19.2 The Quantum Mechanical Atom

Bohr's model of the atom very successfully explained many of the confusing properties of the atom — it marked a monumental first step into the quantum nature of the atom. Nevertheless, the model was incomplete. For example, a very precise examination of the spectrum of hydrogen showed that what had at first appeared to be individual lines in the spectrum were actually several lines that were extremely close together. As illustrated in Figure 19.9, this "fine structure," as it is sometimes called, could best be explained if one or more energy levels was broken up into several very closely spaced energy levels.

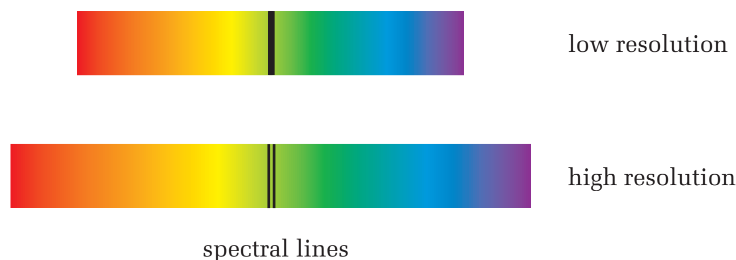


Figure 19.9 Very close examination of the lines in the hydrogen spectrum showed that some of the lines were made up of several fine lines that were very close together.

Another feature of emission spectra that the Bohr atom could not explain was observed in 1896 by Dutch physicist Pieter Zeeman (1865–1943). He placed a sodium flame in a strong magnetic field and then examined the emission spectrum of the flame with a very fine diffraction grating. He observed that the magnetic field caused certain spectral lines to "split" — what had been one line in the spectrum became two or more lines when a magnetic field was present. This phenomenon, illustrated in Figure 19.10, is now called the **Zeeman effect**.

Several physicists attempted with some success to modify the Bohr model to account for the fine structure and the Zeeman effect. The greatest success, however, came from an entirely different approach to modelling the atom: De Broglie's concept of matter waves paved the way to the new quantum mechanics or, as it is often called, "wave mechanics."

When de Broglie proposed his hypothesis about matter waves (about 10 years after Bohr had developed his model of the atom), he applied the ideas to the Bohr model. De Broglie suggested that when electrons were moving in circular orbits around the nucleus, the associated "pilot waves," as de Broglie named them, must

SECTION OUTCOMES

- Outline the development of scientific models from Bohr's model of the hydrogen atom to present-day theories of atomic structure.
- Describe how the development of quantum theory has led to technological advances such as lasers.

KEY TERMS

- Zeeman effect
- Schrödinger wave equation
- wave function
- orbital
- orbital quantum number
- magnetic quantum number
- spin quantum number
- Pauli exclusion principle
- ground state

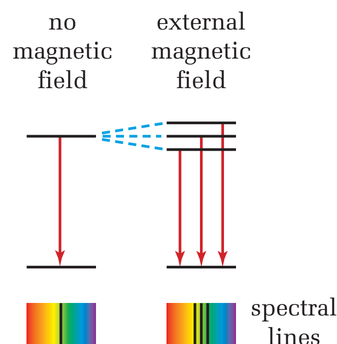


Figure 19.10 When a sample is placed in a magnetic field, some individual spectral lines become a set of closely spaced lines.

form standing waves. Otherwise, destructive interference would eliminate the waves. To form a standing wave on a circular path, the length of the path would have to be an integral number of wavelengths, as shown in Figure 19.11. The procedure that follows the illustration will guide you through the first few steps of de Broglie's method for determining the radius of the orbit of the electron matter waves around the nucleus.

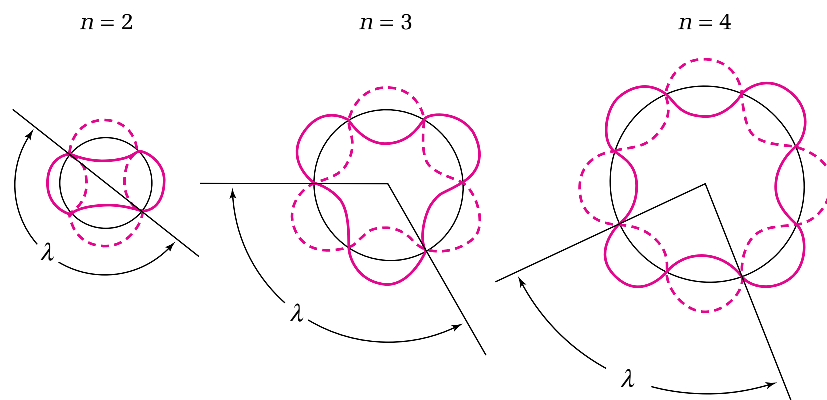


Figure 19.11 The number of wavelengths of matter waves that lie on the radius of an electron orbit is equal to the value of *n* for that energy level. No other wavelengths are allowed because they would interfere destructively with themselves.

- Write the formula for the circumference of a circle and set it equal to any integer (n) times the wavelength. $2\pi r_n = n\lambda$, where $n = 1, 2, 3, \ldots$
- Write de Broglie's formula for the wavelength of a matter wave. $\lambda = \dfrac{h}{mv}$
- Substitute de Broglie's wavelength of an electron into the first equation. $2\pi r_n = n\dfrac{h}{m_e v_n}$
- Divide both sides of the equation by 2π. $r_n = \dfrac{nh}{2\pi m_e v_n}$
- Multiply both sides of the equation by $m_e v_n$ $m_e v_n r_n = \dfrac{nh}{2\pi}$

COURSE CHALLENGE: SCANNING TECHNOLOGIES

Waves and Particles

The process of science continues to discover truths about the nature of our universe. How far have we really come? How well are we able to describe our world? Refer to your e-book for ideas to help you incorporate philosophical debate into your *Course Challenge*.

Notice that the last equation is the same as Bohr's expression for the quantization of angular momentum. From this point on, the derivation of the equation for the radius of allowed orbits would be exactly the same as Bohr's derivation. Using two entirely different approaches to the quantization of electron orbits, Bohr's and de Broglie's results were identical.

In 1925, Viennese physicist Erwin Schrödinger (1887–1961) read de Broglie's thesis with fascination. Within a matter of weeks, Schrödinger had developed a very complex mathematical equation that can be solved to produce detailed information about matter waves and the atom. The now-famous equation, called the **Schrödinger wave equation**, forms the foundation of quantum mechanics. When you insert data describing the potential energy of an electron or electrons in an atom into the wave equation and solve the equation, you obtain mathematical expressions called "wave functions." These **wave functions**, represented by the Greek letter ψ (psi), provide information about the allowed orbits and energy levels of electrons in the atom.

Wave functions account for most of the details of the hydrogen spectra that the original Bohr model could not explain. However, Schrödinger's wave functions could not predict one small, magnetic "splitting" of energy levels. British physicist Paul Adrien Maurice Dirac (1902–1984) realized that electrons travelling in the lower orbits in an atom would be travelling at excessively high speeds, high enough to exhibit relativistic effects. In 1928, Dirac modified Schrödinger's equation to account for relativistic effects. The equation could then account for all observed properties of electrons in atomic orbits. In addition, it predicted many phenomena that had not yet been discovered when the equation was developed.

You are probably wondering, "What are wave functions and what do the amplitude and velocity of a matter wave describe?" Many physicists in the early 1900s asked the same question.

Wave functions do not describe such properties as the changing pressure of air in a sound wave or the changing electric field strength in an electromagnetic wave. In fact, wave functions cannot describe any real property, because they contain the imaginary number i ($i = \sqrt{-1}$, which does not exist). You must carry out a mathematical operation on the wave functions to eliminate the imaginary number in order to describe anything real about the atom.

The result of this operation, symbolized $\psi^*\psi$, represents the probability that the electron will occupy a certain position in the atom at a certain time. You could call the wave function a "wave of probability." You can no longer think of the electron as a solid particle that is moving in a specific path around the nucleus of an atom, but rather must try to envision a cloud such as the one shown in Figure 19.12 (A) and interpret the density of the cloud as the probability that the electron is in that location. These "regions in space" occupied by an electron are often called **orbitals**. If the orbital of the electron is pictured as solid in appearance, as shown in Figure 19.12 (B), it means that there is a 95% probability that the electron is within the enclosed space.

PHYSICS FILE

Solutions to Dirac's modification of the Schrödinger wave equation predicted twice as many particles as were known to exist in the systems for which the equation was defined. Dirac realized that one stage in the solution contained a square root that yielded both positive and negative values. For example, $\sqrt{16y^4} = \pm 4y^2$. You have probably solved problems involving projectile motion or some other form of motion and found both positive and negative values for time. You simply said that a negative time had no meaning and you chose the positive value. Dirac tried this approach, but it changed the final results. Dirac's original results seemed erroneous because they predicted the existence of antiparticles, which had not yet been discovered. Soon after, antiparticles were observed experimentally by other scientists.

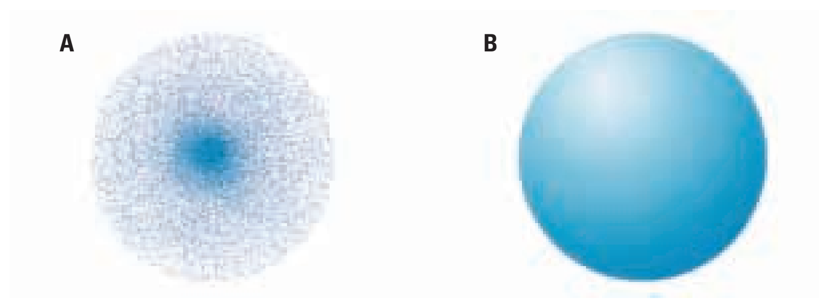
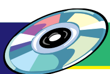


Figure 19.12 When you plot $\psi^*\psi$, you obtain orbitals such as these. **(A)** Orbitals drawn in this manner show the probability of finding the electron. **(B)** Often orbitals are drawn with solid outlines. The probability that the electron is within the enclosed space is 95%.

You might also wonder if the Bohr model was wrong and should be discarded. The answer to that question is a resounding no. The wave functions — that is, the solutions to the Schrödinger wave equation — give the same energy levels and the same principal quantum number (n) that the Bohr model gave. Also, the distance from the nucleus for which the probability of finding the electron is greatest is exactly the same as the Bohr radius. These results show that the general features of the Bohr model are correct and that it is a very useful model for general properties of the atom. The wave equation is necessary only in the finer details of structure.

ELECTRONIC LEARNING PARTNER



Your Electronic Learning Partner contains an excellent reference source of emission and absorption spectra for every element in the periodic table.

Quantum Numbers

The wave functions obtained from Schrödinger's wave equation include two more quantum numbers in addition to the principal quantum number, n. Dirac's relativistic modification of the Schrödinger equation adds another quantum number, making a total of four quantum numbers that specify the characteristics of each electron in an atom. Each quantum number represents one property of the electron that is quantized.

The principal quantum number, n, represents exactly the same property of the atom in both the Bohr model and the Schrödinger model and specifies the energy level of the electron. The value of n can be any positive integer: 1, 2, 3, 4, … . These energy levels are sometimes referred to as "shells."

The **orbital quantum number**, ℓ, specifies the shape of the orbital. The value of ℓ can be any non-negative integer less than n. For example, when $n = 1$, $\ell = 0$. When $n = 2$, ℓ can be 0 or 1. In chemistry, orbitals with different values of ℓ (0, 1, 2, 3, ...) are assigned the letters s, p, d, f, … . Figure 19.13 shows the shapes of orbitals for the first three values of ℓ.

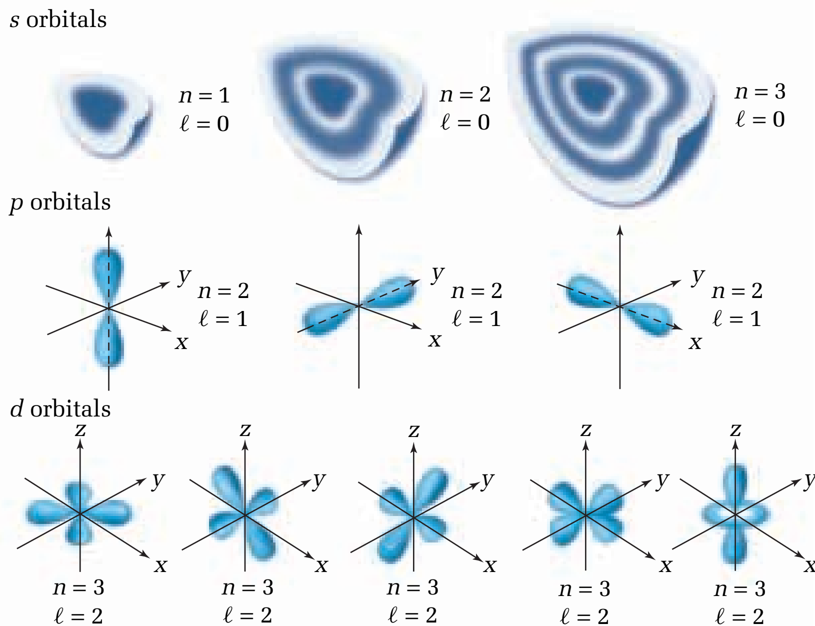


Figure 19.13 Orbitals for which $\ell = 0$ (s orbitals) are always spherical. When $\ell = 1$ (p orbitals), each orbital has two lobes. Four of the $\ell = 2$ (d) orbitals have four lobes and the fifth $\ell = 2$ orbital has two lobes plus a disk.

The orbital quantum number is sometimes called the "angular momentum quantum number," because it determines the angular momentum of the electron. If an electron was to move along a curved path, it would have angular momentum. Although it is not accurate to think of the electron as a tiny, solid piece of matter orbiting around the nucleus, some properties of the electron clouds of orbitals with ℓ greater than zero give angular momentum to the electron cloud. Electrons that have the same value of n but have different values of ℓ possess slightly different energies. As illustrated in Figure 19.14, these closely spaced energy levels account for the fine structure in an emission spectrum of the element.

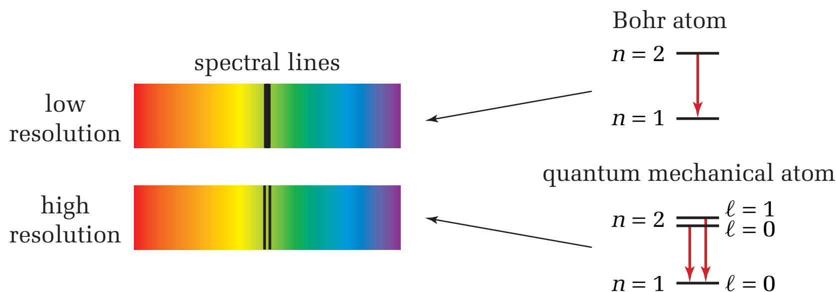


Figure 19.14 For any energy level (shell) for which $n > 0$, there is more than one value of the orbital quantum number, ℓ. The orbitals for each value of ℓ have slightly different energies. These closely spaced energies account for the fine structure, that is, the presence of more than one spectral line very close together.

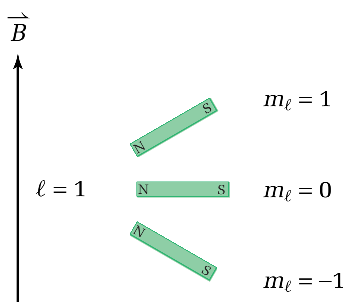


Figure 19.15 In the absence of an external magnetic field, the ℓ orbitals can take any random orientation in space. When a sample is placed in a magnetic field, the ℓ orbitals take on specific orientations in relation to the external field.

The **magnetic quantum number**, m_ℓ, determines the orientation of the orbitals when the atom is placed in an external magnetic field. To develop a sense of what this quantum number means, it is once again helpful, although not entirely accurate, to think of the electron in its cloud as an electric current flowing around the nucleus. As you know, a current flowing in a loop creates a magnetic field. The magnetic quantum number determines how this internal field is oriented if the atom is placed in an external magnetic field. In Figure 19.15, the electron's magnetic field is represented by a small bar magnet with different orientations in an external magnetic field.

The **spin quantum number**, m_s, results from the relativistic form of the wave equation. The term "spin" is used because the effect is the same as it would be if the electron was a spherical charged object that was spinning. A spinning charge creates its own magnetic field in much the same way that a circular current does. The value of m_s can be only $+\frac{1}{2}$ or $-\frac{1}{2}$. Similar to the magnetic quantum number, the spin quantum number has an effect on the energy of the electron only when the atom is placed in an external magnetic field. The two orientations in the external magnetic field are often called "spin up" and "spin down." Figure 19.16 illustrates the two possible orientations of the electron spin and its effect on the electron's energy and spectrum in an external magnetic field.

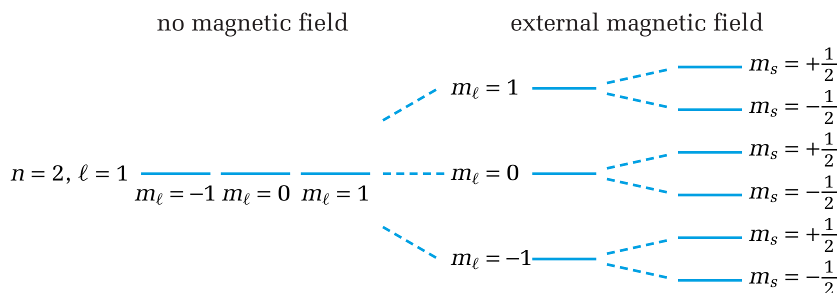


Figure 19.16 The electron spin can assume any orientation in the absence of an external magnetic field, but can take only two orientations when placed in a magnetic field — spin up or spin down.

These four quantum numbers and the associated wave functions can explain and predict essentially all of the observed characteristics of atoms. Two questions might arise, however: If almost all of the mass of an atom is confined to a very tiny nucleus and electrons, with very little mass, are in "clouds" that are enormous compared to the nucleus, why does matter seem so "solid"? Why cannot atoms be compressed into much smaller volumes?

Austrian physicist Wolfgang Pauli (1900–1958) answered those questions in 1925. According to the **Pauli exclusion principle**, *no two electrons in the same atom can occupy the same state*. An easier way of saying the same thing is that *no two electrons in the same atom can have the same four quantum numbers*. Electron clouds of atoms cannot overlap.

The Pauli exclusion principle also tells us how many electrons can fit into each energy level of an atom. The tree diagrams in Figure 19.17 show how many electrons can fit into the first three energy levels, $n = 1$, $n = 2$, and $n = 3$.

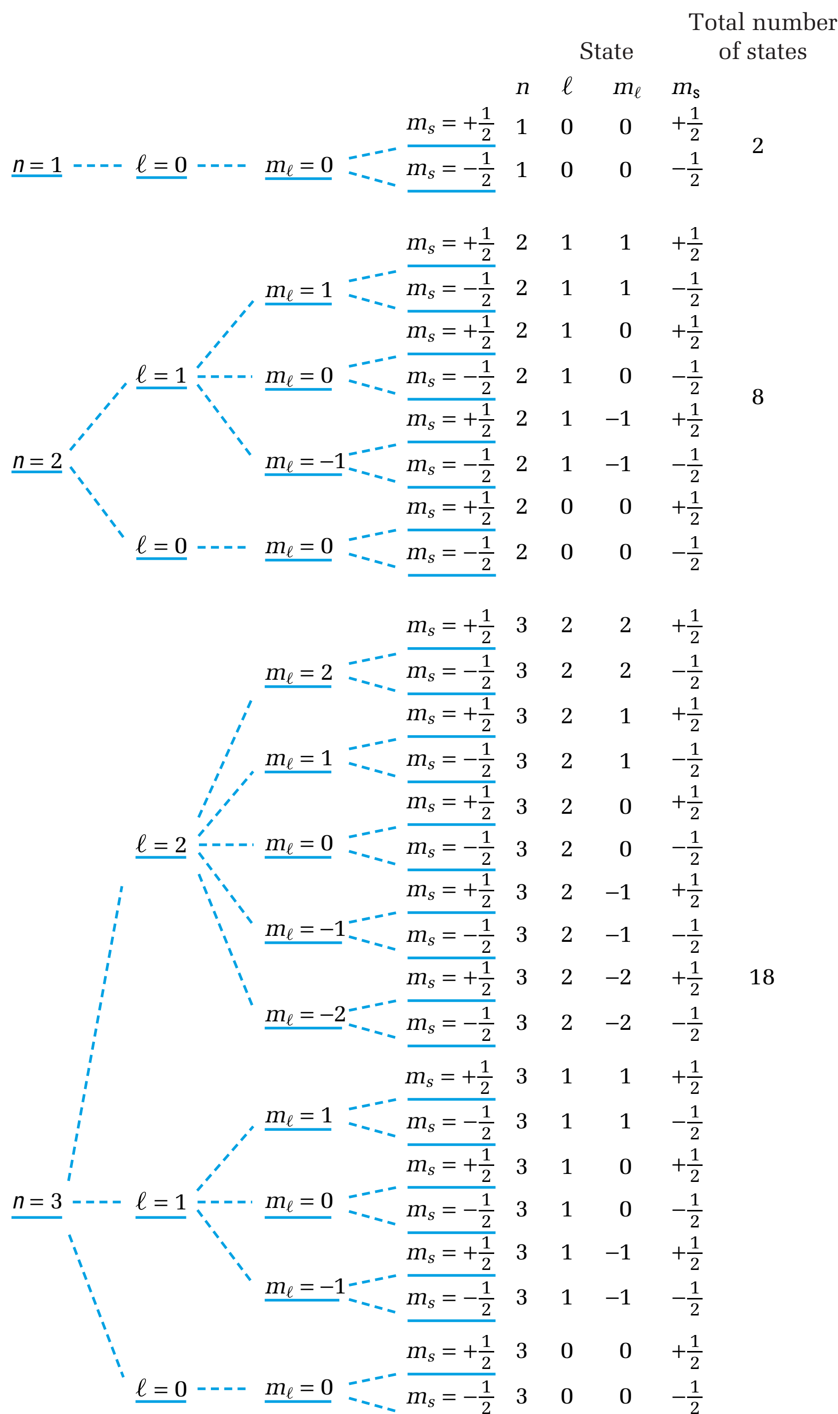


Figure 19.17 These tree diagrams show the energy levels, both in the absence and the presence of an external magnetic field, for the first three values of the principal quantum number, n.

Conceptual Problem

- Study Figure 19.17 and then draw a tree diagram for the next energy level, $n = 4$. How many electrons will fit into the fourth energy level?

Hydrogen has only one proton in the nucleus, and thus one electron in an orbital. When a hydrogen atom is not excited, the electron is in the $n = 1$, $\ell = 0$ energy level. However, the atom can absorb energy and become excited and the electron can "jump" up to any allowed orbital. All elements other than hydrogen have more than one electron. When atoms are not excited, the electrons are in the lowest possible energy levels that do not conflict with the Pauli exclusion principle. Figure 19.18 gives examples of three different elements with their electrons in the lowest possible energy levels. This condition is called the **ground state** of the atom. Similar to the electron in hydrogen, the electrons of other elements can absorb energy and rise to higher energy levels.

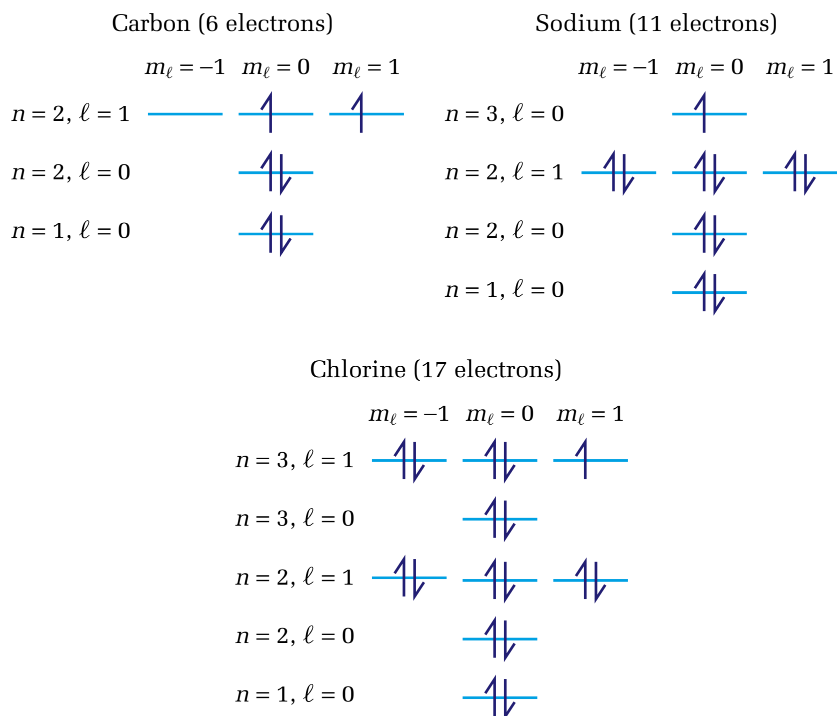


Figure 19.18 Electrons "fill" the energy levels from the lowest upward until there are as many electrons in orbitals as there are protons in the nucleus.

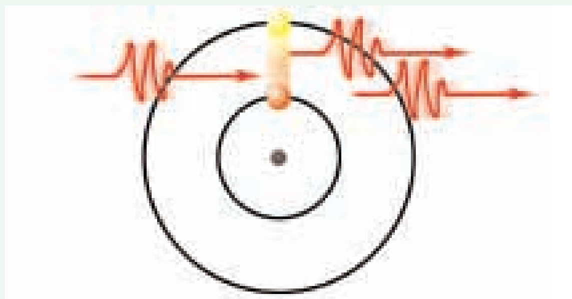
PHYSICS & TECHNOLOGY

TARGET SKILLS

- Hypothesizing
- Analyzing and interpreting

Atoms and Lasers

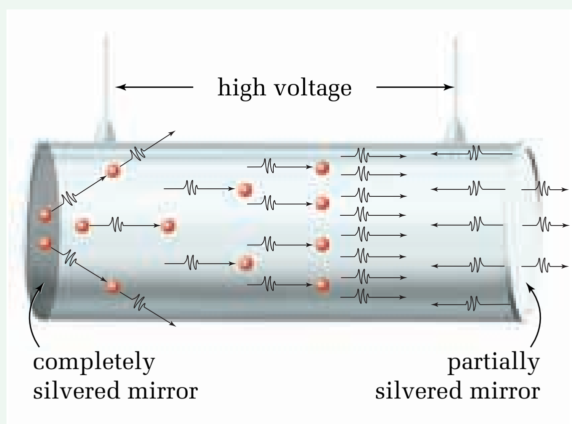
A thorough understanding of the energy levels of electrons in atoms and of transitions between these states was necessary before anyone could even imagine that a laser could be developed. Another critical property of electrons that was necessary in order to develop lasers was predicted by Einstein in 1917 — the stimulation of emission of a photon. As shown in the diagram, if an electron is in an excited state (that is, in a higher energy level), a photon with an energy level equal to the difference in allowed energy levels will stimulate the electron to drop to the lower energy level and emit another identical photon. In addition, the two photons are perfectly in phase.



If more electrons exist in the excited state than in the ground state, it is more probable that a photon will stimulate an emission instead of being absorbed. Two conditions are necessary in order to create and maintain this condition. Normally, most electrons are in the ground state at room temperature, so a stimulus is needed to excite the electrons. This stimulus can be provided by a high voltage that will accelerate free electrons, and then collisions with atoms will excite their electrons. The process is called "optical pumping."

If the excited electrons spend a longer than normal time in the excited state, stimulated emission will be more probable than spontaneous emission. This condition is met by selecting atoms of elements that have specific energy levels called the "metastable state." Electrons remain in metastable states for about 10^{-3} s, rather than the normal 10^{-8} s.

A typical gas laser tube is shown in the diagram. A high voltage excites the electrons in the gas, maintaining more atoms in an excited state than the ground state. As some photons are emitted spontaneously, they stimulate the emission of other photons. The ends of the laser tube are silvered to reflect the photons. This reflection causes more photons to stimulate the emission of a very large number of photons. Any photons that are not travelling parallel to the sides of the tube exit the tube and do not contribute to the beam. One end of the tube is only partially reflecting, and a fraction of the photons escape. These escaping photons have the same wavelength and frequency and are all in phase, creating a beam of what is called "coherent light."



Analyze

1. The word "laser" is an acronym for "light amplification by stimulated emission of radiation." Explain the significance of each term in the name.
2. Laser beams remain small and do not spread out, as does light from other sources. Based on the unique characteristics of laser light, try to explain why the beams do not spread out.
3. List as many applications of laser as you can.

The years from 1900 to 1930 were exciting ones in physics. No longer could physicists speak of waves and particles as separate entities — the boundary between the two became blurred. The long-standing Dalton model of the atom gave way to the Thomson model, which was soon usurped by the Rutherford model and, soon thereafter, by the Bohr model. Eventually, all models that represented electrons as discrete particles yielded to the quantum mechanical model described by the Schrödinger wave equation.

Today, the wave equation is still considered to be the most acceptable model. In fact, physicists have been able to show that the wave equation can give information about the nucleus and particles that was not known to exist when Schrödinger presented his equation. In the next chapter, you will learn about properties of the nucleus and particles that exist for time intervals as small as 10^{-20} s.

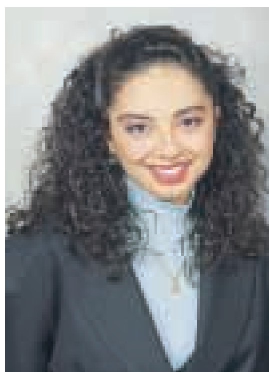
19.2 Section Review

1. K/U How did Dirac improve Schrödinger's wave equation?
2. K/U What is a wave function and what type of information does a wave function provide about atoms?
3. K/U List and define the four quantum numbers.
4. C Balmer's work on the spectrum of hydrogen helped Bohr to modify Rutherford's model of the atom. Explain how he did this.
5. K/U Write down Rydberg's modification of Balmer's formula and define the terms.
6. K/U What can cause an electron in the Bohr model to "jump" to a higher energy level?
7. K/U Explain the term "principal quantum number."

CAREERS IN PHYSICS

The Invisible Universe

Go outside on a cloudless night and look up. You might see the Moon, a few planets, and many stars. The universe stretches before you, but your eyes are not taking in the full picture. Astronomer Dr. Samar Safi-Harb and her colleagues see a very different universe by using instruments that detect X rays and several other wavelengths of electromagnetic radiation that are invisible to the human eye.



Dr. Samar Safi-Harb

Dr. Safi-Harb is an assistant professor with the Department of Physics and Astronomy at the University of Manitoba. She uses the instruments aboard satellites such as NASA's Chandra X-ray Observatory to research the death throes of super-massive stars. When a super-massive star runs out of nuclear energy, it collapses under its own weight and its outer layers burst into space in a violent explosion called a "supernova." In some cases, the mass left behind compacts into a neutron star. This astounding type of star is so dense that all of its matter fits into a volume no larger than that of a city. A neutron star, along with its strong magnetic field, spins incredibly fast — up to several dozen times per second!

A neutron star is a remarkable source of electromagnetic radiation. As its magnetic field spins through space, it creates an electric field that generates powerful beams of electromagnetic waves, ranging from radio waves to gamma rays. If the beams sweeps past Earth, astronomers detect them as pulses, like a lighthouse beacon flashing past. Such neutron stars are called "pulsars."

The Crab Nebula is one of Dr. Safi-Harb's favourite objects in the sky. It is the remains of a star that went supernova in 1054 A.D. The Crab Nebula is energized by fast-moving particles emitted from its central pulsar. "It looks different at different wavelengths," she explains. "The radio image reveals a nebula a few light-years across that harbours low-energy electrons. The diffuse optical nebula shines by intermediate energy particles, showing a web of filaments that trace the debris of the explosion. The X-ray image reveals a smaller nebula — the central powerhouse — containing very energetic particles. Its jets, rings, and wisp-like structures unveil the way pulsars dump energy into their surroundings."

In part, the ground-breaking work of Jocelyn Bell, the discoverer of pulsars, inspired Dr. Safi-Harb to follow this line of research. Although an astronomer, she has a doctorate in physics from the University of Wisconsin, Madison. Few universities today have astronomy programs that stand alone from physics.

Going Further

1. Earth is orbited by a wide array of satellites that explore the sky at high-energy and low-energy wavelengths. Research two or more of these satellites and describe how images taken by them enhance our understanding of the universe.

2. When two objects in space approach or recede from one another at great speed, light emitted from either object appears altered by the time it reaches the other object. Research and describe what astronomers mean when they talk about a "red shift" or a "blue shift" in light.

Web Link

www.mcgrawhill.ca/links/atlphysics

Radio, infrared, optical, X-ray, and gamma-ray images of our galaxy, the Milky Way, can be found on the Internet. You can also learn more about Dr. Safi-Harb's work and see images of several of her favourite objects in space by going to the above Internet site and clicking on **Web Links**.