Chapter 4: Wave Mechanics

4.1. Time-dependent Schrödinger equation

In quantum mechanics, the state of any physical system is specified at each time “t”, by a state vector $|\Psi(t)\rangle$ in a Hilbert space $\mathcal{H}$, where $|\Psi(t)\rangle$ contains all the needed information about the system. The time evolution of the state vector $|\Psi(t)\rangle$ of a system is governed by the time-dependent Schrödinger equation

$$\hat{H}(\vec{r},t)|\Psi(t)\rangle = i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t} \qquad \text{......(4-1-1)}$$

Where $\hat{H}$ is the Hamiltonian operator corresponding to the total energy of the system defined as:

$$\hat{H}(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t) \qquad \text{......(4-1-2)}$$

The spectrum of the Hamiltonian, which consists of the entire set of its eigenvalues, is real. This spectrum can be discrete, continuous, or a mixture of both. In the case of bound states, the Hamiltonian has a discrete spectrum of values and a continuous spectrum for unbound states.

In the position representation, the time-dependent Schrödinger equation (4-1-1) for a particle of mass “m” moving in a time-dependent potential $V(\vec{r},t)$ can be written as follows:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r},t)\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) \qquad \text{......(4-1-3)}$$

Recall that, according to the probabilistic interpretation of Born, the quantity $|\Psi(\vec{r},t)|^2 d\tau$ is the probability of finding the system at time t in the elementary volume $d\tau$ surrounding the point r. Since the total probability is 1, we have

$$\int|\Psi(\vec{r},t)|^2 d\tau = 1 \qquad \text{......(4-1-4)}$$

4.2. Stationary states: Time-independent potentials

In a large class of problems, the Schrödinger potential $V(\vec{r},t)$ has no time dependence and it is simply a function $V(\vec{r})$ of position. In this case the Hamiltonian operator will also be time independent, and hence the Schrödinger equation will have solutions that are separable, i.e. solutions that consist of a product of two functions, one depending only on $\vec{r}$ and the other only on time:

$$\Psi(\vec{r},t)=\psi(\vec{r})\Phi(t) \quad \text{......(4-2-1)}$$

Substitute eq.(4-2-1) into eq.(4-1-3), and dividing both sides by $\psi(\vec{r})\Phi(t)$, we obtain

$$\frac{1}{\psi}\left[-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V(\vec{r})\psi(\vec{r})\right]=\frac{i\hbar}{\Phi}\frac{d\Phi}{dt} \quad \text{......(4-2-2)}$$

The left side of the above equation depends only on the variable "$\vec{r}$", while the right side depends only on the variable "t", since "$\vec{r}$" and "t" are independent variable, then both sides must be equal a quantity which depend on neither "$\vec{r}$" nor "t". Thus, both sides must be equal to the same separation constant "c", the right side:

$$\frac{i\hbar}{\Phi}\frac{d\Phi}{dt}=c \quad \text{......(4-2-3)}$$

with solution

$$\Phi(t)=e^{\frac{-iEt}{\hbar}} \quad \text{......(4-2-4)}$$

while the left side

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V(\vec{r})\psi(\vec{r})=E\psi(\vec{r}) \quad \text{......(4-2-5)}$$

This equation is known as the time-independent Schrödinger equation for a particle of mass m moving in a time-independent potential $V(\vec{r})$. Equation (4-2-5) can be rewritten as:

$$\hat{H}\psi(\vec{r})=E\psi(\vec{r}) \quad \text{......(4-2-6)}$$

Hence the state (4-2-1) becomes

$$\Psi(\vec{r},t)=\psi(\vec{r})e^{\frac{-iEt}{\hbar}} \quad \text{......(4-2-7)}$$

A state described by a wavefunction (4-2-7) in which the spatial and temporal parts are separable is called stationary state, stationary because physical observables of the state are actually time independent.

The probability density of the stationary state is time independent (stationary)

$$\rho(\vec{r}) = \left|\Psi(\vec{r},t)\right|^2 = \left|\psi(\vec{r})e^{\frac{-iEt}{\hbar}}\right|^2 = \left|\psi(\vec{r})\right|^2 \qquad ......(4\text{-}2\text{-}8)$$

The most general solution to the time-dependent Schrödinger equation (4-1-3) can be written as an expansion in terms of the stationary states $\Psi(\vec{r},t) = \psi_n(\vec{r})e^{\frac{-iE_n t}{\hbar}}$

$$\Psi(\vec{r},t) = \sum_n c_n \psi_n(\vec{r})e^{\frac{-iE_n t}{\hbar}} \qquad \textbf{Prove} \qquad (4\text{-}2\text{-}9)$$

Where

$$c_n = \langle \psi_n | \Psi(t=0) \rangle = \int \psi_n^*(\vec{r})\psi_n(\vec{r})d^3r \qquad (4\text{-}2\text{-}10)$$

The general solution (4-2-9) is not a stationary state, because a linear superposition of stationary states is not necessarily a stationary state.

HW. Prove that the probability density is time dependent for linear superposition of stationary states.

HW. Prove that the expectation value of the Hamiltonian operator $\hat{H}$ is time independent for linear superposition of stationary states, where $\hat{H}\phi_n(x) = E_n\phi_n(x)$.

4.3. The harmonic oscillator

Consider a particle subject to a restoring force $F = -kx$, as might arise for a mass-spring system obeying Hooke's Law. The potential is then

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \qquad ......(4\text{-}3\text{-}1)$$

With $\omega = \sqrt{\frac{k}{m}}$, hence, the corresponding one-dimensional Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right)\psi(x) = E\psi(x) \qquad ......(4\text{-}3\text{-}2)$$

There are two approaches that are used to find solutions to this equation. One approach involves using power series (analytical approach). The second approach makes use of Ladder operators.

4.3.1. Analytical approach (Power series method)

As shown in B.Sc. course of quantum mechanics, after some efforts, eq.(4-3-2) can be written

$$\frac{d^2\psi(\zeta)}{d\zeta^2}+\left(\varepsilon-\zeta^2\right)\psi(\zeta)=0 \qquad \textbf{(prove)} \qquad \ldots\ldots(4\text{-}3\text{-}3)$$

Where we have chosen a new measure of length and a new measure of energy, each of which is dimensionless, such that

$$\zeta=\left(\frac{m\omega}{\hbar}\right)^{1/2}x \quad \text{and} \quad \varepsilon=\frac{2E}{\hbar\omega} \qquad \ldots\ldots(4\text{-}3\text{-}4)$$

The solution (normalized eigenfunctions) to eq.(4-3-3) is

$$\psi_n(\zeta)=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}\cdot e^{-\zeta^2/2}\cdot H_n(\zeta) \qquad \ldots\ldots(4\text{-}3\text{-}5)$$

Where $H_n(\zeta)$ is a Hermite polynomial of degree "n", given by

$$H_n(\zeta)=(-1)^n e^{\zeta^2}\frac{d^n}{d\zeta^n}e^{-\zeta^2} \qquad \ldots\ldots(4\text{-}3\text{-}6)$$

The energy of the eigenstate is given by

$$E_n=\hbar\omega\left(n+\frac{1}{2}\right) \ , \ n=0,\ 1,\ 2,\ \ldots \qquad \ldots\ldots(4\text{-}3\text{-}7)$$

The energy levels are equally spaced $\hbar\omega$ apart. Even the lowest energy state (the ground state), has a nonzero energy of $\hbar\omega/2$ known as the zero-point energy. The higher energy states correspond to larger amplitudes of oscillation, and vice versa for the lower energy states.

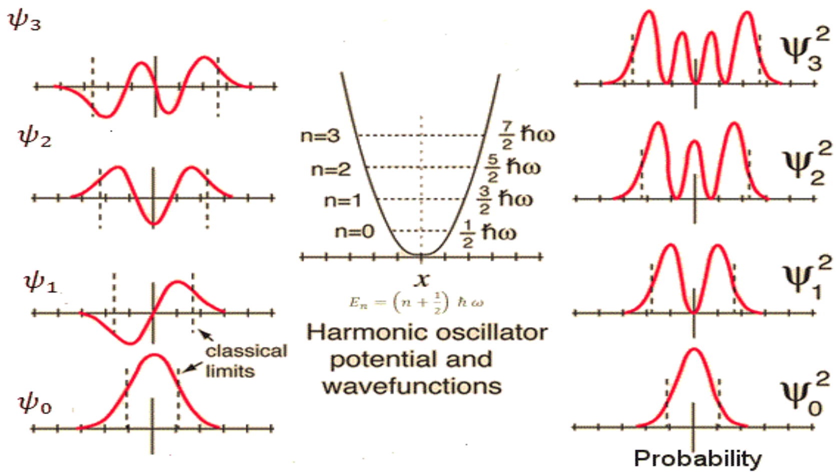

Fig.(1): The energy eigenvalues of a particle in one-dimensional harmonic oscillator potential.

4.3.2. Ladder operators approach (Algebraic method)

Another method may use to solve the problem of H.O. in sense of Q.M. usually called operator treatment. According to this approach Schrödinger equation expressed in formula (4-3-3), which may write as follows:

$$\left(\frac{d^2}{d\zeta^2} - \zeta^2\right)\psi(\zeta) = -\varepsilon\psi(\zeta) \qquad \text{……(4-3-8)}$$

Since $\frac{d^2}{d\zeta^2} - \zeta^2 = \left(\frac{d}{d\zeta} - \zeta\right)\left(\frac{d}{d\zeta} + \zeta\right) - 1$, equation (4-3-8) becomes;

$$\left[\left(\frac{d}{d\zeta} - \zeta\right)\left(\frac{d}{d\zeta} + \zeta\right) - 1\right]\psi(\zeta) = -\varepsilon\psi(\zeta) \qquad \text{……(4-3-9)}$$

Using $\varepsilon = \frac{2E}{\hbar\omega}$ equation (4-3-9) becomes

$$\hbar\omega\left[\frac{1}{\sqrt{2}}\left(\zeta - \frac{d}{d\zeta}\right)\cdot\frac{1}{\sqrt{2}}\left(\zeta + \frac{d}{d\zeta}\right) + \frac{1}{2}\right]\psi(\zeta) = E\,\psi(\zeta) \qquad \text{……(4-3-10)}$$

Let $\hat{a}^+ = \frac{1}{\sqrt{2}}\left(\zeta - \frac{d}{d\zeta}\right)$ and $\hat{a}^- = \frac{1}{\sqrt{2}}\left(\zeta + \frac{d}{d\zeta}\right)$, equation (4-3-10) becomes:

$$\hbar\omega\left(\hat{a}^+\hat{a}^- + \frac{1}{2}\right)\psi(\zeta) = E\,\psi(\zeta) \qquad \text{……(4-3-11)}$$

One can write the Hamiltonian operator as

$$\hat{H} = \hbar\omega(\hat{a}^{+}\hat{a}^{-} + \frac{1}{2}) \qquad \text{……(4-3-12)}$$

Also, one can deduce the commutation relation between $\hat{a}^{+}$ and $\hat{a}^{-}$

$$\left[\hat{a}^{-}, \hat{a}^{+}\right] = \hat{a}^{-}\hat{a}^{+} - \hat{a}^{+}\hat{a}^{-} = 1 \qquad \text{……(4-3-13)}$$

From eqs. (4-3-12) and (4-3-13), the Hamiltonian operator can be rewritten as:

$$\hat{H} = \hbar\omega\left(\hat{a}^{-}\hat{a}^{+} - \frac{1}{2}\right) \qquad \text{……(4-3-14)}$$

HW. Prove that: $\hat{a}^{+} = (2m\omega\ \hbar)^{-\frac{1}{2}}(m\omega\ \hat{x} - i\hat{p}_x)$ and $\hat{a}^{-} = (2m\omega\ \hbar)^{-\frac{1}{2}}(m\omega\ \hat{x} + i\hat{p}_x)$.

HW. Express $\hat{x}$ and $\hat{p}_x$ in terms of both lowering and raising operators.

HW. Formulate in matrix form the position operator, momentum operator and number operator of the 1-dimensional harmonic oscillator.

In order to explore the action of both $\hat{a}^{+}$ and $\hat{a}^{-}$ on ψ, let suppose, if ψ is a solution of the Schrödinger equation corresponding to energy E, then $\left(\hat{a}^{+}\psi\right)$ is also a solution to the Schrödinger equation

$$\hat{H}\left(\hat{a}^{+}\psi\right) = \hbar\omega\left(\hat{a}^{+}\hat{a}^{-} + \frac{1}{2}\right)\left(\hat{a}^{+}\psi\right)$$

$$\hat{H}\left(\hat{a}^{+}\psi\right) = \hbar\omega\ \hat{a}^{+}\left(\hat{a}^{-}\hat{a}^{+}\psi + \frac{1}{2}\psi\right) \qquad \text{……(4-3-15)}$$

Using eq. (4-3-14): $\hat{H} = \hbar\omega\left(\hat{a}^{-}\hat{a}^{+} - \frac{1}{2}\right)$ → $\hat{a}^{-}\hat{a}^{+} = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$ and substitute into eq.(4-3-15)

$$\hat{H}\left(\hat{a}^{+}\psi\right) = \hbar\omega\ \hat{a}^{+}\left(\left(\frac{\hat{H}}{\hbar\omega} + \frac{1}{2}\right)\psi + \frac{1}{2}\psi\right)$$

$$\hat{H}\left(\hat{a}^{+}\psi\right) = \left(E + \hbar\omega\right)\left(\hat{a}^{+}\psi\right) \qquad \text{……(4-3-16)}$$

This means, $\left(\hat{a}^{+}\psi\right)$ is a solution to the Schrödinger equation but for energy $\left(E + \hbar\omega\right)$. Similarly, if ψ is a solution of the Schrödinger equation corresponding to energy E, then $\left(\hat{a}^{-}\psi\right)$ is also a solution to the Schrödinger equation but for energy $\left(E - \hbar\omega\right)$.

$\hat{H}(\hat{a}^{-}\psi)=(E-\hbar\omega)(\hat{a}^{-}\psi)$ **(Prove)** ……(4-3-17)

i.e., Both states $(\hat{a}^{+}\psi)$ and $(\hat{a}^{-}\psi)$ are eigenfunctions for the Hamiltonian operator with eigenvalues $(E+\hbar\omega)$ and $(E-\hbar\omega)$, respectively.

The operators $\hat{a}^{+}$ and $\hat{a}^{-}$ are called ladder operators, because the action of the raising (creation) operator $\hat{a}^{+}$ on an energy eigenstate is to turn it into another energy eigenstate of higher energy and the action of lowering (annihilation) operator $\hat{a}^{-}$ on an energy eigenstate is to turn it into another energy eigenstate of lower energy.

One can summarize the action of operators $\hat{a}^{+}$ and $\hat{a}^{-}$ on the energy eigenstate ψ_n are

$\hat{a}^{-}\psi_n = c_{-}\psi_{n-1}$ and $\hat{a}^{+}\psi_n = c_{+}\psi_{n+1}$

Or can be rewritten in Dirac notation

$\hat{a}^{-}|n\rangle = c_{-}|n-1\rangle$ and $\hat{a}^{+}|n\rangle = c_{+}|n+1\rangle$

Where c_{-} and c_{+} are constants of proportionality (not eigenvalues)

Since the minimum value of the potential energy is zero and occurs at a single value of x, the lowest energy for the quantum harmonic oscillator must be greater than zero. Let the wave function for the minimum energy be $|0\rangle$. Since there is no energy level below this minimum value, we must have

$$\hat{a}^{-}|0\rangle = 0 \qquad ……(4\text{-}3\text{-}18)$$

This equation allows us to find $|0\rangle$, since it gives

$$(2m\omega\ \hbar)^{-\frac{1}{2}}(m\omega\ \hat{x}+i\hat{p}_x)|0\rangle = 0 \qquad ……(4\text{-}3\text{-}19)$$

The normalized solution is found to be

$$|0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\cdot e^{\frac{-m\omega x^2}{2\hbar}} \qquad ……(4\text{-}3\text{-}20)$$

The energy of this state is easily found by applying the Hamiltonian operator given by eq. (4-3-12), this gives

$$H|0\rangle = \hbar\omega\left(\hat{a}^{+}\hat{a}^{-}+\frac{1}{2}\right)|0\rangle = \frac{1}{2}\hbar\omega|0\rangle \qquad ……(4\text{-}3\text{-}21)$$

$$E_o = \frac{1}{2}\hbar\omega$$

Application of the raising operator to the ground state generate the state $|1\rangle$ with energy E_1, whilst n applications of the raising operator generate the $|n\rangle$ state with energy E_n

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \text{ , n=0, 1, 2, …} \qquad \text{……(4-3-22)}$$

To find c_- and c_+

$$\langle n'|\hat{a}^{+\dagger}\hat{a}^{+}|n\rangle = \langle n'|\hat{a}^{-}\hat{a}^{+}|n\rangle$$

$$\langle n'+1|c_+'^{*}c_+|n+1\rangle = \langle n'|\frac{\hat{H}}{\hbar\omega} + \frac{1}{2}|n\rangle$$

$$c_+'^{*}c_+\delta_{n'n} = \left(\frac{E_n}{\hbar\omega} + \frac{1}{2}\right)\delta_{n'n}$$

$$c_+ = \sqrt{n+1}$$

$$\hat{a}^{+}|n\rangle = \sqrt{n+1}|n+1\rangle \qquad \text{…..(4-3-23)}$$

Similarly, $c_- = \sqrt{n}$

$$\hat{a}^{-}|n\rangle = \sqrt{n}|n-1\rangle \qquad \text{…..(4-3-24)}$$

HW. Try to apply the raising operator to the ground state wavefunction to generate the first excited state wavefunction and in turn deduces the energy of the first excited state.

HW. Verify the following commutation relations $[\hat{H},\hat{a}^{+}] = \hbar\omega\hat{a}^{+}$ and $[\hat{H},\hat{a}^{-}] = -\hbar\omega\hat{a}^{-}$.

HW. If the number operator is defined as $\hat{N} = \hat{a}^{+}\hat{a}^{-}$, Verify the following commutation relations $[\hat{N},\hat{a}^{+}] = \hat{a}^{+}$ and $[\hat{N},\hat{a}^{-}] = -\hat{a}^{-}$.

HW. Verify the uncertainty principle $\Delta x\Delta p_x \geq \frac{\hbar}{2}$ for a particle in harmonic oscillator potential.