Skills to Develop

- To introduce the concept of electron spin and demonstrated it is quantized

The process of describing each atom’s electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table. All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin.

The Stern-Gerlach Experiment

The quantum numbers \( (n, l, m) \) are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers \( (n, l, m) \) and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the figure 8.9.1. A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an intrinsic magnetic moment \( M \) arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to a spin, \( S \); unlike position and momentum, which have clear classical analogs, spin does not.

The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, \( m_s \) in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.
Electron Spin

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually pairs of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers $n$, $l$, and $m_l$. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

**Figure 8.9.2: Electron Spin.** In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 8.9.2). These are described by a fourth quantum number ($m_s$), which for any electron can have only two possible values, designated $+\frac{1}{2}$ (up) and $-\frac{1}{2}$ (down) to indicate that the two orientations are opposites; the subscript $s$ is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers ($n$, $l$, $m_l$, $m_s$).*

By giving the values of $n$, $l$, and $m_l$, we also specify a particular orbital (e.g., $1s$ with $n = 1$, $l = 0$, $m_l = 0$). Because $m_s$ has only two possible values ($+\frac{1}{2}$ or $-\frac{1}{2}$), two electrons, _and only two electrons_, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was
originally based on the physical and chemical properties of the known elements.

Example 8.9.2

List all the allowed combinations of the four quantum numbers \((n, l, m_l, m_s)\) for electrons in a \(2p\) orbital and predict the maximum number of electrons the \(2p\) subshell can accommodate.

**Given:** orbital

**Asked for:** allowed quantum numbers and maximum number of electrons in orbital

**Strategy:**

A. List the quantum numbers \((n, l, m_l)\) that correspond to an \(n = 2p\) orbital. List all allowed combinations of \((n, l, m_l)\).

B. Build on these combinations to list all the allowed combinations of \((n, l, m_l, m_s)\).

C. Add together the number of combinations to predict the maximum number of electrons the \(2p\) subshell can accommodate.

**Solution:**

A For a \(2p\) orbital, we know that \(n = 2, l = n - 1 = 1,\) and \(m_l = -l, (-l + 1), \ldots, (l - 1), l.\) There are only three possible combinations of \((n, l, m_l)\): \((2, 1, 1), (2, 1, 0),\) and \((2, 1, -1)\).

B Because \(m_s\) is independent of the other quantum numbers and can have values of only \(+\frac{1}{2}\) and \(-\frac{1}{2}\), there are six possible combinations of \((n, l, m_l, m_s)\): \((2, 1, 1, +\frac{1}{2}), (2, 1, 1, -\frac{1}{2}), (2, 1, 0, +\frac{1}{2}), (2, 1, 0, -\frac{1}{2}), (2, 1, -1, +\frac{1}{2}),\) and \((2, 1, -1, -\frac{1}{2})\).

C Hence the \(2p\) subshell, which consists of three \(2p\) orbitals (\(2p_x, 2p_y,\) and \(2p_z\)), can contain a total of six electrons, two in each orbital.

Exercise 8.9.2

List all the allowed combinations of the four quantum numbers \((n, l, m_l, m_s)\) for a \(6s\) orbital, and predict the total number of electrons it can contain.

**Answer:** \((6, 0, 0, +\frac{1}{2}), (6, 0, 0, -\frac{1}{2});\) two electrons

**Summary**

In addition to the three quantum numbers \((n, l, m_l)\) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number \((m_s)\), which can have values of \(+\frac{1}{2}\) or \(-\frac{1}{2}\) for any electron, corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin).