

2. THE OLD QUANTUM THEORY: WILSON-SOMMERFELD QUANTIZATION RULES

Wilson⁴ and Sommerfeld⁵ independently discovered a method of quantizing the action integrals of classical mechanics, and this method was subsequently applied to a number of physical systems. A necessary condition for the application of this method is that each generalized coordinate q_k and its conjugate momentum p_k must be periodic functions of time. Then the action integral taken over one cycle of the motion is quantized; that is,

$$\oint p_k dq_k = n_k h. \quad (4.1)$$

To illustrate the method, consider a one-dimensional simple harmonic oscillator whose equation of motion is

$$m\ddot{x} + kx = 0,$$

or

$$\ddot{x} + \omega^2 x = 0,$$

where

$$\omega^2 = \frac{k}{m}.$$

Then,

$$x = x_0 \sin \omega t$$

and

$$p_x = m\dot{x} = m\omega x_0 \cos \omega t.$$

Equation 4.1 becomes

$$\begin{aligned} nh &= \oint p_x dx = \int_0^T m\omega^2 x_0^2 \cos^2 \omega t dt \\ &= m\omega x_0^2 \int_0^{2\pi} \cos^2 \theta d\theta \\ &= m\omega\pi x_0^2. \end{aligned}$$

Therefore,

$$x_0^2 = \frac{nh}{\omega m \pi},$$

or the amplitudes are quantized. The energy states are

$$\begin{aligned} E &= T + V = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 \\ &= \frac{1}{2}m\omega^2 x_0^2, \end{aligned}$$

or,

$$E_n = n\omega\hbar = nh\nu. \quad (4.2)$$

⁴ W. Wilson, *Phil. Mag.* **29**, 795 (1915).

⁵ A. Sommerfeld, *Ann. Phys.* **51**, 1 (1916).

In both the classical theory and the old quantum theory, the ground state energy of an oscillator is incorrectly given as zero. However, the level spacings are correct in these older theories. From the oscillator energy levels obtained in Equation 4.2, there is no information about which transitions are most likely to occur, or in fact, whether any are forbidden. Information of this kind goes under the general heading of *selection rules* and is readily obtained in the new quantum mechanics. However, in the old theory, selection rules were inferred by comparing the system with the behavior of a classical system; that is, by employing what is called *Bohr's correspondence principle*. Thus, since a classical oscillator will emit only one frequency (and no harmonics), if a quantum mechanical oscillator is to correspond to the classical result in the limit of large n , then we must have the selection rule $\Delta n = \pm 1$. We had already assumed transitions between adjacent levels in our discussion of Planck's oscillators in section 3 of Chapter 2.

If we treat a two-dimensional harmonic oscillator as two independent one-dimensional oscillators in the x - and y -directions, the energy levels are

$$E_{n_x, n_y} = \hbar(n_x\omega_x + n_y\omega_y).$$

If the oscillator is isotropic ($k_x = k_y$), then $\omega_x = \omega_y = \omega$, and

$$E_n = n\hbar\omega,$$

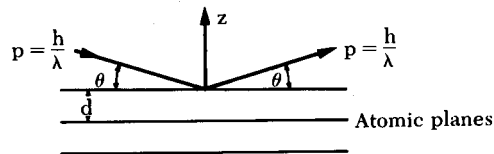
where $n = n_x + n_y$. But $n = 1$ now corresponds to the two states ($n_x = 0, n_y = 1$) and ($n_x = 1, n_y = 0$), which have the same energy. The two states are said to be *degenerate*. In general, the level of energy E_n is $(n + 1)$ -fold degenerate. Similarly, the energy of the n^{th} level of a three-dimensional isotropic oscillator is also given by Equation 4.2 with $n = n_x + n_y + n_z$. The degeneracy in this case is $\frac{1}{2}(n + 1)(n + 2)$.

Duane and Compton⁶ applied the Wilson-Sommerfeld method to a corpuscular model for the diffraction of x -rays by a crystal. If the z -direction is normal to a set of identical atomic planes of separation d , then the quantum condition becomes

$$\oint p_z dz = \int_0^d p_z dz = p_z d = nh, \tag{4.3}$$

in the absence of forces. A photon of momentum h/λ incident at the angle θ , as shown in Figure 4-1, will be reflected at the same angle and will transfer an

Figure 4-1 Bragg reflection of a photon by a crystal.



⁶ W. Duane, *Proc. Nat. Acad. Sci.* **9**, 158 (1923); A. H. Compton, *ibid.* **9**, 359 (1923).

114 THE DEVELOPMENT OF WAVE MECHANICS

amount of momentum in the z -direction equal to $(2h/\lambda) \sin \theta$. But the momentum must satisfy the quantum conditions given by Equation 4.3, so we have

$$n\lambda = 2d \sin \theta, \quad (4.4)$$

the well-known Bragg equation.

One can obtain the equivalent Bragg expression for electrons by letting $p_z = 2mv \sin \theta$ in Equation 4.3 to obtain

$$n \frac{h}{mv} = 2d \sin \theta. \quad (4.5)$$

By comparing Equation 4.4 and Equation 4.5, it is apparent that the de Broglie wavelength, $\lambda = h/mv$, could also have been predicted by this theory.

PROBLEM 4-1

Use the Wilson-Sommerfeld method to obtain the energy levels of a rigid rotator of angular momentum, $p_\theta = I\omega$, where I is its moment of inertia about the rotation axis.
(Ans.: $E_n = n^2 \hbar^2 / 2I$.)

PROBLEM 4-2

Use the Wilson-Sommerfeld method to obtain the energy states of a perfectly elastic particle in a cubic box of edge a and with perfectly rigid walls.
(Ans.: $E_n = n^2 \hbar^2 / 8ma^2$, where $n^2 = n_x^2 + n_y^2 + n_z^2$.)

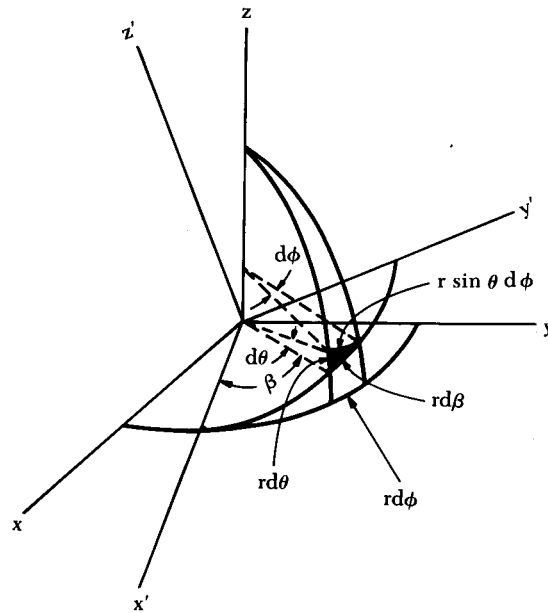
PROBLEM 4-3

Find the energy states of a perfectly elastic ball bouncing in the gravitational field by applying the Wilson-Sommerfeld quantization condition.
(Ans.: $E_n = (9g^2 \hbar^2 mn^2 / 32)^{1/2}$.)

3. SOMMERFELD'S RELATIVISTIC THEORY OF THE HYDROGEN ATOM

Although the Bohr theory was quite successful in predicting the spectrum of hydrogen, there remained an unexplained fine structure or splitting of the lines. This splitting amounts to about one part in 10^4 and cannot be seen in spectrometers of low resolving power. Sommerfeld proposed that if elliptical

Figure 4-2 Relationship between the planar and spherical coordinates. The angle β is the azimuthal angle in the $x'-y'$ -plane, ϕ is the azimuthal angle about the z -axis, and θ is the polar angle measured from the z -axis.



as well as circular orbits were allowed, the electron's velocity in an orbit of large eccentricity could become relativistic. He showed that the energy correction resulting from the relativistic treatment was of the proper order of magnitude to account for the fine structure splitting of hydrogen. Unfortunately, Sommerfeld's theory is not the correct explanation for the fine structure of atomic spectra. We now know that the fine structure is due to the fact that the electron has an intrinsic spin angular momentum which produces the so-called spin-orbit interaction. This will be treated in detail in the discussion of the quantum mechanical theory of radiation. In spite of the shortcomings of the Sommerfeld theory, it is of such great historical importance that it is worth sketching briefly here.

Consider an electron of reduced mass μ to be revolving about a fixed nucleus. Since the motion in a given orbit is confined to a plane, we will describe the position of the electron by the planar coordinates (r, β) measured in the plane of the orbit. In Figure 4-2, the x', y' -plane is the plane of the orbit and the unprimed system is used as the frame for a set of spherical polar coordinates. The relationship between the planar angle and the spherical coordinates is obtained by considering an infinitesimal angular displacement $d\beta$. Then the arc $r d\beta$ is the hypotenuse of an infinitesimal spherical triangle whose legs are $r d\theta$ and $r \sin \theta d\phi$. Then we have

$$(r d\beta)^2 = (r d\theta)^2 + (r \sin \theta d\phi)^2, \tag{4.6}$$

which we will need later in our discussion of the quantization rules.

The equation of the motion in the x', y' -plane is

$$\mu \ddot{r} = \mu r \dot{\beta}^2 - \frac{Ze^2}{r^2}.$$

Using the fact that $p_\beta = \mu r^2 \dot{\beta} = \ell = \text{constant}$, we obtain

$$\mu \ddot{r} = \frac{\ell^2}{\mu r^3} - \frac{Ze^2}{r^2}.$$

Multiplying by \dot{r} and integrating,

$$\mu \int \dot{r} dr = \int \left(\frac{\ell^2}{\mu r^3} - \frac{Ze^2}{r^2} \right) dr,$$

or

$$\frac{1}{2} \mu \dot{r}^2 = -\frac{\ell^2}{2\mu r^2} + \frac{Ze^2}{r} + E. \quad (4.7)$$

The constant of integration E is the total energy of the system. In order to get the path equation we eliminate the time by means of the substitution

$$\dot{r} = \frac{dr}{d\beta} \frac{d\beta}{dt} = \frac{\ell}{\mu r^2} \frac{dr}{d\beta}.$$

Substituting this into Equation 4.7 and multiplying by $2\mu/\ell^2$ results in

$$\left(\frac{1}{r^2} \frac{dr}{d\beta} \right)^2 = -\frac{1}{r^2} + \frac{2\mu Ze^2}{\ell^2 r} + \frac{2\mu E}{\ell^2}.$$

Introducing $u = 1/r$,

$$\frac{du}{d\beta} = -\frac{1}{r^2} \frac{dr}{d\beta} = \pm \sqrt{-u^2 + \frac{2\mu Ze^2}{\ell^2} u + \frac{2\mu E}{\ell^2}}$$

and

$$\pm d\beta = \frac{du}{\sqrt{\frac{2\mu E}{\ell^2} + \frac{2\mu Ze^2}{\ell^2} u - u^2}}.$$

Integrating,

$$u = \frac{1}{r} = \frac{\mu Ze^2}{\ell^2} + \sqrt{\frac{\mu^2 Z^2 e^4}{\ell^4} + \frac{2\mu E}{\ell^2}} \cdot \sin(\beta - \beta_0), \quad (4.8)$$

for negative total energy. The equation of an ellipse of semiaxes a and b , eccentricity ϵ and orientation β_0 is

$$u = \frac{1}{r} = \frac{1 + \epsilon \sin(\beta - \beta_0)}{a(1 - \epsilon^2)} = \frac{a}{b^2} + \frac{\sqrt{a^2 - b^2}}{b^2} \sin(\beta - \beta_0),$$

where $b/a = \sqrt{1 - \epsilon^2}$. Comparing this with Equation 4.8 we immediately

obtain the following results:

$$\left. \begin{aligned} a &= -\frac{Ze^2}{2E} \\ b &= \frac{\ell}{\sqrt{-2\mu E}} \\ 1 - \epsilon^2 &= -\frac{2E\ell^2}{\mu Z^2 e^4} \end{aligned} \right\} \quad (4.9)$$

PROBLEM 4-4

Show that the time averages of T and V satisfy the same relation as that satisfied by circular Bohr orbits, namely, $\bar{E} = \frac{1}{2}\bar{V} = -\bar{T}$.

Applying the quantization condition given in Equation 4.1 to the planar angle and the three spherical coordinates, we have

$$\oint p_\beta d\beta = kh \quad (4.10a)$$

$$\oint p_\phi d\phi = mh \quad (4.10b)$$

$$\oint p_\theta d\theta = n_\theta h \quad (4.10c)$$

$$\oint p_r dr = n_r h \quad (4.10d)$$

Equation 4.10a can be integrated immediately since $p_\beta = \ell = \text{constant}$, and the axis about which ℓ is measured is fixed in space. Then,

$$p_\beta = \ell = k\hbar. \quad (4.11a)$$

Similarly, p_ϕ is a constant and the z -axis about which it is measured is fixed, so

$$p_\phi = m\hbar. \quad (4.11b)$$

The quantum number m is called the *magnetic quantum number* because of the role it plays in distinguishing the energy levels of the atom in the presence of a magnetic field. Since the axis about which p_θ is measured is neither unique nor stationary, we must transform Equation 4.10c before it can be integrated.

If Equation 4.6 is multiplied by μ/dt , we obtain

$$\mu r^2 \dot{\beta} d\beta = \mu r^2 \sin^2 \theta \cdot \dot{\phi} d\phi + \mu r^2 \dot{\theta} d\theta,$$

or

$$p_\beta d\beta = p_\phi d\phi + p_\theta d\theta.$$

Substituting this into Equation 4.10c,

$$\oint (p_\beta d\beta - p_\phi d\phi) = n_\theta h = (k - m)h,$$

or,

$$k = n_\theta + m. \quad (4.11c)$$

The integer k is called the *azimuthal quantum number*. It can take on the values 1, 2, 3, . . . , with zero excluded.

Sommerfeld's integration of Equation 4.10d will not be repeated here but we will merely state his result, namely,

$$kh \left(\frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right) = n_r h,$$

or

$$\frac{a}{b} = \frac{n_r + k}{k} = \frac{n}{k}. \quad (4.11d)$$

The quantity n in the last expression is called the *total quantum number*, since it is defined as the sum of the radial and azimuthal quantum numbers, which is to say that

$$n = n_r + n_\theta + m.$$

Combining Equations 4.9, 4.11a, and 4.11d, we obtain the equalities

$$\frac{a}{b} = \frac{n\hbar}{\ell} = -\frac{Ze^2}{\ell} \sqrt{\frac{-\mu}{2E}},$$

from which the quantized orbits and energies are given by:

$$a = \frac{n^2 a_0}{Z},$$

$$b = \frac{ka}{n} = \frac{kna_0}{Z},$$

and

$$E_n = -\frac{w_0 Z^2}{n^2},$$

(4.12)

where the constants a_0 and w_0 were defined in section 4 of Chapter 3. Note that the semimajor axis, a , is the counterpart of the radius of a circular orbit

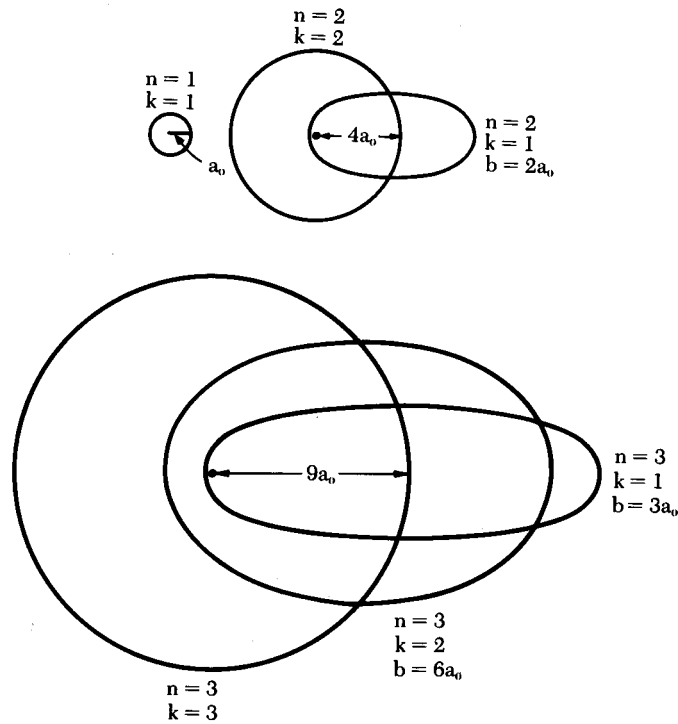


Figure 4-3 Sommerfeld's orbits for $n = 1, 2,$ and $3.$

in the Bohr theory. Furthermore, the energy of an orbit is independent of the value of the semiminor axis. This means that all of the orbits of different eccentricities associated with the same n value are degenerate. A few of these orbits are depicted in Figure 4-3.

It was at this point that Sommerfeld introduced a relativistic correction for the mass of the electron. For an orbit of large eccentricity the electron would pass close to the nucleus at a very high velocity such that the relativistic increase of mass would become noticeable. With this refinement to the theory the revised energies become

$$E_n = -\frac{w_0 Z^2}{n^2} \left[1 + \frac{\alpha^2 Z^2}{n} \left(\frac{1}{k} - \frac{3}{4n} \right) \right]. \quad (4.13)$$

The quantity

$$\alpha = \frac{e^2}{\hbar c} = 7.297 \times 10^{-3} \sim \frac{1}{137}$$

is called the *fine structure constant* since the term in Equation 4.13 in which α appears, correctly accounted for the fine structure splitting of the lines of the hydrogen spectrum.

Although the old quantum theory achieved many successes in atomic and molecular spectroscopy, it was an incomplete theory in the sense that none of its recipes for quantization were derived from first principles. Since it

could not be applied to aperiodic systems, most collision and scattering problems were beyond its pale. Furthermore, it contained errors, contradictions, and ambiguities.⁷ It did have some virtues, however. It predicted a large body of experimental results from a few simple rules, and it set the stage for the new quantum mechanics which soon replaced it. We will now proceed to discuss the wave mechanics of de Broglie and Schrödinger.

4. THE WAVE NATURE OF PARTICLES

The idea of associating both a wave and particle nature with the electron was first proposed by de Broglie in his doctoral thesis in 1925.⁸ His work was motivated by the mystery of the Bohr orbits, which he attempted to explain by fitting a standing wave around the circumference of each orbit. Thus, de Broglie required that $n\lambda = 2\pi r$, where λ is the wavelength associated with the n^{th} orbit and r is its radius. Combining this with Equation 3.25 we immediately obtain the result that

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

Assuming the existence of a natural symmetry in the properties of matter and energy, he proposed that a material particle of total energy E and momentum p must be accompanied by a phase wave, analogous to that ascribed to the photon, whose wavelength is given by $\lambda = h/p$ and whose frequency is given by the Planck formula, $\nu = E/h$. The Planck and de Broglie relations may be expressed in the useful forms,

$$E = \hbar\omega$$

and

$$p = \hbar k,$$

(4.14)

where $\hbar = h/2\pi$, $k = 2\pi/\lambda$, and $\omega = 2\pi\nu$.

The physical nature of such a particle wave was not clearly described by de Broglie. Unlike a classical wave, the energy E of the particle wave is not thought of as spread out over the extent of the wave, but is regarded as localized with the particle. However, the accompanying wave is essential in order to account for the phenomena of interference and diffraction.

The concept of the de Broglie wavelength is one of the cornerstones of modern quantum theory, and the simple relationship

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

holds for photons as well as for both relativistic and non-relativistic material particles, provided that the appropriate expression for p is used.

⁷ Albert Messiah, *Quantum Mechanics*, North-Holland Publishing Co., Amsterdam (1958), Chapter 1.

⁸ L. de Broglie, *Ann. Phys. (Paris)* **3**, 22 (1925).