Hydrogen Atom Wave Equation

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1. Introduction

In 1909, Ernest Rutherford performed his most famous work, the gold foil experiment, in which, an alpha particle beam is scattered when it strikes a thin metal foil. The result suggests that the structure of the atom should be a dense nucleus with electrons orbiting around it[8]. However, there is a problem with this model. In classical electromagnetism, any accelerating charge radiates energy. Therefore, an electron orbiting around a nucleus with circular motion experiences a centripetal acceleration, thus it should radiates energy and lose its kinetic energy, and would rapidly spiral into the nucleus within $1.6 \times 10^{-11} s$[6]. However, in reality, most atoms are quite stable. This means a better model is needed to study atom.

In 1913, in order to correct the classical model, Niels Bohr made a number of assumption[2]:

> 1. Electrons can only be in certain, discrete circular orbits or stationary states, thereby having a discrete set of possible radii and energies.

> 2. Electrons do not emit radiation while in one of these stationary states.

> 3. An electron can gain or lose energy by jumping from one discrete orbital to another.

This model is known as the Bohr model. With the above assumptions, there is no need to worry about collapse of atoms. In addition, the model matched experimental measuring of hydrogen spectral series, as well as spectral of hydrogen-like atoms (any atom ionized with only one electron left). Yet, Bohr model is still not perfect to explain some phenomena such as spectral details result from fine structure or hyperfine structure, Zeeman Effect, and etc. These issues were then resolved with further development of quantum mechanics.

In 1925, Erwin Schrödinger derived the equation later named after himself, the Schrödinger Equation. The equation can be understood mathematically as a linear partial differential equation that describes a physical system. The most general form of the equation is Time-dependent Schrödinger Equation (TDSE), which is able to describe how a system evolves with time. With TDSE, one is able to study the development of a quantum system, and thus, give exact analytical information of the non-relativistic hydrogen atom.

2. Derivation of the PDE

In this paper, for simplicity, the time-independent form of Schrödinger Equation is considered, and in general it can be expressed as:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{1}$$

where $\hat{H}$ is the Hamiltonian operator, which 'extract' the information about energy from the system, and its exact form is depend on which system is studied; $|\Psi\rangle$ is the state vector, or the wave equation,

representing the system being studied; and E is a constant equal to the total energy of the system. The above equation can also be understand as an operator and an eigenstate.

From the relation of momentum and kinetic energy, the Hamiltonian operator can be written in the form:

$$\hat{H} = \frac{\mathbf{p}^2}{2\mu} + V(r) \tag{2}$$

where $V(r)$ is the potential energy, μ is the reduced mass, and $\mathbf{p}$ is the momentum operator defined as:

$$\hat{p} = -i\hbar\nabla \tag{3}$$

where $\hbar$ is the reduced Planck constant, and ∇ is the gradient operator.

Then the Hamiltonian operator becomes:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r) \tag{4}$$

Since hydrogen atom is spherically symmetric, work in spherically coordinates should be a relatively easier way to approach the hydrogen wave equation. The Laplacian operator in spherical coordinates is:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} \tag{5}$$

Substitute the Hamiltonian operator into the time-independent Schrödinger Equation:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi)$$
$$= E\psi(r,\theta,\phi) \tag{6}$$

In quantum mechanics, there is an $\mathbf{L}^2$ operator, which is used to 'extract' squared L^2 norm of angular momentum vector from a system, and $\mathbf{L}^2$ in spherical coordinates is:

$$\hat{L^2} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{7}$$

(The notation is kind of confusing, but $\mathbf{L}^2$ operator has not much to do with L^2 norm, in physics angular momentum is commonly represent by letter $\mathbf{L}$ as in the $\mathbf{L}^2$ operator).

With $\mathbf{L}^2$ operator, the Schrödinger Equation can be written in a more compact form:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\boldsymbol{L}^2\right]\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \tag{8}$$

3. Solution of hydrogen wave equation

Now we have the partial differential equation of hydrogen wave equation, and we are about to solve it. A popular way to handle this equation is to use separation of variables first, and then to solve each ordinary differential equation.

The following few sections of solving hydrogen wave equation are based on works in *Introduction to Quantum Mechanics* by David Griffiths, *Quantum Mechanics* by David McIntyre et al, and *Quantum Mechanics* by Claude Cohen-Tannoudji et al.

3.1 Separation of variables

Assuming the solution of $\psi(r,\theta,\phi)$ can be written as product of functions that depends on only one variable. First, try the separate the radial solution $R(r)$ that only depend on r from $\psi(r,\theta,\phi)$:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{9}$$

The PED in Eq. (8) then becomes:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{1}{\hbar^2 r^2}R(\boldsymbol{L}^2 Y)\right] + V(r)RY = ERY \tag{10}$$

Divide both sides by RY:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{1}{Y}\frac{1}{\hbar^2 r^2}(\boldsymbol{L}^2 Y)\right] + V(r) = E \tag{11}$$

Place all terms with r on one side, and terms with θ and ϕ on the other side:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}(E - V(r))r^2 = \frac{1}{Y}\frac{1}{\hbar^2}(\boldsymbol{L}^2 Y) \tag{12}$$

Since one side of Eq. (12) depends only on r and the other side depends on θ and ϕ, this equation should equal to a constant, A. Therefore, we have radial equation and angular equation as follow:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}(E - V(r))r^2 = A \tag{13}$$

$$\frac{1}{Y}\frac{1}{\hbar^2}(\boldsymbol{L}^2 Y) = A \tag{14}$$

Rearrange Eq. (14) gives:

$$\boldsymbol{L}^2 Y(\theta,\phi) = A\hbar^2 Y(\theta,\phi) \tag{15}$$

In quantum mechanics, the $\boldsymbol{L}^2$ operator acting on an eigenstate has eigenvalue $l(l+1)$, where l is the angular quantum number, so in principle, $A = l(l+1)$.

At this point, we have successfully separate radial equation form the PDE. Now, we can also try to separate θ and ϕ dependences from angular equation. Again, assuming $Y(\theta,\phi)$ can be expressed as product of functions that depend on one variable only:

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi) \tag{16}$$

Plugging Eq. (16) into the angular equation, Eq. (15):

$$\boldsymbol{L}^2 \Theta\Phi = l(l+1)\hbar^2 \Theta\Phi \tag{17}$$

Substitute in the $\mathbf{L}^2$, and rearrange slightly:

$$\left\{\frac{1}{\Theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)\right] + l(l+l)\sin^2\theta\right\} = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \tag{18}$$

Since one side of Eq. (13) depends only on θ and the other side depends on ϕ, this equation should also equal to a constant, B. Thus, the Theta equation and Phi equation are:

$$\frac{1}{\Theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)\right] + l(l+l)\sin^2\theta = B \tag{19}$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -B \tag{20}$$

The PDE is now separated into three ODE:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{1}{\hbar^2 r^2}L^2\right]\psi(r,\theta,\phi)+V(r)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

$$\downarrow$$

$$\begin{cases}\dfrac{1}{R}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial R}{\partial r}\right)-\dfrac{2\mu}{\hbar^2}(E-V(r))r^2=l(l+1)\\[2mm]\dfrac{1}{\Theta}\left[sin\theta\dfrac{\partial}{\partial\theta}\left(sin\theta\dfrac{\partial\Theta}{\partial\theta}\right)\right]+l(l+l)\sin^2\theta=B\\[2mm]\dfrac{1}{\Phi}\dfrac{\partial^2\Phi}{\partial\phi^2}=-B\end{cases}$$

The next step is to solve these ODE, and combine the solutions of each ODE to give the wave equation of hydrogen.

3.2 Azimuthal Solution

Start from the easiest ODE. General solution for differential equation Eq. (20) is:

$$\Phi(\phi)=Ne^{\pm i\sqrt{B}\phi} \tag{21}$$

where N is the normalization constant (since in quantum mechanics, wave equation is related to probability, and inner product of wave equations thus should not exceed 1). To ensure the function is continuous, we also have the restriction $\Phi(\phi)=\Phi(\phi+2\pi)$. This restriction requires $\sqrt{B}$ to be an integer:

$$\sqrt{B}=m=0,\pm1,\pm2\dots$$

Like l, m also have some physical meaning, in quantum mechanics, m is the orbital magnetic quantum number.

Therefore, eigenfunctions for the ODE Eq. (20) are:

$$\Phi_m(\phi)=Ne^{im\phi} \tag{22}$$

Inner product of a wave function with itself over would space should equal to 1, since the total probability equals 1. The inner product in quantum mechanics is defined as the integration of a wave equation and complex conjugate of another wave equation over certain region. Therefore, we are able to get the normalization constant N:

$$1=\int_0^{2\pi}\Phi_m^*(\phi)\Phi_m(\phi)d\phi=\int_0^{2\pi}N^*e^{-im\phi}Ne^{im\phi}d\phi=2\pi|N|^2 \tag{23}$$

One valid normalization constant can be:

$$N=\frac{1}{\sqrt{2\pi}} \tag{24}$$

The solutions are thus:

$$\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi} \tag{22}$$

3.3 Polar Solution

During solving phi solution, we found that $\sqrt{B} = m$, so the differential equation Eq. (19) can be rewritten as:

$$\left[sin\theta \frac{\partial}{\partial \theta} \left(sin\theta \frac{\partial \Theta}{\partial \theta} \right) \right] + l(l+l) \sin^2 \theta \Theta - m^2 \Theta = 0 \tag{23}$$

Rearrange:

$$\left[\frac{1}{sin\theta} \frac{\partial}{\partial \theta} \left(sin\theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} \right] \Theta = -l(l+l)\Theta \tag{24}$$

One method used by many references to deal with the above differential equation is changing variable. By switch from spherical coordinates back to Cartesian coordinates, we have $z = cos\theta$ inside a unit sphere (since we have not consider the radial solution yet, so the radius does not matter). From trigonometric identity $\sin^2 \theta + \cos^2 \theta = 1$, we also have $sin\theta = \sqrt{1-z^2}$. Now, use the chain rule:

$$\frac{d}{d\theta} = \frac{dz}{d\theta} \frac{d}{dz} = -sin\theta \frac{d}{dz} = -\sqrt{1-z^2} \frac{d}{dz} \tag{25}$$

Multiply both side of the above equation by $sin\theta = \sqrt{1-z^2}$:

$$sin\theta \frac{d}{d\theta} = -(1-z^2) \frac{d}{dz} \tag{26}$$

Then we are able to replace all θ in Eq. (24) by z:

$$\begin{aligned}
&\left[\frac{1}{sin\theta} \frac{\partial}{\partial \theta} \left(sin\theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) + l(l+l)\Theta(\theta) \\
&= \left[\frac{1}{sin\theta} \frac{\partial}{\partial \theta} \left(-(1-z^2) \frac{d}{dz} \right) - \frac{m^2}{1-z^2} \right] \Theta(\theta) + l(l+l)\Theta(\theta) \\
&= \left[\frac{d}{dz} \left(-(1-z^2) \frac{d}{dz} \right) - \frac{m^2}{1-z^2} \right] P(z) + l(l+l)P(z) \\
&= \left[(1-z^2) \frac{d^2}{dz^2} - 2z \frac{d}{dz} + l(l+1) - \frac{m^2}{1-z^2} \right] P(z) = 0
\end{aligned} \tag{27}$$

The differential equation after changing variable is a standard form of the associated Legendre equation. According to *Method of Mathematical Physics* by David Hilbert, the equation has nontrivial and nonsingular solution on [-1, 1] only if l and m are integers. The solutions to this differential equation are denoted $P_l^m(z)$, which is defined as derivatives of ordinary Legendre polynomials:

$$P_l^m(z) = (-1)^m (1-z)^{\frac{m}{2}} \frac{d^m}{dz^m} (P_l(z)) \tag{28}$$

The ordinary Legendre polynomials has form:

$$P_l(z) = \frac{1}{2^l l!} \frac{d^l}{dz^l} (z^2 - 1)^l \tag{29}$$

Plugging the ordinary Legendre polynomial into Eq. (28) and simplify:

$$P_l^m(z) = (-1)^m \frac{1}{2^l l!} (1-z)^{\frac{m}{2}} \frac{d^{m+l}}{dz^{m+l}} (z^2 - 1)^l \tag{30}$$

Again, since the equation is related to probability, a normalization factor is required to ensure its inner product with itself is 1.

$$\int_{-1}^{1} P_l^m(z)P_n^m(z)dz = \frac{2}{2l+1}\frac{(l+m)!}{(1-m)!}\delta_{ln} \tag{31}$$

Therefore the normalization factor is $\sqrt{\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}}$. Then switching back to spherical coordinate by replacing all z by θ gives the polar solution:

$$\Theta_l^m(\theta) = \sqrt{\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}}P_l^m(cos\theta) \tag{32}$$

with l and m are both integers.

Also, the ordinary Legendre polynomial is a polynomial of order l, if $m>l$, the associated Legendre polynomial vanishes, so we have $m \in \{-l, -l+1, ..., -1,0,1, ..., l-1, l\}$.

3.4 Spherical harmonics

The combination of azimuthal solution Eq. (22) and polar solution Eq. (32) gives:

$$Y_l^m(\theta, \phi) = (-1)^{\frac{m+|m|}{2}}\sqrt{\frac{2l+1}{4}\frac{(l-m)!}{(l+m)!}}P_l^m(cos\theta)e^{im\phi} \tag{33}$$

which solve the angular equation Eq. (14). Equation in the form of Eq. (33) is called the spherical harmonics.

The spherical harmonics has several important properties:

- Orthogonality

$$\int_0^{2\pi}\int_0^{\pi} Y_{l_1}^{m_1*}(\theta, \phi)Y_{l_2}^{m_2}(\theta, \phi)sin\theta d\theta d\phi = \delta_{l_1 l_2}\delta_{m_1 m_2} \tag{34}$$

where δ is the Kronecker delta.

The orthogonality of m comes from the complex exponential function part of azimuthal solution. The orthogonality of l comes from the Legendre equation.

- Completeness
  The spherical harmonics are able to expand any sufficiently smooth function on a unit sphere:

$$\psi(\theta, \phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}c_{lm}Y_l^m(\theta, \phi) \tag{35}$$

where c_{lm} are coefficients that can be found by projecting the function $\psi(\theta, \phi)$ onto each $Y_l^m(\theta, \phi)$:

$$c_{lm} = \int_0^{2\pi}\int_0^{\pi} Y_l^{m*}(\theta, \phi)\psi(\theta, \phi)sin\theta d\theta d\phi \tag{36}$$

The idea is much like we can expand a continuous function with piecewise continuous derivative to a Fourier series in one dimension.

3.5 Radial solution

For radial equation:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}\left(E - V(r)\right)r^2 = l(l+1) \tag{13}$$

first we need to find out the potential energy *V(r)*. Potential energy comes in two parts in hydrogen atom problem. Electromagnetic interaction between the electron and the nucleus contributes to one part, and another part is caused by the 'circular motion' of the electron around nucleus, which is called centrifugal barrier (the 'circular motion' is in quotation mark since the electron is not really in circular motion, it is just a classical way to interpret the behavior of an electron). The potential energy can be expressed as:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2\mu r^2} \tag{37}$$

where *Ze* is the nuclear charge (although hydrogen atom has nuclear charge *e*, the hydrogen atom wave equation in principle applied to all hydrogen-like atoms as mentioned in introduction. For example He$^+$, the helium +1 ion, has nuclear charge 2*e*), ϵ_0 is permittivity of free space, $\hbar$ is the reduced Planck constant, and μ is the reduced mass (in two body problem, in this case electron and nucleus, electron is not orbiting around nucleus, but center of mass of the system. So in the reference frame centered at nucleus, to be precise, reduced mass is used instead).

In Bohr model, Niels Bohr already gives a good approximate radius of electron orbital radius, which is often refer to Bohr radius (and in fact, it is the most probable radius calculated using wave equation!):

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \tag{38}$$

To make the radius more general to deal with case when nuclear charge is not *e*, we define a length scale parameter *a* as:

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu Z e^2} = \frac{a_0}{Z} \tag{39}$$

Mathematicians usually ignoring constant when solving problems for simplicity as rescaling the wave equation from $u_{tt} = c^2 u_{xx}$ to $u_{tt} = u_{xx}$ and so on. Similarly, physicists like to dealing with dimensionless quantity for clarity. Therefore, we define a dimensionless radius to be:

$$\rho = \frac{r}{a} \tag{40}$$

And characteristic energy scale which is also dimensionless:

$$-\gamma^2 = \frac{E}{\left(\dfrac{\hbar^2}{2\mu a^2}\right)} \tag{41}$$

The radial equation becomes:

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left(-\gamma^2 + \frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right)R = 0 \tag{42}$$

To solve Eq. (41), one approach is to start with considering asymptotic solution.
- For large ρ, inside parentheses of Eq. (41), term with ρ^{-1} and ρ^{-2} can be neglected, and the differential equation becomes:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \gamma^2 R = 0 \tag{43}$$

which has solution:

$$R(\rho) \sim e^{-\gamma\rho} \tag{44}$$

- For small ρ, inside parentheses, ρ^{-2} term dominates, Eq. (41) becomes:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R = 0 \tag{45}$$

Suppose that the solution has the form $R(\rho) = \rho^q$ for some constant q. Plugging $R(\rho) = \rho^q$ into Eq. (41):

$$q(q-1)\rho^{q-2} + \frac{2}{\rho}q\rho^{q-1} - \frac{l(l+1)}{\rho^2}\rho^q = 0$$
$$q(q+1) = l(l+1) \tag{46}$$

Therefore, $q = l$ or $q = -l - 1$. To keep the solution finite when ρ small, q is can only be 1, thus the solution is:

$$R(\rho) \sim \rho^l \tag{47}$$

At this point, we have the approximate solution near the nucleus, and at the infinity. The actual solution should be the combination of Eq. (43), Eq. (46), and another term that describing the solution in between. Suppose that the actual solution is:

$$R(\rho) = \rho^l e^{-\gamma\rho} H(\rho) \tag{48}$$

Plugging Eq. (47) back into the differential equation Eq. (41), and collect terms of $H(\rho)$ and its derivatives:

$$\rho\frac{d^2H}{d\rho^2} + 2(l + 1 - \gamma\rho)\frac{dH}{d\rho} + 2(1 - \gamma - \gamma l)H = 0 \tag{49}$$

Assume $H(\rho)$ can be expand as a power series:

$$H(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \tag{50}$$

Then it has derivatives:

$$H'(\rho) = \sum_{j=1}^{\infty} jc_j\rho^{j-1} = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j \tag{51}$$

$$H''(\rho) = \sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1} \tag{52}$$

Substituting Eq. (50) and Eq. (51) into Eq. (48):

$$\rho\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1} + 2(l+1-\gamma\rho)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j + 2(1-\gamma-\gamma l)\sum_{j=0}^{\infty}c_j\rho^j = 0 \tag{53}$$

To ensure the summation is zero, we need the coefficient of each power of ρ to be zero. Consider the ρ^j term:

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2\gamma jc_j + 2(1-\gamma-\gamma l)c_j = 0$$

$$c_{j+1} = \frac{2\gamma(1+j+l) - 2}{(j+1)(j+2l+2)} c_j \tag{54}$$

The idea behind the above few step in fact is similar to how coefficient of Legendre polynomials is determined. We can use similar way to find an expression for polar solution as well.

However, there is a problem of the coefficient we found. It does not guarantee the convergence of the series, the solution is then to terminate the series at certain point. This requires $c_{jmax} + 1 = 0$, and therefore:

$$c_{jmax+1} = \frac{2\gamma(1+j_{max}+l) - 2}{(j_{max}+1)(j_{max}+2l+2)} c_{jmax} = 0$$

$$2\gamma(1+j_{max}+l) - 2 = 0 \tag{55}$$

Since j and l are both integers, $(1 + j_{max} + l)$ is also an integer, which we can denote as n. In quantum mechanics, n is the principle quantum number. By how n is defined, we can see $n \geq l + 1$, so we have $l \in \{0,1,2,\dots,n-1\}$.

And the radial solution can now be safely written as:

$$R_{n,l} = \rho^l e^{-\gamma\rho} H(\rho)$$
$$= \left(\frac{Zr}{a_0}\right)^l e^{-\frac{Zr}{na_0}} H\left(\frac{Zr}{a_0}\right) \tag{56}$$

The radial equation are usually expressed in terms of the associated Laguerre polynomials, which are defined as:

$$L_q^p(x) = \frac{d^p}{dx^p} L_p(x) \tag{57}$$

where $L_p(x)$ is the ordinary Laguerre polynomials, that are defined as:

$$L_q(x) = e^x \frac{d^q}{dx^q}(x^q e^{-x}) \tag{58}$$

Using above definition for associated Laguerre polynomials, radial solution are:

$$R_{n,l}(r) = \left(\left(\frac{2z}{na_0}\right)^3 \frac{(b-l-1)!}{2n\left((n+l)!\right)^3}\right)^{\frac{1}{2}} e^{-\frac{Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) \tag{59}$$

4. Hydrogen wave functions

Finally, by combining the spherical harmonics, Eq. (33), and radial solution, Eq. (59), we can have the full wave function:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi) \tag{60}$$

Clearly, the partial differential equation, Eq. (8) is solved by the above equation, thus solution exists. Though the derivation of the wave function, we introduced three integer quantum number n, l, and m:

$$n \in \mathbb{N}$$

$$l \in \{0,1,2,\dots,n\}$$

$$m \in \{-l, -l+1, \ldots 0, \ldots, l-1, l\}$$

Therefore, the solution to the differential equation is not unique.

It is hard to see the stability of the solution, since we use time-independent form of Schrödinger Equation, and we cannot use energy method in the way we normally used in class. Yet, there are some conserved quantities can be found:

- As we demand in Eq. (17), $\mathbf{L}^2$ operator acting on the spherical harmonics returns $l(l+1)\hbar^2$. Since $\mathbf{L}^2$ operator does not have any r dependence, acting it on the full wave function would still gives $l(l+1)\hbar^2$.

$$\mathbf{L}^2\psi_{nlm}(r,\theta,\phi) = l(l+1)\hbar^2\psi_{nlm}(r,\theta,\phi) \tag{61}$$

  This means the squared L^2 norm of angular momentum vector is constant for a wave equation with specified quantum number n, l, and m.

- Since squared L^2 norm of angular momentum vector is conserved, we are expecting projection of angular momentum vector in any direction is conserved.
  Angular momentum operator, $\mathbf{L}$, in Cartesian coordinates are defined as:

$$\mathbf{L} = \hat{r} \times \hat{p} = (yp_z - zp_y, zp_x - xp_z, xp_y - yp_x) \tag{62}$$

  with $\hat{p} = -i\hbar\nabla$ as defined in Eq. (3).
  Switch to spherical coordinate, we have[1]:

$$\begin{cases} \widehat{L_x} = i\hbar(sin\phi\dfrac{\partial}{\partial\theta} + cot\theta cos\phi\dfrac{\partial}{\partial\phi}) \\ \widehat{L_y} = i\hbar(-cos\phi\dfrac{\partial}{\partial\theta} + cot\theta sin\phi\dfrac{\partial}{\partial\theta}) \\ \widehat{L_z} = -i\hbar\dfrac{\partial}{\partial\phi} \end{cases} \tag{63}$$

  The easiest one is z component. Since it only involves partial with respect to ϕ, acting it on wave equation, only azimuthal solution matters, and it will return $m\hbar$. For other two components, it is hard to show results rigorously. However in reality, there is no one direction marked z, so we can use spherical symmetry to rotate the system, and the rest two component should behave just like z component. Thus we have:

$$\widehat{L_z}\psi_{nlm}(r,\theta,\phi) = m\hbar\psi_{nlm}(r,\theta,\phi) \tag{64}$$

  This means angular momentum is constant for a wave equation with specified quantum number n, l, and m.

- We have conserved quantities related to l and m. We should expect there is a conserved quantity related to n as well, and there is one!
  By Eq. (55) and with definition $n = (1 + j_{max} + l)$:

$$\gamma = \frac{1}{n} \tag{65}$$

  γ is defined in Eq. (41), so we have the relation between n and energy. Solving Eq. (41) and Eq. (65) yields:

$$E_n = -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\frac{\mu}{\hbar^2} \tag{66}$$

This means, the energy operator, or the Hamiltonian operator, has eigenvalue $-\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\frac{\mu}{\hbar^2}$.

$$\hat{H}\psi_{nlm}(r,\theta,\phi) = (-\frac{\hbar^2}{2\mu}\nabla^2 + V(r))\psi_{nlm} = -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\frac{\mu}{\hbar^2}\psi_{nlm}(r,\theta,\phi) \qquad (67)$$

This means energy is constant for a wave equation with specified quantum number n, l, and m. Energy levels of hydrogen atom, and hydrogen-like atoms can be determined using Eq. (67), and this also explain the spectrum of hydrogen-like atoms.

5. Conclusion

Quantum mechanics is an essential tool to deal with problems in microscopic world. Using Schrödinger Equation we can learn much about atoms. Yet, with all the discussion above, we are not even at the fine structure level of atom. To deal with fine structure or hyperfine structure level problem, we run out of tools for the exact solution. A method called perturbation theory is introduced to approximate, by starting from a relatively simpler but similar problem, then adding correction terms. However, when problem becomes more complicated, for example, the Helium atom, which is a three body problem involving two electrons and a nucleus, perturbation theory starts to fail. It seems like there is still a long way to go on the exploration and discovery.

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