Chapter 5

Quantization of Atomic Energy Levels

5.1 Introduction

In Chapter 4 we described the discovery of the quantization of light, which made clear that classical electromagnetic theory is incorrect on the microscopic level. In the present chapter we describe the corresponding failure of classical mechanics when applied to microscopic systems. With hindsight, we can see that the evidence for this breakdown of classical mechanics goes back to the discovery of atomic spectra in the middle of the nineteenth century, as we describe in Sections 5.2 and 5.3. However, it was not until 1913 that any satisfactory explanation of atomic spectra was found — by the Danish physicist Niels Bohr — and it became clear that a substantial revision of classical mechanics was required.

Bohr’s work was originally prompted by a problem concerning the stability of Rutherford’s model of the atom (a problem we describe briefly in Section 5.4), but he quickly found that many properties of atomic spectra could easily be explained if one assumed that the total energy of the electrons in an atom is quantized. This quantization of atomic energies has no classical explanation, and to account for it, Bohr developed a mechanics that is now called the Bohr model, or the old quantum theory. As Bohr was well aware, his ideas were not really a complete theory, and they have now been superseded by modern quantum mechanics. Nevertheless, Bohr’s ideas were a crucial step in the development of modern quantum mechanics and were correct in several important respects. For these reasons, we describe the Bohr theory and some of its successes in the last six sections of this chapter.
5.2 Atomic Spectra

Perhaps the most famous spectrum of all time was the one discovered in 1666 by Isaac Newton, who shone a narrow beam of white light through a glass prism, producing the well-known ribbon of rainbow colors, as shown in the first spectrum at the front of this book. This established that what we perceive as white light is a mixture of different colors, or different wavelengths as we would now say.

In 1814 the German physicist Joseph von Fraunhofer discovered that when viewed more closely, the spectrum of sunlight is crossed by dark lines, like those in the second spectrum at the front of this book (though narrower and much more numerous). This showed that certain colors, or wavelengths, are missing from the light that reaches us from the sun. Today we know that this is because the gases in the sun’s outer atmosphere absorb light at certain discrete wavelengths. The light with these wavelengths is therefore removed from the white light coming from deeper down, and this causes the dark lines observed by Fraunhofer.

By the middle of the nineteenth century it was known that all gases absorb light at wavelengths that are characteristic of the atoms and molecules they contain. For example, if white light is shone through a gas containing just one kind of atom, the gas will absorb certain wavelengths characteristic of that atom; if the transmitted light is then passed through a prism or diffraction grating, it will produce an absorption spectrum consisting of a bright ribbon of rainbow colors crossed with dark absorption lines, like Fraunhofer’s. Furthermore, it is found that if the same gas is heated sufficiently, it will emit light. Moreover, the wavelengths of this emitted light are the same as those that the gas absorbed when illuminated with white light. If this emitted light is passed through a prism, it will produce an emission spectrum, consisting of bright emission lines against a dark background.

The absorption and emission spectra produced by atomic hydrogen are shown in color at the front of this book. (At ordinary temperatures hydrogen gas consists of H₂ molecules; to produce the atomic spectra shown, one must use gas that is heated enough — by an electric discharge, for example — to dissociate the molecules into atoms.) The same spectra are shown schematically in Fig. 5.1, where the pictures (a) and (c) show the emission and absorption spectra themselves, while (b) and (d) are the corresponding graphs of intensity against wavelength.

**FIGURE 5.1**

Emission and absorption spectra of atomic hydrogen. (a) The emission spectrum; the white stripes represent bright lines against a dark background. (b) The corresponding graph of intensity against wavelength, on which the spikes correspond to the bright lines of the spectrum itself (The relative intensities of the four lines depend on the temperature.) (c) The absorption spectrum, with dark lines against a bright background. (d) The corresponding graph, on which the dips correspond to the dark lines of the spectrum.
The atoms and molecules of any one chemical species emit and absorb light at wavelengths characteristic of that species. Thus emission and absorption spectra act like fingerprints, uniquely identifying the atom or molecule that produced them. By about 1870 spectroscopy had become a powerful tool of chemical analysis and had led to the discovery of several previously unknown elements. In particular, it was, and still is, the only way to determine the chemical composition of the sun, other stars, and interstellar matter.

Despite the many successful applications of spectroscopy in the nineteenth century, there was no satisfactory theory of atomic spectra. Classically, emission and absorption were easy to understand: An atom would be expected to emit light if some source of energy, such as collisions with other atoms, caused its electrons to vibrate and produce the oscillating electric fields that constitute light. Conversely, if light were incident on an atom, the oscillating electric field would cause the electrons to start vibrating and hence to absorb energy from the incident light. The observation that light is emitted and absorbed only at certain characteristic frequencies was understood to imply that the atomic electrons could vibrate only at these same frequencies; but no completely satisfactory classical model was ever found that could explain (let alone predict) these characteristic frequencies of vibration.

As we will see, Bohr’s ideas (and likewise modern quantum mechanics) explain the characteristic spectra in a quite different way. First, the characteristic frequencies, \( f_a, f_b, \ldots \) of light emitted by an atom imply that atoms emit photons with characteristic energies, \( h f_a, h f_b, \ldots \). (This connection between frequency and energy was, of course, completely unknown in the nineteenth century.) These characteristic energies are explained by establishing that the total energy of the electrons in an atom is quantized, with discrete allowed values \( E_1, E_2, E_3, \ldots \), as illustrated in the energy-level diagrams of Fig. 5.2. An atom emits or absorbs light by making an abrupt jump from one energy state to another — for example, by changing from energy \( E_2 \) to \( E_1 \), or vice versa. If \( E_2 > E_1 \) and the atom changes from \( E_2 \) to \( E_1 \) it must release the excess energy \( E_2 - E_1 \) and it does so in the form of a photon of energy \( h f = E_2 - E_1 \), as shown symbolically in Fig. 5.2(a); similarly, it can only change from \( E_1 \) to \( E_2 \) if it is supplied with energy \( E_2 - E_1 \) and one way this can happen is by absorption of a photon of energy \( h f = E_2 - E_1 \), as in Fig. 5.2(b). The characteristic energies of the photons emitted and absorbed by an atom are thus explained as the differences in the characteristic quantized energies of the atom. Before we explore Bohr’s explanation of atomic spectra further, we relate a little more history.

**FIGURE 5.2**
The possible energies of an atom are found to be quantized, with discrete values \( E_1, E_2, E_3, \ldots \). In these energy-level diagrams, energy is plotted upward, and the allowed energies are represented as the rungs of a ladder. (a) If the atom is initially in level \( E_2 \), it can drop to level \( E_1 \) by emitting a photon of energy \( h f = E_2 - E_1 \). (b) If it is initially in the level \( E_1 \), it can absorb a photon of energy \( h f = E_2 - E_1 \), which will lift it to the level \( E_2 \).
5.3 The Balmer–Rydberg Formula

The simplest of all atoms is hydrogen and it is therefore not surprising that the spectrum of atomic hydrogen was the first to be thoroughly analyzed. By 1885 the four visible lines shown in Fig. 5.1 had been measured very accurately by the Swedish astronomer and physicist Anders Ångstrom. These measurements were examined by a Swiss school teacher Johann Balmer, who found (in 1885) that the observed wavelengths fitted the formula

$$\frac{1}{\lambda} = R \left( \frac{1}{4} - \frac{1}{n^2} \right) \quad (5.1)$$

where $R$ was a constant (with the dimension length$^{-1}$), which Balmer determined as

$$R = 0.0110 \text{ nm}^{-1} \quad (5.2)$$

and $n$ was an integer equal to 3, 4, 5, and 6 for the four lines in question. Ångstrom had measured these wavelengths to four significant figures, and Balmer’s formula fitted them to the same accuracy. Balmer guessed (correctly, as we now know) that such an excellent fit could not be a coincidence and that there were probably other lines given by other values of the integer $n$ in the formula (5.1). For example, if we take $n = 7$, then (5.1) gives

$$\lambda = 397 \text{ nm}$$

a wavelength near the violet edge of the visible spectrum; with $n = 8, 9, \ldots$, Eq. (5.1) predicts shorter wavelengths in the ultraviolet. One can imagine Balmer’s delight when he discovered that several more lines had already been observed in the spectrum of hydrogen and that they were indeed given by his formula with $n = 7, 8, 9, \ldots$.

We can rewrite Balmer’s formula (5.1) in the form

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad (n = 3, 4, 5, \ldots) \quad (5.3)$$

It is tempting to guess that this is just a special case of the more general formula

$$\frac{1}{\lambda} = R \left( \frac{1}{n'^2} - \frac{1}{n^2} \right) \quad (n > n', \text{ both integers}) \quad (5.4)$$

and that the spectrum of atomic hydrogen should contain all wavelengths given by all integer values of $n'$ and $n$. Balmer himself had guessed that some such generalization might be possible, but the form (5.4) was apparently first written down by the Swedish physicist Johannes Rydberg, for whom (5.4) is usually called the Rydberg formula and $R$, the Rydberg constant. If we take $n' = 1$ and $n = 2$, for example, Rydberg’s formula predicts

$$\lambda = 121 \text{ nm}$$
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a wavelength well into the ultraviolet; with \( n' = 3, n = 4 \), we get

\[ \lambda = 1870 \text{ nm} \]

in the infrared. In fact, all of the additional wavelengths predicted by (5.4) (with \( n' \) any integer other than Balmer’s original value of 2) are either in the ultraviolet or the infrared. It was several years before any of these additional lines were observed, but in 1908 the German physicist Louis Paschen found some of the infrared lines with \( n' = 3 \), and in 1914 the American Theodore Lyman found some of the ultraviolet lines with \( n' = 1 \). Today, it is well established that the Rydberg formula (5.4) accurately describes all of the wavelengths in the spectrum of atomic hydrogen.

**Example 5.1**

Conventional spectrometers with glass components do not transmit ultraviolet light (\( \lambda \leq 380 \text{ nm} \)). Explain why none of the lines predicted by (5.4) with \( n' = 1 \) could be observed with a conventional spectrometer.

For the case \( n' = 1, n = 2 \), Eq. (5.4) predicts that

\[
\frac{1}{\lambda} = R \left( \frac{1}{1} - \frac{1}{4} \right) = \frac{3}{4} R
\]

and hence

\[
\lambda = \frac{4}{3R} = \frac{4}{3 \times (0.0110 \text{ nm}^{-1})} = 121 \text{ nm}
\]

as stated earlier. Similarly, for \( n' = 1 \) and \( n = 3 \), one finds that \( \lambda = 102 \text{ nm} \), and inspection of (5.4) shows that the larger we take \( n \), the smaller the corresponding wavelength, with \( \lambda \to 91 \text{ nm as } n \to \infty \). Therefore, all lines with \( n' = 1 \) lie in the range \( 91 < \lambda < 121 \text{ nm} \), well into the ultraviolet, and are unobservable with a conventional spectrometer.

It is often convenient to rewrite the Rydberg formula (5.4) in terms of photon energies rather than wavelengths. Since the energy of a photon is \( E_\gamma = \frac{hc}{\lambda} \), we have only to multiply (5.4) by \( hc \) to give

\[
E_\gamma = \frac{hcR \left( \frac{1}{n^2} - \frac{1}{n'^2} \right)}{n' > n, \text{ both integers} \quad (5.5)}
\]

These are the energies of the photons emitted or absorbed by a hydrogen atom.

It is important to recognize that neither Balmer, Rydberg, nor anyone else prior to 1913 could explain why the formula (5.5) gave the spectrum of hydrogen. It was perhaps Bohr’s greatest triumph that his theory predicted the Rydberg formula (5.5), including the correct value of the Rydberg constant \( R \), in terms of known fundamental constants.

*The subscript \( \gamma \) is traditionally used to identify variables pertaining to any kind of photon, since “gamma” (\( \gamma \)) is one of the many names for a photon (although this is a little inconsistent since the name gamma is usually reserved for photons of very high energy).*
Section 5.5 • Bohr’s Explanation of Atomic Spectra

**5.4 The Problem of Atomic Stability**

A satisfactory theory of atomic spectra obviously required a correct knowledge of the structure of the atom. It is therefore not surprising that atomic spectra lacked any explanation until Rutherford had proposed his nuclear model of the atom in 1911, nor that Bohr’s explanation came soon after that proposal, in 1913. Curiously enough, the nuclear model posed a serious problem of its own, and it was in solving this problem that Bohr succeeded in explaining atomic spectra as well.

As Rutherford himself was aware, his model of the atom raises an awkward problem of stability. Superficially, Rutherford’s atom resembles the solar system, and electrons can orbit around the nucleus just as planets orbit around the sun. According to classical mechanics, the planets’ orbits are circles or ellipses and are stable: Once a planet is placed in a given orbit it will remain there indefinitely (if we ignore small effects like tidal friction). Unfortunately, the same is not true in an atom. A clear prediction of classical electromagnetic theory is that an accelerating charge should radiate electromagnetic waves. The electron has an electric charge and should have a centripetal acceleration in its “planetary” orbit. Therefore, the orbiting electron should radiate electromagnetic waves and hence gradually lose energy. This implies that its orbital radius should steadily shrink and its orbital frequency increase. The steady increase in orbital frequency means that the frequency of emitted light should keep changing — in sharp contrast to the observed spectrum, with its discrete, fixed frequencies. Worse still, one can estimate the rate at which the radius will shrink, and one finds that all electrons should collapse into the nucleus in a time of order $10^{-11}$ s. (See Section 11.2.) That is, stable atoms, as we know them, could not exist.* This was the problem that Bohr originally set out to solve.

**5.5 Bohr’s Explanation of Atomic Spectra**

To solve the problem of atomic stability, Bohr proposed that the laws of classical mechanics must be modified and that among the continuum of electron orbits that classical mechanics predicts, only a certain discrete set is actually possible. He gave these allowed orbits the name stationary orbits or stationary states. Since the possible orbits were discrete, their energies would also be discrete; that is, the energies of the electrons in an atom would be quantized, and the only possible energies of the whole atom would be a discrete set $E_1, E_2, E_3, \ldots$. If this were true, it would be impossible for the atom to lose energy steadily and continuously, as required by classical electromagnetic theory. Therefore, Bohr simply postulated that an electron in one of the allowed stationary orbits does not radiate energy and remains in exactly the same orbit as long as it is not disturbed.

Bohr could not show why the electrons in his stationary states do not radiate, and one cannot really say that he explained the stability of atoms.

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*In theory, we should consider the same problem with respect to the solar system. As the planets move in their orbits, they should radiate gravitational waves, analogous to the electromagnetic waves radiated by electrons. However, gravitational radiation is so small that it has not yet (2002) been detected directly, and its effect on the planetary orbits is certainly unimportant.
Nevertheless, his ideas come very close to being correct, and his phrase “stationary state” has proved remarkably apt. In modern quantum mechanics we will find that the electron does not have a classical orbit at all; rather, it is (in a sense we’ll explain in Chapter 6) distributed continuously through the atom and can be visualized as a cloud of charge surrounding the nucleus. The stable states of the atom — corresponding to Bohr’s stationary orbits — are states in which the distribution of charge in this cloud actually is stationary and does not radiate.

Having solved the problem of atomic stability (by simply postulating his quantized stationary states, in which electrons did not radiate), Bohr realized that his theory gave a beautiful explanation of atomic spectra. As we have already described, if the total energy of the electrons in an atom is quantized, with allowed values $E_1, E_2, E_3, \ldots$, the energy can change only by making a discontinuous transition from one value $E_n$ to another $E_{n'}$,

$$E_n \rightarrow E_{n'}$$

Bohr did not try to explain the detailed mechanisms by which such a transition can occur, but one method is certainly the emission or absorption of a photon. If $E_n > E_{n'}$, a photon of energy $E_n - E_{n'}$ must be emitted. If $E_n < E_{n'}$, a photon of energy $E_{n'} - E_n$ must be absorbed. Either way, the photon’s energy must be the difference of two of the allowed energies, $E_n$ and $E_{n'}$ of the atom. This immediately explains why the energies (and hence frequencies) of the emitted and absorbed photons are the same. Further, one would naturally expect the allowed energies $E_1, E_2, E_3, \ldots$ to be different for different atomic species. Thus, the same should be true of the differences $E_n - E_{n'}$, and this would explain why each atomic species emits and absorbs with its own characteristic spectrum.

**Example 5.2**

The helium atom has two stationary states, designated $3p$ and $2s$, with energies

$$E_{3p} = 23.1 \text{ eV} \quad \text{and} \quad E_{2s} = 20.6 \text{ eV}$$

measured on a scale in which the lowest energy state has an energy set to zero. (We will see the significance of the designations $3p$ and $2s$ later.) What will be the wavelength of a photon emitted when the atom makes a transition from the $3p$ state to the $2s$?

In moving from the $3p$ state to the $2s$, the atom loses energy $E_{3p} - E_{2s}$. This is therefore the energy of the emitted photon

$$E_\gamma = E_{3p} - E_{2s} = 2.5 \text{ eV}$$

so the wavelength is

$$\lambda = \frac{hc}{E_\gamma} = \frac{1240 \text{ eV} \cdot \text{nm}}{2.5 \text{ eV}} \approx 500 \text{ nm}$$

Light with this wavelength is blue-green, and the $3p \rightarrow 2s$ transition is, in fact, responsible for the blue-green line that is visible in the helium spectrum inside the front cover.

*We will discuss this further in Section 7.3.*
The Bohr Model of the Hydrogen Atom

It was obviously desirable that Bohr find a way to predict the allowed energies, \( E_1, E_2, \ldots \), of an atom, and in the case of hydrogen he was able to do so. In fact, he produced several different arguments, all of which gave the same answer for the allowed energies. All these arguments were, as Bohr himself acknowledged, quite tentative, and their main justification was that they produced the right answer; that is, they predicted certain energy levels, which in turn led to the Rydberg formula for the spectrum of hydrogen.

We will describe one of Bohr’s arguments, which is the simplest and, in many ways, the closest to modern quantum mechanics. Since Bohr assumed that the possible orbits of the electron were a subset of the classical orbits, we begin by reviewing the classical mechanics of an orbiting electron.

Our system consists of an electron of mass \( m \) and charge \(-e\), which orbits around a proton of charge \(+e\), as shown in Fig. 5.3. For simplicity, we will treat the case where the electron moves in a circular orbit, and because the proton is so much heavier than the electron, we will make the approximation that the proton is fixed in position. (In reality, the proton moves a little, and this requires a very small correction to our answers, as we discuss later.)

The electron’s acceleration is the centripetal acceleration, \( a = \frac{v^2}{r} \), and the only force acting on the electron is the Coulomb attraction of the proton,

\[
F = \frac{ke^2}{r^2}
\]

where \( k \) is the Coulomb force constant, \( k = 1/(4\pi\varepsilon_0) = 8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2 \). Thus Newton’s second law implies that

\[
(m) \times (\text{centripetal acceleration}) = \text{Coulomb force}
\]

or

\[
m\frac{v^2}{r} = \frac{ke^2}{r^2}
\]

This condition is a relation between \( v \) and \( r \), which can be solved to give \( v \) in terms of \( r \) or vice versa.

In classical mechanics (5.6) is the only constraint between \( v \) and \( r \), so neither \( v \) nor \( r \) is fixed. On the contrary, the possible values of \( v \) and \( r \) range continuously from 0 to \( \infty \), and this means that the energy of the electron is not quantized. To see this explicitly, we note that (5.6) implies that

\[
mv^2 = \frac{ke^2}{r}
\]

Now, the electron’s kinetic energy \( K \) is \( K = \frac{1}{2}mv^2 \), while the potential energy of an electron (charge \(-e\)) in the field of a proton (charge \(+e\)) is

\[
U = -\frac{ke^2}{r}
\]
if we define $U$ to be zero when the electron is far from the proton (that is, when $r = \infty$). Thus (5.7) implies that for an electron in a circular orbit

$$K = -\frac{1}{2}U$$

(This result was well known in classical mechanics and is an example of the so-called virial theorem.) The total energy is therefore

$$E = K + U = \frac{1}{2}U = -\frac{1}{2} \frac{ke^2}{r}$$

(5.10)

Notice that the total energy is negative, as it has to be since the electron is bound to the proton and cannot escape to infinity. Since $r$ can have any value in the range $0 < r < \infty$, it is clear from (5.10) that the energy of our bound electron can have any value in the range $-\infty < E < 0$.

Our analysis so far has been purely classical. Some new hypothesis was needed if the allowed energies were to be quantized. To understand the hypothesis that Bohr proposed, we note that Planck’s constant has the same dimensions as angular momentum (remember that since $E = hf$, $h$ has the units of energy/ frequency or energy $\times$ time):

$$[h] = \text{energy} \times \text{time} = \frac{ML^2}{T^2} \times T = \frac{ML^2}{T}$$

and

$$[\text{angular momentum}] = [mv] = M \times \frac{L}{T} \times L = \frac{ML^2}{T}$$

(5.11)

This suggests that the electron’s angular momentum could be quantized in multiples of $h$; and Bohr proposed specifically that its allowed values are integer multiples of $h/(2\pi)$:

$$L = \frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \ldots$$

(5.12)

where $L$ denotes the electron’s angular momentum. Bohr was led to propose these values for $L$ by what he called the correspondence principle, which we will describe briefly in Problem 11.12. For the moment, we simply accept (5.12) as a judicious guess that, like Planck’s hypothesis that light is quantized in multiples of $hf$, was principally justified by the fact that it led to the correct answers. When we go on to discuss modern quantum mechanics we will be able to prove that **Bohr’s quantization condition** (5.12) is essentially correct. *

The combination $h/(2\pi)$ in (5.12) appears so frequently that it is often given its own symbol:

$$h = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{J} \cdot \text{s}$$

(5.13)

*The hypothesis (5.12) is not exactly correct. We will prove, rather, that any component of the vector $\mathbf{L}$ is an integer multiple of $h/(2\pi)$. However, for the present this comes to the same thing because we can take the electron’s orbit to lie in the $xy$ plane, in which case the total angular momentum is the same as its $z$ component.
where $\hbar$ is read as “$h$ bar.” Thus, we can rewrite the quantization condition (5.12) as

\[ L = n\hbar \quad (n = 1, 2, 3, \ldots) \quad (5.14) \]

For the circular orbits, which we are discussing, the angular momentum is $L = mvr$, and (5.14) can be rewritten as

\[ mvr = n\hbar \quad (n = 1, 2, 3, \ldots) \quad (5.15) \]

This condition is a second relation between $r$ and $v$. [The first was (5.7), which expressed Newton’s second law.] With two equations for two unknowns we can now solve to find the allowed values of $r$ (or $v$). If we solve (5.15) to give $v = n\hbar/(mr)$ and then substitute into (5.7), we find

\[ m\left(\frac{n\hbar}{mr}\right)^2 = \frac{ke^2}{r} \]

whence

\[ r = \frac{n^2\hbar^2}{ke^2m} \quad (5.16) \]

That is, the values of $r$ are quantized, with values given by (5.16), which we write as

\[ r = n^2a_B \quad (n = 1, 2, 3, \ldots) \quad (5.17) \]

Here we have defined the **Bohr radius** $a_B$, which is easily evaluated to be (Problem 5.7)

\[ a_B = \frac{\hbar^2}{ke^2m} = 0.0529 \text{ nm} \quad (5.18) \]

Knowing the possible radii of the electron’s orbits, we can immediately find the possible energies from (5.10).

\[ E = -\frac{ke^2}{2r} = -\frac{ke^2}{2a_B} \frac{1}{n^2} \quad (n = 1, 2, 3, \ldots) \quad (5.19) \]

We see that the possible energies of the hydrogen atom are quantized. If we denote the energy (5.19) by $E_n$, then, as we argued in Section 5.5, the energy of a photon emitted or absorbed by hydrogen must have the form

\[ E_\gamma = E_n - E_n' = \frac{ke^2}{2a_B} \left( \frac{1}{n^2} - \frac{1}{n'^2} \right) \quad (5.20) \]

which has precisely the form of the Rydberg formula (5.5)

\[ E_\gamma = \hbar c R \left( \frac{1}{n^2} - \frac{1}{n'^2} \right) \quad (5.21) \]
Comparing (5.20) and (5.21), we see that Bohr’s theory predicts both the Rydberg formula and the value of the Rydberg constant, \( R = \frac{ke^2}{2a_B(hc)} = \frac{1.44 \text{ eV} \cdot \text{nm}}{2 \times (0.0529 \text{ nm}) \times (1240 \text{ eV} \cdot \text{nm})} = 0.0110 \text{ nm}^{-1} \) in perfect agreement with the observed value (5.2).

Because of its close connection with the Rydberg constant, the energy \( hcR = ke^2/(2a_B) \) in (5.21) and (5.20) is called the Rydberg energy and is denoted \( E_R \). Its value and several equivalent expressions for it are (as you should check for yourself in Problem 5.8)

\[
E_R = \frac{ke^2}{2a_B} = \frac{m(k\frac{e^2}{2})^2}{2\hbar^2} = 13.6 \text{ eV} \quad (5.22)
\]

In terms of \( E_R \), the allowed energies (5.19) of the electron in a hydrogen atom are

\[
E_n = -\frac{E_R}{n^2} \quad (5.23)
\]

This is the most important result of the Bohr model, and we take up its implications in the next section.

### 5.7 Properties of the Bohr Atom

As compared to the modern quantum-mechanical view, Bohr’s model of the hydrogen atom is not completely correct. Nevertheless, it is correct in several important features and is often easier to visualize and remember than its modern counterpart. For these reasons we review some of its properties.

Bohr’s model predicts (and modern quantum mechanics agrees) that the possible energies of an electron in a hydrogen atom are quantized, their allowed values being \( E_n = -E_R/n^2 \), where \( n = 1, 2, \ldots \). The lowest possible energy is that with \( n = 1 \) and is

\[
E_1 = -E_R = -13.6 \text{ eV} \quad (5.24)
\]

This state of lowest energy is called the ground state. It is the most stable state of the atom and is the state into which an isolated atom will eventually find its way. The significance of the energy \( E_1 = -13.6 \text{ eV} \) is that an energy \( +13.6 \text{ eV} \) must be supplied to remove the electron entirely from the proton. That is, the Bohr theory predicts that the binding energy of the hydrogen atom is 13.6 eV, in excellent agreement with its observed value.

According to (5.17) the radius of the \( n = 1 \) orbit is just the Bohr radius \( a_B \):

\[
r = a_B = 0.0529 \text{ nm} \quad (5.25)
\]

*In evaluating this, we have used the two useful combinations \( ke^2 = 1.44 \text{ eV} \cdot \text{nm} \) and \( hc = 1240 \text{ eV} \cdot \text{nm} \). (See Problem 5.4.) These are listed, along with many other physical constants, inside the front cover.*
This agrees well with the observed size of the hydrogen atom and was regarded by Bohr as an important accomplishment of his theory. The primary significance of \( a_B \) is that it gives the radius of the ground state of hydrogen. However, we will find that it also gives the order of magnitude of the outer radius of all atoms in their ground states. For this reason, the Bohr radius \( a_B \) is often used as a unit of distance in atomic physics.

The orbits with energies greater than the ground-state energy are called excited states. Their energies are given by \( E_n = -\frac{E_R}{n^2} \), with \( n = 2, 3, \ldots \) that is,

\[
E_2 = -\frac{E_R}{4} = -3.4 \text{ eV} \quad E_3 = -\frac{E_R}{9} = -1.5 \text{ eV}
\]

and so on. These allowed energies, or energy levels, are traditionally displayed graphically as in Fig. 5.4. In these energy-level diagrams, the energy is plotted vertically upward, and the allowed energies are shown as horizontal lines, somewhat like the rungs of a ladder.

Energy-level diagrams provide a convenient way to represent transitions between the energy levels. For example, if the atom is in the lowest state, \( n = 1 \), the only possible change is an upward transition, which will require the supply of some energy. If, for instance, we were to shine photons of energy 10.2 eV on a hydrogen atom, the photons would have exactly the right energy to lift the electron to the \( n = 2 \) level and the atom could make the transition, absorbing one photon in the process. This transition is indicated in Fig. 5.4 by an arrow between the levels concerned. The energy 10.2 eV is called the first excitation energy of hydrogen, since it is the energy required to raise the atom to its first excited state; similarly, the second excitation energy is \( E_3 - E_1 = 12.1 \text{ eV} \), and so on.

If the atom is in an excited state \( n \) (with \( n > 1 \)), it can drop to a lower state \( n' \) (with \( n' < n \)) by emitting a photon of energy \( E_n - E_{n'} \). If, for example, the original level is \( n = 3, 4, 5, \ldots \) and the electron drops to the \( n = 2 \) orbit, the photon will have energy

\[
E_{\gamma} = E_n - E_2 = E_R \left( \frac{1}{2^2} - \frac{1}{n'^2} \right) \quad (5.26)
\]

These are, of course, the photon energies implied by Balmer’s original formula (5.1). For this reason, the spectral lines given by this formula (with the lower

---

*We will see later that in modern quantum mechanics there is no uniquely defined radius of the electron’s orbit. However, the average radius is about \( a_B \); thus in this sense, Bohr’s theory agrees with modern quantum mechanics.*
level being \( n' = 2 \) are often called the **Balmer series**. The transitions in which the lower level is the ground state \((n' = 1)\) are called the Lyman series, and those in which the lower level is \( n' = 3 \), the Paschen series (after their respective discoverers). These three series are illustrated in Fig. 5.5.

According to (5.17), the radius of the \( n \)th circular orbit is proportional to \( n^2 \):

\[
r = n^2 a_B
\]

Thus the radii of the Bohr orbits increase rapidly with \( n \), as indicated in Fig. 5.6. This agrees qualitatively with modern quantum theory and with experiment: In the excited states of hydrogen atoms (and all other atoms, in fact) the electrons tend to be much farther away from the nucleus than they are in their ground states.

In addition to the circular orbits that we have discussed, Bohr’s theory also allowed certain elliptical orbits. However, Bohr was able to show that the allowed energies of these elliptical orbits were the same as those of the circular orbits. Thus, for our present purposes the elliptical orbits do not add any important further information. Since the precise details of the Bohr orbits are not correct anyway, we will not discuss the elliptical orbits any further.

---

**Example 5.3**

Modern atomic physicists have observed hydrogen atoms in states with \( n > 100 \). What is the diameter of a hydrogen atom with \( n = 100 \)?

The diameter is

\[
d = 2r = 2n^2 a_B = 2 \times 10^4 \times (0.05 \text{ nm}) = 1 \mu\text{m}.
\]
By atomic standards this is an enormous size — 10^4 times the diameter in the ground state. For comparison, we note that a quartz fiber with this diameter is visible to the naked eye. Atoms with these high values of \( n \) — called Rydberg atoms — can exist only in a good vacuum since the interatomic spacing at normal pressures is of order 3 nm and leaves no room for atoms this large. (See Problem 5.14.)

## 5.8 Hydrogen-Like Ions

For several years, at least, it appeared that Bohr’s theory gave a perfect account of the hydrogen atom. The important problem was to generalize the theory to atoms with more than one electron, and in this no one succeeded. In fact, the Bohr theory was never successfully generalized to explain multielectron atoms, and a satisfactory quantitative theory had to await the development of modern quantum mechanics around 1925. Nevertheless, the Bohr theory did give a successful quantitative account of some atomic problems besides the spectrum of atomic hydrogen. In this and the next section we describe two of these successes.

In Section 5.6 we found the allowed radii and energies of a hydrogen atom, that is, a single electron in orbit around a proton of charge +e. The arguments given there started with Bohr’s quantization condition that the allowed values of angular momentum are integer multiples of \( \hbar \). Starting from this same assumption, we can modify those arguments to apply to any hydrogen-like ion, that is, any atom that has lost all but one of its electrons and therefore comprises a single electron in orbit around a nucleus of charge +Ze. We might consider, for example, the He\(^+\) ion (an electron and a helium nucleus of charge +2e) or the Li\(^{2+}\) ion (an electron and a lithium nucleus of charge +3e).

To adapt the arguments of Section 5.6 to hydrogen-like ions, we have only to note that the force \( ke^2/r^2 \) on the electron in hydrogen must be replaced by

\[
F = \frac{Zke^2}{r^2}
\]

In other words, wherever \( ke^2 \) appears in Section 5.6, it must be replaced by \( Zke^2 \). For example, the allowed orbits of hydrogen had radii given by (5.16) as

\[
r = n^2 \frac{\hbar^2}{ke^2m} = n^2a_B
\]

therefore, the orbits of an electron moving around a charge Ze are

\[
r = n^2 \frac{\hbar^2}{Zke^2m} = n^2 \frac{a_B}{Z}
\]

(5.27)

We see that the radius of any given orbit is inversely proportional to \( Z \). The larger the nuclear charge \( Z \), the closer the electron is pulled in toward the nucleus, just as one might expect.

The potential energy of the hydrogen-like ion is \( U = -Zke^2/r \). The total energy is, according to (5.10), \( E = K + U = U/2 \) or

\[
E = -\frac{Zke^2}{2r}
\]

(5.28)
Inserting (5.27) for the radius of the \( n \)th orbit, we find that

\[
E_n = -Z^2 \frac{ke^2}{2a_B} \frac{1}{n^2}
\]

or

\[
E_n = -Z^2 \frac{E_R}{n^2}
\]  

That is, the allowed energies of the hydrogen-like ion with nuclear charge \( Ze \) are \( Z^2 \) times the corresponding energies in hydrogen. [The two factors of \( Z \) are easy to understand: One is the \( Z \) in the expression (5.28) for the energy, the other comes from the \( 1/Z \) in the allowed radii.]

The result (5.29) implies that the energy levels of the \( \text{He}^+ \) ion should be four times those in hydrogen. Thus the energies of the photons emitted and absorbed by \( \text{He}^+ \) should be

\[
E_\gamma = 4E_R \left( \frac{1}{n^2} - \frac{1}{n'^2} \right)
\]  

(that is, four times those of the hydrogen atom). This formula looks so like the Rydberg formula for hydrogen that when the spectrum of \( \text{He}^+ \) had been observed in 1896 in light from the star Zeta Puppis, it had been wrongly interpreted as a new series of lines for hydrogen. It was another of the triumphs for Bohr’s theory that he could explain these lines as belonging to the spectrum of once-ionized helium. Today, the spectra of hydrogen-like ions ranging from \( \text{He}^+ \) and \( \text{Li}^{+2} \) to \( \text{Fe}^{+25} \) (iron with 25 of its 26 electrons removed) have been observed and are in excellent agreement with the Bohr formula (5.29).

There is a small but interesting correction to (5.29) that we should mention. So far we have supposed that our one electron orbits around a fixed nucleus; in reality, the electron and nucleus both orbit around their common center of mass. Because the electron is so light compared to the nucleus, the center of mass is very close to the nucleus. Thus the nucleus is very nearly stationary, and our approximation is very good. Nonetheless, the nucleus does move, and this motion is fairly easily taken into account. In particular, it can be shown (Problem 5.21) that the allowed energies are still \( E = -Z^2 E_R/n^2 \) and that the Rydberg energy is still given by (5.22) as

\[
E_R = \frac{m(ke^2)^2}{2\hbar^2}
\]  

provided that the mass \( m \) of the electron is replaced by the so-called reduced mass, usually denoted \( \mu \):

\[
\mu = \text{reduced mass} = \frac{m}{1 + m/m_{\text{nuc}}}
\]  

where \( m \) is the electron mass and \( m_{\text{nuc}} \), the mass of the nucleus. (See Problem 5.21.) In the case of hydrogen, the nucleus is a proton and \( m/m_{\text{nuc}} \approx 1/1800 \). Therefore, the energy levels in hydrogen are all reduced by about 1 part in 1800 as a result of this correction. This is a rather small change, but one that can be easily detected by the careful spectroscopist.
The interesting thing (for the present discussion) is that the correction represented by (5.32) is different for different nuclei. In He⁺ the nucleus is four times heavier than in hydrogen, and the factor \( m/m_{\text{nuc}} \) is four times smaller. Because of this difference, the ratio of the He⁺ frequencies to those of hydrogen is not exactly 4 but is about 4.002. This small difference was observed and added further weight to Bohr’s interpretation.

**Example 5.4**

Hydrogen has an isotope, \(^2\text{H}\), called deuterium or heavy hydrogen, whose nucleus is almost exactly twice as heavy as that of ordinary hydrogen since it contains a proton and a neutron. It was discovered because its spectrum is not exactly the same as that of ordinary hydrogen. Calculate the Balmer \( \alpha \) wavelengths of ordinary hydrogen and of deuterium, both to five significant figures, and compare.

Since \(^1\text{H}\) and \(^2\text{H}\) have the same nuclear charge, they would have identical spectra, if it were not for the motion of the nuclei. In particular, the Balmer \( \alpha \) line would be given by the Rydberg formula (5.4) with \( n = 3, n' = 2 \), and \( R = 0.0109737 \, \text{nm}^{-1} \) (to six significant figures); this would give

\[
\lambda = 656.114 \, \text{nm}
\]

However, all energy levels of each atom must be corrected in accordance with (5.32) and (5.31) by dividing by the factor \( (1 + m/m_{\text{nuc}}) \). Since wavelength is inversely proportional to energy, the correct wavelengths are found by multiplying by this same factor. Therefore, for ordinary hydrogen, the Balmer \( \alpha \) wavelength is really

\[
\lambda(^1\text{H}) = (656.114 \, \text{nm}) \left(1 + \frac{m}{m(^1\text{H})}\right) = (656.114 \, \text{nm}) \left(1 + \frac{1}{1800}\right) = 656.48 \, \text{nm}
\]

For deuterium the corresponding wavelength is

\[
\lambda(^2\text{H}) = (656.114 \, \text{nm}) \left(1 + \frac{1}{3600}\right) = 656.30 \, \text{nm}
\]

a difference of about 1 part in 4000.

Since natural hydrogen contains 0.015% deuterium, its spectrum has a very faint component with these slightly shorter wavelengths. It was by observing these lines that the American chemist Harold Urey proved the existence of deuterium in 1931.

The reduced mass (5.32) is always less than the mass of the electron, and the difference is bigger for lighter nuclei. The extreme case is the system called positronium, which is a hydrogen-like “atom” with the electron bound to a positron. (Positrons were described in Section 2.8.) In this case the “nuclear” mass is equal to the electron mass, and the reduced mass is exactly half the electron mass. Thus the energy levels of positronium are just half those of hydrogen. (See Problem 5.18.) The other interesting thing about positronium is that it is very unstable since the electron and positron eventually annihilate, producing a 1.22 MeV of electromagnetic energy.
The quantitative successes of Bohr’s theory all concerned systems in which a single electron moves in the field of a single positive charge. The most obvious example is the hydrogen-like ion discussed in Section 5.8, but another system that fits the description, at least approximately, is the innermost electron of a multielectron atom. To the extent that the charge distribution of the other outer electrons is spherical (which is actually true to a fair approximation), the outer electrons exert no net force on the innermost electron. Therefore, the latter feels only the force of the nuclear charge $Ze$, and its allowed energies should be given by (5.29) as about

$$E_n = -Z^2 \frac{E_R}{n^2}$$  \hspace{1cm} (5.33)

The factor $Z^2$ means that for medium and heavy atoms the inner electron is very tightly bound. For example, in zinc, with $Z = 30$, the energy needed to remove the innermost electron from the $n = 1$ orbit is about

$$Z^2E_R = (30)^2 \times (13.6 \text{ eV}) \approx 12,000 \text{ eV}$$

Thus, atomic transitions that involve the inner electrons would be expected to involve energies of order several thousand eV; in particular, a photon emitted or absorbed in such a transition should be an X-ray photon. This fact was recognized by the young British physicist Henry Moseley, who, within a few months of Bohr’s paper, had shown that the Bohr theory gave a beautiful explanation of the characteristic X-rays that were produced at discrete frequencies, characteristic of the anode material of an X-ray tube, as discussed in Section 4.5.

Moseley’s explanation of the characteristic X-rays was very simple: In an X-ray tube, the anode is struck by high-energy electrons, which can eject one or more of the electrons in the anode. If an electron in the $n = 1$ orbit is ejected, this will create a vacancy in the $n = 1$ level, into which an outer atomic electron can now fall.1 If, for example, an $n = 2$ electron falls into this $n = 1$ vacancy, a photon will be emitted with energy given by (5.33) as

$$E_\gamma = E_2 - E_1 = Z^2E_R \left(1 - \frac{1}{4}\right) = \frac{3}{4}Z^2E_R$$  \hspace{1cm} (5.34)

Transitions between $n = 2$ and $n = 1$ are traditionally identified as the $K_a$ transitions. Using this terminology, we can say that the Bohr theory predicts the $K_a$ photons emitted or absorbed by an atom should have energy $E_\gamma = 3Z^2E_R/4$. If one observes several different elements and measures the
frequencies of their $K_a$ X-rays (or any other definite X-ray line), then the photon energies, and hence frequencies, should vary like the square of the atomic number $Z$; that is, we should find $f \propto Z^2$, or equivalently

$$\sqrt{f} \propto Z \quad (5.35)$$

Moseley measured the $K_a$ lines of some 20 elements. By plotting $\sqrt{f}$ against the known values of $Z$ and showing that the data fitted a straight line (Fig. 5.7), he verified the prediction (5.35) and gave strong support to the Bohr theory. At that time (1913) the significance of the atomic number $Z$ as the number of positive charges on the nucleus was only just becoming apparent, and Moseley’s work settled this point conclusively. The atomic numbers of several elements were still in doubt, and Moseley’s data, plotted as in Fig. 5.7, allowed these numbers to be determined unambiguously. Moseley was also able to identify three atomic numbers for which the corresponding elements had not yet been found — for example, $Z = 43$, technetium, which does not occur naturally and was first produced artificially in 1937.

A close look at Fig. 5.7 shows that the data do not confirm the prediction (5.35) exactly. If $\sqrt{f} \propto Z$, the line in Fig. 5.7 should pass through the origin, which it does not quite do. The line shown (which is a least-squares best fit) meets the $Z$ axis close to $Z = 1$. That is, the data show that $\sqrt{f} \propto (Z - 1)$, or equivalently,

$$E_g \propto (Z - 1)^2 \quad (5.36)$$

This small discrepancy was explained (and, in fact, anticipated) by Moseley, as follows: The prediction that the X-ray frequencies of a given line should be proportional to $Z^2$ was based on the assumption that the inner electron feels only the force of the nuclear charge $Ze$ and is completely unaffected by any of the other electrons. This is a fair approximation, but certainly not perfect. An inner electron does experience some repulsion by the other electrons, and this slightly offsets, or screens, the attraction of the nucleus. This amounts to a small reduction in the nuclear charge, which we can represent by replacing $Ze$ with $(Z - \delta)e$, where $\delta$ is some (unknown) small number. In this case the energy levels of the inner electron, and hence the X-ray energies, should be proportional to $(Z - \delta)^2$ rather than $Z^2$; specifically, (5.34) should be replaced by

$$E_g = \frac{3}{4}(Z - \delta)^2E_R \quad (5.37)$$

According to (5.36), the observed data fit this prediction perfectly, with a screening factor $\delta$ close to $\delta = 1$.

As we have seen, the dependence of the characteristic X-ray frequencies on atomic number is very simple (namely, $f$ approximately proportional to $Z^2$). Also, because the transitions involve the inner electrons, the frequencies are independent of the external conditions of the atom (for example, whether it is bound to other atoms in a molecule or a solid). Further, Moseley found that with an impure anode he could easily detect the X-ray lines of the impurities. For all these reasons, he predicted that X-ray spectroscopy would “prove a powerful method of chemical analysis.” This prediction has proved correct. In modern X-ray spectroscopy, a sample (a biological tissue, for example) is put in a beam of electrons, protons, or X-rays. The beam ejects inner electrons of many of the atoms in the sample, which then emit X-rays. By measuring the wavelengths emitted, one can identify all elements in the sample, down to the “trace” level of one part per million, or even less.
Example 5.5

Most X-ray spectrometers have a thin window through which the X-rays must pass. Although high-energy X-rays pass easily through such windows, low-energy X-rays are severely attenuated and cannot be analyzed. A certain spectrometer, which is used for chemical analysis, cannot detect X-rays with $E_x \leq 2.4 \text{ keV}$. If an unambiguous identification requires that one observe the $K_a$ line of an element, what is the lightest element that can be identified using this spectrometer?

The energy of a $K_a$ photon emitted by an element $Z$ is given by (5.37) as $E_y = 3(Z - \delta)^2E_R/4$ (with $\delta = 1$). The lowest detectable element is found by equating this energy to 2.4 keV and solving for $Z$, to give

$$Z = \delta + \sqrt{\frac{4E_y}{3E_R}} = 1 + \sqrt{\frac{4 \times (2.4 \times 10^3 \text{ eV})}{3 \times (13.6 \text{ eV})}} = 16.3$$

We see from the table inside the back cover that the element with $Z = 17$ is chlorine and that with $Z = 16$ is sulfur. Therefore, our spectrometer can detect chlorine, but cannot detect sulfur.

5.10 Other Evidence for Atomic Energy Levels*

*This section can be omitted without loss of continuity.

Although atomic spectroscopy gives abundant evidence for the quantization of atomic energy levels, one might hope to find other types of evidence as well. And, in fact, almost any process that transfers energy to or from an atom provides us with such evidence.

Imagine, for example, we fire a stream of electrons, all with the same kinetic energy $K_0$, at a target of stationary atoms; and suppose, for simplicity, that all the atoms are in their ground state, with energy $E_1$. The possible collisions between any one electron and an atom can be divided into two classes, the elastic and the inelastic. An elastic collision is defined as one in which the atom’s internal state of motion is unaltered; this means that the total kinetic energy (of the incident electron plus the atom) does not change. Since the atom can recoil as a whole, it can gain some kinetic energy; but because the atom is so heavy compared to the electron, this recoil energy is very small (Problem 5.27). Therefore, for most purposes, an elastic collision can be characterized as one in which the scattered electron is deflected by the atom but suffers no appreciable loss of kinetic energy.

An inelastic collision is one in which the atom is excited to a different energy level and there is a corresponding reduction of the electron’s kinetic energy. Because the atomic energy levels are quantized, the same must be true of the energy lost by the electron. Specifically, the electron can lose kinetic energy only in amounts equal to $E_n - E_1$, where $E_n$ is an allowed energy of the atom. In particular, if the original kinetic energy $K_0$ is less than the first excitation energy, $E_2 - E_1$ of the atom, the electrons cannot excite the atoms at all and only elastic scattering is possible. Obviously, by studying electron scattering at various incident energies and by measuring how much energy the electrons lose, one should be able to demonstrate and measure the allowed energies of the atoms.
The Franck–Hertz Experiment

The first experiment along these lines was carried out by the German physicists James Franck and Gustav Hertz in 1914 and is duplicated in many undergraduate teaching laboratories today. In this experiment a stream of electrons is passed through a tube of mercury vapor, as shown schematically in Fig. 5.8(a). The electrons leave a heated cathode and are attracted toward the grid by an adjustable accelerating potential $V_0$. Those electrons that pass through the grid will reach the anode provided that they have enough energy to overcome the small retarding potential $\Delta V$. The current $i$ reaching the anode is measured, and the observed behavior of $i$ as a function of the accelerating potential $V_0$ is shown in Fig. 5.8(b). This behavior is easily explained in terms of the quantized energy levels of the mercury atom; in particular, the abrupt drop in the current each time the accelerating potential reaches a multiple of 4.9 V shows that the first excitation energy of mercury is 4.9 eV, as we now argue.

Even when the accelerating potential $V_0$ is zero, the heated cathode emits some electrons, but these collect in a cloud around the cathode, and the resulting field prevents the emission of any more electrons; so no steady current flows. When $V_0$ is slowly increased, some of the electrons in this cloud are drawn away, which allows more electrons to be emitted, and a current now flows. When an electron is accelerated by a potential difference $V_0$, it acquires an energy $V_0 e$. As long as this energy is less than the first excitation energy of the mercury atom, only elastic collisions are possible, and there is no way for the electrons to lose any energy to the vapor. (See Problem 5.27.) Thus, until $V_0 e$ reaches the first excitation energy, the anode current increases steadily as we increase $V_0$. Once $V_0 e$ reaches the excitation energy, some electrons can excite the mercury atoms and lose most of their energy as a result. When these electrons reach the grid, they have insufficient energy to overcome the retarding potential $\Delta V$ and cannot reach the anode. Thus when $V_0 e$ reaches the first excitation energy, we expect a drop in the current $i$. The fact that the drop is observed when $V_0 = 4.9$ eV shows that the first excitation energy of mercury is 4.9 eV.

When $V_0$ increases beyond 4.9 V, the current increases again. But when $V_0 e$ reaches twice the excitation energy, some electrons can undergo two inelastic collisions between the cathode and grid, and the current drops again. This process continues, and it is possible under favorable conditions to observe 10 or more drops in the current, regularly spaced at intervals of 4.9 V. *

*One can sometimes observe drops in $i$ at voltages corresponding to the excitation of higher levels as well. However, the experiment is usually arranged in such a way that the probability for exciting the first excited state is very large and, hence, that very few electrons acquire enough energy to excite any higher levels.
This interpretation of the Franck–Hertz experiment can be confirmed by examining the optical spectrum of mercury. If 4.9 eV is the first excitation energy, the mercury atom should be able to emit and absorb photons of energy 4.9 eV. That is, the spectrum of mercury should include a line whose wavelength is

$$\lambda = \frac{hc}{E_g} = \frac{1240 \text{ eV} \cdot \text{nm}}{4.9 \text{ eV}} = 250 \text{ nm}$$

and this is, indeed, the wavelength of a prominent line in the spectrum of mercury. Better still, one finds that the mercury vapor in the Franck–Hertz experiment begins emitting this line just as soon as $V_0$ passes 4.9 V and excitation of the first excited state becomes possible.

**Energy-Loss Spectra**

Today, energy levels of atoms (and, even more, nuclei) are routinely measured by finding the energy lost by inelastically scattered particles. Figure 5.9(a) is a schematic diagram of an arrangement for measuring the energy levels of the helium atom using inelastically scattered electrons. A beam of electrons, all with the same incident kinetic energy, is fired through a container of helium gas. Those electrons scattered at some convenient angle are sent through a magnetic field, which bends them into circular paths whose radii depend on their energies. [See Equation (2.48).] Therefore, a photographic film placed as shown lets one determine how many electrons are scattered at each different energy.

Figure 5.9(b) is a schematic plot of the number of scattered electrons as a function of their energy lost in the collision. This kind of plot is called an “energy-loss spectrum” — a natural generalization of the word “spectrum,” which in the context of light, this refers to numbers of photons as a function of their energy. The large peak on the left, which occurs at zero energy loss, corresponds to the many electrons that scatter elastically and hence lose no energy. The next peak occurs at an energy loss of 19.8 eV, indicating that the first excited state of helium is 19.8 eV above the ground state. The subsequent peaks indicate further excited states at 20.6 eV, 21.2 eV, and so on. All of the energies shown in Fig. 5.9 agree with the energy levels deduced from the optical spectrum, within the accuracy of the measurements.

Experiments like the Franck–Hertz experiment and the energy-loss measurements just described add confirmation (if any is needed) to Bohr’s hypothesis that atomic energy levels are quantized. In particular, they demonstrate clearly that the quantized energies of atomic spectra are more than just a property of the light emitted and absorbed by atoms; rather, as suggested by Bohr, they reflect the quantization of the atomic energy levels themselves.
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### PROBLEMS FOR CHAPTER 5

#### SECTION 5.3 (The Balmer–Rydberg Formula)

5.1 • Find the wavelength of the light emitted by hydrogen, as predicted by the Rydberg formula (5.4) with \( n = 4 \) and \( n' = 3 \). What is the nature of this radiation? (Visible? X-ray? etc.)

5.2 • Find the wavelength of the light emitted by hydrogen as predicted by the Rydberg formula (5.4) with \( n = 4 \) and \( n' = 1 \). What is the nature of this radiation? (Visible? X-ray? etc.)

5.3 • Use Equation (5.5) to calculate the upper limit of the energies of photons that can be emitted by a hydrogen atom (in eV). (This energy is called the Rydberg energy, as discussed in Section 5.6.) What is the lower limit?

5.4 • Starting from the SI values of \( k, e, h, \) and \( c \), find the values of \( ke^2 \) and \( hc \) in eV \( \cdot \) nm. Prove, in particular, that \( ke^2 = 1.44 \text{ eV} \cdot \text{nm} \)

5.5 ** Using the Rydberg formula (5.4), classify all of the spectral lines of atomic hydrogen as UV, visible, or IR.

5.6 ** The spectral lines of atomic hydrogen are given by the Rydberg formula (5.4). Those lines for which \( n' = 1 \) are called the Lyman series. Since \( n \) can be any integer greater than 1, there are (in principle, at least) infinitely many lines in the Lyman series. (a) Calculate the five longest wavelengths of the Lyman series. Mark the positions of these five lines along a linear scale of wavelength. (b) Prove that the successive lines in the Lyman series get closer and closer together, approaching a definite limit (the series limit) as \( n \to \infty \). Show this limit on your plot. What kind of radiation is the Lyman series? (Visible? X-ray? etc.)

#### SECTION 5.6 (The Bohr Model of the Hydrogen Atom)

5.7 • (a) Find the value of the Bohr radius \( a_B = h^2/(ke^2m) \) (where \( m \) is the electron’s mass) by substituting the SI values of the constants concerned. (b) It is usually easier to do such calculations by using common combinations of constants, which can be memorized in convenient units \( (ke^2 = 1.44 \text{ eV} \cdot \text{nm}, \) for example). Find the value of the convenient combination \( hc \) in eV \( \cdot \) nm from your knowledge of \( hc \). [The value of \( hc \) was given in equation 4.8. Both \( hc \) and \( hc^2 \) are worth remembering in eV \( \cdot \) nm.] Now calculate \( a_B \) by writing it as \( (hc)^2/(ke^2mc^2) \) and using known values of \( hc, ke^2, \) and \( mc^2 \).

5.8 • Two equivalent definitions of the Rydberg energy \( E_R \) are

\[
E_R = \frac{ke^2}{2a_B} = \frac{m(ke^2)^2}{2\hbar^2}
\]

(a) Using the definition (5.18) of \( a_B \), verify that these two definitions are equivalent. (b) Find the value of \( E_R \) from each of these expressions. (In the first case use \( ke^2 = 1.44 \text{ eV} \cdot \text{nm} \) and the known value of \( a_B \); in the second, multiply top and bottom by \( c^2 \), and then use the known values of \( mc^2, ke^2, \) and \( hc \).)
5.9 Consider a charge \( q_1 \) with mass \( m \) in a circular orbit around a fixed charge \( q_2 \), with \( q_1 \) and \( q_2 \) of opposite sign. Show that the kinetic energy \( K \) is \(-1/2\) times the potential energy \( U \) and hence that \( E = K + U = U/2 \).

Your arguments can parallel those leading to (5.10). The point is for you to make sure you understand those arguments and to check that the conclusion is true for any two charges of opposite sign.

5.10 (a) Derive an expression for the electron’s speed in the \( n \)th Bohr orbit. (b) Prove that the orbit with highest speed is the \( n = 1 \) orbit, with \( v_1 = ke^2/h \).

Compare this with the speed of light, and comment on the validity of ignoring relativity (as we did) in discussing the hydrogen atom. (c) The ratio \( \alpha = \frac{v_1}{c} = \frac{ke^2}{hc} \) (5.38)
is called the “fine-structure constant” (for reasons that are discussed in Problems 9.22 and 9.23) and is generally quoted as \( \alpha \approx 1/137 \). Verify this value.

SECTION 5.7 (Properties of the Bohr Atom)

5.11 Find the range of wavelengths in the Balmer series of hydrogen. Does the Balmer series lie completely in the visible region of the spectrum? If not, what other regions does it include?

5.12 Find the range of wavelengths in each of the Lyman, Balmer, and Paschen series of hydrogen. Show that the lines in the Lyman series are all in the UV region, those of the Paschen are all in the IR region, while the Balmer series is in the visible and UV regions. (Note that visible light ranges from violet at about 400 nm to deep red at about 700 nm.) Show that these three series do not overlap one another but that the next series, in which the lower level is \( n = 4 \), overlaps the Paschen series.

5.13 The negative muon is a subatomic particle with the same charge as the electron but a mass that is about 207 times greater: \( m_\mu \approx 207 m_e \). A muon can be captured by a proton to form a “muonic hydrogen atom,” with energy and radius given by the Bohr model, except that \( m_e \) must be replaced by \( m_\mu \).

(a) What are the radius and energy of the first Bohr orbit in a muonic hydrogen atom? (b) What is the wavelength of the Lyman \( \alpha \) line in muonic hydrogen? What sort of electromagnetic radiation is this? (Visible? IR? etc.) Treat the proton as fixed (although this is not such a good approximation here — see Problem 5.17).

5.14 The average distance \( D \) between the atoms or molecules in a gas is of order \( D \approx 3 \) nm at atmospheric pressure and room temperature. This distance is much larger than typical atomic sizes, and it is, therefore, reasonable to treat an atom as an isolated system, as we did in our discussion of hydrogen. However, the Bohr theory predicts that the radius of the \( n \)th orbit is \( n^2 a_B \). Thus for sufficiently large \( n \), the atoms would be larger than the spaces between them and our simple theory would surely not apply. Therefore, one would not expect to observe energy levels for which the atomic diameter \( 2n^2 a_B \) is of order \( D \) or more. (a) At normal densities (with \( D \approx 3 \) nm) what is the largest \( n \) that you would expect to observe? (b) If one reduced the pressure to 1/1000 of atmospheric, what would be the largest \( n \)? (Remember that the spacing \( D \) is proportional to (pressure)\(^{-1/2} \) for constant temperature.) (c) Modern experiments have found hydrogen atoms in levels with \( n \approx 100 \). What must be the pressure in these experiments?

SECTION 5.8 (Hydrogen-Like Ions)

5.15 (a) What are the energy and wavelength of photons in the Lyman \( \alpha \) line of \( \text{Fe}^{25+} \) (an iron nucleus with all but one of its 26 electrons removed)? What kind of electromagnetic radiation is this? (Visible? UV? etc.)

(b) What is the radius of the \( n = 1 \) orbit in the \( O^{7+} \) ion? What are the wavelength and energy of photons in the Lyman \( \alpha \) line of \( O^{7+} \)?

5.16 In most of this chapter we treated the atomic nucleus as fixed. This approximation (often a very good one) can be avoided by using the reduced mass, as described in connection with Equations (5.31) and (5.32). (a) What percent error do we make in the energy levels of ordinary hydrogen when we treat the proton as fixed? (b) Answer the same question for muonic hydrogen, which is a negative muon bound to a proton. (See Problem 5.13.)

5.17 (a) In most of this chapter we treated the atomic nucleus as fixed. This approximation (often a very good one) can be avoided by using the reduced mass, as described in connection with Equations (5.31) and (5.32). (a) What percent error do we make in the energy levels of ordinary hydrogen when we treat the proton as fixed? (b) Answer the same question for muonic hydrogen, which is a negative muon bound to a proton. (See Problem 5.13.)

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5.18 What is the ground-state energy of positronium, the bound state of an electron and a positron?

[HINT: Here you must allow for the motion of the “nucleus” (that is, the positron) by using the reduced mass, as described in connection with Equations (5.31) and (5.32).]

5.19 When the spectrum of once-ionized helium, \( \text{He}^+ \), was first observed, it was interpreted as a newly discovered part of the hydrogen spectrum. The following two questions illustrate this confusion: (a) Show that alternate lines in the Balmer series of \( \text{He}^+ \) — that is, those lines given by the Rydberg formula (5.30) with the lower level \( n' = 2 \) — coincide with the lines of the Lyman series of hydrogen. (b) Show that all lines of \( \text{He}^+ \) could be interpreted (incorrectly) as belonging to hydrogen if one supposed that the numbers \( n \) and \( n' \) in the Rydberg formula for hydrogen could be half-integers as well as integers.

5.20 The negative pion, \( \pi^- \), is a subatomic particle with the same charge as the electron but mass \( m_\pi = 273 m_e \). A \( \pi^- \) can be captured into Bohr orbits around an atomic nucleus, with radius given by the Bohr formula (5.27), except that \( m_e \) must be replaced by \( m_\pi \).

(a) What is the orbital radius for a \( \pi^- \) captured in the \( n = 1 \) orbit by a carbon nucleus? (b) Given that the carbon nucleus has radius \( R \approx 3 \times 10^{-15} \) m, can this orbit be formed? (c) Repeat parts (a) and (b) for a lead nucleus (nuclear radius \( \approx 7 \times 10^{-15} \) m). (The required atomic numbers can be found in Appendix C.)

5.21 In Section 5.6 we treated the H atom as if the electron moves around a fixed proton. In reality, both the electron and proton orbit around their center of
mass as shown in Fig. 5.10. Using this figure, you can repeat the analysis of Section 5.6, including the small effects of the proton’s motion, as follows:

\[
\text{FIGURE 5.10} \\
(\text{Problem 5.21})
\]

(a) Write down the distances \( r_e \) and \( r_p \) in terms of \( r, m_e, \) and \( m_p \).

(b) Because both \( e \) and \( p \) move, it is easiest to work with the angular velocity \( \omega \), in terms of which \( v_e \) and \( v_p \) are as given in Fig. 5.10. Write down the total kinetic energy \( K = K_e + K_p \) and prove that

\[
K = \frac{1}{2} \mu r^2 \omega^2, \quad (5.39)
\]

where \( \mu \) is the reduced mass,

\[
\mu = \frac{m_mm_e}{m_p + m_e} = \frac{m_e}{1 + (m_e/m_p)} \approx 0.9995 m_e. \quad (5.40)
\]

Notice that the expression (5.39) for \( K \) differs from its fixed proton counterpart, \( K = (1/2)m_r r^2 \omega^2 \), only in the replacement of \( m_e \) by \( \mu \).

(c) Show that Newton’s law, \( F = ma \), applied to either the electron or proton gives

\[
\frac{k e^2}{r^2} = \mu \omega^2 r. \quad (5.41)
\]

(Again, this differs from the fixed proton equivalent only in that \( \mu \) has replaced \( m_e \).)

(d) Use (5.39) and (5.41) to show that \( K = -U/2 \) and \( E = U/2 \).

(e) Show that the total angular momentum is

\[
L = L_e + L_p = \mu r^2 \omega \quad (5.42)
\]

(in place of \( L = m_r r^2 \omega \) if the proton is fixed).

(f) Assuming that the allowed values of \( L \) are \( L = nh \), where \( n = 1, 2, 3, \ldots \), use (5.41) and (5.42) to find the allowed radii \( r \), and prove that the allowed energies are given by the usual formula \( E = -\frac{\mu}{\hbar^2} \), except that

\[
E_R = \frac{\mu (k e^2)^2}{2\hbar^2}. \quad (5.43)
\]

This is the result quoted without proof in (5.31) and (5.32).

(g) Calculate the energy of the ground state of hydrogen using (5.43), and compare with the result of using the fixed-proton result \( E_p = (\mu (k e^2)^2)/(2\hbar^2) \). (Give five significant figures in both answers.) The difference in your answers is small enough that we are usually justified in ignoring the proton’s motion. Nevertheless, the difference can be detected, and the result (5.43) is found to be correct.

**SECTION 5.9 (X-ray Spectra)**

5.22 * Use Equation (5.37) to predict the slope of a graph of \( \sqrt{n} \) against \( Z \) for the \( K \) frequencies. Do the data in Fig. 5.7 bear out your prediction?

5.23 * The \( K \) line from a certain element is found to have wavelength 0.475 nm. Use Equation (5.37), with \( \delta \approx 1 \), to determine what the element is.

5.24 * The \( K \) series of X-rays consists of photons emitted when an electron drops from the \( n \)th Bohr orbit to the first \((n \to 1)\). (a) Use (5.33) to derive an expression for the wavelengths of the \( K \) series. [This will be approximate, since (5.33) ignores effects of screening.] (b) Find the wavelengths of the \( K_a, K_b, \) and \( K_c \), lines \((n = 2, 3, 4)\) of uranium. (For the atomic numbers of uranium and other elements, see the periodic table inside the back cover or the alphabetical lists in Appendix C.)

5.25 * What is the approximate radius of the \( n = 1 \) orbit of the innermost electron in the lead atom? Compare with the radius of the lead nucleus, \( R \approx 7 \times 10^{-15} \text{ m} \).

5.26 ** Suppose that a negative muon (see Problem 5.13) penetrates the electrons of a silver atom and is captured in the first Bohr orbit around the nucleus. (a) What is the radius \((\text{in fm})\) of the muon’s orbit? Is it a good approximation to ignore the atomic electrons when considering the muon? (The muon’s orbital radius is very close to the nuclear radius. For this reason, the details of the muon’s orbit are sensitive to the charge distribution of the nucleus, and the study of muonic atoms is a useful probe of nuclear properties.) (b) What are the energy and wavelength of a photon emitted when a muon drops from the \( n = 2 \) to the \( n = 1 \) orbit?

**SECTION 5.10 (Other Evidence for Atomic Energy Levels)**

5.27 *** When an electron with initial kinetic energy \( K_0 \) scatters elastically from a stationary atom, there is no loss of total kinetic energy. Nevertheless, the electron loses a little kinetic energy to the recoil of the atom.

(a) Use conservation of momentum and kinetic energy to prove that the maximum kinetic energy of the recoiling atom is approximately \((4m/M)K_0\), where \( m \) and \( M \) are the masses of the electron and atom.

[HINT: The maximum recoil energy is in a head-on collision. Remember that \( m \ll M \), and use nonrelativistic mechanics.]

(b) If a 3-eV electron collides elastically with a mercury atom, what is its maximum possible loss of kinetic energy? (Your answer should convince you that it is a good approximation to say that the electrons in the Franck–Hertz experiment lose no kinetic energy in elastic collisions with atoms.)