
LECTURE 3

The Old Quantum Theory - Further Developments

- Line Spectra and Early Atomic Models
 - The Correspondence Principle
 - The Demise of the Old Quantum Theory
-

3.1 Line Spectra and Early Atomic Models

In 1859, Robert Bunsen (1811-1899) and Gustav Kirchhoff (1824-1887) developed an instrument to study the emission spectra from luminous sources. It was called the *spectroscope* and consisted of a prism to disperse incoming light and a telescope through which to observe the resulting spectrum. Bunsen and Kirchhoff were the first to discover that each chemical element possesses a unique characteristic line spectrum. That is, each element possesses a spectrum of lines occurring at certain wavelengths. The particular set of lines emitted is peculiar to the element, and can be used for identification purposes. For example, the emission spectrum from incandescent hydrogen vapors shows three characteristic lines in the visible region at 6563, 4861, and 4340 Å.

Many attempts were made to work out formulas that predicted the unique set of wavelengths of the radiation emitted from each different element. Most attempts were unsuccessful. In 1884 Johann Balmer energized hydrogen atoms and examined the radiation with a spectroscope. By studying the wavelengths of the observed spectrum, he produced an empirical relationship that gave the correct wavelengths for lines observed in the hydrogen spectrum. Just as important, it *did not* predict the existence of lines *that were not observed* as other formulas had. The *Balmer formula* which gives wavelengths of the lines observed in the *visible* hydrogen spectrum is

$$\lambda = 3645.6 \left[\frac{n^2}{n^2 - 4} \right] \times 10^{-8} \text{ cm} \quad (n = 3, 4, 5, \dots). \quad (3.1)$$

Question 3-1: Verify that the Balmer formula predicts the three characteristic wavelengths mentioned above.

In 1890, Rydberg saw that the Balmer formula could be written in such a way as to suggest more lines in the hydrogen spectrum. It is straightforward to show that equation (3.1) can be written as

$$\frac{1}{\lambda} = 27430 \left[1 - \frac{4}{n^2} \right] \text{ cm}^{-1}$$

or

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \quad (n = 3, 4, 5, \dots). \quad (3.2)$$

where R is known as Rydberg's constant, and to be consistent with equation (3.1), it must equal $109,720 \text{ cm}^{-1}$.

Rydberg suggested that the Balmer formula was actually a specific case for a more general formula of the form

$$\frac{1}{\lambda} = R \left[\frac{1}{n'^2} - \frac{1}{n^2} \right] \quad (n = n' + 1, n' + 2, \dots) \quad (3.3)$$

Indeed, in 1908 Lyman discovered the series that corresponds to $n' = 1$ with the corresponding wavelengths in the ultraviolet regions. In 1908, Paschen discovered the series corresponding to $n' = 3$; in 1922, Brackett discovered the series corresponding to $n' = 4$, and in 1924 Pfund observed the series corresponding to $n' = 5$.

Question 3-2: To which regions of the electromagnetic spectrum do the emissions lines in each series correspond? (a) Paschen series; (b) Brackett series; (c) Pfund series.

Attempts to Explain Atomic Emission Spectra

While the Rydberg formula correctly predicts the wavelengths of the lines in the various series of the hydrogen spectrum, it was developed, in somewhat the same spirit as Planck's blackbody formula, to match purely empirical observations. If our understanding of matter and radiation is accurate, it should be possible to derive this relationship from purely theoretical considerations. Since these emission lines occur from atomic processes, it is necessary to have a clear model of atomic structure.

The earliest theory of atoms was proposed in 1803 by John Dalton. According to his theory, all matter was composed of small, dense, indivisible particles of matter that resemble tiny billiard balls. Dalton called these particles *atoms*. He proposed that each element was composed of a different kind of atom. Furthermore, he proposed that the varying properties of different elements was due to the differences in their constituent atoms. While Dalton's theory provided a satisfactory explanation for the mass relationships in chemical reactions, it could not explain why atoms combined in certain ratios in reactions, nor could it explain atomic emission spectra.

During the nineteenth century, a number of experiments involving electric decomposition of solutions and electric decomposition of gases in sealed tubes indicated that atoms were divisible, and that they were composed of electrically charged particles. The charged particles were later called *electrons* and *protons*.

The first reasonable model of atomic structure was proposed by J. J. Thomson (1856 - 1940). He proposed that atoms consist of solid positively charged spheres with electrons dispersed throughout the volume of positive charge much like plums in plum pudding or raisins in a raisin cake. For obvious reasons, Thomson's model became known as the "plum pudding" or "raisin cake" model. With this model, Thomson was somewhat successful in providing a *qualitative* explanation for atomic emission spectra. In the lowest possible state, the electrons would be fixed in some equilibrium position. In materials at high temperatures, the electrons would vibrate about their equilibrium positions due to thermal motion. According to classical radiation theory, any accelerated charge will radiate electromagnetic radiation; thus, a vibrating electron would emit radiation at its vibrational frequency.

Question 3-3: Suppose that an electron in a raisin cake atom vibrates about its equilibrium position in simple harmonic motion with frequency 3.0×10^{15} Hz. (a) What is the wavelength of the emitted radiation? (b) To which region of the electromagnetic spectrum does this radiation correspond?

Although Thomson's model did provide a qualitative explanation for emission spectra, quantitative agreement was clearly lacking (see for example, *Eisberg and Resnick's* text, Example 4-1). In 1911, Lord Ernest Rutherford provided conclusive evidence that Thomson's model was structurally incorrect. In a series of experiments in which Rutherford bombarded thin sheets of gold foil with alpha particles, Rutherford concluded that

1. atoms were composed of mostly empty space, and
2. the positive charge was concentrated in a small dense region which he called the *nucleus*.
3. The negatively charged electrons orbit the nucleus and *the region over which they orbit constitutes the "volume" of the atom*.

The details of Rutherford's experiments, as well as his proposed theory based on those experiments are described in sections 4-1 and 4-2 of *Eisberg and Resnick's* text. The main point, though, is that the concept of the *nuclear atom* had been born. Rutherford's predictions based on a detailed theory of a *point* nucleus was completely verified in 1913 in the celebrated experiments of Geiger and Marsden.

Unfortunately, Rutherford's nuclear atom could not be explained on the basis of classical physics. The argument is straightforward. Any orbiting electron is accelerated. Accelerated charges radiate (and therefore give off energy). As an accelerated charge continues to radiate, its orbit would become smaller as its energy decreases, and it would eventually spiral into the nucleus. In other words, a Rutherford atom would collapse. To make matters worse, the collapse would occur over a very "short" time compared those of human comprehension - about 10^{-10} s. The observed stability of our universe (it is at least stable on that time scale) indicates a flaw in the Rutherford model, or in our understanding of matter and radiation, or in both.

In 1913 Neils Bohr (1885 - 1962) used Rutherford's concept of the "nuclear atom," ideas from Planck's quantum explanation of radiation, and a set of *ad hoc* postulates to develop a model of atomic structure that enabled him to derive the Rydberg formula for the hydrogen atom and all hydrogen-like species (that is, species with one valence electron, He^+ , Li^{++} , etc.).

3.2 The Bohr Atom

Geiger and Marsden's experiments clearly indicated that the basic structure of Rutherford's nuclear atom was consistent with experimental evidence. The main problem with Rutherford's model was that it was inconsistent with classical radiation theory -- a theory which we have seen is inadequate to explain both blackbody radiation and the photoelectric

effect. To circumvent the problems that arose from classical theory and to incorporate the ideas of quantization proposed by Planck and Einstein, Bohr made the following postulates:

1. An atomic system possesses a number of permitted states in which no emission of energy radiation takes place, even if the particles are in motion relative to each other (even though such an emission is to be expected in ordinary electrodynamics).
2. The dynamical equilibrium of the system in these permitted states is governed by the ordinary laws of mechanics, while these laws do not hold for the transition from one permitted states to another.
3. Any emission or absorption of radiation will correspond to the transition between two permitted states. The radiation emitted during such a transition is homogeneous and the frequency is determined by the relation

$$h\nu = E_1 - E_2$$

where h is Planck's constant and E_1 and E_2 are the energies of the system in the two permitted states.

4. The only permitted states of a system consisting of an electron rotating around a positive nucleus are those for which the orbital angular momentum of the electron is an integral multiple of $h/2\pi$ where h is Planck's constant.

Essentially, Bohr's first postulate accounts for the fact that atoms do not collapse. It simply states that classical electrodynamics does not apply to atoms. The second postulate states that in the "allowed" states of the system, classical mechanics can be applied. The third postulate describes the only instance in which an atom will radiate and incorporates the Einstein quantization condition. The fourth postulate says that the *angular momentum of the electrons in an atom are quantized*.

Bohr's postulates seem to provide a plausible qualitative explanation for the existence of line spectra. Each element has a unique spectrum because each element is composed of atoms with different permitted states that selectively follow rules of classical physics. A spectral line will be produced when an excited electron drops from a permitted state of higher energy to one with lower energy, thereby emitting electromagnetic radiation of a specific frequency and wavelength. We now see if there is quantitative agreement between Bohr's predictions for the wavelength of the emitted radiation and the Rydberg formula.

Quantitative Predictions of the Bohr Model

We will consider a hydrogenic species as a single electron of mass m , charge $-e$ in a circular orbit of radius r about an infinitely massive nucleus composed of Z protons, and thereby having charge $+Ze$.

The classical picture of such a system is illustrated in figure 3-1 with the sizes of both the nucleus and the electron greatly exaggerated.

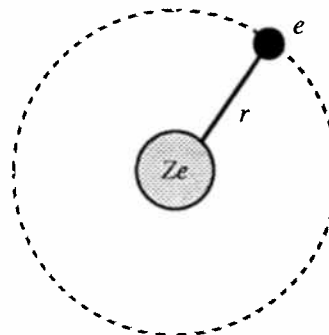


Figure 1-3

If this system obeys classical mechanics, then the centripetal force required to keep the electron in its circular orbit about the nucleus must be provided by the Coulombic attraction between the nucleus and the electron, or

$$\frac{mv^2}{r} = \frac{kZe^2}{r^2} \quad (3.4)$$

where $k = (4\pi\epsilon_0)^{-1}$ is the electric constant of free space.

It follows from equation (3.4) that the kinetic energy, T , of the electron is given by

$$\frac{1}{2} mv^2 = \frac{kZe^2}{2r} \quad (3.5)$$

The electrical potential energy, V , of the electron in this orbit is given by $-e\Phi$ where Φ is the electric potential caused by the nucleus at the location of the electron:

$$-e\Phi = -\frac{kZe^2}{r} \quad (3.6)$$

The total energy of the system is, from equations (3.5) and (3.6)

$$E = T + V = -\frac{kZe^2}{2r} \quad (3.7)$$

Equation (3.7) gives us the energy of an electron in such a system at any distance r from the nucleus. Thus far, the approach has incorporated only classical mechanics and Coulomb's law (postulate 2). In Bohr's theory, however, *not all values of r are permissible*. The only permissible values of r are those for which the orbital angular momentum of the electron is quantized as proposed by postulate 4.

We will now proceed to find the allowed values of r . The orbital angular momentum, L of the electron is mvr . Using equation (3.4) once again, we find

$$mvr = \sqrt{kZmre^2}.$$

According to postulate 4, this quantity must equal an integral multiple of $h/2\pi$:

$$\sqrt{kZmre^2} = n \frac{h}{2\pi} \quad (n = 1, 2, 3, \dots) \quad (3.8)$$

Since this particular combination of Planck's constant divided by 2π appears throughout all areas of quantum physics, it is reasonable to define a new quantity $\hbar = h/2\pi$. Equation (3.8) then becomes

$$\sqrt{kZmre^2} = n \hbar \quad (n = 1, 2, 3, \dots) \quad (3.9)$$

Solving equation (3.9) for r yields an expression for the permissible or allowed values of r :

$$r_n = \frac{n^2 \hbar^2}{k Z m e^2} \quad (n = 1, 2, 3, \dots) \quad (3.10)$$

Since each permissible value of r depends on a particular value of n , the value of n is usually used as a subscript for identification purposes.

When equation (3.10) is substituted into equation (3.7), we see that the electron is permitted only certain energy values, and these are the energies of the permitted states of the atomic system:

$$E_n = - \frac{k^2 Z^2 m e^4}{2 n^2 \hbar^2} \quad (n = 1, 2, 3, \dots) \quad (3.11)$$

In other words, Bohr's postulate of *angular momentum quantization* leads to *energy quantization*. Each permitted state of the hydrogen atom system is characterized by a *definite energy* determined by equation (3.11). The integer n is called the *quantum number* of the state and is used to identify the state. The state corresponding to $n = 1$ has energy E_1 and is called the *ground state* of the system. The state corresponding to $n = 2$ has energy E_2 and is called the *first excited state* of the system. The states corresponding to $n = 3, 4, 5, \dots$ are called the *second, third, and fourth excited states* and so on. The energy of the system is said to be *quantized* because it can change only by discrete amounts. The only permitted energy values of this system are E_1, E_2, E_3, \dots with all other value excluded.

Question 3-4: What is the significance of the minus sign in equation (3.11)?

How does this model explain the characteristic lines in atomic emission spectra? To answer this question, suppose that an atomic electron begins in the permitted state with energy E_2 and drops to a state of lower energy E_1 . According to postulate 3, the atom will emit electromagnetic radiation of frequency ν , where

$$\nu = \frac{E_2 - E_1}{h}$$

Using expressions for E_1 and E_2 obtained from equation (3.11) we obtain

$$\nu = \frac{k^2 Z^2 m e^4}{4\pi \hbar^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (3.12)$$

If it is valid to treat this radiation classically, $\nu = c/\lambda$, and we have

$$\frac{1}{\lambda} = \frac{k^2 Z^2 m e^4}{4\pi c \hbar^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (3.13)$$

which bears a remarkable resemblance to the Rydberg formula that was based on purely empirical observations.

Question 3-5: (a) What is the numerical value of the coefficient of the bracketed terms in equation (3.13) for the case $Z = 1$ (atomic hydrogen)?
 (b) What is the physical significance of this coefficient?

The Rydberg constant for hydrogen, as determined by the Bohr theory, is $109677.578 \pm 0.012 \text{ cm}^{-1}$, which is in agreement with spectroscopic observations; Rydberg's original value was slightly higher.

Corrections for Finite Nuclear Mass and Motion of the Nucleus

If your computations for *Question 3-5* were correct you should have obtained a value of $109737.318 \text{ cm}^{-1}$ for the coefficient of the bracketed terms. Clearly, this value is in disagreement with the value of the Rydberg constant quoted above. The reason for the discrepancy lies in our choice of model for a Bohr atom. In our calculation, we assumed that the nucleus was infinitely massive; in other words, we neglected the motion of the nucleus during one revolution of the electron. The nucleus of a hydrogen atom consists of a single proton. The mass of a proton is about 1836 times greater than that of an electron. We would expect that the nuclear motion should be small compared to that of the electron over one revolution. To first approximation this is true and we have a fairly good model. Even at the turn of the century, however, atomic spectroscopy could be performed to a level of precision that would produce discrepancies with our model.

The main features of our model are correct and consistent with the postulates of Bohr. To obtain agreement with spectroscopic measurement, however, we must consider the finite mass of the nucleus and its resulting motion.

The classical motion of two particles of mass m_1 and m_2 , some distance r apart, takes place about a point called the *center of mass of the system*. If the center of mass is at rest, the total energy of the system of two particles is the same as that of a *fictitious* particle called the *relative particle*, which has mass (called the *reduced mass*)

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (3.14)$$

Question 3-6: (a) What is the reduced mass of the electron-proton system that makes up the hydrogen atom? (b) How does this compare with the mass of the electron?

The problem is equivalent then to that of a particle of reduced mass μ which orbits the fixed center of mass at a distance r . In other words, the energy of a Bohr atom is the same as that of the *relative particle of reduced mass* given by equation (3.14) that orbits a fixed point (the center of mass) at a distance r . Note that the distance between the electron and the nucleus is the same as the radial orbit of the *relative particle* about the center of mass.

Question 3-7: How could we modify equation (3.13) to include the finite nuclear mass without redoing the calculation?

Question 3-8: How much error is introduced in the ground state energy of the hydrogen atom by using the electron mass instead of the reduced mass?

It can be shown that all of the results of the previous section are valid if the electron mass m is everywhere replaced by the reduced mass μ of the hydrogenic system under consideration. The permitted energy levels of any hydrogenic system are given by

$$E_n = - \frac{k^2 Z^2 \mu e^4}{2 n^2 \hbar^2} \quad (n = 1, 2, 3, \dots) \quad (3.15)$$

and the corresponding relationship that determines the wavelength of the radiation emitted when the electron drops from any level n_2 to any lower level n_1 is

$$\frac{1}{\lambda} = \frac{k^2 Z^2 \mu e^4}{4\pi c \hbar^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (3.16)$$

The combination $ke^2/\hbar c$ is a dimensionless number, very close to $1/137$. It is called the *fine structure constant* and is denoted by the symbol α . Then, equation (3.16) can be expressed as

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (3.17)$$

where R is the Rydberg constant for the hydrogenic species with reduced mass μ and nuclear charge Z :

$$R = \frac{Z^2 \mu c^2 \alpha^2}{2 hc} \quad (3.18)$$

The Hydrogen Spectrum

One of the great successes of the Bohr model of atomic structure was its predictions of the spectrum of the hydrogen atom. Equation (3.15) can be written as follows:

$$\begin{aligned} E_n &= - \frac{\mu c^2}{2} \frac{\alpha^2 Z^2}{n^2} \\ &= - \frac{5.11 \times 10^5 \text{ eV}}{2} \frac{1}{137} \frac{Z^2}{n^2} \\ &= - \frac{Z^2 13.6 \text{ eV}}{n^2} \end{aligned}$$

Thus, for the hydrogen atom ($Z = 1$), the ground state energy is -13.6 eV. Since this is the state normally occupied by the electron, this is also the *ionization energy*, or the work required to free the electron. The excited states of the hydrogen atom have energies $-13.6/4$ eV, $-13.6/9$ eV, and so on. These values are in agreement with experiment.

It is customary to display these graphically in an *energy level diagram* as shown in Figure 3-2. The horizontal axis has no physical meaning. The vertical axis shows the values of

the allowed energies with the lowest energy on the bottom. In practice, such diagrams are usually drawn to scale along the vertical axis. Also shown in Figure 3-2 are transitions that give rise to the first four lines in each of the Lyman, Balmer, and Paschen Series.

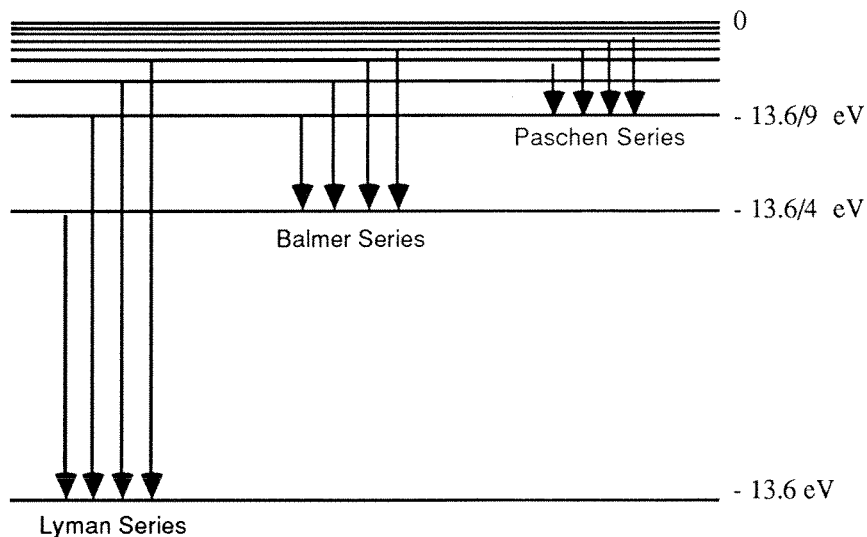


Figure 3-2

3.3 The Franck-Hertz Experiment - Direct Evidence of Discrete Energy Levels

A correct interpretation of Planck's blackbody formula, as well as Bohr's atomic theory, *predict* that electrons in cavity walls and in atoms possess quantized energy states. Furthermore, the discrete frequencies in atomic spectra *provides compelling evidence* that atoms possess discrete energy levels, provided that Einstein's equation, $E = h\nu$ is accepted. *Direct confirmation* of the quantization of atomic energy states was presented by James Franck and Gustav Hertz in 1914.

In their celebrated experiment, Franck and Hertz investigated the effect of collisions between electrons and the atoms of mercury vapor¹. While radiation was not involved in the transfer of energy between the electrons and the atoms, the results of their experiment showed that the electrons lost energy only in *discrete* amounts through inelastic collisions with the atoms. In 1925, Franck and Hertz were awarded the Nobel Prize for their efforts, and their contribution to the field of quantum physics. Ironically, Franck once explained in a filmed presentation that when he and Hertz performed the original experiment, they had not yet heard of Bohr's atomic theory.

¹James Franck and Gustav Hertz, Verh. Dtsch. Phys. Ges. **16**, 512 (1914)

Figure 3-3 shows the apparatus used by Franck and Hertz in their famous experiment. Electrons from a hot cathode C are accelerated through mercury vapor toward grid G . The electrons that pass through the grid can reach the anode A provided that they have sufficient kinetic energy to overcome a small retarding potential between the grid and the anode. The resistance of the apparatus is adjustable so that the accelerating voltage between the cathode and the grid, V_G can be increased or decreased in a continuous fashion. The circuit contains a volt meter and an ammeter to measure the grid voltage V_G , and the anode current respectively. If there were no mercury vapor present, an increase in the grid voltage V_G would always result in an increase in the anode current, as it will in any vacuum tube.

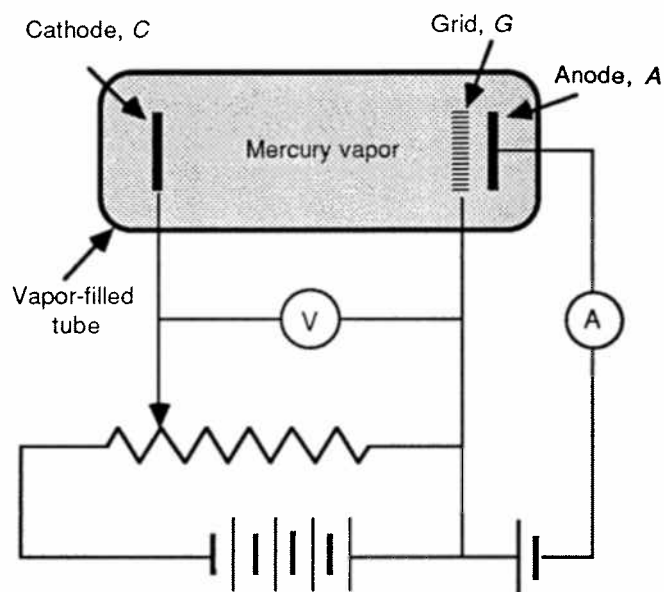


Figure 3-3

As shown in Figure 3-4, when the grid voltage is increased from zero, the anode current increases, as expected, until a grid voltage close to 5.0 V is reached. If the grid voltage is increased beyond this value, the current drops abruptly. If the grid voltage is still increased the current again rises until a grid voltage close to 10 V is reached. If the grid voltage is increased beyond 10 V, another abrupt drop is observed in the anode current. How do these observations imply the existence of discrete energy levels? Apparently, when the kinetic energy of the electrons is lower than 5.0 eV, they undergo *elastic* collisions with the atoms of the mercury vapor thereby retaining their kinetic energies. These electrons have enough kinetic energy to overcome the retarding potential and reach the anode thereby causing current to flow through the anode branch of the circuit. At a kinetic energy of 5 eV, however, the collisions with the vapor atoms results in an *inelastic* collision in which the electrons lose their kinetic energy to the atoms. After such a collision, the electrons do not possess enough kinetic energy to overcome the retarding potential, so they cannot reach the anode. Apparently, inelastic collisions excite the atoms of the vapor.

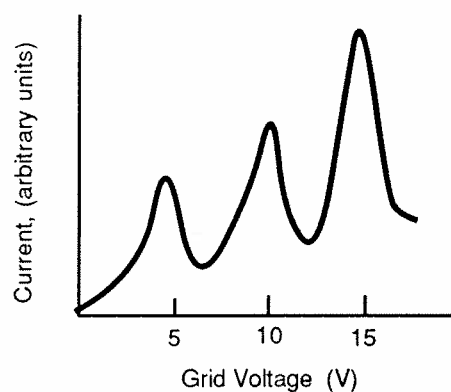


Figure 3-4

If the energy levels of the atom are quantized, then the atom can only absorb certain *discrete* amounts of energy. These results seem to indicate that the first excited state of the mercury atoms is about 5 eV above the ground state. If an electron with less than 5 eV collides with a mercury atom, none of the energy can be absorbed. If an electron with energy 5 eV or more collides with a mercury atom, then the energy will be absorbed and excite the atom. These conclusions are in agreement with the spectroscopic evidence that the first excited state in mercury is 4.86 eV above the ground state.

Question 3-9: Suppose an electron with 6 eV collides with a mercury atom. What happens to the extra energy?

Question 3-10: In the actual Franck-Hertz experiment, the first drop in current occurs at a grid voltage 6.6 or 6.7 V while subsequent drops occur at 5 V intervals. That is, the first drop in the anode current occurs at 6.7 V. The current is then observed to drop around 11.7 V, 16.7 V, etc. Explain.

3.4 Quantization and the Wilson-Sommerfeld Rule

Although Bohr's theory was in excellent agreement with experiment for the hydrogen atom, and the Franck-Hertz experiment confirmed the existence of quantized atomic energy states, the appearance of quantization on a microscopic level was still a mystery. In 1915, W. Wilson and A. Sommerfeld provided a theoretical explanation. They independently proposed that quantization will be apparent in any system for which the coordinates are periodic functions of time. Formally, the *Wilson-Sommerfeld quantization rule* states that *for any physical system for which the coordinates are periodic functions of the time, there is a quantization rule*

$$\oint_C p_q dq = n_q h \quad (3.19)$$

where q is the coordinate, p_q is the corresponding momentum, n_q is an integer called a quantum number, and h is Planck's constant and the integration is carried out over one cycle of the motion. Note that this rule can be applied to the electrons in the walls of a blackbody cavity, as well as to the electron in a Bohr atom. Both systems represent electrons that undergo periodic motion (simple harmonic in the former case, and uniform circular motion in the latter case). It will be left as a student exercise to show that Planck's quantization of the total energy of the electrons and Bohr's quantization of the angular momentum of an orbiting electron are special cases of (3.19).

3.5 The Correspondence Principle

As students of physics, you are now in an awkward position. You have two different radiation laws, each of which seems to work in certain circumstances. Classical electrodynamics predicts one radiation law for the radiation emitted from an accelerated charge which works well in a variety of situations. It works quite well, for example, in predicting the radiation field both near to and far from a transmitting dipole antenna. Yet, it fails miserably if one tries to use it to predict the radiation emitted from an electron in a Bohr atom. The obvious question at this point is "how do we know when to use classical electrodynamics and when to use Bohr's postulates?"

Bohr answered this question in 1923 when he stated an auxiliary postulate called the *correspondence principle*. This principle states that *the result of any quantum theory must approach the classical result in the limit in which the corresponding quantum number approaches infinity*. Eisberg and Resnick carry through the correspondence for a harmonic

oscillator in section 4-11 of their text; the correspondence principle is applied to the hydrogen atom in *Example 4-11*.

3.6 The Demise of the Old Quantum Theory

Bohr's atomic theory showed great promise with its prediction of the hydrogen spectrum that agreed with experiment. Unfortunately, it failed miserably when it was applied to neutral helium, the next element in the periodic table. It also became apparent that when the hydrogen spectrum is examined closely, the spectral lines are actually a set or multiplet of two or more lines. Bohr's theory had no explanation for this *fine structure*. In 1916, A. Sommerfeld attempted to explain the fine structure of hydrogen in terms of elliptical orbits. Although Sommerfeld's theory was somewhat successful for the hydrogen atom, his success was purely coincidental. Like Bohr's original theory, it could not be extended to multi-electron atoms. While the Wilson-Sommerfeld rules do lead to a number of successful predictions, they can only be applied to periodic systems; there are many systems of physical interest that are not periodic in time. It became clear between the years 1920 and 1925, that a more comprehensive theory must be proposed to explain and predict the behavior of systems that exhibit energy quantization. The historical development of the quantum theory of atoms can be summarized somewhat generally as follows:

1913 - 1920	The origin and (extensive) application of the old quantum theory of the atom
1920 - 1925	The decline of the old quantum theory
1925 - 1926	The development of the new <i>quantum mechanics</i> and its application to simple physical systems
1927 -	The application of <i>quantum mechanics</i> to chemical systems

We now proceed to examine the events and theories that led to the development of *modern quantum mechanics* and its application to atomic systems.

References and Suggested Reading

Early atomic models including Rutherford's model of the nuclear atom are discussed in
 Eisberg and Resnick, Chapter 4, sections 1 and 2.
 Serway and Moses, Chapter 3, section 3.

Atomic spectra and the Bohr atom, and a need for a "non-classical" atomic theory are discussed in
 Eisberg and Resnick, Chapter 4, sections 3 through 7.
 Serway and Moses, Chapter 3, section 4.

The Franck-Hertz experiment is discussed in
 Eisberg and Resnick, Chapter 4, section 8.

The Wilson-Sommerfeld Quantization rules, the correspondence principle, and a critique of the Old Quantum Theory can be found in
 Eisberg and Resnick, Chapter 4, sections 9 through 12