Chapter 4 (Lecture 9-10)

Schrödinger Equation in Spherical coordinate system and Angular Momentum Operator

In this section we will construct 3D Schrödinger equation and we give some simple examples. In this course we will consider problems where the partial differential equations are separable.

Cartesian coordinate

In previous chapters we have solved one dimensional problems, by using the time dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi$$

Time part of the equation can be separated by substituting $\Psi = \psi e^{-\frac{iE}{\hbar}t}$ and we obtain time independent equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi$$

The equation can be extended in three dimensions (3D) by introducing 3D kinetic energy operator and potential:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + V(x,y,z)\psi = E\psi$$

Where the operator

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

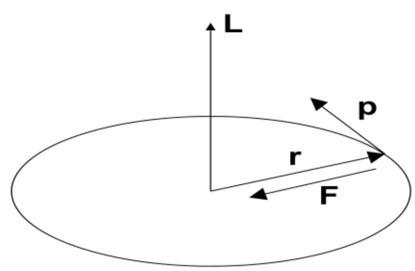
Is square of gradient operator. It is obvious that 3D momentum operator can be written as

$$p = -i\hbar\left(\frac{\partial}{\partial x}i + \frac{\partial}{\partial y}j + \frac{\partial}{\partial z}k\right) = -i\hbar\nabla$$

Angular Momentum

In quantum mechanics, the **angular momentum operator** is an operator analogous to classical angular momentum.

$$\vec{L} = \vec{r} \times \vec{p}$$



Where $\vec{r}$ is position vector and $\vec{p}$ is the momentum vector. The angular momentum operator plays a central role in the theory of atomic physics and other quantum problems involving rotational symmetry.

In quantum mechanics angular momentum is quantized. This is because at the scale of quantum mechanics, the matter analyzed is best described by a wave equation or probability amplitude, rather than as a collection of fixed points or as a rigid body.

Quantum angular momentum (cartesian)

As it is known, observables in quantum physics are represented by operators. In quantum mechanics we get **linear Hermitian angular momentum operators** from the classical expressions using the postulates

$$\vec{L} = -i\hbar\vec{r} \times \vec{\nabla}$$

When using Cartesian coordinates, it is customary to refer to the three spatial components of the angular momentum operator as:

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right);\ L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right);\ L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

Square of the total angular momentum is defined as the square of the components:

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

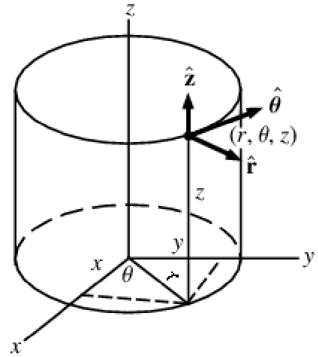
Commutation relation

Different components of the angular momentum do not commute with another while all of the components commute with square of the total angular momentum.

$$[L_x, L_y] = i\hbar L_z; \; [L_y, L_z] = i\hbar L_x \; [L_z, L_x] = i\hbar L_y$$

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$$

Cylindrical coordinate system (optional)



In terms of Cartesian variables we can write

$$x = r cos\theta; y = r sin\theta; and\ z = z$$

We can obtain the relations:

$$r^2 = x^2 + y^2; tan\theta = \frac{y}{x}; z = z.$$

In order to obtain partial derivative $\frac{\partial}{\partial x}$ we use

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial z}{\partial x}\frac{\partial}{\partial z}; \quad \frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial z}{\partial y}\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial z}{\partial z}\frac{\partial}{\partial z}$$

Since z is independent from x and y we can write

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial z}$$

We can easily obtain

$$\frac{\partial r}{\partial x} = \frac{x}{r}; \frac{\partial \theta}{\partial x} = -\frac{y}{x^2}\cos^2\theta; \frac{\partial z}{\partial x} = 0 \ and \ \frac{\partial r}{\partial y} = \frac{y}{r}; \frac{\partial \theta}{\partial y} = \frac{1}{x}\cos^2\theta; \frac{\partial z}{\partial y} = 0$$

Then using the relation

$$\frac{\partial^2}{\partial x^2} = \left(cos\theta\frac{\partial}{\partial r} - \frac{sin\theta}{r}\frac{\partial}{\partial \theta}\right)\left(cos\theta\frac{\partial}{\partial r} - \frac{sin\theta}{r}\frac{\partial}{\partial \theta}\right)$$

$$\frac{\partial^2}{\partial y^2} = \left(sin\theta\frac{\partial}{\partial r} - \frac{cos\theta}{r}\frac{\partial}{\partial \theta}\right)\left(sin\theta\frac{\partial}{\partial r} - \frac{cos\theta}{r}\frac{\partial}{\partial \theta}\right)$$

We obtain kinetic energy operator in cylindrical coordinate system:

$$KE = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2}\right)$$

And Hamiltonian takes the form

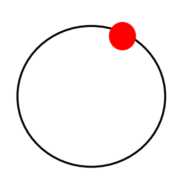
$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2}\right) + V(r, \theta, z)$$

Example: Particle in a ring

In quantum mechanics, the case of a **particle in a one-dimensional ring** is similar to the particle in a box. The Schrödinger equation for a free particle which is restricted to a ring of radius r, in polar coordinate is

$H = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}; H\psi = E\psi$

The wave function be periodic in θ with a period 2π and that they be normalized leads to the conditions



$$\int_0^{2\pi} |\psi|^2 d\theta = 1$$

And boundary condition(quantization)

$$\psi(\theta) = \psi(\theta + 2\pi)$$

Under these conditions, the solution to the Schrödinger equation is given by

$$\psi_{\pm}(\theta) = \frac{1}{\sqrt{2\pi}} e^{\pm i\frac{r}{\hbar}\sqrt{2mE}\theta}$$

Quantization conditions leads to the

$$e^{\pm i\frac{r}{\hbar}\sqrt{2mE}\theta} = e^{\pm i\frac{r}{\hbar}\sqrt{2mE}(\theta+2\pi)}$$

$$1 = e^{\pm i\frac{r}{\hbar}\sqrt{2mE}(2\pi)} = e^{\pm i(2\pi n)}$$

Then energy and eigenfunction of the particle is given by:

$$\psi = e^{\pm in\theta}$$

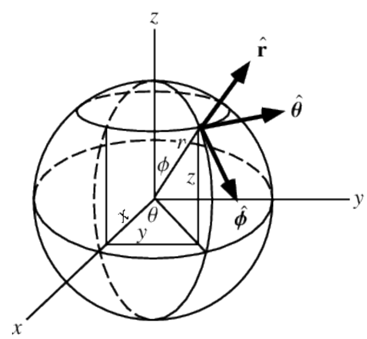
$$E = \frac{n^2\hbar^2}{2mr^2} \; where \; n = \pm 1, \pm 2, \pm 3, \ldots$$

Therefore, there are two degenerate quantum states for every value of n The case of a particle in a one-dimensional ring is an instructive example when studying the quantization of angular momentum for, say, an electron orbiting the nucleus.

This simple model can be used to find approximate energy levels of some ring molecules, such as benzene.

Spherical coordinates

Cartesian-spherical and spherical-Cartesian relation can be written as:



$$x = rsin\theta cos\phi; \; y = rsin\theta sin\phi; \; z = rcos\theta;$$

And

$$r^2 = x^2 + y^2 + z^2; \; tan\phi = \frac{y}{x}; \;\; cos\theta = \frac{z}{r}$$

Using the analogy given in the previous section we can obtain the Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{1}{sin\,\theta}\frac{\partial}{\partial\theta}sin\,\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + V(r,\theta,\phi)$$

where m is mass of the particle If the potential seen by the particle depends only on the distance r, then the Schrodinger equation is separable in Spherical coordinates. In order to separate coordinate system let us introduce a wave function of the form:

$$\Psi(r,\theta,\phi) = R(r)Q(\phi)P(\theta)$$

Then the eigenvalue equation $H\Psi = E\Psi$ becomes:

$$\frac{\hbar^2}{2m}\left(\frac{1}{Rr^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + \frac{1}{Pr^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}sin\,\theta\frac{\partial P}{\partial\theta} + \frac{1}{Qr^2}\frac{1}{\sin^2\theta}\frac{\partial^2 Q}{\partial\phi^2}\right) - V(r) + E = 0$$

Multiply both sides by $r^2\sin^2\theta$ we separate $Q(\phi)$

$$\frac{1}{Q}\frac{\partial^2 Q}{\partial\phi^2} = -m_l^2$$

Then we can write

$$\frac{\hbar^2}{2m}\left(\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + \frac{sin\,\theta}{P}\frac{\partial}{\partial\theta}sin\,\theta\frac{\partial P}{\partial\theta} - m_l^2\right) - r^2\sin^2\theta\,(V(r) - E) = 0$$

Divide both sides by $\sin^2\theta$ we obtain:

$$\frac{\hbar^2}{2m}\left(\frac{1}{P\,sin\,\theta}\frac{\partial}{\partial\theta}sin\,\theta\frac{\partial P}{\partial\theta} - \frac{m_l^2}{\sin^2\theta}\right) = -\frac{L^2}{2m}$$

$$\frac{\hbar^2}{2m}\left(\frac{1}{R}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}-L^2\right)-r^2(V(r)-E)=0$$

Where m_l^2 *and* L^2 are constants of separations and L is corresponding to angular momentum operator.

Angular momentum in spherical coordinate

Using the analogy given in the previous section (3D Schrödinger equation) we can calculate $\frac{\partial}{\partial x},\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$ then components of the angular momentum are given by:

$$L_x = i\hbar\left(sin\phi\frac{\partial}{\partial\theta}+\frac{cos\phi}{tan\theta}\frac{\partial}{\partial\phi}\right)$$

$$L_y = i\hbar\left(-cos\phi\frac{\partial}{\partial\theta}+\frac{sin\phi}{tan\theta}\frac{\partial}{\partial\phi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

We can obtain total angular momentum operator in spherical coordinate system:

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

Solutions of the angular parts of the equations are given by:

$$Q\sim\frac{1}{\sqrt{2\pi}}e^{im_l\phi}$$

$$P\sim P_l^{m_l}(cos\theta)$$

The eigenvalue equations are

$$L^2\left(P_l^{m_l}(cos\theta)\right)=l(l+1)\hbar^2\left(P_l^{m_l}(cos\theta)\right)$$

Where l is orbital angular momentum quantum operator. It takes values $l = 0, 1, 2, \ldots$.

$$L_z\left(\frac{1}{\sqrt{2\pi}}e^{im_l\phi}\right)=m_l\hbar\left(\frac{1}{\sqrt{2\pi}}e^{im_l\phi}\right)$$

Where m_l is called magnetic quantum number restricted to the values $-l, \ldots, +l$. The product of P and Q occurs so frequently in quantum mechanics that it is known as a spherical harmonic:

$$Y_l^m(\theta,\phi)=\epsilon\left[\frac{(2l+1)(l-|m_l|)!}{4\pi(l+|m_l|)!}\right]^{\frac{1}{2}}e^{im_l\phi}P_l^{m_l}(cos\theta)$$

Where $\epsilon = (-1)^m\ for\ m \geq 0\ and\ \epsilon = 1\ for\ m < 0$. Note that spherical harmonics are orthonormal:

$$\int_0^\pi sin\theta d\theta\int_0^{2\pi}[Y_l^m(\theta,\phi)]^*Y_{l'}^{m'}(\theta,\phi)d\phi=\delta_{ll'}\delta_{mm'}$$

Table shows spherical Harmonic functions for a few values of l.

l	m_l	Function
0	0	$\frac{1}{2\sqrt{\pi}}$
1	-1	$\frac{1}{2}e^{-i\phi}\sqrt{\frac{3}{2\pi}}\text{Sin}[\theta]$
	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\text{Cos}[\theta]$
	1	$-\frac{1}{2}e^{i\phi}\sqrt{\frac{3}{2\pi}}\text{Sin}[\theta]$

Dirac notation

As we mentioned before quantum systems can be described by quantum numbers. The quantum numbers can be represented by Dirac notation. We have already solved angular parts of the Schrödinger equation in spherical coordinate and the solution can be described by two quantum numbers. We can express the solution:

$$Y_l^m(\theta,\phi) = \epsilon\left[\frac{(2l+1)(l-|m_l|)!}{4\pi(l+|m_l|)!}\right]^{\frac{1}{2}} e^{im_l\phi}P_l^{m_l}(cos\theta) => |lm_l\rangle$$

The action of operators on state is given by

$$L^2\left|lm_l\right\rangle = l(l+2)\hbar^2\left|lm_l\right\rangle\ and\ L_z|lm_l\rangle = m_l\hbar|lm_l\rangle$$

Example. In a system rotation of an operator is defined by:

$$H = \frac{L^2}{2I}$$

Where I is moments of inertia.

a) Find eigenvalues of H acting on the state $|lm_l\rangle$.
b) Find number of degeneracies for $l = 0,1, and\ 2$.

Solution: a)

$$H|lm_l\rangle = \frac{L^2}{2I}|lm_l\rangle = \frac{1}{2I}l(l+1)\hbar^2|lm_l\rangle$$

Then eigen values of H is $\frac{1}{2I}l(l+1)\hbar^2$

b) When $l=0$, $m_l=0$ non degenerate

When $l=1$, $m_l=-1, 0,1$; 3 degeneracy

When $l=2$, $m_l=-2, -1, 0,1,2$; 5 degeneracy

Radial part of the equation can be simplified by substituting: $u(r) = rR(r)$:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \left(V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)u = Eu$$

With the normalization:

$$\int_{-\infty}^{\infty}|u|^2 dr = 1$$

This is now referred to as the radial wave equation, and would be identical to the one-dimensional Schrödinger equation were it not for the term $\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$ added to V , which pushes the particle away from the origin and is therefore often called `the centrifugal potential' or 'centrifugal barrier.

Note that a good place to find the summary of spherical harmonics is http://mathworld.wolfram.com/SphericalHarmonic.html

Spherical harmonics are used when there are spherical symmetry.

Terminology in spectroscopy: $\ell = 0, 1, 2, 3, 4, \ldots$ are called s, p, d f, and g, ….

Let's consider some specific examples.

Where does the centrifugal barrier come from?

In classical physics fixed l corresponds to fixed angular momentum $L = mvr$ for the electron.

so as r becomes small, must increase in order to maintain L. This causes an increase in the apparent outward force (the 'centrifugal' force). For circular motion:

$$F = \frac{mv^2}{r} = \frac{L^2}{mr^3}$$

$$V = \frac{L^2}{2mr^2}$$

Alternatively, we can say that the energy required to supply the extra angular speed must come from the radial motion so this decreases as if a corresponding outward force was being applied.

The rigid rotator

A very simple system is interesting to study at this point. Consider a quantum particle held at a fixed distance R_0 from a central point, but free to move in all directions. Its moment of inertia is $I = mR_0^2$, and its classical total energy is given by

$$E = \frac{1}{2}mv^2 = \frac{m^2 R_0^2 v^2}{2mR_0^2} = \frac{L^2}{2I}$$

Therefore its Schroedinger equation can be written as

$$\frac{L^2}{2I}\psi(\theta,\varphi) = E\psi(\theta,\varphi).$$

This is just the eigenvalue equation for total angular momentum, so we find that the eigenfunctions are the spherical harmonics, and the allowed energy levels are

$$E_l = \frac{\hbar^2}{2I} l(l+1); l = 0,1,2,3,\ldots$$

In the next section we will solve radial part of the Schrödinger equation for Hydrogen atom.

Free-particle solutions (optional)

For V(r)=0, the equation takes the form

$$-\frac{\partial^2 R}{\partial r^2} - \frac{2}{r}\frac{\partial R}{\partial r} + \frac{l(l+1)}{r^2}R = \frac{2m_0}{\hbar^2}ER$$

There are two independent solutions,

$$R(r) = Aj_l(kr) + Bn_l(kr)$$

Where , $j_l(kr)$ *and* $n_l(kr)$ are the **spherical Bessel functions** and **spherical Neumann functions**, respectively. To first order, at large kr, they are like sine functions and cosine functions, respectively. At small kr, is finite but diverges. They can be generated from the relations

$$j_l(x) = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{sinx}{x}$$

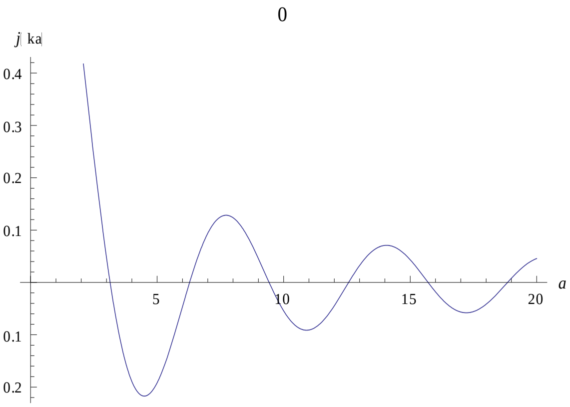
$$n_l(x) = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{cosx}{x}.$$

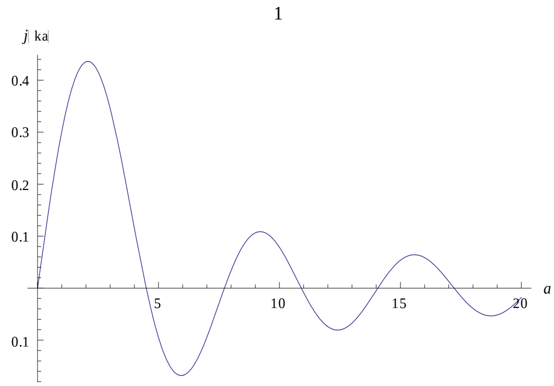
The 3D infinite potential well

If the particle is confined to a sphere of radius a, clearly the radial wavefunction which if finite at $r = 0$ is given by $j_l(kr)$ Because $n_l(kr)$, unstable at the origin. The condition that it vanishes at $r = a$ requires that

$$j_l(ka) = 0$$

Thus the allowed energies are related to the zero's of the spherical Bessel functions. These are can be obtained from the followowing graphs.(This will be discussed in detail in the exercise section)





Harmonic Oscillator in in spherical coordinate (optional)

We have already solved the problem of a 3D harmonic oscillator by separation of variables in Cartesian coordinates. It is instructive to solve the same problem in spherical coordinates and compare the results. In the previous section we have discussed Schrödinger equation in spherical coordinate and we have shown that for radial potentials Schrödinger equation can be separated. Solution of the angular part of the Schrödinger equation is given by:

$$Y_l^m(\theta,\phi) = \epsilon\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{\frac{1}{2}} e^{im\phi}P_l^m(cos\theta)$$

Radial part of the Schrödinger equation is given by:

$$\frac{\hbar^2}{2m_0}\left(-\frac{\partial^2 R}{\partial r^2}-\frac{2}{r}\frac{\partial R}{\partial r}+\frac{l(l+1)}{r^2}R\right)+V(r)R = ER$$

3D harmonic oscillator potential in spherical coordinate is given by

$$V = \frac{1}{2}m_0\omega^2 r^2$$

Solution of the radial part of the Schrödinger equation can be obtained using series method and one can obtain the following results:

$$R_{nl} = N_{nl}r^l e^{-\frac{r^2}{2}}L_k^{l+\frac{1}{2}}(r)$$

$$E = \left(2k+l+\frac{3}{2}\right)\hbar\omega = \left(n+\frac{3}{2}\right)\hbar\omega$$

Where N_{nl} is normalization constant with the value:

$$N_{nl} = \left(\frac{2^{n+l+2}}{\sqrt{\pi}}\right)^{\frac{1}{2}}\left(\frac{\left(\frac{1}{2}(n-l)\right)!\left(\frac{1}{2}(n+l)\right)!}{(n+l+1)!}\right)^{\frac{1}{2}}$$

The eigenfunction can be written as:

$$\psi_{nlm} = R_{nl}Y_l^m(\theta,\phi)$$

Where

$$\begin{cases} l = 0, 2, 4, \dots, n \; for\; n\; even \\ l = 1, 3, \dots, n \quad for\; n\; odd \\ \qquad -l \le m \le l \end{cases}$$

Consequently we conclude that:

Energy values can be graphically represented as an energy spectrum.

The energy values of the harmonic oscillator are equally spaced, with a constant energy difference of $\hbar\omega$ between successive levels.

$$E_N - E_{(N+1)} = \hbar\omega$$

The ground state of lowest energy has nonzero kinetic and potential energy.

In the case of 2 od 3 dimensional oscillators for any energy level above the ground state, there is more than one eigenstate that produces that energy.

The table shows the quantum numbers for the states of each energy for our separation in spherical coordinates, and for separation in Cartesian coordinates. Remember that there are $l + 1$ states.

n	E	nlm	$n_x n_y n_z$	$\#particle\ N$
0	3/2	000	000	1
1	5/2	11-1 110 111	100 010 001	3
2	7/2	200 22-2 22-1 220 221 222	110 101 011 200 020 001	6

Values of Generalized Laguerre polynomial $L_{(n-l)/2}^{l+\frac{1}{2}}$ are givenin the table

l \ n	0	2	4
0	1	$\frac{3}{2} - r^2$	$\frac{1}{8}(15 - 20r^2 + 4r^4)$
2		1	$\frac{7}{2} - r^2$
4			1

l \ n	1	3	5
1	1	$\frac{5}{2} - r^2$	$\frac{1}{8}(35 - 28r^2 + 4r^4)$
3		1	$\frac{9}{2} - r^2$

5			1

Correspondence Principle

In physics, the correspondence principle states that the behavior of systems described by the theory of quantum mechanics (or by the old quantum theory) reproduces classical physics in the limit of large quantum numbers.

You provide a demonstration of how large quantum numbers for harmonic oscillator can give rise to classical (continuous) behavior.