Chapter 6 (Lecture 9)

Schrödinger Equation in 3D 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 \( \Psi = \psi e^{-i\frac{E}{\hbar}t} \) 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

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

Example: Free particles in a box--separable in Cartesin coordinates

If the particle is confined in a box \( L^3 \), clearly the wavefunction is given by

\[ \psi_{n_1,n_2,n_3} = \left( \frac{2}{L} \right)^\frac{3}{2} \sin \frac{n_1\pi x}{L} \sin \frac{n_2\pi y}{L} \sin \frac{n_3\pi z}{L} \]

and the energies are given by

\[ E = \frac{\hbar^2 \pi^2}{2mL^2} \]

Thus there are three quantum numbers, \( n_1, n_2, n_3 \) to denote a given state and since the energy depends is given by , there are degeneracy in that different eigenstates can have the same energy. (learn the degenerate states)

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

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

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

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

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.

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

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

**Cylindrical coordinate system**

In terms of Cartesian variables we can write

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

We can obtain the relations:

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

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

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

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

Since $z$ is independent from $x$ and $y$ we can write

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

We can easily obtain

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

Then using the relation

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

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

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

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

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

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

Then the eigenvalue equation \( H\Psi = E\Psi \) becomes:

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

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

\[ \frac{1}{Q} \frac{\partial^2 Q}{\partial \phi^2} = -m_i^2 \]

Then we can write

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

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

\[ \frac{\hbar^2}{2m} \left( \frac{1}{P \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{m_i^2}{\sin^2 \theta} \right) = -\frac{\hbar^2 L^2}{2m_0} \]

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

Where \( m_i^2 \) 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:

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

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

\[ L_z = -i\hbar \frac{\partial}{\partial \phi} \]

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

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

Values of the \( L^2 = l(l+1) \). Solutions of the angular parts of the equations are given by:

\[ Q \sim \frac{1}{\sqrt{2\pi}} e^{im_1 \phi} \]

\[ P \sim P_l^{m_1}(\cos \theta) \]

The eigenvalue equations are

\[ L^2 \left( P_l^{m_1}(\cos \theta) \right) = l(l+1)\hbar^2 \left( P_l^{m_1}(\cos \theta) \right) \]

\[ L_z \left( \frac{1}{\sqrt{2\pi}} e^{im_1 \phi} \right) = m_1 \hbar \left( \frac{1}{\sqrt{2\pi}} e^{im_1 \phi} \right) \]

Where \( m_1 \) is restricted to the range \( -l, ..., l \). associated Legendre functions. The product of \( P \) and \( Q \) occurs so frequently in quantum mechanics that it is known as a spherical harmonic:

\[ Y_l^m(\theta, \phi) = e^{i(m_1 \phi)} \frac{(2l+1)(l-|m_1|)!}{4\pi(l+|m_1|)!} P_l^{m_1}(\cos \theta) \]

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

\[ \int_0^\pi \sin \theta d\theta \int_0^{2\pi} \left[ Y_l^m(\theta, \phi) \right]^* Y_l^m(\theta, \phi) d\phi = \delta_{ll} \delta_{mm}. \]

Table shows spherical Harmonic functions for a few values of \( l \).
Radial part of the equation can be simplified by substituting: \( u(r) = rR(r) \):

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

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 \( \frac{\hbar^2}{2m} l(l+1) \) 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](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:

\[
F = m\frac{v^2}{r} = \frac{L^2}{mr^2}
\]

\[
V = \frac{L^2}{2mr^2}
\]

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 Schrödinger 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

<table>
<thead>
<tr>
<th>( l )</th>
<th>( m_l )</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>( \frac{1}{2\sqrt{\pi}} )</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>( \frac{1}{2} e^{-i\phi} \sqrt{\frac{3}{2\pi}} \sin[\theta] )</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>( \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos[\theta] )</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>( -\frac{1}{2} e^{i\phi} \sqrt{\frac{3}{2\pi}} \sin[\theta] )</td>
</tr>
</tbody>
</table>
\[ E_l = \frac{\hbar^2}{2I} l(l+1); l = 0,1,2,3, \ldots \]

**Free-particle solutions**

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,

\[ R(r) = A j_l(kr) + B n_l(kr) \]

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

\[ j_l(x) = (-x)^l \left( \frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin x}{x} \]

\[ n_l(x) = (-x)^l \left( \frac{1}{x} \frac{d}{dx} \right)^l \frac{\cos x}{x} \]

**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 following graphs. (This will be discussed in detail in the exercise section)