

Mathematical equations are the language of scientists as they try to model natural phenomena. Schrödinger's wave equation is a very complex equation. It describes the quantized energies of the electron in an atom as well as wave functions that determine the probability of finding electrons in various regions in an atom. In this section, you will explore the results of Schrödinger's equations.

## The Four Quantum Numbers

Solutions to Schrödinger's equation for the hydrogen atom give many wave functions that describe various types of orbitals. Each of these types of orbitals has a set of four numbers called **quantum numbers**, which describe various properties of the orbital. These numbers are like addresses for locating the position of an electron by its city, street, number, and apartment number. In this subsection, you will learn about the four quantum numbers and what each quantum number represents.

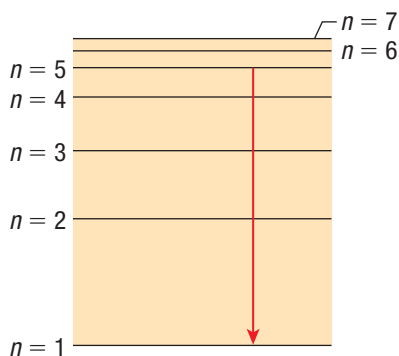
**quantum numbers** numbers that describe the quantum mechanical properties of orbitals; from the solutions to Schrödinger's wave equation

### The Principal Quantum Number ( $n$ )

Energy levels in an atom are sometimes called **shells**. Bohr devised this numbering system and called the shell number the principal quantum number. The **principal quantum number ( $n$ )** is the quantum number that describes the size and energy of an atomic orbital. It has whole-number values (1, 2, 3, and so on). It is important to note that the spaces between atomic shells are not equal (**Figure 1**). As  $n$  increases, the energy required for an electron to occupy that orbital increases. Each successive orbital is larger, meaning that an electron occupying that orbit spends more time farther from the nucleus. This also means that electrons with higher energy are less tightly bound to the nucleus.

**shell** an atom's main energy level, where the shell number is given by the principal quantum number,  $n = 1, 2, 3, \dots$

**principal quantum number ( $n$ )** the quantum number that describes the size and energy of an atomic orbital

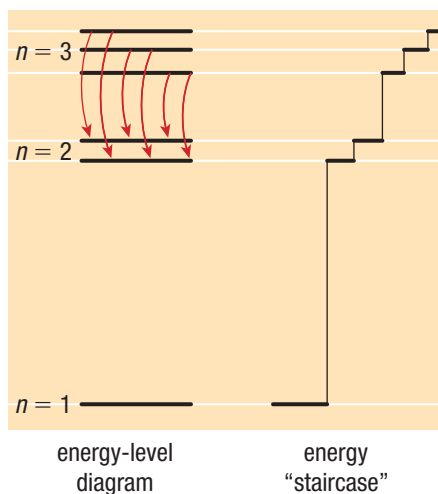


**Figure 1** The principal quantum number,  $n$ , represents the position of an electron in an atom. If an electron moves from a higher shell, such as  $n = 5$ , to a lower shell, such as  $n = 1$ , the energy difference between the shells is released as a photon.

Recall that Bohr took up the challenge of explaining the line spectrum of the hydrogen atom. Bohr's success led other scientists to pursue the investigation of line spectra in detail because there were observations that still required explanation. In 1891, Albert Michelson discovered that the distinct lines in the hydrogen atom's spectrum actually consisted of many smaller lines. These smaller lines were difficult to see and were unexplained for many years. In 1915, a German physicist, Arnold Sommerfeld, studied the hydrogen atom's spectrum in detail. To explain the extra lines, Sommerfeld proposed the secondary quantum number as a way to describe electron energy sublevels, or **subshells**.

**subshells** orbitals of different shapes and energies, as given by the secondary quantum number; often referred to as  $s$ ,  $p$ ,  $d$ , and  $f$

Subshells are part of the primary energy level. If an energy level is described as a staircase, one regular step actually represents a group of several smaller energy steps (Figure 2).



**Figure 2** Sommerfeld's atomic model includes multiple energy levels within shells, called subshells, except when  $n = 1$ .

**secondary quantum number ( $l$ )** the quantum number that describes the shape and energy of an atomic orbital, with whole-number values from 0 to  $n - 1$  for each value of  $n$

### The Secondary Quantum Number ( $l$ )

The **secondary quantum number ( $l$ )** describes the shape of an atomic orbital. It has whole-number values from 0 to  $n - 1$  for each value of  $n$ . This quantum number also describes the energy of atomic orbitals. When  $n = 1$ ,  $l = 0$ . When  $n = 3$ ,  $l = 0, 1$ , and 2. The numbers used to describe  $l$  are usually replaced by letters to avoid confusion with  $n$ . These letters are given in Table 1.

**Table 1** Secondary Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals

Value of $l$	0	1	2	3	4
Letter used	$s$	$p$	$d$	$f$	$g$
Name	sharp	principal	diffuse	fundamental	

In other words, at an energy level of  $n = 1$ , only an  $s$  orbital exists. However, at the third energy level ( $n = 3$ ), there can be  $s$ ,  $p$ , and  $d$  orbitals. Each of these orbital types is a subshell. Higher-energy subshell symbols follow the alphabet ( $g, h, i$ ), but no stable element in its ground state has electrons in subshells higher than  $f$ . This system of using letters to identify the various subshells arises from early spectral studies.

Compared to different values of  $n$ , different values of  $l$  represent smaller differences in the amount of energy an electron requires to occupy any of the orbitals.

### The Magnetic Quantum Number ( $m_l$ )

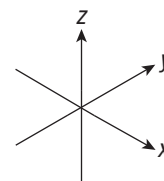
**magnetic quantum number ( $m_l$ )** the quantum number that describes the orientation of an atomic orbital in space relative to the other orbitals in the atom, with whole-number values between  $+l$  and  $-l$ , including 0

The **magnetic quantum number ( $m_l$ )** is the quantum number that describes the orientation of an atomic orbital in space relative to the other orbitals in the atom. It has whole-number values between  $+l$  and  $-l$ , including 0. The value of  $m_l$  is related to the orientation of an orbital in space relative to the other orbitals in the atom. The number of different values that  $m_l$  can have equals the number of orbitals that are possible.

For example, when  $l = 1$ , there are three possible orbitals:  $+1$ ,  $0$ , and  $-1$  (Table 2). These three types of orbital are all  $p$  orbitals, but they differ from each other by their orientation in space. Think about an  $xyz$  coordinate system (Figure 3).

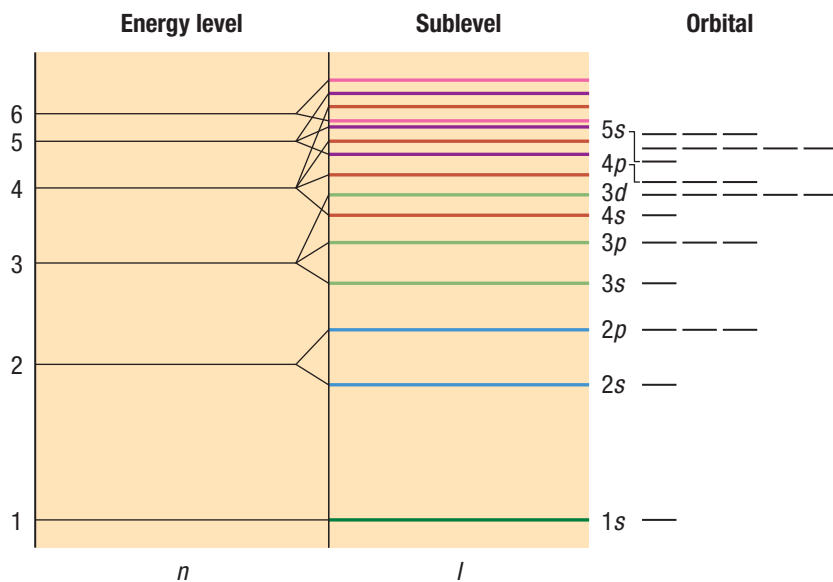
**Table 2** Quantum Numbers for the First Four Levels of Orbitals of Hydrogen

$n$	$l$	Sublevel designation	$m_l$	Number of orbitals	Number of electrons in each energy level ( $2n^2$ )
1	0	1s	0	1	2
2	0	2s	0	1	8
	1	2p	-1, 0, 1	3	
3	0	3s	0	1	18
	1	3p	-1, 0, 1	3	
	2	3d	-2, -1, 0, 1, 2	5	
4	0	4s	0	1	32
	1	4p	-1, 0, 1	3	
	2	4d	-2, -1, 0, 1, 2	5	
	3	4f	-3, -2, -1, 0, 1, 2, 3	7	



**Figure 3** The magnetic quantum number describes an orbital's orientation in three-dimensional space.

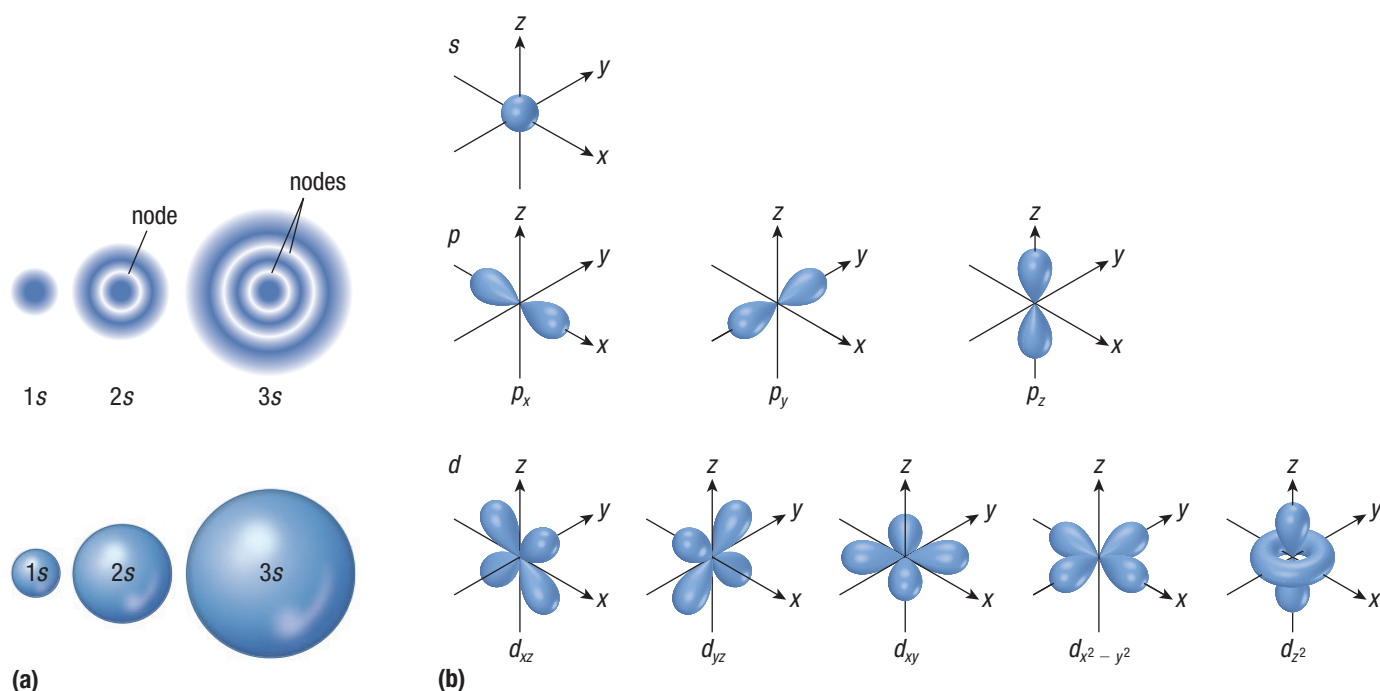
Figure 4 shows the relative energies of the  $s$ ,  $p$ , and  $d$  orbitals in their respective energy levels.



**Figure 4** The energies of orbitals relative to each other. The farther the orbitals are from the nucleus, the closer together they are, and the subshells “overlap.”

## Shapes and Orientations of Orbitals

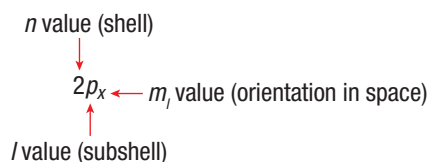
You have read that orbitals represent electron probability distributions and that each orbital has a unique probability distribution, shape, and orientation. Note that the  $2s$  and  $3s$  orbitals contain areas of high probability separated by areas of zero probability (**Figure 5(a)**, top). These areas of zero probability are called nodes. For simplicity, you can think of  $s$  orbitals in terms of their overall spherical shape, which becomes larger as the value of  $n$  increases. **Figure 5(a)**, bottom, illustrates the characteristic spherical shape of each of the  $s$  orbitals.



**Figure 5** (a) In these representations of the hydrogen  $1s$ ,  $2s$ , and  $3s$  orbitals, the nodes are the areas of zero probability. The top diagram is a cross section of the electron probability distribution; the nodes are spherical, too. Bottom: the surface contains 90 % of the total electron probability (the size of the orbital, by definition). (b) Shapes and orientations of  $s$ ,  $p$ , and  $d$  orbitals

The  $p$  orbitals are not spherical like  $s$  orbitals, but have two *lobes* separated by a node at the nucleus (**Figure 5(b)**). The  $p$  orbitals can exist in any of the three dimensions and are labelled using the  $xyz$  coordinate system along which the lobes lie. For example, the  $2p$  orbital with its lobes centred along the  $x$ -axis is the  $2p_x$  orbital.

**Figure 6** shows how the  $2p_x$  orbital is identified using the first three quantum numbers.



**Figure 6**

The  $3p$  orbitals have the same boundary surface shapes shown in Figure 5(b), except that they are larger because the value of  $n$  is greater.

The  $d$  orbitals ( $l = 2$ ) first occur in level  $n = 3$ . The five  $3d$  orbitals have the shapes shown in Figure 5(b). Four of the orbitals ( $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ , and  $d_{x^2-y^2}$ ) have four lobes centred in the plane indicated in the orbital label. Note that  $d_{xy}$  and  $d_{x^2-y^2}$  are both centred in the  $xy$  plane, but the lobes of  $d_{x^2-y^2}$  lie *along* the  $x$ - and  $y$ -axes, whereas the lobes of  $d_{xy}$  lie *between* the axes. The fifth orbital,  $d_{z^2}$ , has a unique shape with two lobes along the  $z$ -axis and a belt centred in the  $xy$  plane. The  $d$  orbitals for levels  $n > 3$  look like the  $3d$  orbitals but have larger lobes.

### Investigation 3.4.1

#### Simulation of Electron Orbitals (page 181)

You have learned about the first three quantum numbers related to the model of the atom. This observational study will give you an opportunity to use the numbers to simulate electron orbitals.

## The Spin Quantum Number ( $m_s$ )

Samuel Goudsmit and George Uhlenbeck, graduate students at the University of Leiden in the Netherlands, found that a fourth quantum number (in addition to  $n$ ,  $l$ , and  $m_l$ ) was necessary to account for the details of the emission spectra of atoms. The spectral data indicated that the atom has a magnetic property, called a magnetic moment, when the atom is placed in an external magnetic field. The magnetic moment of an atom has two orientations. Since they knew from classical physics that a spinning charge produces a magnetic moment, it seemed reasonable to assume that the electron could have two oppositely directed “spin states” (Figure 7). The new quantum number related to the spin of an electron, called the electron **spin quantum number** ( $m_s$ ), can have one of two values:  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . These two values mean that the electron can spin in one of two opposite directions, although other interpretations have been suggested.

### Research This

#### Magnetic Fields and Sunspots

**Skills:** Researching, Analyzing, Communicating, Identifying Alternatives

SKILLS  
HANDBOOK  A5.1

Sunspots are temporary dark spots on the surface of the Sun. They are areas of intense magnetic activity at a reduced temperature. Solar activity and sunspot cycles are important factors in forecasting space weather, which can affect satellite communications.

Energy levels in atoms, transitions between energy levels, and associated spectral lines of energy levels are assumed not to be under the influence of any magnetic field. However, when a magnetic force is present, the energy levels split into sublevels, and so do the spectral lines. This splitting is called the Zeeman effect. The idea of magnetic quantum numbers was developed to explain the Zeeman effect.

The Zeeman effect is a way to identify, explain, and measure characteristics of sunspots. Since the distance between the spectral lines produced by the split energy sublevels is proportional to the strength of the magnetic field, scientists can use the Zeeman effect to measure the magnetic fields of the Sun and other stars.

1. Research sunspots and their spectrographs. Find an image of a sunspot and its associated spectrograph.
  2. Determine what the spectrograph shows and how it relates to the sunspot.
  3. Research how scientists use this information and why it is important.
- A. Summarize your research. Provide an image, and describe your sunspot and spectrograph. C A
- B. What else do you think this technology could be used for? Are there any examples of this application? C A



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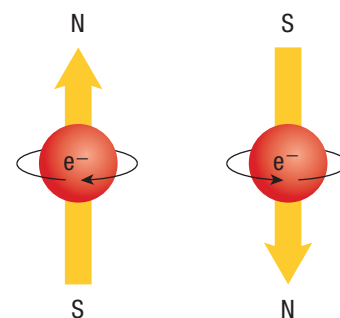
## The Pauli Exclusion Principle

The Austrian physicist Wolfgang Pauli (1900–1958) formulated an important principle, the **Pauli exclusion principle**, which states the following:

### Pauli Exclusion Principle

In a given atom, no two electrons can have the same set of four quantum numbers ( $n$ ,  $l$ ,  $m_l$ , and  $m_s$ ).

Since electrons in the same orbital have the same values of  $n$ ,  $l$ , and  $m_l$ , the Pauli exclusion principle implies that they must have different spin quantum numbers,  $m_s$ . Since only two values of  $m_s$  are allowed, *an orbital can hold only two electrons, which must have opposite spins*. This principle will have important implications when you apply the quantum mechanical atomic model to account for electron arrangements of the atoms in the periodic table.



**Figure 7** (a) By spinning in one direction, the electron produces a magnetic field oriented toward north. (b) By spinning in the opposite direction, the electron produces a magnetic field in the opposite orientation.

**spin quantum number** ( $m_s$ ) the quantum number that relates to the spin of the electron; limited to  $+\frac{1}{2}$  or  $-\frac{1}{2}$

**Pauli exclusion principle** the principle that no two electrons in the same atom can be in the same quantum state

### UNIT TASK BOOKMARK

Refer to the Pauli exclusion principle as you work on the Unit Task on page 268.

## Tutorial 1 Working with Quantum Numbers

By working with the quantum numbers in this Tutorial, you will better understand the rules that govern their use.

### Sample Problem 1: Solving the Secondary Quantum Number

For principal quantum number  $n = 5$ , determine the value(s) of the secondary quantum number,  $l$ , and the types of orbitals in each case.

#### Solution

For  $n = 5$ , the allowed values of  $l$  are 0 to  $n - 1$ , or 0, 1, 2, 3, and 4. The types of orbitals in each case are shown in **Table 3**.

Table 3

$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
5s	5p	5d	5f	5g

### Sample Problem 2: Solving the Magnetic Quantum Number

How many possible values of  $m_l$  are there for  $l = 0, 1, 2$ , and 3? What pattern do you notice in these numbers?

#### Solution

The principal quantum number,  $n$ , determines the values of the secondary quantum number,  $l$ , which in turn determines the possible values of the magnetic quantum number,  $m_l$ .

The magnetic quantum number  $m_l$  is equal to whole numbers from  $l$  to  $-l$ .

For  $l = 0, 1, 2$ , and 3, the values of  $m_l$  are shown in **Table 4**.

Table 4

$l$	$m_l$
0	0
1	1, 0, -1
2	2, 1, 0, -1, -2
3	3, 2, 1, 0, -1, -2, -3

### Practice

- For  $n = 7$ , what are the possible values for the quantum numbers  $l$  and  $m_l$ ? K/U T/I

[ans:  $l = 0$  to 6;  $m_l = 6$  to  $-6$ ]

- Identify which of the following orbital designations do not exist: 1s, 1p, 7d, 3f, 4f, 2d K/U T/I

[ans: 1p, 3f, 2d] CAREER LINK

## 3.4 Review

### Summary

- Four quantum numbers,  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ , define the electron's position in the atom.
- The principal quantum number,  $n$ , represents the main energy levels, or shells, the electrons can occupy in an atom and has whole-number values 1, 2, 3, ....
- The secondary quantum number,  $l$ , represents subshells, gives the shape of the orbital, has values 0 to  $n - 1$ , and letters *spdf*.
- The magnetic quantum number,  $m_l$ , represents the orientations of the subshells and has values  $-l$  to  $+l$ .
- The spin quantum number,  $m_s$ , represents electron spin and has a value of either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .
- The Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers ( $n$ ,  $l$ ,  $m_l$ ,  $m_s$ ).

### Questions

1. What are quantum numbers? Create a chart showing the information you can obtain from the quantum numbers  $n$ ,  $l$ , and  $m_l$ . K/U C
2. Suggest an analogy not mentioned in this section to help explain the four quantum numbers. Share it with a classmate and get his or her feedback. Revise your analogy if necessary. K/U T/I C A
3. How do  $2p$  orbitals differ from each other? How do  $2p$  and  $3p$  orbitals differ from each other? K/U
4. Draw a sketch to compare the following orbitals. In a few words, highlight the similarities and differences. K/U C
  - (a)  $1s$  and  $3s$
  - (b)  $2p_x$  and  $3p_y$
  - (c)  $2s$  and  $2p_z$
5. What are the possible values for the quantum numbers  $n$ ,  $l$ , and  $m_l$  in the first three shells? K/U T/I A
6. List all the possible quantum numbers for an electron in the
  - (a)  $2s$  orbital
  - (b)  $6s$  orbital
  - (c)  $5f$  orbital K/U T/I A
7. Which of the following orbital designations do not exist? Explain your answer. K/U T/I
  - (a)  $1d$
  - (b)  $0p$
  - (c)  $4g$
  - (d)  $5s$
  - (e)  $2f$
8. Which of the following sets of quantum numbers are not allowed? For each set that is not allowed, explain why it is not allowed. K/U T/I A
  - (a)  $n = 3, l = 2, m_l = 2$
  - (b)  $n = 4, l = 3, m_l = 4$
  - (c)  $n = 0, l = 0, m_l = 0$
  - (d)  $n = 2, l = -1, m_l = 1$
  - (e)  $n = 1, l = 1, m_l = 2$
9. Which of the following sets of quantum numbers are not allowed? For each set that is not allowed, explain why it is not allowed. K/U T/I A
  - (a)  $n = 3, l = 3, m_l = 0, m_s = -\frac{1}{2}$
  - (b)  $n = 4, l = 3, m_l = 2, m_s = -\frac{1}{2}$
  - (c)  $n = 4, l = 1, m_l = 1, m_s = +\frac{1}{2}$
  - (d)  $n = 2, l = 1, m_l = -1, m_s = -1$
  - (e)  $n = 5, l = -4, m_l = 2, m_s = +\frac{1}{2}$
  - (f)  $n = 3, l = 1, m_l = 2, m_s = -\frac{1}{2}$
10. Science looks for ways to explain what is observed; theoretical knowledge forms the basis of these explanations. Explain the fourth quantum number. Why was it needed? K/U T/I A
11. The second energy shell ( $n = 2$ ) in an atom can hold no more than 8 electrons. Explain this limitation. K/U
12. Every electron requires four unique quantum numbers. How many different sets of these numbers are there for  $n = 1$  and  $n = 2$ ? K/U T/I A