that space. For example, the particle in a box model describes a particle free to move in a small space surrounded by impenetrable barriers. This is true in blackbody radiators (atoms and molecules) as well as in atomic and molecular spectra. Various atoms and molecules will have different sets of electron orbits, depending on the size and complexity of the system. When a system is large, such as a grain of sand, the tiny particle waves in it can fit in so many ways that it becomes impossible to see that the allowed states are discrete. Thus the correspondence principle is satisfied. As systems become large, they gradually look less grainy, and quantization becomes less evident. Unbound systems (small or not), such as an electron freed from an atom, do not have quantized energies, since their wavelengths are not constrained to fit in a certain volume.

PHET EXPLORATIONS

Quantum Wave Interference

When do photons, electrons, and atoms behave like particles and when do they behave like waves? Watch waves spread out and interfere as they pass through a double slit, then get detected on a screen as tiny dots. Use quantum detectors to explore how measurements change the waves and the patterns they produce on the screen.

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PhET

30.7 Patterns in Spectra Reveal More Quantization

LEARNING OBJECTIVES

By the end of this section, you will be able to:

- State and discuss the Zeeman effect.
- Define orbital magnetic field.
- Define orbital angular momentum.
- Define space quantization.

High-resolution measurements of atomic and molecular spectra show that the spectral lines are even more complex than they first appear. In this section, we will see that this complexity has yielded important new information about electrons and their orbits in atoms.

In order to explore the substructure of atoms (and knowing that magnetic fields affect moving charges), the Dutch physicist Hendrik Lorentz (1853–1930) suggested that his student Pieter Zeeman (1865–1943) study how spectra might be affected by magnetic fields. What they found became known as the **Zeeman effect**, which involved spectral lines being split into two or more separate emission lines by an external magnetic field, as shown in Figure <u>30.47</u>. For their discoveries, Zeeman and Lorentz shared the 1902 Nobel Prize in Physics.

Zeeman splitting is complex. Some lines split into three lines, some into five, and so on. But one general feature is that the amount the split lines are separated is proportional to the applied field strength, indicating an interaction with a moving charge. The splitting means that the quantized energy of an orbit is affected by an external magnetic field, causing the orbit to have several discrete energies instead of one. Even without an external magnetic field, very precise measurements showed that spectral lines are doublets (split into two), apparently by magnetic fields within the atom itself.



FIGURE 30.47 The Zeeman effect is the splitting of spectral lines when a magnetic field is applied. The number of lines formed varies, but the spread is proportional to the strength of the applied field. (a) Two spectral lines with no external magnetic field. (b) The lines split when the field is applied. (c) The splitting is greater when a stronger field is applied.

Bohr's theory of circular orbits is useful for visualizing how an electron's orbit is affected by a magnetic field. The circular orbit forms a current loop, which creates a magnetic field of its own, B_{orb} as seen in Figure 30.48. Note that the **orbital magnetic field B**_{orb} and the **orbital angular momentum** L_{orb} are along the same line. The external magnetic field and the orbital magnetic field interact; a torque is exerted to align them. A torque rotating a system through some angle does work so that there is energy associated with this interaction. Thus, orbits at different angles to the external magnetic field have different energies. What is remarkable is that the energies are quantized—the magnetic field splits the spectral lines into several discrete lines that have different energies. This means that only certain angles are allowed between the orbital angular momentum and the external field, as seen in Figure 30.49.



FIGURE 30.48 The approximate picture of an electron in a circular orbit illustrates how the current loop produces its own magnetic field, called \mathbf{B}_{orb} . It also shows how \mathbf{B}_{orb} is along the same line as the orbital angular momentum \mathbf{L}_{orb} .



FIGURE 30.49 Only certain angles are allowed between the orbital angular momentum and an external magnetic field. This is implied by the fact that the Zeeman effect splits spectral lines into several discrete lines. Each line is associated with an angle between the external magnetic field and magnetic fields due to electrons and their orbits.

We already know that the magnitude of angular momentum is quantized for electron orbits in atoms. The new insight is that the *direction of the orbital angular momentum is also quantized*. The fact that the orbital angular momentum can have only certain directions is called **space quantization**. Like many aspects of quantum mechanics, this quantization of direction is totally unexpected. On the macroscopic scale, orbital angular momentum, such as that of the moon around the earth, can have any magnitude and be in any direction.

Detailed treatment of space quantization began to explain some complexities of atomic spectra, but certain patterns seemed to be caused by something else. As mentioned, spectral lines are actually closely spaced doublets, a characteristic called **fine structure**, as shown in Figure 30.50. The doublet changes when a magnetic field is applied, implying that whatever causes the doublet interacts with a magnetic field. In 1925, Sem Goudsmit and George Uhlenbeck, two Dutch physicists, successfully argued that electrons have properties analogous to a macroscopic charge spinning on its axis. Electrons, in fact, have an internal or intrinsic angular momentum called **intrinsic spin S**. Since electrons are charged, their intrinsic spin creates an **intrinsic magnetic field B**_{int}, which interacts with their orbital magnetic field **B**_{orb}. Furthermore, *electron intrinsic spin is quantized in magnitude and direction*, analogous to the situation for orbital angular momentum. The spin of the electron can have only one magnitude, and its direction can be at only one of two angles relative to a magnetic field, as seen in Figure 30.51. We refer to this as spin up or spin down for the electron. Each spin direction has a different energy; hence, spectroscopic lines are split into two. Spectral doublets are now understood as being due to electron spin.



FIGURE 30.50 Fine structure. Upon close examination, spectral lines are doublets, even in the absence of an external magnetic field. The electron has an intrinsic magnetic field that interacts with its orbital magnetic field.



FIGURE 30.51 The intrinsic magnetic field **B**_{int} of an electron is attributed to its spin, **S**, roughly pictured to be due to its charge spinning on its axis. This is only a crude model, since electrons seem to have no size. The spin and intrinsic magnetic field of the electron can make only one of two angles with another magnetic field, such as that created by the electron's orbital motion. Space is quantized for spin as well as for orbital angular momentum.

These two new insights—that the direction of angular momentum, whether orbital or spin, is quantized, and that electrons have intrinsic spin—help to explain many of the complexities of atomic and molecular spectra. In magnetic resonance imaging, it is the way that the intrinsic magnetic field of hydrogen and biological atoms interact with an external field that underlies the diagnostic fundamentals.

30.8 Quantum Numbers and Rules

LEARNING OBJECTIVES

By the end of this section, you will be able to:

- Define quantum number.
- Calculate angle of angular momentum vector with an axis.
- Define spin quantum number.

Physical characteristics that are quantized—such as energy, charge, and angular momentum—are of such importance that names and symbols are given to them. The values of quantized entities are expressed in terms of **quantum numbers**, and the rules governing them are of the utmost importance in determining what nature is and

does. This section covers some of the more important quantum numbers and rules—all of which apply in chemistry, material science, and far beyond the realm of atomic physics, where they were first discovered. Once again, we see how physics makes discoveries which enable other fields to grow.

The energy states of bound systems are quantized, because the particle wavelength can fit into the bounds of the system in only certain ways. This was elaborated for the hydrogen atom, for which the allowed energies are expressed as $E_n \propto 1/n^2$, where n = 1, 2, 3, ... We define *n* to be the principal quantum number that labels the basic states of a system. The lowest-energy state has n = 1, the first excited state has n = 2, and so on. Thus the allowed values for the principal quantum number are

$$n = 1, 2, 3, \dots$$
 30.41

This is more than just a numbering scheme, since the energy of the system, such as the hydrogen atom, can be expressed as some function of *n*, as can other characteristics (such as the orbital radii of the hydrogen atom).

The fact that the magnitude of angular momentum is quantized was first recognized by Bohr in relation to the hydrogen atom; it is now known to be true in general. With the development of quantum mechanics, it was found that the magnitude of angular momentum L can have only the values

$$L = \sqrt{l(l+1)} \frac{h}{2\pi} \quad (l = 0, 1, 2, ..., n-1),$$
 30.42

where *l* is defined to be the **angular momentum quantum number**. The rule for *l* in atoms is given in the parentheses. Given *n*, the value of *l* can be any integer from zero up to n - 1. For example, if n = 4, then *l* can be 0, 1, 2, or 3.

Note that for n = 1, l can only be zero. This means that the ground-state angular momentum for hydrogen is actually zero, not $h/2\pi$ as Bohr proposed. The picture of circular orbits is not valid, because there would be angular momentum for any circular orbit. A more valid picture is the cloud of probability shown for the ground state of hydrogen in Figure 30.46. The electron actually spends time in and near the nucleus. The reason the electron does not remain in the nucleus is related to Heisenberg's uncertainty principle—the electron's energy would have to be much too large to be confined to the small space of the nucleus. Now the first excited state of hydrogen has n = 2, so that l can be either 0 or 1, according to the rule in $L = \sqrt{l(l+1)}\frac{h}{2\pi}$. Similarly, for n = 3, l can be 0, 1, or 2. It is often most convenient to state the value of l, a simple integer, rather than calculating the value of L from $L = \sqrt{l(l+1)}\frac{h}{2\pi}$. For example, for l = 2, we see that

$$L = \sqrt{2(2+1)}\frac{h}{2\pi} = \sqrt{6}\frac{h}{2\pi} = 0.390h = 2.58 \times 10^{-34} \text{ J} \cdot \text{s.}$$
 30.43

It is much simpler to state l = 2.

As recognized in the Zeeman effect, the *direction of angular momentum is quantized*. We now know this is true in all circumstances. It is found that the component of angular momentum along one direction in space, usually called the *z*-axis, can have only certain values of L_z . The direction in space must be related to something physical, such as the direction of the magnetic field at that location. This is an aspect of relativity. Direction has no meaning if there is nothing that varies with direction, as does magnetic force. The allowed values of L_z are

$$L_z = m_l \frac{h}{2\pi} \quad (m_l = -l, -l+1, ..., -1, 0, 1, ..., l-1, l),$$
 30.44

where L_z is the *z*-component of the angular momentum and m_l is the angular momentum projection quantum number. The rule in parentheses for the values of m_l is that it can range from -l to l in steps of one. For example, if l = 2, then m_l can have the five values -2, -1, 0, 1, and 2. Each m_l corresponds to a different energy in the presence of a magnetic field, so that they are related to the splitting of spectral lines into discrete parts, as discussed in the preceding section. If the *z*-component of angular momentum can have only certain values, then the angular momentum can have only certain directions, as illustrated in Figure 30.52.



FIGURE 30.52 The component of a given angular momentum along the *z*-axis (defined by the direction of a magnetic field) can have only certain values; these are shown here for l = 1, for which $m_l = -1$, 0, and +1. The direction of *L* is quantized in the sense that it can have only certain angles relative to the *z*-axis.

EXAMPLE 30.3

What Are the Allowed Directions?

Calculate the angles that the angular momentum vector **L** can make with the *z*-axis for l = 1, as illustrated in Figure 30.52.

Strategy

Figure 30.52 represents the vectors L and L_z as usual, with arrows proportional to their magnitudes and pointing in the correct directions. L and L_z form a right triangle, with L being the hypotenuse and L_z the adjacent side. This means that the ratio of L_z to L is the cosine of the angle of interest. We can find L and L_z using $L = \sqrt{l(l+1)} \frac{h}{2\pi}$ and $L_z = m \frac{h}{2\pi}$.

Solution

We are given l = 1, so that m_l can be +1, 0, or -1. Thus L has the value given by $L = \sqrt{l(l+1)} \frac{h}{2\pi}$.

$$L = \frac{\sqrt{l(l+1)}h}{2\pi} = \frac{\sqrt{2}h}{2\pi}$$
 30.45

 L_z can have three values, given by $L_z = m_l \frac{h}{2\pi}$.

$$L_{z} = m_{l} \frac{h}{2\pi} = \begin{cases} \frac{h}{2\pi}, & m_{l} = +1\\ 0, & m_{l} = 0\\ -\frac{h}{2\pi}, & m_{l} = -1 \end{cases}$$
 30.46

As can be seen in Figure 30.52, $\cos \theta = L_z/L$, and so for $m_l = +1$, we have

$$\cos \theta_1 = \frac{L_Z}{L} = \frac{\frac{n}{2\pi}}{\frac{\sqrt{2h}}{2\pi}} = \frac{1}{\sqrt{2}} = 0.707.$$
 30.47

Thus,

$$\theta_1 = \cos^{-1} 0.707 = 45.0^{\circ}.$$
 30.48

Similarly, for $m_l = 0$, we find $\cos \theta_2 = 0$; thus,

$$\theta_2 = \cos^{-1}0 = 90.0^{\circ}.$$
 30.49

And for $m_l = -1$,

$$\cos \theta_3 = \frac{L_Z}{L} = \frac{-\frac{h}{2\pi}}{\frac{\sqrt{2}h}{2\pi}} = -\frac{1}{\sqrt{2}} = -0.707,$$
 30.50

so that

$$\theta_3 = \cos^{-1}(-0.707) = 135.0^{\circ}.$$
 30.51

Discussion

The angles are consistent with the figure. Only the angle relative to the *z*-axis is quantized. *L* can point in any direction as long as it makes the proper angle with the *z*-axis. Thus the angular momentum vectors lie on cones as illustrated. This behavior is not observed on the large scale. To see how the correspondence principle holds here, consider that the smallest angle (θ_1 in the example) is for the maximum value of $m_l = 0$, namely $m_l = l$. For that smallest angle,

$$\cos\theta = \frac{L_z}{L} = \frac{l}{\sqrt{l(l+1)}},$$
30.52

which approaches 1 as *l* becomes very large. If $\cos \theta = 1$, then $\theta = 0^{\circ}$. Furthermore, for large *l*, there are many values of m_l , so that all angles become possible as *l* gets very large.

Intrinsic Spin Angular Momentum Is Quantized in Magnitude and Direction

There are two more quantum numbers of immediate concern. Both were first discovered for electrons in conjunction with fine structure in atomic spectra. It is now well established that electrons and other fundamental particles have *intrinsic spin*, roughly analogous to a planet spinning on its axis. This spin is a fundamental characteristic of particles, and only one magnitude of intrinsic spin is allowed for a given type of particle. Intrinsic angular momentum is quantized independently of orbital angular momentum. Additionally, the direction of the spin is also quantized. It has been found that the **magnitude of the intrinsic (internal) spin angular momentum**, *s*, of an electron is given by

$$S = \sqrt{s(s+1)} \frac{h}{2\pi} \quad (s = 1/2 \text{ for electrons}),$$
 30.53

where *s* is defined to be the **spin quantum number**. This is very similar to the quantization of *L* given in $L = \sqrt{l(l+1)} \frac{h}{2\pi}$, except that the only value allowed for *s* for electrons is 1/2.

The *direction of intrinsic spin is quantized*, just as is the direction of orbital angular momentum. The direction of spin angular momentum along one direction in space, again called the *z*-axis, can have only the values

$$S_z = m_s \frac{h}{2\pi} \left(m_s = -\frac{1}{2}, +\frac{1}{2} \right)$$
 30.54

for electrons. S_z is the *z*-component of spin angular momentum and m_s is the spin projection quantum number. For electrons, *s* can only be 1/2, and m_s can be either +1/2 or -1/2. Spin projection m_s =+1/2 is referred to as *spin up*, whereas m_s = -1/2 is called *spin down*. These are illustrated in Figure 30.51.

Intrinsic Spin

In later chapters, we will see that intrinsic spin is a characteristic of all subatomic particles. For some particles s is half-integral, whereas for others s is integral—there are crucial differences between half-integral spin particles and integral spin particles. Protons and neutrons, like electrons, have s = 1/2, whereas photons have s = 1, and other particles called pions have s = 0, and so on.

To summarize, the state of a system, such as the precise nature of an electron in an atom, is determined by its particular quantum numbers. These are expressed in the form (n, l, m_l, m_s) —see <u>Table 30.1</u> For electrons in atoms, the principal quantum number can have the values n = 1, 2, 3, ... Once n is known, the values of the angular momentum quantum number are limited to l = 1, 2, 3, ..., n - 1. For a given value of l, the angular momentum projection quantum number can have only the values $m_l = -l, -l + 1, ..., -1, 0, 1, ..., l - 1, l$. Electron spin is independent of n, l, and m_l , always having s = 1/2. The spin projection quantum number can have two values, $m_s = 1/2$ or -1/2.

Name	Symbol	Allowed values
Principal quantum number	n	1, 2, 3,
Angular momentum	l	$0, 1, 2, \dots n-1$
Angular momentum projection	m _l	$-l, -l + 1,, -1, 0, 1,, l - 1, l (or 0, \pm 1, \pm 2,, \pm l)$
Spin ¹	S	1/2(electrons)
Spin projection	m_s	-1/2, +1/2

TABLE 30.1 Atomic Quantum Numbers

Figure 30.53 shows several hydrogen states corresponding to different sets of quantum numbers. Note that these clouds of probability are the locations of electrons as determined by making repeated measurements—each measurement finds the electron in a definite location, with a greater chance of finding the electron in some places rather than others. With repeated measurements, the pattern of probability shown in the figure emerges. The clouds of probability do not look like nor do they correspond to classical orbits. The uncertainty principle actually prevents us and nature from knowing how the electron gets from one place to another, and so an orbit really does not exist as such. Nature on a small scale is again much different from that on the large scale.



FIGURE 30.53 Probability clouds for the electron in the ground state and several excited states of hydrogen. The nature of these states is determined by their sets of quantum numbers, here given as (n, l, m_l) . The ground state is (0, 0, 0); one of the possibilities for the second excited state is (3, 2, 1). The probability of finding the electron is indicated by the shade of color; the darker the coloring the greater the chance of finding the electron.

We will see that the quantum numbers discussed in this section are valid for a broad range of particles and other systems, such as nuclei. Some quantum numbers, such as intrinsic spin, are related to fundamental classifications of subatomic particles, and they obey laws that will give us further insight into the substructure of matter and its interactions.

30.9 The Pauli Exclusion Principle

LEARNING OBJECTIVES

By the end of this section, you will be able to:

- Define the composition of an atom along with its electrons, neutrons, and protons.
- Explain the Pauli exclusion principle and its application to the atom.
- Specify the shell and subshell symbols and their positions.
- Define the position of electrons in different shells of an atom.
- State the position of each element in the periodic table according to shell filling.

Multiple-Electron Atoms

All atoms except hydrogen are multiple-electron atoms. The physical and chemical properties of elements are directly related to the number of electrons a neutral atom has. The periodic table of the elements groups elements