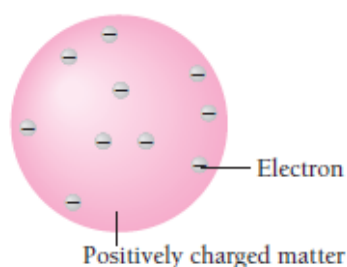# Chapter 4: Atomic Structure

- Structure of the atom is responsible for nearly all the properties of matter that have shaped the world around us.
- Every atom consists of a small nucleus of protons and neutrons with a number of electrons some distance away.
- It is tempting to think that the electrons circle the nucleus as planets do the sun, but classical electromagnetic theory denies the possibility of stable electron orbits.
- Niels Bohr applied quantum ideas to atomic structure in 1913 (inspired from Balmer's formula).

4.1 THE NUCLEAR ATOM

- An atom is largely empty space.
- Late nineteenth century: It was known that all atoms contain electrons.
  - Since electrons carry negative charges whereas atoms are neutral, positively charged matter of some kind must be present in atoms.
  - But what kind? And arranged in what way?
- Thomson model (Plum pudding model): One suggestion, made by the British physicist J. J. Thomson (Discovery of electron) in 1898, was that atoms are just positively charged lumps of matter with electrons embedded in them, like raisins in a fruitcake (Fig. 4.1).
  - Because Thomson had played an important role in discovering the electron, his idea was taken seriously.
 - But the real atom turned out to be quite different.

Joseph John Thomson 1856-1940 Nobel Prize in Physics in 1906

Figure 4.1 The Thomson model of the atom. The Rutherford scattering experiment showed it to be incorrect.

- What is inside a fruitcake?
- Rutherford model: Hans Geiger and Ernest Marsden used as probes the fast alpha particles in 1911 at the suggestion of Ernest Rutherford (Discovery of alpha and beta radioactivity and discovery of atomic nucleus)
  - Fast alpha particles emitted by certain radioactive elements.
  - Alpha particles are helium atoms that have lost two electrons each, leaving them with a charge of +2e.
- Geiger and Marsden placed a sample of an alpha-emitting substance behind a lead screen with a small hole in it, as in Fig. 4.2, so that a narrow beam of alpha particles was produced.
  - This beam was directed at a thin gold foil.
- It was expected that the alpha particles would go right through the foil with hardly any deflection. This follows from the Thomson model!!

Ernest Rutherford 1871-1937 Nobel Prize in Chemistry in 1908
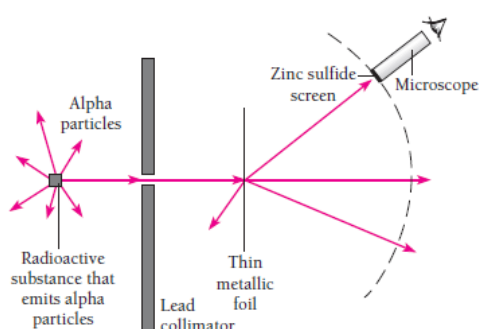
- With only weak electric forces exerted on them, alpha particles that pass through a thin foil ought to be deflected only slightly, 1° or less.

Figure 4.2 The Rutherford scattering experiment.

- What Geiger and Marsden actually found was that although most of the alpha particles indeed were not deviated by much, a few were scattered through **very large angles.**
- Some were even scattered in the backward direction.
- Alpha particles are relatively heavy (almost 8000 electron masses) and those used in this experiment had high speeds (typically 2×10^7 m/s).
- It was clear that powerful forces were needed to cause such marked deflections.
- The only way to explain the results, Rutherford found, was to picture an atom as being composed of a tiny nucleus in which its positive charge and nearly all its mass are concentrated, with the electrons some distance away (Fig. 4.3).
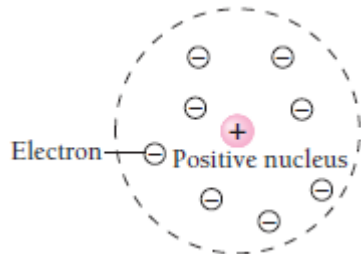
- With an atom being largely empty space, it is easy to see why most alpha particles go right through a thin foil.
- However, when an alpha particle happens to come near a nucleus, the intense electric field there scatters it through a large angle.
- The atomic electrons, being so light, do not appreciably affect the alpha particles.

Figure 4.3 The Rutherford model of the atom.

- All the atoms of any one element turned out to have the same unique nuclear charge, and this charge increased regularly from element to element in the periodic table.
- The nuclear charges always turned out to be multiples of +e; the number Z of unit positive charges in the nuclei of an element is called the atomic number of the element.
- We know now that protons, each with a charge +e, provide the charge on a nucleus, so the atomic number of an element is the same as the number of protons in the nuclei of its atoms.

Nuclear Dimensions

- Rutherford assumed that the size of a target nucleus is small compared with the minimum distance R to which incident alpha particles approach the nucleus before being deflected away.
- Rutherford scattering therefore gives us a way to find an upper limit to nuclear dimensions.
- An alpha particle will have its smallest R when it approaches a nucleus head on, which will be followed by a 180° scattering.
- At the instant of closest approach the initial kinetic energy KE of the particle is entirely converted to electric potential energy, and so at that instant

$$KE_{initial} = PE = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{R}$$

- since the charge of the alpha particle is 2e and that of the nucleus is Ze. Hence

Distance of closest approach

$$R = \frac{2Ze^2}{4\pi\epsilon_0 KE_{initial}} \qquad (4.2)$$

The maximum KE found in alpha particles of natural origin is 7.7 MeV, which is 1.2×10^{12} J. Since $1/4\pi\epsilon_0 = 9.0 \times 10^9$ Nm²/C²,

$$R = \frac{(2)(9.0 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2 Z}{1.2 \times 10^{-12} \text{ J}}$$

$$= 3.8 \times 10^{-16} Z \text{ m}$$

when Z=79

$R \text{ (Au)} = 3.0 \times 10^{-14}$ m *: Radius of gold nucleus*

4.2 ELECTRON ORBITS

- The planetary model of the atom and why it fails.
- The Rutherford model of the atom, so convincingly confirmed by experiment,
  - pictures a tiny, massive, positively charged nucleus surrounded at a relatively great distance by enough electrons
  - enough electrons to render the atom electrically neutral as a whole.
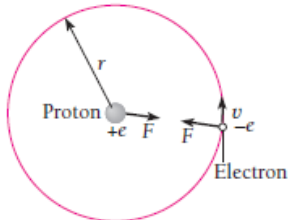
- The electrons <u>cannot</u> be stationary in this model, because there is nothing that can keep them in place against the electric force pulling them to the nucleus.
- If the electrons are in motion, however, dynamically stable orbits like those of the planets around the sun are possible (Fig. 4.5).

Figure 4.5 Force balance in the hydrogen atom.

- Let us look at the classical dynamics of the hydrogen atom, whose single electron makes it the simplest of all atoms.
  - We assume a circular electron orbit for convenience, though it might as reasonably be assumed to be elliptical in shape.
  - The centripetal force holding the electron in an orbit r from the nucleus is provided by

$$F_e = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2}$$

between them. The condition for a dynamically stable orbit is

$$F_c = F_e$$

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} \qquad (4.3)$$

The electron velocity v is therefore related to its orbit radius r by the formula

Electron velocity $\qquad\qquad v = \dfrac{e}{\sqrt{4\pi\epsilon_0 mr}} \qquad (4.4)$

The total energy E of the electron in a hydrogen atom is the sum of its kinetic and potential energies, which are

$$KE = \frac{1}{2}mv^2 \qquad PE = -\frac{e^2}{4\pi\epsilon_0 r}$$

(The minus sign follows from the choice of PE $= 0$ at $r = \infty$, that is, when the electron and proton are infinitely far apart.) Hence

$$E = KE + PE = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0 r}$$

Substituting for v from Eq. (4.4) gives

$$E = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r}$$

Total energy of hydrogen atom $\qquad\qquad E = -\dfrac{e^2}{8\pi\epsilon_0 r} \qquad (4.5)$

- The total energy of the electron is negative.
  - ° This holds for every atomic electron and reflects the fact that it is <u>bound to the nucleus</u>.
  - ° If E were greater than zero, an electron would not follow a closed orbit around the nucleus.

Example 4.1

Experiments indicate that 13.6 eV is required to separate a hydrogen atom into a proton and an electron; that is, its total energy is E=-13.6 eV. Find the orbital radius and velocity of the electron in a hydrogen atom.

Solution

Since 13.6 eV $= 2.2 \times 10^{-18}$ J, from Eq. (4.5)

$$r = -\frac{e^2}{8\pi\epsilon_0 E} = -\frac{(1.6 \times 10^{-19} \text{ C})^2}{(8\pi)(8.85 \times 10^{-12} \text{ F/m})(-2.2 \times 10^{-18} \text{ J})}$$
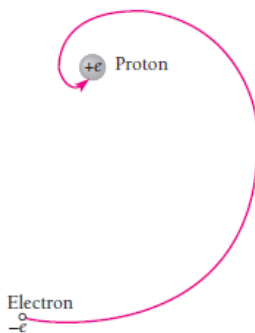$$= 5.3 \times 10^{-11} \text{ m}$$

An atomic radius of this magnitude agrees with estimates made in other ways. The electron's velocity can be found from Eq. (4.4):

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 m r}} = \frac{1.6 \times 10^{-19} \text{ C}}{\sqrt{(4\pi)(8.85 \times 10^{-12} \text{ F/m})(9.1 \times 10^{-31} \text{ kg})(5.3 \times 10^{-11} \text{ m})}}$$
$$= 2.2 \times 10^6 \text{ m/s}$$

Since $v \ll c$, we can ignore special relativity when considering the hydrogen atom.

The Failure of Classical Physics

- The analysis above is a straightforward application of Newton's laws of motion and Coulomb's law of electric force (classical physics) and is in accord with the experimental observation that atoms are stable.
- However, it is not in accord with electromagnetic theory (another classical physics) which predicts that accelerated electric charges radiate energy in the form of em waves.
- An electron pursuing a curved path is accelerated and therefore should continuously lose energy, spiraling into the nucleus in a fraction of a second (Fig. 4.6).

Figure 4.6 An atomic electron should, classically, spiral rapidly into the nucleus as it radiates energy due to its acceleration

- But atoms do not collapse.
- This contradiction further illustrates what we saw in the previous two chapters,
  - ° The laws of physics that are valid in the macroworld do not always hold true in the microworld of the atom.

4.3 ATOMIC SPECTRA

- Each element has a characteristic line spectrum
- The existence of spectral lines is an important aspect of the atom that finds no explanation in classical physics.
- We saw in Chap. 2 that condensed matter (solids and liquids) at all temperatures emits em radiation in which all wavelengths are present, though with different intensities.
  - ° Witnessing the collective behavior of a great many interacting atoms rather than the characteristic behavior of the atoms of a particular element.
  - ° At the other extreme, the atoms or molecules in a rarefied gas are so far apart on the average that they only interact during occasional collisions. Under these circumstances,

we would expect any emitted radiation <u>to be characteristic</u> of the particular atoms or molecules present, which turns out to be the case.
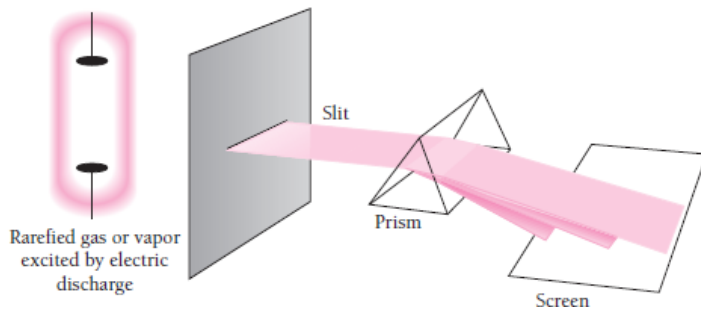
- When an atomic gas or vapor at somewhat less than atmospheric pressure is suitably "excited," usually by passing an electric current through it, the emitted radiation has a spectrum which contains certain specific wavelengths only.

Figure 4.7 An idealized spectrometer.

- An idealized arrangement for observing such atomic spectra is shown in Fig. 4.7; actual spectrometers use diffraction gratings.
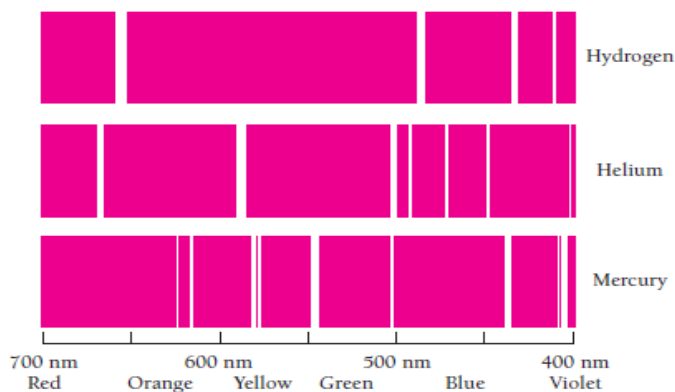
- Figure 4.8 shows the emission line spectra of several elements.
- Every element displays a unique line spectrum when a sample of it in the vapor phase is excited.
- **Spectroscopy is therefore a useful tool for analyzing the composition of an unknown substance**.

Figure 4.8 Some of the principal lines in the emission spectra of hydrogen, helium, and mercury

- When white light is passed through a gas, the gas is found to absorb light of certain of the wavelengths present in its emission spectrum.
- The resulting **absorption line spectrum** consists of a bright background crossed by dark lines that correspond to the missing wavelengths (Fig. 4.9); emission spectra consist of bright lines on a dark background.
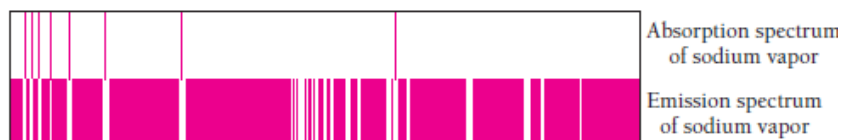

Figure 4.9 The dark lines in the absorption spectrum of an element correspond to bright lines in its

- The number, intensity, and exact wavelengths of the lines in the spectrum of an element depend upon temperature, pressure, the presence of electric and magnetic fields, and the motion of the source.
- It is possible to tell by examining its spectrum not only what elements are present in a light source but much about their physical state.

Spectral Series

- A century ago the wavelengths in the spectrum of an element were found to fall into sets called **spectral series**.
- The first such series was discovered by J. J. Balmer in 1885 in the course of a study of the visible part of the hydrogen spectrum.

- Figure 4.10 shows the Balmer series.

656.3 nm   364.6 nm

H_α H_β H_γ H_δ H_∞
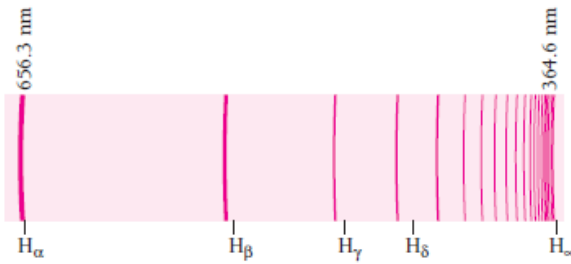
- As the wave-length decreases, the lines are found closer together and weaker in intensity until the series limit at 364.6 nm is reached,
- beyond which there are no further separate lines but only a faint continuous spectrum.

Figure 4.10 The Balmer series of hydrogen. The $H_\square$ line is red, the $H_\square$ line is blue, the H_γ and $H_\square$ lines are violet, and the other lines are in the near ultraviolet.

- Balmer's formula for the wavelengths of this series is

Balmer
$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, \ldots \tag{4.6}$$

The quantity R, known as the **Rydberg constant,** has the value

Rydberg constant
$$R = 1.097 \times 10^7 \text{ m}^{-1} = 0.01097 \text{ nm}^{-1}$$

- What is n for $H_\square$? What happens for n=$\square$?
- The Balmer series contains wavelengths in the visible portion of the hydrogen spectrum.
- The spectral lines of hydrogen in the ultraviolet and infrared regions fall into several other series. In the ultraviolet the Lyman series contains the wavelengths given by the formula

Lyman
$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad n = 2, 3, 4, \ldots \tag{4.7}$$

In the infrared, three spectral series have been found whose lines have the wavelengths specified by the formulas

Paschen
$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad n = 4, 5, 6, \ldots \tag{4.8}$$

Brackett
$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \quad n = 5, 6, 7, \ldots \tag{4.9}$$

Pfund
$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right) \quad n = 6, 7, 8, \ldots \tag{4.10}$$

These spectral series of hydrogen are plotted in terms of wavelength in Fig. 4.11; the Brackett series evidently overlaps the Paschen and Pfund series. The value of R is the same in Eqs. (4.6) to (4.10).

These observed regularities in the hydrogen spectrum, together with similar regularities in the spectra of more complex elements, pose a definitive test for any theory of atomic structure.
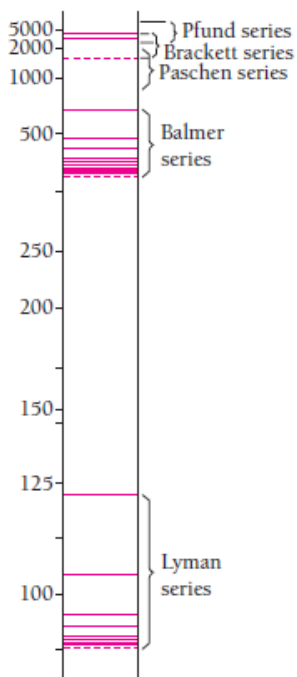
Figure 4.11 The spectral series of hydrogen. The wavelengths in each series are related by simple formulas.

4.4 THE BOHR ATOM

- Electron waves in the atom.

- The first theory of the atom to meet with any success was put forward in 1913 by Niels Bohr.
- The concept of matter waves leads in a natural way to this theory, as de Broglie found.
- Bohr himself used a different approach, since de Broglie's work came a decade later.
- Start by examining the wave behavior of an electron in orbit around a hydrogen nucleus.
- Since the electron velocities are much smaller than c (v<<c), we will assume that γ=1 and for simplicity omit γ from the various equations.
- The de Broglie wavelength of this electron is

Niels Henrik David Bohr 1885-1962 Nobel Prize in Physics in 1922

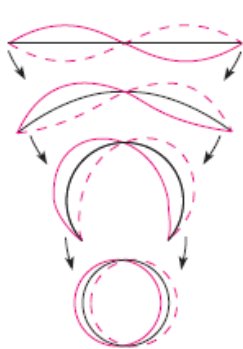$$\lambda = \frac{h}{mv}$$

where the electron velocity v is that given by Eq. (4.4):

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$$

Hence

Orbital electron wavelength

$$\lambda = \frac{h}{e}\sqrt{\frac{4\pi\epsilon_0 r}{m}} \qquad (4.11)$$
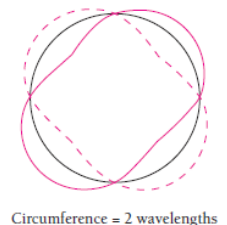
By substituting 5.3x10^{-11} m for the radius r of the electron orbit (see Example 4.1), we find the electron wavelength to be
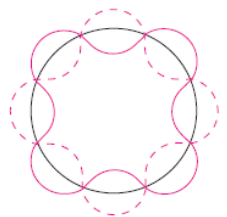
$$\lambda = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{1.6 \times 10^{-19} \text{C}} \sqrt{\frac{(4\pi)(8.85 \times 10^{-12} \text{ C}^2/\text{N} \cdot \text{m}^2)(5.3 \times 10^{-11}\text{m})}{9.1 \times 10^{-31} \text{ kg}}}$$

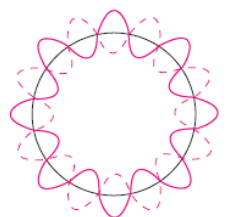$$= 33 \times 10^{-11} \text{ m}$$

Circumference = 2 wavelengths

- This wavelength is exactly the same as the circumference of the electron orbit, $2\pi r = 33 \times 10^{-11}$ m.
- The orbit of the electron in a hydrogen atom corresponds to one complete electron wave joined on itself (Fig. 4.12).

— Electron path
— De Broglie electron wave

Figure 4.12 The orbit of the electron in a hydrogen atom corresponds to a complete electron de Broglie wave joined on itself.

Circumference = 4 wavelengths

- The fact that the electron orbit in a hydrogen atom is one electron wavelength in circumference provides the clue we need to construct a theory of the atom.
- If we consider the vibrations of a wire loop (Fig. 4.13), we find that their wavelengths always fit an integral number of times into the loop's circumference so that each wave joins smoothly with the next.
- If the wire were perfectly elastic, these vibrations would continue indefinitely.
- Why are these the only vibrations possible in a wire loop?

Circumference = 8 wavelengths

Figure 4.13 Some modes of vibration of a wire loop. In each case a whole number of wavelengths fit into the circumference of the loop.

- If a fractional number of wavelengths is placed around the loop, as in Fig. 4.14, destructive interference will occur as the waves travel around the loop, and the vibrations will die out rapidly.
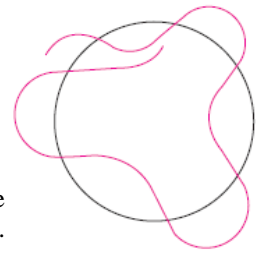

Figure 4.14 A fractional number of wavelengths cannot persist because destructive interference will occur.

- By considering the behavior of electron waves in the hydrogen atom as analogous to the vibrations of a wire loop, then, we can say that
- An electron can circle a nucleus only if its orbit contains an integral number of de Broglie wavelengths.
- This statement combines both the particle and wave characters of the electron since the electron wavelength depends upon the orbital velocity needed to balance the pull of the nucleus.
- It is easy to express the condition that an electron orbit contain an integral number of de Broglie wavelengths. The circumference of a circular orbit of radius r is $2\pi r$, and so the condition for orbit stability is

Condition for orbit stability $\qquad n\lambda = 2\pi r_n \qquad n = 1, 2, 3, \ldots \qquad$ (4.12)

where r_n designates the radius of the orbit that contain n wavelengths. The integer n is called the **quantum number** of the orbit. Substituting for λ, the electron wavelength given by Eq. (4.11), yields

$$\frac{nh}{e}\sqrt{\frac{4\pi\epsilon_0 r_n}{m}} = 2\pi r_n$$

and so the possible electron orbits are those whose radii are given by

Orbital radii in Bohr atom $\qquad r_n = \dfrac{n^2 h^2 \epsilon_0}{\pi m e^2} \qquad n = 1, 2, 3, \ldots \qquad$ (4.13)

The radius of the innermost orbit is customarily called the *Bohr radius* of the hydrogen atom and is denoted by the symbol a_0:

Bohr radius $\qquad a_0 = r_1 = 5.292 \times 10^{-11}\,\text{m}$

The other radii are given in terms of a_0 by the formula

$$r_n = n^2 a_0 \qquad (4.14)$$

4.5 ENERGY LEVELS AND SPECTRA

- A photon is emitted when an electron jumps from one energy level to a lower level
- The various permitted orbits involve different electron energies. The electron energy E_n is given in terms of the orbit radius r_n by Eq. (4.5) as
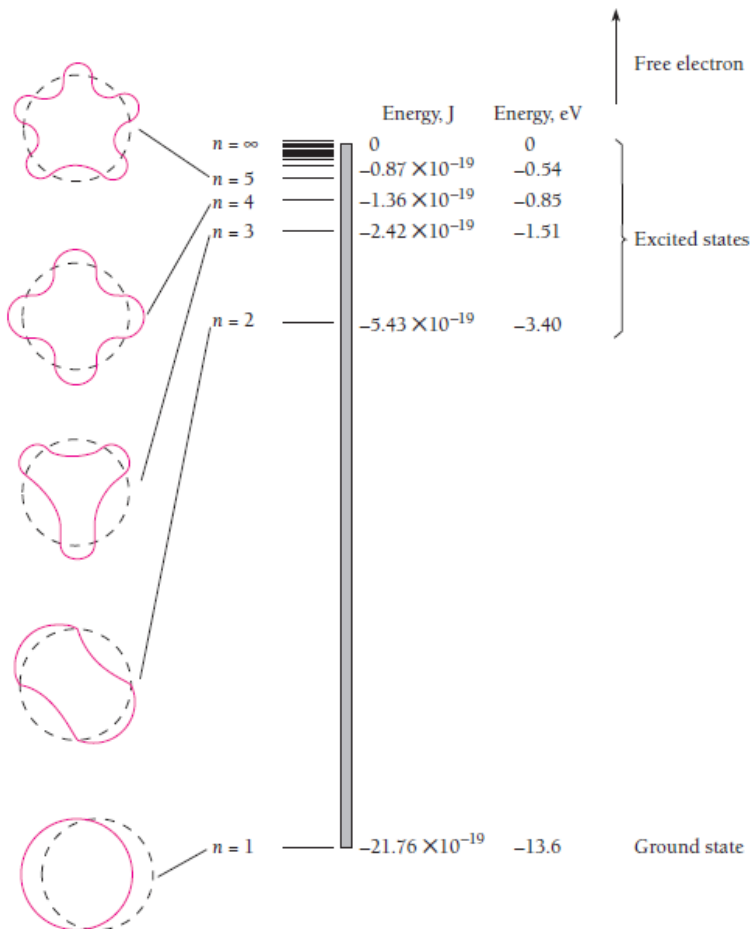
$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n}$$

Substituting for r_n from Eq (4.13), we see that

Energy levels $\qquad E_n = -\dfrac{me^4}{8\epsilon_0^2 h^2}\left(\dfrac{1}{n^2}\right) = \dfrac{E_1}{n^2} \qquad n = 1, 2, 3, \ldots \qquad (4.15)$

$$E_1 = -2.18 \times 10^{-18}\,\text{J} = -13.6\,\text{eV}$$

	Energy, J	Energy, eV	
$n = \infty$	0	0	Free electron
$n = 5$	-0.87×10^{-19}	-0.54	
$n = 4$	-1.36×10^{-19}	-0.85	
$n = 3$	-2.42×10^{-19}	-1.51	Excited states
$n = 2$	-5.43×10^{-19}	-3.40	
$n = 1$	-21.76×10^{-19}	-13.6	Ground state

Figure 4.15 Energy levels of the hydrogen atom.

- The energies specified by Eq. (4.15) are called the energy levels of the hydrogen atom and are plotted in Fig. 4.15.
- An atomic electron can have only these energies and no others.
- The lowest energy level E_1 is called the **ground state** of the atom, and the higher levels E_2, E_3, E_4, . . . are called **excited states**.
- As the quantum number n increases, the corresponding energy E_n approaches closer to 0.
- The work needed to remove an electron from an atom in its ground state is called its **ionization energy**.
- The ionization energy is accordingly equal to $-E_1$, the energy that must be provided to raise an electron from its ground state to an energy of E=0, when it is free.
- For hydrogen, it is 13.6 eV.

Example 4.2
An electron collides with a hydrogen atom in its ground state and excites it to a state of n=3. How much energy was given to the hydrogen atom in this inelastic (KE not conserved) collision?

Solution

From Eq. (4.15) the energy change of a hydrogen atom that goes from an initial state of quantum number n_i to a final state of quantum number n_f is

$$\Delta E = E_f - E_i = \frac{E_1}{n_f^2} - \frac{E_1}{n_i^2} = E_1\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Here $n_i = 1$, $n_f = 3$, and $E_1 = -13.6$ eV, so

$$\Delta E = -13.6\left(\frac{1}{3^2} - \frac{1}{1^2}\right)\text{eV} = 12.1\,\text{eV}$$

Example 4.3
Hydrogen atoms in states of high quantum number have been created in the laboratory and observed in space. They are called Rydberg atoms. (a) Find the quantum number of the Bohr orbit in a hydrogen atom whose radius is 0.0100 mm. (b) What is the energy of a hydrogen atom in this state?

Solution

(a) From Eq. (4.14) with $r_n = 1.00 \times 10^{-5}$ m,

$$n = \sqrt{\frac{r_n}{a_0}} = \sqrt{\frac{1.00 \times 10^{-5} \text{ m}}{5.29 \times 10^{-11} \text{ m}}} = 435$$

(b) From Eq. (4.15),

$$E_n = \frac{E_1}{n^2} = \frac{-13.6 \text{ eV}}{(435)^2} = -7.19 \times 10^{-5} \text{ eV}$$

Rydberg atoms are obviously extremely fragile and are easily ionized, which is why they are found in nature only in the near-vacuum of space. The spectra of Rydberg atoms range down to radio frequencies and their existence was established from radio telescope data.

Origin of Line Spectra

- The presence of discrete energy levels in the hydrogen atom suggests the connection.
- According to our model, electrons cannot exist in an atom except in certain specific energy levels.
- The jump of an electron from one level to another, with the difference in energy between the levels being given off all at once in a photon rather than in some more gradual manner, fits in well with this model.
- Recall that E_1 is a negative quantity (-13.6 eV), so $-E_1$ is a positive quantity. The frequency of the photon released in this transition is therefore

$$\nu = \frac{E_i - E_f}{h} = -\frac{E_1}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{4.17}$$

Since $\lambda = c/\nu$ ➔ **Hydrogen spectrum**

$$\frac{1}{\lambda} = -\frac{E_1}{ch}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{4.18}$$
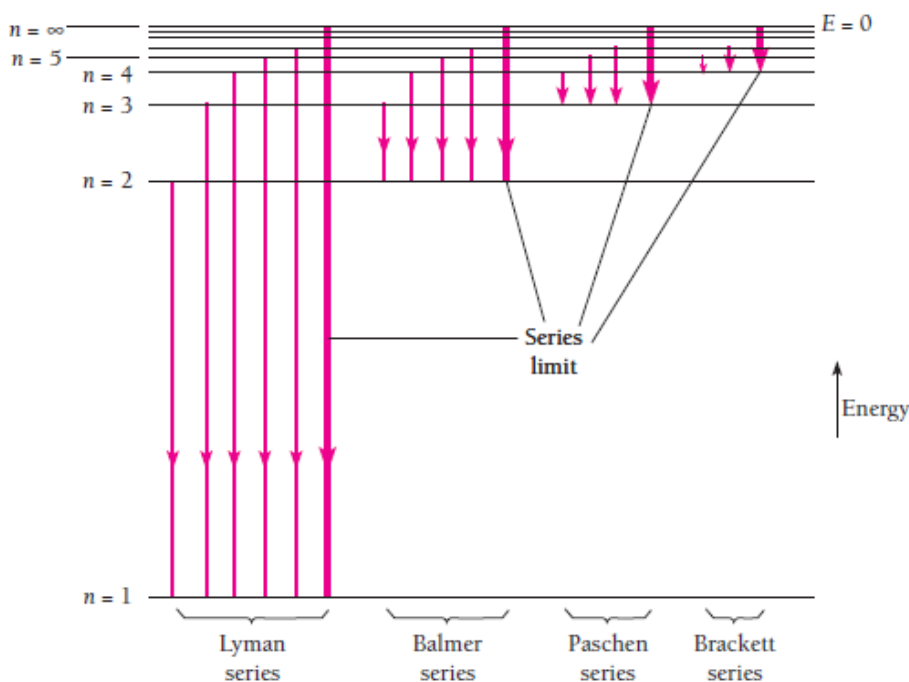
- Equation (4.18) states that the radiation emitted by excited hydrogen atoms should contain certain wavelengths only.
- These wavelengths, furthermore, fall into definite sequences that depend upon the quantum number n_f of the final energy level of the electron (Fig. 4.16).

Figure 4.16 Spectral lines originate in transitions between energy levels. Shown are the spectral series of hydrogen. When n=∞, the electron is free.

- Since $n_i > n_f$ in each case, in order that there be an excess of energy to be given off as a photon, the calculated formulas for the first five series are

Lyman $\quad n_f = 1: \quad \dfrac{1}{\lambda} = -\dfrac{E_1}{ch}\left(\dfrac{1}{1^2} - \dfrac{1}{n^2}\right) \quad n = 2, 3, 4, \ldots$

Balmer $\quad n_f = 2: \quad \dfrac{1}{\lambda} = -\dfrac{E_1}{ch}\left(\dfrac{1}{2^2} - \dfrac{1}{n^2}\right) \quad n = 3, 4, 5, \ldots$

Paschen $\quad n_f = 3: \quad \dfrac{1}{\lambda} = -\dfrac{E_1}{ch}\left(\dfrac{1}{3^2} - \dfrac{1}{n^2}\right) \quad n = 4, 5, 6, \ldots$

Brackett $\quad n_f = 4: \quad \dfrac{1}{\lambda} = -\dfrac{E_1}{ch}\left(\dfrac{1}{4^2} - \dfrac{1}{n^2}\right) \quad n = 5, 6, 7, \ldots$

Pfund $\quad n_f = 5: \quad \dfrac{1}{\lambda} = -\dfrac{E_1}{ch}\left(\dfrac{1}{5^2} - \dfrac{1}{n^2}\right) \quad n = 6, 7, 8, \ldots$

Example 4.4

Find the longest wavelength present in the Balmer series of hydrogen, corresponding to the H_α line.

Solution

In the Balmer series the quantum number of the final state is $n_f = 2$. The longest wavelength in this series corresponds to the smallest energy difference between energy levels. Hence the initial state must be $n_i = 3$ and

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 0.139R$$

$$\lambda = \frac{1}{0.139R} = \frac{1}{0.139(1.097 \times 10^7 \mathrm{m}^{-1})} = 6.56 \times 10^{-7}\mathrm{m} = 656 \text{ nm}$$

This wavelength is near the red end of the visible spectrum.

4.8 ATOMIC EXCITATION

- How atoms absorb and emit energy.
- There are two main ways in which an atom can be excited to an energy above its ground state and thereby become able to radiate.
1) One of these ways is by a collision with another particle in which part of their joint kinetic energy is absorbed by the atom.
   o Such an excited atom will return to its ground state in an average of 10^{-8} s by emitting one or more photons (Fig. 4.18).
   o Energy transfer is a maximum when the colliding particles have the same mass: the electrons in such a discharge are more effective than the ions in providing energy to atomic electrons.
2) Another excitation mechanism is involved when an atom absorbs a photon of light whose energy is just the right amount to raise the atom to a higher energy level. This process explains the origin of absorption spectra (Fig. 4.19).
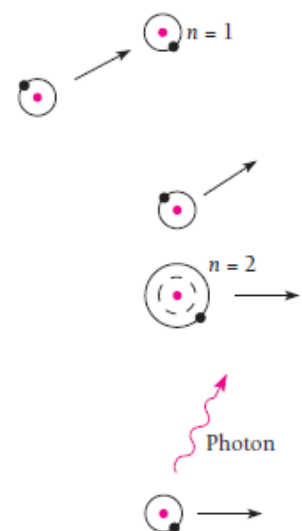

Figure 4.18 Excitation by collision. Some of the available energy is absorbed by one of the atoms, which goes into an excited energy state. The atom then emits a photon in returning to its ground (normal) state.
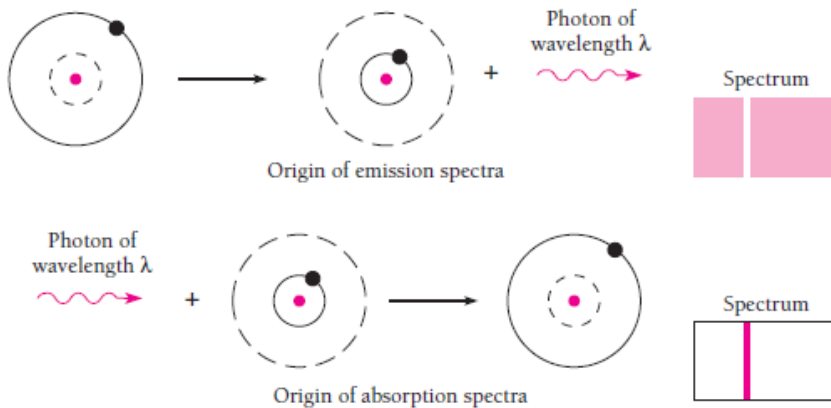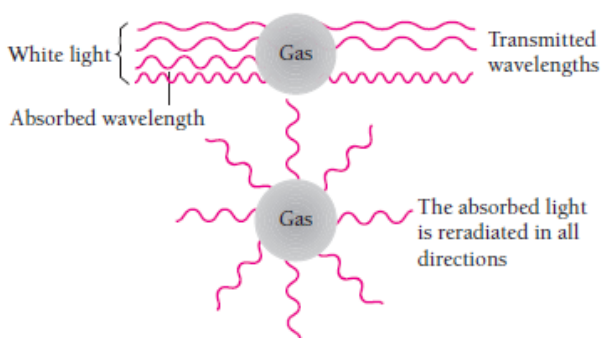
Figure 4.19 How emission and absorption spectral lines originate.

- When white light, which contains all wavelengths, is passed through hydrogen gas, photons of those wavelengths that <u>correspond to transitions between energy levels</u> are absorbed.


- The resulting excited hydrogen atoms reradiate their excitation energy almost at once, but these photons come off in random directions with only a few in the same direction as the original beam of white light (Fig. 4.20).

Figure 4.20 The dark lines in an absorption spectrum are never totally dark

4.9 THE LASER

- How to produce light waves all in step.
- The laser is a device that produces a light beam with some remarkable properties:
1. The light is very nearly monochromatic.
2. The light is coherent, with the waves all exactly in phase with one another (Fig.4.23).
3. A laser beam diverges hardly at all. Such a beam sent from the earth to a mirror left on the moon remained narrow enough to be detected on its return to the earth, a total distance of over three-quarters of a million kilometers.
4. The beam is extremely intense, more intense by far than the light from any other source
- The last two of these properties follow from the second of them.
- The term laser stands for Light Amplification by Stimulated Emission of Radiation.

Figure 4.23 A laser produces a beam of light whose waves all have the same frequency (monochromatic) and are in phase with one another (coherent). The beam is also well collimated and so spreads out very little, even over long distances.
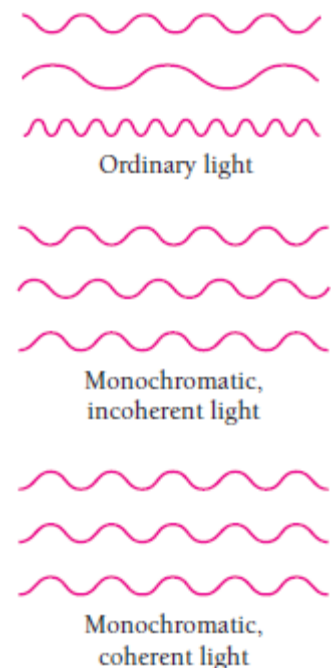
- The key to the laser is the presence in many atoms of one or more excited energy levels whose lifetimes may be 10^{-3} s or more instead of the usual 10^{-8} s.
- Such relatively long-lived states are called metastable (temporarily stable); see Fig. 4.24.
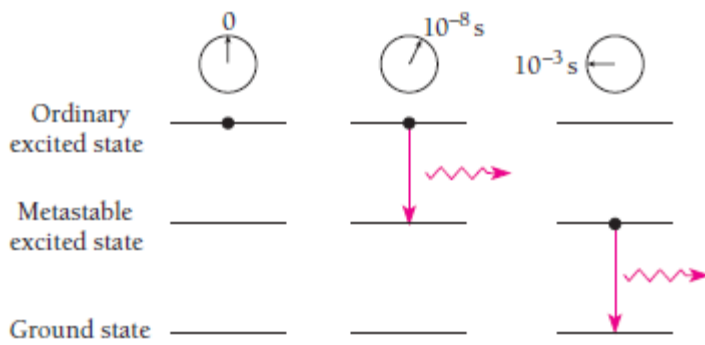
Figure 4.24 An atom can exist in a metastable energy level for a longer time before radiating than it can in an ordinary energy level.

- Three kinds of transition involving electromagnetic radiation are possible between two energy levels, E_0 and E_1, in an atom (Fig. 4.25).
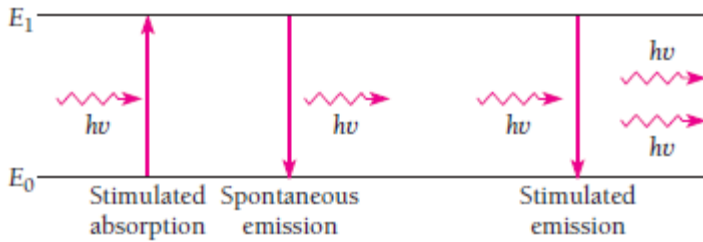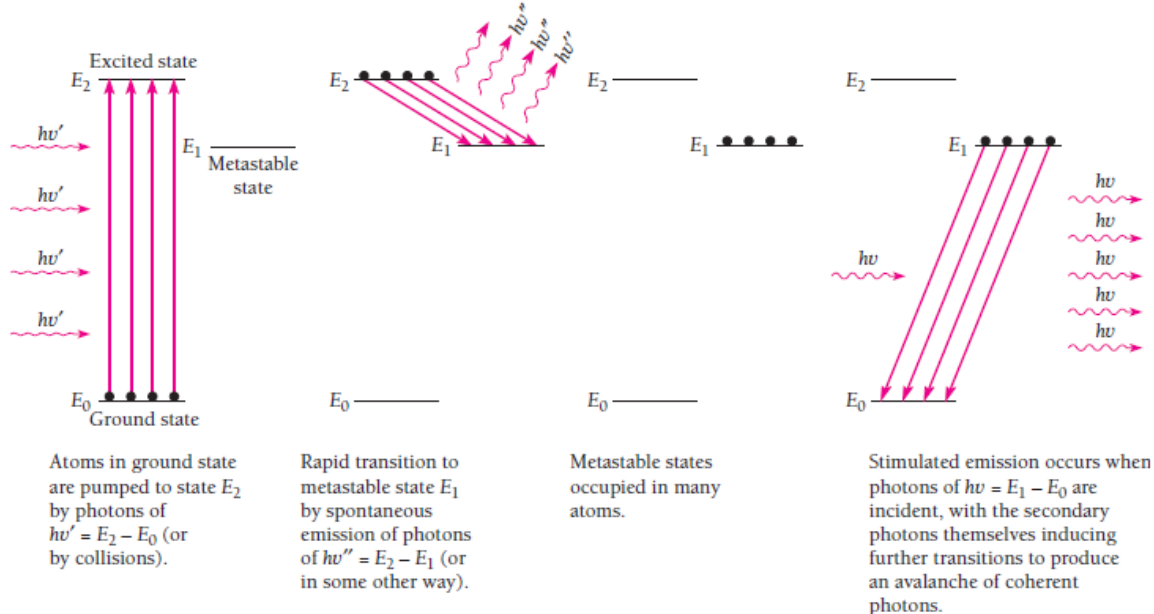

Figure 4.25 Transitions between two energy levels in an atom can occur by stimulated absorption, spontaneous emission, and stimulated emission.

1. **Stimulated absorption**. If the atom is initially in the lower state E_0, it can be raised to E_1 *by absorbing a photon* of energy $E_1 - E_0 = h\nu$.
2. **Spontaneous emission**. If the atom is initially in the upper state E_1, it can drop to E_0 *by emitting a photon* of energy $h\nu$.
3. **Stimulated emission** (Einstein, in 1917, was the first to point out a third possibility). An incident photon of energy $h\nu$ causes a transition from E_1 to E_0.
   - In stimulated emission, the radiated light waves are exactly in phase with the incident ones, so the result is an enhanced beam of coherent light.
   - A photon of energy $h\nu$ incident on an atom in the upper state E_1 has the same likelihood of causing the emission of another photon of energy $h\nu$ as its likelihood of being absorbed if it is incident on an atom in the lower state E_0.
- **A three-level laser**, the simplest kind, uses an assembly of atoms (or molecules) that have a metastable state $h\nu$ in energy above the ground state and a still higher excited state that decays to the metastable state (Fig. 4.26).

Figure 4.26 The principle of the laser.

Atoms in ground state are pumped to state E_2 by photons of $h\nu' = E_2 - E_0$ (or by collisions).

Rapid transition to metastable state E_1 by spontaneous emission of photons of $h\nu'' = E_2 - E_1$ (or in some other way).

Metastable states occupied in many atoms.

Stimulated emission occurs when photons of $h\nu = E_1 - E_0$ are incident, with the secondary photons themselves inducing further transitions to produce an avalanche of coherent photons.

- What we want is more atoms in the metastable state than in the ground state.

- If we can arrange this and then shine light of frequency ν on the assembly, there will be more stimulated emissions from atoms in the metastable state than stimulated absorptions by atoms in the ground state.
- The result will be an amplification of the original light. This is the concept that underlies the operation of the laser.
- The term **population inversion** describes an assembly of atoms in which the majority are in energy levels above the ground state; normally the ground state is occupied to the greatest extent.