Example 4.7

Atomic hydrogen in its lowest energy state absorbs a photon, raising the electron to an $n = 3$ state. If we assume the lifetime of the excited state is 10^{-10} s, and if we make the rudimentary assumption that the electron orbits around the proton, how many revolutions does the electron make in the excited state before returning to a lower energy state?

Strategy We know both the electron's speed v_3 and the radius r_3 of the orbit. From these we can find the time T it takes the electron to go one orbit. To find the number of rotations, we divide the lifetime by the time T.

Solution The velocity of the electron will be

$$v = \frac{\text{circumference}}{\text{period}} = \frac{2\pi r}{T}$$

Therefore

$$T = \frac{2\pi r_3}{v_3} = \frac{(2\pi)(9a_0)(3)(4\pi\epsilon_0\hbar)}{e^2}$$

$$T = \frac{(54\pi)(0.53 \times 10^{-10}\ \text{m})(1.055 \times 10^{-34}\ \text{J}\cdot\text{s})}{(1.6 \times 10^{-19}\ \text{C})^2\left(9 \times 10^9\ \dfrac{\text{N}\cdot\text{m}^2}{\text{C}^2}\right)}$$

$$= 4.1 \times 10^{-15}\ \text{s}$$

$$\text{Number of revolutions} = \frac{10^{-10}\ \text{s}}{4.1 \times 10^{-15}\ \text{s}} = 2.4 \times 10^4$$

The electron revolves many times in the excited state before decaying to a lower energy state.

The Correspondence Principle

Early in the 1900s physicists had trouble reconciling well-known and well-understood classical physics results with the new quantum ones. Sometimes completely different results were valid in their own domains. For example, there were two radiation laws: one used classical electrodynamics to determine the properties of radiation from an accelerated charge, but another explanation was expressed in Bohr's atomic model. Physicists proposed various kinds of correspondence principles to relate the new modern results with the old classical ones that had worked so well in their own domain. In his 1913 paper Bohr proposed perhaps the best *correspondence principle* to guide physicists in developing new theories. This principle was refined several times over the next few years.

Bohr's correspondence principle

Bohr's correspondence principle: In the limits where classical and quantum theories should agree, the quantum theory must reduce to the classical result.

To illustrate this principle, let us examine the predictions of the two radiation laws. The frequency of the radiation produced by the atomic electrons in the Bohr model of the hydrogen atom should agree with that predicted by classical electrodynamics in a region where the finite size of Planck's constant is unimportant—for large quantum numbers n where quantization effects are minimized. To see how this works we recall that classically the frequency of the radiation emitted is equal to the orbital frequency f_{orb} of the electron around the nucleus:

$$f_{classical} = f_{orb} = \frac{\omega}{2\pi} = \frac{1}{2\pi}\frac{v}{r} \tag{4.33a}$$

where for circular motion the angular velocity is $\omega = v/r$. If we substitute for v from Equation (4.19), we find

$$f_{classical} = \frac{1}{2\pi}\left(\frac{e^2}{4\pi\epsilon_0 m r^3}\right)^{1/2} \tag{4.33b}$$

We make the connection to the Bohr model by inserting the orbital radius r from Equation (4.24) into Equation (4.33b). We then know the classical frequency in terms of fundamental constants and the principal quantum number n.

$$f_{\text{classical}} = \frac{me^4}{4\epsilon_0^2\hbar^3}\frac{1}{n^3} \tag{4.34}$$

In the Bohr model, the nearest we can come to continuous radiation is a cascade of transitions from a level with principal quantum number $n + 1$ to the next lowest and so on:

$$n + 1 \rightarrow n \rightarrow n - 1 \rightarrow \cdots$$

The frequency of the transition from $n + 1 \rightarrow n$ is

$$f_{\text{Bohr}} = \frac{E_0}{h}\left[\frac{1}{n^2} - \frac{1}{(n+1)^2}\right]$$
$$= \frac{E_0}{h}\left[\frac{n^2 + 2n + 1 - n^2}{n^2(n+1)^2}\right] = \frac{E_0}{h}\left[\frac{2n+1}{n^2(n+1)^2}\right]$$

which for large n becomes

$$f_{\text{Bohr}} \approx \frac{2nE_0}{hn^4} = \frac{2E_0}{hn^3}$$

If we substitute E_0 from Equation (4.26), the result is

$$f_{\text{Bohr}} = \frac{me^4}{4\epsilon_0^2\hbar^3}\frac{1}{n^3} = f_{\text{classical}} \tag{4.35}$$

Equivalence of Bohr and classical frequencies

so the frequencies of the radiated energy agree between classical theory and the Bohr model for large values of the quantum number n. Bohr's correspondence principle is verified for large orbits, where classical and quantum physics should agree.

By 1915, as Bohr's model gained widespread acceptance, the critics of the quantum concept were finding it harder to gain an audience. Bohr had demonstrated the necessity of Planck's quantum constant in understanding atomic structure, and Einstein's conception of the photoelectric effect was generally accepted as well. The *assumption* of quantized angular momentum $L_n = n\hbar$ led to the quantization of other quantities r, v, and E. We collect the following three equations here for easy reference.

Orbital radius $$r_n = \frac{4\pi\epsilon_0\hbar^2}{me^2}n^2 \tag{4.24}$$

Velocity $$v_n = \frac{n\hbar}{mr_n} \tag{4.22b}$$

Energy $$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \tag{4.25}$$

4.5 Successes and Failures of the Bohr Model

As we briefly mentioned in the previous section, the Bohr atomic model was a first step in understanding the structure of the atom. We will discuss the correct description of the hydrogen atom in Chapter 7 after we introduce quantum theory in Chapter 6. Wavelength measurements for the atomic spectrum of hydrogen are precise and exhibit a small disagreement with the Bohr model results just presented. These disagreements can be corrected by looking more carefully at our original assumptions, one of which was to assume an infinite nuclear mass.

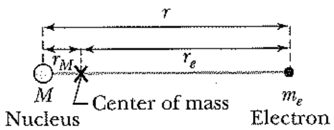

Figure 4.17 Because the nucleus does not actually have an infinite mass, the electron and nucleus rotate about a common center of mass that is located very near the nucleus.

Reduced Mass Correction

The electron and hydrogen nucleus actually revolve about their mutual center of mass as shown in Figure 4.17. This is a two-body problem, and our previous analysis should be in terms of r_e and r_M instead of just r. A straightforward analysis derived from classical mechanics shows that this two-body problem can be reduced to an equivalent one-body problem in which the motion of a particle of mass μ_e moves in a central force field around the center of mass. The only change required in the results of Section 4.4 is to replace the electron mass m_e by its **reduced mass** μ_e where

Reduced mass

$$\mu_e = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + \dfrac{m_e}{M}} \tag{4.36}$$

and M is the mass of the nucleus (see Problem 53). In the case of the hydrogen atom, M is the proton mass, and the correction for the hydrogen atom is $\mu_e = 0.999456\ m_e$. This difference can be measured experimentally. The Rydberg constant for infinite nuclear mass, R_∞, defined in Equation (4.29), should be replaced by R, where

$$R = \frac{\mu_e}{m_e} R_\infty = \frac{1}{1 + \dfrac{m_e}{M}} R_\infty = \frac{\mu_e e^4}{4\pi c \hbar^3 (4\pi\epsilon_0)^2} \tag{4.37}$$

The Rydberg constant for hydrogen is $R_H = 1.096776 \times 10^7\ m^{-1}$.

Example 4.8

Calculate the wavelength for the $n_u = 3 \rightarrow n_\ell = 2$ transition (called the H_α *line*) for the atoms of hydrogen, deuterium, and tritium.

Strategy We use Equation (4.30) but with R_∞ replaced by the Rydberg constant expressed in Equation (4.37). In order to use Equation (4.37) we will need the masses for hydrogen, deuterium, and tritium.

Solution The following masses are obtained by subtracting the electron mass from the atomic masses given in Appendix 8.

Proton = 1.007276 u

Deuteron = 2.013553 u

Triton (tritium nucleus) = 3.015500 u

The electron mass is $m_e = 0.0005485799$ u. The Rydberg constants are

$$R_H = \frac{1}{1 + \dfrac{0.0005486}{1.00728}} R_\infty = 0.99946 R_\infty \qquad \text{Hydrogen}$$

$$R_D = \frac{1}{1 + \dfrac{0.0005486}{2.01355}} R_\infty = 0.99973 R_\infty \qquad \text{Deuterium}$$

$$R_T = \frac{1}{1 + \dfrac{0.0005486}{3.01550}} R_\infty = 0.99982 R_\infty \qquad \text{Tritium}$$

The calculated wavelength for the H_α line is

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 0.13889R$$

$$\lambda(H_\alpha, \text{hydrogen}) = 656.47 \text{ nm}$$

$$\lambda(H_\alpha, \text{deuterium}) = 656.29 \text{ nm}$$

$$\lambda(H_\alpha, \text{tritium}) = 656.23 \text{ nm}$$

Deuterium was discovered when two closely spaced spectral lines of hydrogen near 656.4 nm were observed in 1932. These proved to be the H_α lines of atomic hydrogen and deuterium.

The Bohr model may be applied to any single-electron atom (hydrogen-like) even if the nuclear charge is greater than 1 proton charge ($+e$), for example He^+ and Li^{++}. The only change needed is in the calculation of the Coulomb force, where e^2 is replaced by Ze^2 to account for the nuclear charge of $+Ze$. Bohr applied his model to the case of singly ionized helium, He^+. The Rydberg Equation (4.30) now becomes

$$\frac{1}{\lambda} = Z^2R\left(\frac{1}{{n_\ell}^2} - \frac{1}{{n_u}^2}\right) \tag{4.38}$$

where the Rydberg constant is given by Equation (4.37). We emphasize that Equation (4.38) is valid only for single-electron atoms (H, He^+, Li^{++}, and so on) and does not apply to any other atoms (for example He, Li, Li^+). Charged atoms, such as He^+, Li^+, and Li^{++}, are called *ions*.

In his original paper of 1913, Bohr predicted the spectral lines of He^+ although they had not yet been identified in the lab. He showed that certain lines (generally ascribed to hydrogen) that had been observed by Pickering in stellar spectra, and by Fowler in vacuum tubes containing both hydrogen and helium, could be identified as singly ionized helium. Bohr showed that the wavelengths predicted for He^+ with $n_\ell = 4$ are almost identical to those of H for $n_\ell = 2$, except that He^+ has *additional lines* between those of H (see Problem 35). The correct explanation of this fact by Bohr gave credibility to his model.

Example 4.9

Calculate the shortest wavelength that can be emitted by the Li^{++} ion.

Strategy The shortest wavelength occurs when the electron changes from the highest state (unbound, $n_u = \infty$) to the lowest state ($n_\ell = 1$). We use Equation (4.38) to calculate the wavelength.

Solution Equation (4.38) gives

$$\frac{1}{\lambda} = (3)^2R\left(\frac{1}{1^2} - \frac{1}{\infty}\right) = 9R$$

$$\lambda = \frac{1}{9R} = 10.1 \text{ nm}$$

When we let $n_u = \infty$, we have what is known as the *series limit*, which is the shortest wavelength possibly emitted for each of the named series.

Other Limitations

As the level of precision increased in optical spectrographs, it was observed that each of the lines, originally believed to be single, actually could be resolved into two or more lines. Arnold Sommerfeld adapted the special theory of relativity (assuming some of the electron orbits were elliptical) to Bohr's hypotheses and was able to account for some of the "splitting" of spectral lines. Subsequently it has been found that other factors (especially the electron's *spin*, or *intrinsic angular momentum*) also affect the fine structure of spectral lines.

It was soon observed that external magnetic fields (the Zeeman effect) and external electric fields (the Stark effect) applied to the radiating atoms affected the spectral lines, splitting and broadening them. Although classical electromagnetic theory could quantitatively explain the (normal) Zeeman effect (see Chapter 7), it was unable to account for the Stark effect; for this the quantum model of Bohr and Sommerfeld was necessary.

Although the Bohr model was a great step forward in the application of the new quantum theory to understanding the tiny atom, it soon became apparent that the model had its limitations:

Limitations of Bohr model

1. It could be successfully applied only to single-electron atoms (H, He^+, Li^{++}, and so on).
2. It was not able to account for the intensities or the fine structure of the spectral lines.
3. Bohr's model could not explain the binding of atoms into molecules.

We discuss in Chapter 7 the full quantum mechanical theory of the hydrogen atom, which accounts for all of these phenomena. The Bohr model was an ad hoc theory to explain the hydrogen spectral lines. Although it was useful in the beginnings of quantum physics, we now know that the Bohr model does not correctly describe atoms. Despite its flaws, Bohr's model should not be denigrated. It was the first step from a purely classical description of the atom to the correct quantum explanation. As usually happens in such tremendous changes of understanding, Bohr's model simply did not go far enough—he retained too many classical concepts. Einstein, many years later, noted* that Bohr's achievement "appeared to me like a miracle and appears as a miracle even today."

4.6 Characteristic X-Ray Spectra and Atomic Number

By 1913 when Bohr's model was published, little progress had been made in understanding the structure of many-electron atoms. It was believed that the general characteristics of the Bohr-Rutherford atom would prevail. We discussed the production of x rays from the bombardment of various materials by electrons in Section 3.7. It was known that an x-ray tube with an anode made from a given element produced a continuous spectrum of bremsstrahlung x rays upon which are superimposed several peaks whose frequencies are characteristic of that element (see Figure 3.19).

Characteristic x-ray wavelengths

We can now understand these **characteristic x-ray wavelengths** by adopting Bohr's *electron shell* hypothesis. Bohr's model suggests that an electron shell based on the radius r_n can be associated with each of the principal quantum numbers n. Electrons with lower values of n are more tightly bound to the nucleus than those with higher values. The radii of the electron orbits increase in proportion to n^2 [Equation (4.24)]. A specific energy is associated with each value of n. We may assume that when we add electrons to a fully ionized many-electron atom, the inner

*P. A. Schillp, ed., *Albert Einstein, Philosopher-Scientist*, La Salle, IL: The Open Court, 1949.