

Chapter 2

The Hydrogen Atom

2.1 Central Potential Hamiltonian

2.1.1 Hamiltonian for central potential problem in spherical coordinates

Central potential problems relate to potentials that depend only on the distance between the origin and the particle r , such as the Coulomb potential felt by an electron bound to an atomic nucleus (see Chapter 1.2). In this case, the potential is independent of the direction, and it is useful to describe the angular momentum operators in spherical coordinates. First, we note that

$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta,\end{aligned}\tag{2.1}$$

from which we derive the relationship

$$\begin{aligned}r &= \sqrt{x^2 + y^2 + z^2} \\ \theta &= \arctan(\sqrt{x^2 + y^2}/z) \\ \phi &= \arctan(y/x).\end{aligned}\tag{2.2}$$

The partial derivatives between the coordinates can be computed as

$$\begin{aligned}\frac{\partial r}{\partial x} &= \frac{x}{r}, & \frac{\partial r}{\partial y} &= \frac{y}{r}, & \frac{\partial r}{\partial z} &= \frac{z}{r} \\ \frac{\partial \theta}{\partial x} &= \frac{\cos \theta \cos \phi}{r}, & \frac{\partial \theta}{\partial y} &= \frac{\cos \theta \sin \phi}{r}, & \frac{\partial \theta}{\partial z} &= -\frac{\sin \theta}{r} \\ \frac{\partial \phi}{\partial x} &= -\frac{y \cos^2 \phi}{x^2}, & \frac{\partial \phi}{\partial y} &= \frac{\cos^2 \phi}{x}, & \frac{\partial \phi}{\partial z} &= 0.\end{aligned}\tag{2.3}$$

The partial derivatives in the Cartesian coordinates translate to derivatives in spherical coordinates as

$$\begin{aligned}
\frac{\partial}{\partial x} &= \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} = \frac{x}{r} \frac{\partial}{\partial r} + \frac{\cos \theta \cos \phi}{r} \frac{\partial}{\partial \theta} - \frac{y \cos^2 \phi}{x^2} \frac{\partial}{\partial \phi}, \\
\frac{\partial}{\partial y} &= \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi} = \frac{y}{r} \frac{\partial}{\partial r} + \frac{\cos \theta \sin \phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos^2 \phi}{x} \frac{\partial}{\partial \phi}, \\
\frac{\partial}{\partial z} &= \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} = \frac{z}{r} \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta}.
\end{aligned} \tag{2.4}$$

Thus, the angular momentum operators can be rewritten as

$$\begin{aligned}
\hat{L}_x &= -i\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] = -i\hbar \left[-\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right] \\
\hat{L}_y &= -i\hbar \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] = -i\hbar \left[\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right] \\
\hat{L}_z &= -i\hbar \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right] = -i\hbar \frac{\partial}{\partial \phi} \\
\hat{\mathbf{L}}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right].
\end{aligned} \tag{2.5}$$

This is an alternative way to derive Eq. 1.24. If we let the radial component of the momentum operator $\hat{p}_r = -i\hbar \left(\frac{1}{r} \frac{\partial}{\partial r} r \right)$, the Hamiltonian with central potential $V(r)$ in Eq. 1.25 can be written as

$$\hat{H} = \frac{\hat{p}_r^2}{2mr} + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(r). \tag{2.6}$$

2.1.2 Spherical harmonics

We can multiply the expression of the Hamiltonian with central potential, Eq. 2.6, by r^2 . Then, the first and the third terms will only depend on r , and the second term will only depend on the angles θ and ϕ . We consider the eigenvalue equation corresponding to the orbital angular momentum operators $\hat{\mathbf{L}}^2$ and \hat{L}_z , parametrized with two quantum numbers l and m , written as

$$\hat{\mathbf{L}}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi), \tag{2.7}$$

$$\hat{L}_z Y_l^m(\theta, \phi) = \hbar m Y_l^m(\theta, \phi). \tag{2.8}$$

These are explicit functional forms of the eigen equations for the orbital angular momentum operator discussed in the previous chapter, in Eq. 1.36. In terms of Dirac notations, the eigenstates of the orbital angular momentum operators $|l, m\rangle$ can be expressed in spatial coordinates by projecting it with a position eigenfunction $|r\rangle$

$$\langle r | l, m \rangle = Y_l^m(\theta, \phi). \tag{2.9}$$

These eigenstates are called *spherical harmonics* of degree l and order m . Next, we solve the Eqs. 2.7 and 2.8 to find the explicit functional form of the spherical harmonics. Noting the form of the $\hat{\mathbf{L}}^2$ operator given in Eq. 2.5, we note that when we multiply it by $\sin^2 \theta$, the first (second) term becomes completely independent of ϕ (θ). This means we can separate variables again. We let $Y_l^m(\theta, \phi) \equiv \Theta_l^m(\theta) \Phi_m(\phi)$, and rewrite Eq. 2.7 as

$$-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Theta_l^m(\theta)\Phi_m(\phi)=l(l+1)\Theta_l^m(\theta)\Phi_m(\phi). \quad (2.10)$$

Dividing the equation by $\Theta_l^m(\theta)\Phi_m(\phi)/\sin^2\theta$ yields

$$-\frac{1}{\Phi_m(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi_m(\phi)=\frac{1}{\Theta_l^m(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+l(l+1)\sin^2\theta\right]\Theta_l^m(\theta). \quad (2.11)$$

Since the left (right) hand side of this equation only depends on ϕ (θ), each of these terms must be a constant. Letting these equal to m^2 and replacing partial derivative to a full derivative, we get two equations

$$\frac{d^2}{d\phi^2}\Phi_m(\phi)=-m^2\Phi_m(\phi) \quad (2.12)$$

$$\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)+l(l+1)\sin^2\theta\right]\Theta_l^m(\theta)=m^2\Theta_l^m(\theta). \quad (2.13)$$

The solution to Eq. 2.12 is straightforward: $\Phi_m(\phi)=e^{\pm im\phi}$. Given that in real space, the solution has to wrap itself around every 2π , we conclude that m has to be an integer. We can rewrite Eq. 2.13 by replacing the variable $t=\cos\theta$, and noting that $\frac{d}{d\theta}=\frac{dt}{d\theta}\frac{d}{dt}=-\sin\theta\frac{d}{dt}$, we get

$$\left[\frac{d}{dt}\left((1-t^2)\frac{d}{dt}\right)+l(l+1)-\frac{m^2}{1-t^2}\right]\Theta_l^m(t)=0. \quad (2.14)$$

This equation is called the Legendre equation, and its solutions are the associated Legendre polynomials $P_l^m(t)$. Therefore, the spherical harmonics can be written as $Y_l^m(\theta,\phi)=A_{lm}P_l^m(\cos\theta)e^{im\phi}$, where A_{lm} is the normalization factor. Enforcing the normalization condition

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}Y_l^mY_{l'}^{m'*}d\Omega=\delta_{ll'}\delta_{mm'}, \quad (2.15)$$

we conclude that

$$Y_l^m(\theta,\phi)=\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}. \quad (2.16)$$

2.1.3 Solution to free Hamiltonian

A quantum particle in free space, in the absence of any potential, is readily solved in Cartesian coordinate system, as the spatial variables $\{x, y, z\}$ separate readily. The solution is a linear superposition of plan waves

$$\psi_{pqr}(x, y, z)=A_{pqr}\exp[-i(k_px+k_qy+k_rz)], \quad (2.17)$$

where the momentum vector $\vec{k} = (k_p, k_q, k_r)$ describes the quantum numbers determined by the boundary conditions of how the free space is quantized.

In spherical coordinates, we seek the solution to the time-independent Schrödinger equation with three quantum numbers k, l, m as

$$\hat{H}\psi_{klm}(r, \theta, \phi) = E_{klm}\psi_{klm}(r, \theta, \phi) = E_{klm}R_{kl}(r)Y_l^m(\theta, \phi), \quad (2.18)$$

where we further separated the radial and the angular variables into two functions $R_{kl}(r)$ that only depends on radial variable and $Y_l^m(\theta, \phi)$ that only depends on the angular variables. This is justified because the Hamiltonian does not have any terms that mixes the radial and angular operators (r appears in the second term of Eq. 2.6, but acts as a scalar rather than an operator). The Schrödinger equation can be reduced to

$$\frac{\hbar^2}{2m} \left[- \left(\frac{1}{r} \frac{\partial}{\partial r} r \right)^2 + \frac{\hat{\mathbf{L}}^2}{\hbar^2 r^2} \right] R_{kl}(r)Y_l^m(\theta, \phi) = E_{klm}R_{kl}(r)Y_l^m(\theta, \phi). \quad (2.19)$$

Dividing both sides by $\frac{\hbar^2}{2mr^2}R_{kl}(r)Y_l^m(\theta, \phi)$ gives

$$- \frac{r^2}{R_{kl}(r)} \left(\frac{1}{r} \frac{\partial}{\partial r} r \right)^2 R_{kl}(r) - r^2 E_{klm} + \frac{1}{\hbar^2 Y_l^m(\theta, \phi)} \hat{\mathbf{L}}^2 Y_l^m(\theta, \phi) = 0. \quad (2.20)$$

The first and second terms on the left hand side of Eq. 2.20 are independent of the angular coordinates θ and ϕ , and the third term is independent of the radial coordinate r . This means that the third term has to be a constant (i.e., no coordinate dependence), which can potentially depend on the quantum numbers l and m . Letting this to be C_{lm} , we get the eigenvalue equation for the $\hat{\mathbf{L}}^2$ operator

$$\hat{\mathbf{L}}^2 Y_l^m(\theta, \phi) = \hbar^2 C_{lm} Y_l^m(\theta, \phi). \quad (2.21)$$

The solution of this equation is $C_{lm} = l(l+1)$, where l is a non-negative integer or non-negative half-integer (Eq. 1.43). Putting this value back into Eq. 2.20 yields the differential equation for the radial coordinates

$$\left[- \left(\frac{1}{r} \frac{\partial}{\partial r} r \right)^2 + \frac{l(l+1)}{r^2} \right] R_{kl}(r) = \frac{2mE_{klm}}{\hbar^2} R_{kl}(r). \quad (2.22)$$

We define k such that $2mE_{klm} \equiv k^2$ and let $x \equiv kr$, then Eq. 2.22 simplifies to

$$\frac{d^2}{dx^2} R_l(x) + \frac{2}{x} \frac{d}{dx} R_l(x) + \left[1 - \frac{l(l+1)}{x^2} \right] R_l(x) = 0, \quad (2.23)$$

where the index k has dropped since the equation is now independent of k . This differential equation is known as the spherical Bessel equation. There are two types solutions to this

equation, known as the spherical Bessel functions $j_l(x)$ and the spherical Neumann functions $n_l(x)$. These functions can be generated from simple elementary functions, as

$$j_l(x) = (-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \left(\frac{\sin x}{x} \right), \quad (2.24)$$

$$n_l(x) = -(-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \left(\frac{\cos x}{x} \right). \quad (2.25)$$

The spherical Bessel and spherical Neumann functions have the following asymptotic behavior near $x = 0$:

$$\begin{aligned} \lim_{x \rightarrow 0} |j_l(x)| &< \infty \\ \lim_{x \rightarrow 0} |n_l(x)| &\rightarrow \infty. \end{aligned} \quad (2.26)$$

So, we choose the spherical Bessel function as the solution, so that

$$\psi_{klm}(r, \theta, \phi) = j_l(kr) Y_l^m(\theta, \phi) \quad (2.27)$$

and $E_{klm} = \hbar^2 k^2 / 2m \equiv E_k$, where the wavefunction is properly normalized. Upon measurement of energy, \hat{L}^2 and \hat{L}_z the wavefunction yields E_k , $l(l+1)\hbar^2$ and $m\hbar$, respectively.

2.2 Hamiltonian for the Hydrogen Atom

2.2.1 Two particle problem

A hydrogen atom is the simplest atom, with one (negatively-charged) electron bound to the nucleus of the atom consisting of one (positively-charged) proton. This is an example of a two-particle system, where the interaction between the two particles depends on the relative position of the two particles. We let m_1 , $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{p}}_1$ (m_2 , $\hat{\mathbf{r}}_2$ and $\hat{\mathbf{p}}_2$) be the mass, position and momentum of the proton (electron), respectively. Then, the total Hamiltonian of the system is given by

$$\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V(|\vec{r}_1 - \vec{r}_2|). \quad (2.28)$$

We now define the relative position operator $\hat{\mathbf{r}} \equiv \hat{\mathbf{r}}_2 - \hat{\mathbf{r}}_1$ and the total momentum operator $\hat{\mathbf{P}} \equiv \hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_2$. We note that these two operators commute, by checking $[\hat{\mathbf{r}}, \hat{\mathbf{P}}] = [\hat{\mathbf{r}}_2, \hat{\mathbf{p}}_2] - [\hat{\mathbf{r}}_1, \hat{\mathbf{p}}_1] = 0$. We then find the conjugate variables for these two operators, the relative momentum operator $\hat{\mathbf{p}}$ and the total position operator $\hat{\mathbf{R}}$ such that each component of the operators satisfy the commutation relations

$$[\hat{r}_i, \hat{p}_j] = [\hat{R}_i, \hat{P}_j] = i\hbar\delta_{ij}, \quad (2.29)$$

where the subscripts here show the x , y or z component of each operator. Letting the operators be linear combinations of the component operators $\hat{\mathbf{R}} = a\hat{\mathbf{r}}_1 + b\hat{\mathbf{r}}_2$ and $\hat{\mathbf{p}} = c\hat{\mathbf{p}}_1 + d\hat{\mathbf{p}}_2$, and enforcing the commutation relation given by Eq. 2.29, we find that

$$\hat{\mathbf{R}} = \frac{m_2}{m_1 + m_2}\hat{\mathbf{r}}_2 + \frac{m_1}{m_1 + m_2}\hat{\mathbf{r}}_1 \quad (2.30)$$

$$\hat{\mathbf{p}} = \frac{m_1}{m_1 + m_2}\hat{\mathbf{p}}_2 - \frac{m_2}{m_1 + m_2}\hat{\mathbf{p}}_1 \quad (2.31)$$

One can readily check that the kinetic energy portion of the Hamiltonian then becomes

$$\frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu}, \quad (2.32)$$

where $M = m_1 + m_2$ and $\mu = m_1m_2/(m_1 + m_2)$ are the total mass and the reduced mass of the two-particle system, respectively. The total Hamiltonian in Eq. 2.28 now breaks down into two parts $\hat{H} = \hat{H}_{CM} + \hat{H}_{rel}$, where

$$\hat{H}_{CM} = \frac{\hat{\mathbf{P}}^2}{2M} \quad (2.33)$$

$$\hat{H}_{rel} = \frac{\hat{\mathbf{p}}^2}{2\mu} + V(|r|) \quad (2.34)$$

are the center-of-mass and relative Hamiltonian that describes the center-of-mass motion and relative motion of the two particles, respectively.

2.2.2 Potential energy for the hydrogen atom

The potential energy between the electron and the nucleus (proton) for the hydrogen atom is given by, in SI units,

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{q^2}{r} = -\frac{e^2}{r}, \quad (2.35)$$

where $q = 1.602 \times 10^{-19}\text{C}$ is the elementary charge (magnitude of the charge of an electron), ϵ_0 is the electrical permittivity of vacuum, and $e^2 \equiv q^2/4\pi\epsilon_0$ is defined for simplicity. The electron mass ($m_e = 9.109 \times 10^{-31}\text{kg}$) is much smaller than the proton mass ($m_p = 1.67 \times 10^{-27} \text{ kg} \approx 1,836m_e$), so the total mass $M \approx m_p$ and the reduced mass $\mu \approx m_e$.

The total Hamiltonian of the hydrogen atom reduces to

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{r}. \quad (2.36)$$

The first term simply describes the motion of the atom (that includes both electron and the nucleus) in free space, and is not very interesting at this time. The interesting aspect we would like to focus on is the internal state of the electron, bound by the Coulomb interaction with the nucleus. So, we focus on the relative Hamiltonian

$$\hat{H}_{rel} = \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{r}. \quad (2.37)$$

This is a particle in a central potential, and can be described using spherical coordinates, as shown in Eq. 2.6.

2.3 Solution of the hydrogen atom

2.3.1 Radial Schrödinger equation and its solutions

Using the separation of variable technique similar to that used for the free particle in Section 2.1.3 and recognizing that the eigen energy of the solution is negative (binding energy, noted by $-E$, where E is a positive number), the radial portion of the Schrödinger equation for the electron in a hydrogen atom becomes

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{1}{r} \frac{d}{dr} r \right)^2 + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{e^2}{r} + E \right] R_{nl}(r) = 0, \quad (2.38)$$

where we choose two quantum numbers n and l to identify the radial function R_{nl} . If we define a different radial function $u_{nl}(r) = rR_{nl}(r)$, Eq. 2.38 can be rewritten as

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2\mu e^2}{\hbar^2 r} + \frac{2\mu E}{\hbar^2} \right] u_{nl}(r) = 0. \quad (2.39)$$

If we define κ as $E \equiv \hbar^2 \kappa^2 / 2\mu$ and rescale the radial variable using κ as $\rho \equiv 2\kappa r$, the equation reduces to

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \left(\frac{\lambda}{\rho} - \frac{1}{4} \right) \right] u_{nl}(\rho) = 0, \quad (2.40)$$

where

$$\lambda^2 = \left(\frac{\mu e^2}{\hbar^2 \kappa} \right)^2 = \frac{\mu e^4}{2\hbar^2} \frac{2\mu}{\hbar^2 \kappa^2} \equiv \frac{\mathbb{R}}{E}. \quad (2.41)$$

If we define the Bohr radius $a_0 \equiv \hbar^2 / \mu e^2 \approx 0.53 \text{ \AA}$, we can express $\mathbb{R} = \mu e^4 / 2\hbar^2 = \hbar^2 / 2\mu a_0^2$, which is called the Rydberg constant ($\mathbb{R} = 2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$).

We solve the radial Schrödinger equation 2.40. We first look for the asymptotic solution. When $\rho \gg 1$, we can ignore the $1/\rho$ and $1/\rho^2$ terms, and the equation simplifies to

$$\frac{d^2 u_{nl}}{d\rho^2} - \frac{1}{4} u_{nl} = 0. \quad (2.42)$$

The solution to this equation, which does not diverge at large ρ values, is given by $u_{nl}(\rho) \sim e^{-\rho/2}$. Next, we look at asymptotic solutions when $\rho \ll 1$, where $1/\rho \ll 1/\rho^2$. In this limit, the equation simplifies to

$$\frac{d^2 u_{nl}}{d\rho^2} - \frac{l(l+1)}{\rho^2} u_{nl} = 0. \quad (2.43)$$

The solution to this equation, which does not diverge at small ρ values, is given by $u_{nl}(\rho) \sim \rho^{l+1}$. So, we use the ansatz for the solution to take the form

$$u_{nl}(\rho) = e^{-\rho/2} \rho^{l+1} F(\rho), \quad (2.44)$$

where $F(\rho) = \sum_{i=0}^{i_{max}} C_i \rho^i$. The polynomial expansion of the function $F(\rho)$ must terminate after finite number of terms to ensure that the boundary condition $|u_{nl}(\rho)| < \infty$ as $\rho \rightarrow \infty$. Plugging the solution form Eq. 2.44 into the radial equation in Eq. 2.40 gives a differential equation for the function $F_n(\rho)$

$$\rho \frac{d^2}{d\rho^2} F(\rho) + (2l + 2 - \rho) \frac{d}{d\rho} F(\rho) + (\lambda - l - 1) F(\rho) = 0. \quad (2.45)$$

This differential equation is called the Laguerre equation, and the solutions to this equation are called the generalized (or associated) Laguerre polynomials. The condition that the function $F(\rho)$ is finite everywhere leads to a requirement that the parameter λ is quantized to an integer, such that $\lambda = i_{max} + l + 1$. We define the principal quantum number $n \equiv i_{max} + l + 1 \geq 1$. Then, from Eq. 2.41, we find that the binding energy of the electron to the nucleus in the hydrogen atom is quantized as

$$E_n = -\frac{\mathbb{R}}{n^2} = -\frac{13.6 \text{ eV}}{n^2}. \quad (2.46)$$

With these quantum numbers, the solution $F(\rho)$ is the associated Laguerre polynomial $L_{n-l-1}^{2l+1}(\rho)$, where $\rho = 2\kappa_n r$ and $\kappa_n = 1/(a_0 n)$.

2.3.2 Properties of the solutions of the hydrogen atom

In this section, we summarize the implications of the solutions. First we note that the summation for the polynomial $F(\rho)$ terminates at $i_{max} = n - l - 1 \geq 0$. From this condition, we conclude that $l \leq n - 1$. For a fixed n , there are n possible values of the orbital angular momentum quantum number $l = 0, 1, 2, \dots, n-1$. For each l value, there are $2l+1$ distinct values of $m = -l, -l+1, \dots, l-1, l$. So, the degeneracy of the quantum states (total number of states with the same energy) at E_n is $\sum_{l=0}^{n-1} (2l+1) = n^2$.

The final wavefunction of the electron in a hydrogen atom is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi) = \frac{A_{nl} u_{nl}}{r} Y_l^m(\theta, \phi) = A'_{nl} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^m(\theta, \phi), \quad (2.47)$$

where A'_{nl} is the normalization constant for the radial function and $\rho = 2\kappa_n r$.

For the nucleus with total charge of Zq , the binding energy of the electron is quantized at $E_n = -Z^2 \mathbb{R} / n^2$.

For example, let's consider the ground state of the hydrogen atom, where $n = 1$. we also see that $l = 0$ and $m = 0$, and the wavefunction is given by

$$\psi_{100}(r, \theta, \phi) = A'_{10} e^{-\rho/2} L_0^1(\rho) Y_0^0(\theta, \phi) = \frac{A'_{10}}{\sqrt{4\pi}} e^{-r/a_0}, \quad (2.48)$$

given that $L_0^1(\rho) = 1$, $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$ and $\kappa_1 = 1/a_0$. we find from the normalization condition that

$$|A'_{nl}|^2 \int_0^\infty e^{-2r/a_0} r^2 dr = 1, \quad (2.49)$$

from which we derive $|A'_{nl}| = 2/a_0^{3/2}$. Therefore, the ground state wavefunction of the hydrogen atom is given by

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \quad (2.50)$$

The fully generalized form of the hydrogen wavefunction is given by

$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^m(\theta, \phi), \quad (2.51)$$