Revisiting Bohr’s quantization hypothesis for the atomic orbitals

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We deduce the quantization of the atomic orbit for the hydrogen’s atom model proposed by Bohr without using his hypothesis of angular momentum quantization. We show that his hypothesis can be deduced from and is a consequence of the Planck’s energy quantization.

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I. INTRODUCTION

The existence of an atomic nucleus was confirmed in 1911 by E. Rutherford in his classic scattering experiment [1]. Before that time, it was believed that an atom was something like a positively charged dough and negatively charged raisins scattered here and there within the dough, or an ice-cream with chocolate chip flakes in it, where the ice-cream would be the positive charge (protons) and the chocolate chip flakes the negative charge (electrons); an atomic model proposed by J.J. Thomson in 1904. However, this atomic model had many problems. And it became untenable as E. Rutherford showed the inconsistencies of such a model in face of his experiments of alpha particle (ionized helium) scattering by thin sheets of gold as targets. The main objection to that model being that scattering experiments indicated a far more ”dilute” type of matter constituents and ”empty” space within objects.

Then, Rutherford himself proposed the orbital model for the atom, in which there was a central nucleus populated by positively charged particles – protons – and negatively charge particles – electrons – moving around the nucleus in orbital trajectories, similar to the solar system with the sun at the center and planets orbiting it, described by the mechanics of celestial bodies acted on under central forces among them. Later on, the concept of neutral particles – neutrons – within the nucleus came to be added into the model.

The planetary model, however, was not free of problems. The main objection was that in such a model, electrons moving around the nucleus would radiate energy and therefore, classically, such an atom would collapse into itself after electrons radiated all their energy. Therefore, the model proposed by Rutherford had to be modified, and here comes the contribution of N. Bohr, which proposed the hypothesis for quantization of electron orbits making it possible to better understand the properties of atoms and of the stuff with which they are made of.

A comment may be in order here: At that time, the atomic nucleus was understood as a “storage” of mass and positive charge of the atom. There was no need to know neither a hint as to what was the internal structure of the nucleus [2]. These concepts came into play afterwards, as experiments got more sophisticated and more deeply concerned as to the internal structure of atoms.

II. THOMSON’S MODEL

In the model proposed by J.J. Thomson [3] in 1904, the atom was considered like a fluid with continuous spherical distribution of positive charges where electrons with negative charges were embedded, in a number sufficient to neutralize the positive charges. This model had an implicit underlying assumption: that of the existence of stable configurations for the electrons around which they would oscillate. However, according to the classical electromagnetic theory, there can be no stable configuration in a system of charged particles if the only interaction among them is of the electromagnetic character. Moreover, since any electrically charged particle in an accelerated movement emits electromagnetic radiation, his model had an additional hypothesis that the normal modes for the oscillating electrons would have the same frequencies as those observed associated with the lines of the atomic spectrum. However, there was not found any configuration for the electrons for any atom whose normal modes had any one of the expected frequencies. Therefore, Thomson’s model for the atom was abandoned because there was no agreement between its assumptions/predictions and the experimental results obtained by H. Geiger and E. Marsden [4].
III. THE PLANETARY ATOMIC MODEL

The discoveries that occurred by the end of XIX century led the physicist Ernest Rutherford to do scattering experiments that culminated in a proposal for the planetary model for atoms.

According to this model, all positive charge of a given atom, with approximately 99% of its mass, would be concentrated in the atomic nucleus. Electrons would be moving around the nucleus in circular orbits and these would be the carriers of the negative charges. Knowing that the charge of an electron and the charge of a proton are the same in modulus, and that the nucleus has \( Z \) protons, we can define the charge of the nucleus as \( Ze^- \).

Experimentally we observe that in an atom the distance \( r \) between the electron orbit and the nucleus is of the order \( 10^{-10} \text{m} \).

In this section, we build the planetary model for the atom and analyse its predictions compared to experimental data.

Using Coulomb’s law

\[
F = \frac{Ze^-}{4\pi\varepsilon_0 r^2} \tag{1}
\]

and the centripetal force acting on the electron in its circular orbit

\[
F_c = \frac{m_e v^2}{r} \tag{2}
\]

results in

\[
\frac{Ze^-}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r} \tag{3}
\]

\[
v = \sqrt{\frac{e^2}{4\pi\varepsilon_0 m_e r Z}} \tag{4}
\]

where we have used the shorthand notation \( |e^-| = e \).

From (4) we can estimate the radius for the electron orbit,

\[
r = \frac{e^2}{4\pi\varepsilon_0 m_e v^2 Z}, \tag{5}
\]

which means that the radius depends on the total number of protons in the nucleus, \( Z \), and also on the electron’s velocity. Here we can make some definite estimates and see whether our estimates are reasonable, i.e., agrees or does not violate experimental data. According to the special theory of relativity, no greater velocity can any particle possess than the speed of light. More precisely, for particles with mass like electrons, we know that their velocity is limited by \( v < c \) where \( c \) is the speed of light in vacuum. Substituting for velocity \( v = c = 3 \times 10^8 \text{m/s} \), electric charge \( e = 1.602 \times 10^{-19} \text{m/s} \), mass of the electron \( m_e = 9.109 \times 10^{-31} \text{kg} \) and \( \varepsilon_0 = 8.854 \times 10^{-12} \text{F/m} \), we have

\[
r > 2.813 \times 10^{-15} \text{m},
\]

where we have taken \( Z = 1 \) and didn’t consider the relativistic mass. This means that we have a lower limit for the radius of an electron’s orbit around the central nucleus, which is consistent with the experimental observed data where radius of electronic orbits are typically of the order \( 10^{-10} \text{m} \).

A. Limitations of the model

Even though this model could explain some features of the atomic structure concerning the scattering data, there was nonetheless problems that could not be explained just by classical mechanics analysis. Since protons and electrons are charged particles, electromagnetic forces do play their role in this interaction, and according to Maxwell’s equations, an accelerated electron emits radiation (and therefore energy), so that electrons moving around the nucleus would be emitting energy. This radiated energy would of course lead to the downspiraling of electrons around the nucleus until hitting it. Classical theoretical calculations done predicted that all electrons orbiting around a nucleus would hit it in less than a second!

However, what we observe is that there is electronic stability, and therefore the model had to be reviewed.
IV. BOHR’S HYPOTHESIS

Analysis of the hydrogen spectrum which showed that only light at certain definite frequencies and energies were emitted led Niels Bohr to postulate that the circular orbit of the electron around the nucleus is quantized, that is, that its angular momentum could only have certain discrete values, these being integer multiples of a certain basic value $\hbar$. This was his “ad hoc” assumption, introduced by hand into the theory. In 1913, therefore, he proposed the following for the atomic model:

1. The atom would be composed of a central nucleus where the positive charges (protons) are located;
2. Around the central nucleus revolved the electrons in equal number as the positive charges present in the nucleus. The electrons orbiting such a nucleus had discrete quantized energies, which meant that not any orbit is allowed but only certain specific ones satisfying the energy quantization requirements;
3. The allowed orbits also would have quantized or discrete values for orbital angular momentum, according to the prescription $|L| = n\hbar$ where $\hbar = \frac{\hbar}{2\pi}$ and $n = 1, 2, 3, ...$, which meant the electron’s orbit would have specific minimum radius, corresponding to the angular momentum quantum number $n = 1$. That would solve the problem of collapsing electrons into the nucleus.

Observe that Bohr did not use the value $n = 0$ because this does not define an electronic orbit around the nucleus, although in Plank’s hypothesis

$$E = nhf$$

where $n = 0, 1, 2, 3, ...$ the value $n = 0$, is perfectly allowed. The reason why Bohr left out this first quantum number out of his hypothesis comes from experiment, since spectroscopic studies of many chemical elements show that these numbers start with $n = 1$.

Two colloraries following Bohr’s assumptions do follow: First, from item 2. above, the laws of classical mechanics cannot describe the transition of an electron from one orbit to another, and second, when electrons do make a transition from one orbit to another, the energy difference is either supplied (transition from lower to higher energy orbits) or carried away (transition from higher to lower energy orbits) by a single quantum of light - the photon - which has the same energy as the energy difference between the two orbits.

In this short work we propose that Bohr’s atomic orbit quantization hypothesis is not necessarily needed as an “ad hoc” assumption, but that this can be arrived at using only Planck’s assumption of energy quantization.

First, let us follow the usual pathway where Bohr’s quantization is introduced. Using Newton’s second law for the electron moving in a circular orbit around the nucleus, and thus subject to Coulomb’s law, we have:

$$\frac{e^2}{4\pi \varepsilon_0 r^2} = \frac{mv^2}{r}. \quad (6)$$

This allows us to calculate the kinetic energy of the electron in such an orbit:

$$E_k = \frac{1}{2}mv^2 = \frac{e^2}{8\pi \varepsilon_0 r}. \quad (7)$$

The potential energy for the system proton-electron on the other hand is given by

$$E_p = -\frac{e^2}{4\pi \varepsilon_0 r}, \quad (8)$$

where $r$ is the radius of the electronic orbit.

Therefore, the total energy for the system is

$$E = -\frac{e^2}{8\pi \varepsilon_0 r}. \quad (9)$$

This result would suggest that, since the radius can have any value, the same should happen with the angular momentum $L$.

$$L = pr \sin \theta = pr, \text{ where } \theta = 90^0 \quad (10)$$

that is, the angular momentum depends on the radius. The linear momentum of the electron is given by

$$p = mv. \quad (11)$$
Therefore the problem of quantizing the angular momentum $L$ reduces to the quantizing of the radius $r$, which depends on the total energy $E$. Just here Bohr introduced an additional hypothesis, in that the angular momentum of the electron is quantized, i.e.,

$$ L = n\hbar, \quad (12) $$

where $\hbar = \frac{h}{2\pi}$. In this manner he was able to quantize the other physical quantities such as the total energy. This is the usual pathway wherein the textbooks normally follow in their sequence of calculations.

V. ORIGIN OF ORBITAL QUANTIZATION

In this work we show another way, in which we do not need the additional Bohr’s assumption input for angular momentum quantization, but stress the importance of Planck’s original energy quantization, from which angular momentum quantization follows as a consequence. So, from Planck’s hypothesis to quantize the energy

$$ E = nhf, \quad (13) $$

we have that the total energy for the electron-proton system is quantized accordingly, i.e.,

$$ nhf = E_n, \quad (14) $$

so that if we take the derivative of $E_n$ with respect to the frequency $f$ we get

$$ \left. \frac{dE_n}{df} \right|_{\text{Planck}} = nh. \quad (15) $$

According to the deduction given in the Appendix, modulus its sign, the total energy for the system electron-proton is

$$ E_n = \frac{mv^2}{2} \quad (16) $$

Knowing that the scalar orbital velocity is

$$ v = 2\pi fr, \quad (17) $$

where $f$ is the frequency and $r$ is the radius of the electronic orbit. Substituting this $v$ into (16) we then have:

$$ E_n = 2\pi^2 mr^2 f^2 \quad (18) $$

so the ratio of the system’s total energy variation with respect to the frequency is

$$ \left. \frac{dE_n}{df} \right|_{\text{System}} = 4\pi^2 mr^2 f. \quad (19) $$

From (17), (10) and (11), we rewrite (19), so that

$$ \left. \frac{dE_n}{df} \right|_{\text{System}} = 2\pi L. \quad (20) $$

Using now (15) in (20) we obtain

$$ L = nh. \quad (21) $$

We see that the ratio of the system’s total energy variation with respect to the frequency plus the Planck’s hypothesis of energy quantization leads to Bohr’s assumption.
VI. CONCLUSIONS

In this work we have shown that Planck’s fundamental assumption of energy quantization is more fundamental than Bohr’s assumption of angular momentum quantization. In fact, we have shown that Bohr’s rule for angular momentum quantization can be dispensed of altogether if we consider Planck’s energy quantization and that the former can be derived from this latter one.

The identity (15) can be further clarified by Wilson-Sommerfeld’s rules for quantization [8]. They proposed a set of rules to quantize any physical system whose coordinates are periodic functions of time. Their rules are the following: For all physical systems whose coordinates are periodic functions of time there exists a quantum condition for each coordinate expressed as:

\[ \oint p_i dq_i = n_i \hbar \]  

(22)

where \( i \) labels any one of the coordinates, \( p_i \) the conjugate momentum associated with such coordinate and \( n_i \) a quantum number attributed to such a coordinate.

In our case, we have,

\[ \oint p_i dq_i = L \oint d\theta = 2\pi L \]

and by (22)

\[ 2\pi L = n\hbar \]

that is,

\[ L = n\hbar \]

obtaining therefore our result (21).

VII. APPENDIX

In this Appendix we will show that the total energy for the system electron-proton depends on the scalar orbital velocity of the electron. From classical mechanics, an electron orbiting a proton in a circular orbit obeys the following equilibrium of forces:

\[ \frac{e^2}{4\pi \varepsilon r^2} = \frac{mv^2}{r} \]  

(23)

which results in

\[ \frac{e^2}{4\pi \varepsilon r} = mv^2 \]  

(24)

The total energy \( E_n \) for the electron-proton system is equal to the sum of its kinetic energy \( E_k \) and its potential energy \( E_p \).

\[ E_n = E_k + E_p \]  

(25)

where

\[ E_k = \frac{mv^2}{2} \]  

(26)

and

\[ E_p = -\frac{e^2}{4\pi \varepsilon r} \]  

(27)
The negative sign for the potential energy indicates that our zero reference for it is at infinity. Substituting these in (25) we have:

\[ E_n = \frac{mv^2}{2} - \frac{e^2}{4\pi\varepsilon r} \]  

(28)

From (24), we obtain:

\[ E_n = \frac{mv^2}{2} - mv^2 = -\frac{mv^2}{2} \]

Therefore, the total energy \( E_n \) for the electron-proton system is:

\[ E_n = -\frac{mv^2}{2} \]

Again, the negative sign here defines the bound state of the atom.

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