Lecture 7 Particle Waves in Three Dimensions

SCPY152, Second Semester 2021-22

Udom Robkob, Physics-MUSC

February 8, 2022

Topics

1. Schrodinger equation in three dimensions-Cartesian system
2. Schrodinger equation in three dimensions-spherical system
3. Spherical harmonics
4. Free particle
5. Infinite potential sphere
6. Degeneracy

SE in 3 dimensions in Cartesian system

Cartesian system of coordinate $\vec{r} = (x, y, z)$. The gradient

$$\nabla = \hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z}$$

The Laplace operator is

$$\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

SE in three dimension, in Cartesian system, is

$$-\frac{\hbar^2}{2m}\nabla^2\varphi(x, y, z) + U(x, y, z)\varphi(x, y, z) = E\varphi(x, y, z) \qquad (1)$$

For practical propose we should have separation of variables of the potential $U(x, y, x) = U(x) + U(y) + U(x)$, then we can separate variables of the wave function

$$\varphi(x, y, z) = A(x)B(y)C(z)$$

With separated energy

$$E = E_x + E_y + E_z$$

Equation (25) will become three separated independent equations

$$-\frac{\hbar^2}{2m}A''(x) + U(x)A(x) = E_x A(x) \tag{2}$$

$$-\frac{\hbar^2}{2m}B''(y) + U(y)B(y) = E_y B(y) \tag{3}$$

$$-\frac{\hbar^2}{2m}C''(z) + U(z)C(z) = E_z C(z) \tag{4}$$

For example of free particle wave in 3-dimension, in a large cube of size L

$$E_{k_x,k_y,k_z} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \tag{5}$$

$$\varphi_{k_x,k_y,k_z}(x,y,z) = \frac{1}{\sqrt{L^3}} e^{ik_x x + ik_y y + ik_z z} \tag{6}$$

For example of infinite potential cube of volume $V = a^3$, the quantum energy and particle wave function will be

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2), \;\; n_x, n_y, n_z = 1, 2, 3, ... \tag{7}$$

$$\varphi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{1}{a^3}} \sin(\frac{n_x\pi}{a}x) \sin(\frac{n_y\pi}{a}y) \sin(\frac{n_z\pi}{a}z) \tag{8}$$

Pause For example of 3-dimensional isotropic harmonic potential well, the quantum energy and particle wave function will be

$$E_{n_x,n_y,n_z} = \hbar\omega(n_x + n_y + n_z + \frac{3}{2}) \tag{9}$$

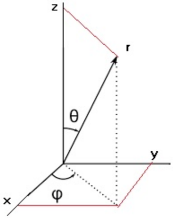
$$\begin{aligned}\varphi_{n_x n_y n_z}(x, y, z) = C_{n_x} C_{n_y} C_{n_z} e^{-\frac{\alpha^2}{2}(x^2+y^2+z^2)} \\ \times H_{n_x}(\alpha x) H_{n_y}(\alpha y) H_{n_z}(\alpha z)\end{aligned} \tag{10}$$

when $\alpha = \sqrt{\frac{m\omega}{\hbar}}$ and C_n appears in equation (25).
Exercise: Try to write quantum energy and particle wave function in 2-dimensions for all of these example potential problems.

SE in 3 dimensions in spherical system

In spherical coordinate system $\vec{r} = \{r, \theta, \phi\}$, and it is related to Cartesian system (x, y, z) as

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



The gradient in spherical system is

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi} \tag{11}$$

The Laplace operator is

$$\nabla^2 V = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial V}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial V}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 V}{\partial \phi^2} \tag{12}$$

SE in spherical coordinate system will appear in ready to solve form as

$$\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\varphi(r,\theta,\phi)$$
$$+\frac{2m}{\hbar^2}[E-U(r,\theta,\phi)]\varphi(r,\theta,\phi)=0 \tag{13}$$

In case of the central potential problem, $U=U(r)$, the particle wave function in spherical system $\varphi(r,\theta,\phi)$ will be separate into radial and angular parts as

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

Insertion into (13) and separate equation into radial and angular equations, we will get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}[E-U(r)]$$
$$=-\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right) \tag{14}$$

LHS and RHS are equations of independent variables, equality can only occur through some constant. Let us assume from (14)

$$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)=-\alpha^2$$

$$\mapsto\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)+\alpha^2 Y=0 \tag{15}$$

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

$$\mapsto\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{2m}{\hbar^2}[E-U(r)]-\frac{\alpha^2}{r^2}\right)R=0 \tag{16}$$

(15) is angular equation for angular function $Y(\theta,\phi)$, and (16) is radial equation for radial function $R(r)$.

Spherical harmonics

From the angular equation (15) for angular function $Y(\theta, \phi)$, let us do the separation of variable one more time as

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

Insertion back into (15), we get

$$\frac{1}{\Theta}\left(\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right) + \alpha^2\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \equiv m^2 \qquad (17)$$

With a similar reason as before, we can observe immediately that solution of the right hand side equation will be

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \mapsto \Phi(\phi) = e^{im\phi} \qquad (18)$$

where $m = 0, \pm 1, \pm 2, ...$ (are integers, in order to be the quantum numbers, and any constants of integration are assumed to be one for simplicity)

From equation (16)

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\alpha^2-\frac{m^2}{\sin^2\theta}\right)\Theta=0 \tag{19}$$

Change of variable $x=\cos\theta \mapsto dx=-\sin\theta d\theta$, then

$$\frac{d}{dx}\left((1-x^2)\frac{d\Theta(x)}{dx}\right)+\left(\alpha^2-\frac{m^2}{1-x^2}\right)\Theta(x)=0$$

$$(1-x^2)\frac{d^2\Theta(x)}{dx^2}-2x\frac{d\Theta}{dx}+\left(\alpha^2-\frac{m^2}{1-x^2}\right)\Theta(x)=0 \tag{20}$$

Ask Wolfram Alpha, we observe that (20) is a kind of *associated Lengendre equation* for $y(x)$ appears as

$$(1-x^2)y''-2xy'+\left(l(l+1)-\frac{m^2}{1-x^2}\right)y=0 \tag{21}$$

with a condition $l=0,1,2,...$(are integers) and $0\leq|m|\leq l$. Solution of (21) is called *associated Lengendre polynomial* $P_l^m(\cos\theta)$.

The first few associated Legendre functions $P_l^{|m|}(x)$

$$P_0^0(x) = 1$$

$$P_1^0(x) = x = \cos\theta$$

$$P_1^1(x) = (1 - x^2)^{1/2} = \sin\theta$$

$$P_2^0(x) = \tfrac{1}{2}(3x^2 - 1) = \tfrac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^1(x) = 3x(1 - x^2)^{1/2} = 3\cos\theta\sin\theta$$

$$P_2^2(x) = 3(1 - x^2) = 3\sin^2\theta$$

$$P_3^0(x) = \tfrac{1}{2}(5x^3 - 3x) = \tfrac{1}{2}(5\cos^3\theta - 3\cos\theta)$$

$$P_3^1(x) = \tfrac{3}{2}(5x^2 - 1)(1 - x^2)^{1/2} = \tfrac{3}{2}(5\cos^2\theta - 1)\sin\theta$$

$$P_3^2(x) = 15x(1 - x^2) = 15\cos\theta\sin^2\theta$$

$$P_3^3(x) = 15(1 - x^2)^{3/2} = 15\sin^3\theta$$

With parity

$$P_l^{-|m|}(x) = (-)^m \frac{(l-m)!}{l+m)!} P_l^{|m|}(x)$$

Spherical harmonic

Form (20,21), we can have $\alpha = l(l+1)$, and our solution of (20) will be in the form of associated Legendre polynomial $P_l^m(\theta, \phi)$ with $l = 0, 1, 2, ...$ and $m = 0, \pm 1, \pm 2, ..., \pm l$.
The *spherical harmonic* $Y_{lm}(\theta, \phi)$ is defined form the combined angular solutions

$$Y_{lm}(\theta, \phi) = C_{lm} P_l^m(\cos\theta) e^{im\phi} \tag{22}$$

$$\text{with } C_{lm} = (-)^m \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} \tag{23}$$

It is the normalization constant.

The First Few Spherical Harmonics, $Y_J^m(\theta, \phi)$ [a]

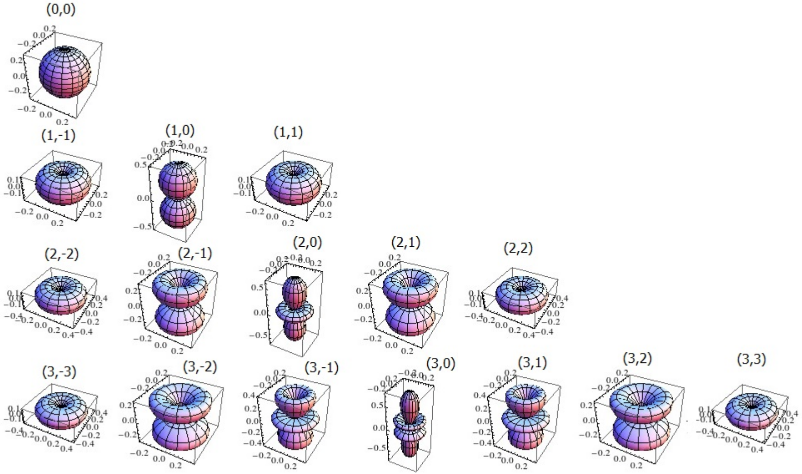
$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$	$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
$Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$	$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{i\phi}$
$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{-i\phi}$	$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}$
$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$	

a. The negative signs in $Y_1^1(\theta, \phi)$ and $Y_2^1(\theta, \phi)$ are simply a convention.

Mathematica command call for SphericalHarmonic

$$\mathrm{SphericalHarmonicY}[\mathrm{l}, \mathrm{m}, \theta, \phi] \mapsto Y_l^m(\theta, \phi)$$

The first few $|Y_{lm}|$ plots



Free particle wave in spherical system

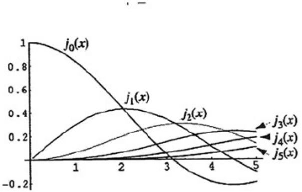
In case of free particle wave in spherical system, the particle potential energy is $U = 0$ and its radial equation (16) will become

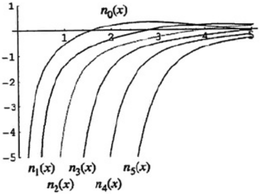
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \left(k^2 - \frac{l(l+1)}{r^2}\right)R(r) = 0$$

$$\rho^2 R'' + 2\rho R' + \left(\rho^2 - l(l+1)\right)R = 0,\ \ \rho = kr \tag{24}$$

Wolfram Alpha can tell you that equation (24) is known in the name of *spherical Bessel equation*, and its solution are called *spherical Bessel functions of the first and second kinds*, as

$$R_l(\rho) = C_1 j_l(\rho) + C_2 n_l(\rho) \tag{25}$$





From the figure, we do not need $n_l(\rho)$ because it diverges at origin so we will set $C_2 = 0$. So that we will have our radial appropriate radial solution for free particle wave in spherical system in the form

$$R_l(r) = C_1 j_l(kr) \tag{26}$$

Examples of the first few spherical Bessel functions of the first kind

$$j_0(kr) = \frac{\sin kr}{kr}$$

$$j_1(kr) = \frac{\sin kr}{(kr)^2} - \frac{\cos kr}{kr}$$

$$j_2(kr) = \frac{3\sin kr}{(kr)^3} - \frac{3\cos kr}{(kr)^2} - \frac{\sin kr}{kr}$$

Infinite spherical potential well

In case of particle wave inside infinite spherical potential well

$$U(r) = \begin{cases} 0, & 0 < r < a \\ \infty, & r > a \end{cases}$$

In this case we cannot have particle wave outside the sphere but will be standing spherical wave inside the sphere.
We can use our previous equation (24) for this case but its solution must vanish at the boundary of the sphere

$$R(a) = C_1 j_l(ka) = 0$$

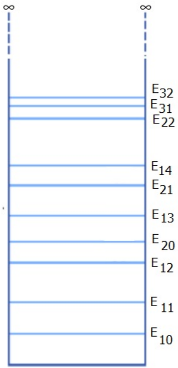
Form figure above, you can see the zero points of $j_l(kr)$, and this will be listed by integer $n = 1, 2, ..$ for each l^{th} order of the spherical Bessel function $j_l(kr)$.

List of zeros of the spherical Bessel function of the first kind

Number of zero; n	$j_0(x)$	$j_1(x)$	$j_2(x)$	$j_3(x)$	$j_4(x)$
1	3.14159 [1]	4.49341 [2]	5.76346 [3]	6.98793 [5]	8.18256 [7]
2	6.28319 [4]	7.72525 [6]	9.09501 [8]	10.4171	11.7049
3	9.42478 [9]	10.9041 [10]	12.3229	13.6980	15.0397
4	12.5664	14.0662	15.5146	16.9236	18.3013
5	15.7080	17.2208	18.6890	20.1218	21.5254

The ordering of these zeros are indicated with numbers (n, l), as Z_{nl}, which are quantum numbers of the system. The corresponding quantum energy will be

$$ka = Z_{nl} \mapsto k_{nl} = \frac{Z_{nl}}{a}, \; E_{nl} = \frac{\hbar^2 k_{nl}^2}{2m} = \frac{\hbar^2 Z_{nl}^2}{2ma^2} \tag{27}$$



Example: Ground state energy of and electron being in infinite spherical potential well with radius $a = 0.5^0 A$.

$$E_{10} = \frac{(\hbar c)^2 Z_{10}^2}{2(mc^2)a^2} = \frac{(1.97 \times 10^{-7} eV \cdot m)^2 (3.14)^2}{2(0.512 \times 10^6 eV)(0.5 \times 10^{-10} m)^2} = 3.88 eV$$

Degeneracy

Degeneracy is the number of quantum states appear with have the same energy. With some degeneracy occur in the system, it will be called *degenerated system*.

Degeneracy comes from *symmetry* of the system, i.e., central potential system with spherical symmetry, its angular degeneracy appear for each l with $2l + 1$ values of m.

Exercise: Let count the degeneracy of free particle and infinite spherical potential systems.