Hydrogen Atom

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1 Bohr Model

Bohr assumed that the angular momentum L of the electron in orbit around the proton in a hydrogen atom is quantized [2],

$$L = n\hbar, \quad n = 1, 2, 3, ... \tag{1-1}$$

Bohr postured that the electron with charge $-e$ moves in a circular orbit of radius a at speed v around the fixed proton (with charge e) in a hydrogen atom. The proton is fixed because it is much more massive than the electron (1836 times heavier).

We can show that the electron moves in quantized orbits and the quantized energy is given by [2]

$$\boxed{E_n = -\frac{e^2}{2a_0}\frac{1}{n^2} = -\frac{me^4}{2\hbar^2}\frac{1}{n^2}, \; n = 1, 2, 3, ...} \tag{1-2}$$

where a_0 is the Bohr radius defined by [2]

$$a_0 := \frac{\hbar^2}{me^2} = 5.3\times 10^{-11} \text{ m.} \tag{1-3}$$

When $n = 1$, the electron is in the ground state radius a_0 and energy

$$\boxed{E_1 = -\frac{e^2}{2a_0} = -13.6 \text{ eV} = 2.179\times 10^{-18} \text{ J.}} \tag{1-4}$$

The radius of the nth orbit is

$$a_n = n^2 a_0, \; n = 2, 3, ... \tag{1-5}$$

The *fine structure constant* is given by

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}. \tag{1-6}$$

The energy can be expressed in terms of the fine structure constant by

$$\boxed{E_n = -\frac{e^2}{2a_0}\frac{1}{n^2} = -\frac{\alpha^2 mc^2}{2}\frac{1}{n^2}, \; n = 1, 2, 3, ...} \tag{1-7}$$

2 Schrödinger Equation for Hydrogen Atom

The time-independent Schrödinger equation for the hydrogen tom **is** atom is

$$H\psi = E\psi, \tag{2-1}$$

where

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}, \tag{2-2}$$

Since the problem has spherical symmetry, it is preferable to use the spherical polar coordinates ((r,θ,φ) to express ∇^2 [1], [3-4]

$$\nabla^2\psi = \nabla\cdot\nabla\psi = \frac{1}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]. \tag{2-3}$$

Solution of the Schrödinger equation gives the eigenvalues and normalized eigenfunctions as [3], [4]

$$H\psi_{nlm}(r,\theta,\varphi) = E_n\psi_{nlm}(r,\theta,\varphi), \tag{2-4}$$

$$\boxed{E_n = -\frac{e^2}{2a_0}\frac{1}{n^2} = -\frac{me^4}{2\hbar^2}\frac{1}{n^2},\ \ n = 1,2,3,\ldots} \tag{2-5}$$

$$\boxed{\psi_{nlm}(r,\theta,\varphi) = A_{nl}\exp(-r/na_0)\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)Y_{lm}(\theta,\varphi),} \tag{2-6}$$

where

n is the principal quantum number, $n = 1,2,3,\ldots$

l is the orbital quantum number, $l = 0,1,2,\ldots,n-1.$

m is the magnetic quantum number, $m = -l, -l+1, \ldots -1, 0, 1, \ldots, l-1, l,$

A_{nl} is a normalization constant,

Y_{lm} is the spherical harmonic,

L_{n-l-1}^{2l+1} is an associated Laguerre polynomial defined by [1], [3,4]

$$L_{q-p}^{p}(x) := (-1)^p\left(\frac{d}{dx}\right)^p L_q(x), \tag{2-7}$$

and where $L_q(x)$ is a Legendre function defined by [1], [3,4]

$$L_q(x) = e^x\left(\frac{d}{dx}\right)^q(e^x x^q). \tag{2-8}$$

The normalization constant is given by [4]

$$\boxed{A_{nl} = \left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2[(n+l)!]^3}.} \tag{2-9}$$

The orthonormality of the wave functions is described by

$$\int \psi^*_{nlm}(r,\theta,\varphi)\psi_{n'l'm'}(r,\theta,\varphi)r^2 \sin\theta drd\theta d\varphi = \delta_{nn'}\delta_{ll'}\delta_{mm'}. \tag{2-10}$$

The spherical harmonic Y_{lm} can be written as

$$Y_{lm}(\theta,\varphi) = (-1)^m \sqrt{\frac{2n+1}{2}\frac{(n-m)!}{(n+m)!}} L^p_{q-p}(\cos\theta)\Phi_m(\varphi), \tag{2-11}$$

where the azimuthal eigenfunction satisfies

$$\frac{d^2}{d\varphi^2}\Phi_m(\varphi) = -m^2\Phi_m(\varphi), \tag{2-12}$$

with

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(im\varphi). \tag{2-13}$$

Orthonormality conditions are given by

$$\int_{\varphi=0}^{2\pi} \Phi_m(\varphi)\Phi_{m'}(\varphi)d\varphi = \delta_{mm'}, \tag{2-14}$$

$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi} Y^*_{lm}(\theta,\varphi)\psi_{l'm'}(\theta,\varphi) = \sin\theta drd\theta d\varphi = \delta_{ll'}\delta_{mm'}. \tag{2-15}$$

Remark 1. Comparing the energy in (1-2) from the Bohr model with the eigenvalue in (2-5) obtained from the solution of the Schrödinger equation; we find that they are the same. Hence we can easily get the eigenvalues of the Schrödinger equation easily from the Bohr model.

Remark 2. The eigenvalue in (2-5) only depends on the principal quantum number n, and is independent of l and m.

Remark 3. For a given n, the number of degenerate states is n^2.

For a given n, l takes values $0,1,...,n-1.$ For a given l, m takes $2l+1$ values $-l,-l,+1,...,0,...,l.$ Hence the number of degenerate states is

$$\sum_{l=0}^{n-1}(2l+1) = n + 2\sum_{l=0}^{n-1} l = n + 2(n-1)n/2 = n^2. \tag{2-16}$$

References

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