-Quantum Theory of the Hydrogen Atom

The hydrogen atom is the simplest atomic system in nature, consisting of a single proton (positively charged) and a single electron (negatively charged) bound together by the Coulomb electrostatic force. Despite its simplicity, it plays a fundamental role in quantum mechanics because it is one of the very few systems that can be solved exactly using the Schrödinger equation.

Classically, according to classical electrodynamics, an electron orbiting a nucleus should continuously lose energy by emitting radiation, causing it to spiral into the nucleus. However, this does not happen in reality. The stability of the hydrogen atom was one of the key problems that led to the development of quantum mechanics.

When Schrödinger's equation is applied to the hydrogen atom, it is found that the electron does not move in fixed orbits as in the classical model, but instead exists in regions of space called orbitals. An **orbital** is a region in space around the nucleus where the probability of finding the electron is high. These orbitals arise directly from the solutions of Schrödinger's equation (wave functions), where each orbital has a specific shape and a particular probability distribution of the electron.

One of the most important results of solving Schrödinger's equation for the hydrogen atom is the concept of quantization.

Quantization means that the energy of the electron does not take arbitrary or continuous values, but is restricted to specific discrete values called energy levels

In other words, the electron cannot have any energy it wants; it can only move between certain allowed energy levels. This explains the appearance of discrete spectral lines in the hydrogen atom spectrum, where the electron absorbs or emits a specific amount of energy when it transitions from one level to another.

واحدة من أهم نتائج حل معادلة شرودنغر لذرة الهيدروجين هي مفهوم التكميم (Quantization)

التكميم: يعني أن طاقة الإلكترون لا تأخذ أي قيمة عشوائية أو مستمرة، بل تقتصر على قيم محددة ومنفصلة تُسمّى مستويات الطاقة. بمعنى آخر، لا يستطيع الإلكترون أن يمتلك أي طاقة يشاء، بل يمكنه فقط الانتقال بين مستويات الطاقة المسموح بها. وهو ما يفسّر ظهور الخطوط الطيفية المنفصلة في طيف الهيدروجين، حيث يمتص أو يصدر الإلكترون طاقة محددة عند الانتقال بين المستويات.

-Schrödinger Equation for the Hydrogen Atom

The Schrödinger equation is the heart of quantum mechanics, describing the state of the electron in the hydrogen atom. The time-independent form is:

$\hat{H}\,\psi(r) = E\,\psi(r)$

$\hat{H}$: Hamiltonian operator, representing the total energy (kinetic + potential).

$\psi(r)$: Electron wave function, determines the probability of finding the electron at position r.

E: Energy of the electron.

r: Position vector (x, y, z).

Hamiltonian of the Electron in the Hydrogen Atom

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_\circ r}$$

Where the first term is the kinetic energy, while the second term is the potential energy due to the Coulomb force.

$\hbar=\frac{h}{2\pi}$: Reduced Planck constant

m: Mass of the electron

e: Electron charge

$\epsilon_\circ$: Vacuum permittivity

r: Distance between electron and nucleus

∇^2: 3D Laplacian (sum of second derivatives with respect to x, y, z)

Conversion to Spherical Coordinates

Since the potential energy depends only on the distance r from the nucleus

$$V = -\,\frac{e^2}{4\pi\epsilon_\circ r},$$

We use spherical coordinates (r, θ, ϕ).

The expression of the Laplacian operator in spherical coordinates:

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

$$\because\ \hat{\mathrm{H}} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_\circ r}$$

$$\therefore\ \hat{\mathrm{H}} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{e^2}{4\pi\epsilon_\circ r}$$

$$\hat{H}\,\psi(r) = E\,\psi(r)$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\epsilon_\circ r}\Psi = E\Psi$$

To simplify the equation, we apply separation of variables

$$\Psi(r, \theta, \phi) = R(r)\,\boldsymbol{\theta}(\theta)\,\boldsymbol{\phi}(\phi)$$

$$\frac{\partial\Psi}{\partial r} = \boldsymbol{\theta}\,\boldsymbol{\phi}\,\frac{dR}{dr}\ , \qquad \frac{\partial\Psi}{\partial\theta} = R\boldsymbol{\phi}\frac{d\boldsymbol{\theta}}{d\theta}, \qquad \frac{\partial^2\Psi}{\partial\phi^2} = R\,\boldsymbol{\theta}\,\frac{d^2\boldsymbol{\phi}}{d\phi^2}$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{dR}{dr}\right)\boldsymbol{\theta}\,\boldsymbol{\phi} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right)R\boldsymbol{\phi} + \frac{1}{r^2\sin^2\theta}\,\frac{d^2\boldsymbol{\phi}}{d\phi^2}\right]R\,\boldsymbol{\theta} - \frac{e^2}{4\pi\epsilon_\circ r}R\,\boldsymbol{\theta}\boldsymbol{\phi} = ER\,\boldsymbol{\theta}\boldsymbol{\phi}$$

R(r): Radial part, determines the electron distribution with distance

θ (θ) **ϕ** (ϕ): Angular part, determines the shape and orientation of the orbital

Substituting into the equation, and dividing both sides by R **θ ϕ** we get:

$$-\frac{\hbar^2}{2m}[\frac{1}{Rr^2}\frac{d}{dr}\left(r^2\frac{d\mathrm{R}}{dr}\right)+\frac{1}{\boldsymbol{\theta}\, r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right)+\frac{1}{\boldsymbol{\phi}\, r^2\sin^2\theta}\frac{d^2\boldsymbol{\phi}}{d\phi^2}]-\frac{\mathrm{e}^2}{4\pi\epsilon_\circ r}=E$$

$$-\frac{\hbar^2}{2m}[\frac{1}{Rr^2}\frac{d}{dr}\left(r^2\frac{d\mathrm{R}}{dr}\right)+\frac{1}{\boldsymbol{\theta}\, r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right)+\frac{1}{\boldsymbol{\phi}\, r^2\sin^2\theta}\frac{d^2\boldsymbol{\phi}}{d\phi^2}]=(E+\frac{\mathrm{e}^2}{4\pi\epsilon_\circ r})$$

Multiply by $\frac{2\mathrm{mr}^2}{\hbar^2}$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{d\mathrm{R}}{dr}\right)+\frac{2\mathrm{mr}^2}{\hbar^2}\left(E+\frac{\mathrm{e}^2}{4\pi\epsilon_\circ r}\right)+\frac{1}{\boldsymbol{\theta}\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right)+\frac{1}{\boldsymbol{\phi}\sin^2\theta}\frac{d^2\boldsymbol{\phi}}{d\phi^2}]=0$$

Now we begin by separating the variable

1- **Azimuthal (magnetic) part ϕ**

$$\boldsymbol{\frac{1}{\phi}\frac{d^2\phi}{d\phi^2}}$$

$$\boldsymbol{\frac{d^2\phi}{d\phi^2}} = -m^2\,\boldsymbol{\varphi} = \boldsymbol{\frac{d^2\phi}{d\phi^2}}+m^2\,\boldsymbol{\varphi}=\mathbf{0}$$

$\Phi\,(\boldsymbol{\phi}) = \boldsymbol{e^{-im\phi}}$

The periodicity condition:

$\Phi\,(\phi+2\pi) = \Phi\,(\boldsymbol{\phi})$

m=0, ±1, ± 2,...

2- Polar angular part θ

$$\frac{1}{\boldsymbol{\theta}\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right)+\frac{1}{\boldsymbol{\phi}\sin^2\theta}\frac{d^2\boldsymbol{\phi}}{d\phi^2}]$$

$$\frac{1}{\boldsymbol{\theta}\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right)-\frac{m^2}{\sin^2\theta}=-l(l+1)$$

Multiply by $\boldsymbol{\theta}$:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right)+[l(l+1)-\frac{m^2}{\sin^2\theta}]\boldsymbol{\theta}=0$$

l: Angular quantum number, determines the orbital shape

This is the associated Legendre differential equation, and its solution is given by:

$\boldsymbol{\theta}$ (θ) = p_l^m(cos θ)

From this, we obtain**:** $l=0,1,2,3,\dots\dots$

3- Radial part

The radial equation determines the energy levels of the electron

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{d\mathrm{R}}{dr}\right)+\frac{2\mathrm{mr}^2}{\hbar^2}\left(E+\frac{\mathrm{e}^2}{4\pi\epsilon_\circ r}\right)-l(l+1)=0$$

Multiply by R:

$$\frac{d}{dr}\left(r^2\frac{d\mathrm{R}}{dr}\right)+\frac{2\mathrm{mr}^2}{\hbar^2}\left(E+\frac{\mathrm{e}^2}{4\pi\epsilon_\circ r}\right)R-l(l+1)R=0$$

Assume that $u_{(r)} = r\,R_{(r)}$ to simplify the solution

$$\frac{d^2u}{dr^2}+\left[\frac{2m}{\hbar^2}\left(E+\frac{\mathrm{e}^2}{4\pi\epsilon_\circ r}\right)-\frac{l(l+1)}{\mathrm{r}^2}\right]u=0$$

The solution of this series gives n=1, 2, 3,…..

The final result for the energy :

$$E_n = -\frac{13.6}{n^2} \text{ eV} \qquad n=1, 2, 3,...$$

n: Principal quantum number

E_n : Energy of the electron at level n

The solution of the Schrödinger equation for the hydrogen atom introduces three quantum numbers that completely describe the state of the electron:

1-Principal Quantum Number (n):

Determines the energy level of the electron. Takes positive integer values:

$n=1, 2, 3,\ldots$

2-Angular Momentum Quantum Number (*l*):

Determines the shape of the orbital. Takes values:

$l = 0, 1, 2,\ldots, (n-1)$

3-Magnetic Quantum Number (m):

Determines the orientation of the orbital in space. Takes values:

$m= -l, -(l-1),\ldots, 0,\ldots,+(l-1),+l$

These quantum numbers arise naturally from the separation of variables in the Schrödinger equation

The solution of the Schrödinger equation provides a complete description of the hydrogen atom, including energy levels, orbitals, and quantum numbers.

H.W:

1. Why did the classical model fail to explain atomic stability?
2. What is the difference between a classical orbit and a quantum mechanical orbital?