Expanding the Model of the Atom

In science, theoretical models and experimental evidence are always linked. For example, early scientists believed that rotting meat generated maggots. This seemed reasonable, since exposed meat becomes infested with maggots. Experiments proved, however, that if the meat was protected from flies, no maggots appeared. Thus, rotting meat didn't generate maggots; flies did. When a model fails to explain experimental evidence, scientists must discard or modify that model. The model of the atom is no exception.

Emission Spectra

In Chapter 2, you used a diffraction grating to observe the spectra of various elements. These elements were sealed in gas discharge tubes. The spectra resulted from electrons in atoms moving from higher energy levels to lower energy levels and releasing energy as light.

Each wavelength of visible light is associated with a colour. When white light is shone through a gas discharge tube, it produces a line spectrum. A line spectrum is a series of narrow lines having specific colours (energy), separated by colourless spaces. Each element produces a different and characteristic emission spectrum. You can see several examples of these spectra in Figure D.1. Scientists who were thinking about how to describe the atom needed to take the emission spectra into account.

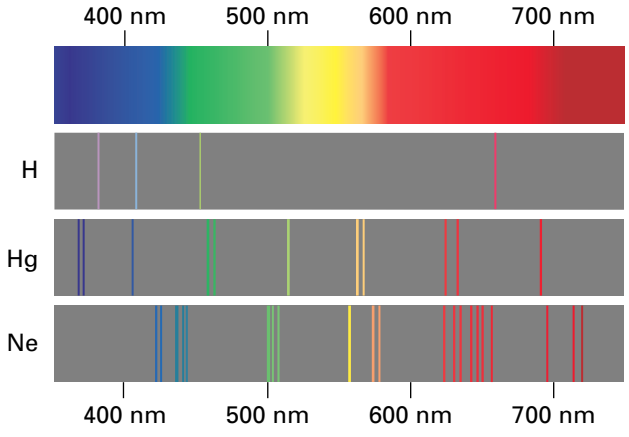

Figure D.1 **The top spectrum is the continuous spectrum of white light. The others are emission spectra for hydrogen, mercury, and neon. Each element has its own distinct spectrum, which is like a "fingerprint" for that element.**

Bohr's Model of the Atom

In 1913, the Danish physicist Niels Bohr developed a model of the atom that explained the hydrogen emission spectrum. In Bohr's model, electrons orbit the nucleus in the same way that Earth orbits the Sun, as shown in Figure D.2. The following three points of Bohr's theory help to explain hydrogen's emission spectrum.

1. In Bohr's model, atoms have specific allowable energy levels. He called these energy levels *stationary states*. Each of these levels corresponds to a fixed, circular orbit around the nucleus.
2. An atom does not give off energy when its electrons are in a stationary state.
3. An atom changes stationary states by giving off or absorbing a quantity of light energy exactly equal to the difference in energy between the two stationary states.

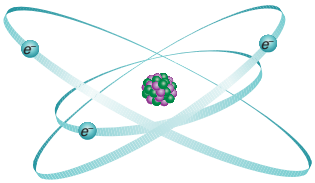

Figure D.2 **In Bohr's atomic model, electrons move around the nucleus with fixed, circular orbits.**

Bohr's model was revolutionary, because he proposed that the energy absorbed or emitted by an atom needed to have specific values. The energy change was quantized, rather than continuous. When something is *quantized*, it means that it is limited to discrete amounts or multiples of discrete amounts. Two great scientists paved the way for this surprising idea. German physicist Max Planck had already suggested that energy in general was quantized, meaning that it exists in "packets." Building on this idea, Einstein proposed that light could behave as particles, which he called *photons*.

The energy associated with the light in a line spectrum corresponds with the change in energy of an electron as it moves up or down an energy level. For example, when electrons in hydrogen atoms that have been excited to the third energy level subsequently drop to the second energy level, they emit light that has a specific energy. They emit photons of red light that have a wavelength of 656.3 nm. These photons cause the red line on the line spectrum for hydrogen, which you can see in Figure D.1.

Why a New Model?

So what was the problem? Bohr's model worked beautifully, correctly predicting the line spectrum for

hydrogen. It also worked fine for ions with one electron, such as He^{+}, Li^{2+}, Be^{3+}, etc. The model failed, however, when it was applied to the emission spectra of atoms that had more than one electron. Bohr's model needed to be modified, because it was too simple to explain the experimental evidence.

Sublevels

The spectra of many-electron atoms suggested that a more complex structure was needed. Notice in Figure D.1 that spectra for these more complex atoms have groups of lines close together. The groups are separated by spaces. The large spaces represent the energy differences between energy levels, while the smaller spaces represent energy differences within the levels.

If the electrons are changing energy within the levels, this suggests that there are *sublevels* within each level, each with its own slightly different energy. The idea of energy levels 1, 2, 3, 4, etc. remains, but each energy level is split up into sublevels called *s*, *p*, *d*, and *f*. Examine Table D.1 to see how electrons are arranged in sublevels for energy levels 1 to 4.

Table D.1 Distribution of Electrons in Energy Levels and Sublevels

Energy level	Number of electrons in energy level	Sublevel	Number of electrons in sublevel
1	2	1*s*	2
2	8	2*s*	2
		2*p*	6
3	18	3*s*	2
		3*p*	6
		3*d*	10
4	32	4*s*	2
		4*p*	6
		4*d*	10
		4*f*	14

Each sublevel has its own energy. Examine Figure D.3 to see the relative energies of the levels and sublevels.

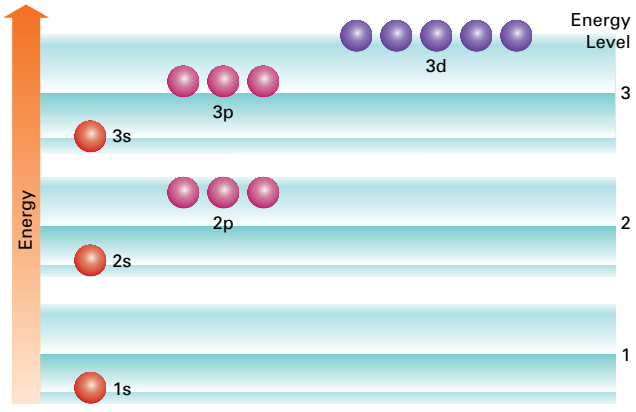

Figure D.3 **This figure shows the relative energies of sublevels in energy levels 1, 2, and 3.**

Visualizing the New Model

But where do you find the electrons in this new model? How are the sublevels oriented in space? Several theories enabled scientists to describe what the newly conceived atom "looked like."

Particles with Wave-Like Properties

In 1924, Louis de Broglie, a young physics student, suggested that all matter had wave-like properties. This seemed to follow from Planck and Einstein's idea that electromagnetic radiation has matter-like properties. De Broglie developed an equation that allowed him to calculate the wavelength of the matter wave associated with any object, from a bowling ball to an electron. Objects that we can see and can interact with have calculated wavelengths that are smaller than electrons. Their wavelengths are so tiny compared to their size that they do not have any measurable effect on the motion of the objects.

For very tiny moving particles, however, such as electrons, the wavelength becomes very significant. In fact, an electron moving at an average speed has a wavelength even larger than the size of the entire hydrogen atom!

De Broglie's theory was proven by experiment when streams of electrons produced diffraction patterns similar to those produced by electromagnetic radiation, which was already known to travel in waves.

Orbitals

In 1926, Erwin Schrödinger used de Broglie's idea that matter has wavelike properties. Schrödinger proposed what is now known as the *quantum mechanical model of the atom*. In this new model, he abandoned the notion of the electron as a small particle orbiting the nucleus. Instead, he took into account the particle's wavelike properties, and described the behaviour of electrons in terms of wave functions.

The imprecise nature of Schrödinger's model was supported shortly afterwards by a principle proposed by Werner Heisenberg, in 1927. Heisenberg demonstrated that it is impossible to know both an electron's pathway and its exact location. *Heisenberg's uncertainty principle* is a mathematical relationship that shows that you can never know both the position and the momentum of an object beyond a certain measure of precision.

CHEM FACT

The momentum of an object is its mass multiplied by its velocity. An object's momentum is directly related to the amount of energy it has.

Heisenberg also showed that if you could know either velocity or position precisely, then the other property would be uncertain. Therefore, when talking about where electrons are found in an atom, you cannot talk in terms of certainties, but only in terms of probabilities.

Schrödinger used a mathematical wave equation to define the probability of finding an electron within an atom. There are multiple solutions to this wave equation and Schrödinger called these solutions wave functions, or *orbitals*. Each solution provides information about the energy and location of an electron within an atom. Each orbital has a specific energy associated with it, and each contains information about where, inside the atom, the electrons would spend most of their time. The actual paths of the moving electrons cannot be determined. However, the solutions can be used to show where, for each orbital, there is a high probability of finding an electron.

Imagine you were able to take many exact measurements of the position of an electron in the 1*s* sublevel at fixed intervals. At each second, you would mark the electron's position on a graph. After a while, your graph might look something like the first diagram in Figure D.4. If someone tried to use your graph to determine where the electron was, they would not be able to state its position exactly. They would, however, be able to see that the probability of finding the electron would be greater near the nucleus and would decrease farther away from the nucleus.

The probability graph is "fuzzy," because the probability of finding an electron anywhere in a 1*s* sublevel is never zero. The probability becomes extremely small when it is far away from the nucleus, but it never quite reaches zero. Therefore, to obtain an exact shape for an orbital, you need to choose a level of probability. For example, drawing a contour that encompasses 95 percent of the probability graph results in a spherical shape, like the third diagram in Figure D.4. In other words, at any time, there is a 95 percent chance of finding the electron within the spherical contour.

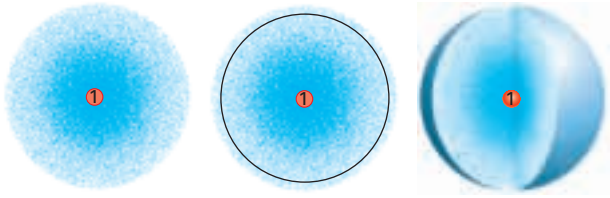

Figure D.4 **These three figures represent the probability of finding an electron at any point in a hydrogen atom. The two-dimensional drawing on the left shows that the electron spends most of its time fairly close to the nucleus. The circle around the cloud in the centre encompasses 95 percent of the two-dimensional cloud. The diagram on the right shows the 95 percent probability contour in three dimensions.**

Shapes of Orbitals

The shapes of the probability graphs from Schrödinger's wave functions are the shapes of the orbitals in which electrons reside in atoms. You can visualize orbitals as electron clouds. The shape of each cloud is based on probability—it tells you where the electron spends most of its time.

Examine Figure D.5. The *s* orbitals are spherical in shape, as described above. Each of these spherical shells contains two electrons. There are three *p* orbitals for each sublevel, each with a capacity for two electrons. Each orbital is shaped something like a dumbbell. For each sublevel, the *p* orbitals are oriented along the *x*, *y*, and *z* axes. Therefore, the three *p* orbitals in each sublevel are sometimes designated with subscripts to show this. For example, the 2*p* orbitals may be designated $2p_x$, $2p_y$, $2p_z$.

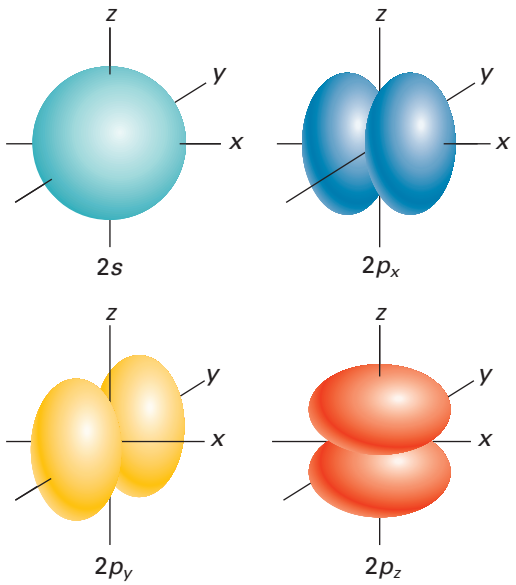

Figure D.5 **This figure shows the shapes of the 2*s* and 2*p* orbitals.**

The *d* and *f* orbitals are quite complex in shape. Each *d* sublevel contains five *d* orbitals, while each *f* sublevel contains seven *f* orbitals.

Filling the Orbitals

Why is it that each orbital can contain only two electrons? A hypothesis suggests that electrons spin around their own axes as they move around the nucleus, generating magnetic fields. They can spin either in a positive direction or in a negative direction. In 1925, Wolfgang Pauli proposed that only two electrons of opposite spin could occupy an orbital. This idea became known as the *Pauli exclusion principle*.

How do electrons fill orbitals within atoms? They do so in such a way as to minimize the potential energy of the atom.

1. They will fill orbitals with the lowest energy first. The 1*s* orbital will fill before the 2*s* orbital, which will fill before the 2*p* orbitals.
2. When occupying two or more orbitals with the same energy (for example, any of the three 2*p* orbitals), electrons will half fill each orbital until all are half filled before adding a second electron to each one. This is called *Hund's rule*.

You can show how electrons fill orbitals, using superscripts. For example, a boron atom contains five electrons. Here's how you show the electron configuration:

$$1s^2\,2s^2,\ 2p_x^1$$

How would you show the electron configuration of a nitrogen atom? Remember Hund's rule:

$$1s^2,\ 2s^2,\ 2p_x^1,\ 2p_y^1,\ 2p_z^1$$

Using the Model

The quantum mechanical model of the atom is useful for explaining phenomena in addition to emission spectra. For example, in Chapter 2, you learned about trends in ionization energy. You learned that, in general, ionization energy increases across a period. Figure D.6 shows the ionization energy as a function of atomic number for the first 18 elements. In most cases, the ionization energy follows the trend. There are some exceptions, however, such as oxygen, boron, and sulfur. You can use the quantum model of the atom to explain these discrepancies.

First Ionization Energy versus Atomic Number

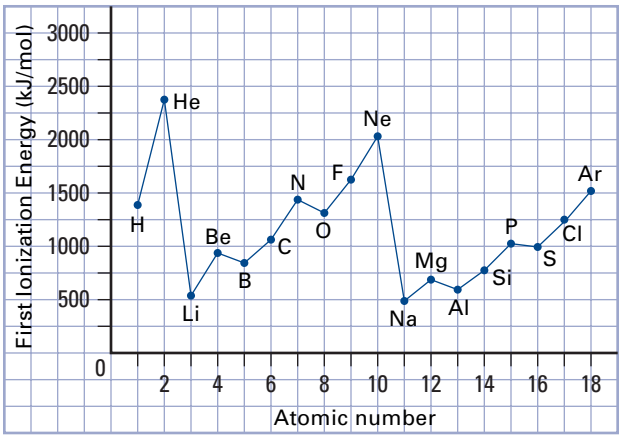

Figure D.6 **This graph shows the relationship between first ionization energy and atomic number for the first 18 elements.**

Practice Problems

1. Write the electron configurations for the following atoms:
   - **(a)** carbon
   - **(b)** oxygen
   - **(c)** fluorine
   - **(d)** sodium
   - **(e)** silicon
   - **(f)** hydrogen
2. Explain why the ionization energy of the following elements is less than the element that precedes it, even though its nucleus has a greater positive charge.
   - **(a)** oxygen has a lower ionization energy than nitrogen
   - **(b)** boron has a lower ionization energy than beryllium
   - **(c)** sulfur has a lower ionization energy than phosphorus

PROBLEM TIP

Keep in mind two things when answering question 2:

(a) A completely filled sublevel is favourable in terms of energy.

(b) When removing electrons from the same sublevel, it is easier to remove an electron from a filled orbital than from a half-filled orbital. In spite of their opposite spins, the negative charges of electrons together in a filled orbital repel each other more than those in half-filled orbitals.

3. Explain why Bohr's model of the atom explained emission spectra for one-electron atoms, but failed to explain emission spectra for many-electron atoms.