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A simple relativistic Bohr atom

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Abstract

A simple concise relativistic modification of the standard Bohr model for hydrogen-like atoms with circular orbits is presented. As the derivation requires basic knowledge of classical and relativistic mechanics, it can be taught in standard courses in modern physics and introductory quantum mechanics. In addition, it can be shown in a class that one straightforward prediction of this relativistic version of Bohr's model is the impossibility of finding atoms in nature with atomic number larger than a critical value.

1. Introduction

The standard textbooks in modern physics and introductory quantum mechanics treat Bohr's atom semi-classically [1–3], which is the way Bohr presented his theory in his historic papers investigating the hydrogen atom and other hydrogenic atoms [4]. Bohr, in his study of the H-atom, studied the motion of the single electron around the assumed fixed nucleus classically (i.e. applied Newton's classical mechanics). But in order to perform an investigation based on classical mechanics, one either needs to know in advance that the speed of the moving electron is much smaller than the speed of light or perform the calculation classically and then check to ensure that the result is consistent with the assumption. Moreover, in class, during the presentation of the standard Bohr model, the question of a relativistic treatment may arise. Actually, this is the most appropriate time for presenting a relativistic model for Bohr's atom in class, as special relativity is usually taught in the previous or same semester, either as an individual course or as part (the very first lessons) of a modern physics course [5].

In this paper we present a concise derivation of the predictions of Bohr's theory, describing the dynamics of the atoms using special relativity. We treat both the hydrogen atom (the simplest atom in nature) and hydrogenic atoms (ions of one electron with a complex nucleus). For the hydrogen atom, it is shown that for most practical cases the main results do not differ appreciably from the findings of the classical model. In contrast, it is revealed that for hydrogen-like atoms with heavy nuclei, the predictions of the relativistic model differ significantly compared to the prediction of the classical Bohr model.

In the development of this relativistic approach, we assume all Bohr's basic assumptions are valid [1–4]. Hence, (a) radiation is not emitted or absorbed as expected from classical electrodynamics for accelerated charges, (b) the dynamics of the system is determined by the

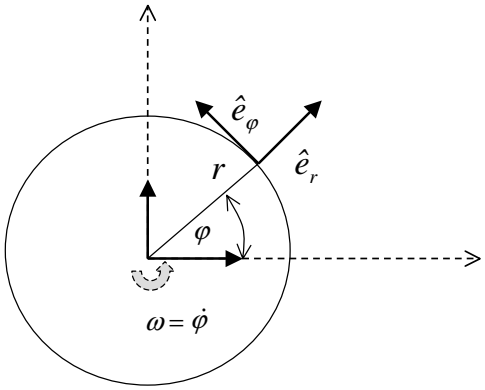

Figure 1. Definition of polar coordinates (r, φ) and unit vectors $(\hat{e}_r, \hat{e}_\varphi)$ used in circular motion of the electron in the H-atom. The z-axis is perpendicular to the plane of circular motion, with unit vector $\hat{z} = \hat{x} \times \hat{y} = \hat{e}_r \times \hat{e}_\varphi$.

ordinary law of classical (here relativistic) mechanics and (c) the various stationary states, in the case of circular orbits, are determined by the condition that the angular momentum of the electron revolving around the nucleus is an integer multiple of $\hbar$.

2. Hydrogen atom

Initially, we focus on the hydrogen atom. The generalization for any hydrogen-like atom is straightforward and it will be presented in the next section.

In the following procedure, as the mass of the nucleus (proton) is much larger than the mass of the electron, it is assumed that the nucleus is not moving. The relativistic law of the rate of change of the momentum of the moving electron is given by the well-known relativistic expression

$$\vec{F} = \frac{\mathrm{d}\vec{p}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{m\vec{v}}{\sqrt{1 - v^2/c^2}}\right), \tag{1}$$

where m is the rest mass of the electron ($mc^2 \approx 511$ keV), $\vec{v}$ is the velocity of the electron, $v \equiv |\vec{v}|$ is the speed of the electron and $\vec{F}$ is the force on the electron. Following Bohr's assumptions, we accept circular orbits with constant angular frequency ω (i.e. $\omega = \dot{\varphi} = \mathrm{d}\varphi/\mathrm{d}t$ and the speed is constant given by the expression $v = \omega r$). In this model, once we assume circular orbits (constant radius, r), the angular frequency should be constant as otherwise $\vec{F} = \mathrm{d}\vec{p}/\mathrm{d}t = -(1 - v^2/c^2)^{-1/2} r(\mathrm{d}\varphi/\mathrm{d}t)\hat{e}_r + (1 - v^2/c^2)^{-3/2} r(\mathrm{d}^2\varphi/\mathrm{d}t^2)\hat{e}_\varphi$ has a part (second term) which is not compensated by the centripetal force (parallel to $-\hat{e}_r$; for the definition of the unit vectors, $\hat{e}_r$ and $\hat{e}_\varphi$, see figure 1). Moreover, if the angular frequency is not constant, the angular momentum will be time dependent $|\vec{l}| = m(1 - r^2(\mathrm{d}\varphi/\mathrm{d}t)^2/c^2)^{-1/2} r^2(\mathrm{d}\varphi/\mathrm{d}t)$, as $\mathrm{d}\varphi/\mathrm{d}t$ is time dependent and it cannot be equal to a constant ($\hbar n$).

In this case the speed is time independent; equation (1) can be written as

$$\vec{F} = \frac{m}{\sqrt{1 - v^2/c^2}} \frac{\mathrm{d}\vec{v}}{\mathrm{d}t}. \tag{1a}$$

For circular motion

$$\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = \frac{\mathrm{d}(r\omega\hat{e}_\varphi)}{\mathrm{d}t} = r\omega\frac{\mathrm{d}\hat{e}_\varphi}{\mathrm{d}t} = r\omega\frac{\mathrm{d}(-\sin\varphi\hat{x} + \cos\varphi\hat{y})}{\mathrm{d}t}$$
$$= r\omega\frac{\mathrm{d}\varphi}{\mathrm{d}t}(-\cos\varphi\hat{x} - \sin\varphi\hat{y}) = -\frac{v^2}{r}\hat{e}_r,$$

and the relativistic force causing the circular motion of the electron has the following form:

$$\vec{F} = \frac{m}{\sqrt{1 - v^2/c^2}}\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = -\frac{mv^2}{r\sqrt{1 - v^2/c^2}}\hat{e}_r. \tag{1b}$$

In the hydrogen atom the physical origin of this force is the electrostatic attraction from the fixed nucleus. Hence the Coulomb force should be equal to the force needed for the circular motion with constant speed.

It is well known in the special theory of relativity (actually an experimental fact) that Coulomb's law is unchanged for a moving charge [6]. In other words, *Coulomb's law is valid for a moving charge,* even if its speed is approaching the speed of light, provided the source charge (here the nucleus) is at rest.

By equating these forces (i.e. the centripetal force and the electrostatic force) we get a relation between the radius of the circular orbit and its speed:

$$\frac{e^2}{r^2} = \frac{mv^2}{r\sqrt{1 - v^2/c^2}} \quad \Rightarrow \quad \frac{e^2}{r} = \frac{mv^2}{\sqrt{1 - v^2/c^2}}. \tag{2}$$

We work with the CGS system of measurement, where the Coulomb force has a unity coefficient. Then we follow Bohr's treatment using the quantization of the angular momentum ($|\vec{l}| = \hbar n$, where n is a positive integer). Hence the orbit of the electron is described by the equation

$$|\vec{l}| = |\vec{r} \times \vec{p}| = \left| r\hat{e}_r \times \frac{mv\hat{e}_\varphi}{\sqrt{1 - v^2/c^2}} \right| = \left| \frac{mvr\hat{z}}{\sqrt{1 - v^2/c^2}} \right| = \frac{mvr}{\sqrt{1 - v^2/c^2}} = \hbar n. \tag{3}$$

By combining equations (2) and (3), we eliminate the radius and find an expression for the speed, in various orbits specified by the quantum number *n:*

$$v_n = \frac{e^2}{\hbar}\frac{1}{n}, \tag{4}$$

which is *identical* to the expression found by Bohr in the classical treatment [1–4]. We can use this expression to check the validity of the classical treatment. We easily find that the relativistic treatment give minor corrections (i.e. it is in most cases practically unnecessary). The reason is that $v_n = e^2/\hbar n = ce^2/c\hbar n$, which shows that the speed of the electron is, even for the smallest $n(=1)$, much smaller than the speed of light (as α[fine-structure constant] $\equiv e^2/\hbar c \sim 1/137.036$ and $v_n/c = \alpha/n \sim 1/137.036n$).

Then the radius of each circular orbit is found using either equation (2) or (3):

$$r_n = \frac{\hbar^2}{me^2}n\sqrt{n^2 - \alpha^2} = a_0 n\sqrt{n^2 - \alpha^2}, \tag{5}$$

where α is the fine-structure constant and $a_0 \equiv \hbar^2/me^2$ is the first Bohr orbit for hydrogen, usually called the hydrogen-atom Bohr radius (symbolized as a_0 [≈ 0.529 Å] in most textbooks).

Practically, because of the small value of $\alpha^2 \sim 0.000\,0533$ and especially for large values of the quantum number n, the expression for the radius of the circular orbits is almost identical (derived from equation (5), assuming $\sqrt{n^2-\alpha^2} \sim n$) to the one found in the classical treatment ($r_n = a_0 n^2$).

Our last step is to find the total energy of the system, using the relativistic expressions. As the nucleus is assumed stationary the total energy of the hydrogen atom (bound state of the electron–proton system) is

$$\begin{aligned} E &= Mc^2 + mc^2/\sqrt{1-v^2/c^2} - e^2/r \quad \xrightarrow{\text{Equation (2)}} \\ E &= Mc^2 + mc^2/\sqrt{1-v^2/c^2} - mv^2/\sqrt{1-v^2/c^2} \\ &= Mc^2 + mc^2\sqrt{1-v^2/c^2} \quad \xrightarrow{\text{Equation (4)}} \\ E_n &= Mc^2 + mc^2(1-\alpha^2/n^2)^{1/2}. \end{aligned} \tag{6}$$

As $\alpha/n \ll 1$, even for the lowest value of n, we can expand equation (6) and keep the lowest term. In this case we get

$$E_n \simeq Mc^2 + mc^2(1-\alpha^2/2n^2) = Mc^2 + mc^2 - me^4/2\hbar^2 n^2, \tag{6a}$$

which, after subtracting the energies describing the relativistic rest mass energies, is identical to the expression found in the standard 'classical' derivation (third term in equation (6*a*)).

Hence, the relativistic correction is

$$E_n - Mc^2 - mc^2(1-\alpha^2/2n^2) = mc^2[(1-\alpha^2/n^2)^{1/2} - (1-\alpha^2/2n^2)], \tag{6b}$$

with the most important correction term given by the second term in the Taylor expansion of the square root term being equal to $-mc^2\alpha^4/8n^4$.

3. Hydrogen-like atoms

The classical Bohr model is valid for any hydrogen-like atom [7, 8], i.e. for any atom with one electron and a nucleus with atomic number Z (number of protons). Obviously, these one-electron atoms are ions with total charge of $(Z-1)e$ (the only neutral hydrogen-like atom is hydrogen). These ions can be found in nature, for example on the surface of the sun or other stars, or they are produced in the lab as uranium hydrogen-like ions [9]. Since the early days of atomic physics, it has been shown experimentally that the classical Bohr model predicts correctly the spectra of the three lightest hydrogenic ions, helium (He^+), lithium (Li^{2+}) and beryllium (Be^{3+}) [10]. In this section, we extend the previously presented relativistic model for the hydrogen-like atoms. In the theoretical treatment of the hydrogenic atoms, basically we have to change the expression in the Coulomb force from e^2/r^2 to Ze^2/r^2; then the speed becomes (combining the modified equation (2) and equation (3)) $v_n = Ze^2/\hbar n = Z\alpha c/n$ (hence for large Z, at least the first orbit $n = 1$ can approach the speed of light). Then the radius is modified as $r_n = a_0 n\sqrt{n^2 - Z^2\alpha^2}/Z$ (now for the first orbit and for $Z > 1/\alpha$ we get a square root of a negative number), and the total energy is $E_n = Mc^2 + mc^2\sqrt{1 - Z^2\alpha^2/n^2}$ (again, for the first orbit and for $Z > 1/\alpha$ we get a square root of a negative number).

The significance of the relativistic treatment can be illustrated in class with the example of ionization energy. Hence for the hydrogen atom ($Z = 1$) the prediction of the classical and the relativistic model is practically identical. But for Ag (silver, $Z = 47$), the classical model predicts an ionization energy of 30.0534 keV and the relativistic model an energy of 30.9824 keV, almost 1 keV larger (3.1% relative difference). For heavier atoms such as Hg (mercury, $Z = 80$) the energies are 87.072 keV and 96.0738 keV, with a relative difference of greater than 10%. For even heavier ions the relative difference can be close to 20%, as

for example for Fm (fermium, $Z = 100$), with energies of 136.02 keV and 161.614 keV, respectively.

A final example, revealing the significance of the relativistic treatment, is related to the radius of the atom. The size (diameter) of the nucleus is in the range of 1.6 fm (fm $= 10^{-15}$ m) (for a proton in light hydrogen) to about 15 fm (for the heaviest atoms, such as uranium). These dimensions are much smaller than the size of the atom itself by a factor of about 23 000 (uranium) to about 145 000 (hydrogen). When we apply the relativistic model the circular orbit of the uranium hydrogen-like ion has a radius of 426 fm. In this case the electron is now much closer to the nucleus and the finite size of the nucleus should be accounted for.

The expressions found for the velocity, radius and energy of the hydrogen-like atoms suggest that, in order not to contradict special relativity (speed of electrons higher than speed of light) or not to achieve square roots of negative numbers (implying imaginary radius and energy), the quantity $Z\alpha$ should be smaller than unity. Hence, the relativistic version of Bohr's model for the hydrogen-like ions suggests that $Z < 1/\alpha \sim 137$. This relation sets an upper limit on the atomic number of atoms in nature. This is in agreement with present-day experimental facts, since the largest observed atom has an atomic number of 118 (Ununoctium, discovered in 2006)[1].

Finally, it becomes obvious from the energy expression that the relativistic model predicts a very different spectrum for the hydrogen-like ions with very heavy nuclei (large Z). Today it is an experimental fact that these deviations from the classical model are found even for not very large ions, such as, for example, gallium with atomic number $Z = 31$ [11].

4. Nucleus with finite mass and non-zero velocity

Finally, we discuss the case where the mass of the nucleus is not infinite. This is a very complicated case as in the relativistic model it is not possible to follow the classical treatment by introducing the reduced mass. This can be seen easily as $\mathrm{d}\vec{p}/\mathrm{d}t = d(m\vec{v}/\sqrt{1 - v^2/c^2})/\mathrm{d}t$; it can never take the form of $\mathrm{d}^2\vec{r}/\mathrm{d}t^2$, which is the starting point for obtaining a simple differential equation of the relative position vector $(\vec{r}_e - \vec{r}_{\text{nucleus}})$. Moreover, the reduced mass method cannot be carried on, as when the nucleus has a finite mass, it will certainly be moving, and hence it will produce an electric and a magnetic field, resulting in forces on each particle that are not of equal magnitude and opposite sign. These arguments are explained in detail for the hydrogen atom in the following paragraphs.

We start with a short review of the reduced mass method. Newton's law for the acceleration of the electron and the proton (with rest mass M) is described by the equations $m\frac{\mathrm{d}^2\vec{r}_e}{\mathrm{d}t^2} = \vec{F}_{e-p}$ and $M\frac{\mathrm{d}^2\vec{r}_p}{\mathrm{d}t^2} = \vec{F}_{p-e}$, where the forces $\vec{F}_{e-p}$ (electrostatic force on the electron due to the proton) and $\vec{F}_{p-e}$ (electrostatic force on the proton due to the electron) are opposite forces (action–reaction). By eliminating the masses from the left-hand side of each equation and subtracting the two equivalent equations we get

$$\frac{\mathrm{d}^2\vec{r}_e}{\mathrm{d}t^2} - \frac{\mathrm{d}^2\vec{r}_p}{\mathrm{d}t^2} = \frac{\vec{F}_{e-p}}{m} - \frac{\vec{F}_{p-e}}{M} = \left(\frac{1}{m} + \frac{1}{M}\right)\vec{F}_{e-p} \quad \Rightarrow \quad \left(\frac{mM}{M+m}\right)\frac{\mathrm{d}^2(\vec{r}_e - \vec{r}_p)}{\mathrm{d}t^2} = \vec{F}_{e-p}.$$

This equation shows that the relative position vector of the electron with respect to the proton has a motion caused by the electron–proton electrostatic force but for an equivalent mass,

[1] A complete and updated periodic table of elements can be found in the web page of the chemistry division at the Los Alamos National Laboratory (http://periodic.lanl.gov/default.htm). In this table one can find, interactively, the history, properties, resources, uses, isotopes, forms and other information for each element.

$mM/(M+m)$, called reduced mass. In addition, in the relativistic version of Bohr's atom, the equations of motion are very different. The reason is that in the case of both charges moving, apart from the electric fields, magnetic fields are also introduced. The equations become [12]

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{m\vec{v}_e}{\sqrt{1-v_e^2/c^2}}\right) &= -e(\vec{E}_p + \vec{v}_e \times \vec{B}_p) \\ \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{M\vec{v}_p}{\sqrt{1-v_p^2/c^2}}\right) &= e(\vec{E}_e + \vec{v}_p \times \vec{B}_e), \end{aligned} \tag{7}$$

where $\vec{E}_{p(e)}$ and $\vec{B}_{p(e)}$ are the electric and magnetic fields created by the proton (electron). The expressions for the electric and magnetic fields are quite complicated since retardation effects, originating from the finite speed of propagation of any interaction in nature, become important at high velocities [13]. The right-hand terms are not of the form of action and reaction as in classical mechanics. The absence of opposite forces on the right-hand side of the equations of motion is another reason why the reduced mass method cannot be applied in the relativistic version of Bohr's model.

A first attempt to study this problem appeared in [14], with a much larger nucleur mass and few terms in the expansion of the complicated expression for the forces.

Another attempt to study the relativistic corrections was presented in [15], but results and predictions for the H-like atoms were not emphasized.

5. Elliptic orbits in the semi-classical model

It is well known that in all atomic spectra that splitting of the spectral lines into several distinct components can be observed, and is termed fine structure [16, 17]. In an effort to explain this fine structure, Sommerfeld assumed that the electron could move in elliptic orbits. He evaluated the size and shape of the elliptical orbits and the energy of these orbits by applying the laws of the classical mechanics and the generalized quantization rules that he proposed with Wilson in 1916 (the Wilson–Sommerfeld quantization rules, which include both Bohr quantization for the H-atom and Planck quantization for the harmonic oscillator as special cases). The generalized quantization rules introduced two quantum numbers: the principal and the azimuthal one. The relationship between these two quantum numbers determines the shape of the elliptic orbits with the special case of the circular orbit corresponding to equal quantum numbers. Sommerfeld found that despite the very different paths followed by an electron moving in the elliptical orbits, they all show the same total energy provided the principal quantum number is the same (i.e. all orbits with given principal quantum number are degenerate, with degeneracy equal to the azimuthal quantum number) [16]. This degeneracy in the total energy is the result of a very delicate balance between potential and kinetic energy, which is a characteristic for the inverse square law of force. Actually, this degeneracy and the simple form of the energy spectrum of the non-relativistic hydrogen atom have been explained in terms of the dynamic symmetry approach [18].

Sommerfeld removed the degeneracy of the elliptic orbits by treating the problem with the theory of relativistic mechanics [14, 16]. In the context of the relativistic model the fine structure of the hydrogen spectrum has been explained partially. However, a full explanation of the atomic spectrum had to wait for a quantum mechanical treatment.

6. Quantum mechanical treatment of one-electron atoms

The correct treatment of the hydrogen and hydrogen-like atoms corresponds to a quantum mechanical one. The Bohr model is an important first step. But basic assumptions of the Bohr model are completely contrary to the basic premises of quantum mechanics. For example, the ground state orbital angular momentum of the H-atom is zero according to quantum mechanics rather than $\hbar$ (Bohr's model for $n = 1$). In the quantum mechanical treatment the starting point is the Schrödinger equation for the one-electron atom, which is well known and presented in all quantum mechanics textbooks [19–24]. The simple form of the eigenenergies found for the H-atoms and H-like atoms can be explained by means of the dynamic symmetry, a very useful method in atomic and nuclear physics [25–27]. Actually, the non-relativistic hydrogen atom consists the oldest example of a dynamic symmetry application in quantum mechanics [18]. It has been shown that the H-atom has a four-dimensional space O(4) symmetry. The Hamiltonian can be written in terms of one of the Casimir operators of an algebra, O(4), whose elements are the three components of the angular momentum and the three components of the Runge–Lenz vector. The presence of this dynamic symmetry manifests itself in the closed form of the energy eigenvalues which produces a regular pattern of energy levels and in the occurrence of degeneracies in addition to those due to rotational invariance.

Although the energy levels obtained from the standard H-atom Hamiltonian, which includes the kinetic and potential energy terms, are in good agreement with experiment, the very precise measurements carried out in atomic physics demonstrate the existence of several effects which cannot be derived from this Hamiltonian and require the addition of correction terms [28, 29]. First, it introduces the relativistic correction to the kinetic energy (i.e. the most significant term in the expansion of the relativistic kinetic energy, proportional to the fourth power of the momentum). The next important correction is the spin–orbit interaction, which describes the interaction of the electron's spin with its motion (angular momentum), detectable as a splitting of spectral lines. The Lamb shift is another subtle effect, which is an energy shift that is explained in the context of quantum electrodynamics, and can be interpreted as the influence of virtual photons that have been emitted and re-absorbed by the atom. Then, it appears the Darwin term. The physical origin of the Darwin term is a phenomenon in relativistic Dirac theory called zitterbewegung, whereby the electron does not move smoothly but instead undergoes extremely rapid small-scale fluctuations, causing the electron to see a smeared-out Coulomb potential of the nucleus [28].

Finally, we consider various small corrections such as the hyperfine structure splitting and the volume effect, which take into account the fact that the nucleus is not simply a point charge, but has a finite size, and may possess an intrinsic angular momentum (spin), a magnetic dipole moment, an electric quadrupole moment and so on [28]. The inclusion of these effects gives an improvement in the agreement between theory and experiment to about seven significant digits. A further improvement is achieved when a quantization of the internal electric and magnetic fields is included. The corrections due to these effects bring agreement to the higher significant digits (8 or 9), which is the limit of accuracy of current measurement techniques.

The Schrödinger equation is based on a non-relativistic ansatz, i.e. it is invariant under Galilei transformation, but not under Lorentz transformation. In order to obtain a relativistic wave equation we start with the relativistic relation between the energy, the momentum and the mass of a particle. The correct relativistic equation for the electron in hydrogenic atoms is the Dirac equation, which in addition includes spin property [30–32].

Closing, we recall that it is well known in the scientific community that the correct approach to the hydrogen-like atoms is not a semi-classical one (except for large quantum

number [33]), but a quantum mechanical one in which all properties and interactions of the electron and proton should be considered [34–36].

7. Conclusions

A simple concise relativistic version of the Bohr model for hydrogen-like atoms with circular orbits is presented. As the derivation requires basic knowledge of classical and relativistic mechanics, it can be taught in standard first courses in modern physics and introductory quantum mechanics. It is explained that the method of the reduced mass is not applicable in the relativistic version for the exact case of non-stationary nucleus with finite mass.

One of the predictions of the relativistic model is that the inverse of the fine-structure constant ($1/\alpha \sim 137$) sets an upper limit for the atomic number of atomic elements.

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