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The rule of radius averaging in hydrogen atom

Abdurrouf

Department of Physics, Brawijaya University, Jl. Veteran Malang, Indonesia 65145

*Corresponding author: abdurrouf@ub.ac.id

Abstract. According to quantum mechanics, electrons do not have a fixed position in an atom, and therefore orbitals have no definite radii. However, electrons have characteristic wave functions from which the radius of their orbits can be calculated or averaged. Depending on the average method, there are three most popular expressions for orbital radius, namely the average radius, the root mean square (rms) radius, and the most probable radius. Unfortunately, for hydrogen atom, none of those three radii is equal to the classical radius, even for large principal quantum numbers called the classical regime. Here, by using energy analysis, we propose a harmonic radius and show that the results well agree with the classical radius for each principal and orbital quantum numbers.

1. Introduction

The Bohr atomic model is one of the atomic models that is very successful in explaining the behavior of atoms. The model can well explain the energy spectrum of hydrogen atom, well known as the Lyman, Balmer, Paschen, Bracket, Pfund, and Humphreys series, and also can derive Rydberg's semi-empirical equation. In developing his model, Bohr assumed that each atom's electron moves in an orbit around the nucleus under the influence of the electrostatic force of the nucleus; in circular orbits. Instead, a continuum orbits allowed in classical mechanics, electron can orbit in discrete orbits only, called stationary states, with definite angular momentum, $L_n = n\hbar$, where $\hbar$ is Planck's constant h divided by 2π. As a consequence, the stationary states have definite energy $E_n = E_0/n^2$ and definite radius $r_n = n^2 a_0$, where E_0 and a_0 stand for ionization energy and radius of first orbit in Bohr's atom, respectively. These assumptions violate classical physics but successfully explain many properties of the hydrogen atom [1,2].

The rapid development of quantum mechanics, initiated its application to atomic models. In contrast to the Bohr atomic model which considers electrons as radially fixed particles, quantum mechanics represents electron in a wave function. As a consequence, electrons are considered to spread throughout space, and therefore do not have a fixed radial position. However, using the corresponding wave function, it is possible to calculate the expectation value of energy, whose should be the same as the result in the Bohr model.

For the atomic radius, the situation is different, where there is a discrepancy between quantum calculations and Bohr's value. Along the popular way of averaging, neither mean radius, root squared mean radius, nor most probable radius are the same as the radius of the Bohr atom [1-3]. As quantum mechanics is believed to be true, it is assumed that this failure is due to the way of averaging. To overcome, it is necessary to propose a different average model for the atomic radius, as well as its variance. This new average model can be also applied for other hydrogen like atom, as well as the other physical quantities.

2. The popular way of averaging radius

Based on quantum mechanical approach, the time-independent electronic wave function of hydrogen atom in state (nlm) is given by [1]

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) \tag{1}$$

In above, $R_{nl}(r)$ and $Y_{lm}(\theta,\varphi)$ are the radial and spherical part of the electronic wave function of hydrogen atom, respectively. $Y_{lm}(\theta,\varphi)$ is also well known as spherical harmonic. The expectation value of power p of radius r, $\langle r^p \rangle$, is then given by

$$\langle r^p \rangle = \int r^p |\psi(r,\theta,\varphi)|^2 d\Omega.$$

Using Eq. (1), it is instructive to express $\langle r^p \rangle$ as

$$\langle r^p \rangle = \int_0^\infty r^p r^2 |R_{nl}(r)|^2 dr \int_0^{2\pi} \int_0^\pi |Y_{lm}(\theta,\varphi)|^2 \sin\theta \, d\theta d\varphi.$$

Then, by utilizing orthonormal properties of spherical harmonics $\int_0^{2\pi}\int_0^\pi |Y_{lm}(\theta,\varphi)|^2 \sin\theta \, d\theta d\varphi = 1$ and by defining $r^2|R_{nl}(r)|^2 \equiv P(r)$ as the radial probability of finding electron in hydrogen atom, then we obtain

$$\langle r^p \rangle = \int_0^\infty r^p P(r)dr. \tag{2}$$

The radial wave function for hydrogen atom for an orbital (nl) is given by

$$R_{nl}(r) = -\left(\frac{2}{na_0}\right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right), \tag{3}$$

where $L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$ is the associated Laguerre polynomial and reads as

$$L_{n+l}^{2l+1}(r) = \frac{d^{2l+1}}{dr^{2l+1}}\left[e^r \frac{d^{n+l}}{dr^{n+l}}\left(r^{n+l}e^{-r}\right)\right]. \tag{4}$$

The expression of $R_{nl}(r)$ as well as $L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$ are listed in the References [1-2].

To obtain the average radius of orbital (nl) in hydrogen atom, one should take the average of r^p following Eq. (2). There are two popular ways of averaging, those are mean radius $(\bar{r})$ and root mean square (rms) radius (r_{rms}). In the mean radius, one simply involves taking the integration of a multiplication of r and $P(r)$. Mathematically mean radius $(\bar{r})$ reads

$$\bar{r} = \langle r \rangle = \int_0^\infty rP(r)dr. \tag{5}$$

In the root mean square (rms) average, one involves taking the integration of a squared r multiplied $P(r)$ then taking its root square. Mathematically root mean square (rms) average reads

$$r_{rms} = \sqrt{\langle r^2 \rangle} = \left[\int_0^\infty r^2 P(r)dr\right]^{1/2}. \tag{6}$$

Comparing Eqs (5) and (6), it is clear that mean radius, $\bar{r}$, is actually the first order mean arithmetic radius whereas root mean square (rms) radius, r_{rms}, is the second order mean arithmetic radius. In addition, there is another type of radius, known as the most probable radius r_m. The r_m is obtained when the $P(r)$ reaches maximum. Mathematically it follows

$$\frac{\partial(P(r))}{\partial r} = 0 \text{ and } \frac{\partial^2(P(r))}{\partial r^2} < 0 \rightarrow r = r_m. \tag{7}$$

In case $P(r)$ has more than one peaks, r_m is the value of r gives the highest value of $P(r)$.

In this study, we analyze the value of those three average radii $\bar{r}$, r_{rms}, and r_m, and compare with the classical radius of atom given by

$$r_c = n^2 a_0, \tag{8}$$

where a_0 is Bohr's radius.

Let first evaluate the mean radius, $\bar{r}$. Along analytical derivation, the value of $\bar{r}$ for orbital (nl) is given by [2]

$$\bar{r} = \frac{1}{2}[3n^2 - l(l+1)]na_0 \tag{9}$$

Then let express l in term of n as $l = n - t$ where $t = 1,2,\dots n$. The mean radius now can be expressed as

$$\bar{r} = \begin{cases} \frac{1}{2}[2n^2 + 2nt - t^2 - n + t]a_0 & \text{for } 1 \le t \le n-1 \quad \text{satisfies } l = 1,2,\dots n-1 \\ \frac{3}{2}n^2 a_0 = \frac{3}{2}r_c & \text{for } t = n \text{ satisfies } l = 0 \end{cases} \tag{10}$$

Furthermore, let observe the classical limit of mean radius, occuring when For $n \to \infty$. In this condition, mean radius reads

$$\bar{r} = \begin{cases} r_c & \text{for } 1 \le t \le n-1 \text{ satisfies } l = 1,2,..,n-1 \\ \frac{3}{2}r_c & \text{for } t = n \text{ satisfies } l = 0 \end{cases} \tag{11}$$

Let continu evaluating root mean square radius, r_{rms}. Along analytical derivation, the value of r_{rms} is given by [2]

$$r_{rms} = n \sqrt{\frac{5n^2 - 3l(l+1)+1}{2}} \, a_0 \tag{12}$$

Lets express l in term of n as $l = n - t$ where $t = 1,2,\dots n$. The root mean square radius now can be expressed as

$$r_{rms} = \begin{cases} \sqrt{1 + \frac{1}{n^2} - \frac{3t^2}{2n^2} + \frac{t}{n^2} + \frac{2t}{n} - \frac{3}{2n}} \, r_c & \text{for } 1 \le t \le n-1 \quad \text{satisfies } l = 1,2,\dots n-1 \\ \sqrt{\frac{5}{2} - \frac{1}{n} + \frac{1}{2n^2}} r_c & \text{for } t = n \text{ satisfies } l = 0 \end{cases} \tag{13}$$

Now, let observe the classical limit of root mean square radius, r_{rms}, occuring when $n \to \infty$. In this condition, the root mean square radius reads

$$r_{rms} = \begin{cases} r_c & \text{for } 1 \le t \le n-1 \quad \text{satisfies } l = 1,2,\dots n-1 \\ \sqrt{\frac{5}{2}}r_c & \text{for } t = n \text{ satisfies } l = 0 \end{cases} \tag{14}$$

Table 1 The calculated value of average radius for few lowest orbitals in hydrogen atom. The radius is presented in units of Bohr's radius a_0. The starred orbital indicates orbital whose $P(r)$ has only one peak.

Orbital	$\bar{r}$	r_{rms}	r_{mp}	r_c
1s (*)	1.5	1.73	1.00	1
2s	6.0	6.48	5.24	4
2p (*)	5.0	5.48	4.00	4
3s	13.5	14.39	13.07	9
3p	12.5	13.42	12.00	9
3d (*)	10.5	11.22	9.00	9
4s	24.0	25.43	24.60	16
4p	23.0	24.49	23.58	16
4d	21.0	22.45	21.12	16
4f (*)	18.0	18.97	16.00	16

We continu with the most probable radius, r_{mp}. To understand the value of r_m let first evaluate the radial wave function, in Eq. (4), where $R_{nl}(r) \infty \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$. The associated Laguerre polynomial $L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$ is a polynomial of $\left(\frac{2r}{na_0}\right)$ whose highest order is $(n+l) - (2l+1) = n - l - 1$. Then the radial wave function is $R_{nl}(r)$ is proportional to $\left(\frac{2r}{na_0}\right)^{n-1} e^{-r/na_0}$. As a consequence, the highest order of the density probability $P_{nl}(r)$ is proportional to $\left(\frac{2r}{na_0}\right)^{2n} e^{-2r/na_0}$. Then, setting

$\frac{dP_{nl}(r)}{dr} = \frac{d}{d\left(\frac{2r}{na_0}\right)}\left[\left(\frac{2r}{na_0}\right)^{2n} e^{-2r/na_0}\right] = 0$, one obtains for orbital $(n, l = n - 1)$ whose peak only one,
$r_m = n^2 a_0$. [2]

The value of average radius of few lowest orbitals in hydrogen atom, calculated by using Eqs. (5-8) are given in Tab. 1. In general, the calculated $\bar{r}$ and r_{rms} are not equal to r_c. In other hand, $\boldsymbol{r_{mp} = r_c}$ for $\boldsymbol{l = n - 1}$ orbital, such as orbital $\boldsymbol{1s}$, $\boldsymbol{2p}$, $\boldsymbol{3d}$, $\boldsymbol{4f}$, etc.

3. Harmonic averaging radius

Comparing the value of mean radius, root mean square radius, and most probable radius with the classical radius, it is clear that:

- For lower n, both $\bar{r}$ and r_{rms} give the value of r which is not equal to classical radius r_c. In classical limit $(n \to \infty)$, $\bar{r}$ and r_{rms} are equal the classical radius r_c, for $l \neq 0$ orbital only. For $l = 0$ orbital, we have $\bar{r} = \frac{3}{2}r_c$ and $r_{rms} = \sqrt{\frac{5}{2}}r_c$.

- The r_{mp} is equal the classical radius r_c, for $l = n - 1$ orbital only.   For $l < n - 1$ orbital, we have $r_{mp} > r_c$.

These facts shows that neither $\bar{r}$, r_{rms}, nor r_{mp} represent classical radius r_c, eventhough in cassical regime. Then we need other formulae for averaging radius that are consistent with classical radius.

To understanding these facts, let discuss the following facts. First, quantum mechanics is based on Schrodinger equation, which is actually quantum mechanics expression of Hamiltonian or total energy equation. Second, quantum mechanics exactly produce the classical energy, $E_n = -\frac{E_0}{n^2}$. Third, the classical radius is obtained by energy approach, by means it is obtained to explain spectrum of hydrogen atom which is observed in energy response. Therefore, it is reasonable to conclude the following. First, the proper and operational average for energy is the mean average $\bar{E}$. Second the proper and operational average of any other quantities refers to their relation to energy.

According to quantum mechanics, the expectation of mechanic energy $\langle E \rangle$ is a sum of the expectation of kinetic energy $\langle T \rangle$ and potential energy $\langle V \rangle$. Having $\langle T \rangle = -\frac{1}{2}\langle V \rangle$, we have

$$\langle E \rangle = \frac{1}{2}\langle V \rangle = \langle -\frac{e^2}{8\pi\varepsilon_0}\frac{1}{r} \rangle,$$

or

$$\langle E \rangle = -\frac{e^2}{8\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle \tag{15}$$

Eq. (15) tells us that $\langle E \rangle \propto \left\langle \frac{1}{r} \right\rangle$ and tells us that $\bar{r}$ and r_{rms} are not proper averaging for radius. It is also instructive to conclude that proper and operational average for radius, r, is harmonic average, r_h, defined as $r_h = \left\langle \frac{1}{r} \right\rangle^{-1}$, or

$$r_h = \left[\int_0^\infty \frac{1}{r}P(r)dr\right]^{-1}. \tag{16}$$

Comparing Eq. (16) with Eqs (5) and (6), it is clear that harmonic average, r_h, is the mean arithmetic order -1 [4]. Along analytical derivation, the value of r_h is given by [2]

$$r_h = n^2 a_0 \tag{17}$$

It is now clear that r_h is equal to r_c, for any orbital (n, l), in both quantum and classical regime.

For completeness and following Eq. (15), it is worthwhile to propose a new variance satisfies

$\Delta E = -\frac{e^2}{8\pi\varepsilon_0}\frac{1}{\Delta r}$. Having $\Delta E = -\frac{e^2}{8\pi\varepsilon_0}\left[\left\langle \frac{1}{r^2} \right\rangle - \left\langle \frac{1}{r} \right\rangle^2\right]^{1/2}$, it is instructive to define harmonic variance as

$$\Delta r_h = \left[\left\langle \frac{1}{r^2} \right\rangle - \left\langle \frac{1}{r} \right\rangle^2\right]^{-1/2}. \tag{18}$$

Using $\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(l+\frac{1}{2}\right)n^3 a_0{}^2}$ and $\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0}$, it is found that

$$\Delta r_h = \left[\frac{\left(l+\frac{1}{2}\right)}{n-\left(l+\frac{1}{2}\right)} \right]^{1/2} n^2 a_0. \tag{19}$$

For comparison, we also calculate the standard covariance $\Delta r = \left[\overline{|r - \langle r \rangle|^2} \right]^{1/2} = [\langle r^2 \rangle - \langle r \rangle^2]^{1/2}$. Using Eq. (10-11), we obtain

$$\Delta r = [n^2(n^2 + 2) - l^2(l+1)^2]^{1/2} \frac{a_0}{2}. \tag{20}$$

The calculated value of mean and harmonic radius and their covariance for few lowest orbitals in hydrogen atom is listed in Tab. 2.

Table 2. The calculated value of mean and harmonic radius and their covariance for few lowest orbitals in hydrogen atom. The radius is presented in units of Bohr's radius a_0.

Orbital	$r_h \pm \Delta r_h$	$\bar{r} \pm \Delta r$
$1s$ (*)	1.00 ± 1.00	1.50 ± 0.87
2s	4.00 ± 0.58	6.00 ± 2.45
2p (*)	4.00 ± 1.73	5.00 ± 2.24
3s	9.00 ± 0.45	13.50 ± 4.97
3p	9.00 ± 1.00	12.50 ± 4.87
3d (*)	9.00 ± 2.24	$10.50 \pm .3.97$
4s	16.00 ± 0.38	24.00 ± 8.49
4p	16.00 ± 0.77	23.00 ± 8.43
4d	16.00 ± 1.29	21.00 ± 7.96
4f (*)	16.00 ± 2.65	18.00 ± 6.00

It is now very challenging to apply energy approach in defining the proper and operational average of other physical quantities. For any quantities proportional to energy, such as frequency, it is recommended to use mean average. If the squared quantities are proportional to energy, such as speed, momentum, position in harmonic oscillator potential problem, it is recommended to use root mean square average. On the other hand, there are some physical quantities whose invers values are proportional to energy, such as position in Coulomb potential problem and wavelength. For these properties, the proper and operational average is harmonic average. It is also challenging to define rms variance and harmonic variance, as well as mean variance.

4. Conclusion

As a conclusion, it is demonstrated that for hydrogen atom neither $\bar{r}$, $\boldsymbol{r_{rms}}$, and $\boldsymbol{r_m}$, both in quantum and classical regime, reproduce classical radius $\boldsymbol{r_c}$, except for vey limited case. To overcome it is proposed to use harmonic average $\boldsymbol{r_h}$, that clearly produces the classical radius $\boldsymbol{r_c}$. As a cosequence of using harmonic avearge, it is also recomended to use harmonic variance for radius.

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