corresponds to the d (l = 2) subshell.

The periodic table also gives information on molecular bonding. To see this, consider atoms in the left-most column (the so-called alkali metals including: Li, Na, and K). These atoms contain a single electron in the 2s subshell, which is easily donated to other atoms. In contrast, atoms in the second-to-right column (the halogens: for example, Cl, F, and Br) are relatively stingy in sharing electrons. These atoms would much rather accept an electron, because they are just one electron shy of a filled shell ("of being noble").

Therefore, if a Na atom is placed in close proximity to a Cl atom, the Na atom freely donates its 2s electron and the Cl atom eagerly accepts it. In the process, the Na atom (originally a neutral charge) becomes positively charged and the Cl (originally a neutral charge) becomes negatively charged. Charged atoms are called ions. In this case, the ions are Na⁺ and Cl⁻, where the superscript indicates charge of the ion. The electric (Coulomb) attraction between these atoms forms a NaCl (salt) molecule. A chemical bond between two ions is called an **ionic bond**. There are many kinds of chemical bonds. For example, in an oxygen molecule O_2 electrons are equally shared between the atoms. The bonding of oxygen atoms is

an example of a **covalent bond**.

8.5 Atomic Spectra and X-rays

Learning Objectives

By the end of this section, you will be able to:

- Describe the absorption and emission of radiation in terms of atomic energy levels and energy differences
- Use quantum numbers to estimate the energy, frequency, and wavelength of photons produced by atomic transitions in multi-electron atoms
- · Explain radiation concepts in the context of atomic fluorescence and X-rays

The study of atomic spectra provides most of our knowledge about atoms. In modern science, atomic spectra are used to identify species of atoms in a range of objects, from distant galaxies to blood samples at a crime scene.

The theoretical basis of atomic spectroscopy is the transition of electrons between energy levels in atoms. For example, if an electron in a hydrogen atom makes a transition from the n = 3 to the n = 2 shell, the atom emits a photon with a wavelength

$$\lambda = \frac{c}{f} = \frac{h \cdot c}{h \cdot f} = \frac{hc}{\Delta E} = \frac{hc}{E_3 - E_2},$$
(8.36)

where $\Delta E = E_3 - E_2$ is energy carried away by the photon and $hc = 1940 \text{ eV} \cdot \text{nm}$. After this radiation passes through a spectrometer, it appears as a sharp spectral line on a screen. The Bohr model of this process is shown in **Figure 8.18**. If the electron later absorbs a photon with energy ΔE , the electron returns to the n = 3 shell. (We examined the Bohr model earlier, in **Photons and Matter Waves**.)



Figure 8.18 An electron transition from the n = 3 to the n = 2 shell of a hydrogen atom.

To understand atomic transitions in multi-electron atoms, it is necessary to consider many effects, including the Coulomb repulsion between electrons and internal magnetic interactions (spin-orbit and spin-spin couplings). Fortunately, many properties of these systems can be understood by neglecting interactions between electrons and representing each electron by its own single-particle wave function ψ_{nlm} .

Atomic transitions must obey **selection rules**. These rules follow from principles of quantum mechanics and symmetry. Selection rules classify transitions as either allowed or forbidden. (Forbidden transitions do occur, but the probability of the typical forbidden transition is very small.) For a hydrogen-like atom, atomic transitions that involve electromagnetic interactions (the emission and absorption of photons) obey the following selection rule:

$$\Delta l = \pm 1, \tag{8.37}$$

where *l* is associated with the magnitude of orbital angular momentum,

$$L = \sqrt{l(l+1)}\hbar. \tag{8.38}$$

For multi-electron atoms, similar rules apply. To illustrate this rule, consider the observed atomic transitions in hydrogen (H), sodium (Na), and mercury (Hg) (Figure 8.19). The horizontal lines in this diagram correspond to atomic energy levels, and the transitions allowed by this selection rule are shown by lines drawn between these levels. The energies of these states are on the order of a few electron volts, and photons emitted in transitions are in the visible range. Technically, atomic transitions can violate the selection rule, but such transitions are uncommon.



Figure 8.19 Energy-level diagrams for (a) hydrogen, (b) sodium, and (c) mercury. For comparison, hydrogen energy levels are shown in the sodium diagram.

The hydrogen atom has the simplest energy-level diagram. If we neglect electron spin, all states with the same value of n have the same total energy. However, spin-orbit coupling splits the n = 2 states into two angular momentum states (s and p) of slightly different energies. (These levels are not vertically displaced, because the energy splitting is too small to show up in this diagram.) Likewise, spin-orbit coupling splits the n = 3 states into three angular momentum states (s, p, and d).

The energy-level diagram for hydrogen is similar to sodium, because both atoms have one electron in the outer shell. The valence electron of sodium moves in the electric field of a nucleus shielded by electrons in the inner shells, so it does not experience a simple 1/r Coulomb potential and its total energy depends on both n and l. Interestingly, mercury has two separate energy-level diagrams; these diagrams correspond to two net spin states of its 6s (valence) electrons.

Example 8.6

The Sodium Doublet

The spectrum of sodium is analyzed with a spectrometer. Two closely spaced lines with wavelengths 589.00 nm and 589.59 nm are observed. (a) If the doublet corresponds to the excited (valence) electron that transitions from some excited state down to the 3s state, what was the original electron angular momentum? (b) What is the energy difference between these two excited states?

Strategy

Sodium and hydrogen belong to the same column or chemical group of the periodic table, so sodium is "hydrogen-like." The outermost electron in sodium is in the 3s (l = 0) subshell and can be excited to higher energy levels. As for hydrogen, subsequent transitions to lower energy levels must obey the selection rule:

$$\Delta l = \pm 1$$

We must first determine the quantum number of the initial state that satisfies the selection rule. Then, we can use this number to determine the magnitude of orbital angular momentum of the initial state.

Solution

a. Allowed transitions must obey the selection rule. If the quantum number of the initial state is l = 0, the transition is forbidden because $\Delta l = 0$. If the quantum number of the initial state is l = 2, 3, 4,...the transition is forbidden because $\Delta l > 1$. Therefore, the quantum of the initial state must be l = 1. The orbital angular momentum of the initial state is

$$L = \sqrt{l(l+1)}\hbar = 1.41\hbar$$

b. Because the final state for both transitions is the same (3*s*), the difference in energies of the photons is equal to the difference in energies of the two excited states. Using the equation

$$\Delta E = hf = h\left(\frac{c}{\lambda}\right),$$

we have

$$\Delta E = hc \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)$$

= $(4.14 \times 10^{-15} \text{ eVs})(3.00 \times 10^8 \text{ m/s}) \times \left(\frac{1}{589.00 \times 10^{-9} \text{ m}} - \frac{1}{589.59 \times 10^{-9} \text{ m}}\right)$
= $2.11 \times 10^{-3} \text{ eV}$

Significance

To understand the difficulty of measuring this energy difference, we compare this difference with the average energy of the two photons emitted in the transition. Given an average wavelength of 589.30 nm, the average energy of the photons is

$$E = \frac{hc}{\lambda} = \frac{(4.14 \times 10^{-15} \text{ eVs})(3.00 \times 10^8 \text{ m/s})}{589.30 \times 10^{-9} \text{ m}} = 2.11 \text{ eV}.$$

The energy difference ΔE is about 0.1% (1 part in 1000) of this average energy. However, a sensitive spectrometer can measure the difference.

Atomic Fluorescence

Fluorescence occurs when an electron in an atom is excited several steps above the ground state by the absorption of a high-energy ultraviolet (UV) photon. Once excited, the electron "de-excites" in two ways. The electron can drop back to

the ground state, emitting a photon of the same energy that excited it, or it can drop in a series of smaller steps, emitting several low-energy photons. Some of these photons may be in the visible range. Fluorescent dye in clothes can make colors seem brighter in sunlight by converting UV radiation into visible light. Fluorescent lights are more efficient in converting electrical energy into visible light than incandescent filaments (about four times as efficient). **Figure 8.20** shows a scorpion illuminated by a UV lamp. Proteins near the surface of the skin emit a characteristic blue light.



Figure 8.20 A scorpion glows blue under a UV lamp. (credit: Ken Bosma)

X-rays

The study of atomic energy transitions enables us to understand X-rays and X-ray technology. Like all electromagnetic radiation, X-rays are made of photons. X-ray photons are produced when electrons in the outermost shells of an atom drop to the inner shells. (Hydrogen atoms do not emit X-rays, because the electron energy levels are too closely spaced together to permit the emission of high-frequency radiation.) Transitions of this kind are normally forbidden because the lower states are already filled. However, if an inner shell has a vacancy (an inner electron is missing, perhaps from being knocked away by a high-speed electron), an electron from one of the outer shells can drop in energy to fill the vacancy. The energy gap for such a transition is relatively large, so wavelength of the radiated X-ray photon is relatively short.

X-rays can also be produced by bombarding a metal target with high-energy electrons, as shown in **Figure 8.21**. In the figure, electrons are boiled off a filament and accelerated by an electric field into a tungsten target. According to the classical theory of electromagnetism, *any* charged particle that accelerates emits radiation. Thus, when the electron strikes the tungsten target, and suddenly slows down, the electron emits **braking radiation**. (Braking radiation refers to radiation produced by any charged particle that is slowed by a medium.) In this case, braking radiation contains a continuous range of frequencies, because the electrons will collide with the target atoms in slightly different ways.

Braking radiation is not the only type of radiation produced in this interaction. In some cases, an electron collides with another inner-shell electron of a target atom, and knocks the electron out of the atom—billiard ball style. The empty state is filled when an electron in a higher shell drops into the state (drop in energy level) and emits an X-ray photon.



Figure 8.21 A sketch of an X-ray tube. X-rays are emitted from the tungsten target.

Historically, X-ray spectral lines were labeled with letters (*K*, *L*, *M*, *N*, ...). These letters correspond to the atomic shells (n = 1, 2, 3, 4, ...). X-rays produced by a transition from any higher shell to the *K* (n = 1) shell are labeled as *K* X-rays. X-rays produced in a transition from the *L* (n = 2) shell are called K_{α} X-rays; X-rays produced in a transition from the *M* (n = 3) shell are called K_{β} X-rays; X-rays produced in a transition from the *N* (n = 4) shell are called K_{γ} X-rays; and so forth. Transitions from higher shells to *L* and *M* shells are labeled similarly. These transitions are represented by an energy-level diagram in **Figure 8.22**.



The distribution of X-ray wavelengths produced by striking metal with a beam of electrons is given in **Figure 8.23**. X-ray transitions in the target metal appear as peaks on top of the braking radiation curve. Photon frequencies corresponding to the spikes in the X-ray distribution are called characteristic frequencies, because they can be used to identify the target metal. The sharp cutoff wavelength (just below the K_{γ} peak) corresponds to an electron that loses all of its energy to a single

photon. Radiation of shorter wavelengths is forbidden by the conservation of energy.



Figure 8.23 X-ray spectrum from a silver target. The peaks correspond to characteristic frequencies of X-rays emitted by silver when struck by an electron beam.

Example 8.7

X-Rays from Aluminum

Estimate the characteristic energy and frequency of the K_{α} X-ray for aluminum (Z = 13).

Strategy

A K_{α} X-ray is produced by the transition of an electron in the L (n = 2) shell to the K (n = 1) shell. An electron in the L shell "sees" a charge Z = 13 - 1 = 12, because one electron in the K shell shields the nuclear charge. (Recall, two electrons are not in the K shell because the other electron state is vacant.) The frequency of the emitted photon can be estimated from the energy difference between the L and K shells.

Solution

The energy difference between the *L* and *K* shells in a hydrogen atom is 10.2 eV. Assuming that other electrons in the *L* shell or in higher-energy shells do not shield the nuclear charge, the energy difference between the *L* and *K* shells in an atom with Z = 13 is approximately

$$\Delta E_{L \to K} \approx (Z - 1)^2 (10.2 \text{ eV}) = (13 - 1)^2 (10.2 \text{ eV}) = 1.47 \times 10^3 \text{ eV}.$$
(8.39)

Based on the relationship $f = (\Delta E_{L \to K})/h$, the frequency of the X-ray is

$$f = \frac{1.47 \times 10^3 \text{ eV}}{4.14 \times 10^{-15} \text{ eV} \cdot \text{s}} = 3.55 \times 10^{17} \text{ Hz}.$$

Significance

The wavelength of the typical X-ray is 0.1–10 nm. In this case, the wavelength is:

$$\lambda = \frac{c}{f} = \frac{3.0 \times 10^8 \text{ m/s}}{3.55 \times 10^{17} \text{ Hz}} = 8.5 \times 10^{-10} = 0.85 \text{ nm}.$$

Hence, the transition $L \rightarrow K$ in aluminum produces X-ray radiation.

X-ray production provides an important test of quantum mechanics. According to the Bohr model, the energy of a K_{α} X-ray depends on the nuclear charge or atomic number, *Z*. If *Z* is large, Coulomb forces in the atom are large, energy differences (ΔE) are large, and, therefore, the energy of radiated photons is large. To illustrate, consider a single electron in a multielectron atom. Neglecting interactions between the electrons, the allowed energy levels are

$$E_n = -\frac{Z^2(13.6 \,\mathrm{eV})}{n^2},\tag{8.40}$$

where n = 1, 2, ... and Z is the atomic number of the nucleus. However, an electron in the L (n = 2) shell "sees" a charge Z - 1, because one electron in the K shell shields the nuclear charge. (Recall that there is only one electron in the K shell because the other electron was "knocked out.") Therefore, the approximate energies of the electron in the L and K shells are

$$E_L \approx -\frac{(Z-1)^2 (13.6 \text{ eV})}{2^2}$$

 $E_K \approx -\frac{(Z-1)^2 (13.6 \text{ eV})}{1^2}.$

The energy carried away by a photon in a transition from the *L* shell to the *K* shell is therefore

$$\Delta E_{L \to K} = (Z - 1)^2 (13.6 \text{ eV}) \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$
$$= (Z - 1)^2 (10.2 \text{ eV}),$$

where Z is the atomic number. In general, the X-ray photon energy for a transition from an outer shell to the K shell is

$$\Delta E_{L \to K} = hf = \text{constant} \times (Z - 1)^2,$$

or

$$(Z-1) = \text{constant}\sqrt{f},$$
(8.41)

where *f* is the frequency of a K_{α} X-ray. This equation is **Moseley's law**. For large values of *Z*, we have approximately

 $Z \approx \text{constant}\sqrt{f}$.

This prediction can be checked by measuring *f* for a variety of metal targets. This model is supported if a plot of *Z* versus \sqrt{f} data (called a **Moseley plot**) is linear. Comparison of model predictions and experimental results, for both the *K* and *L*

series, is shown in **Figure 8.24**. The data support the model that X-rays are produced when an outer shell electron drops in energy to fill a vacancy in an inner shell.



8.3 Check Your Understanding X-rays are produced by bombarding a metal target with high-energy electrons. If the target is replaced by another with two times the atomic number, what happens to the frequency of X-rays?



Moseley Plot of Characteristic X-Rays



Example 8.8

Characteristic X-Ray Energy

Calculate the approximate energy of a K_{α} X-ray from a tungsten anode in an X-ray tube.

Strategy

Two electrons occupy a filled *K* shell. A vacancy in this shell would leave one electron, so the effective charge for an electron in the *L* shell would be Z - 1 rather than *Z*. For tungsten, Z = 74, so the effective charge is 73. This number can be used to calculate the energy-level difference between the *L* and *K* shells, and, therefore, the energy carried away by a photon in the transition $L \rightarrow K$.

Solution

The effective *Z* is 73, so the K_{α} X-ray energy is given by

$$E_{K\alpha} = \Delta E = E_i - E_f = E_2 - E_1,$$

where

$$E_1 = -\frac{Z^2}{1^2}E_0 = -\frac{73^2}{1}(13.6 \,\mathrm{eV}) = -72.5 \,\mathrm{keV}$$

and

$$E_2 = -\frac{Z^2}{2^2}E_0 = -\frac{73^2}{4}(13.6 \text{ eV}) = -18.1 \text{ keV}.$$

Thus,

$$E_{K_{\alpha}} = -18.1 \text{ keV} - (-72.5 \text{ keV}) = 54.4 \text{ keV}.$$

Significance

This large photon energy is typical of X-rays. X-ray energies become progressively larger for heavier elements because their energy increases approximately as Z^2 . An acceleration voltage of more than 50,000 volts is needed to "knock out" an inner electron from a tungsten atom.

X-ray Technology

X-rays have many applications, such as in medical diagnostics (**Figure 8.25**), inspection of luggage at airports (**Figure 8.26**), and even detection of cracks in crucial aircraft components. The most common X-ray images are due to shadows. Because X-ray photons have high energy, they penetrate materials that are opaque to visible light. The more energy an X-ray photon has, the more material it penetrates. The depth of penetration is related to the density of the material, as well as to the energy of the photon. The denser the material, the fewer X-ray photons get through and the darker the shadow. X-rays are effective at identifying bone breaks and tumors; however, overexposure to X-rays can damage cells in biological organisms.



Figure 8.25 (a) An X-ray image of a person's teeth. (b) A typical X-ray machine in a dentist's office produces relatively low-energy radiation to minimize patient exposure. (credit a: modification of work by "Dmitry G"/Wikimedia Commons)



Figure 8.26 An X-ray image of a piece of luggage. The denser the material, the darker the shadow. Object colors relate to material composition—metallic objects show up as blue in this image. (credit: "IDuke"/Wikimedia Commons)

A standard X-ray image provides a two-dimensional view of the object. However, in medical applications, this view does not often provide enough information to draw firm conclusions. For example, in a two-dimensional X-ray image of the body, bones can easily hide soft tissues or organs. The CAT (computed axial tomography) scanner addresses this problem by collecting numerous X-ray images in "slices" throughout the body. Complex computer-image processing of the relative absorption of the X-rays, in different directions, can produce a highly detailed three-dimensional X-ray image of the body.

X-rays can also be used to probe the structures of atoms and molecules. Consider X-rays incident on the surface of a crystalline solid. Some X-ray photons reflect at the surface, and others reflect off the "plane" of atoms just below the surface. Interference between these photons, for different angles of incidence, produces a beautiful image on a screen (**Figure 8.27**). The interaction of X-rays with a solid is called X-ray diffraction. The most famous example using X-ray diffraction is the discovery of the double-helix structure of DNA.



Figure 8.27 X-ray diffraction from the crystal of a protein (hen egg lysozyme) produced this interference pattern. Analysis of the pattern yields information about the structure of the protein. (credit: "Del45"/Wikimedia Commons)

8.6 | Lasers

Learning Objectives

By the end of this section, you will be able to:

- Describe the physical processes necessary to produce laser light
- Explain the difference between coherent and incoherent light
- Describe the application of lasers to a CD and Blu-Ray player

A **laser** is device that emits coherent and monochromatic light. The light is coherent if photons that compose the light are in-phase, and **monochromatic** if the photons have a single frequency (color). When a gas in the laser absorbs radiation, electrons are elevated to different energy levels. Most electrons return immediately to the ground state, but others linger in what is called a **metastable state**. It is possible to place a majority of these atoms in a metastable state, a condition called a **population inversion**.

When a photon of energy disturbs an electron in a metastable state (**Figure 8.28**), the electron drops to the lower-energy level and emits an addition photon, and the two photons proceed off together. This process is called **stimulated emission**. It occurs with relatively high probability when the energy of the incoming photon is equal to the energy difference between the excited and "de-excited" energy levels of the electron ($\Delta E = hf$). Hence, the incoming photon and the photon produced

by de-excitation have the same energy, *hf*. These photons encounter more electrons in the metastable state, and the process repeats. The result is a cascade or chain reaction of similar de-excitations. Laser light is coherent because all light waves in laser light share the same frequency (color) and the same phase (any two points of along a line perpendicular to the direction