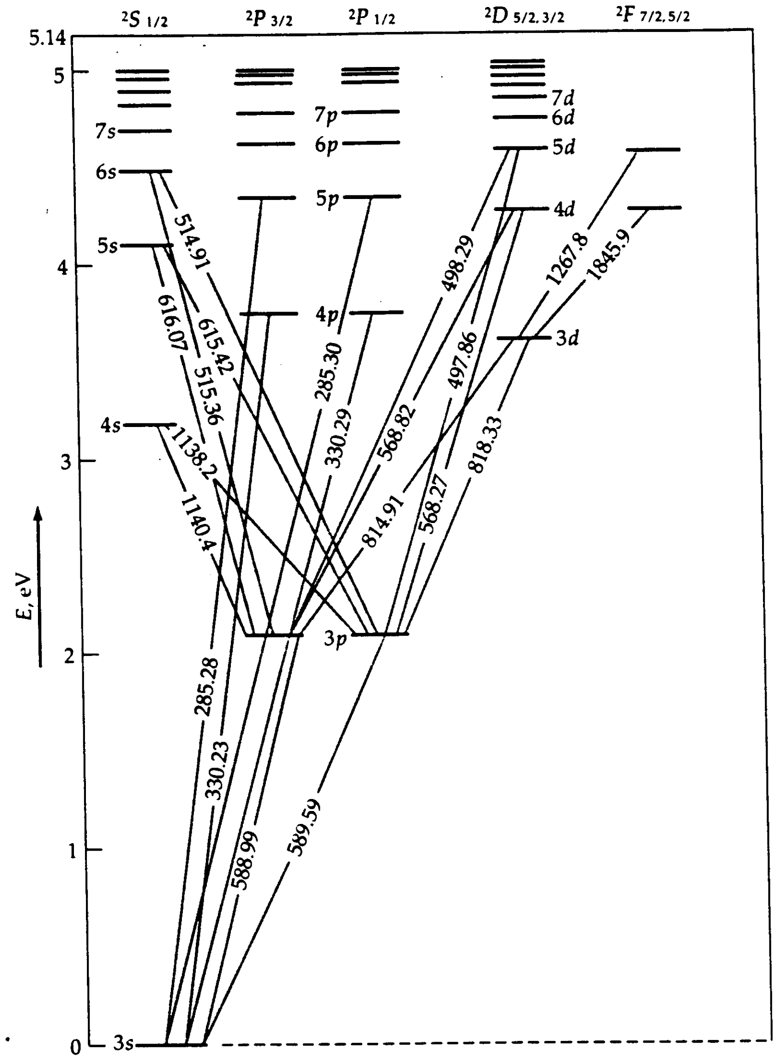

Figure 37-18 Energy-level diagram for sodium. The diagonal lines show observed optical transitions, with wavelengths given in nanometers. The energy of the ground state has been chosen as the zero point for the scale on the left.

states. One of these is ruled out by a selection rule on j, which is

$$\Delta j = \pm 1 \text{ or } 0 \qquad \text{allowed}$$

but

$$j = 0 \rightarrow j = 0 \qquad \text{forbidden}$$

Transitions between doublet states therefore result in triplet spectral lines. The energy levels and optical spectra of the other alkali metals are similar to those for sodium.

The optical spectra for elements that have two outer electrons, such as helium, beryllium, and magnesium, are considerably more complex because of the interaction between the two outer electrons.

X-Ray Spectra

The energy needed to excite an inner, core electron, for example, an electron in the $n = 1$ state (K shell), is much greater than that needed to excite an outer, valence electron. An inner electron cannot be excited to any of the filled states, such as the $n = 2$ states in sodium, because of the Pauli exclusion principle. Therefore, the energy required to excite an inner electron to an unoccupied state is typically of the order of several thousand electron volts (keV). An inner electron can be excited by bombarding the atom with a high-energy electron beam in, for example, an x-ray tube. If an electron is knocked out of the $n = 1$ (K) shell, there is a vacancy left in this shell. This vacancy can be filled by an electron from the L shell or a higher shell that makes a transition to the K shell. The photons emitted by electrons making such transitions have energies of the order of 1 keV. They constitute the **characteristic x-ray spectrum** of an element, appearing as sharp peaks in the continuous x-ray spectrum of the element, as shown for molybdenum in Figure 37-19. Spectral lines arising from transitions that end at the $n = 1$ (K) shell make up the K series of the characteristic x-ray spectrum of an element. For instance, the K_α line in the figure arises from transitions from the $n = 2$ (L) shell to the $n = 1$ (K) shell, and the K_β line arises from transitions from the $n = 3$ shell to the $n = 1$ shell. A second series, the L series, is produced by transitions from higher energy states to a vacated place in the $n = 2$ (L) shell.

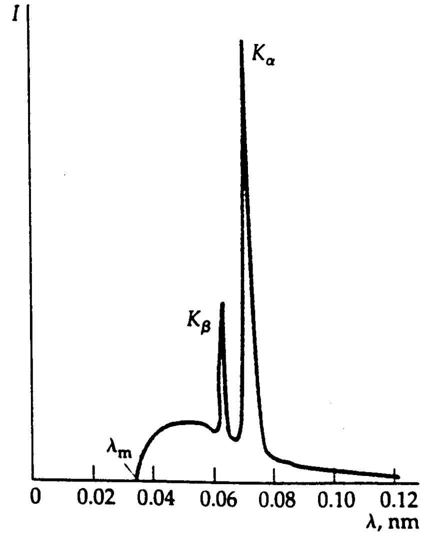

Figure 37-19 X-ray spectrum of molybdenum. The sharp peaks labeled K_α and K_β are characteristic of the element. The cutoff wavelength λ_m is independent of the target element and is related to the voltage V of the x-ray tube by $\lambda_m = hc/eV$.

We can use the Bohr theory to calculate the approximate frequencies of characteristic x-ray spectra. According to the Bohr model, the energy of a single electron in a state n is given by Equation 37-9:

$$E_n = -Z^2 \frac{13.6 \text{ eV}}{n^2}$$

Since for any atom other than hydrogen there are two electrons in the innermost shell, the K shell, the effective charge seen by one of the electrons is less than Ze because of the shielding due to the other electron. If the effective charge is $(Z - 1)e$, the energy of an electron in the K shell is given by this equation when $n = 1$ and Z is replaced by $Z - 1$:

$$E_1 = -(Z - 1)^2(13.6 \text{ eV})$$

The energy of an electron in state n (provided that the effective charge is the same) is given by

$$E_n = -(Z - 1)^2 \frac{13.6 \text{ eV}}{n^2} \qquad 37\text{-}30$$

When an electron from state n drops into the vacated state in the $n = 1$ shell, a photon of energy $E_n - E_1$ is emitted. The wavelength of this photon is

$$\lambda = \frac{hc}{E_n - E_1} = \frac{hc}{(Z - 1)^2(13.6 \text{ eV})(1 - 1/n^2)} \qquad 37\text{-}31$$

In 1913, the English physicist H. Moseley measured the wavelengths of the characteristic x-ray spectra for about 40 elements. From his data he was able to determine the atomic number Z for each element.

Example 37-7

Calculate the wavelength of the K_α x-ray line for molybdenum ($Z = 42$) and compare it with the value $\lambda = 0.0721$ nm measured by Moseley.

The K_α line corresponds to a transition from $n = 2$ to $n = 1$. The wavelength is given by Equation 37-31 with $Z = 42$ and $n = 2$:

$$\lambda = \frac{hc}{(41)^2(13.6 \text{ eV})(1 - \frac{1}{4})} = \frac{1240 \text{ eV}\cdot\text{nm}}{(41)^2(13.6 \text{ eV})(3/4)} = 0.0723 \text{ nm}$$

This result is in good agreement with the measured value.