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The Physical Constant Called the Rydberg Constant Does Not Exist

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Abstract

In classical quantum theory, the Rydberg constant is a fundamental physical constant that plays an important role. It comes into play as an indispensable physical constant in basic formulas for describing natural phenomena. However, relativity is not taken into account in this Rydberg formula for wavelength. If the special theory of relativity is taken into account, R_∞ can no longer be regarded as a physical constant. That is, we have continued to conduct experiments to this day in an attempt to determine the value of a physical constant, the Rydberg constant, which does not exist in the natural world.

Keywords

Rydberg Constant, Rydberg Formula, Classical Quantum Theory, Einstein's Energy-Momentum Relationship

1. Introduction

In the classical quantum theory of Bohr, the energy levels of the hydrogen atom are given by the following formula [1].

$$E_{\mathrm{BO},n} = -\frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{m_e e^4}{\hbar^2} \cdot \frac{1}{n^2} \tag{1}$$

Here, E_{BO} refers to the total mechanical energy predicted by Bohr.

Bohr thought the following quantum condition was necessary to find the energy levels of the hydrogen atom.

$$m_e v_n \cdot 2\pi r_n = 2\pi n\hbar. \tag{2}$$

The total mechanical energy of the hydrogen atom is also given by the following formula.

$$E = K + V(r) = -K = \frac{1}{2}V(r) = -\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}. \quad (3)$$

If E in Formula (1) is substituted into Formula (3), then the following formula can be derived as the orbital radius of the electron.

$$r_n = 4\pi\varepsilon_0 \frac{\hbar^2}{m_e e^2} n^2, \quad n = 1, 2, \cdots. \quad (4)$$

The photonic energy emitted during a transition between energy levels $\left(E_{\mathrm{BO},n} - E_{\mathrm{BO},m}\right)$ and wavelength $\lambda_{n,m}$ for principal quantum numbers n and m can be expressed as follows.

$$\begin{aligned} E_{\mathrm{BO},n} - E_{\mathrm{BO},m} &= h\nu = \frac{hc}{\lambda_{n,m}} \\ &= hcR_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right), \quad m = 1, 2, \cdots, \ n = m+1, m+2, \cdots. \end{aligned} \quad (5)$$

The Rydberg formula can be derived from Formula (5) as indicated below.

$$\frac{1}{\lambda_{n,m}} = \frac{E_{\mathrm{BO},n} - E_{\mathrm{BO},m}}{hc} = R_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right), \quad m = 1, 2, \cdots, \quad n = m+1, m+2, \cdots. \quad (6)$$

This R_∞ is the Rydberg constant. Its value is fixed, and does not depend on the spectra series or atom. The physical status of this empirical formula, which was obtained experimentally, was indicated by Bohr. In Bohr's theory of the hydrogen atom, R_∞ is given by the following formula.

$$R_\infty = \frac{2\pi^2 m_e e^4}{ch^3} = 10973731.568160\ \mathrm{m}^{-1}. \quad \text{(NIST CODATA 2018 value)} \quad (7)$$

Around the end of the 19th century, Balmer, Rydberg, and others discovered Formula (6).

However, Formula (6) is a nonrelativistic formula, and the theory of relativity is not taken into account. Thus, the objective of this paper is to derive a relativistic formula for wavelength.

The energy-momentum relationship in the special theory of relativity (STR) holds in an isolated system in free space. Here, if m_0 is rest mass and m relativistic mass, the relationship can be written as follows [2].

$$\left(m_0c^2\right)^2 + p^2c^2 = \left(mc^2\right)^2. \quad (8)$$

Incidentally, Sommerfeld once defined kinetic energy as the difference between the relativistic energy mc^2 and rest mass energy m_0c^2 of an object [3]. That is,

$$K_{\mathrm{re}} = mc^2 - m_0c^2 = m_0c^2\left[\frac{1}{\left(1-\beta^2\right)^{1/2}} - 1\right], \quad \beta = \frac{v}{c}. \quad (9)$$

Sommerfeld believed that Formula (9), which can be derived from Formula (8), can also be applied to the electron in a hydrogen atom.

In Formula (9), energy takes continuous values. To derive a quantum theoretic formula, discontinuity must be incorporated into Formula (9). This problem is solved in the following section.

2. A New Quantum Condition and the Relativistic Energy Levels of a Hydrogen Atom

The Planck constant h can be written as follows [4]:

$$\hbar = \frac{h}{2\pi} = \frac{m_e c \lambda_C}{2\pi}. \tag{10}$$

Here, λ_C is the Compton wavelength of the electron.

Also, the fine-structure constant α is defined as follows.

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}. \tag{11}$$

When Formula (10) is used, α can be expressed as follows.

$$\alpha = \frac{e^2}{2\varepsilon_0 m_e c^2 \lambda_C}. \tag{12}$$

Also, the classical electron radius r_e is defined as follows.

$$r_e = \frac{e^2}{4\pi\varepsilon_0 m_e c^2}. \tag{13}$$

If r_e/α is calculated here,

$$\frac{r_e}{\alpha} = \frac{\lambda_C}{2\pi}. \tag{14}$$

If Formula (4) is written using r_e and α, the result is as follows.

$$r_n = 4\pi\varepsilon_0 \frac{\hbar^2}{m_e e^2} n^2 = \frac{e^2}{4\pi\varepsilon_0 m_e c^2}\left(\frac{4\pi\varepsilon_0 \hbar c}{e^2}\right)^2 n^2 = \frac{r_e}{\alpha^2} n^2. \tag{15}$$

Next, if $\hbar$ in Formula (10) and r_n in Formula (15) are substituted into Formula (2),

$$m_e v_n \cdot 2\pi \frac{r_e}{\alpha^2} n^2 = 2\pi n \frac{m_e c \lambda_C}{2\pi}. \tag{16}$$

If Formula (14) is also used, then Formula (16) can be written as follows.

$$m_e v_n \cdot 2\pi \frac{r_e}{\alpha^2} n^2 = 2\pi n \frac{m_e c r_e}{\alpha}. \tag{17}$$

Rearranging Formula (17), we obtain the following.

$$2\pi r_e m_e \frac{v_n n^2}{\alpha^2} = 2\pi r_e m_e \frac{nc}{\alpha}. \tag{18}$$

From this, the following relationship can be derived [5].

$$\frac{v_n}{c} = \frac{\alpha}{n}. \tag{19}$$

Here, let us express the absolute energy possessed by an electron whose principal quantum number is in state n as $m_n c^2$, and the relativistic energy levels of a hydrogen atom as $E_{\mathrm{re},n}$. Using the relationship in Formula (19), Formula (9) can be written as follows.

$$E_{\mathrm{re},n} = -K_{\mathrm{re},n} = m_{\mathrm{e}}c^2 - m_n c^2 = m_{\mathrm{e}}c^2\left[1-\left(1-\frac{\alpha^2}{n^2}\right)^{-1/2}\right], \quad n = 1, 2, \cdots. \tag{20}$$

Formula (20) is a quantum theoretic formula incorporating discontinuity into the relativistic formula for energy.

Now, if a Taylor expansion is performed on the right side of Formula (20),

$$\begin{aligned} E_{\mathrm{re},n} &= m_{\mathrm{e}}c^2\left[1-\left(1+\frac{\alpha^2}{2n^2}+\frac{3\alpha^4}{8n^4}+\frac{5\alpha^6}{16n^6}+\cdots\right)\right] \\ &= -\frac{\alpha^2 m_{\mathrm{e}}c^2}{2n^2}\left(1+\frac{3\alpha^2}{4n^2}+\frac{5\alpha^4}{8n^4}+\cdots\right). \end{aligned} \tag{21}$$

If Equation (1) is rewritten as a formula containing α, the result is as follows.

$$E_{\mathrm{BO},n} = -\frac{\alpha^2}{2n^2}m_{\mathrm{e}}c^2. \tag{22}$$

Comparing Formulas (21) and (22), it is evident that Formula (22) is an approximation of Formula (21). That is,

$$E_{\mathrm{re},n} \approx E_{\mathrm{BO},n}. \tag{23}$$

3. A Relativistic Formula for Wavelength and the Rydberg Constant

The differences in energy between different energy levels in the hydrogen atom can be found with the following formula.

$$\begin{aligned} &E_{\mathrm{re},n} - E_{\mathrm{re},m} = \left(m_{\mathrm{e}}c^2 - m_n c^2\right) - \left(m_{\mathrm{e}}c^2 - m_m c^2\right) = m_m c^2 - m_n c^2 \\ &= m_{\mathrm{e}}c^2\left[\left(1-\frac{\alpha^2}{m^2}\right)^{-1/2} - \left(1-\frac{\alpha^2}{n^2}\right)^{-1/2}\right], \quad m = 1, 2, \cdots, \quad n = m+1, m+2, \cdots. \end{aligned} \tag{24}$$

The following equation is also known.

$$\lambda_{\mathrm{C}} = \frac{h}{m_{\mathrm{e}}c}. \tag{25}$$

Taking into account Formula (25),

$$m_{\mathrm{e}}c^2 = \frac{hc}{\lambda_{\mathrm{C}}}. \tag{26}$$

Based on this, Formula (24) can be written as follows.

$$\begin{aligned} \frac{1}{\lambda_{n,m}} &= \frac{E_{\mathrm{re},n} - E_{\mathrm{re},m}}{hc} \\ &= \frac{1}{\lambda_{\mathrm{C}}}\left[\left(1-\frac{\alpha^2}{m^2}\right)^{-1/2} - \left(1-\frac{\alpha^2}{n^2}\right)^{-1/2}\right], \quad m = 1, 2, \cdots, \quad n = m+1, m+2, \cdots. \end{aligned} \tag{27}$$

However, the relativistic formula for wavelength was not derived for the first time in this paper. This formula has already been derived by Dr. Haug [6] [7].

Formula (27) is the formula for wavelength, taking into account the STR. If the Taylor expansion of Formula (27) is taken, the following formula is obtained.

$$\begin{aligned}\frac{1}{\lambda_{n,m}} &= \frac{1}{\lambda_C}\left[\left(1+\frac{\alpha^2}{2m^2}+\frac{3\alpha^4}{8m^4}+\frac{5\alpha^6}{16m^6}+\cdots\right)-\left(1+\frac{\alpha^2}{2n^2}+\frac{3\alpha^4}{8n^4}+\frac{5\alpha^6}{16n^6}+\cdots\right)\right] \\ &= \frac{\alpha^2}{2\lambda_C}\cdot\frac{2}{\alpha^2}\left[\left(1+\frac{\alpha^2}{2m^2}+\frac{3\alpha^4}{8m^4}+\frac{5\alpha^6}{16m^6}+\cdots\right)-\left(1+\frac{\alpha^2}{2n^2}+\frac{3\alpha^4}{8n^4}+\frac{5\alpha^6}{16n^6}+\cdots\right)\right].\end{aligned} \tag{28}$$

The following relationship is used here.

$$R_\infty = \frac{\alpha^2}{2\lambda_C}. \tag{29}$$

Formula (28) can then be written as follows.

$$\begin{aligned}\frac{1}{\lambda_{n,m}} &= R_\infty\left[\left(\frac{1}{m^2}+\frac{3\alpha^2}{4m^4}+\frac{5\alpha^4}{8m^6}+\cdots\right)-\left(\frac{1}{n^2}+\frac{3\alpha^2}{4n^4}+\frac{5\alpha^4}{8n^6}+\cdots\right)\right] \\ &\approx R_\infty\left(\frac{1}{m^2}-\frac{1}{n^2}\right)+R_\infty\left(\frac{3\alpha^2}{4m^4}-\frac{3\alpha^2}{4n^4}+\frac{5\alpha^4}{8m^6}-\frac{5\alpha^4}{8n^6}\right).\end{aligned} \tag{30}$$

It is evident from this that the previously-known Formula (6) is an approximation of Formula (27).

Next, Formulas (6) and (27) are further compared. If, in Formula (27), the values of the Compton wavelength λ_C and fine-structure constant α are determined, it is possible to calculate the spectra wavelengths. Of course, Formula (6) too must predict the spectra wavelengths. However, at present, the spectra wavelengths are first measured, and then the value of R_∞ is determined based on those values. Formula (6) is not for calculating wavelengths, but for determining the Rydberg constant.

Next, the following table summarizes the energies of a hydrogen atom obtained from Formulas (6) and (27) (**Table 1**).

The following values of CODATA were used when calculating energies.

$$R_\infty = 10973731.568160\ \text{m}^{-1}.$$

$$\alpha = 7.2973525693\times10^{-3}.$$

$$\lambda_C = 2.42631023867\times10^{-12}\ \text{m}.$$

Incidentally, the relativistic formula for wavelength previously derived by the author is not Formula (27) [8] [9]. However, the formula derived by the author has still not been accepted by physicists.

Table 1. Wavelength values predicted by Bohr's theory and this paper.

	Bohr's Theory	This Paper	Remark
$\lambda_{2,1}$	121.502 nm	121.496 nm	Lyman α
$\lambda_{3,1}$	1.02518 nm	1.02513 nm	Lyman β
$\lambda_{3,2}$	656.112 nm	656.103 nm	
$\lambda_{4,2}$	486.009 nm	486.003 nm	

If the aim is only to achieve the purpose of this paper, there is no need to use the formula previously derived by the author. Thus, this paper demonstrates that the Rydberg constant is not a physical constant by using Formula (27), which is acceptable to physicists.

First, Formula (27) is rewritten in a like Formula (6). That is,

$$\frac{1}{\lambda_{n,m}}=R\left(\frac{1}{m^2}-\frac{1}{n^2}\right),\quad R\neq R_\infty. \tag{31}$$

Also, in this paper it is checked whether this R can maintain the status of a physical constant.

Formula (27) can be written as follows taking Formula (29) into account.

$$\frac{1}{\lambda_{n,m}}=R_\infty\cdot\frac{2}{\alpha^2}\left[\frac{m}{\left(m^2-\alpha^2\right)^{1/2}}-\frac{n}{\left(n^2-\alpha^2\right)^{1/2}}\right]. \tag{32}$$

Also, Formula (32) can be written as follows.

$$\frac{1}{\lambda_{n,m}}=R_\infty\cdot\frac{2}{\alpha^2}\left[\frac{m}{\left(m^2-\alpha^2\right)^{1/2}}-\frac{n}{\left(n^2-\alpha^2\right)^{1/2}}\right]\frac{m^2n^2}{n^2-m^2}\left(\frac{1}{m^2}-\frac{1}{n^2}\right). \tag{33}$$

However,

$$\frac{m^2n^2}{n^2-m^2}\left(\frac{1}{m^2}-\frac{1}{n^2}\right)=1,\quad m=1,2,\cdots,\quad n=m+1,m+2,\cdots. \tag{34}$$

Here, the following $R_{n,m}$ is defined.

$$\begin{aligned}R_{n,m}&=R_\infty\cdot\frac{2}{\alpha^2}\cdot\frac{m^2n^2}{n^2-m^2}\left[\frac{m}{\left(m^2-\alpha^2\right)^{1/2}}-\frac{n}{\left(n^2-\alpha^2\right)^{1/2}}\right]\\&=\frac{1}{\lambda_{\mathrm{C}}}\cdot\frac{m^2n^2}{n^2-m^2}\left[\frac{m}{\left(m^2-\alpha^2\right)^{1/2}}-\frac{n}{\left(n^2-\alpha^2\right)^{1/2}}\right].\end{aligned} \tag{35}$$

As is clear from Formula (35), $R_{n,m}$ is not a constant. Thus, in Formula (35), R has subscripts n, m.

If $R_{n,m}$ is defined similar to Formula (35), then Formula (31) can be written as follows.

$$\begin{aligned}\frac{1}{\lambda_{n,m}}&=\frac{1}{\lambda_{\mathrm{C}}}\cdot\frac{m^2n^2}{n^2-m^2}\left[\frac{m}{\left(m^2-\alpha^2\right)^{1/2}}-\frac{n}{\left(n^2-\alpha^2\right)^{1/2}}\right]\left(\frac{1}{m^2}-\frac{1}{n^2}\right)\\&=R_{n,m}\left(\frac{1}{m^2}-\frac{1}{n^2}\right),\quad m=1,2,\cdots,\quad n=m+1,m+2,\cdots.\end{aligned} \tag{36}$$

Here, if R_∞ and $R_{n,m}$ are compared,

$$\frac{R_{n,m}}{R_\infty}=\frac{2}{\alpha^2}\cdot\frac{m^2n^2}{n^2-m^2}\left[\frac{m}{\left(m^2-\alpha^2\right)^{1/2}}-\frac{n}{\left(n^2-\alpha^2\right)^{1/2}}\right]. \tag{37}$$

Table 2. Relation between the Rydberg constant R_∞ and $R_{n,m}$. The values of R_∞ and $R_{n,m}$ are almost equal, but it is always the case that $R_\infty < R_{n,m}$.

	$R_{n,m}/R_\infty$	Theoretical value of $R_{n,m}$
$R_{2,1}$	1.000049925	10974279.4 m^{-1}
$R_{3,1}$	1.000044378	10974218.6 m^{-1}
$R_{3,2}$	1.000014422	10973889.8 m^{-1}

It is thus evident that the value we try to determine by measuring spectra wavelengths is not R_∞ in Formula (6) but $R_{n,m}$ in Formula (36). However, that fact has not been noticed by anyone thus far. Furthermore, $R_{n,m}$ is not a physical constant, as is evident from Formula (35).

Next, the following table summarizes the values of $R_{n,m}$ when $m = 1, 2$ and $n = 2, 3$ (**Table 2**).

Ordinarily, we determine the value of the Rydberg constant in Formula (6) by measuring the spectra wavelengths. If this value matches with the theoretical value (Formula (7)), then the validity of Bohr's model of the atom is confirmed.

However, the value we try to determine through experiment is the value of $R_{n,m}$ not the value of the Rydberg constant R_∞. Therefore, if more precise measurement becomes possible, it will become clear that the theoretical value (Formula (7)) and experimental value (Formula (35)) do not match exactly.

Originally, Formula (6) is given as follows.

$$\frac{1}{\lambda_{n.m}} = \frac{2\pi^2 m_e e^4}{ch^3}\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{38}$$

However, writing out the right side of Formula (7) is bothersome, and for reasons of convenience, this expression was replaced with the single symbol R_∞. (However, this is not a description of the actual history.) Therefore, R_∞ is not a physical constant on a par with c or e. It is also not the case that we discovered a physical constant R_∞. R_∞ came into common use in the world of nonrelativistic classical quantum theory. If the theory of relativity is taken into account, R_∞ can no longer be regarded as a physical constant.

4. Conclusions

In classical quantum theory, the wavelengths of the line spectra of a hydrogen atom are described by the following formula.

$$\frac{1}{\lambda_{n,m}} = R_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right), \quad m = 1, 2, \cdots, \quad n = m+1, m+2, \cdots. \tag{39}$$

If the special theory of relativity is incorporated into Formula (39), and expressed with an equation similar to Formula (39), the result is the following formula.

$$\frac{1}{\lambda_{n,m}} = R_{n,m}\left(\frac{1}{m^2} - \frac{1}{n^2}\right), \quad m = 1, 2, \cdots, \quad n = m+1, m+2, \cdots. \tag{40}$$

At this time, $R_{n,m}$ is defined as follows.

$$R_{n,m}=\frac{1}{\lambda_{\mathrm{C}}}\cdot\frac{m^2n^2}{n^2-m^2}\left[\frac{m}{\left(m^2-\alpha^2\right)^{1/2}}-\frac{n}{\left(n^2-\alpha^2\right)^{1/2}}\right]\neq const. \tag{41}$$

What we try to determine by measuring spectra wavelengths is not actually the value of the Rydberg constant R_∞ but the value $R_{n,m}$ of Formula (41). $R_{n,m}$ cannot take a fixed value.

R_∞ came into common use in the world of nonrelativistic classical quantum theory. If the STR is taken into account, R_∞ can no longer be regarded as a physical constant. That is, we have continued to conduct experiments to this day in an attempt to determine the value of a physical constant, the Rydberg constant, which does not exist in the natural world.

If we wish to include constants in the wavelength formula incorporating the special theory

$$\frac{1}{\lambda_{n,m}}=\frac{1}{\lambda_C}\left[\left(1-\frac{\alpha^2}{m^2}\right)^{-1/2}-\left(1-\frac{\alpha^2}{n^2}\right)^{-1/2}\right],\quad m=1,2,\cdots,\quad n=m+1,m+2,\cdots. \tag{42}$$

As is clear from a comparison of Formulas (40) and (42), the physical constant that is important for determining the wavelengths of the line spectra of a hydrogen atom is not the Rydberg Constant, but rather the Compton wavelength of the electron.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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