Chapter 12
Spin

12.1 Classical Magnetic Moment

I have completed most of the material typically covered in a one-semester course on quantum mechanics. There is one additional topic, however, that needs to be discussed, that of intrinsic angular momentum or *spin*. Spin arises naturally when one considers the relativistic version of the Schrödinger equation, namely the Dirac equation. In that equation the wave function for a free electron has four components, two of which correspond to positive energy solutions. The two positive energy solutions can be associated with two spin components of the electron (the negative energy solutions correspond to anti-particles). Historically, spin was deduced from atomic spectra. In turned out that the spectra could be explained if one assigned an intrinsic angular momentum to the electron. Today we know that all elementary particles possess such an intrinsic angular momentum (which can be zero for some particles). *Fermions* (named after Enrico Fermi) are particles whose intrinsic angular momentum quantum number corresponds to half integral values of intrinsic spin (measured in units of $\hbar$) while *bosons* (named after Satyendra Nath Bose) are particles whose intrinsic angular momentum quantum number corresponds to integral values of intrinsic spin.

Before discussing spin, it is useful to recall the relationship between the magnetic moment of a charged particle and its angular momentum relative to some origin. The magnetic moment of an electron circulating about the origin is given by

$$\begin{aligned}\boldsymbol{\mu} &= \frac{1}{2}\int \mathbf{r}'\times\mathbf{J}(\mathbf{r}')d\mathbf{r}' = -\frac{e}{2}\int \mathbf{r}'\times\mathbf{v}(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}' = -\frac{e\mathbf{r}\times\mathbf{v}}{2} \\ &= -\frac{e\mathbf{r}\times m_e\mathbf{v}}{2m_e} = -\frac{e\mathbf{r}\times\mathbf{p}}{2m_e} = -\frac{e\mathbf{L}}{2m_e},\end{aligned} \tag{12.1}$$

where $\mathbf{J}(\mathbf{r}') = -e\mathbf{v}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ is the (electric) current density associated with an electron located at position $\mathbf{r}$ moving with velocity $\mathbf{v}$. Remember that e is the

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magnitude of the charge of the electron—the magnetic moment of an electron and its angular momentum are in opposite directions. When a particle having a magnetic moment $\boldsymbol{\mu}$ is placed in a magnetic field characterized by a field induction vector $\mathbf{B}$, there is an energy

$$V = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{e\mathbf{L} \cdot \mathbf{B}}{2m_e} \tag{12.2}$$

associated with the magnetic moment–magnetic field interaction. If the field is taken to be along the z axis, then

$$V = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{eBL_z}{2m_e} = \beta_0 B \frac{L_z}{\hbar}, \tag{12.3}$$

where

$$\beta_0 = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}\ \mathrm{J\,T^{-1}} = 5.79 \times 10^{-5}\ \mathrm{eV\,T^{-1}} \tag{12.4}$$

is the *Bohr magneton.* In frequency units,

$$\frac{\beta_0}{h} = 14.0\ \mathrm{GHz/T} = 1.40\ \mathrm{MHz/Gauss}. \tag{12.5}$$

In the quantum problem, the magnetic moment becomes an operator and the potential is replaced by the operator

$$\hat{V} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = \frac{eB\hat{L}_z}{2m_e} = \beta_0 B \frac{\hat{L}_z}{\hbar}. \tag{12.6}$$

For the electron in hydrogen, the energy levels characterized by a given value of ℓ are $(2\ell + 1)$-fold degenerate in the absence of the magnetic field. In the presence of an external magnetic field these degenerate levels are split into $(2\ell + 1)$ distinct energy levels, with the spacing between adjacent levels of order $\Delta E_m = \beta_0 B$. I will derive explicit expressions for this so-called *Zeeman splitting* in Chap. 21. In the Earth's magnetic field, which is typically of order 0.5 Gauss, the splittings are of order 1 MHZ.

12.2 Spin Magnetic Moment

Since ℓ is integral, each state of a given ℓ splits into an *odd* number of states in a magnetic field. This is referred to as the *normal* Zeeman effect. However, in some cases it is observed that the splitting is into an *even* number of levels. This is referred to as the *anomalous* Zeeman effect. In order to explain this and other observed

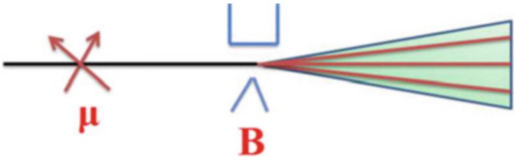

Fig. 12.1 Schematic representation of the Stern-Gerlach experiment. A beam of atoms having randomly oriented magnetic moments are passed through a region where there is a magnetic field gradient. Classically, there is a continuous range of deflection angles. For atoms having quantized angular momentum characterized by the quantum number ℓ, one would expect $(2\ell + 1)$ distinct traces

features of atomic structure, Goudsmit and Uhlenbeck proposed the concept of an intrinsic angular momentum or *spin* for the electron.[1] This also helped to explain an apparent anomaly in another experiment.

The other experiment is the Stern-Gerlach experiment carried out in 1921 (see Fig. 12.1).[2] If a beam of neutral particles, each having a magnetic moment $\boldsymbol{\mu}$, is sent into an *inhomogeneous* magnetic field $\mathbf{B}(\mathbf{r})$, there is a force on each particle given by

$$\mathbf{F}(\mathbf{r},t) = \nabla\left[\boldsymbol{\mu}(t)\cdot\mathbf{B}(\mathbf{r})\right] = \nabla\left[\mu_x(t)B_x(\mathbf{r}) + \mu_y(t)B_y(\mathbf{r}) + \mu_z(t)B_z(\mathbf{r})\right]. \tag{12.7}$$

Owing to its interaction with the field, the magnetic moment becomes a function of time. In the experiment of Stern and Gerlach, neutral atoms moving in the x direction pass through a region in which there is a magnetic field having a large homogeneous component in the z direction and smaller spatially varying components in all directions (the field components must satisfy $\nabla \cdot \mathbf{B} = 0$). An atom can possess a magnetic moment owing to the motion of its electrons about the nucleus. The magnetic moment precesses about the large homogeneous field component in the z direction, resulting in values of $\mu_x(t)$ and $\mu_y(t)$ that effectively average to zero and to a value of μ_z that is approximately constant, such that the resulting force on an atom produced by the field gradient is given approximately by

$$\mathbf{F} \approx \mu_z \frac{\partial B_z}{\partial z}\mathbf{u}_z \approx \mu_z \frac{\partial B}{\partial z}\mathbf{u}_z. \tag{12.8}$$

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[1] See, for example, George E. Uhlenbeck and Samuel A. Goudsmit, *Spinning Electrons and the Structure of Spectra*, Nature **117,** 264–265 (1926). For an interesting paper on this discovery, see the article by Abraham Pais, *George Uhlenbeck and the discovery of electron spin,* Physics Today **42**, 34–40 (1989).

[2] Walter Gerlach and Otto Stern, *Der experimentelle Nachweis der Richtungsquantelung im Magnetfeld* (*Experimental Proof of Space Quantization in a Magnetic Field*), Zeitschrift für Physik. **9**, 349–352 (1922); an English translation can be found at http://www.applet-magic.com/sterngerlach.htm.

Classically, we would expect a beam of particles having a magnetic moment $\boldsymbol{\mu}$ oriented in random directions to be deflected over a continuous range in the z-direction corresponding to the range of values $-\mu \leq \mu_z \leq \mu$ in the incoming beam.

In the quantum case, μ_z is replaced by the expectation value of the z-component of the magnetic moment operator which, in turn, is proportional to the expectation value of $\hat{L}_z$. Thus, owing to the gradient force, atoms having an angular momentum quantum number ℓ should be split into $(2\ell + 1)$ *discrete* paths after passing through the magnetic field region, each path corresponding to a different value of the z-component of angular momentum or magnetic moment. It was found, however, that when silver atoms were sent through the apparatus, *two* paths were detected even though ground state silver atoms were known to have $\ell = 0$.

Compton and Pauli had previously suggested that the electron could possess an intrinsic magnetic moment, but the credit for the explanation usually goes to Goudsmit and Uhlenbeck (although they never won the Nobel prize for the discovery of spin). To fit the experimental data, the operator $\hat{\boldsymbol{\mu}}_s$ associated with intrinsic magnetic moment of the electron and the operator $\hat{\mathbf{S}}$ associated with the intrinsic spin angular momentum of the electron must be related by

$$\boldsymbol{\mu}_s = -g_e \frac{e\mathbf{S}}{2m_e}; \tag{12.9}$$

moreover, it is necessary that the spin operator $\hat{\mathbf{S}}$ appearing in Eq. (12.9) corresponds to an angular momentum quantum number $s = 1/2$. The quantity g_e appearing in Eq. (12.9) is referred to as the *electron g-factor*. To fit the spectroscopic data, Goudsmit and Uhlenbeck took $g_e = 2$. It turns out that g_e is *approximately* equal to 2, but there are corrections related to the interaction of the electron with the vacuum field. The electron g-factor is one of the most precisely determined constants in physics with

$$g_e = 2.0023193043622 \pm 0.0000000000015, \tag{12.10}$$

and is in agreement with theoretical calculations. I will take $g_e = 2$.

It is natural to talk about spin using Dirac notation. The spin state of an electron can be described by the eigenket $|sm_s\rangle$ where $s = 1/2$, $m_s = \pm 1/2$. The state with $m_s = +1/2$ is referred to as *spin up* and that with $m_s = -1/2$ as *spin down*. As for any angular momentum,

$$\hat{S}^2 |sm_s\rangle = \hbar^2 s(s+1) |sm_s\rangle = \frac{3}{4}\hbar^2 |sm_s\rangle; \tag{12.11a}$$

$$\hat{S}_z |\pm 1/2\rangle = m_s \hbar |\pm 1/2\rangle = \pm \frac{1}{2}\hbar |\pm 1/2\rangle; \tag{12.11b}$$

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar \hat{S}_z; \tag{12.11c}$$

$$\hat{S}_+ \left|-1/2\right\rangle = \left(\hat{S}_x + i\hat{S}_y\right) \left|-1/2\right\rangle = \hbar \left|1/2\right\rangle; \tag{12.11d}$$

$$\hat{S}_- \left|1/2\right\rangle = \left(\hat{S}_x - i\hat{S}_y\right) \left|1/2\right\rangle = \hbar \left|-1/2\right\rangle; \tag{12.11e}$$

$$\hat{S}_+ \left|1/2\right\rangle = 0; \quad \hat{S}_- \left|-1/2\right\rangle = 0. \tag{12.11f}$$

(the s quantum number is suppressed in most of these equations since it always equals 1/2). It is important to remember that electron spin is an *intrinsic* spin and has nothing to do with motion of charge—any classical models based on a rotating charge give meaningless results. Thus, spin acts in its own *abstract* space, independent of the orbital angular momentum of the particle. The intrinsic magnetic moment of the spin is a direction opposite to its intrinsic spin angular momentum.

In the $|m_s\rangle$ basis, the spin operators are 2 × 2 matrices

$$\underset{\sim}{\mathrm{S}}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \tag{12.12a}$$

$$\underset{\sim}{\mathrm{S}}_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \tag{12.12b}$$

$$\underset{\sim}{\mathrm{S}}_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \tag{12.12c}$$

$$\underset{\sim}{\mathrm{S}}_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \tag{12.12d}$$

$$\underset{\sim}{\mathrm{S}}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad \underset{\sim}{\mathrm{S}}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \tag{12.12e}$$

where the order of the matrix indices is

$$\left|1/2\right\rangle = \left|\uparrow\right\rangle; \qquad \left|-1/2\right\rangle = \left|\downarrow\right\rangle \tag{12.13}$$

(that is, $\left(\underset{\sim}{\mathrm{S}}_z\right)_{11} = \left(\underset{\sim}{\mathrm{S}}_z\right)_{\uparrow\uparrow}$) and $|\uparrow\rangle$ and $|\downarrow\rangle$ are referred to as spin up and spin down eigenkets, respectively. It is customary to write

$$\underset{\sim}{\mathrm{S}} = \hbar\boldsymbol{\sigma}/2, \tag{12.14}$$

where

$$\boldsymbol{\sigma} = \sigma_x \mathbf{u}_x + \sigma_y \mathbf{u}_y + \sigma_z \mathbf{u}_z, \tag{12.15}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \tag{12.16a}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \tag{12.16b}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{12.16c}$$

and the components of $\boldsymbol{\sigma}$ are referred to as *Pauli matrices*. Together with the identity,

$$1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{12.17}$$

the Pauli matrices form a complete basis set for all 2 × 2 Hermitian matrices. Note that

$$\mathrm{Tr}\,(\sigma_x) = \sum_{i=1}^{3} (\sigma_x)_{ii} = 0; \tag{12.18a}$$

$$\sigma_x^2 = 1; \tag{12.18b}$$

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0; \tag{12.18c}$$

$$\left[\sigma_x, \sigma_y\right] = 2i\sigma_z; \tag{12.18d}$$

$$\sigma_x \sigma_y = i\sigma_z, \tag{12.18e}$$

along with all cyclic variations of these equations with $x \to y$, $y \to z$, and $z \to x$. Since they satisfy Eq. (12.18c), the Pauli matrices are said to *anti-commute*.

A general spin state can be written as

$$|\chi\rangle = \alpha\,|\uparrow\rangle + \beta\,|\downarrow\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \tag{12.19}$$

The corresponding wave functions for spin up and spin down can be written as χ_+ and χ_-, respectively, although these wave functions *have no meaning in coordinate space*. They are defined only in the abstract spin vector space. Thus, the eigenfunctions of the electron in the hydrogen atom can be written as $\psi_{n\ell m}(\mathbf{r})\,\chi_\pm$ and the eigenkets as

$$|n\ell m; s = 1/2, m_s = \pm 1/2\rangle = |n\ell m\rangle\,|sm_s\rangle\,. \tag{12.20}$$

Spin is a strange quantity. To help you understand why, I will look at the way in which the spin components transform under a rotation of the coordinate system. Although the spin wave functions are not functions in coordinate space, they *will* change under a rotation of the coordinate system since the $x, y, z,$ components of the spin are inter-mixed. Imagine that we have a Stern-Gerlach experiment that picks out spin up relative to some quantization axis. We now pass these atoms through a second Stern-Gerlach magnet that is oriented at an angle $\theta \leq \pi$ relative to the first (that is, the spin is now defined relative to a new axis that is at an angle θ relative to the first). The question is, "What is the spin state after passing through the second magnet?"

Before answering this question let us think about what happens in a similar situation with the electric field vector of light, which is a vector quantity. After passing through a polarizer whose axis is in the z direction (the light is propagating in the y direction) and an *analyzer* in the $x - z$ plane whose axis is at an angle $\theta \leq \pi$ relative to the z-axis, the field intensity after passing through the analyzer is proportional to $\cos^2 \theta$. That is, if the analyzer is rotated by π relative to the polarizer, the intensity is unchanged. If the analyzer is rotated by $\pi/2$ (crossed polarizers), no light gets through.

But what happens with spin? In the spin experiment, the first magnet has $\mathbf{B} = B_0 \mathbf{u}_z$ and the second

$$\mathbf{B} = B_0 \left(\mathbf{u}_z \cos\theta + \mathbf{u}_x \sin\theta \right). \tag{12.21}$$

To see what occurs, I must express the original state vector in terms of the new state vectors defined relative to the new direction of the field. In other words, I need to look at the interaction of the spin magnetic moment with the new field,

$$\hat{V} = -\hat{\boldsymbol{\mu}}_s \cdot \mathbf{B} = \frac{e\hat{\mathbf{S}} \cdot \mathbf{B}}{m_e} = \frac{eB_0}{m_e} \left(\hat{S}_x \sin\theta + \hat{S}_z \cos\theta \right); \tag{12.22}$$

$$\underset{\sim}{V} = \frac{eB_0\hbar}{2m_e} \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} = \beta_0 B_0 \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}. \tag{12.23}$$

It is a simple matter to diagonalize this matrix. The eigenvalues are $\pm\beta_0 B_0$ and the eigenkets are (work this out)

$$|\uparrow\rangle' = \cos\left(\frac{\theta}{2}\right) |\uparrow\rangle + \sin\left(\frac{\theta}{2}\right) |\downarrow\rangle; \tag{12.24a}$$

$$|\downarrow\rangle' = -\sin\left(\frac{\theta}{2}\right) |\uparrow\rangle + \cos\left(\frac{\theta}{2}\right) |\downarrow\rangle. \tag{12.24b}$$

Expressing the original ket in terms of the new ket, I find

$$|\uparrow\rangle = \cos\left(\frac{\theta}{2}\right) |\uparrow\rangle' - \sin\left(\frac{\theta}{2}\right) |\downarrow\rangle'. \tag{12.25}$$

Thus the probability to find the atom in spin up after the second magnet is $\cos^2(\theta/2)$ instead of being proportional to $\cos^2\theta$ as I found for the electric field case. It takes a rotation of π to block the passage of the spin up component emerging from the second magnet [only a spin down component (with respect to the new quantization axis) is transmitted], whereas it takes a rotation of $\pi/2$ to (totally) block the emerging optical field. It is not difficult to understand why a rotation of π leads to no transmission of a spin up component—when it enters the second magnet, there is no longer any spin up component with respect to the new quantization axis.

In order to see the effect of rotation on the spin state vector from a somewhat different perspective, imagine an electron having its magnetic moment aligned along a strong homogeneous magnetic field, taken to be in the z-direction. Now slowly rotate the magnetic field about the y-axis. For sufficiently slow rotations, the magnetic moment will stay aligned with the field. As a consequence, after a rotation of π the spin has been flipped from down to up (recall that spin angular momentum and magnetic moment differ in sign for an electron) relative to the original quantization axis. After a rotation of 2π, the magnetic moment is again aligned along the positive z-direction, *but the sign of the spin state vector has changed* [see Eq. (12.25) with $\theta = 2\pi$]. It takes a rotation of 4π to return the state vector to its original value. The state vector is said to transform as a *spinor* under rotation. Rotations are discussed in more detail in Chaps. 19 and 20.

12.3 Spin-Orbit Coupling in Hydrogen

If we put ourselves in the rest frame of the electron in a hydrogen atom, we would see the proton undergoing orbital motion. This orbital motion produces a magnetic field at the position of the electron. Since the electron has a magnetic moment, there is *spin–orbit interaction* in hydrogen that adds a term to the Hamiltonian that is given classically by

$$H_{\text{so}} = -\boldsymbol{\mu} \cdot \mathbf{B}_{\text{proton}}. \tag{12.26}$$

There are two ways to evaluate H_{so} that both give the same (wrong) answer. First we can look at the field produced by the proton at the position $\mathbf{r}_e$ of the electron. From the Biot-Savart law, the magnetic induction can be calculated as

$$\mathbf{B}(\mathbf{r}_e) = \frac{\mu_0}{4\pi} \int d\mathbf{r}' \frac{\mathbf{J}_p(\mathbf{r}') \times (\mathbf{r}_e - \mathbf{r}')}{|\mathbf{r}_e - \mathbf{r}'|^3}, \tag{12.27}$$

where the current density $\mathbf{J}_p(\mathbf{r}')$ of the proton is given by

$$\mathbf{J}_p(\mathbf{r}') = e\left(\mathbf{v}_p - \mathbf{v}_e\right)\delta\left(\mathbf{r}' - \mathbf{r}_p\right) = -e\mathbf{v}\delta\left(\mathbf{r}' - \mathbf{r}_e + \mathbf{r}\right), \tag{12.28}$$

$\mathbf{v}_p$ is the velocity of the proton, $\mathbf{v}_e$ is the electron velocity, $\mathbf{r}_p$ is proton's coordinate, and

$$\mathbf{r} = \mathbf{r_e} - \mathbf{r_p}; \qquad \mathbf{v} = \mathbf{v_e} - \mathbf{v}_p \tag{12.29}$$

are the position and velocity of the electron relative to the proton. As a consequence,

$$\mathbf{B}(\mathbf{r}_e) = -e\frac{\mu_0 \mathbf{v}\times\mathbf{r}}{4\pi r^3} = \frac{e}{4\pi\epsilon_0}\frac{\mathbf{r}\times\mathbf{v}}{r^3c^2}. \tag{12.30}$$

This leads to

$$\begin{aligned} H_{\text{so}} &= -\boldsymbol{\mu}\cdot\mathbf{B}(\mathbf{r_e}) = \frac{1}{4\pi\epsilon_0}\frac{e^2\mathbf{S}}{m_e}\cdot\frac{\mathbf{r}\times\mathbf{v}}{r^3c^2} \\ &= \frac{1}{4\pi\epsilon_0}\frac{e^2\mathbf{S}\cdot\mathbf{L}}{m_e^2r^3c^2}. \end{aligned} \tag{12.31}$$

Alternatively, we can use the relativistic formula for the magnetic induction in the electron's instantaneous rest frame produced by the static electric field $\mathbf{E}_p(\mathbf{r})$ in the proton's rest frame, namely

$$\mathbf{B}(\mathbf{r}) \approx -\frac{\mathbf{v}\times\mathbf{E}_p(\mathbf{r})}{c^2} = -\frac{e}{4\pi\epsilon_0}\frac{\mathbf{v}\times\mathbf{r}}{r^3c^2}, \tag{12.32}$$

a result that agrees with Eq. (12.30).

Both methods give a result which is *twice* the correct result. There is a correction, known as the *Thomas Precession*,[3] connected with the fact that the electron is in an accelerating reference frame. Why the correction factor is *exactly* one/half remains somewhat of a mystery to me.[4] In any event the correct spin–orbit interaction is

$$\hat{H}_{\text{so}} = \frac{1}{8\pi\epsilon_0}\frac{e^2\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}}{m_e^2r^3c^2}, \tag{12.33}$$

where classical variables have been replaced by quantum-mechanical operators. As I have mentioned, the correct spin-orbit coupling emerges naturally in Dirac's relativistic treatment of the bound states of hydrogen. In Chap. 21, I use perturbation theory within the framework of the Schrödinger equation to calculate the changes in the energy levels resulting from the spin-orbit coupling.

12.4 Coupling of Orbital and Spin Angular Momentum

Since the spin and orbital angular momentum act in different Hilbert spaces, they commute,

$$\left[\hat{S}_i, \hat{L}_j\right] = 0. \tag{12.34}$$

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[3] It is discussed in Sect. 11.8 in Jackson *Classical Electrodynamics*, but the derivation is too involved to reproduce here.

[4] But see this link, http://aether.lbl.gov/www/classes/p139/homework/seven.pdf.

Thus, I can label the eigenkets as

$$|\ell, s; m_\ell, m_s\rangle = |\ell, m_\ell\rangle\, |s, m_s\rangle\,, \tag{12.35}$$

which are eigenkets of $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$. For an isolated atom, however, it turns out that $\hat{L}_z$ and $\hat{S}_z$ need not be constants of the motion when the spin-orbit interaction given by Eq. (12.33) is included. On the other hand, the *total angular momentum*

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \tag{12.36}$$

is a constant of the motion. As a result, it is often convenient to use eigenkets of the commuting operators $\hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z$, denoted by $|\ell, s, ; j, m\rangle$. They are related to the product state eigenkets by

$$|\ell, s, ; j, m\rangle = \sum_{m_\ell, m_s} \langle \ell, m_\ell; s, m_s\; |\ell, s; j, m\rangle\, |\ell, s; m_\ell, m_s\rangle\,, \tag{12.37}$$

where the expansion coefficients,

$$\langle \ell, s; m_\ell, m_s\; |\ell, s; j, m\rangle \equiv \begin{bmatrix} \ell & s & j \\ m_\ell & m_s & m \end{bmatrix}, \tag{12.38}$$

are referred to as *Clebsch-Gordan coefficients*. These coefficients, as well as the associated 3-J symbols, are discussed in detail in Chap. 20. The Clebsch-Gordan coefficients are built-in functions in many symbolic mathematical programs, which use a closed form expression to evaluate them.

For $s = 1/2$, owing to the properties of the Clebsch-Gordan coefficients, only two terms enter the sum,

$$\begin{aligned} \left|\ell, \frac{1}{2}, ; j = \ell \pm \frac{1}{2}, m\right\rangle &= \begin{bmatrix} \ell & 1/2 & \ell \pm \frac{1}{2} \\ m - 1/2 & 1/2 & m \end{bmatrix} \left|\ell, \frac{1}{2}; m - \frac{1}{2}, \frac{1}{2}\right\rangle \\ &+ \begin{bmatrix} \ell & 1/2 & \ell \pm \frac{1}{2} \\ m + 1/2 & -1/2 & m \end{bmatrix} \left|\ell, \frac{1}{2}; m + \frac{1}{2}, -\frac{1}{2}\right\rangle \\ &= \pm\sqrt{\frac{\ell \pm m + 1/2}{2\ell + 1}} \left|\ell, \frac{1}{2}; m - \frac{1}{2}, \frac{1}{2}\right\rangle \\ &+ \sqrt{\frac{\ell \mp m + 1/2}{2\ell + 1}} \left|\ell, \frac{1}{2}; m + \frac{1}{2}, -\frac{1}{2}\right\rangle. \end{aligned} \tag{12.39}$$

It is not really possible to write an equivalent expression for the wave functions since the ket $\left|\ell, \frac{1}{2}, ; j = \ell \pm \frac{1}{2}, m\right\rangle$ represents a mixture of orbital and spin states. Of course you could define the wave function by taking the inner product of this equation with $\langle \mathbf{r}|$. In this way the eigenfunctions of hydrogen, including spin can be written as

$$\begin{aligned}\psi_{n,\ell,j=\ell\pm\frac{1}{2},m}(\mathbf{r}) &= \left\langle \mathbf{r} \left| n,\ell,\frac{1}{2},;j=\ell\pm\frac{1}{2},m \right.\right\rangle \\ &= \pm\sqrt{\frac{\ell\pm m+1/2}{2\ell+1}}\psi_{n\ell,m-1/2}(\mathbf{r})\,\chi_+ \\ &+\sqrt{\frac{\ell\mp m+1/2}{2\ell+1}}\psi_{n\ell,m+1/2}(\mathbf{r})\,\chi_-, \end{aligned} \tag{12.40}$$

where the $\psi_{n\ell m_\ell}(\mathbf{r})$ are eigenfunctions of the hydrogen atom without spin.

States of hydrogen are labeled as nL_J where n is the energy or electronic quantum number, L is the ℓ quantum number in an old-fashioned scheme in which $\ell = 0$ is S (sharp), $\ell = 1$ is P (principal), $\ell = 2$ is D (diffuse), $\ell = 3$ is F (fundamental), $\ell = 4$ is G, etc., and J is the j value. Thus $2P_{3/2}$ is the state having $n = 2$, $\ell = 1$, and $j = 3/2$.

12.5 Spin and Statistics

Most of the discussion to date has focused on the quantum mechanics of a single particle. I did look at the eigenfunctions of a Hamiltonian that was the sum of two commuting Hamiltonians in Chap. 5. That result is strictly valid only if the particles governed by each of the Hamiltonians are distinguishable. But what happens if they are indistinguishable, such as the two electrons in the helium atom?

The eigenfunctions of a two-particle system can be written as $\psi_E(\mathbf{r}_1,\mathbf{r}_2)$ where $\mathbf{r}_j$ is the coordinate of particle j. If the particles are indistinguishable, there is an *exchange degeneracy* in this system. I can define an operator that interchanges the coordinates of the two particles. This exchange or *permutation operator* is Hermitian and commutes with the Hamiltonian so it is possible to find simultaneous eigenfunctions of the Hamiltonian and the permutation operator. Let me denote the exchange or permutation operator that interchanges particle 1 and 2 by $\hat{P}_{12}$ and its eigenfunctions by $\psi_{E,P}(\mathbf{r}_1,\mathbf{r}_2)$. Clearly

$$\hat{P}_{12}^2\psi_{E,P}(\mathbf{r}_1,\mathbf{r}_2) = \psi_{E,P}(\mathbf{r}_1,\mathbf{r}_2) \tag{12.41}$$

and, since $\hat{P}_{12}$ is Hermitian, this implies that the eigenvalues of $\hat{P}_{12}$ must equal ±1. This, in turn, implies that either

$$\psi_{E,P}(\mathbf{r}_2,\mathbf{r}_1) = \psi_{E,P}(\mathbf{r}_1,\mathbf{r}_2) \tag{12.42}$$

or

$$\psi_{E,P}(\mathbf{r}_2, \mathbf{r}_1) = -\psi_{E,P}(\mathbf{r}_1, \mathbf{r}_2) . \tag{12.43}$$

It turns out that the wave functions of all elementary particles satisfy either Eq. (12.42) or (12.43). Particles having integral intrinsic spin that satisfy Eq. (12.42) and are called *bosons* (photon, graviton, mesons) while particles having half-integral intrinsic spin satisfy Eq. (12.43) and are called *fermions* (electron, neutrino, quarks, baryons).

For multi-particle systems, the eigenfunctions for bosons must be symmetric on the interchange of any two particles and that for fermions must be antisymmetric on the interchange of any two particles. In practice you can show that you need not worry about this symmetrization of the wave function if the spatial wave functions for the particles never overlap.

For two spin 1/2 particles moving in a potential, it is always possible to write the eigenfunctions as a product of a symmetric (antisymmetric) spatial wave function multiplied by an antisymmetric (symmetric) spin state. The spin eigenkets of the two particles are eigenkets of the total spin operator, $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$, and can be expressed in terms of Clebsch-Gordan coefficients as

$$|s_1, s_2, ; s, m\rangle = \sum_{m_1, m_2} \begin{bmatrix} s_1 & s_2 & s \\ m_1 & m_2 & m \end{bmatrix} |s_1 m_1\rangle \, |s_2 m_2\rangle , \tag{12.44}$$

where the ket $|s_1, s_2, ; s, m\rangle$ is a simultaneous eigenket of the operators $\hat{S}_1^2, \hat{S}_2^2, \hat{S}^2, \hat{S}_z$. Using this equation with $s_1 = s_2 = 1/2$, I find that the coupled spin eigenkets of two electrons consist of an antisymmetric or spin *singlet* state

$$\left| \frac{1}{2}, \frac{1}{2}; s = 0, m_s = 0 \right\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) , \tag{12.45}$$

and a spin *triplet* state

$$\left| \frac{1}{2}, \frac{1}{2}; s = 1, m_s = 1 \right\rangle = |\uparrow\uparrow\rangle ; \tag{12.46a}$$

$$\left| \frac{1}{2}, \frac{1}{2}; s = 1, m_s = 0 \right\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) ; \tag{12.46b}$$

$$\left| \frac{1}{2}, \frac{1}{2}; s = 1, m_s = 1 \right\rangle = |\downarrow\downarrow\rangle , \tag{12.46c}$$

where the first arrow in the kets on the right-hand side of the equation refers to particle 1 and the second to particle 2. For N spin 1/2 particles, with $N > 2$, it is no longer possible to construct total spin eigenkets all of which are symmetric or antisymmetric on the exchange of any two particles. There is no totally antisymmetric spin state for $N > 2$. Of the 2^N total spin eigenkets, only $(N + 1)$ are totally symmetric on the interchange of any two particles and these correspond the the spin state having total spin $s = N/2$.

There is a profound difference in the allowed energy levels of a system of indistinguishable particles, depending on whether the particles are fermions or bosons. A simple example will suffice to illustrate this idea. Imagine we have three non-interacting particles in a one-dimensional infinite square well potential. You are asked to obtain the ground state energy and eigenfunction of the system assuming (1) the particles are bosons and (2) the particles are spin $1/2$ fermions. If the particles are bosons they can all be in the same energy state so the ground state energy is simply $3E_0$, where E_0 is the ground state energy of a single particle in the well. The ground state wave function is simply a product of the ground state wave functions for each particle, multiplied by a symmetric state of the spins of the particles.

On the other hand, if the particles are spin 1/2 fermions, they cannot all have the same ground state spatial wave function. Such a wave function is symmetric on exchange of any two particles, which would require that the spin wave function be antisymmetric on the exchange of any two particles. It is impossible to form such a state for three particles that is non-vanishing. Thus the third particle must be in the first excited state of the well having energy E_1. The total energy of this 3-particle system is $E = 2E_0 + E_1$, while the wave function is

$$\psi_E(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_0(x_1)\chi_\uparrow(1) & \psi_0(x_1)\chi_\downarrow(1) & \psi_1(x_1)\chi_\uparrow(1) \\ \psi_0(x_2)\chi_\uparrow(2) & \psi_0(x_2)\chi_\downarrow(2) & \psi_1(x_2)\chi_\uparrow(2) \\ \psi_0(x_3)\chi_\uparrow(3) & \psi_0(x_3)\chi_\downarrow(3) & \psi_1(x_3)\chi_\uparrow(3) \end{vmatrix}, \tag{12.47}$$

where the determinant is referred to as a *Slater determinant* and is manifestly antisymmetric on the exchange of any two particles. (The third state could have equally well been spin down rather than spin up.)

As a second example of the role of spin and statistics, consider a conductor that is modeled as a sea of free electrons confined to a volume. If I take the volume to be a cube having side L and assume that the wave function vanishes on the surfaces of the cube, the energy levels of a *single* electron in this volume are given by

$$E_n = \frac{\hbar^2 k_n^2}{2m_e} = \frac{\hbar^2 n^2 \pi^2}{2m_e L^2} = \frac{\hbar^2 \left(n_x^2 + n_y^2 + n_z^2\right) \pi^2}{2m_e L^2}, \tag{12.48}$$

where m_e is the electron mass and n_x, n_y, n_z take on all positive integral values, with $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$. If there are N electrons in the volume, then two electrons can occupy the lowest energy level $(n_x = n_y = n_z = 1)$, *six* electrons can occupy the next highest energy level $[(n_x = n_y = 1; n_z = 2)$ or $(n_x = n_z = 1; n_y = 2)$ or $(n_y = n_z = 1; n_x = 2)]$, etc. If N is large and the electrons occupy the lowest possible energy state, then the total number of particles in the *Fermi sphere* is given by

$$N = 2 \times \frac{1}{8} \frac{4\pi n_F^3}{3} \tag{12.49}$$

where the factor of 2 is for two spin states for each value of $\left(n_x, n_y, n_z\right)$, while the factor of $1/8$ is required since only one quadrant of the sphere is permitted for positive $\left(n_x, n_y, n_z\right)$. The quantity n_F is the smallest value of n that is needed to accommodate the N electrons. For an electron density $\mathfrak{N} = N/L^3$, the corresponding k value and energy corresponding to n_F are given by

$$k_f = \frac{\pi n_F}{L} = \left(3\pi^2\mathfrak{N}\right)^{1/3}; \tag{12.50a}$$

$$E_f = \frac{\hbar^2 k_f^2}{2m_e} = \frac{\hbar^2\left(3\pi^2\mathfrak{N}\right)^{2/3}}{2m_e}. \tag{12.50b}$$

The quantities k_f and E_f are referred to as the magnitude of the *Fermi k-vector* and *Fermi energy*, respectively. The total energy of all the electrons is equal to

$$E_{\text{total}} = \int_0^N E_f(N')dN' = E_f\int_0^N (N'/N)^{2/3}dN' = \frac{3}{5}NE_f \tag{12.51}$$

and the average energy of an electron is

$$\langle E\rangle = \frac{E_{\text{total}}}{N} = \frac{3}{5}E_f. \tag{12.52}$$

12.6 Summary

The concept of electron spin was introduced. The electron possesses an intrinsic angular momentum corresponding to a spin angular momentum quantum number $s = 1/2$. Some of the properties of spin were discussed, as were the modifications to the energy levels of hydrogen resulting from spin. Finally, systems of identical particles were considered and were found to obey either Bose or Fermi statistics, depending on their intrinsic spin angular momentum. No two identical fermions can possess all the same quantum labels since their wave function must be antisymmetric on exchange of particles. The fact that no two *electrons* can possess all the same quantum numbers is often referred to as the *Pauli Exclusion Principle*, based on a proposal of Pauli to explain the shell structure of atoms.

12.7 Problems

1. Consider an electron in a magnetic induction $\mathbf{B} = B_0\mathbf{u}_x$. Find the eigenkets and eigenvalues for the Hamiltonian $\hat{H} = 2\beta_0\mathbf{B}\cdot\hat{\mathbf{S}}/\hbar$. Calculate the state vector as a function of time if the electron is in its spin down state at $t = 0$. Neglect any center-of-mass motion of the electron—consider only its spin components.

2. Suppose that the lowest energy eigenvalue for a single electron moving in a one-dimensional infinite potential well is 1.0 eV. The well is located between $x = 0$ and $x = a$ so the eigenfunctions for a single electron are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right); \qquad n = 1, 2, 3, \ldots.$$

(a) For two *non-interacting* electrons moving in this potential find the ground state eigenfunction and eigenenergy. You must include the fact that electrons are fermions.
(b) Calculate the next highest energy and explain why there are four eigenfunctions having this energy.
(c) Calculate the third highest energy and explain why this energy state is nondegenerate.

3. Two *non-interacting* particles, each having mass m move in a one-dimensional oscillator potential characterized by frequency ω.

(a) If the particles have spin zero write the eigenfunctions and eigenenergies for the three lowest energy state manifolds of the two-particle system.
(b) If the particles have spin $1/2$ write the eigenfunctions and eigenenergies for the three lowest energy state manifolds of the two-particle system.

In each case, you can express your answers in terms on the single particle eigenfunctions $\psi_{n_1}(x_1)$ and $\psi_{n_2}(x_2)$. By "three lowest energy state manifolds" I mean all and any degenerate states having one of the three lowest energies. Explain your reasoning.

4. Consider the protons in water as independent spin 1/2 particles. The spin of the proton is equal to 1/2, its g factor of 5.59, and its magnetic moment operator is

$$\hat{\boldsymbol{\mu}}_p = 5.59 \frac{e}{2m_p} \hat{\mathbf{S}}_p,$$

where $m_p = 1.67 \times 10^{-27}$ kg is the proton mass and $\hat{\mathbf{S}}_p$ is its spin operator. Note, the nuclear Bohr magneton $\beta_n = \beta_0 \frac{m_e}{m_p} = 5.05 \times 10^{-27}$ J·T^{-1}

(a) Calculate the energy level splitting in frequency units for the spin states of protons in a static magnetic field of 1.0 T.
(b) Assume the protons are in thermal equilibrium at room temperature (about 300 °K). Estimate the population ratio of the two spin states according to Boltzmann's law, $W(E) \sim \exp(-E/k_B T)$. Even though the population difference is small, it is still sufficient to use for *magnetic resonance imaging* (MRI) since there are so many protons present. In MRI, a radio frequency magnetic field is applied to drive transitions between the spin states.

5. The Hamiltonian for a spin in a magnetic induction $\mathbf{B}$ is $\hat{H} = 2\beta_0 \mathbf{B} \cdot \hat{\mathbf{S}}/\hbar$, where β_0 is the Bohr magneton and $\hat{\mathbf{S}}$ is the spin operator. Prove that

$$\frac{d\left\langle \hat{\mathbf{S}} \right\rangle}{dt} = \boldsymbol{\omega} \times \left\langle \hat{\mathbf{S}} \right\rangle$$

and obtain an expression $\boldsymbol{\omega}$.

6. Write all the eigenfunctions for the electron in the $n = 3$ state of hydrogen using the $\left| n\ell j m_j \right\rangle$ basis.

7–8. Prove that the eigenkets of $\hat{S}_x$ and $\hat{S}_y$ can be written in terms of the eigenkets of $\hat{S}_z$ as

$$\begin{aligned} |\pm\rangle_x &= \frac{1}{\sqrt{2}} \left(|\uparrow\rangle \pm |\downarrow\rangle \right); \\ |\pm\rangle_y &= \frac{1}{\sqrt{2}} \left(|\uparrow\rangle \pm i\, |\downarrow\rangle \right), \end{aligned}$$

where the $+$ refers to spin up and $-$ to spin down. For a quantization axis defined by

$$\mathbf{u}\left(\theta, \phi, \psi\right) = \cos\psi \mathbf{u}_\theta + \sin\psi \mathbf{u}_\varphi,$$

prove that the eigenkets of the operator $\hat{S}_{\theta,\phi,\psi} = \hat{\mathbf{S}} \cdot \mathbf{u}\left(\theta, \phi, \psi\right)$ can be written in terms of the eigenkets of $\hat{S}_z$ as

$$\begin{aligned} |+\rangle_{\theta,\phi,\psi} &= \sqrt{\frac{1 - \cos\psi \sin\theta}{2}}\, |\uparrow\rangle + e^{i\phi} \frac{\cos\psi \cos\theta + i \sin\theta}{\sqrt{2\left(1 - \cos\psi \sin\theta\right)}}\, |\downarrow\rangle; \\ |-\rangle_{\theta,\phi,\psi} &= e^{-i\phi} \frac{\cos\psi \cos\theta - i \sin\theta}{\sqrt{2\left(1 - \cos\psi \sin\theta\right)}}\, |\uparrow\rangle - \sqrt{\frac{1 - \cos\psi \sin\theta}{2}}\, |\downarrow\rangle. \end{aligned}$$

The angles θ and ϕ are the polar and azimuthal angles of a spherical coordinate system, while ψ is the angle of the quantization axis relative to the $\mathbf{u}_\theta$ direction in a plane perpendicular to $\mathbf{u}_r$.

9–10. (a) Use Eq. (12.44) with $s = s_{12}$ to prove Eqs. (12.45) and (12.46) for a two-electron system.
(b) Now add a third electron to the system and form total spin eigenkets of a three-electron system defined by

$$|s_1, s_2, s_3, s_{12}; s, m\rangle = \sum_{m_{12}, m_3} \begin{bmatrix} s_{12} & s_3 & s \\ m_{12} & m_3 & m \end{bmatrix} |s_{12}, s_3, ; m_{12}, m_3\rangle,$$

where the ket $|s_1, s_2, s_{3,}s_{12}; s, m\rangle$ is a simultaneous eigenket of the operators $\hat{S}_1^2, \hat{S}_2^2, \hat{S}_3^2, \hat{S}_{12}^2, \hat{S}^2, \hat{S}_z$ and

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3 = \hat{\mathbf{S}}_{12} + \hat{\mathbf{S}}_3$$

is the total spin operator. Express your answer in terms of the eigenkets $|s_1, s_2, s_3; m_1, m_2, m_3\rangle$ and show that eigenkets having $s = 3/2$ are totally symmetric on the interchange of any two particles, but the other eigenkets are neither symmetric nor antisymmetric on the interchange of any two particles. You will have to look up the needed values of the Clebsch-Gordan coefficients.