3.5: Quantum Mechanics and The Atom

> **◫ Learning Objectives**
>
> - To apply the results of quantum mechanics to electrons in atoms

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies.

Schrödinger started with the simple requirement that the total energy of the electron is the sum of its kinetic and potential energies:

$$E = \underbrace{\frac{mv^2}{2}}_{\text{kinetic energy}} + \underbrace{\frac{-e^2}{r}}_{\text{potential energy}} \tag{3.5.1}$$

The second term represents the potential energy of an electron (whose charge is denoted by e) at a distance r from a proton (the nucleus of the hydrogen atom). In quantum mechanics it is generally easier to deal with equations that use momentum ($p = mv$) rather than velocity, so the next step is to make this substitution:

$$E = \frac{p^2}{2m} - \frac{e^2}{r} \tag{3.5.2}$$

This is still an entirely classical relation, as valid for the waves on a guitar string as for those of the electron in a hydrogen atom. The third step takes into account the wavelike character of the electron in the atom, a mathematical expression that describes the position and momentum of the electron at all points in space is applied to both sides of the equation. The function, denoted by ψ, "modulates" the equation of motion of the electron so as to reflect the fact that the electron manifests itself with greater probability in some locations that at others. This yields the celebrated **Schrödinger equation**

$$\left(\frac{mv^2}{2} - \frac{e^2}{r} \right) \psi = E\psi \tag{3.5.3}$$

which is often written as

$$H\psi = E\psi \tag{3.5.4}$$

where H is the **Hamiltonian** operator, E is the total energy of the electron, and ψ is the **wavefunction** of the electron. The Hamiltonian is a combination of operations that are used to extract the total energy of the system (e.g., the sum of kinetic an potential energies) and the wavefunction is a mathematical description of the quantum state of an isolated quantum system. The wavefunction is a complex-valued probability amplitude, and the probabilities for the possible results of measurements made on the system can be derived from it. Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

> **⚲ Erwin Schrödinger (1887–1961)**
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> Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Solutions to the Schrödinger Equation for the Hydrogen Atom

A wavefunction is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular energy E. The properties of wavefunctions derived from quantum mechanics are summarized here:

A wavefunction uses three variables to describe the position of an electron. A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates *x*, *y*, and *z*), and one specifies the time at which the object is at the specified location. For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point. Many wavefunctions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wavefunction (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wavefunction should *not* be confused with a positive or negative electrical charge.

The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space. The square of the wavefunction (ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] and is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wavefunction Ψ and its complex conjugate Ψ*, in which all terms that contain i are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure $3.5.2$.

Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wavefunction. From the patterns of one- and two-dimensional standing waves shown previously, you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wavefunctions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wavefunctions), each of which is specified by a set of numbers called quantum numbers.

Each wavefunction is associated with a particular energy. As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.
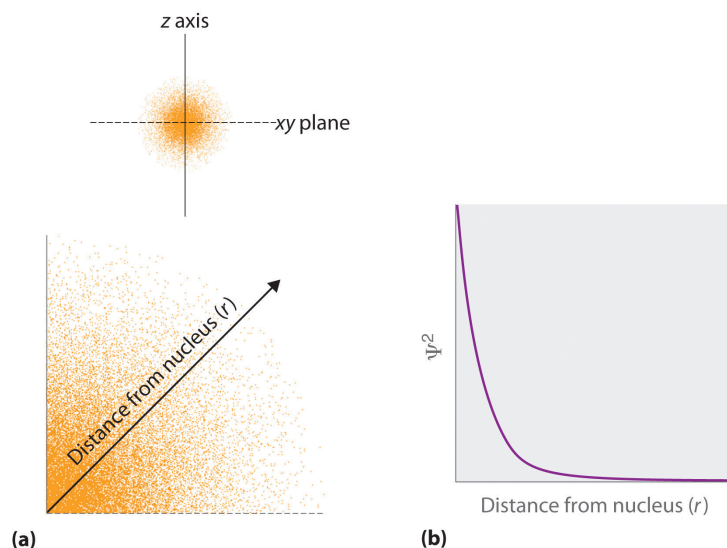

Figure $3.5.2$: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but *not* zero.

Schrödinger's approach uses three quantum numbers (n, l, and m_l) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l and m_l are allowed for a given value of n.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{3.5.5}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wavefunctions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number (l)**. The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to $n − 1$:

$$l = 0, 1, 2, \ldots, n-1 \tag{3.5.6}$$

For example, if $n = 1$, l can be only 0; if $n = 2$, l can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from $−l$ to l in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{3.5.7}$$

For example, if $l = 0$, m_l can be only 0; if $l = 1$, m_l can be −1, 0, or +1; and if $l = 2$, m_l can be −2, −1, 0, +1, or +2.

Each wavefunction with an allowed combination of n, l, and m_l values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

The Spin Quantum Number

> ✔ **Example 3.5.1: n=4 Shell Structure**
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> How many subshells and orbitals are contained within the principal shell with $n = 4$?
>
> **Given:** value of n
>
> **Asked for:** number of subshells and orbitals in the principal shell
>
> **Strategy:**
>
> A. Given $n = 4$, calculate the allowed values of l. From these allowed values, count the number of subshells.
> B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.
>
> **Solution:**
>
> **A** We know that l can have all integral values from 0 to $n − 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2 = 16$

? Exercise 3.5.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer

three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l =	0	1	2	3
Designation	s	p	d	f

The principal quantum number is named first, followed by the letter s, p, d, or f as appropriate. (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental.) A $1s$ orbital has $n = 1$ and $l = 0$; a $2p$ subshell has $n = 2$ and $l = 1$ (and has three $2p$ orbitals, corresponding to $m_l = -1$, 0, and +1); a $3d$ subshell has $n = 3$ and $l = 2$ (and has five $3d$ orbitals, corresponding to $m_l = -2, -1, 0, +1,$ and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible ($1s$); for $n = 2$, there are two subshells ($2s$ and $2p$); for $n = 3$, there are three subshells ($3s$, $3p$, and $3d$); and so forth. Every shell has an ns subshell, any shell with $n \geq 2$ also has an np subshell, and any shell with $n \geq 3$ also has an nd subshell. Because a $2d$ subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a $2d$ subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all ns subshells contain a single s orbital, all np subshells contain three p orbitals, all nd subshells contain five d orbitals, and all nf subshells contain seven f orbitals.

> *Each principal shell has n subshells, and each subshell has 2l + 1 orbitals.*

Table 3.5.1: Values of n, l, and ml through n = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	−1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	−1, 0, 1	3	
	2	3d	−2, −1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	−1, 0, 1	3	
	2	4d	−2, −1, 0, 1, 2	5	
	3	4f	−3, −2, −1, 0, 1, 2, 3	7	

Summary

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wavefunctions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wavefunctions have five important properties:

1. the wavefunction uses three variables (Cartesian axes x, y, and z) to describe the position of an electron;
2. the magnitude of the wavefunction is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wavefunction at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and
5. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n-1$; it describes the shape of the electron distribution. wavefunctions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l+1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wavefunction with a given set of values of n, l, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.