INTRODUCTION TO ATOMIC SPECTRA

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CHAPTER III

SOMMERFELD'S ELLIPTIC ORBITS AND SPACE QUANTIZATION

Soon after Bohr put forward his famous theory of the hydrogen atom Sommerfeld¹ extended the model so as to include elliptic orbits. The importance of this extension may be attributed directly to the accuracy with which his resultant equations, with suitable relativity corrections, account for the fine structure of the energy levels and spectrum lines in hydrogen and hydrogen-like atoms.

In order to quantize any proposed atomic system Wilson² and Sommerfeld postulated, about the same time and quite independently, that each degree of freedom must be quantized separately. In other words

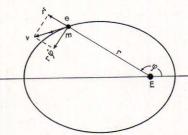


Fig. 3.1.—Elliptic orbit.

each degree of freedom should be fixed by its own separate quantum number.

3.1. Two Degrees of Freedom.— Following Sommerfeld, the motion of an electron in an elliptic orbit, with the nucleus at one focus, presents a system with two degrees of freedom and hence two quantum conditions. In polar coordinates the position of the electron is given by the azimuth angle φ (see

Fig. 3.1) and the electron-nuclear distance r. Assuming that the potential energy is zero when the electron is removed to infinity,

$$V = -\frac{eE}{r} = -\frac{e^2Z}{r},\tag{3.1}$$

where e and E are the charges on the electron and nucleus, respectively, and Z is the atomic number. The kinetic energy is given by

$$T = \frac{1}{2}mv^2 = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\varphi}^2) = \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\varphi}^2.$$
 (3.2)

These equations involve two displacement coordinates, φ and r, and two momentum coordinates,

$$p_{\varphi} = mr^2\dot{\varphi} \text{ and } p_{\tau} = m\dot{r}.$$
 (3.3)

Corresponding to these two degrees of freedom two phase-space diagrams (see Figs. 2.4 and 3.3) can be drawn in such a way that the

¹ SOMMERFELD, A., Ann. d. Phys., 51, 1, 1916.

² Wilson, W., Phil. Mag., 29, 795, 1915.

motion of the electron is represented by two graph points, one moving on one diagram and one on the other. Applying the quantum conditions [see Eq. (2.9)] to these two degrees of freedom,

$$\oint p_{\varphi} d\varphi = kh \tag{3.4}$$

and

$$\oint p_r dr = rh,$$
(3.5)

where k and r take integral values only and are called the *azimuthal* and radial quantum numbers, respectively.

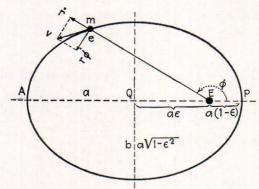


Fig. 3.2.—Elliptic orbit.

According to Kepler's second law of planetary motion the angular momentum p_{φ} remains constant throughout the motion so that the first integral is readily evaluated. Integrating over a complete cycle,

$$\int_0^{2\pi} p_{\varphi} d\varphi = 2\pi p_{\varphi} = 2\pi m r^2 \dot{\varphi} = kh. \tag{3.6}$$

This result is identical with Bohr's quantum conditions for circular orbits [Eq. (2.20)]. The quantized angular momentum for elliptic orbits may therefore be represented by a graph point traversing one of the paths in the phase space given for circular orbits in Fig. 2.4.

3.2. The Radial Quantum Number.—In order to quantize the radial motion of the electron the left-hand side of Eq. (3.5) must be evaluated. The object of this section is to present Sommerfeld's method of evaluating this integral. The starting point is the general equation of an ellipse in polar coordinates,

$$\frac{1}{r} = C_1 + C_2 \cos \varphi, \tag{3.7}$$

where C_1 and C_2 are constants to be determined for every ellipse. If the eccentricity ϵ of an ellipse (see Fig. 3.2) is defined as the ratio EQ/a, where a is the semimajor axis, then

$$EQ = a\epsilon. (3.8)$$

In terms of the eccentricity ϵ , it is readily shown that the perihelion distance EP, the aphelion distance EA, and the semiminor axis b become:

Perihelion
$$EP = a(1 - \epsilon)$$
.
Aphelion $EA = a(1 + \epsilon)$.
Semiminor axis $b = a\sqrt{1 - \epsilon^2}$. (3.9)

With the electron at perihelion, $\varphi = 0$, Eq. (3.7) becomes

$$\frac{1}{a(1-\epsilon)} = C_1 + C_2 \tag{3.10}$$

while at aphelion, $\varphi = \pi$, Eq. (3.7) becomes

$$\frac{1}{a(1+\epsilon)} = C_1 - C_2. {(3.11)}$$

With these two equations, C_1 and C_2 can be evaluated

$$C_1 = \frac{1}{a(1 - \epsilon^2)}$$
 and $C_2 = \frac{\epsilon}{a(1 - \epsilon^2)}$, (3.12)

and the equation of the ellipse written

$$\frac{1}{r} = \frac{1 + \epsilon \cos \varphi}{a(1 - \epsilon^2)}. (3.13)$$

Taking the log of each side of this equation and differentiating, we get

$$\frac{1}{r}\frac{dr}{d\varphi} = \frac{\epsilon \sin \varphi}{1 + \epsilon \cos \varphi}.$$
(3.14)

Remembering that $p_{\varphi} = mr^2\dot{\varphi}$,

$$p_r = m\dot{r} = m\frac{dr}{d\varphi}\dot{\varphi} = \frac{p_\varphi}{r^2}\frac{dr}{d\varphi}.$$
 (3.15)

Since

$$dr = \frac{dr}{d\varphi}d\varphi,\tag{3.16}$$

one obtains

$$p_r dr = p_{\varphi} \frac{1}{r^2} \left(\frac{dr}{d\varphi} \right)^2 d\varphi = p_{\varphi} \epsilon^2 \frac{\sin^2 \varphi}{(1 + \epsilon \cos \varphi)^2} d\varphi. \tag{3.17}$$

The phase integral, Eq. (3.5), now becomes

$$\oint p_r dr = p_{\varphi} \epsilon^2 \int_0^{2\pi} \frac{\sin^2 \varphi}{(1 + \epsilon \cos \varphi)^2} d\varphi = rh.$$
(3.18)

Now, from Eq. (3.6),

$$p_{\varphi} = \frac{kh}{2\pi},\tag{3.19}$$

so that

$$\frac{\epsilon^2}{2\pi} \int_{-\infty}^{2\pi} \frac{\sin^2 \varphi}{(1 + \epsilon \cos \varphi)^2} d\varphi = \frac{r}{k}.$$
 (3.20)

Integrating by parts, we get

$$\frac{1}{\sqrt{1-\epsilon^2}} - 1 = \frac{r}{k} \tag{3.21}$$

which upon transposing and squaring becomes, from the definition of the semiminor axis [Eq. (3.9)],

$$1 - \epsilon^2 = \frac{k^2}{(k+r)^2} = \frac{b^2}{a^2}.$$
 (3.22)

Since k and r take integral values only, we may write

$$k + r = n$$
, where $n = 1, 2, 3, \cdots$ (3.23)

is the so-called total quantum number.

In terms of this new quantum number n, Eq. (3.22) leads to the very interesting and simple result that

$$\frac{k}{n} = \frac{b}{a}. (3.24)$$

Out of all the classically possible ellipses the quantum conditions allow only those for which the ratio of the major and minor axes is that of two

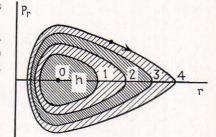


Fig. 3.3.—Phase-space diagram for the radial motion.

integers, viz., the quantum numbers n and k.

The radial motion of the electron may be represented by a graph point traversing one of the curves in the phase space shown in Fig. 3.3.

3.3. The Total Energy W.—The total energy of each stationary state has yet to be calculated. From Eqs. (3.1) and (3.2),

$$W = T + V = \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\varphi}^2 - \frac{e^2Z}{r}$$
 (3.25)

which in terms of p_r and p_{φ} [Eqs. (3.3) and (3.15)] gives

$$W = \frac{1}{2m} \left(p_r^2 + \frac{p_\varphi^2}{r^2} \right) - \frac{e^2 Z}{r},\tag{3.26}$$

$$W = \frac{p_{\varphi}}{2mr^2} \left[\left(\frac{1}{r} \frac{dr}{d\varphi} \right)^2 + 1 \right] - \frac{e^2 Z}{r}. \tag{3.27}$$

By direct substitution of Eqs. (3.13) and (3.14),

$$W = \frac{p_{\varphi}}{ma^{2}(1-\epsilon^{2})^{2}} \left(\frac{1+\epsilon^{2}}{2} + \epsilon \cos \varphi\right) - \frac{e^{2}Z(1+\epsilon \cos \varphi)}{a(1-\epsilon^{2})}.$$
 (3.28)

For a conservative system the total energy is constant and is independent of the time and of the angle φ . Since the total energy is constant and $\cos \varphi$ varies, the coefficient of $\epsilon \cos \varphi$ must vanish. Collecting terms in $\epsilon \cos \varphi$ and equating to zero,

$$\epsilon \cos \varphi \left(\frac{p_{\varphi}}{ma^2(1-\epsilon^2)^2} - \frac{e^2Z}{a(1-\epsilon^2)} \right) = 0.$$
 (3.29)

This gives

$$\frac{p_{\varphi}}{ma^{2}(1-\epsilon^{2})^{2}} = \frac{e^{2}Z}{a(1-\epsilon^{2})}$$
(3.30)

from which

$$a = \frac{p_{\varphi}}{me^2 Z(1 - \epsilon^2)}.$$
(3.31)

With the values of p_{φ} and $1 - \epsilon^2$ from Eqs. (3.6) and (3.22), respectively, the semimajor axis

$$a = \frac{h^2}{4\pi^2 m e^2 Z} (k+r)^2 = a_1 \frac{n^2}{Z},$$
(3.32)

and with Eq. (3.9) the semiminor axis

$$b = \frac{h^2}{4\pi^2 m e^2 Z} k(k+r) = a_1 \frac{kn}{Z}.$$
 (3.33)

Here a_1 is the radius of the first Bohr circular orbit [see Eq. (2.33)], and n is the total quantum number.

With the value of a from Eq. (3.31), the total energy [Eq. (3.28)] becomes

$$W = \frac{e^2 Z}{a(1 - \epsilon^2)} \left\{ \frac{1 + \epsilon^2}{2} - 1 \right\} = -\frac{e^2 Z}{2a}.$$
 (3.34)

Substituting a from Eq. 3.32,

$$W = -\frac{2\pi^2 m e^4 Z^2}{h^2 (k+r)^2} = -\frac{2\pi^2 m e^4 Z^2}{h^2 n^2},$$
 (3.35)

This equation is of particular interest in that the energy is exactly the same as that obtained by Bohr for circular orbits [see Eq. (2.23)].

3.4. General Characteristics of Sommerfeld's Elliptic Orbits.—While the introduction of elliptic orbits has thus far introduced no new energy states for the hydrogen atom, the electron may now move in different orbits. For any given value of the energy, corresponding to the total quantum number n, there are n different quantized orbits for the electron. If, for example, n = 5, the azimuthal quantum number k may take on one of the five values 1, 2, 3, 4, or 5, while the radial quantum number r takes on the values 4, 3, 2, 1, or 0, respectively. A study of the possibility

of states with k=0 shows that the ellipse reduces to motion along a straight line with the nucleus at one end. Sommerfeld therefore excluded such states on the grounds that the electron would collide with the nucleus. As the quantum mechanics leads to a model of hydrogen-like atoms which possess features than can be described in terms of elliptic orbits, the size and shape of Sommerfeld's electron orbits are of interest and will be given here in somewhat more detail.

From Eqs. (3.32) and (3.33) it is seen that the semimajor axis a is proportional to n^2 , and to 1/Z, and the semiminor axis b is proportional

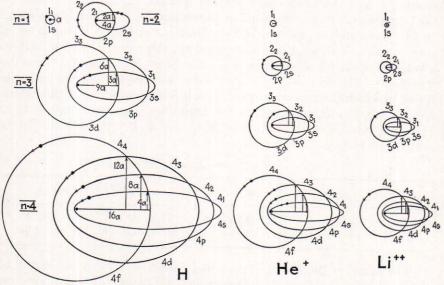


Fig. 3.4.—Relative dimensions of the Sommerfeld elliptic orbits.

to nk, and to 1/Z. Starting with the smallest orbits of hydrogen with Z=1, ionized helium with Z=2, doubly ionized lithium with Z=3, etc., we place n=1, k=1 and r=0. These are circles of radius $a_1, a_1/2, a_1/3$, etc., shown at the top of Fig. 3.4, and are exactly the same as Bohr's circular orbits. With n=2 there are two possibilities for each atom, k=2, r=0 and k=1, r=1. The first set of quantum numbers gives Bohr's circular orbits of radius $4a_1, 4a_1/2, 4a_1/3$, etc., and the second set gives elliptic orbits with semimajor axes the same as for the circles, $4a_1, 4a_1/2, 4a_1/3$, etc., and semiminor axes $2a_1, 2a_1/2, 2a_1/3$, etc.

For the next higher states of H, He II, Li III, etc., with n=3, there are three types of orbits possible, k=3, r=0; k=2, r=1; and k=1, r=2. The first set gives Bohr's circular orbits of radius $9a_1$, $9a_1/2$, $9a_1/3$, etc. The second set (k=2, r=1) gives elliptic orbits with semimajor axes the same as for the circles and semiminor axes two-thirds

as large. The third set (k = 1, r = 2) gives elliptic orbits with semimajor axes the same as for the circles but with semiminor axes one-third as large. In general, a and b vary as the reciprocal of the atomic number Z, i.e., as 1/Z, so that by reducing the hydrogen orbits (Fig. 3.4) to one-half and one-third their dimensions they become identical with the orbits of He II and Li III, respectively.

TABLE 3.1.—ELECTRON-ORBIT NOTATION

	n = 1	n = 2	n = 3	n = 4
n_k	11	21 22	31 32 38	41 42 43 44
nk	18	2s 2p	3s 3p 3d	4s 4p 4d 4f

The origin of the letters s, p, d, and f goes back to the discovery of sharp, principal, diffuse, and fundamental series, in the alkali spectra, and to the designation of such series by Rydberg formulas. These have been treated at some length in Chap. I.

It is convenient to remember that, for a given n it is the s orbit which comes closest to, and recedes farthest from, the nucleus, *i.e.*, it is the most elliptic of any family of orbits having the same major axis. Next in eccentricity come the p electron orbits with k=2, followed by d electrons with k=3, f electrons with k=4, etc.

3.5. Space Quantization.—Up to this point the motion of a single electron of a hydrogen-like atom has been confined to two degrees of freedom. In this special case an electron orbit or energy state is determined by two of the three quantum numbers n, k, and r. As a more general case, however, the motion of the electron is three-dimensional. With three degrees of freedom the Wilson-Sommerfeld quantum conditions require three quantum numbers to describe each energy state in place of two. It should be pointed out at the outset, however, that the introduction of a third quantum number does not change the size

or shape of the Bohr-Sommerfeld orbits but simply determines their orientation with respect to some direction in space.

In order to set up a fixed axis in space we first imagine the atom placed in a uniform magnetic field H. Let the vertical axis in Fig. 3.5 be the direction of the applied field, and let α be the angle between this axis and the normal to the plane of the orbit. As a result of the applied field the plane of the orbit precesses about H, just as a mechanical top precesses in a gravitational field and p_{ψ} , the orbital angular momentum

vector, generates a cone about the vertical axis. The quantum conditions imply that the orbit is spacequantized, i.e., that α takes on certain discrete values only. It will be shown in the following section, how, for any given orbit, the precession frequency depends upon H. If now the field His gradually reduced to zero, the angle α remains constant (α is independent of H), while the rate at which p_{ψ} precesses about H decreases to zero. In this rather indirect way the atom is left with the plane of the electron orbit, or the orbit angular momentum p_{ψ} , in one of a discrete set of orienta-

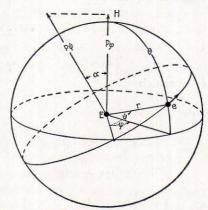


Fig. 3.5.—The motion of the electron with three degrees of freedom.

tions in space, but the energy is identical with that obtained by quantizing the field-free atom.

Now in the two-dimensional problem, treated in the preceding sections, the kinetic energy in terms of the coordinates r and φ is $(\varphi$ is now replaced by ψ) (see Fig. 3.5)

$$T = \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\psi}^2 = \frac{1}{2}(p_r\dot{r} + p_\psi\dot{\psi})$$
 (3.36)

and is subject to the quantum conditions that

$$\oint p_{\psi}d\psi = kh \text{ and } \oint p_{r}dr = rh,$$
(3.37)

where the radial quantum number $r=0,\,1,\,2,\,3,\,\cdots$ and the azimuthal quantum number $k=1,\,2,\,3,\,4,\,\cdots$. The potential energy is given by

$$V = -\frac{e^2 Z}{r}. (3.38)$$

In the three-dimensional problem, let the position of the electron be given by the polar coordinates r, θ , and φ . With the potential energy exactly the same as it is in the two-dimensional problem, we need only

write down the kinetic energy. In terms of the corresponding momenta, the kinetic energy T is

$$T = \frac{1}{2}(p_r \dot{r} + p_\theta \dot{\theta} + p_\varphi \dot{\varphi}). \tag{3.39}$$

The quantum conditions in terms of the phase integrals are

$$\oint p_r dr = rh, \qquad \oint p_\theta d\theta = th, \qquad \oint p_\varphi d\varphi = mh,$$
(3.40)

where the quantum numbers r, t, and m take integral values only.

Since the total energy W=T+V in the $r,\,\psi$ coordinates is just the same as in the $r,\,\theta,\,\varphi$ coordinates, it follows from Eqs. (3.36) and (3.39) that

$$p_r \dot{r} + p_\phi \dot{\psi} = p_r \dot{r} + p_\phi \dot{\varphi} + p_\theta \dot{\theta} \tag{3.41}$$

from which

$$p_{\psi}d\psi = p_{\varphi}d\varphi + p_{\theta}d\theta \tag{3.42}$$

or

$$\oint p_{\psi}d\psi = \oint p_{\varphi}d\varphi + \oint p_{\theta}d\theta.$$
(3.43)

The quantum conditions for each of the phase integrals are most easily expressed in terms of their corresponding quantum numbers k, m, and t, respectively. It follows that

$$k = t + m. (3.44)$$

Since the total angular momentum of the electron p_{ψ} is constant, p_{φ} , its projection on the φ axis, is also constant, so that

$$p_{\varphi} = p_{\psi} \cos \alpha. \tag{3.45}$$

The angle between p_{φ} and p_{ψ} is therefore determined by the quantum numbers m and k,

$$\cos \alpha = \frac{p_{\varphi}}{p_{\psi}} = \frac{m}{k}, \tag{3.46}$$

where the magnetic quantum number

$$m = \pm 1, \pm 2, \pm 3, \pm 4, \cdots \pm k$$
 (3.47)

and the azimuthal quantum number

$$k = 1, 2, 3, 4, \cdots n.$$
 (3.48)

It is customary to represent the space quantization of an electron orbit by means of the orbit normal and to treat this as a vector. Equation (3.47) shows that the number of possible m values is limited by the value of k. In Fig. 3.6, the space diagram for s electrons (i.e., k = 1) shows two possible orientations of p_{φ} . Similar diagrams for $p = d_{\varphi}d$ electrons show four and six possible orientations, respectively. By

drawing the oriented vector of length $k=2\pi p_{\varphi}/h$ in place of p_{φ} , the projection will always be just the magnetic quantum number m. The state m=0 in this early work was always excluded on the ground that the application of an electric field would cause the electron to collide with the nucleus. We shall see later that on the quantum mechanics the states m=0 are allowed. Experimental proof of the space quanti-

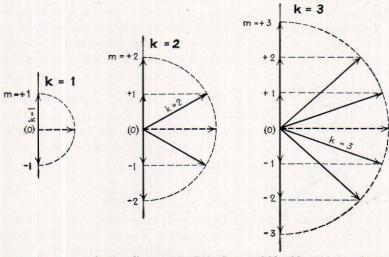


Fig. 3.6.—Space-quantization diagrams for Bohr-Sommerfeld orbits with k=1, 2, and 3.

zation of atoms in a magnetic field is to be found in the admirable experiments of Stern and Gerlach.¹

3.6. Larmor's Theorem.—Just as a mechanical top precesses in a gravitational field, so an electron in an orbit would be expected classically to precess in a magnetic field. This precession is called the *Larmor precession* and the relation expressing the frequency of precession is called *Larmor's theorem*. This theorem, derived on the classical theory of electrodynamics, states that to a first approximation the change in the motion of an electron about a nucleus produced by the introduction of a magnetic field of intensity H is a precession of the orbit about the field direction with uniform angular velocity

$$\omega_L = H \cdot \frac{e}{2mc} \tag{3.49}$$

or with a uniform frequency

$$\nu_L = H \cdot \frac{e}{4\pi mc}.\tag{3.50}$$

Phys., 8, 110, 1921; 9. 349, 1922; Stern, O., Zeits. f. Phys., 41, 563, 1927.

Fig. 3.7.—Larmor pre-

cession of an electron orbit in an external mag-

netic field, H.

This theorem is of considerable importance in atomic structure as it enables an easy calculation of energy levels in the presence of an external magnetic field. The classical theory shows that, as the magnetic field starts from zero and gradually increases, there is no change in the size or shape of the electron orbit. The picture formed therefore is the one shown in Fig. 3.7. As the orbit precesses with angular velocity ω_L , the orbit normal describes a cone about the field direction H.

The quantum conditions presented in the previous section show that, if we represent the orbital angular momentum $p_{\psi} = kh/2\pi$ by a

vector of length k, the projection of k on the field direction H must be integral-valued, *i.e.*,

$$m = \pm 1, \pm 2, \pm 3, \cdots \pm k.$$
 (3.51)

3.7. Magnetic Moment and the Bohr Magneton.—It will here be shown classically that, in terms of electron orbits, the ratio between the magnetic moment μ and the orbital angular momentum p is given by

$$\frac{\mu}{p} = \frac{e}{2mc} \cdot \tag{3.52}$$

Hereafter we shall frequently refer to the orbital angular momentum p as the mechanical moment. An elementary principle in electrodynamics states that the magnetic moment μ (in electromagnetic units) of a current in a single loop or circuit is

equal to the area of the circuit A, times the current I (in electrostatic units) divided by the velocity of light c:

$$\mu = \frac{\text{area} \cdot I}{c}.$$
 (3.53)

In terms of the moving charge e and its period of revolution T, the current I is given by

$$I = \frac{e}{T}. (3.54)$$

Now the area of a Kepler ellipse in terms of the mass of the electron m, its mechanical moment p, and the period T is

Area =
$$\frac{T}{2m}p = \frac{T}{2m} \cdot k \cdot \frac{h}{2\pi}$$
 (3.55)

¹ It is not difficult to show from classical electrodynamics that, when a field is applied normal to the plane of a circular electron orbit, the electron speeds up without a change in the radius of the orbit. This unexpected result is due to the balance between the increased centrifugal force and the radial force on the electron due to the magnetic field H. Since the radius remains unchanged, the moment of inertia $I = mr^2$ remains constant.

giving for the magnetic moment, just as stated above in Eq. (3.52),

$$\mu = k \cdot \frac{h}{2\pi} \cdot \frac{e}{2mc} = k \frac{eh}{4\pi mc}$$
 (3.56)

According to this result the magnetic moment of a hydrogen atom should always be equal to an integral number of units:

$$\frac{eh}{4\pi mc} \cdot \frac{\text{ergs}}{\text{gauss}}$$
 (3.57)

This unit of magnetic moment is called the *Bohr magneton* and is equal to 0.918×10^{-20} erg gauss⁻¹. Returning to Larmor's theorem [Eq. (3.49)], we see that the angular velocity of the Larmor precession is equal to the field strength H, times the ratio between the magnetic and mechanical moments:

$$\omega_L = H \cdot \frac{\mu}{p} = H \cdot \frac{e}{2mc}. \tag{3.58}$$

Similarly the precession frequency

$$\nu_L = \frac{H}{2\pi} \cdot \frac{\mu}{p} = H \cdot \frac{e}{4\pi mc}.$$
 (3.59)

It is interesting to note in passing that the frequency of precession is independent of the orientation angle between the orbit normal and the field direction (see Fig. 3.7).

Problems

- 1. Derive a general expression for the period of the electron in any of the Bohr-Sommerfeld orbits. Compare this formula with the one obtained in Chap. II, Prob. 6, for the Bohr circular orbits.
- 2. From the definition of the eccentricity as given by Eq. (3.8), show that the perihelion, aphelion, and semiminor axis are given by the relations in Eq. (3.9).