the s quantum number from which the magnitude of the spin angular momentum $\sqrt{s(s+1)}\,\hbar$ is easily calculated.

It is customary to refer to the spin angular momentum quantum number as the spin. Electrons, protons, and neutrons all have spin 1/2. Photons have spin 1. Gravitons have spin 2.

The Semiclassical Vector Model for Spin

Since there is no good classical analog for the spin, it is difficult to describe. The semiclassical vector model is useful, just as it was for orbital angular momentum. The classical picture for the Bohr hydrogen atom had an electron orbiting a proton as shown in Figure 13.1. Both the electron and the proton are charged particles. So, the classical orbit of the electron around the proton is a current loop, which classically generates a magnetic moment associated with the orbit. In addition, since the electron and the proton have intrinsic spin, they both have a magnetic moment associated with the spin. The interaction energy between a magnetic moment and a magnetic field is given by $U = -\vec{\mu} \cdot \vec{B}$. Because the instrinsic spin can have different orientations relative to the applied field, the coupling of the magnetic moments associated with the spin to a magnetic field will result in different energies.

In addition, the relative motions of the proton and electron create an internal magnetic field, and the coupling between the intrinsic spin magnetic moment and the orbital magnetic moment also results in different energies. Compared to the energy differences associated with n, the splittings due to the spin-orbit interaction are much smaller and produce the atomic fine structure. The differences in the energy levels for fine structure splitting is on the order of 10^{-2} eV. The interaction between the magnetic moments associated with the proton and the electron produces a further splitting of the energy levels which is called the hyperfine splitting. The differences in the energy levels for hyperfine structure splitting is on the order of 10^{-7} eV.

The shifts in the energy levels due to these effects can be observed in the hydrogen spectrum. Figure 13.2 illustrates the energy level splittings due to the spin–orbit coupling (fine structure), and due to the spin–spin coupling (hyperfine structure). The degeneracy of the hydrogen energy levels is (largely) removed when these magnetic effects are included.

How Big is an Electron—and How Fast Does it Spin?

The Bohr radius is given by

$$a_0 = \frac{\hbar^2}{\mu e^2} = \frac{\hbar}{\mu c}\,\frac{\hbar c}{e^2} = \frac{\lambda_c}{2\pi\,\alpha} \qquad (13-1)$$

where

$$\alpha = \frac{e^2}{\hbar c} \qquad (13-2)$$

is known as the fine structure constant, and where

$$\lambda_c = 2\pi\,\frac{h}{\mu c}$$

is known as the Compton wavelength The fine structure constant emerges naturally from the explanation of the spin–orbit spectral line splitting using the Bohr model of the hydrogen atom. It relates the basic constants of electromagnetism (the charge on the electron), relativity (the speed of light), and quantum mechanics (Planck's constant). It is a dimensionless number with a value of approximately 1/137. Because it is dimensionless, its value is always 1/137 for any choice of units! In quantum electrodynamics α describes the coupling between electrons and photons.

Example 13–1: Calculate the Compton wavelength of an electron.

$$\lambda_c = 2\pi\;a_0\;\alpha = 2\pi\;\left(0.529\,\mathring{A}\right)\left(\frac{1}{137}\right) \approx 2.43\times 10^{-2}\,\mathring{A}.$$

The Compton wavelength λ_c was one of the early estimates of the electron radius, known as the Compton radius r_c.

Example 13–2: We now believe the electron to be a point particle. This means that the electron has no size in any spatial direction. However, another early mental picture of an electron was as a small spinning charged ball. The associated classical radius of the electron r_e was estimated by setting the Coulomb energy equal to the rest energy.

Calculate the velocity at the equator of a small charged spinning ball with an intrinsic spin angular momentum along z equal to $\hbar/2$.

Set the Coulomb energy equal to electron rest energy,

$$\frac{e^2}{r_e} = m_e c^2 \quad \Rightarrow \quad r_e = \frac{e^2}{m_e c^2} \approx 3\times 10^{-5}\,\text{Å},$$

which seems reasonable for atoms with radii on the order of an Angstrom. How fast does this electron spin? Equivalently, what is the speed of a point on the equator of this electron? Setting the angular momentum of a solid sphere equal to $\hbar/2$,

$$L = I\omega = \frac{2}{5}m_e r_e^2\left(\frac{v}{r_e}\right) = \frac{2}{5}m_e r_e^2 v = \frac{\hbar}{2}$$

$$\Rightarrow \quad v = \frac{5}{4}\frac{\hbar}{m_e r_e} = \frac{5}{4}\frac{\hbar}{m_e\left(e^2/m_e c^2\right)} = \frac{5}{4}\left(\frac{\hbar c}{e^2}\right)c = \frac{5}{4}(137)c \approx 171\;c.$$

This velocity is clearly superluminal, and so we do not believe this model.

Example 13–3: Calculate the speed of a point on the equator of a spinning charged ball model for the electron if its radius is equal to the Compton radius of the electron?

$$v = \frac{5}{4}\frac{\hbar}{m_e r_c} = \frac{5}{4}\frac{\hbar}{m_e(2\pi r_e)} = \frac{5}{8\pi}\big(137\big)c \approx 27\ c.$$

The velocity is again superluminal, and so we do not believe this model either.

The Gyromagnetic Ratio

The intent of this section is to introduce some terminology, and more importantly, to illustrate how the angular momentum associated with a charged particle results in a magnetic moment.

The classical definition of the gyromagnetic ratio is the ratio of the magnetic moment to the angular momentum. In other words

$$\mu = \gamma \vec{L},$$

where γ is the gyromagnetic ratio.

Example 13–4: Calculate the gyromagnetic ratio for a single electron in a circular orbit using classical arguments.

This example illustrates how the angular momentum and the magnetic moment are related. A circular current loop has a circumference of $2\pi r$ and an area of πr^2. For a current I in a circular loop of area A, the magnetic moment is $\vec{\mu} = I\vec{A}$. If the current is composed of one electron completing a cycle during period T,

$$\vec{\mu} = I\vec{A} \quad \Rightarrow \quad \big|\,\vec{\mu}\,\big| = \mu = IA = \frac{e}{T}\,\pi r^2,$$

where the direction is normal to the plane of the circle in accordance with the right hand rule. One circumference is traversed each period, or $2\pi r = vT$, so

$$\mu = \frac{ev}{2\pi r}\,\pi r^2 = \frac{1}{2}\,evr.$$

The classical ngular momentum is given by $\vec{L} = \vec{r} \times m\vec{v} \Rightarrow \big|\,\vec{L}\,\big| = L = mvr$. Since the direction of the magnetic moment and angular momentum are parallel we can simply use the magnitudes. This means that

$$\mu = \left(\frac{e}{2m}\right) L \qquad (13-3)$$

$$\Rightarrow \quad \frac{\mu}{L} = \gamma = \frac{e}{2m}$$

is the gyromagnetic ratio for a single electron in a circular orbit. This is a classical argument for the orbital angular momentum, but it is but a useful mnemonic.

If angular momentum is anticipated to be quantized in units of $\hbar$, it would make sense to define a magnetic moment expressed in terms of $\hbar$, like

$$\mu_B = \frac{e}{2m}\,\hbar$$

where μ_B is the known as the Bohr magnetron. The Bohr magnetron is nothing more than a specific magnetic moment which is given numerically by $\mu_B = 9.274 \times 10^{-24}, J/T$. In terms of the gyromagnetic ratio, the magnetic moment and orbital angular momentum are related by

$$\vec{\mu} = \left(\frac{e}{2m}\right)\vec{L} = \gamma\vec{L}.$$

Analogously, the spin magnetic moment is given by

$$\vec{\mu}_s = \frac{e}{m}\vec{S}, \qquad (13-4)$$

where S is the spin angular momentum. Note that the gyromagnetic ratios given by equations (13–3) and (13–4) differ by a factor of 2. There is no classical explanation for this difference. In terms of the spin gyromagnetic ratio,

$$\mu_s = \left(\frac{e}{m}\right)\vec{S} = \gamma_s\vec{S},$$

where $\gamma_s/\gamma = g$. The quantity g is known as the g-factor.

The right way to derive this is to use the relativistic Dirac equation, however relativistic quantum mechanics is beyond the scope of this book. The non–relativistic arguments which follow instead are due to Wolfgang Pauli, who postulated spin as an additional degree of freedom to explain the known experimental results before Dirac developed his equation. Pauli's theory is the classical limit of Dirac's theory. When the spin is included using Pauli's formalism, we call the resulting equation the Pauli-Schrodinger equation instead of simply the Schrodinger equation.

Spin Space

Pauli showed that the effects of spin can be included via additional degrees of freedom. The space that these additional degrees of freedom live in is known as the spin state space or spin space.

Ultimately, we will need to combine the new spin space with good old three-dimensional space to form the full state space. We will denote good old three-dimensional space by $\xi_{\vec{\mathrm{r}}}$, the spin state space by ξ_{s}, and the full state space by ξ. The full state space is spanned by the eigenvectors of good old three-dimensional space when properly combined with the eigenvectors of spin space. Schematically, the combination of 3d space and spin space can be labelled by the combined quantum numbers:

$$\begin{array}{lcl} & & \{\mathcal{X},\mathcal{Y},\mathcal{Z}\} \\ \xi_{\vec{\mathrm{r}}} & \longrightarrow & \{\mathcal{P}_x,\mathcal{P}_y,\mathcal{P}_z\} \\ & & \{\mathcal{H},\mathcal{L}^2,\mathcal{L}_z\} \\ \\ \xi_s & \longrightarrow & \{\mathcal{S}^2,\mathcal{S}_z\} \end{array} \qquad\qquad \xi \longrightarrow \begin{array}{c} \{\mathcal{X},\mathcal{Y},\mathcal{Z},\mathcal{S}^2,\mathcal{S}_z\} \\ \{\mathcal{P}_x,\mathcal{P}_y,\mathcal{P}_z,\mathcal{S}^2,\mathcal{S}_z\} \\ \{\mathcal{H},\mathcal{L}^2,\mathcal{L}_z,\mathcal{S}^2,\mathcal{S}_z\} \end{array}$$

The combination of spaces is done by forming the direct product of the component spaces. We write $\xi = \xi_{\vec{\mathrm{r}}} \bigotimes \xi_{\mathrm{s}}$, to denote the direct product. The direct product is a generalization of the outer product of vectors to spaces. In general,

$$\mathcal{A}\bigotimes\mathcal{B} = \mathcal{C} \quad \Rightarrow \quad C_{ikjl} = A_{ij}B_{kl}.$$

If both $\mathcal{A}$ and $\mathcal{B}$ are represented by 2×2 matrices,

$$\mathcal{A}\bigotimes\mathcal{B}=\begin{pmatrix} a_{11}\begin{pmatrix} b_{11} & b_{12}\\ b_{21} & b_{22}\end{pmatrix} & a_{12}\begin{pmatrix} b_{11} & b_{12}\\ b_{21} & b_{22}\end{pmatrix}\\ a_{21}\begin{pmatrix} b_{11} & b_{12}\\ b_{21} & b_{22}\end{pmatrix} & a_{22}\begin{pmatrix} b_{11} & b_{12}\\ b_{21} & b_{22}\end{pmatrix}\end{pmatrix}=\begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12}\\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22}\\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12}\\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22}\end{pmatrix}.$$

You can imagine why this is an impractical calculation to do explicitly when one of the component spaces is an infinite-dimensional Hilbert space. Instead, we will first develop just the spin space, and then later we will combine the results explicitly for the wavefunctions of hydrogen.

Although we will develop the spin eigenvalues and eigenvectors for any value of the spin, spin 1/2 particles will dominate our discussion. We can represent the operators of the spin spaces in subspaces. In particular, spin 1/2 uses a two-dimensional subspace. Therefore, our discussion of spin space will involve a number of 2×2 matrix operators.

The Ladder Operators for Spin

We are going to treat the spin angular momentum using a development very similar to our treatment of the orbital angular momentum in Chapter 9. The parallels are striking. In fact, the spin angular momentum arguments are precisely the same as the arguments we made for orbital angular momentum. The reason for this is because the algebra of the operators is identical. The commutators of the components of spin are

$$\big[\,\mathcal{S}_x,\,\mathcal{S}_y\,\big]=i\hbar\,\mathcal{S}_z,\qquad \big[\,\mathcal{S}_y,\,\mathcal{S}_z\,\big]=i\hbar\,\mathcal{S}_x,\qquad \text{and}\qquad \big[\,\mathcal{S}_z,\,\mathcal{S}_x\,\big]=i\hbar\,\mathcal{S}_y. \tag{13-5}$$

Like orbital angular momentum, the square of the spin angular momentum operator commutes with all its components,

$$\big[\,\mathcal{S}^2,\,\mathcal{S}_i\,\big]=0, \tag{13-6}$$

where the subscript i indicates any of the three components x, y, or z. Again like orbital angular momentum, the spin angular momentum is related to its components by

$$\mathcal{S}^2=\mathcal{S}_x^2+\mathcal{S}_y^2+\mathcal{S}_z^2\quad\Rightarrow\quad\mathcal{S}^2-\mathcal{S}_z^2=\mathcal{S}_x^2+\mathcal{S}_y^2.$$

The sum of the two components $\mathcal{S}_x^2+\mathcal{S}_y^2$ would appear to factor

$$\big(\mathcal{S}_x+i\mathcal{S}_y\big)\big(\mathcal{S}_x-i\mathcal{S}_y\big).$$

Again, these operators do not commute, so this is not actually factoring, but it is a good mnemonic. These are the raising and lowering operators for spin angular momentum, so

$$\mathcal{S}_+=\mathcal{S}_x+i\mathcal{S}_y,\qquad\text{and}\qquad\mathcal{S}_-=\mathcal{S}_x-i\mathcal{S}_y.$$

Here

$$\big[\mathcal{S}^2,\,\mathcal{S}_\pm\big]=0,$$
$$\big[\mathcal{S}_z,\,\mathcal{S}_\pm\big]=\pm\hbar\,\mathcal{S}_\pm.$$

Example 13–5: Show that $\big[\mathcal{S}^2,\, \mathcal{S}_+\big] = 0$.

$$\big[\mathcal{S}^2,\, \mathcal{S}_+\big] = \big[\mathcal{S}^2,\, \mathcal{S}_x + i\mathcal{S}_y\big] = \big[\mathcal{S}^2,\, \mathcal{S}_x\big] + i\big[\mathcal{S}^2,\, \mathcal{S}_y\big] = 0 + i(0) = 0.$$

Example 13–6: Show that $\big[\mathcal{S}_z,\, \mathcal{S}_+\big] = \hbar\,\mathcal{S}_+$.

$$\big[\mathcal{S}_z,\, \mathcal{S}_+\big] = \big[\mathcal{S}_z,\, \mathcal{S}_x + i\mathcal{S}_y\big] = \big[\mathcal{S}_z,\, \mathcal{S}_x\big] + i\big[\mathcal{S}_z,\, \mathcal{S}_y\big] = i\hbar\mathcal{S}_y + i\big(-i\hbar\mathcal{S}_x\big) = \hbar\big(\mathcal{S}_x + i\mathcal{S}_y\big) = \hbar\mathcal{S}_+.$$

The $\mathcal{S}^2$ and $\mathcal{S}_z$ operators will have different eigenvalues when they operate on the same basis vector, so there will be two indices for each basis vector. The first index is the eigenvalue for $\mathcal{S}^2$, denoted by α, and the second index is the eigenvalue for $\mathcal{S}_z$ denoted by β. The form of the eigenvalue equations must be

$$\mathcal{S}^2\big|\alpha,\, \beta\big> = \alpha\big|\alpha,\, \beta\big>, \tag{13-7}$$

$$\mathcal{S}_z\big|\alpha,\, \beta\big> = \beta\big|\alpha,\, \beta\big>\,. \tag{13-8}$$

Equations (13–7) and (13–8) are the spin space analogs to equations (9–15) and (9–16) for orbital angular momentum. Using arguments similar to those of chapter 9, $S_\pm\big|\alpha,\, \beta\big>$ is an eigenvector of both S^2 and S_z.

Example 13–7: Show that $S_+\big|\alpha,\, \beta\big>$ is an eigenvector of S_z.

This calculation is a carbon copy of those following equations (9–15) and (9–16). Example 13–6 gave us

$$\big[\mathcal{S}_z,\, \mathcal{S}_+\big] = \mathcal{S}_z\,\mathcal{S}_+ - \mathcal{S}_+\,\mathcal{S}_z = \hbar\,\mathcal{S}_+$$

$$\Rightarrow \quad \mathcal{S}_z\,\mathcal{S}_+ = \mathcal{S}_+\,\mathcal{S}_z + \hbar\,\mathcal{S}_+$$

$$\begin{aligned}
\Rightarrow \quad \mathcal{S}_z\,\mathcal{S}_+\big|\alpha,\, \beta\big> &= \big(\mathcal{S}_+\,\mathcal{S}_z + \hbar\,\mathcal{S}_+\big)\big|\alpha,\, \beta\big> \\
&= \mathcal{S}_+\,\mathcal{S}_z\big|\alpha,\, \beta\big> + \hbar\,\mathcal{S}_+\big|\alpha,\, \beta\big> \\
&= \mathcal{S}_+\,\beta\big|\alpha,\, \beta\big> + \hbar\,\mathcal{S}_+\big|\alpha,\, \beta\big> \\
&= \big(\beta + \hbar\big)\mathcal{S}_+\big|\alpha,\, \beta\big>,
\end{aligned}$$

$$\Rightarrow \quad \mathcal{S}_z\big(\mathcal{S}_+\big|\alpha,\, \beta\big>\big) = \big(\beta + \hbar\big)\big(\mathcal{S}_+\big|\alpha,\, \beta\big>\big).$$

Example 13–8: Show that $S_+\big|\alpha,\, \beta\big>$ is an eigenvector of $\mathcal{S}^2$.

This is a carbon copy of example 9–12. Here

$$\big[\mathcal{S}^2,\, \mathcal{S}_+\big] = \mathcal{S}^2\,\mathcal{S}_+ - \mathcal{S}_+\,\mathcal{S}^2 = 0$$

$$\Rightarrow \quad \mathcal{S}^2\,\mathcal{S}_+ = \mathcal{S}_+\,\mathcal{S}^2.$$

$$\Rightarrow \quad \mathcal{S}^2\,\mathcal{S}_+\big|\alpha,\, \beta\big> = \mathcal{S}_+\,\mathcal{S}^2\big|\alpha,\, \beta\big> = \mathcal{S}_+\,\alpha\big|\alpha,\, \beta\big> = \alpha\,\mathcal{S}_+\big|\alpha,\, \beta\big>,$$

$$\Rightarrow \quad \mathcal{S}^2\big(\mathcal{S}_+\big|\alpha,\, \beta\big>\big) = \alpha\big(\mathcal{S}_+\big|\alpha,\, \beta\big>\big).$$

The Eigenvalues of Spin

The linear algebra arguments for the spin angular momentum are the same as those for the orbital angular momentum: the operator S takes the place of the operator L. This is because the commutation relations are the same. Were we to follow the calculations of chapter 9, explicitly substituting $\mathcal{S}$ for $\mathcal{L}$, we would arrive at the spin analogs to equations (9–22) and (9–23),

$$\alpha = \beta_{\max}^2 + \hbar\beta_{\max},$$

and

$$\alpha = \beta_{\min}^2 - \hbar\beta_{\min}.$$

Equating these two equations and solving for $\beta_{\max}$ results in

$$\beta_{\max} = -\beta_{\min},$$

which is the maximum ladder separation. It gives us the top and bottom of the ladder. We assume the rungs of the ladder are separated by $\hbar$, because that is the amount of change indicated by the raising and lowering operators. If there is other than minimum separation, say there are n steps between the bottom and top rungs of the ladder, there is a total separation of $n\hbar$ between the bottom and the top. From figure 13–5 we expect

$$2\beta_{\max} = n\hbar \quad \Rightarrow \quad \beta_{\max} = \frac{n\hbar}{2}.$$

$$\begin{aligned} \Rightarrow \quad \alpha &= \beta_{\max}\big(\beta_{\max} + \hbar\big) \\ &= \frac{n\hbar}{2}\left(\frac{n\hbar}{2} + \hbar\right) \\ &= \hbar^2\left(\frac{n}{2}\right)\left(\frac{n}{2} + 1\right). \end{aligned} \tag{13-9}$$

We are going to re–label, letting $j = n/2$ again, so

$$\alpha = \hbar^2 j\big(j+1\big).$$

We find that j can be half-integral or integral and the rungs of the ladder will be separated by $\hbar$. Remember that the ladder steps depend on the z–component of the spin, and that the z–component is quantized in units of $\hbar/2$.

The linear algebra arguments have actually given us the solution in terms of total angular momentum. Total angular momentum is

$$\vec{J} = \vec{L} + \vec{S}.$$

Because the total angular momentum, the orbital angular momentum and the spin angular momentum all obey analogous commutation relations, we have accidentally arrived at the solution

for the most general case which is the case of total angular momentum. Spin brings the argument of chapter 9 to partial fruition. In the next chapter, we will discuss the total angular momentum, and the argument will be completed.

Using the possible values of $n = 0, 1, 2, 3, \ldots,$ equation (13–9) gives us the eigenvalues of the square of spin angular momentum, which are

$$\alpha = \hbar^2 \frac{n}{2}\left(\frac{n}{2}+1\right) = 0, \quad \frac{3}{4}\hbar^2, \quad 2\hbar^2, \quad \frac{15}{4}\hbar^2, \ldots$$

These are the possible values of spin angular momentum. For a particle with spin 0, the only possible value of n is 0; for a particle with spin 1/2, the only possible value of n is 1; for a particle with spin 2, the only possible value of n is 2; and so on. There is only one possible eigenvalue for the square of the spin angular momentum operator. The convention is to use the value of $n/2$ as the quantum number of the particle, to label this s, and to write equation (13–9) as

$$\alpha = \hbar^2\, s\left(s+1\right). \qquad (13-10)$$

Equation (13–10) gives the eigenvalues of $\mathcal{S}^2$ for all particles. It is conventional to refer to the spin quantum number of the particle instead of to the eigenvalue of the square of the spin angular momentum operator. The $\mathcal{S}^2$ eigenvalue can always be easily calculated using equation (13–10).

We refer to a particle as "a spin 1 particle" or as a "spin 1/2 particle" which implies that only one eigenvalue of the $\mathcal{S}^2$ can result from equation (13–10) for that particle...and that is correct. The value of $\mathcal{S}^2$ for a spin 1 photon is always $2\hbar^2$. The value of $\mathcal{S}^2$ for a spin 1/2 electron is always $3\hbar^2/4$.

The primary constituents of atoms are electrons, protons, and neutrons; all of which have spin 1/2. This motivates our upcoming concentration on spin 1/2 calculations.

The Eigenvalues of the Spin Projections

The ladder used in the above argument is constructed from the eigenvalues of the $\mathcal{S}_z$ operator. The spin ladder has a bottom rung and a top rung, which are given by

$$\beta_{\min} = -s\hbar, \qquad\qquad \beta_{\max} = s\hbar,$$

where s is the spin quantum number. The eigenvalues of $\mathcal{S}_z$ are multiples of $\hbar/2$ ranging from $-s$ to s. The symbol conventionally used to denote the $\mathcal{S}_z$ quantum number, for which we have used a generic β, is m_s which is known as the spin magnetic moment quantum number. The associated eigenvalue/eigenvector equation

$$\mathcal{S}_z\big|\alpha,\, \beta\!>\, = m_s\hbar\big|\alpha,\, \beta\!>\, . \qquad (13-11)$$

Example 13–9: What are the possible results of a measurement of $\mathcal{S}^2$ for an electron?

An electron is a spin 1/2 particle, so has $s = 1/2$. The only possible result of a measurement of $\mathcal{S}^2$ is

$$\hbar^2\, s\,(s+1) = \hbar^2\,\frac{1}{2}\,\left(\frac{1}{2}+1\right) = \hbar^2\,\frac{1}{2}\,\left(\frac{3}{2}\right) = \frac{3}{4}\hbar^2.$$

There is only one possible result of a measurement of $\mathcal{S}^2$.

Example 13–10: What are the possible results of a measurement of $\mathcal{S}_z$ for an electron?

For a particle of spin 1/2, the "bottom of the ladder" is at $-s\hbar = -\hbar/2$, which is one possible result of a measurement. The result of example 13–7 is

$$\mathcal{S}_z\big(\mathcal{S}_+|\alpha,\,\beta>\big) = \big(\beta+\hbar\big)\big(\mathcal{S}_+|\alpha,\,\beta>\big),$$

which is

$$\mathcal{S}_z\big(\mathcal{S}_+|s,\,m_s>\big) = \big(m_s\hbar+\hbar\big)\big(\mathcal{S}_+|s,\,m_s>\big)$$

using the result of example 13–8 and conventional notation for spin quantum numbers. This means that the next higher eigenvalue is $\hbar$ greater than the last, or $-\hbar/2+\hbar = \hbar/2$. Therefore $\hbar/2$ is a possible result of a measurement of $\mathcal{S}_z$. But this saturates the range since the top of the ladder is $s\hbar = \hbar/2$. For a spin 1/2 particle, the possible results of a measurement of $\mathcal{S}_z$ are $-\hbar/2$ or $\hbar/2$.

Two comments are relevant concerning examples 13–9 and 13–10. First, there are two eigenstates possible for a spin 1/2 particle. That is all. Since protons, neutrons, and electrons are all spin 1/2 particles, spin 1/2 is encountered frequently. There are many different notations for these two eigenstates. Some conventional ways of writing the eigenvector associated with the positive value of the $\mathcal{S}_z$ eigenvalue are

$$\Big|\frac{1}{2},\,\frac{1}{2}>,\quad \Big|\frac{1}{2}>,\quad \Big|\frac{1}{2},\,+>,\quad |+>,\quad \Big|\frac{1}{2},\,\uparrow>,\quad |\uparrow>\,.$$

Some conventional ways of writing the eigenvector associated with the negative value of the $\mathcal{S}_z$ eigenvalue are

$$\Big|\frac{1}{2},\,-\frac{1}{2}>,\quad \Big|-\frac{1}{2}>,\quad \Big|\frac{1}{2},\,->,\quad |->,\quad \Big|\frac{1}{2},\,\downarrow>,\quad |\downarrow>\,.$$

Notice that half of these contain only one symbol. This is reasonable because the spin quantum number s does not change for any given spin 1/2 particle. When there is only one possible value, the second index uniquely identifies the eigenstate. The up/down arrows are from the convention that for the predominant case of spin 1/2, (electrons, protons, neutrons), the two possible state are referred to as spin up or spin down.

Example 13–11: Show for a particle of spin s, that there are $2s+1$ possible eigenstates.

For a particle of spin s, there is only one eigenvalue of $\mathcal{S}^2$ and the only quantity which can assume different values is m_s. The number of eigenstates is the number of different values that m_s can assume. The allowed values of m_s range from $-s$ to $+s$ in integer steps. There are as many eigenstates which are negative as are positive. The quantum number s is the same as the maximum positive value as m_s. This explains the $2s$ term in $2s+1$.

Next, is zero included or not? For integral spin particles zero is included. This is described by the 1 in $2s+1$. If the spin quantum number is half integral— for example, 1/2, 3/2, or 5/2—zero is not a possible value of m_s. The effect of the "last half integer," the 1/2 in $5/2 = 2 + 1/2$ for instance, is to count one additional eigenstate, and the effect of the 1 in $2s+1$ is to count the opposite value of m_s, and not to count zero.

The total number of possible eigenstates for a particle of spin s is therefore $2s+1$.

The Spin Eigenvalue/Eigenvector Equations

With equation (13–10) and spin/spin magnetic moment quantum numbers, the eigenvalue/ eigenvector equation for the square of spin angular momentum is

$$\mathcal{S}^2\big|s,\, m_s\big> = \hbar^2\, s\big(s+1\big)\big|s,\, m_s\big> \,. \qquad (13-12)$$

The eigenvalue/eigenvector equation for the z–component of spin angular momentum is

$$\mathcal{S}_z\big|s,\, m_s\big> = m_s\hbar\big|s,\, m_s\big> \,. \qquad (13-13)$$

The magnitude of spin angular momentum is

$$\big|\,\mathcal{S}\,\big| = \sqrt{\mathcal{S}^2} = \hbar\sqrt{s(s+1)}. \qquad (13-14)$$

From an argument identical to that for the raising and lowering operators of orbital angular momentum, the normalized eigenvalue/eigenvector equations for the raising and lowering operators for spin are

$$\mathcal{S}_\pm\big|s,\, m_s\big> = \sqrt{s(s+1) - m_s(m_s \pm 1)}\,\hbar\big|s,\, m_s \pm 1\big> \,. \qquad (13-15)$$

Examples of the use of these are included in the text and in the examples. Examples 13–17 and 13–18 use equations (13–13) and (13–15).

Spinors

The section, and most of the remainder of the chapter, will deal only with spin 1/2 particles. This reduces the scope of the discussion, but since protons, neutrons, and electrons are all spin 1/2 particles, it also has the advantage of being practical.

A spin 1/2 particle has two possible eigenstates,

$$\big|s,\, m_s\big> \;\rightarrow\; \Big|\frac{1}{2},\, \pm\frac{1}{2}\Big> \,.$$

Since we have specified spin 1/2, the only possible value of of s is $s = 1/2$, so s is uniquely identified and we do not need to refer to it explicitly. The notation

$$|s,\, m_s> \;\rightarrow\; \Big|\, \pm\frac{1}{2}>,$$

contains the same information if $s = 1/2$ is understood. In fact, if $s = 1/2$ is understood, the only possible values of m_s are $\pm 1/2$, so the only symbol that changes is the sign of m_s between the two states. Keeping track of the sign of m_s uniquely specifies the eigenstate, so we can write

$$|s,\, m_s> \;\rightarrow\; |\pm>,$$

if $s = 1/2$ is understood. This is the convention we will use for spin 1/2 particles. Further, using a classical analogy, it is conventional to refer to these as spin up or spin down eigenstates, where $|+>$ specifies spin up and $|->$ specifies spin down.

Since angular momentum is observable, $\mathcal{S}$ is Hermitian, and we can take $|+>$ and $|->$ to be orthonormal, *i.e.*,

$$<+|+> = <-|-> = 1,$$

and

$$<+|-> = <-|+> = 0.$$

A two eigenstate system can be described in a two-dimensional subspace of the infinite-dimensional Hilbert space. We can represent $|+>$ and $|->$ as orthonormal two-dimensional unit vectors

$$|+> \;\rightarrow\; \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{and} \quad |-> \;\rightarrow\; \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

These unit vectors are often denoted χ_+ and χ_-.

We indicated the space appropriate to both orbital state space and spin space is the direct product of both spaces. However, you may have gleaned from the calculation of $\mathcal{A} \bigotimes \mathcal{B}$ that the effect is to expand the space where the new eigenstates are all possible product eigenstates. If we have a representation of an eigenstate in orbital state space, say $\psi(\vec{r})$, and we know it has spin up we can write

$$\Psi(\vec{r}) = \psi(\vec{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \psi_+(\vec{r}) \\ 0 \end{pmatrix},$$

where the subscript $+$ indicates spin up, and the upper case Ψ indicates spin is included. If we know the particle is spin down, we can write

$$\Psi(\vec{r}) = \psi(\vec{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ \psi_-(\vec{r}) \end{pmatrix},$$

similarly. If know only we are dealing with a spin 1/2 particle and do not know if it is in a spin up or down eigenstate, we can write

$$\Psi(\vec{r}) = \begin{pmatrix} \psi_+(\vec{r}) \\ \psi_-(\vec{r}) \end{pmatrix},$$

where the last two component object is known as a spinor.

Example 13–12: Construct the spinor for the $\psi_{3,1,-1}(r,\theta,\phi)$ spin down state of the hydrogen atom.

The position space representation for $\psi_{3,1,-1}(r,\theta,\phi)$ (see example 10–12) is given by

$$\psi_{3,1,-1}(r,\theta,\phi) = \frac{2}{27\sqrt{\pi}} a_0^{-3/2} \left(1 - \frac{r}{6a_0}\right) \frac{r}{a_0} \sin\theta\, e^{-r/3a_0 - i\phi},$$

so the associated spinor wavefunction is given by

$$\Psi_{3,1,-1}(r,\theta,\phi) = \begin{pmatrix} 0 \\ \frac{2}{27\sqrt{\pi}} a_0^{-3/2} \left(1 - \frac{r}{6a_0}\right) \frac{r}{a_0} \sin\theta\, e^{-r/3a_0 - i\phi} \end{pmatrix}.$$

Spin Calculations using Dirac Notation

We can write any vector in the Hilbert space using Dirac notation. If the direct product of this Hilbert space and the spin state space is made, earlier denoted by $\xi = \xi_{\vec{r}} \bigotimes \xi_s$, we can simply include additional indices to denote the additional degrees of freedom. For example, $<\vec{r}, s, m_s|\,\psi> = \psi_{m_s}(\vec{r})$.

For a spin 1/2 particle, m_s can only have one of two values; these two values are often denoted by $+$ and $-$. If we knew the particle had spin up or spin down, we could write the two representations as

$$<\vec{r},\,+|\,\psi> = \psi_+(\vec{r}), \quad \text{or} \quad <\vec{r},\,-|\,\psi> = \psi_-(\vec{r}).$$

Combining this with the notation of the previous section, we can write the spinor wavefunction as

$$<\vec{r},\,\pm|\,\psi> = \Psi(\vec{r}).$$

Example 13–13: Write the orthonormality condition for ξ.

The orthonormality condition for $\xi_{\vec{r}}$ is given by

$$<\vec{r}\,'\,\big|\,\vec{r}> = \delta(\vec{r}\,' - \vec{r}).$$

The orthonormality condition for ξ_s is given by

$$<m_s'\,\big|\,m_s> = \delta_{m_s',\,m_s}.$$

So, the orthonormality condition for the direct product space ξ is given by

$$<\vec{r}\,',\,m_s'\big|\vec{r},\,m_s> = \delta_{m_s',\,m_s}\,\delta(\vec{r}\,' - \vec{r}).$$

Example 13–14: Write the completeness relation for a vector in the space ξ where spin 1/2 particles are being described.

The completeness relation for $\xi_{\vec{r}}$ is

$$\int d^3r \big| \vec{r} \big\rangle \big\langle \vec{r} \big| = \mathcal{I}.$$

The completeness relation for ξ_s is

$$\sum_{m_s} \big| \, m_s \big\rangle \big\langle m_s \, \big| = \mathcal{I}.$$

They are combined in the direct product space ξ as

$$\sum_{m_s} \int d^3r \big| \, \vec{r}, \, m_s \big\rangle \big\langle \vec{r}, \, m_s \big| = \mathcal{I}.$$

For spin 1/2 particles specifically,

$$\sum_{m_s} \int d^3r \big| \, \vec{r}, \, \pm \big\rangle \big\langle \vec{r}, \, \pm \big| = \int d^3r \big| \, \vec{r}, \, + \big\rangle \big\langle \vec{r}, \, + \big| \;\; + \;\; \int d^3r \big| \, \vec{r}, \, - \big\rangle \big\langle \vec{r}, \, - \big| = \mathcal{I}.$$

Notice cross terms were not considered, which is a consequence of the orthonormality condition.

Example 13–15: Write the normalization condition for spinors.

The normalization condition is given by

$$\langle \psi \, \big| \, \psi \rangle = 1 = \langle \vec{r}, \, \pm \big| \vec{r}, \, \pm \rangle$$

$$= \langle \vec{r}, \, + \big| \vec{r}, \, + \rangle \;\; + \;\; \langle \vec{r}, \, - \big| \vec{r}, \, - \rangle$$

and we are done. If a specific position space representation is assumed,

$$1 = \int d^3r \Psi(\vec{r})^\dagger \Psi(\vec{r})$$

$$= \int d^3r \big(\psi_+^*(\vec{r}), \;\; \psi_-^*(\vec{r}) \big) \begin{pmatrix} \psi_+(\vec{r}) \\ \psi_+(\vec{r}) \end{pmatrix}$$

$$= \int d^3r \Big(\big| \, \psi_+(\vec{r}) \, \big|^2 + \big| \, \psi_-(\vec{r}) \, \big|^2 \Big).$$

Both forms ignore the cross terms because of the orthonormality condition. Notice there are two terms in both final expressions. That is because there are two eigenstates being described.

Note that the probability density for spin up is given by $\big| \, \psi_+(\vec{r}) \, \big|^2$, and the probability density for spin down is given by $\big| \, \psi_-(\vec{r}) \, \big|^2$.

The Matrix Representations of Spin Operators

The matrix form of the square of the spin 1/2 angular momentum operator is

$$\mathcal{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{3}{4}\hbar^2 \mathcal{I}. \qquad (13-16)$$

Notice that precisely like $\mathcal{L}^2, \mathcal{S}^2$ is proportional to the identity operator. The matrices representing the components of the spin 1/2 angular momentum operators are

$$\mathcal{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \mathcal{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \mathcal{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \qquad (13-17)$$

The matrices, without the constants of $\hbar/2$, are known as the Pauli spin matrices. The Pauli matrices are denoted by σ_i with

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (13-18)$$

. The matrices which represent the ladder operators for spin 1/2 are given by

$$\mathcal{S}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad \mathcal{S}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \qquad (13-19)$$

Example 13–16: Use the eigenvalue/eigenvector equation for the z–component to derive the matrix form of $\mathcal{S}_z$.

Equation (13–13) is

$$\mathcal{S}_z\big|s,\, m_s\big> = m_s\hbar\big|s,\, m_s\big>$$

which we can write as

$$\mathcal{S}_z\big|\pm\big> = \pm\frac{\hbar}{2}\big|\pm\big>$$

for spin 1/2 particles. Spin 1/2 operators must act on two dimensional spinors, so their matrix form must be a 2×2 matrix. The matrix elements will be $<\pm|\,\mathcal{S}_z\,|\pm>$, so

$$\mathcal{S}_z = \begin{pmatrix} <+|\,\mathcal{S}_z\,|+> & <+|\,\mathcal{S}_z\,|-> \\ <-|\,\mathcal{S}_z\,|+> & <-|\,\mathcal{S}_z\,|-> \end{pmatrix} = \begin{pmatrix} <+|\,\frac{\hbar}{2}\,|+> & <+|\,-\frac{\hbar}{2}\,|-> \\ <-|\,\frac{\hbar}{2}\,|+> & <-|\,-\frac{\hbar}{2}\,|-> \end{pmatrix}$$

where we have let $\mathcal{S}_z$ operate on the ket to the right in the last step. Then

$$\mathcal{S}_z = \begin{pmatrix} \frac{\hbar}{2}<+|+> & -\frac{\hbar}{2}<+|-> \\ \frac{\hbar}{2}<-|+> & -\frac{\hbar}{2}<-|-> \end{pmatrix} = \begin{pmatrix} \frac{\hbar}{2}\cdot 1 & -\frac{\hbar}{2}\cdot 0 \\ \frac{\hbar}{2}\cdot 0 & -\frac{\hbar}{2}\cdot 1 \end{pmatrix}$$

because of the orthonormality of the eigenstates, we find

$$\mathcal{S}_z = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

This is consistent with equation (13–17).

Example 13–17: Use the raising and lowering operators to derive the matrix form of $\mathcal{S}_y$.

The eigenvalue/eigenvector equation for the raising and lowering operators is given by equation (13–15),

$$\mathcal{S}_\pm \big| s,\, m_s \big> = \sqrt{s(s+1) - m_s(m_s \pm 1)}\,\hbar \big| s,\, m_s \pm 1 \big> \,.$$

There are enough signs in this equation to easily induce a sign error, so we will work case-by-case. For a spin 1/2 system, there are four cases $\mathcal{S}_+\big|+\big>$, $\mathcal{S}_+\big|-\big>$, $\mathcal{S}_-\big|+\big>$, and $\mathcal{S}_-\big|-\big>$. The first is

$$\mathcal{S}_+\big|+\big> = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{1}{2}\left(\frac{1}{2}+1\right)}\hbar \Big| \frac{1}{2}+1 \Big>,$$

Proceeding,

$$\mathcal{S}_+\big|+\big> = \sqrt{\frac{3}{4} - \frac{3}{4}}\hbar \Big| \frac{3}{2} \Big> = \sqrt{0}\hbar \Big| \frac{3}{2} \Big> = 0.$$

We have tried to step above the top rung of the ladder. Similarly, $\mathcal{S}_-\big|-\big> = 0$. The other cases are

$$\mathcal{S}_+\big|-\big> = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - -\frac{1}{2}\left(-\frac{1}{2}+1\right)}\hbar \Big| -\frac{1}{2}+1 \Big> = \sqrt{\frac{3}{4} + \frac{1}{2}\left(\frac{1}{2}\right)}\hbar \Big| \frac{1}{2} \Big> = \sqrt{1}\hbar\big|+\big> = \hbar\big|+\big> \,.$$

Similarly, $\mathcal{S}_-\big|+\big> = \hbar\big|+\big>$. Remember also $\mathcal{S}_+ = \mathcal{S}_x + i\mathcal{S}_y$, and $\mathcal{S}_- = \mathcal{S}_x - i\mathcal{S}_y$. Therefore

$$\mathcal{S}_-\big|-\big> = \left(\mathcal{S}_x - i\mathcal{S}_y\right)\big|-\big> = 0,$$

$$\mathcal{S}_+\big|-\big> = \left(\mathcal{S}_x + i\mathcal{S}_y\right)\big|-\big> = \hbar\big|+\big> \,.$$

If we subtract the second equation from the first, we get

$$-2i\mathcal{S}_y\big|-\big> = -\hbar\big|+\big> \quad \Rightarrow \quad \mathcal{S}_y\big|-\big> = -i\frac{\hbar}{2}\big|+\big> \,.$$

Similarly, we find

$$\mathcal{S}_y\big|+\big> = i\frac{\hbar}{2}\big|-\big> \,.$$

Forming the matrix following the procedure of the last example, we find

$$\mathcal{S}_y = \begin{pmatrix} <+|\,\mathcal{S}_y\,|+> & <+|\,\mathcal{S}_y\,|-> \\ <-|\,\mathcal{S}_y\,|+> & <-|\,\mathcal{S}_y\,|-> \end{pmatrix} = \begin{pmatrix} <+|\,i\frac{\hbar}{2}\,|-> & <+|\,-i\frac{\hbar}{2}\,|+> \\ <-|\,i\frac{\hbar}{2}\,|-> & <-|\,-i\frac{\hbar}{2}\,|+> \end{pmatrix}$$

when the operator acts to the right. Then

$$\mathcal{S}_y = \begin{pmatrix} i\frac{\hbar}{2}<+|-> & -i\frac{\hbar}{2}<+|+> \\ i\frac{\hbar}{2}<-|-> & -i\frac{\hbar}{2}<-|+> \end{pmatrix} = \begin{pmatrix} 0 & -i\frac{\hbar}{2} \\ i\frac{\hbar}{2} & 0 \end{pmatrix}$$

because of the orthonormality of the eigenstates, we obtain

$$\mathcal{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

$\mathcal{S}_x$ can be derived similarly.

Example 13–18: Derive equation (13–16).

The square of the spin angular momentum operator is the sum of the squares of the component operators, or

$$\begin{aligned}
\mathcal{S}^2 &= \mathcal{S}_x^2 + \mathcal{S}_y^2 = \mathcal{S}_z^2 \\
&= \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\
&= \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
&= \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{3\hbar^2}{4}\mathcal{I}.
\end{aligned}$$

This duplicates equation (13–16).
