Investigation of the Hydrogen Atom

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The physical approach provides very good treatment for the Hydrogen atom, yet unlike mathematics, usually precise details are disregarded in favor of physical properties. This report aims to provide these absent information.

Keywords: Hydrogen atom, Hilbert space, commuting operators

I. INTRODUCTION

At the very beginning, Quantum theory was constructed from the basis of Classical mechanics in which Euclidean space played central role[1]. As the theory depends thoroughly on the empirical measure that requires processing huge amounts of data simultaneously, this framework became obsolete. Then the development of Hilbert spaces has significantly changed the way we approach to this subject as well as many other fields. With representation of measurable quantities by operators and complete information by a vector in a Hilbert space[2], the method facilitates the calculations and allows to find precise meanings.

However, this rigorous formulation seems to be neglected in almost any undergraduate quantum mechanics course due to the sake of accessibility[3,4]. For example, the domain in which the functions are defined is barely stated, or for many times the constants are seemingly forced to put into the equation. This report reviews the model of Hydrogen atom and attempts to add some more description to the story.

II. BACKGROUND

A Hilbert space $\mathcal{H}$ is a complex vector space endowed with a scalar product that associates a complex number to each pair of elements of $\mathcal{H}$[5]. In the context of this paper, we draw interest in $\mathcal{L}^2(\mathbb{R}^3)$, which is a Hilbert space of square-integrable functions. Of most important role is the Hamiltonian operator given by,

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + \hat{V}(\boldsymbol{r}), \tag{1}$$

where Δ is Laplace operator. As the negatively charged electron is moving around the positively charged nucleus, it is under the effect of the Coulomb potential (in Gaussian unit). The potential operator is simply a radial function on $\mathbb{R}^3/\{0\}$,

$$V(r) = -\frac{e^2}{|\boldsymbol{r}|}. \tag{2}$$

Now, we introduce the angular momentum operator $\hat{\boldsymbol{l}}$ on $\mathcal{L}^2(\mathbb{R}^3)$. By considering the spherical coordinate (r, θ, ϕ), it has been shown in[6] that the components of $\hat{\boldsymbol{l}}$ can be expressed in terms of θ and ϕ as follows,

$$\begin{aligned} \hat{l_x} &= i\hbar\Big(\sin\phi\frac{\partial}{\partial\theta}\cot\theta\cos\phi\frac{\partial}{\partial\phi}\Big) \\ \hat{l_y} &= i\hbar\Big(-\cos\phi\frac{\partial}{\partial\theta}\cot\theta\sin\phi\frac{\partial}{\partial\phi}\Big) \\ \hat{l_z} &= -i\hbar\frac{\partial}{\partial\phi} \end{aligned}$$

The square of the angular momentum is also an operator defined by

$$-\frac{\hat{\boldsymbol{l}}^2}{\hbar^2} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \tag{3}$$

As mentioned above, how well physical quantities are measured is of great importance. One of the strange features of quantum mechanics is that not always can the two different quantities be measured with full accuracy. Mathematically speaking, the operators corresponding to these quantities do not commute. To specify,

$$\left[\hat{a}, \hat{b}\right] = \hat{a}\hat{b} - \hat{b}\hat{a} \neq 0. \tag{4}$$

It is easy to check that the components $\hat{l_x}$, $\hat{l_y}$, $\hat{l_z}$ do not mutually commute, in fact, $\left[\hat{l_i}, \hat{l_j}\right] = i\hbar\varepsilon_{ijk}\hat{l_k}$, where ε_{ijk} is Levi-Civita symbol[7]. Fortunately, they commute with both $\hat{H}$ and $\hat{\boldsymbol{l}}^2$.

Proof of commutation relation between $\hat{\boldsymbol{l}}^2$ and $\hat{l_z}$.

$$\hat{l_z}\hat{l_x} - \hat{l_x}\hat{l_z} = i\hbar\hat{l_y}.$$

Multiplying both sides with $\hat{l_x}$ yields

$$\begin{aligned} \hat{l_z}\hat{l_x^2} &= \hat{l_x}\hat{l_y}\hat{l_x} + i\hbar\hat{l_y}\hat{l_x}. \\ \hat{l_x^2}\hat{l_z} &= \hat{l_x}\hat{l_y}\hat{l_x} - i\hbar\hat{l_x}\hat{l_y}. \end{aligned}$$

Taking subtraction, $\hat{l_z}\hat{l_x^2} - \hat{l_x^2}\hat{l_z} = i\hbar(\hat{l_y}\hat{l_x} + \hat{l_x}\hat{l_y})$. Similarly, $\hat{l_z}\hat{l_y^2} - \hat{l_y^2}\hat{l_z} = -i\hbar(\hat{l_x}\hat{l_y} + \hat{l_y}\hat{l_x})$. Also, $\hat{l_z}\hat{l_z^2} - \hat{l_z^2}\hat{l_z} = 0$. Summing them up then we finally get $\left[l_z, \hat{\boldsymbol{l}}^2\right] = 0$. ☐

In addition, it can be shown that $\hat{\boldsymbol{l}}^2$ commutes with $\hat{H}$[8]. As a result, we acquire a set of commuting observables: $\hat{H}$, $\hat{\boldsymbol{l}}^2$, and $\hat{l_z}$. The *compatibility theorem* says that this set projects the quantum state onto a unique vector (eigenstate) in the Hilbert space[9].

III. EIGENVALUES AND EIGENFUNCTIONS

Applying an operator $\hat{A}$ on a function ψ, we may get back that function multiplying with some constant λ.

$$\hat{A}\psi = \lambda\psi. \tag{5}$$

Apparently, given the operator, this relation does not hold for all ψ. To find those non-trivial functions, hereafter called *eigenfunctions*, we need to solve this equation out. The associated constant λ is then an *eigenvalue*. This constant can be either real or complex[10]. In quantum mechanics, we are mainly interested in the so-called Hermitian (self-adjoint) operators because they always have real eigenvalues[11]. An operator $\hat{A}$ is hermitian if

$$\int dx\psi_1^*\hat{A}\psi_2 = \int dx(\hat{A}\psi_1)^*\psi_2.$$

Proof. Suppose that $\hat{A}\psi_1 = \lambda\psi_1$ and $\psi_1 = \psi_2$. We have,

$$\int dx\psi_1^*\hat{A}\psi_1 = \lambda\int dx\psi_1^*\psi_1.$$

$$\int dx(\hat{A}\psi_1)^*\psi_1 = \lambda^*\int dx\psi_1^*\psi_1.$$

If $\hat{A}$ is hermitian, the two terms in left-hand side are equal, $\lambda = \lambda^*$, thus λ is real. □

So far, the introduced operators $\hat{H}$, $\hat{\boldsymbol{l}^2}$, and $\hat{l_z}$ are hermitian[12,13].

One of the very important results of compatibility theorem is that: *If two operators commute, they have the same eigenfunctions.*

Proof. Let $V = \{\psi_n\}$ be a space spanned by the eigenfunctions of the operator $\hat{A}$, with the eigenvalue λ, we have,

$$\hat{A}\psi_n = \lambda\psi_n.$$

Given the operator $\hat{B}$ commuting with $\hat{A}$, then,

$$\hat{A}(\hat{B}\psi_n) = \hat{B}(\hat{A}\psi_n) = \lambda(\hat{B}\psi_n).$$

Hence, $\hat{B}\psi_n$ is an eigenfunction of $\hat{A}$. In case that each eigenvalue of $\hat{A}$ corresponds to one eigenfunction. This implies that there exist a constant β such that $\hat{B}\psi_n = \beta\psi_n$. In other words, ψ_n is also an eigenfunction of $\hat{B}$.

The second case is that an eigenvalue corresponds to more than one eigenfunction. Let us denoted the these eigenfuncions by f_i, where $i = 1, ..., N$. We can write,

$$\hat{A}(\hat{B}\psi_n) = \lambda\sum_{i=1}^{N}\hat{B}f_i.$$

It can be considered that $\hat{B}$ is acting on a subspace of V spanned by f_i. $\hat{B}$ is a hermitian operator in V, it is also hermitian in this subspace. Indeed, we always have $(f_1, \hat{B}f_2) = (\hat{B}f_1, f_2)$. This proposition allows us to choose a basis of eigenfunctions of $\hat{B}$, which span this subspace[14]. Since these eigenfunctions still belong to V of $\hat{A}$. The proof is completed. □

Now we will seek for the eigenvalues of $\hat{\boldsymbol{l}^2}$ and $\hat{l_z}$. Let call them λ and γ, respectively. Considering the ladder operators given by $\hat{L_\pm} = \hat{l_x} \pm \hat{l_y}$. It can be shown quite straightforwardly that they commute with $\hat{\boldsymbol{l}^2}$; meanwhile, $\left[\hat{l_z}, \hat{L_\pm}\right] = \pm\hbar\hat{L_\pm}$. As we have already proved above, these two commuting operators have simultaneous eigenfunction. We set $f_\pm = \hat{L_\pm}f$, the function immediately satisfies,

$$\hat{\boldsymbol{l}^2}f_\pm = \hat{l_\pm}\hat{\boldsymbol{l}^2}f = \lambda f_\pm. \tag{6}$$

$$\hat{l_z}f_\pm = \left[\hat{l_z}, \hat{L_\pm}\right]f + \hat{L_\pm}\hat{l_z}f = (\gamma \pm \hbar)f_\pm. \tag{7}$$

Realize that if we repeat the process t times for $\hat{l_z}$, we can find its eigenvalues $\gamma' = \gamma \pm t\hbar$. However, we want $\gamma' \leq \lambda$. It follows that the set of eigenfunctions is finite, and assume that the maximum among them is denoted by f_{max} such that $\hat{l_+}f_{max}$=0. It corresponds to eigenvalue $\hbar l_{max}$. We also notice that $\hat{\boldsymbol{l}^2}f_{max} = \left[\hat{l_-}\hat{l_+} + \hat{l_z}^2 + \hbar\hat{l_z}\right]f_{max}$. This means that $\lambda = \left[0 + (\hbar l_{max})^2 + \hbar(\hbar l_{max})\right]$, or $\lambda = \hbar^2 l_{max}(l_{max}+1)$. In the same way, we define f_{min} such that $\hat{l_-}f_{min=0}$ and the eigenvalue is $\hbar l_{min}$. Then we find that $\lambda = \hbar^2 l_{min}(l_{min}-1)$. Since λ is invariant, we obtain $l_{min} = -l_{max}$ (the second root $l_{min} = l_{max}+1 > l_{max}$ is excluded). Thus, the eigenvalues of $\hat{l_z}$ range from $-\hbar l$ to $\hbar l$. For short, we take $\gamma = \hbar m$, where $m = -l, ..., l$. Also, λ can be set equal to $\hbar^2 l(l+1)$. If connecting $m = l$ to $m = -l$ by an integer number k of operations, we infer that $l = k/2$, which means that l can be either integer or half-integer.

IV. HYDROGEN ATOM

For simplicity, the problem is reduced to a two-body problem in which we consider the motion of a small particle of mass $\mu = \frac{m_e m_p}{m_e + m_p}$ around a particle of mass $m_e + m_p$ fixed at the origin.

The potential function (2) does not depend on time, therefore, we utilize the time-independent Schrödinger equation. It reads,

$$\left(-\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{|\boldsymbol{r}|}\right)\psi = E\psi. \tag{8}$$

From (3), the Laplacian in spherical coordinate is transformed to,

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\hat{\boldsymbol{l}}^2}{\hbar^2 r^2}. \tag{9}$$

First of all, let assume that the solution is in form of,

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi). \tag{10}$$

Substituting this expression into (8), we obtain,

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{R}\frac{d^2R}{dr^2} + \frac{2}{r}\frac{1}{R}\frac{dR}{dr} - \frac{1}{Y}\frac{\hat{\boldsymbol{l}}^2 Y}{\hbar^2 r^2}\right) - \frac{e^2}{|\boldsymbol{r}|} = E \tag{11}$$

A. Harmonic Oscillators

For the angular part, suppose $Y(\theta,\phi)$ can be written as,

$$Y_m^l(\theta,\phi) = \Theta(\theta)\Phi(\phi), \tag{12}$$

where $0 \le \theta \le \pi$, and $0 \le \phi \le 2\pi$.

1. The Azimuthal Angle Equation

Considering the eigenequation of $\hat{l_z}$ operator

$$\hat{l_z^2}\Phi = \left(-i\hbar\frac{\partial}{\partial\phi}\right)^2\Phi = \hbar^2 m^2\Phi, \tag{13}$$

this leads to

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi. \tag{14}$$

We recognize that the function Φ is periodic with the period of 2π, from which we deduce that the constant m must be an integer. (14) is a second order differential equation, whose characteristic equation is $r^2 = -m^2$. The roots yield $r = \pm im$. The solution is then straightforwardly found as,

$$\Phi(\phi) = e^{\pm im\phi}. \tag{15}$$

2. The Polar Angle Equation

We have already known the eigenequation of $\hat{\boldsymbol{l}}^2$ which is,

$$-\frac{\hat{\boldsymbol{l}}^2}{\hbar^2}Y = -l(l+1)Y. \tag{16}$$

From (3), (11) and the result we obtained for the azimuthal angle. The equation of Θ becomes,

$$\frac{d^2\Theta}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta} + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right]\Theta = 0. \tag{17}$$

Happily, this equation has the form of trigonometric *Associated Legendre equation*. The complete solution is a well-known family of polynomials expressed by the Rodrigues' formula[15],

$$P_l^m(\cos\theta) = \sin^m\theta\frac{d^m}{dx^m}P_l(\cos\theta), \tag{18}$$

where $P_l(\cos\theta)$ is called *Legendre Polynomial*, which is solution to (17) when setting $m = 0$

The angular terms generate the spherical harmonic functions.

$$Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi}. \tag{19}$$

The coefficient is chosen so that it satisfies the Racah's normalization. N the complex conjugate is,

$$Y_l^{m*}(\theta,\phi) = (-1)^m Y_l^{-m}(\theta,\phi). \tag{20}$$

B. The Radial Equation

We denote $r = |\boldsymbol{r}|$, by substituting the constants, the equation for radial function follows,

$$\frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{r}\right)r^2 + \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - l(l+1) = 0. \tag{21}$$

Lets denote,

$$\rho = \frac{r}{a_0}, \quad \epsilon = \frac{E}{E_0}. \tag{22}$$

where $a_0 = \frac{\hbar^2}{\mu c^2}$ is the Bohr radius, and $E_0 = \frac{\mu e^4}{\hbar^2} = \frac{e^2}{a_0}$ corresponds to the ground-state energy level. (21) can be rewritten as,

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[2\epsilon + \frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0. \tag{23}$$

Now, we examine the asymptotic form of the solutions. When $\rho \to 0$, $\frac{l(l+1)}{\rho^2}$ will dominate, (23) reduces to

$$\frac{d^2R}{d\rho^2} - \frac{l(l+1)}{\rho^2}R = 0. \tag{24}$$

Suppose the solution is in form of ρ^s. Substituting this formula, we obtain,

$$s(s-1) = l(l+1).$$

which yields,

$$s_1 = l+1 \text{ and } s_2 = -l.$$

Since the function $R(\rho)$ must be finite, we exclude the second root. Consequently, we have

$$R(\rho) \propto \rho^{l+1} \text{ when } \rho \to 0. \tag{25}$$

When ρ becomes very large, those terms that involve $1/\rho$ and $1/\rho^2$ vanish; approximately,

$$\frac{d^2R}{d\rho^2} + 2\epsilon R = 0. \tag{26}$$

Obviously, the solution depends on the sign of ϵ. If it is positive, we get,

$$R(\rho) = A\exp\left(i\rho\sqrt{2\epsilon}\right) + B\exp\left(-i\rho\sqrt{2\epsilon}\right). \tag{27}$$

The two terms are finite for all value of ρ which means that the motion of particle is continuous. For $\epsilon < 0$, we introduce $\alpha = \sqrt{2|\epsilon|}$. The general solution is,

$$R(\rho) = C\exp\left(-\alpha\rho\right) + D\exp\left(\alpha\rho\right). \tag{28}$$

but $e^{\alpha\rho}$ blows up when $\rho \to 0$, $D = 0$. Therefore, the function $R(\rho)$:

$$R(\rho) = e^{-\alpha\rho}\rho^{l+1}\sum_{k=0}^{\infty} c_k\rho^k. \tag{29}$$

Inserting this expression in (23), we find the recurrence relation for the coefficient c_k

$$c_{k+1} = \frac{2[1-\alpha(k+l+1)]}{l(l+1)-(k+l+2)(k+l+1)}c_k. \tag{30}$$

Assume that the series solution does not terminate, by the ratio test we see that,

$$\lim_{k\to\infty}\frac{c_{k+1}}{c_k} = \frac{2\alpha}{k+l+2}. \tag{31}$$

For values of k larger than some very large number L, it can be deduced from the above relation that,

$$\sum_{k=0}^{\infty} c_k\rho^k \approx (\text{polynomial of } \rho) + e^{2\alpha\rho}. \tag{32}$$

This means that $R(\rho) \propto e^{\alpha\rho}$, which does not satisfy the finite condition. Therefore, there will be some integer $k = n_r$ for which the series vanishes. For short, we take $n = n_r + l + 1$, it follows that the energy of function ψ must satisfy $\alpha = 1/n$, or

$$\epsilon = -\frac{1}{2n^2}. \quad n = 1, 2, 3, ... \tag{33}$$

Since n_r is non-negative, $n \geq l+1$. This infers that for certain n, the maximum possible value of l is $n-1$. The recurrence relation (30) is rewritten as,

$$c_{k+1} = \frac{2}{n}\frac{k-n+l+1}{(k+1)(k+2l+2)}c_k. \tag{34}$$

The radial functions are then determined by,

$$R_{nl}(r) = e^{-r/na_0}r^{l+1}\sum_{k=0}^{n-l-1} c_k r^k \tag{35}$$

The coefficient is determined from the normalization $\int |R|^2 r^2 dr = 1$.

Finally, recalling that the Schrödinger equation $\hat{H}\psi_n = E_n\psi_n$. has the form of (5), is an eigenequation of the Hamiltonian operator. Then E_n is an eigenvalue representing the energy state of the system. From (22) and (33), we obtain,

$$E_n = -\frac{\mu e^4}{2n^2\hbar^2}. \tag{36}$$

It is important to remark that all eigenenergies are discrete and negative. We can say that the associated eigenfunctions for the Hamiltonian ψ_n span negative energy subspace of $\mathcal{L}^2(\mathbb{R}^3)$[16].

V. CONCLUSION

Although topic of this report is about the Hydrogen, our main objective is to provide rigorous background and details to help understand it. We have briefly mentioned some main and basic characteristics of operators in Hilbert space such that hermiticity, commutativity, though just the tip of the iceberg. Through our analysis, we can see how this concept formulates the mathematical structure of quantum mechanics. For example in this case of hydrogen atom, it provides the precise meanings to the quantum numbers n, l, m, not just random constants inserted into the equations to get solvable ones. Lastly, we want to emphasize how mathematics and physics complement each other, yet have their own merits.

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