An alternative solution to the radial quantum condition for the hydrogen atom

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The quantization method applied to the hydrogen atom involves the solution of the phase integral $\oint p_r\, dr = n_r h$, which was named by Sommerfeld as the *radial quantum condition* and it was solved using complex integration. In this work, we present an alternative solution to the *radial quantum condition* using real variable integration methods as an accessible way for students of introductory quantum mechanics courses. In addition, we show that in the Sommerfeld model the degeneracy of the energy levels is related to the geometric properties of the ellipse describing the electron motion around the nucleus.

Keywords: Hydrogen atom; elliptical orbits; phase integral.

La aplicación del método de cuantización al átomo de hidrógeno implica resolver la integral de fase $\oint p_r\, dr = n_r h$, la cual fue denominada por Sommerfeld como la *condición de cuantización radial* y fue resuelta empleando técnicas de integración de variable compleja. En este trabajo, presentamos una solución alternativa para la *condición de cuantización radial*, en la cual se utilizan únicamente métodos de integración de variable real como una forma accesible para los estudiantes de cursos introductorios de mecánica cuántica. Además, mostramos que dentro del modelo de Sommerfeld, la degeneración que presentan los niveles de energía está relacionada con las propiedades geométricas de la trayectoria elíptica del electrón alrededor del núcleo.

Descriptores: Átomo de hidrógeno; órbitas elípticas; integral de fase.

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1. Introduction

One of the pillars of the atomic structure was established by Bohr, by introducing the concept of quantization of circular orbits for the electron around a fixed nucleus and developing a theory, which was in quantitative agreement with the hydrogen spectrum data [1]. Subsequently, Sommerfeld extended Bohr's theory by assuming the existence of elliptical orbits in an attempt to explain the splitting of the spectral lines in the hydrogen spectrum [2–4]. The hydrogen atom was studied by Sommerfeld as a planetary system according to the formulation of Kepler's law in the form: *The electron moves in an ellipse, in one focus of which the nucleus is situated*. Consequently, the motion in the elliptic path represents a problem of two degrees of freedom. For the present analysis, will consider the polar coordinates measured from the nucleus, namely azimuth ϕ and the radius r (see Fig. 1). Thus, the element of orbit ds of the electron is given by

$$ds^2 = dr^2 + r^2 d\phi^2, \tag{1}$$

with kinetic energy, T:

$$T = \frac{m}{2}\left(\dot{r}^2 + r^2\dot{\phi}^2\right), \tag{2}$$

and potential energy, $V(r)$, in CGS is:

$$V = -\frac{Ze^2}{r}, \tag{3}$$

where r represents the distance between the particles. Thus, the total energy $E = T + V$ is given by

$$E = \frac{m}{2}\left(\dot{r}^2 + r^2\dot{\phi}^2\right) - \frac{Ze^2}{r}, \tag{4}$$

which in terms of $p_r = m\dot{r}$ and $p_\phi = mr^2\dot{\phi}$ can be rewritten as

$$E = \frac{1}{2m}\left(p_r^2 + \frac{p_\phi^2}{r^2}\right) - \frac{Ze^2}{r}, \tag{5}$$

where p_r and p_ϕ are the radial and angular momentum, respectively.

The quantization for the phase-space was conducted over many years before the Sommerfeld work [2–4]. First, Planck suggested the rule defined by

$$\int\!\!\int dp\, dq = h, \tag{6}$$

where q is a generalized coordinate and p is the corresponding conjugated momentum. At the same time Sommerfeld proposed that for every molecular process, the exchange quantity of action is

$$\int_0^\tau L\, dt = \frac{h}{2\pi}, \tag{7}$$

where τ is the duration of the process and L is the Lagrangian. It is interesting to mention that Sommerfeld and other involved in the development of the old quantum theory were all experienced in the Hamiltonian formulation of classical dynamics. Therefore, it was natural that they express the generalization of the quantum conditions in that language [2–4]. Hence, Sommerfeld attempted to formulate the idea of quantization in a universal way in order to be applied to any classically finite motion. Thus, the Sommerfeld proposal states that among all possible motions are allowed, only those that satisfies the condition,

$$\int p_k \, dq_k = n_k h, \tag{8}$$

where q and p refer to a pair of canonical variables and the integration is over a full period of classical motion. Consequently, by setting $n_k = 1, 2, \ldots$ in (8) we fix the first, second, etc. quantized phase-orbit of the k-th freedom degree. Interestingly, this quantization rule was proposed independently by Wilson [5], Ishiwara [6], and Sommerfeld [7].

The Wilson-Sommerfeld quantization conditions applied to elliptical orbits wich takes the form [8–10]:

$$\oint p_\phi \, d\phi = n_\phi h, \tag{9}$$

$$\oint p_r \, dr = n_r h, \tag{10}$$

where h is the Planck constant. The number n_ϕ is the azimuthal quantum number and it can take the values: 1, 2, 3, $\cdots$; while n_r is the radial quantum number and it can take the values: 0, 1, 2, $\cdots$. These integrals have to be computed for one complete period. The Eqs. (9) and (10) were called the *azimuthal quantum condition* and the *radial quantum condition* [13], respectively.

From the subject of central forces in classical mechanics, we know that for a particle of mass m moving in a potential $V(r)$, the angular momentum L is a constant of motion [11]. This fact can be easily demonstrated by taking the time derivative of the angular momentum vector, $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, resulting:

$$\frac{d\boldsymbol{L}}{dt} = \boldsymbol{r} \times \boldsymbol{F}. \tag{11}$$

But for the case of a central potential, the general form of the force is given by

$$\boldsymbol{F} = f(r) \, \frac{\boldsymbol{r}}{r}, \tag{12}$$

where $f(r) = -dV/dr$. Thus, substituting this expression for $\boldsymbol{F}$ in (11) we find that $d\boldsymbol{L}/dt = 0$, which means that for the case of a particle moving in a force field derived from a central potential $V(r)$, the angular momentum is a constant of motion. Hence, according to the law of conservation of angular momentum $p_\phi = mr^2\dot{\phi} = L$ is constant [11]. Thus, the integral (9) becomes

$$p_\phi = n_\phi \hbar, \tag{13}$$

where $\hbar = h/2\pi$.

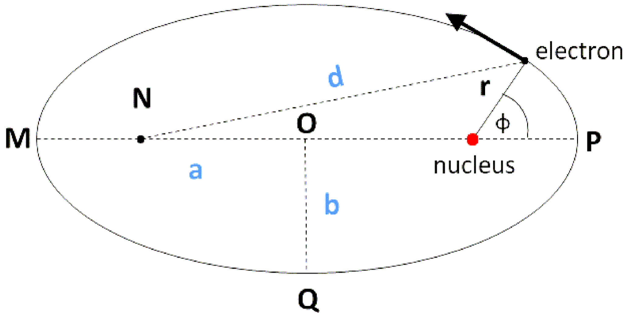

FIGURE 1. Geometrical representation of the hydrogen atom.

The Eq. (10) has to be restated in terms of the orbital equation of the ellipse. From Fig. 1 and according to elementary analytical geometry [12], we have that:

$$\begin{aligned} \overline{\mathrm{OP}} &= a \\ \overline{\mathrm{OQ}} &= b \\ \overline{\mathrm{NP}} &= a(1+\epsilon) \\ \overline{\mathrm{NM}} &= a(1-\epsilon) \\ \overline{\mathrm{NO}} &= a\epsilon, \end{aligned} \tag{14}$$

where a and b are the major and minor axis respectively, and ε is the ellipse eccentricity $(0 < \varepsilon < 1)$, which are related by

$$b = a\sqrt{1-\epsilon^2}. \tag{15}$$

To obtain the equation of the electron orbit around the nucleus, we will start by analyzing Fig. 1. We denote as d the distance between the point N and the point where the electron is located (see Fig. 1), so d can be expressed geometrically as

$$d^2 = r^2 \sin^2\phi + (2a\varepsilon + r\cos\phi)^2 \,, \tag{16}$$

and using the trigonometric identity $\sin^2\phi + \cos^2\phi = 1$, the last equation is reduced to:

$$d^2 = r^2 + 4a\varepsilon \left(a\varepsilon + r\cos\phi\right). \tag{17}$$

But, by construccion, the left and right focal radii obey the relationship $d + r = 2a$. Therefore,

$$\left(2a - r\right)^2 = r^2 + 4a\varepsilon \left(a\varepsilon + r\cos\phi\right). \tag{18}$$

Thus, the parametric formula of the ellipse in polar coordinates is written as:

$$\frac{1}{r} = \frac{1}{a}\left(\frac{1+\varepsilon\cos\phi}{1-\varepsilon^2}\right). \tag{19}$$

Then, before solving the integral in the radial quantum condition (10), we notes that

$$\begin{aligned} p_r &= m\frac{dr}{dt} = m\frac{dr}{d\phi}\frac{d\phi}{dt} \\ &= \frac{1}{r^2}\left(mr^2\frac{d\phi}{dt}\right)\frac{dr}{d\phi} = \frac{L}{r^2}\frac{dr}{d\phi}, \end{aligned} \tag{20}$$

so that

$$\oint p_r\,dr = \int_0^{2\pi} \frac{L}{r^2}\left(\frac{dr}{d\phi}\right)^2 d\phi = n_r h.. \tag{21}$$

From the parametric formula of the ellipse (19), we have that

$$\frac{1}{r^2}\left(\frac{dr}{d\phi}\right)^2 = \frac{\varepsilon^2 \sin^2\phi}{(1+\varepsilon\cos\phi)^2}. \tag{22}$$

Thus, we find that the integral (10) becomes

$$L\varepsilon^2 \int_0^{2\pi} \frac{\sin^2\phi}{(1+\varepsilon\cos\phi)^2} d\phi = n_r h. \tag{23}$$

The constant L, is also so-called *areal constant* and determines the size of the ellipse. Thus, the problem of quantization for the elliptical orbit has been reduced to solve the integral, I, in Eq. (23):

$$I \equiv \int_0^{2\pi} \frac{\sin^2\phi}{(1+\varepsilon\cos\phi)^2} d\phi. \tag{24}$$

This integral was evaluated by Sommerfeld using complex integration on a closed contour [13]. We would like to mention that details of this solution and other alternative methods, based also on complex variable techniques, can be found in reference [14]. In the next section, we show an alternative solution which does not require the use of the complex variable.

2. The radial quantum condition solved using real variable integration methods

In this section we present a solution of the integral (24) using real variable integration methods. We start integrating (24) by parts [15], obtaining

$$\begin{aligned} I &= \int_0^{2\pi} \frac{\sin^2\phi}{(1+\varepsilon\cos\phi)^2} d\phi \\ &= -\frac{1}{\varepsilon}\int_0^{2\pi} \frac{\cos\phi}{1+\varepsilon\cos\phi} d\phi. \end{aligned} \tag{25}$$

Now, we take the right hand integral and separate the interval $[0, 2\pi]$ in two parts $[0, \pi]$ and $[\pi, 2\pi]$. Then we have:

$$-\varepsilon I = \int_0^{\pi} \frac{\cos\phi}{1+\varepsilon\cos\phi} d\phi + \int_{\pi}^{2\pi} \frac{\cos\phi}{1+\varepsilon\cos\phi} d\phi. \tag{26}$$

These integrals are rational functions of $\cos\phi$, then we can performe the following change of variable [16]:

$$u = \tan\frac{\phi}{2}. \tag{27}$$

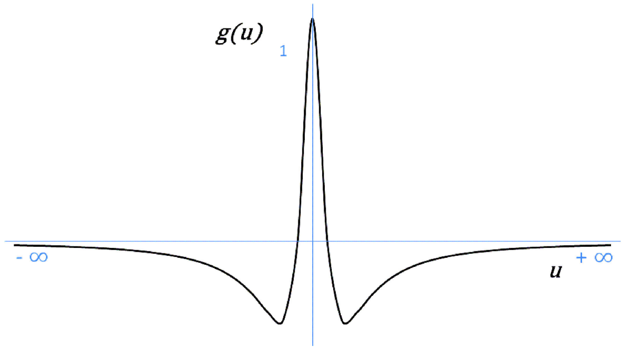

FIGURE 2. Plot of $g(u)$ for $\varepsilon = \sqrt{1/2}$.

Then

$$\cos\phi = \frac{1-u^2}{1+u^2}, \tag{28}$$

and

$$d\phi = \frac{2\,du}{1+u^2}. \tag{29}$$

Because the function (27) presents a discontinuity at $\phi = \pi$, the limits corresponding to the change of variable in the Eq. (26) are as follows:

$$\begin{aligned} -\varepsilon I = &\int_0^{+\infty} \frac{2(1-u^2)du}{(1+u^2)[(1-\varepsilon)u^2+(1+\varepsilon)]} \\ &+ \int_{-\infty}^{0} \frac{2(1-u^2)du}{(1+u^2)[(1-\varepsilon)u^2+(1+\varepsilon)]}. \end{aligned} \tag{30}$$

The integrand in the equation is a function of u that we will denote by $g(u)$. As we can see $g(u) = g(-u)$, that means that g is an even function in u. In order to observe the parity of $g(u)$, in Fig. 2 it is shown the plot of $g(u)$ for $\varepsilon = \sqrt{1/2}$.

Thus, as a result of the parity of $g(u)$ we have that:

$$-\varepsilon I = 2\int_0^{+\infty} \frac{2(1-u^2)du}{(1+u^2)[(1-\varepsilon)u^2+(1+\varepsilon)]}. \tag{31}$$

Now, separating in partial fractions we obtain:

$$-\varepsilon I = 2\int_0^{+\infty} \frac{\frac{2}{\varepsilon}du}{1+u^2} - 2\int_0^{+\infty} \frac{\frac{2}{\varepsilon}du}{(1-\varepsilon)u^2+(1+\varepsilon)}. \tag{32}$$

Manipulating algebraically we arrive to:

$$\begin{aligned} -\varepsilon I = 2\Bigg[&\frac{2}{\varepsilon}\int_0^{+\infty} \frac{du}{1+u^2} - \frac{2}{\varepsilon\sqrt{1-\varepsilon^2}} \\ &\times \int_0^{+\infty} \frac{\sqrt{\frac{1-\varepsilon}{1+\varepsilon}}du}{\left(\sqrt{\frac{1-\varepsilon}{1+\varepsilon}}u\right)^2+1}\Bigg]. \end{aligned} \tag{33}$$

Integrating the two terms of the right side, we obtain:

$$-\varepsilon I = 2 \lim_{u\to+\infty} \left[\frac{2}{\varepsilon} \arctan u - \frac{2}{\varepsilon\sqrt{1-\varepsilon^2}} \arctan\left(\sqrt{\frac{1-\varepsilon}{1+\varepsilon}} u \right) \right]. \tag{34}$$

Finally, we find that:

$$I = \frac{2\pi}{\varepsilon^2} \left(\frac{1}{\sqrt{1-\varepsilon^2}} - 1 \right). \tag{35}$$

Thus, with (35) in (23) we obtain:

$$2\pi L \left(\frac{1}{\sqrt{1-\varepsilon^2}} - 1 \right) = n_r h. \tag{36}$$

This result is the same expression that was obtained by Sommerfeld solving (24) using complex variable methods [13].

3. Quantization of energy orbits

After solving the phase-integral of the radial quantum condition, in this section, we are obtaining the expression for the quantization of energy. We start rewriting (4) using $\dot{\phi} = L^2/mr^2$, to obtain

$$E(r, p_r) = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{Ze^2}{r}. \tag{37}$$

From Fig. 1 we can see that when the electron is at the points P and M, the radial component of the momentum vanishes ($p_r = 0$), because there are turning points [11]. Notice that the distance r at P and M corresponds to $r_P = a(1-\varepsilon)$ and $r_M = a(1+\varepsilon)$, respectively. Thus, evaluating (37) at the points P and M, we obtain:

$$E_P = \frac{L^2}{2ma^2(1-\varepsilon)^2} - \frac{Ze^2}{a(1-\varepsilon)}, \tag{38}$$

$$E_M = \frac{L^2}{2ma^2(1+\varepsilon)^2} - \frac{Ze^2}{a(1+\varepsilon)}. \tag{39}$$

It is important to remember that the total energy is a constant of motion, consequently $E_P = E_M = E$. Hence, in order to find an expression for E in terms of L, we take the difference $(1+\varepsilon)E_M - (1-\varepsilon)E_P$ and we obtain:

$$E = -\frac{L^2}{2ma^2(1-\varepsilon^2)}. \tag{40}$$

On the other hand, to find an expression for E in terms of Z, we take the difference $(1+\varepsilon)^2 E_M - (1-\varepsilon)^2 E_N$ to obtain

$$E = -\frac{Ze^2}{2a}. \tag{41}$$

Now, combaining (36), (40) and (41) the following relation for the energy E can be get

$$E = -\frac{m}{2} \frac{Z^2 e^4}{(n_r \hbar + L)^2}, \tag{42}$$

but $L = p_\phi = n_\phi \hbar$, then

$$E = -\frac{m}{2\hbar^2} \frac{Z^2 e^4}{(n_r + n_\phi)^2}. \tag{43}$$

This result shows that the energy levels of the elliptical orbits are degenerate because there are two quantum numbers (n_r and n_ϕ) in the denominator. In this way, more than one set of values for n_r and n_ϕ are producing the same value for the energy. From here, the total or principal quantum number n rises and corresponds to the sum of the radial and azimuthal quantum numbers:

$$n \equiv n_r + n_\phi. \tag{44}$$

Then the expression of the total energy in terms of the principal quantum number is:

$$E = -\frac{m}{2\hbar^2} \frac{Z^2 e^4}{n^2}. \tag{45}$$

To conclude, a relationship between the quantum numbers and the geometric properties of ellipse can be obtained combining (13), (15) and (36). From that we find

$$\frac{a}{b} = \frac{n_r + n_\phi}{n_\phi}, \tag{46}$$

which can be rewritten as:

$$\frac{a}{b} = \frac{n}{n_\phi}. \tag{47}$$

This result shows that the ratio between semi-major (a) and semi-minor (b) axes of the elliptic orbit is equal to the ratio between the principal and azimuthal quantum numbers.

Finally, we want to mention that the problem of treating a particle in an elliptical orbit as a de Broglie wave conducts to the original quantum conditions proposed by Wilson [5], Ishiwara [6], and Sommerfeld [7]. A didactic exposition of this topic can be found in reference [17].

4. Final remarks

In summary, we presented an alternative solution to the radial quantum condition, based on the Sommerfeld model of the hydrogen atom, using real variable integration methods, which does not require the use of complex variable techniques. Adittionally, we used a simple geometric approach to show that the degeneracy of energy levels in the Sommerfeld model is related to the properties of the ellipse describing the electron motion around the nucleus. Both subjects can be useful for the discussion of the Sommerfeld model in an introductory quantum mechanics courses.

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