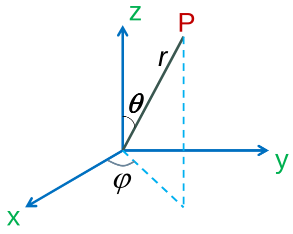
Spherical Co-ordinate System



$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$

Schrödinger Equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right)+$$
$$\frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\phi}{\partial\varphi^2}\right)+$$
$$\frac{2m}{\hbar^2}\left[E-V(r)\right]\ \phi=0$$

Separation of Variables

First separate only radial part. Take trial wave function as follows.

$$\phi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$$

Substitute and multiply by $\frac{r^2}{RY}$.

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[E-V(r)\right]\ r^2+$$
$$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right)=0$$

Radial Part Separated

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[E-V(r)\right]\,r^2=\lambda$$

$$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right)$$

$$=-\lambda$$

Separate other Two Parts

Now we try to separate the angular parts. Take trial wave function as follows.

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\varphi)$$

Substitute and multiply by $\frac{\sin^2\theta}{\Theta\Phi}$.

$$\left(\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\lambda\sin^2\theta\right)$$

$$+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=0$$

Note that λ has become a part of the equation.

The Other Equations Separated

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\lambda\sin^2\theta=m_\ell^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m_\ell^2$$

The Separated Equations

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)$$
$$+\left[\frac{2m}{\hbar^2}[E-V(r)]\ -\frac{\lambda}{r^2}\right]r^2=0$$

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\lambda\sin^2\theta=m_\ell^{\,2}$$
$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m_\ell^{\,2}$$

Solution of Φ Equation

$$\Phi(\varphi)=Ae^{im_\ell\varphi}+Be^{-im_\ell\varphi}$$

As the wave function should be single valued m_ℓ should be integer.

Solution of Θ Equation

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\lambda\sin^2\theta=m_l^{\,2}$$

Substitute $w=\cos\theta$

$$\frac{d\Theta}{d\theta}=\frac{d\Theta}{dw}\frac{dw}{d\theta}=-\sin\theta\frac{d\Theta}{dw}\qquad\text{etc.}$$

Solution of Θ Equation

We write $p \equiv \Theta$, to put in the form of a standard differential equation.

$$\left(1 - w^2\right)\frac{d^2p}{dw^2}$$

$$-2w\frac{dp}{dw} + \left[\lambda - \frac{m_l^{\;2}}{1-w^2}\right]P = 0$$

Legendre Polynomials

The solution is in the form of a series called Associated Legendre Polynomials. For $m_\ell = 0$, they are called Legendre Polynomials. The solution is of the form:

$$P(w) = \left(1-w^2\right)^{\frac{|m_l|}{2}} \sum_{n=0}^{\infty} a_n w^n$$

Next Step

Substitute this in the equation and put the coefficient of *w* to be equal to zero as this equation has to be satisfied for all values of *w*. We then get the following relation.

$$\frac{a_{n+2}}{a_n} = -\frac{\lambda - \left(n+|m_l|\right)\left(n+|m_l|+1\right)}{(n+1)(n+2)}$$

It can be shown that infinite series would diverge for *w* = 1. Hence it has to be limited to a finite number of terms.

Note: If one of the even (odd) coefficient is zero all even (odd) would be zero

So we write the series in the following way.

$$P(w) = \left(1-w^2\right)^{\frac{|m_l|}{2}} [\left(a_0 + a_2 w^2 + a_4 w^4 + \ldots\right) + \left(a_1 w + a_3 w^3 + a_5 w^5 + \ldots\right)]$$

We have only two unknowns in this equation a_o and a_1. Others are related to them by recurrence relation.

Logic

Put one of the coefficients to be zero and restrict other to finite series. In case the series has to be limited to a finite number for some *n*, numerator should be zero.

$$\frac{a_{n+2}}{a_n} = -\frac{\lambda - \left(n + |m_l|\right)\left(n + |m_l| + 1\right)}{(n+1)(n+2)}$$

Let $\lambda \equiv \ell(\ell+1)$, then we must have for some *n (n* is positive*):*

$$\ell = n + |m_\ell|$$

Thus ℓ must be positive integer and

$$|m_\ell| \le \ell$$

$\lambda = \ell(\ell+1)$ with ℓ positive integer and $|m_\ell| \le \ell$

The Radial Equation Rewritten

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left[E - V(r)\right] - \frac{\ell(\ell+1)}{r^2}\right]r^2 = 0$$

Hydrogen Atom

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_o r}\right] - \frac{\ell(\ell+1)}{r^2}\right]r^2 = 0$$

Do the following substitution.

$\rho = \alpha r$

Where α is given as follows.

$$\alpha^2 = \frac{8\mu|E|}{\hbar^2}$$

Further define q as follows.

$$q \equiv \frac{Ze^2}{4\pi\varepsilon_o\hbar}\left(-\frac{\mu}{2E}\right)^{1/2}$$

New form of Radial Equation

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) + \left[-\frac{1}{4} + \frac{q}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]R = 0$$

The solution of the above equation is of the following form.

$$R(\rho) = \rho^{\ell} e^{-\frac{1}{2}\rho} \sum_{n=0}^{\infty} a_n \rho^n$$

Substitute this in the equation. As before, we shall get a recurrence relation amongst the coefficients.

$$\frac{a_{n+1}}{a_n} = \frac{n + \ell + 1 - q}{(n+1)(n + 2\ell + 2)}$$

Again it can be shown that the series would diverge unless it is terminated after a finite number of terms. Hence for some n, numerator must be zero. Thus

$$q = n + \ell + 1$$

Implication

- 'q' should be integer as both n and ℓ are integers.
- As n can not be negative, maximum value of q is $\ell+1$. This is because $\ell+1- q$ should be negative to make numerator zero for a positive n.

$$q = \frac{Ze^2}{4\pi\varepsilon_o \hbar}\left(-\frac{\mu}{2E}\right)^{1/2}$$

$$\therefore E = -\frac{\mu Z^2 e^4}{(4\pi\varepsilon_o)^2 \, 2\hbar^2 q^2}$$

This is same as what Bohr obtained. Later replace q by n as per convention.

Comments

- The energy depends on quantum number n.
- The quantum number ℓ is related to the angular momentum.
- The quantum number m_ℓ is related to the z- component of the angular momentum.
- Spin Quantum Number??

Wave Functions

$n = 1, \ell = 0, m_\ell = 0$ (1s)

$$\phi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_o}\right)^{3/2} e^{-Zr/a_o}$$

$$a_o = \frac{4\pi\varepsilon_o\hbar^2}{\mu e^2}$$ is First Bohr radius

$n = 2, \ell = 0, m_\ell = 0$ (2s)

$$\phi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_o}\right)^{3/2}\left(2 - \frac{zr}{a_o}\right)e^{-Zr/2a_o}$$

$n = 2, \ell = 1, m_\ell = 0$ (2p)

$$\phi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_o}\right)^{3/2}\left(\frac{zr}{a_o}\right)e^{-Zr/2a_o}\cos\theta$$

$n = 2, \ell = 1, m_\ell = \pm 1$ (2p)

$$\phi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{z}{a_o}\right)^{3/2}\left(\frac{zr}{a_o}\right)e^{-Zr/2a_o}(\sin\theta)e^{\pm i\varphi}$$

Symmetry

- Even when potential is spherically symmetrical, many wave functions are not.
- The sum of probability density function for the degenerate states (same *n*) turns out to be spherically symmetrical.

- z-axis can be defined by the perturbation.
- In an unperturbed atom, an arbitrary z-axis may be chosen, but that would have no measurable consequence.