University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Robert Katz Publications

Research Papers in Physics and Astronomy

1-1958

Physics, Chapter 42: Optical Spectra and Atomic Structure

Henry Semat City College of New York

Robert Katz University of Nebraska-Lincoln, rkatz2@unl.edu

Follow this and additional works at: https://digitalcommons.unl.edu/physicskatz



Part of the Physics Commons

Semat, Henry and Katz, Robert, "Physics, Chapter 42: Optical Spectra and Atomic Structure" (1958). Robert Katz Publications. 175.

https://digitalcommons.unl.edu/physicskatz/175

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Robert Katz Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Part Six

ATOMICS AND NUCLEONICS

42

Optical Spectra and Atomic Structure

42-1 Types of Optical Spectra

When light passes through a prism spectroscope or a diffraction-grating spectroscope, an optical spectrum is obtained in which the intensity of the radiation may be analyzed as a function of wavelength. The spectrum may be observed visually in the limited wavelength region to which the eye is sensitive; it may be focused on a photographic plate or upon a thermocouple or thermopile. Our knowledge of the structure of atoms and molecules is largely dependent upon the analyses of optical spectra, for these spectra are characteristic of the emitting atoms or molecules. Even before the spectra of atoms were properly understood in terms of the atomic structure, it was possible to determine the chemical composition of an unknown substance by study of its spectrum.

The spectra obtained from radiating bodies are called *emission spectra* and are classified as *continuous spectra*, *band spectra*, and *line spectra*, according to their appearance in a spectroscope. Continuous spectra are emitted by solids, liquids, and dense opaque gases at high temperatures. The spectrum of the sun, or of a black body, is a continuous spectrum and, as we have seen in Section 18-6, the shape of the black-body spectrum is characteristic of its temperature. Gases at low pressures emit *band* or *line* spectra. Line spectra have their origin in the energy changes which take place in the atoms of a gas, while band spectra are associated with similar changes in the molecules.

To early investigators the line spectra of atoms and the continuous spectra of black bodies posed seemingly insurmountable problems, for all explanations of the wavelengths of the spectral lines, or of the shape of the continuous spectra, were inadequate. For example, by analogy with 782

the properties of organ pipes and vibrating bodies, a black body was assumed to be capable of sustaining electromagnetic vibrations in much the same manner as an organ pipe is capable of generating a fundamental and its overtones, under appropriate excitation, or as a room is capable of sustaining standing waves. Each harmonic was assumed to be a mode of vibration and to have energy kT, as in the case of the specific heats of gases, but the calculated spectrum was in violent disagreement with the observed spectrum. To explain the shape of this spectrum Max Planck proposed, in 1900, that the energy of a given mode of vibration depended upon its frequency in accordance with the relationship

$$\mathcal{E} = hf, \tag{42-1}$$

where \mathcal{E} is the energy, f is the frequency of vibration, and h is a constant now known as Planck's constant whose measured value is

$$h = 6.624 \times 10^{-27} \text{ erg sec.}$$

Planck's conception, in contradiction to the well-established principle of equipartition of energy, successfully predicted the shape of the black-body radiation spectrum. Planck's formula was subsequently interpreted by Einstein as implying that radiation was emitted or absorbed in discrete units called quanta, each of which had an energy given by Equation (42-1). This interpretation helped to explain many phenomena observed in the interaction of radiation and matter such as the photoelectric effect and the emission and absorption of radiation. According to the quantum theory of light, the energy in a beam of monochromatic light of frequency f is determined by the number of quanta hf in the beam rather than by the square of the amplitude of vibration.

From our discussion of black-body radiation we have seen that the efficiency of a body as a radiator of energy is equivalent to the efficiency of the body as an absorber of radiation. Thus we should expect that, when white light irradiated a gas, it would absorb precisely those wavelengths which it was capable of emitting. A spectrum produced in this manner is called an *absorption spectrum*. Contrary to classical expectations it was discovered that only a few of the lines in the emission spectrum of a gas were to be found in its absorption spectrum.

42-2 Spectrum of Hydrogen

Hydrogen, the simplest of the elements, has been investigated most extensively both theoretically and experimentally. The knowledge gained from this study has acted as a guide to the study of more complex elements.

As shown in Figure 42-1, the radiation emitted by hydrogen is a line spectrum, whose wavelengths were shown by Balmer, in 1855, to be related by a formula which may be stated as

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$
 (42-2)

for light in the visible spectrum. In this equation λ is the wavelength, R is a constant known as the *Rydberg constant* whose value for hydrogen is $R = 109,677.76 \text{ cm}^{-1}$, and n is an integer greater than 2. By substituting

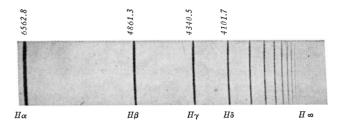


Fig. 42-1 Photograph of the emission spectrum of hydrogen showing the Balmer series lines in the visible and the near ultraviolet regions. The numbers represent the wavelengths of the corresponding lines in angstrom units. (Reprinted by permission from Atomic Spectra and Atomic Structure, by G. Hertzberg, Dover Publications.)

for n in Equation (42-2) the successive values 3, 4, 5, . . . , we obtain the wavelengths of the lines in the visible region and also in the near ultraviolet region. These lines form a series known as the *Balmer series* of hydrogen.

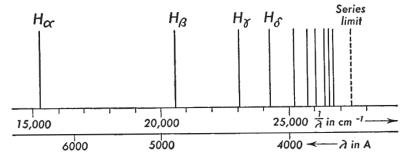


Fig. 42-2 Graph of the positions of the lines of the Balmer series. The upper scale is the reciprocal of the wavelength in centimeters, while the lower scale is the wavelength in angstrom units.

The relative positions of these lines are shown in Figure 42-2. As n approaches infinity, the wavelength difference between adjacent lines gets smaller; the lines crowd together and approach a limit known as the series limit.

In addition to the Balmer series in the visible spectrum, hydrogen emits radiation in the ultraviolet region, in a series known as the *Lyman series*, which is described by a formula like Equation (42-2), except that the first term in the parentheses is replaced by $1/1^2$, and the symbol n is replaced by integers from 2 on; there are lines in the infrared which can be described by a series formula in which the first term in the parentheses is replaced by $1/3^2$, and so on. The other series of hydrogen are shown in Figure 42-3.

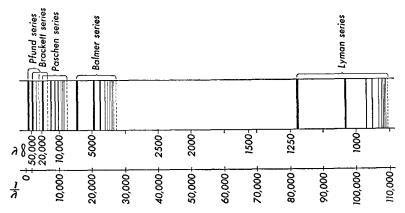


Fig. 42-3 Relative positions of the lines of the different spectral series of hydrogen. The upper scale is in angstrom units, while the lower scale is the reciprocal of the wavelength in centimeters.

None of this great regularity in the spectrum of hydrogen could be explained by classical ideas. In absorption at ordinary temperatures, hydrogen exhibits only the Lyman series in the ultraviolet, while several of the absorption lines in the solar spectrum, known as the *Fraunhofer lines*, lie in the Balmer series. The first quantitatively correct derivation of the Balmer formula was given by Bohr, in 1913, in his model of the hydrogen atom. This theory has played such an important role in the development of atomic physics that, even though it has been modified and extended by later developments, it is worth while presenting the original simplified theory.

42-3 Bohr's Theory of the Hydrogen Atom

In his theory of the hydrogen atom, Bohr chose as a model a positively charged central nucleus, consisting of a proton, about which a negatively charged electron revolved in a circular orbit. In accordance with classical theory, a revolving electron experiences a centripetal acceleration and should radiate electromagnetic waves, so that the electron should lose energy and slowly spiral into the nucleus. Bohr supposed that this would not happen in the atom, and that only certain orbits were permitted the

electron according to special quantum conditions. An allowable orbit was called a *stationary state*, for the electron could remain in a particular allowed orbit without the emission of radiation or without a change in the energy of the system.

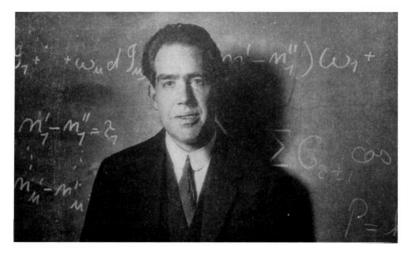


Fig. 42-4 Niels Bohr. He made outstanding contributions to the modern theory of the nuclear structure of the atom and formulated the theory of nuclear processes. (Courtesy of American Institute of Physics.)

If e represents the magnitude of the charge of the electron or the proton, the electrical force between the electron and proton is given by Coulomb's law, expressed in Gaussian (electrostatic) units by

$$F = \frac{e^2}{r^2},$$
 (42-3)

in which r is the radius of the circular orbit. The nucleus, having a mass of 1,836 times that of the electron, is assumed to remain stationary at the center of the circle, as though its mass were infinite. The force on the electron owing to the attraction of the two charges is directed toward the center and supplies the centripetal force necessary to keep the electron in its circular motion. Thus we have

$$\frac{mv^2}{r} = \frac{e^2}{r^2},$$
 (42-4)

in which m is the mass of the electron, and v is its speed.

The energy of this system is partly potential energy and partly kinetic energy. The potential energy of the negatively charged electron in the field of the nucleus is given by the expression $-e^2/r$, while the kinetic

energy is simply equal to $\frac{1}{2}mv^2$. From Equation (42-4) we see that

$$mv^2 = \frac{e^2}{r}$$
,

so that the total energy \mathcal{E} of the electron in the atom is given by

$$\mathcal{E} = \frac{1}{2}mv^2 - \frac{e^2}{r} = -\frac{1}{2}\frac{e^2}{r}.$$
 (42-5)

The minus sign for the total energy indicates that the electron is bound to the nucleus, and that positive work is required to remove the electron to infinity where it has zero energy when at rest.

Nothing thus far in the theory indicates that the radiation should be emitted in the form of sharp spectral lines. Bohr introduced two postulates to account for the emission of sharp spectral lines. The first of these postulates may be stated as follows: Only those orbits are permissible for which the angular momentum of the electron is an integral multiple of $h/2\pi$. Thus we have

$$mvr = n\frac{h}{2\pi}, \qquad (42-6)$$

where n is an integer called a quantum number. The orbits which satisfy this condition are called stationary orbits. The second of Bohr's postulates states that whenever the energy of the atom is decreased from its initial value \mathcal{E}_i to some final value \mathcal{E}_f , the atom emits radiation of frequency f in the form of quanta or photons of energy hf such that the energy of the system of atom plus quantum is conserved, or

$$\boxed{\mathcal{E}_i - \mathcal{E}_f = hf.} \tag{42-7}$$

The radii of the permissible orbits can be obtained by eliminating v from Equations (42-4) and (42-6) and solving for r, yielding

$$r = n^2 \frac{h^2}{4\pi^2 m e^2} {42-8}$$

By substituting known values of h, m, and e, and setting n = 1, we find that the radius of the first orbit is

$$r_1 = 0.529 \times 10^{-8} \text{ cm} = 0.529 \text{ A}.$$

The energy of any orbit characterized by any quantum number n can

be determined by eliminating r from Equations (42-5) and (42-8), yielding

$$\mathcal{E} = -\frac{2\pi^2 m e^4}{n^2 h^2} \cdot \tag{42-9}$$

Applying Bohr's second postulate, we find that the frequency f of the radiation emitted when an electron goes from its initial orbit of quantum number n_i to another orbit n_f is

$$f = \frac{\mathcal{E}_i - \mathcal{E}_f}{h} = \frac{2\pi^2 me^4}{h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \cdot \tag{42-10}$$

Here is a result that can be tested by comparison with experiment. Equation (42-10) may be re-expressed in terms of the wavelength of the emitted line by making use of the equation $\lambda f = c$, where c is the speed of light. We find that

$$\frac{1}{\lambda} = \frac{2\pi^2 me^4}{ch^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \cdot \tag{42-11}$$

This equation can be checked directly against experimental results. On comparison with Equation (42-2), which represents the experimental values of the wavelengths of the Balmer series, we find that our theoretical expression predicts a value for the Rydberg constant R of

$$R = \frac{2\pi^2 me^4}{ch^3} = 109,740 \text{ cm}^{-1},$$

the latter value calculated from known values of the constants in the equation. This value is in remarkably good agreement with the experimental value of R quoted earlier. The Bohr theory thus provided the first successful and satisfying explanation of the emission of sharp spectral lines by hydrogen, not only qualitatively but quantitatively as well. The model not only gave correct values of the wavelengths of the Balmer series, and the other spectral series of hydrogen, but explained the reason for the integers appearing in the wavelength formulas.

The hydrogen atom was pictured as a series of imaginary concentric rings surrounding the nucleus, as shown in Figure 42-5, representing the allowed orbits of the electron. Each ring was characterized by a quantum number n which described the radius of the orbit, the angular momentum of the electron in the orbit, and the energy of the electron in the orbit. At any instant of time a neutral hydrogen atom had an electron in one of these orbits. In emission, an electron could make a spontaneous transition from any of these orbits to any other orbit of lower energy, that is, closer to the nucleus, and in this transition light would be emitted of appropriate energy, or wavelength. Thus if the electron jumped from orbit n=4 to

orbit n=2, the wavelength of the radiation corresponded to the blue line H_{β} ($\lambda=4861.3~\mathrm{A}$) of the Balmer series. In a gaseous discharge tube, collisions between neutral atoms and charged ions caused the atoms to become ionized; that is, the atoms were given sufficient energy in the collision to overcome the binding energy of the electron to the proton. The

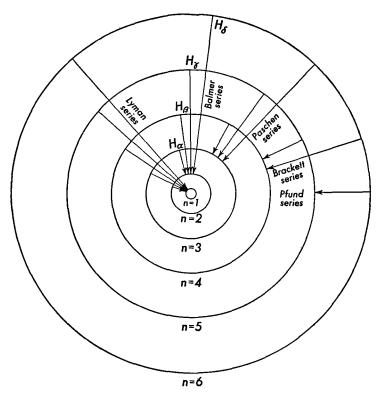


Fig. 42-5 Possible quantum jumps between stationary orbits giving rise to the different spectral series of hydrogen.

electron then had positive energy of any amount. Since any system generally seeks its configuration of lowest potential energy, an unbound electron would tend to drop into one of the unfilled orbits of neutral hydrogen, with the emission of a quantum of radiation. On passing from the outer orbits to the orbit for which n=1, the electron might fall into intermediate orbits for a short time emitting an appropriate quantum of radiation in each transition. Since any small quantity of hydrogen contains an enormous number of atoms, all of the lines of the hydrogen spectrum are emitted simultaneously from a gas discharge tube.

42-4 The Hydrogen Energy-Level Diagram

The results discussed above can be represented in a simple and elegant manner by means of an energy-level diagram, as shown in Figure 42-6. In this diagram the energies of the various orbits corresponding to the different quantum numbers n are plotted on a vertical scale. Two different sets of numbers are shown in the diagram. The numbers on the right are the reciprocals of wavelengths in centimeters, and, when multiplied by the constants ch, will yield the energy $\mathcal E$ in ergs. Differences between these numbers for any two energy levels give the reciprocal of the wavelength, called the wave number (the number of waves per centimeter), of the radiation emitted when an electron goes from an upper level to a lower one. The numbers on the left give the energy in electron volts. Recalling that an electron volt is the energy acquired by an electron in falling through a potential difference of 1 volt, we see that the energy, expressed in electron volts, may be converted to energy expressed in joules by multiplying by the charge of the electron, in coulombs. On the left of the diagram the lowest level, called the *ground state*, is taken as the zero of energy. we see that 13.60 ev of energy must be delivered to a neutral hydrogen atom, in its ground state, to ionize the atom. This is called the ionization potential, for if hydrogen is placed in a gaseous discharge tube which is provided with electrodes, there can be no significant conduction of electricity through the gas until the electrode potential difference is higher than the ionization potential. Beyond the level designated as $n = \infty$, the electron is outside the atom and can have any value of energy; this is the shaded region of the diagram. The numbers on the vertical lines between any two levels represent the wavelength in Angstrom units of the radiation emitted when the energy of the atom changes from one level to another. All lines ending at the same energy level represent spectral lines of the same series. The thickness of the lines in the diagram represents the relative intensities of the spectral lines, although it must be pointed out that one of the failings of the Bohr theory is that it makes no attempt to predict the line intensities. This prediction has been accomplished with the aid of more advanced methods called wave mechanics or quantum mechanics.

The advantage of an energy-level diagram is that it is independent of any particular model of the atom. Such a diagram may be constructed from experimental data using only the wavelengths of the spectral lines of an atom. The construction is based upon Bohr's postulate that the frequency of spectral lines is determined by Equation (42-7), regardless of the particular mechanical model chosen to represent the atom. Thus all spectra, whether atomic, molecular, or nuclear, are analyzed in terms of energy-level diagrams, based upon Bohr's analysis of hydrogen.

At temperatures where the mean translational energy of $\frac{3}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature, is consider-

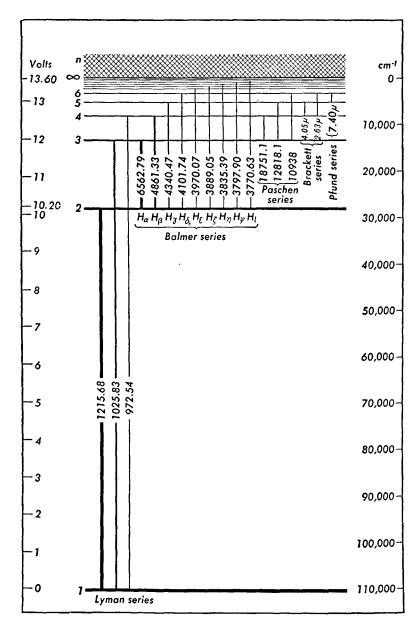


Fig. 42-6 The energy-level diagram for hydrogen.

ably less than the difference in energy of 10.20 ev between the ground state and the first excited state, we would expect to find the vast majority of hydrogen atoms in the ground state, for there is insufficient energy available to raise atoms from the n = 1 state to the n = 2 state. Thus

only lines corresponding to transitions from the n=1 state to higher levels should occur in absorption, at such temperatures. Only when the gas is at sufficiently high temperatures should we expect to find absorption lines of the Balmer series, for only at high temperatures will there be a significant population of hydrogen atoms whose electrons are in the n=2 level. Thus the question of why not all of the spectral lines appear in an absorption spectrum is resolved by the Bohr theory.

If the temperature is sufficiently high, the kinetic energy of translation exceeds 13.6 ev, and the gas is completely ionized. In this event we would expect that the protons and electrons act as separate particles which are not bound to each other and which are free to be much closer together than would be permitted by the Bohr quantum conditions. expect to see no spectral lines from a gas at sufficiently high temperatures. Thus the sun and the stars emit continuous spectra rather than line spectra. The line spectra are formed in absorption when the continuous spectrum passes through the cooler gases in the outer atmospheres of the sun and the stars. Furthermore, the stars and the sun consist of gases at high temperatures, but these gases are of much greater density than the solid matter on earth. On earth we must expect that the closest distance of approach of two hydrogen atoms is approximately the diameter of the first Bohr orbit. At the temperature of a star, the electron is unbound, and there is no such restriction, so that the distance of approach of two protons, or of a proton and an electron, is limited only by their kinetic energies, and stellar densities may seem enormous when compared to the densities of solid substances on earth.

When hydrogen is illuminated with light whose quantum energy is greater than 13.6 ev, each quantum has sufficient energy to liberate an electron from the atom. This is the *photoelectric effect* in a gas. Light of longer wavelength cannot cause ionization of hydrogen gas, no matter how intense the beam or how long the period of illumination. This prediction from the energy-level diagram is in agreement with experimental results but is quite different from our expectations based on classical theory. From a purely classical viewpoint, the energy flux in a light beam is related to its vibration amplitude, so that light of any frequency should be able to liberate photoelectrons if its intensity is sufficiently great. Here too, the quantum viewpoint is in agreement with experiment, while the classical analysis is not.

42-5 Atomic Structure

Attempts to extend the Bohr theory quantitatively to more complex atoms met with failure. The best that could be accomplished was to use the Bohr model of hydrogen as a qualitative guide or, at best, in a semiquantitative way. For example, the Z electrons of a neutral atom of atomic number Z were assumed to be moving in circular orbits about the nucleus. Sommerfeld attempted to generalize Bohr's theory to permit the atom to have elliptic orbits, and while the Sommerfeld theory has been superseded, certain details of the model he used remain useful in implementing our understanding of atomic structure. Sommerfeld supposed that the electrons could move in elliptic orbits and found that the orbit could be described by a principal quantum number n and an azimuthal quantum number which we will call l, corresponding to modern notation. The energy of the electron was found to depend upon n exactly

as in Bohr's calculation as given by Equation (42-9), but the angular momentum depended upon l and was given by $(lh)/(2\pi)$. For each principal quantum number n, the value of l could be any integer between zero and n-1, corresponding to orbits of different eccentricity, as shown in Figure 42-7. Thus where n=3, there are three possible orbits having angular momenta corresponding to l=0, l=1, In the elliptical and l=2. orbit the principal quantum number designates the length of the semimajor axis, as it designates the orbital radius in the Bohr circle. Thus the elliptic orbits fall into shells for which n = 1 (called the K shell),

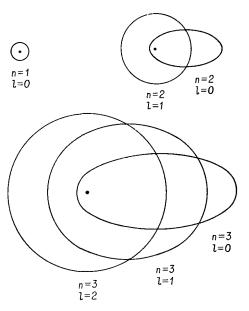


Fig. 42-7 Possible electronic orbits for a given total quantum number n.

n=2 (called the L shell), n=3 (called the M shell), and so on. The orbits within a shell are called S orbits if l=0, P orbits if l=1, D orbits if l=2, and F orbits if l=3. Thus we speak of an electron occupying a D orbit in the M shell, or of a 3D electron, when its orbit has a principal quantum number of 3 and an azimuthal quantum number of 2.

An electron moving in a closed orbit is analogous to a loop of wire carrying current, in that the electron generates a magnetic field and also experiences a force when in a magnetic field which tends to orient the plane of the orbit perpendicular to the external field, as in the case of a galvanometer coil. Experiment has shown that not all orientations are possible for an atomic orbit but that the orbit may take up only certain permitted

orientations, according to a principle known as space quantization. orbit can only take up those orientations in which the projection of the azimuthal quantum number representing the orbital angular momentum vector onto the direction of the magnetic field is itself an integer, called the magnetic quantum number m. Furthermore, the projection of l can be in the direction of the magnetic field or opposed to it. Thus we find that the quantum number m may have 2l+1 values ranging from +lthrough 0 to -l. For an orbit for which l=2, the quantum number m may take on the values 2, 1, 0, -1, -2. In addition to this perplexing number of parameters which we might call orbital quantum numbers, we already have mentioned that the electron has an intrinsic angular momentum called spin, designated by the letter s. Thus each electron in an atom is designated by four quantum numbers n, l, m, and s. The number ndesignates the shell in which the orbit is located, the number l designates the eccentricity of the orbit and its angular momentum, the number mdesignates the orientation of the plane of the orbit with respect to a magnetic field, and the number s designates the spin of the electron, which may be oriented parallel to or opposed to the direction of the magnetic field.

Together with an extremely valuable guiding principle introduced by Pauli in 1925, these quantum numbers serve as a vitally important guide to the problem of atomic structure. We would normally expect a system to fall into its configuration of lowest potential energy. Thus an atom with many electrons would have all of its electrons in the K shell, and all atoms would be essentially indistinguishable from each other, except perhaps through their different masses. But we know experimentally that this is not the case, and that atoms display characteristic valences. Furthermore, we know that the chemical properties of different atoms repeat in cycles in the periodic table.

To solve the problem of how electrons are arranged in the periodic table, Pauli proposed a principle, now known as the Pauli exclusion principle, which states that no two electrons in an atom can exist in the same state. Now the state of any electron can be completely specified by the four quantum numbers n, l, m, and s, so that the Pauli principle states that the group of values assigned to these four numbers must be different for all electrons in the atom. Subject to this condition, the electrons in an atom must occupy the states of lowest energy.

Thus an atom for which Z=1 (hydrogen) must have its electron in the n=1 shell. In this shell the value of l is 0, so that m=0. In an atom for which Z=2 (helium), there are two electrons which must fall into the K shell but which must have their spins oppositely oriented. No more than two electrons can occupy the K shell. An atom for which Z=3 must locate its third electron in the L shell for which n=2. This single electron

in the outermost shell is responsible for the fact that the chemical valence of lithium is +1. The fact that the K shell of helium is filled is responsible for the fact that helium is a noble gas. Thus we would expect that each time a shell is filled we would find an inert gas, and that each time a new shell is begun we would find a substance of valence +1. To fill the K shell requires 2 electrons; to fill the L shell requires 8 electrons, so that the next element of unit valency is sodium for which L = 11.

While there are many complications in the periodic table which require far more elaboration than it is possible to give here, the basic structure and pattern of the table and of the structure of atoms are determined by the energy-level diagram of hydrogen and by our theory of the hydrogen atom. A table of the distribution of electrons in atoms is given as Table 5 in Appendix A, while the periodic table of the elements is given as Table 6 in Appendix A. From Table 5, Appendix A, we may note that the shells fill in regular order until we reach potassium, for which Z=19. At this point we note that the S level in the N shell begins to be occupied before the D level in the M shell. In the case of iron, cobalt, and nickel, the 4S levels are occupied while the 3D levels are being filled. The spins of the 3D electrons may reorient themselves without altering the chemical structure of a molecule, or the crystal structure of a solid, for these depend upon the outermost electrons. It is this distortion in the level structure which is responsible for ferromagnetism. Another interesting aberration occurs in the case of the rare earths, beginning with element 57. Here the outer shells are nearly identically filled, but deep inside the atom, two shells removed from the valence electrons, the electrons populate the 4F subshell, for which n = 4, and l = 3. This results in nearly identical properties for the rare-earth elements and makes purely chemical separation of these elements extremely difficult.

42-6 Changes in Our Fundamental Concepts

Around the beginning of the present century, many changes began to take form in our fundamental concepts of physics. Light, which had been successfully explained as a wave motion, was found to have particlelike characteristics. The electron, which originally was an extremely small charged particle, was found to have spin and a magnetic moment. The concept of electron spin was introduced by Uhlenbeck and Goudsmit in 1925 to explain a fine splitting of atomic energy levels, called the fine structure. This concept was later found to be of great value in explaining the magnetic properties of matter. The Pauli exclusion principle was a special rule for the organization of atoms and electrons which had no classical analogue and which proved invaluable in explaining the electrical properties of metals as well as the periodic table. Another concept which

has played an important role in modern physics is one of the complete indistinguishability of fundamental particles; that is no two electrons can be distinguished from each other. The formal recognition that it is impossible to label individual electrons has had important consequences in theoretical physics, as in the theory of valency.

In 1925 another new concept was introduced by Louis de Broglie to the effect that every particle of mass m moving with speed v has associated with it a wave of wavelength λ given by

$$\lambda = \frac{h}{mv}, \qquad (42-12)$$

where h is Planck's constant. Thus an electron, as well as any other particle, should have a wave associated with it. The existence of waves associated with electrons was verified in a series of remarkable experiments in 1927 and 1928 by Davisson and Germer, and by G. P. Thomson, and has led to an entirely new field of physics known as *electron optics*. These new ideas concerning the spin of the electron and the waves associated with electrons in motion were incorporated into a new theory known as wave mechanics or quantum mechanics, mainly through the work of Heisenberg, Schroedinger, Dirac, and Pauli, beginning about 1926, in which the wave properties of electrons and the quantum character of atomic energy levels was built into the theory, as the inertial character of mass is built into Newton's second law of motion. As a result of these developments, remarkably rapid progress was made in the next few years in describing atoms, molecules, and nuclei. We shall consider these concepts in greater detail in the succeeding chapters.

Problems

- 42-1. The red line of the Balmer series of hydrogen has a wavelength of 6,563 A. Determine the energy of a quantum of this radiation (a) in ergs and (b) in electron volts.
- 42-2. The first line of the Lyman series of hydrogen has a wavelength of 1,216 A and is emitted in a transition from the second to the first Bohr orbits. Calculate the energy, in electron volts, of this transition.
- 42-3. Ultraviolet light of wavelength 800 A is incident upon a tube containing hydrogen. Determine the minimum kinetic energy with which an electron will be ejected from hydrogen.
- 42-4. At what absolute temperature would the mean kinetic energy of molecules of hydrogen in a gas tube equal the energy required to raise hydrogen from the ground state to the first excited state (n = 2)?
- 42-5. The light emitted by sodium atoms in a transition from the first excited state to the ground state is of wavelength 5,896 A. At what temperature

is the mean kinetic energy of sodium atoms equal to the energy required to raise sodium to its first excited state?

- 42-6. A neutron has a mass of 1.67×10^{-24} gm. What is the de Broglie wavelength of a neutron whose velocity may be determined by assuming the neutron to have a kinetic energy corresponding to a temperature of 20°C? [HINT: Assume $\mathcal{E}_k = kT$.]
- 42-7. Derive an equation for the energy with which an electron is bound to a nucleus whose charge is Ze.
- 42-8. From the result of Problem 42-7, find the energy, in electron volts, with which an electron is bound to sodium (Z = 11) in the state for which n = 1.
- 42-9. (a) Find the de Broglie wavelength of an electron in the *n*th Bohr orbit of hydrogen. (b) What is the relationship between this wavelength and the circumference of the *n*th orbit? (c) Is there any relationship between the Bohr condition on the quantization of angular momentum and the result you obtained in part (b).
- 42-10. The earth is 149×10^6 km from the sun and has a mass of 5.98×10^{24} kg. What is the de Broglie wavelength of the earth?
- 42-11. A ball which weighs 5 oz is pitched with a velocity of 100 ft/sec. What is the de Broglie wavelength of the ball? Would you expect such a ball to display predominantly wavelike or particlelike behavior?
- 42-12. An electron has a mass of 9.1×10^{-28} gm and a charge of 4.8×10^{-10} stcoul. What is the de Broglie wavelength of an electron which has been accelerated through a potential difference of 100 volts? Would you expect this electron to display wavelike or particlelike behavior in the presence of obstacles 1 mm in diameter?
- 42-13. The negative μ -meson has a mass of 206 times the mass of the electron and a charge equal to the charge of the electron. Such a meson can form a mesic atom by falling into an appropriate Bohr orbit. Find the radius of the first Bohr orbit of the meson in silver.
- 42-14. According to the correspondence principle of Bohr, we must expect phenomena to look alike from the classical and quantum viewpoints in the limit of large quantum numbers, for we know that the classical picture of matter is reasonably accurate for macroscopic phenomena. Classically, we would expect that the frequency of light emitted from the hydrogen atom would equal the frequency of rotation of the electron in its orbit. Show that, for very large quantum numbers, the frequency of rotation of the electron and the frequency of the radiation emitted when the quantum number changes by unity approach the same value $f = 2cR/n^3$.