

§3.6 Solutions to Eigenvalue Equation and Schrödinger Equation

16. Solution to Eigenvalue Equation and Schrödinger Equation.

Schrödinger equation: $i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}, t)$.

If $V(\vec{r})$ is not explicitly dependent on time t , then we have

$$\psi(\vec{r}, t) = \psi(\vec{r}) T(t).$$

Substituting this into the Schrödinger equation:

$$\frac{i\hbar}{T} \frac{dT}{dt} = \frac{1}{\psi(\vec{r})} \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E$$

↑
total energy

$$\therefore \frac{i\hbar}{T} \frac{dT}{dt} = E \Rightarrow T = T_0 e^{-iEt/\hbar}$$

$$\left\{ \begin{array}{l} \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E \psi(\vec{r}) \end{array} \right.$$

$$\therefore \psi(\vec{r}, t) = \psi(\vec{r}) e^{-iEt/\hbar}$$

Probability density $= |\psi(\vec{r}, t)|^2 = |\psi(\vec{r})|^2$ is independent of t .
i.e., the probability of the particle appearing at position \vec{r} does not change with time!

$$\text{Equation } \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E \psi(\vec{r})$$

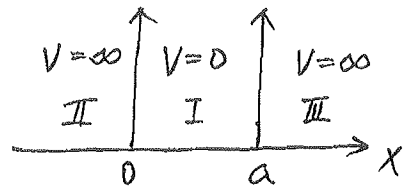
is called the stationary state Schrödinger equation. Essentially, it is the energy eigenvalue equation.

Here, we show a few examples of how to solve the stationary state Schrödinger equation, i.e., the energy eigenvalue equation, to derive the system states and eigenvalues.

(1) 1-Dimension Infinite potential well

The stationary-state Schrödinger equation

$$\text{is: } \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \psi(x) = E \psi(x).$$



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

Since a particle cannot be in an infinite potential, $\therefore \psi = 0$ in regions II and III. (Physics)

In region I, $V = 0$, the equation is simplified to

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

Let $k \equiv \sqrt{\frac{2mE}{\hbar^2}}$, then: $\frac{d^2 \psi}{dx^2} + k^2 \psi = 0$

The general solution to this equation is

$$\psi = A \sin(kx + \delta),$$

where A and δ are constants to be determined from boundary conditions and normalization requirements.

Considering from physics aspects, since the particle cannot be in the $V = \infty$ region, i.e., the probability to be in regions II and III is zero. Therefore, $\psi(x=0) = 0$, $\psi(x=a) = 0$.

At $x=0$, $0 = A \sin \delta$.

Since $A \neq 0$ (otherwise, the solution is no meaning),

$$\therefore \delta = 0$$

At $x=a$, $0 = A \sin ka$.

Since $A \neq 0$, $\therefore \sin ka = 0 \Rightarrow ka = n\pi$ ($n = 1, 2, 3, \dots$)

$$\therefore k = \frac{n\pi}{a}$$

Here, we kick out $n=0$ and $n < 0$ solutions, as they have no meaning in reality. Now: $\psi_n = A \sin\left(\frac{n\pi}{a}x\right)$.

$$\therefore k = \frac{n\pi}{a} = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}, \quad n = 1, 2, 3, \dots$$

$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$ indicates that the particle energy is quantized in the infinite high potential well.

$|\psi(x)|^2$ is the probability density of finding the particle at position x . Since the probability of finding the particle in all space is 1 (i.e., normalization requirement), we have

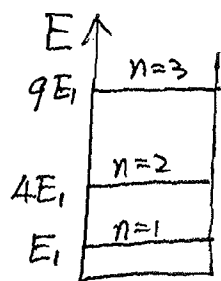
$$\int |\psi(x)|^2 dx = 1$$

$$\therefore \int_0^a A^2 \sin^2 kx dx = \int_0^a A^2 \sin^2 \frac{n\pi}{a} x dx = A^2 \cdot \frac{a}{2} = 1$$

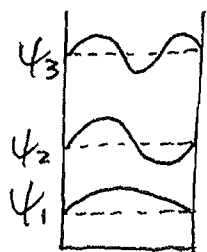
$$\Rightarrow A = \sqrt{\frac{2}{a}}$$

\therefore the normalized wave function (eigen wave function) is

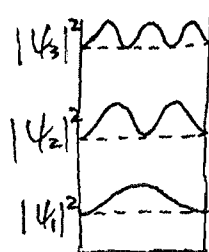
$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad n=1, 2, 3, \dots$$



(a) energy level E_n



(b) ψ_n



(c) $|\psi_n|^2$

Particle's motion in a potential well is a common phenomenon, e.g., the electron in hydrogen atom does 3-D motion in the Coulomb potential, just the wall is not a square, but distributes along $-\frac{1}{r}$.

* Note: the lowest energy $E_1 \neq 0$, which is completely different from classical mechanics. This is due to the wave nature of particle — "a wave at rest" does not exist!

* Note: the full wave function $\psi_n(x,t) \propto \sin\left(\frac{n\pi x}{a}\right) e^{-iE_n t/\hbar}$, which is a standing wave.

(2) Harmonic Oscillator (1-D):

The force that a particle experiences $F = -kx$,
 where x is the displacement of particle relative to its
 balance point 0. $\therefore E_{\text{potential}} = \frac{1}{2} kx^2 = V$.

The stationary-state Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 \right) \psi = E\psi$$

Let $\beta = \alpha x$, where $\alpha = (mk/\hbar^2)^{1/4}$.

$$\therefore \frac{d^2 \psi}{d\beta^2} + (\lambda - \beta^2) \psi = 0$$

where $\lambda = \frac{2mE}{\hbar^2 \alpha^2} = \frac{2E}{\hbar} \sqrt{\frac{m}{k}} = \frac{2E}{\hbar \omega}$. $\omega = \sqrt{k/m}$.

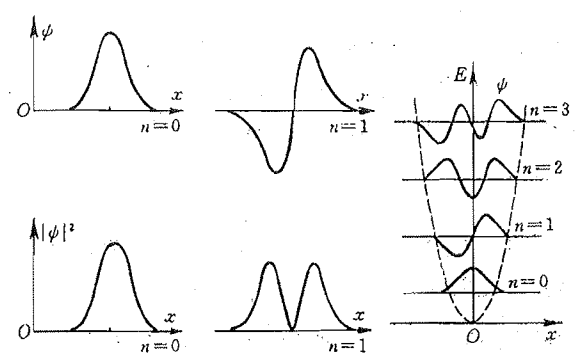
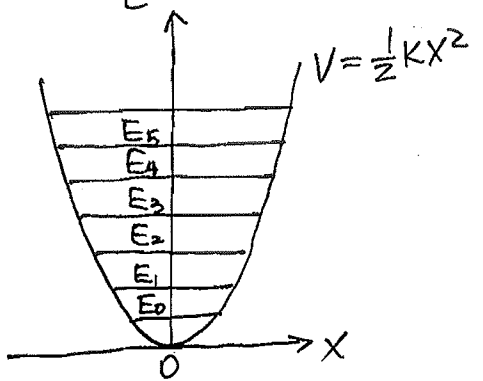
The solution to the equation is:

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega, \quad n=0, 1, 2, \dots$$

$$\psi_n = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} e^{-\frac{1}{2} \alpha^2 x^2} H_n(\alpha x)$$

Where $H_n(\alpha x)$ is Hermitean polynomial

$$H_0(\alpha x) = 1, \quad H_1(\alpha x) = 2\alpha x, \quad H_2(\alpha x) = 4(\alpha x)^2 - 2, \dots$$



① Plot energy levels within the potential energy curve. The length of horizontal lines shows the oscillator motion range.

② When $\hbar = 0$,
 $E_0 = \frac{1}{2} \hbar \omega \neq 0$.
 \Rightarrow no oscillator at rest!

③ E_n are equally separated — similar to Planck's hypothesis — quanta of oscillator energy!

Review on Quantum Mechanics

1. Concepts of Quantum

* Photon has energy and the energy is quantized —

- { Blackbody Radiation
- { Photoelectric Effect
- { Hydrogen Spectra

* Photon has momentum and the momentum is quantized —

- { Compton Effect
- { Radiation Pressure

2. Wave-Particle Duality:

Both photon and matter particles have wave-particle

- Duality —
- { de Broglie matter wave
 - { Relation of E and P in relativity

* Single photon interference or Imagin

Single electron interference or diffraction

— How to explain these experiments?

Try to understand the details of these experiments and useful relations, e.g., blackbody radiation:

$$\left\{ \begin{array}{l} \text{Planck Radiation Law: } P(\nu) = \frac{8\pi h \nu^3}{c^3} \cdot \frac{1}{e^{h\nu/k_B T} - 1} \\ \text{Wien Displacement Law: } \lambda_m T = 2.898 \times 10^{-3} \text{ m} \cdot \text{K} \\ \text{Stefan-Boltzmann Law: } P_{\text{total}} = \int_0^\infty P(\nu) d\nu = \frac{4}{c} \sigma T^4 \end{array} \right.$$

de Broglie Relation: $\left\{ \begin{array}{l} E = h\nu \\ \vec{p} = \hbar \vec{k}, \quad (p = \frac{h}{\lambda}) \end{array} \right.$

$$E = \sqrt{p^2 c^2 + m_0^2 c^4} \quad \text{in relativity theory.}$$

3. Fundamentals of Quantum Mechanics

* QM state : state vector $|\psi(t)\rangle$

* QM observables/variables/physical quantities : operator \hat{A}

* QM measurement : $\hat{A} |\psi(t)\rangle$

— only possible result is one of the eigenvalues of \hat{A} .

* Eigenvalue equation, eigen state, eigenvalues

$$\hat{A} |\psi\rangle = \lambda |\psi\rangle, \text{ where } \lambda \text{ is a complex number.}$$

* Superposition principle:

orthonormal basis $\{|u_n\rangle\}$, $\hat{A} |u_n\rangle = a_n |u_n\rangle$.

eigenvalues $\{a_n\}$ ($\langle u_m | u_n \rangle = \delta_{mn}$)

$$|\psi\rangle = \sum_n (c_n |u_n\rangle), \text{ where } c_n = \langle u_n | \psi \rangle.$$

Probability of obtaining a specific eigenvalue:

$$P(a_n) = \frac{|\langle u_n | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{|c_n|^2}{\langle \psi | \psi \rangle}$$

* Mean value:

$$\bar{A} = \langle \psi | \hat{A} | \psi \rangle$$

$$= \sum_n [P(a_n) a_n]$$

$$= \sum_n \left(\frac{|\langle u_n | \psi \rangle|^2}{\langle \psi | \psi \rangle} a_n \right)$$

(4)

* Representation: When really calculate eigenvalues or mean values, it is common to project states and operators to certain representation, e.g., $\{x, y, z\}$ representation.

$$\hat{A} \psi(x) = a \psi(x)$$

$$1D: \int \psi^*(x) \hat{A}(x) \psi(x) dx$$

$$3D: \int \psi^*(\vec{r}) \hat{A}(\vec{r}) \psi(\vec{r}) d^3r = \iiint \psi^*(x, y, z) \hat{A} \psi(x, y, z) dx dy dz$$

* Uncertainty Principle and commutation relation.

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}, \quad [\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij},$$

($i, j = x, y, z$)

$$\Delta A \cdot \Delta B \geq \frac{1}{2} | \langle [\hat{A}, \hat{B}] \rangle |, \quad \text{e.g., } \Delta Q \cdot \Delta P \geq \frac{\hbar}{2}$$

* Evolution of state — Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle$$

$$\text{Where } \hat{H}(t) = \frac{\hat{p}^2(t)}{2m} + \hat{V}(t)$$

Chapter 4. Introduction to Atomic Structure and Atomic Spectra

1. Overall Atomic Spectroscopy consists of the following aspects:

(1) Quantum Mechanics Fundamentals

(2) Theory of Atomic Structure

[Energy Eigenvalues and Eigenstates of single Atom]

⇒ Resonance central frequency (wavelength λ_0) of spectral line.

(3) Theory of Radiative Transitions

[Transition Probability and Selection Rules of single Atom]

⇒ Intensity (partially), Polarization, and Distribution Direction of spectral line

(4) Theory of Statistical Interaction of an ensemble of atoms with radiation [Quantum Statistical Behavior of an ensemble of atoms]

⇒ Shape, width, Intensity of spectral line.

(5) Applications of atomic spectroscopy.

2. Spectral lines are produced by different processes, e.g., resonant radiative transitions (absorption, stimulated and spontaneous emissions); Scattering, etc.

