

SUMMARY

1. A potential $V(r)$ which depends only on the radial coordinate r and is independent of the angular variables θ, ϕ is called a spherically symmetric potential or a central potential.
2. For a spherically symmetric potential, the wave function $\psi(r, \theta, \phi)$ can be written as a product of two functions; a radial function $R(r)$ and an angular function $Y(\theta, \phi)$:

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

3. The angular function, which is common to all central potentials, is the spherical harmonic $Y_{lm_l}(\theta, \phi)$ discussed in chapter 7. These are eigenfunctions of the operators L^2 and L_z with the eigenvalues $l(l+1)\hbar^2$ and $m_l\hbar$ respectively, where $l = 0, 1, 2, \dots$ and $m_l = l, l-1, \dots, 0, \dots, -l+1, -l$.
4. The radial function $R(r)$ satisfies the equation

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

Its solution depends on the precise form of the potential $V(r)$.

5. For a hydrogenic atom, for which,

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

the normalized radial eigenfunctions are

$$R_{nl}(r) = - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho),$$

where
$$\rho = \left(\frac{2Zme^2}{n(4\pi\epsilon_0)\hbar^2} \right) r$$

and $L_{n+l}^{2l+1}(\rho)$ is the associated Laguerre polynomial. n is called the principal quantum number and can have positive integral values.

6. The complete normalized energy eigenfunctions for a hydrogenic atom are

$$\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) Y_{lm_l}(\theta, \phi)$$

where

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

$$l = 0, 1, 2, \dots, n-1$$

$$m_l = -l, -l+1, \dots, 0, \dots, l-1, l$$

7. The bound-state energies for the hydrogenic atom are

$$E_n = -\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} = -\frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2},$$

+

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

where α is the fine structure constant.

The expression for E_n is same as that obtained in the Bohr model. The energy depends only on the principal quantum number n . Since for each n there are n^2 possible (lm_l) combinations, and hence as many eigenfunctions, the eigenvalues are n^2 -fold degenerate. The m_l -degeneracy is due to spherical symmetry of $V(r)$; the l -degeneracy is characteristic of the Coulomb potential.

The complete normalized energy eigenfunctions for the hydrogenic atoms

$$\begin{aligned} \Psi_{nlm_l}(r, \theta, \phi) &= R_{nl}(r) Y_{lm_l}(\theta, \phi) \\ n &= 1, 2, 3, \dots; \quad l = 0, 1, 2, \dots, n-1 \\ m_l &= -l, -l+1, \dots, 0, \dots, l-1, l \end{aligned}$$

$$R_{nl}(r) = - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

$$Y_{lm_l}(\theta, \phi) = (-1)^{m_l} \left[\frac{(2l+1)(l-m_l)!}{4\pi(l+m_l)!} \right]^{1/2} P_l^{m_l}(\cos \theta) e^{im_l\phi}, \quad m_l \geq 0$$

and

$$Y_{lm_l}(\theta, \phi) = (-1)^{m_l} Y_{l,-m_l}^*(\theta, \phi), \quad m_l \leq 0$$

$P_l^{m_l}$ Legendre function of degree l and order m_l is defined as,

$$P_l^{m_l}(-\xi) = (-1)^{l-m_l} P_l^{m_l}(\xi), \quad m_l = 0, 1, 2, \dots, l$$

For the case $m_l = 0$

$$P_l(-\xi) = (-1)^l P_l(\xi)$$

The first few Legendre polynomials are:

$$\begin{aligned} P_0(\xi) &= 1 \\ P_1(\xi) &= \xi \\ P_2(\xi) &= \frac{1}{2}(3\xi^2 - 1) \\ P_3(\xi) &= \frac{1}{2}(5\xi^3 - 3\xi) \\ P_4(\xi) &= \frac{1}{8}(35\xi^4 - 30\xi^2 + 3) \\ P_5(\xi) &= \frac{1}{8}(63\xi^5 - 70\xi^3 + 15\xi) \end{aligned}$$

For the case $m_l \neq 0$

The first few associated Legendre functions are:

$$\begin{aligned}
 P_1^1(\xi) &= (1 - \xi^2)^{1/2} \\
 P_2^1(\xi) &= 3(1 - \xi^2)^{1/2} \xi \\
 P_2^2(\xi) &= 3(1 - \xi^2) \\
 P_3^1(\xi) &= \frac{3}{2}(1 - \xi^2)^{1/2} (5\xi^2 - 1) \\
 P_3^2(\xi) &= 15\xi(1 - \xi^2) \\
 P_3^3(\xi) &= 15(1 - \xi^2)^{3/2}
 \end{aligned}$$

The first three radial eigenfunctions are:

$$\begin{aligned}
 R_{10} &= 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp \left(-\frac{Zr}{a_0} \right) \\
 R_{20} &= \left(\frac{Z}{2a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) \exp \left(-\frac{Zr}{2a_0} \right) \\
 R_{21} &= \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right) \exp \left(-\frac{Zr}{2a_0} \right)
 \end{aligned}$$

The First Few Spherical Harmonics $Y_{lm_l}(\theta, \phi)$

l	m_l	Spherical Harmonic $Y_{lm_l}(\theta, \phi)$
0	0	$Y_{0,0} = \frac{1}{(4\pi)^{1/2}}$
1	0	$Y_{1,0} = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$
	± 1	$Y_{1,\pm 1} = \mp \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi}$
2	0	$Y_{2,0} = \left(\frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1)$
	± 1	$Y_{2,\pm 1} = \mp \left(\frac{15}{8\pi} \right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$
	± 2	$Y_{2,\pm 2} = \left(\frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$

The complete eigenfunctions for the lowest few states are:

$$\left. \begin{aligned} \psi_{100} &= \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right) \\ \psi_{200} &= \frac{1}{\pi^{1/2}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) \exp\left(\frac{-Zr}{2a_0}\right) \\ \psi_{210} &= \frac{1}{\pi^{1/2}} \left(\frac{Z}{2a_0} \right)^{5/2} r \exp\left(\frac{-Zr}{2a_0}\right) \cos \theta \\ \psi_{21\pm 1} &= \frac{1}{8\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{5/2} r \exp\left(\frac{-Zr}{2a_0}\right) (\sin \theta) e^{\pm i\phi} \end{aligned} \right\}$$

Quantum Number	Symbol	Possible Values
Principal Quantum Number	n	1, 2, 3, ...
Orbital or Angular Quantum Number	l	0, 1, 2, 3, ..., (n - 1)
Magnetic Quantum Number	m_l	-l, ..., 0, 1, ..., l
Spin Quantum Number	m_s	$\pm \frac{1}{2}$

These four quantum numbers are used to describe the probable location of an electron in an atom.