

# 1 A Short Primer on Quantum Mechanics

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Nanomechanics is part of both quantum physics and molecular physics. As this book is aimed at engineering students and engineers, whom we assume have no formal training in quantum physics, we begin our presentation with a short introduction of quantum mechanics, in order to provide the necessary background for later presentations.

## 1.1 Wave–Particle Duality: Law of Physics

Light and matter exhibit wave–particle duality, in other words, all matter and light have two manifestations: discreteness as the deterministic being and continuousness in the sense of probabilistic presence. In our current understanding, such wave–particle duality is the law of physics or first principle, because we do not know, at least to date, any other laws of universe that are more fundamental than it.

The relations between wave and particle properties of any object in the universe may be described by the de Broglie relations,

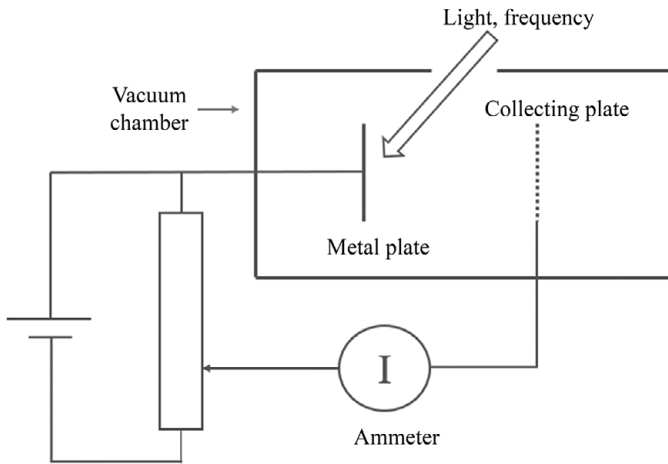
$$E = h\nu, \quad \text{and} \quad p = \frac{h}{\lambda}, \quad (1.1)$$

where  $h$  is the Planck constant, which is a universal constant of nature, and its value is  $h = 6.63 \times 10^{-34}$  Js;  $\lambda$  is the matter wavelength; and  $\nu$  is the matter wave frequency, which is the number of a repeating event, e.g., cycles or temporal wave number per unit time. The unit of frequency is hertz (Hz) (1 Hz means one wave cycle per second). The reciprocal of the frequency is period, which is the time duration of one wave cycle, i.e.,

$$T = \frac{1}{\nu}.$$

At first sight, many of us may experience difficulties understanding such wave–particle proposition because, in our common experience, a finite mass matter is always associated with the discrete particle, whereas the light wave is associated with the continuous electromagnetic field.

However, at the turn of the twentieth century, people had found several counterexamples or evidences that show either (1) light wave behaves like particles, and (2) matter exhibits wave properties.



**Figure 1.1** Illustration of photoelectric effect experiment

Two famous examples showing that light exhibits particle properties are: (1) photoelectric effect and (2) Compton effect.

### 1.1.1 Photoelectric Effect

In 1887, Heinrich Hertz found that when ultraviolet (UV) light is shone on a metal plate in a vacuum, and it emits charged particles (see Fig. 1.1), which were later shown to be electrons by J. J. Thomson (1899).

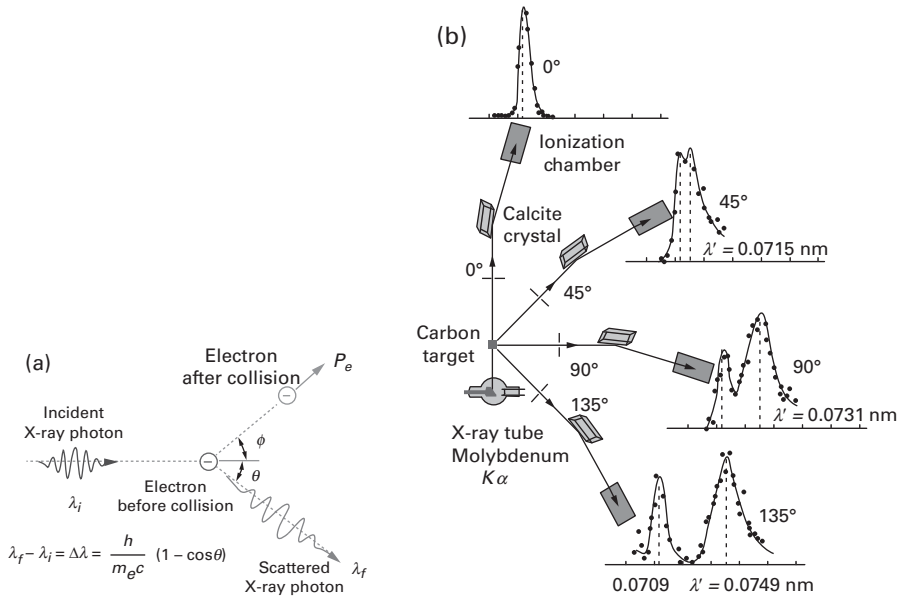
Based on classical electromagnetic theory, electric field  $\mathbf{E}$  of light exerts force  $F = -eE$  on electrons. As the intensity of light increases, the input energy to the metal plate increases as well, which may be absorbed by the electrons inside the metal plate, so that the kinetic energy of electrons inside the metal plate increases too. When the kinetic energy of the electrons reach a critical value, they may escape from the metal plate. From this perspective, electrons should be emitted whatever the frequency  $\nu$  of light is, so long as  $\mathbf{E}$  is sufficiently large; and for very low intensity, one may expect a time lag between light exposure and electron emission, because electrons need to absorb enough energy to escape from the metal plate.

The actual experimental observation shows that the maximum kinetic energy of ejected electrons is independent of light intensity, but dependent on the frequency  $\nu$  of the light. For  $\nu < \nu_0$ , i.e., for frequencies below a cutoff frequency, no electrons are emitted from the metal plate, and there is no time lag when the light intensity is low. However, the rate of ejection of electrons depends on light intensity.

To interpret the experimental results, Albert Einstein theorized that the energy distribution in light is discrete, or light travels in packets of discrete energy, which are referred to as *quanta*, and they are now called as *photons*,<sup>1</sup>

$$E = h\nu. \quad (1.2)$$

<sup>1</sup> Here, we adopt the hypothesis that the group of velocity of light is the velocity of photons.



**Figure 1.2** Compton scattering: (a) schematic illustration and (b) experimental observation

When an electron absorbs a single photon, it may leave the metal plate. The maximum kinetic energy of an emitted electron can then be expressed as

$$K_{max} = h\nu - \varphi,$$

where  $\varphi$  is the work function, which is the minimum energy needed for an electron to escape from the surface of the metal plate of a given metallic material. It is usually 2~5 eV depending on the type of materials, and it may be written as  $\varphi = h\nu_0$ , so that we must have  $\nu > \nu_0$  for the photoelectric effect to occur. Einstein’s theory was later validated by the experiments conducted by Robert Andrews Millikan in 1914.

For his discovery of the law of the photoelectric effect, in 1921 Albert Einstein was awarded the Nobel Prize in Physics.

### 1.1.2 Compton Scattering

The second example is the so-called Compton scattering or the Compton effect, which is the light scattering due to the inelastic collision of photons and electrons. The experiment is illustrated in Fig. 1.2(a). In the experiment, a high-energy X-ray or gamma ray photon beam hits a target with electrons. In this case, classical theory predicts that when light is scattered on a free electron, the incident electromagnetic (EM) wave will shake the electron transversely, and the oscillating electron then radiates in all directions (except the exact direction of 90°). The classical theory predicts that there may be a change of the wavelength of the colliding photons due to the associated Doppler shift, when the light intensity is large.

However, in the Compton scattering experiment, one can observe the change of the wavelength of the scattering light even when the light intensity is very small, which is called the Compton shift. The shift of the wavelength can be calculated by treating the collision of the photon and electron as the elastic collision of two billiard balls. That is, the photon behaves like a particle and, hence, the photon–electron collision obeys the energy conservation and momentum conservation,

$$h\nu + m_e c^2 = h\nu' + (p_e'^2 c^2 + m_e^2 c^4)^{1/2} \quad \text{and} \quad \mathbf{p}_\nu = \mathbf{p}_{\nu'} + \mathbf{p}_e. \quad (1.3)$$

Note that  $(p_e'^2 c^2 + m_e^2 c^4)^{1/2} = m_e c^2$  is Einstein's relativistic energy, which can be derived from Einstein relations,

$$E = mc^2, \quad m = \frac{m_e}{\sqrt{1 - v^2/c^2}}, \quad \text{and} \quad p = mv, \quad \rightarrow \quad p^2 c^2 = -m_e^2 c^4 + (mc^2)^2$$

and  $m_e$  in Eq. (1.3) is the electron's static mass.

From Eq. (1.3), one can find that

$$\lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta) \geq 0. \quad (1.4)$$

In Fig. 1.2(b), one finds the shifted wavelength measurement at different angles. Note that for every fixed angle, there is also an unshifted peak, that is due to collision of the X-ray photon and the core of the atom (the nucleus of the atom plus the immobile electrons) because in that case, based on Eq. (1.3), one can find that

$$\lambda' - \lambda = \frac{h}{m_c c} (1 - \cos \theta) \sim 0, \quad m_c \gg m_e. \quad (1.5)$$

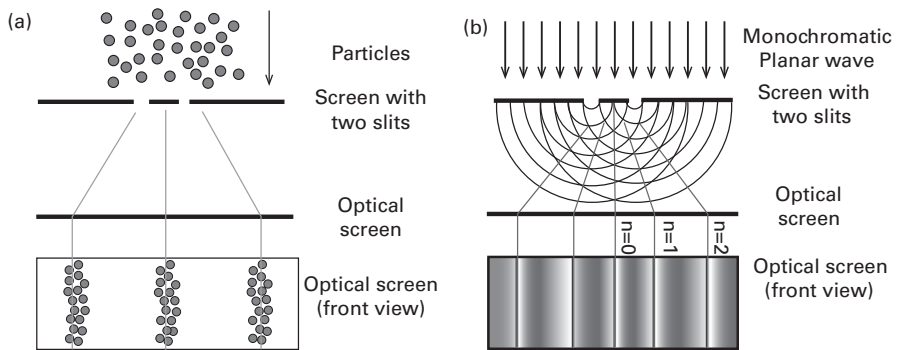
The Compton effect is a strong evidence that the continuous electromagnetic waves may behave like particles. For the discovery of the Compton effect, Arthur Holly Compton earned the 1927 Nobel Prize in Physics.

On the other hand, discrete matter may also behave like continuous waves. In the following, we consider a well-known double-slit diffraction experiment of matter waves.

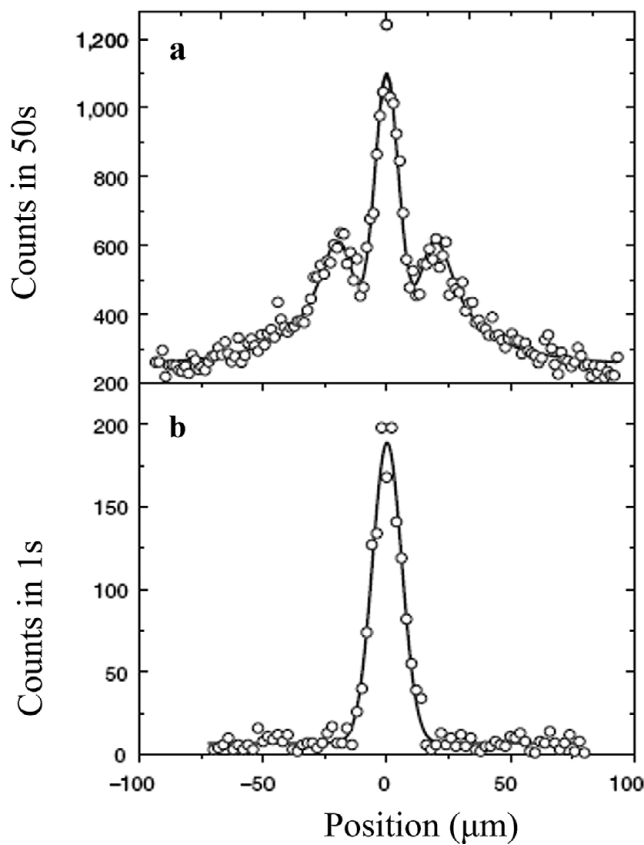
### 1.1.3 Interference of Matter Waves

The double-slit experiment was originally performed by Thomas Young in 1801 in demonstrating the wave nature of light, in which an incoming coherent plane wave is directly hitting a thin plate with two slits, one can observe the wave interference pattern on the screen behind the double-slit plate as shown in Fig. 1.3(b).

On the other hand, if the incoming object is not light, but a beam of particles such as electrons, atoms, or even molecules, what would we expect the measurement result on the back screen to be? A natural expectation on the results of double-slit diffraction of matter waves is depicted in Fig. 1.3(a). However, on the contrary, for matter particle waves, the particle density on the back screen has the same interference pattern as the light wave. Interference pattern produced by a beam of  $C_{60}$  molecules is shown in Fig. 1.4, which demonstrates the wave–particle duality of  $C_{60}$  molecules. It should be



**Figure 1.3** Double-slit experiment: (a) expected result for particles and (b) experimental observation



**Figure 1.4** Interference pattern produced by  $C_{60}$  molecules: (a) experimental recording (open circles) and the fitting curve by using the Kirchhoff diffraction theory (continuous line) – the expected zeroth and first-order maxima can be clearly seen. The details of the theory are discussed in the text; and (b) the molecular beam profile without the grating in the path of the molecules (Arndt et al. (1999))

noted that the position of the matter wave is uncertain, and it is a wave of probability distribution, and it is sometimes called the de Broglie wave. One of the consequences of this probabilistic wave is the uncertainty principle, which is sometimes called the Heisenberg principle. The principle asserts that there is a fundamental limit to the precision with which certain pairs of physical properties of a particle can be simultaneously determined, such as position  $x$  and momentum  $p$ ,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2},$$

where  $\hbar = \frac{h}{2\pi} = 1.05457172610^{-34}$  Js is the reduced Planck constant and  $\sigma_x, \sigma_p$  are standard deviation of position and momentum.

The quantum mechanics uncertainty principle indicates that the more precise the momentum of a particle is determined, the less precise its position can be known, and vice versa. In other words, for a fixed precision of momentum, the precision of the position is bounded below. This is to say that as random variables, position and momentum are intrinsically related, and the product of their variances has a low bound.

To close this section, we note that not only light and matter exhibit wave–particle duality, antimatter also exhibits wave–particle duality.

## 1.2 Schrödinger Equation

The partial differential equation that governs the matter wave motion is called the Schrödinger equation.

### 1.2.1 A Short Heuristic Derivation

Since this is not a quantum mechanics book but an introduction to nanomechanics to engineers, we derived the Schrödinger equation in a heuristic manner.

Before we get into mathematical derivations, we first make the following assumptions:

1. The total energy  $E$  of a particle is

$$E = T + V = \frac{p^2}{2m} + V.$$

This is the energy expression for a classical particle with mass  $m$  where the total energy  $E$  is the sum of the kinetic energy  $T$ , and the potential energy  $V$  (which can vary with position, and time).  $p$  and  $m$  are the momentum and the mass of the particle, respectively.

2. Einstein's light quanta hypothesis (1905) asserts that the energy  $E$  of a photon is proportional to the frequency  $\nu$  (or angular frequency,  $\omega = 2\pi\nu$ ) of the corresponding electromagnetic wave:

$$E = h\nu = \hbar\omega.$$

3. The de Broglie hypothesis (1924) states that any particle can be associated with a wave, and that the momentum  $p$  of the particle is related to the wavelength  $\lambda$  (or wave number  $k$ ) of such a wave by:

$$p = \frac{h}{\lambda} = \hbar k.$$

Expressing  $p$  and wavelength  $k$  as vectors, we have

$$\mathbf{p} = \hbar\mathbf{k}.$$

4. The three assumptions discussed earlier allow one to derive the governing equation for plane waves only. To extend those assumptions to general situations will require the superposition principle, and thus, one must separately postulate that the Schrödinger equation is linear.

Schrödinger's main idea was to express the phase of the matter wave as a complex phase factor so that the matter wave probability function has the following form:

$$\Psi(\mathbf{r}, t) = A \exp i(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad \text{where } \mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z, \quad (1.6)$$

where  $\mathbf{k}$  is the wave number and  $\omega$  is the angular frequency.

Considering that Eq. (1.6) is the intrinsic form of the wave function, we have

$$\frac{\partial}{\partial t} \Psi = -i\omega \Psi$$

and then

$$E\Psi = h\nu\Psi = \hbar\omega\Psi = i\hbar \frac{\partial}{\partial t} \Psi. \quad (1.7)$$

Similarly, for spatial derivatives, we have

$$\frac{\partial}{\partial x} \Psi = ik_x \Psi, \quad \text{and} \quad \frac{\partial^2}{\partial x^2} \Psi = -k_x^2 \Psi.$$

We then have

$$p_x^2 \Psi = (\hbar k_x)^2 \Psi = -\hbar^2 \frac{\partial^2}{\partial x^2} \Psi$$

and hence

$$\mathbf{p}^2 \Psi = (p_x^2 + p_y^2 + p_z^2) \Psi - \hbar^2 \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = -\hbar^2 \nabla^2 \Psi.$$

Recalling the Assumption 1 on total energy,

$$E = T + V = \frac{p^2}{2m} + V \Rightarrow E\Psi = (T + V)\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \quad (1.8)$$

and combining Eqs. (1.7) and (1.8), we obtain the standard form of time-dependent Schrödinger equation for a single particle as,

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t), \quad (1.9)$$

where  $m$  is the mass of the particle,  $-\frac{\hbar^2}{2m}\nabla^2$  is said to be the kinetic energy operator, and  $V(\mathbf{r},t)$  is the potential energy of the particle at position  $\mathbf{r}$  and at time  $t$ .

In passing, we note that the Schrödinger equation, i.e., Eq. (1.9), is a second-order, homogeneous, linear partial differential equation.

## 1.2.2 Wave Function

Further examining the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r},t)\Psi$$

we find that

$$E = T + V = \frac{\mathbf{p} \cdot \mathbf{p}}{2m} + V(\mathbf{r},t) \Rightarrow -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t),$$

which may be viewed as a differential operator, and we name the energy differential operator as *Hamiltonian operator* or simply “Hamiltonian,”

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t). \quad (1.10)$$

Max Born made a physical interpretation of the wave function  $\Psi(\mathbf{r},t)$ : The probability of finding the particle in a small volume  $\delta\Omega$  at position  $\mathbf{r}$  and time  $t$  is equal to  $|\Psi(\mathbf{r},t)|^2\delta\Omega = \Psi(\mathbf{r},t)\Psi^*(\mathbf{r},t)\delta\Omega$ . In other words,  $|\Psi(\mathbf{r},t)|^2$  is the probability distribution of finding the particle in the location  $\mathbf{r}$  at time  $t$ . Since the total probability to find the particle in the space should be one, i.e.,

$$\int_{\mathbf{R}^3} |\Psi(\mathbf{r},t)|^2 d\Omega = 1$$

and a wave function that satisfies this condition is said to be normalized. Suppose that we have a solution of Eq. (1.9), which is not normalized,

$$\int_{\mathbf{R}^3} |\Psi(\mathbf{r},t)|^2 d\Omega = C,$$

we can then normalize it by choosing

$$\Psi(\mathbf{r},t) = \frac{1}{\sqrt{C}}\Psi(\mathbf{r},t).$$



In fact, we can show that the Born interpretation of the wave function

$$P_r = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = \text{const.}$$

is correct by proving  $\frac{dP_r}{dt} = 0$ . We know that

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi. \quad (1.11)$$

By taking the complex conjugate of the above equation, we can have the conjugate Schrödinger equation,

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + V(x,t)\Psi^*. \quad (1.12)$$

Then, multiplying Eq. (1.11) with  $\Psi^*$  and multiplying Eq. (1.12) with  $\Psi$  yield

$$i\hbar \Psi^* \dot{\Psi} = -\frac{\hbar^2}{2m} \Psi^* \frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi^* \Psi, \quad (1.13)$$

$$i\hbar \Psi \dot{\Psi}^* = \frac{\hbar^2}{2m} \Psi \frac{\partial^2 \Psi^*}{\partial x^2} - V(x,t)\Psi \Psi^*. \quad (1.14)$$

By integrating Eqs. (1.13) and (1.14) from  $-\infty$  to  $\infty$  and by integration by parts, we obtain

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \int_{-\infty}^{\infty} |\Psi|^2 dx &= -\frac{\hbar^2}{2m} \Psi^* \frac{\partial \Psi}{\partial x} \Big|_{-\infty}^{\infty} + \frac{\hbar^2}{2m} \Psi \frac{\partial \Psi^*}{\partial x} \Big|_{-\infty}^{\infty} \\ &\quad + \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} (\Psi_{,x}^* \Psi_{,x} - \Psi_{,x} \Psi_{,x}^*) dx = 0, \end{aligned}$$

the last equality is derived by considering the fact that wave function should be convergent, which requires  $\Psi(x)$  and  $\Psi^*(x) \rightarrow 0$ , as  $x \rightarrow \infty$ . This result leads to Born's statistical interpretation,

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = \text{const.}$$

is the probability of finding the particle at time  $t$  along the  $x$ -axis.

## 1.3 Solution Examples of the Schrödinger Equation

In this section, we provide a few benchmark solutions, as well as corresponding solution techniques, of the Schrödinger equation.

### 1.3.1 Time-Independent Schrödinger Equation

There is a large class of problems in which the potential function is independent from time,  $t$ . In one-dimensional (1D) cases, we can write such potential function

as  $V(x, t) = V(x)$ , and the corresponding Schrödinger equation can be written as follows:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi. \quad (1.15)$$

Using separation of variable and substituting  $\Psi(x, t) = \psi(x)T(t)$  into Eq. (1.15), we have

$$i\hbar\psi \frac{dT}{dt} = -\frac{\hbar^2}{2m} T(t) \frac{d^2\psi}{dx^2} + V(x)\psi(x)T(t).$$

Dividing the above equation by  $\psi(x)T(t)$ , we can obtain

$$i\hbar \frac{1}{T} \frac{dT}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V(x) = \text{const.} = A, \quad (1.16)$$

where  $A$  is separation constant.

Equation (1.16) can be separated into two equations, and we can solve the first equation,

$$\frac{dT}{dt} = -i \frac{A}{\hbar} T \rightarrow T(t) = C \exp\left(-i \frac{A}{\hbar} t\right).$$

We know that the matter wave solution should have a factor  $\exp(-i\omega t)$  and  $\omega = E/\hbar$ . Thus, we can now identify that  $A = E$ .

Subsequently, the two ordinary differential equations of Eq. (1.16) can be written as

$$i\hbar \frac{1}{T} \frac{dT}{dt} = E \quad \text{and} \quad -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V(x) = E$$

or

$$i\hbar \frac{dT}{dt} = ET \quad (1.17)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x) = E\psi. \quad (1.18)$$

Equation (1.18) is called the time-independent Schrödinger equation. For time-independent wave function, we always denote  $\psi(\mathbf{r})$ , which is the stationary part of the total wave function.

In three-dimensional (3D) space, the time-independent Schrödinger equation has the following form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad \text{or} \quad \hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (1.19)$$

where the energy  $E$  is a constant. One may find that Eq. (1.19) is an eigenvalue problem.

The solution of Eq. (1.17) is given as

$$T(t) = a \exp\left(-i \frac{Et}{\hbar}\right), \Rightarrow T(t) = a \exp(-i\omega t), \leftarrow \omega = \frac{E}{\hbar}$$

and the probability density becomes

$$\begin{aligned} P(x,t) &= |\Psi(x,t)|^2 = \psi^*(x) \exp(-i\omega t) \psi(x) \exp(-i\omega t) \\ &= \psi^*(x) \psi(x) = |\psi(x)|^2 = P(x), \end{aligned}$$

which indicates that the probability density only depends on the solution of time-independent Schrödinger equation, and hence the probability distribution is spatial and stationary, if  $V(x,t) = V(x)$ .

### 1.3.2 Free Particle Solution

If we let  $V(x) = 0$  in Eq. (1.18), this is the case that a particle freely moves in a 1D space. The solution of Eq. (1.18) in this case is:

$$\psi(x) = b \exp\left(\pm i \frac{\sqrt{2mE}}{\hbar} x\right).$$

Consider that, in this case,

$$E = \frac{p^2}{2m} \text{ and } p = \hbar k \Rightarrow \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = k, \Rightarrow \psi(x) = b \exp(i \pm kx).$$

Therefore, the total solution of the wave function becomes

$$\Psi(x,t) = (a \cdot b) \exp i(\pm kx - \omega t) = C \exp i(\pm kx - \omega t).$$

In the derivation above, the sign of the time term ( $-i\omega t$ ) is fixed by the sign adopted in time-dependent Schrödinger equation, while the sign of the position term  $\pm ikx$  depends on propagation direction of wave:  $+ikx$  term propagates toward  $+\infty$ , while the term  $-ikx$  propagates toward  $-\infty$ .

In fact, in the above heuristic derivation of the Schrödinger equation we have assumed that the general wave function solution has a plane wave form. We say that the derivation is heuristic, because the derivation does not consider the general cases of potential function  $V(\mathbf{r},t) \neq 0$ .

### 1.3.3 Particle in a Finite Potential Well

Assume that a particle is associated with a finite potential well,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi, \text{ where } V(x) = \begin{cases} V_0, & \text{if } x < -a \\ 0, & \text{if } |x| < a \\ V_0, & \text{if } x > a \end{cases} \quad (1.20)$$

The eigen solution for the above problem has the form  $\exp(kx)$  and

$$\begin{aligned} \text{Outside the well: } k &\sim \pm \frac{\sqrt{2m(V_0 - E)}}{\hbar}, \text{ when } V_0 > E, \\ &\sim \pm i \frac{\sqrt{2m(E - V_0)}}{\hbar} \text{ when } V_0 < E, \\ \text{Inside the well: } k &\sim \pm i \frac{\sqrt{2mE}}{\hbar}. \end{aligned}$$

Outside the well, we may discard the eigen solutions

$$\psi \sim \exp\left(\pm i \frac{\sqrt{2m(E - V_0)}}{\hbar}\right)$$

because they are not convergent when  $x \rightarrow \pm\infty$ . However, outside of the well we have convergent solutions,

$$\begin{aligned} \psi &\sim \exp\left(\frac{\sqrt{2m(V_0 - E)}}{\hbar}x\right), \text{ when } x < 0, \\ \text{and } \psi &\sim \exp\left(-\frac{\sqrt{2m(V_0 - E)}}{\hbar}x\right), \text{ when } x > 0. \end{aligned} \quad (1.21)$$

Now, we even have a solution that corresponds to the case  $E < V_0$  outside the well. For classical particles, it is impossible to have a solution when  $E < V_0$ , which means the classical particles can never escape from the energy well, however, for quantum mechanics, this is a valid possibility. Let  $q = \sqrt{2m(V_0 - E)}/\hbar$ . Based on the convergence argument, in  $x < -a$  we have to discard the solution  $\sim \exp(-qx)$  and, for  $x > a$ , we must discard the solution  $\sim \exp(qx)$ .

Finally, we have the convergent wave function solution in the whole domain,

$$\psi(x) = \begin{cases} C \exp(qx), & \forall x < -a \\ A \cos kx + B \sin kx, & \forall -a < x < a \\ D \exp(-qx), & \forall x > a \end{cases} \quad (1.22)$$

where  $A, B, C, D$  are coefficient constants determined by boundary conditions. It may be noted again that inside the well  $V = 0$  and,

$$\psi(x) = A \cos kx + B \sin kx \quad \text{and} \quad E = \frac{k^2 \hbar^2}{2m}.$$

Using the continuity condition,

$$\psi(-a^-) = \psi(-a^+) \text{ and } \frac{d\psi}{dx}(-a^-) = \frac{d\psi}{dx}\psi(-a^+)$$

one can find that the even function solution must satisfy the conditions,

$$C \exp(-qa) = A \cos ka \quad \text{and} \quad \alpha C \exp(-qa) = kA \sin(ka),$$

which lead to

$$q = k \tan(ka). \quad (1.23)$$

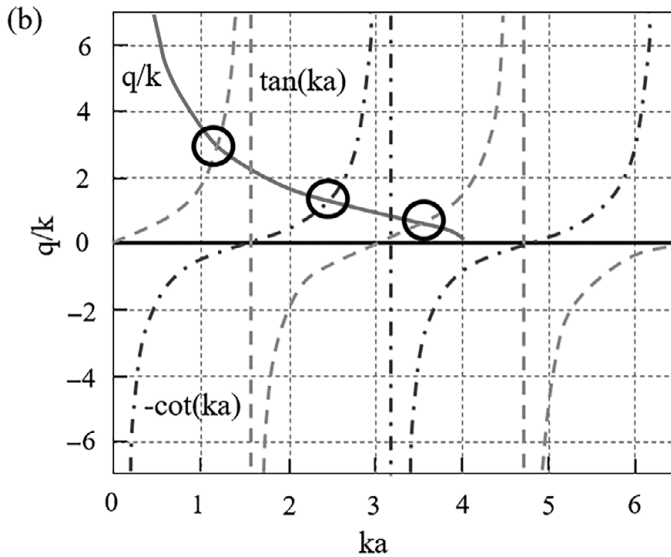


Figure 1.5 Eigenvalue locations for a particle in a finite depth well

While, for the odd function solution

$$\psi(a^-) = \psi(a^+) \text{ and } \frac{d\psi}{dx}(a^-) = \frac{d\psi}{dx}\psi(a^+)$$

it must satisfy the conditions,

$$C \exp(-qa) = B \sin ka \text{ and } -\alpha C \exp(-qa) = kB \cos(ka),$$

which lead to

$$q = -kcot(ka). \tag{1.24}$$

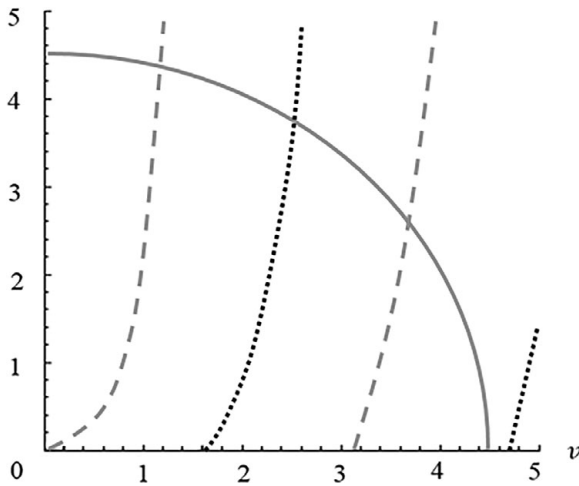
The graph solution of the two characteristic equations for eigenvalues is shown in Fig. 1.5, in which the intersection points are between  $y(ka) = \tan(ka)$  or  $-\cot(ka)$  and  $y(ka) = q/k = \sqrt{k_0^2/k^2 - 1}$ , where  $k_0 = \sqrt{2mV_0}/\hbar$ . Another approach to find the allowable discrete energy level is utilizing the fact that  $q = \sqrt{2m(V_0 - E)}/\hbar$ . Let

$$u = qa, v = ka = \frac{\sqrt{2mE}a}{\hbar} \text{ and } u_0 = \frac{\sqrt{2mV_0}a}{\hbar}.$$

Equations (1.23)–(1.24) may be converted to the following energy balance relation:

$$u_0^2 - u^2 = \begin{cases} (v \tan v)^2 & \text{(symmetric case)} \\ (v \cot v)^2 & \text{(antisymmetric case)}. \end{cases}$$

If we choose  $X = v$  and  $Y = u$ , we can find different energy levels for a fixed depth of the well, i.e.,  $V_0$ , in a plot. In Fig. 1.6, the solid semicircle is the contour for  $u_0^2 = 20$ , and the dash or dotted curves are functions  $u = v \tan v$  or  $u = -v \cot v$ . In this case,



**Figure 1.6** Eigenvalues for a particle in a finite depth well

there are exactly three solutions,  $v_1 = 1.28$ ,  $v_2 = 2.54$ , and  $v_3 = 3.73$ , with the corresponding energies

$$E_n = \frac{\hbar^2 v_n^2}{2ma^2}.$$

Consider a special case that  $V_0 \rightarrow \infty$ . The finite depth of potential well becomes an infinite height potential well, and the solution Eq. (1.22) degenerates to

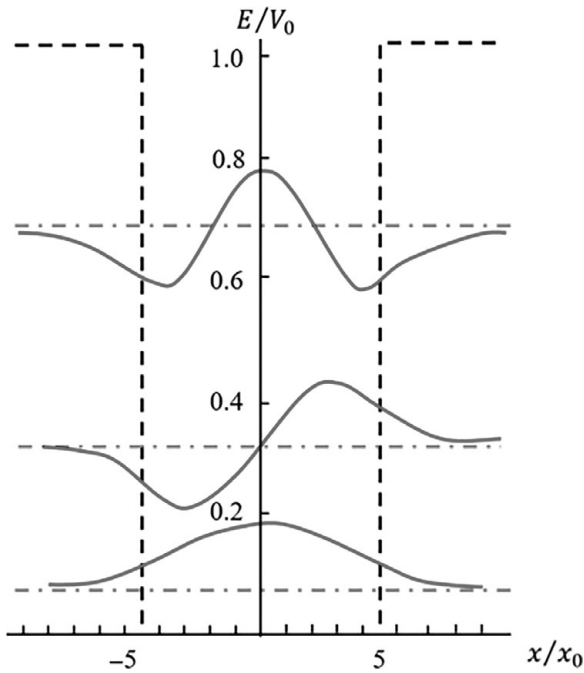
$$\psi(x) = \begin{cases} 0, & \forall x < -a \\ A \cos kx + B \sin kx, & \forall -a < x < a \\ 0, & \forall x > a \end{cases} \quad (1.25)$$

The wave function solution will then become:

$$\text{Even solution: } \psi_n(x) = \sqrt{\frac{1}{a}} \cos\left(\frac{n\pi x}{2a}\right), \quad n = 1, 2, 5, \dots \infty \text{ and}$$

$$\text{Odd solution: } \psi_n(x) = \sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right), \quad n = 2, 4, 6, \dots \infty,$$

which satisfy the boundary conditions  $\psi(-a) = \psi(a) = 0$ , as shown in Fig. 1.7. The energy level for each quantum state  $n$  is  $E_n = \frac{n^2 \hbar^2 \pi^2}{8ma^2}$ . When  $n = 1$   $E_1 = \frac{\hbar^2 \pi^2}{8ma^2}$ , it is the minimum quantum energy state in the well, which we call as the *ground state*. In general, the ground state of a quantum mechanical system is its lowest-energy state and the energy of the ground state is known as the zero-point energy of the system. An excited state is any state with energy greater than the ground state. If more than one ground state exist, they are said to be degenerate. Many systems have degenerate ground states. Mathematically speaking, the ground state eigenvalue has multiplicities. According to the third law of thermodynamics, a system at absolute zero temperature only exists in its ground state. At the ground state, the system's



**Figure 1.7** Different quantum states in an infinite well

entropy is determined by the degeneracy of the ground state. Many systems, such as a perfect crystal lattice, have a unique ground state and, therefore, have zero entropy at absolute zero temperature.

### 1.3.4 Harmonic Oscillator

If we choose the potential energy as the quadratic function

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m^2\omega^2x^2, \quad \leftarrow \text{Recall } \omega^2 = \frac{k}{m},$$

the time-independent Schrödinger equation will take the form

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi. \quad (1.26)$$

Since, in classical mechanics, this is the potential function of the simple harmonic oscillator, we call the solution of Eq. (1.26) the quantum harmonic oscillator.

Choosing  $\psi(x) = \exp(-\alpha^2x^2/2)$  and taking the second-order derivative of the wave function, one may find that

$$\frac{d^2\psi}{dx^2} = -\alpha^2\psi + \alpha^4x^2\psi,$$

and the Schrödinger equation becomes,

$$-\frac{\hbar^2}{2m} \left( -\alpha^2 + \alpha^4 x^2 \right) \psi(x) + \frac{1}{2} m \omega^2 x^2 \psi(x) = E \psi(x).$$

To solve the equation, we obtain

$$\alpha = \sqrt{\frac{m\omega}{\hbar}} \quad \text{and} \quad E_0 = \frac{1}{2} \hbar \omega,$$

which is the lowest achievable energy state or the ground state the particle can occupy.

In general, one can assume the form of solution as  $\psi(x) = H(y) \exp(-y^2/2)$ ,  $y = \alpha x$ , and Eq. (1.26) becomes,

$$\frac{d^2 H}{dy^2} - 2y \frac{dH}{dy} + (\lambda - 1)H = 0, \quad \text{where } \lambda := \frac{2E}{\hbar \omega}.$$

To obtain a convergent solution for this equation (see, e.g., Pilar 1990), the parameter  $\lambda$  has to satisfy the condition

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

and a complete family of solutions may be found as

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left( \frac{m\omega}{\pi \hbar} \right)^{1/4} H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right) \exp \left( -\frac{m\omega x^2}{2\hbar} \right), \quad n = 0, 1, 2, 3, \dots$$

where the function  $H_n$  are the Hermite polynomials

$$H_n(x) = (-1)^n \exp(x^2) \frac{d^n}{dx^n} \left( \exp(-x^2) \right), \quad n = 0, 1, 2, \dots$$

For example,

$$H_0(x) = 1, \quad H_1(x) = 2x, \quad H_2(x) = 4x^2 - 2, \quad H_3(x) = 8x^3 - 12x, \dots$$

### 1.3.5 Physical Meaning of the Operators

The operators of the Schrödinger equation have definite physical meanings relating to the physical properties of the particle that is under investigation.

To study the motion of a subatomic particle, the first thing that you may want to do is to measure its position and velocity, which are related with the position operator and momentum operator. The position operator is an algebraic operator that can be expressed as,

$$\hat{x} = x \quad (\text{in 1D space}) \quad \text{and} \quad \hat{\mathbf{r}} = \mathbf{r}, \quad (\text{in 3D space}).$$

The velocity of a particle is related to the linear momentum operator:

$$\hat{p}_x = i\hbar \frac{\partial}{\partial x} \quad \text{and} \quad \hat{\mathbf{p}} = -i\hbar \left[ \mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \right] = -i\hbar \nabla.$$



Other important operators are:

- Kinetic energy operator

$$T = \frac{\mathbf{p}^2}{2m} \rightarrow \hat{T} = \frac{1}{2m} \left( -i\hbar \frac{\partial^2}{\partial x_i \partial x_i} \right) = -\frac{\hbar^2}{2m} \nabla^2.$$

- Hamiltonian operator

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}).$$

- Angular momentum operator

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \rightarrow \hat{\mathbf{L}} = -i\hbar \mathbf{r} \times \nabla.$$

### 1.3.6 Dirac's Notation: Bra–Ket Notation

The solution of quantum mechanics belongs to a complex Hilbert space. Paul Dirac developed a set of notations for vector operations in the complex Hilbert space, which are essentially analogs of vector operations in linear vector space.

Dirac denoted that vector basis and its complex conjugate or transpose as ket or bra, i.e.,

$$|e_i\rangle := \mathbf{e}_i \quad \text{and} \quad \langle e_i| := \mathbf{e}_i^*$$

where the superscript indicates the complex conjugate.

To illustrate the concept here, we slightly alter the notation, so that we may write a vector in a complex finite dimensional vector space by using the bras and kets as

$$\mathbf{A} = A_1 \mathbf{e}_1 + A_2 \mathbf{e}_2 + A_3 \mathbf{e}_3 = A_1 |e_1\rangle + A_2 |e_2\rangle + A_3 |e_3\rangle = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix}$$

and

$$\mathbf{A}^* = A_1^* \mathbf{e}_1^* + A_2^* \mathbf{e}_2^* + A_3^* \mathbf{e}_3^* = A_1^* \langle e_1| + A_2^* \langle e_2| + A_3^* \langle e_3| = (A_1^*, A_2^*, A_3^*)$$

and you may see that the bra is basically a complex conjugate of row vector, whereas the ket is a complex column vector. Essentially, the bra may be viewed as the complex conjugate transpose of the ket.

The inner product of finite dimensional vector space may be defined as

$$\langle e_i | e_j \rangle := \mathbf{e}_i^* \cdot \mathbf{e}_j = \delta_{ij};$$

and the outer product of bra and ket may be viewed as a tensor product, i.e.,

$$|e_i\rangle \langle e_j| := \mathbf{e}_i \otimes \mathbf{e}_j^*.$$

Using engineering notations, we can express the inner product of bra and ket as the scalar dot product of two vectors,

$$\langle A|B \rangle = (A_1^*, A_2^*, A_3^*) \begin{pmatrix} B_1 \\ B_2 \\ B_3 \end{pmatrix} = A_1^* B_1 + A_2^* B_2 + A_3^* B_3$$

and express the outer product of bra and ket as the following matrix multiplication,

$$|A \rangle \langle B| = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix} (B_1^* B_2^* B_3^*) = \begin{pmatrix} A_1 B_1^* & A_1 B_2^* & A_1 B_3^* \\ A_2 B_1^* & A_2 B_2^* & A_2 B_3^* \\ A_3 B_1^* & A_3 B_2^* & A_3 B_3^* \end{pmatrix}.$$

Moreover, it may be shown that

$$(|A \rangle \langle B|)|C \rangle = \langle B|C \rangle |A \rangle.$$

In the complex Hilbert space, we can define the inner product between two function bases as

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i^*(x) \psi_j(x) dx.$$

As seen previously, the total wave function is the superposition of a complete set of eigenfunctions, which can now be written by using the bra–ket notation,

$$\psi = \sum_{i \in \mathbb{H}} a_i \phi_i \rightarrow |\psi \rangle = \sum_{i \in \mathbb{H}} \langle \phi_i | \psi \rangle |\phi_i \rangle,$$

where, by definition,

$$\langle \phi_i | \psi \rangle = \int_{-\infty}^{\infty} \phi_i^* \psi dx = a_i$$

because  $\int_{-\infty}^{\infty} \phi_i^*(x) \phi_j(x) dx = \delta_{ij}$ ,  $\psi(x) = \sum_i a_i \phi_i(x)$ ,

if we view the eigenfunction as the vector(function) basis.

Similarly, one may write,

$$\psi^* = \sum_{i \in \mathbb{H}} a_i^* \phi_i^* \rightarrow \langle \psi | = \sum_{i \in \mathbb{H}} \langle \phi_i | \langle \psi | \phi_i \rangle, \text{ where } a_i^* = \langle \psi | \phi_i \rangle.$$

### 1.3.7 Measurement and Expectation

In quantum mechanics, a measurable operator, differential or algebraic, is often called the *observable*, by which the state of the physical system can be determined by a sequence of physical measurements. When a measurement of the observable  $\hat{Q}$  is made on a normalized wave function  $\psi$ , i.e.,

$$\hat{Q}\phi_n = q_n \phi_n, \quad \psi = \sum_n a_n \phi_n(\mathbf{r}),$$

the probability of obtaining the eigenvalue  $q_n$  is given by the modulus squared of the overlap integral,

$$P_r(q_n) = |a_n|^2, \quad a_n = \int_{\mathbb{R}^3} \phi_n^*(\mathbf{r})\psi(\mathbf{r})dV.$$

The operator here can be energy, linear momentum, position, angular momentum, and so forth.

Based on the occurrence probability of each eigenvalue, we can define the expectation value of the operator  $\hat{Q}$ , i.e., in an 1D case,

$$\langle Q \rangle := \sum_n P_r(q_n)q_n = \sum_n |a_n|^2q_n, \quad \text{where } a_n = \int_{\mathbb{R}} \phi_n^*(x)\psi(x)dx.$$

One can readily show that

$$\langle Q \rangle = \int_{\mathbb{R}} \psi^* \hat{Q} \psi dx,$$

this is because

$$\begin{aligned} \langle Q \rangle &= \int_{\mathbb{R}} \psi^* \hat{Q} \psi dx = \int_{real} \left[ \sum_i a_i^* \phi_i^* \right] \hat{Q} \left[ \sum_j a_j \phi_j \right] dx \\ &= \int_{real} \left[ \sum_i a_i^* \phi_i^* \right] \left[ \sum_j a_j q_j \phi_j \right] dx \quad \leftarrow \hat{Q} \phi_j = q_j \phi_j \\ &= \sum_i \sum_j a_i^* a_j q_j \int_{\mathbb{R}} \phi_i^* \phi_j dx \\ &= \sum_i |a_i|^2 q_i \quad \leftarrow \int_{\mathbb{R}} \phi_i^* \phi_j dx = \delta_{ij}. \end{aligned}$$

Now, we can write the expectation of a operator  $\hat{Q}$  as

$$\begin{aligned} \langle Q \rangle &= \int_{\mathbb{R}} \psi^* \hat{Q} \psi dx = \int_{\mathbb{R}} \left[ \sum_i a_i^* \phi_i^* \right] \hat{Q} \left[ \sum_j a_j \phi_j \right] dx \\ &= \sum_i \langle \phi_i | \langle \psi | \phi_i \rangle \hat{Q} \sum_j \langle \phi_j | \psi \rangle | \phi_j \rangle . = \langle \psi | \hat{Q} | \psi \rangle . \quad (1.27) \end{aligned}$$

If the wave function is not normalized, i.e.,  $\int \psi^* \psi dx \neq 1$ , the expectation of the operator  $\hat{Q}$  should be written as

$$\langle \hat{Q} \rangle = \frac{\langle \psi | \hat{Q} | \psi \rangle}{\langle \psi | \psi \rangle}.$$

### 1.3.8 Operator, Commutators, and Uncertainty Principle

All the operators in quantum mechanics have definite physical meanings or properties that may be measurable. The operation order of the two different quantum mechanics

operators is not commutable in general, and such incommutable property has profound physical implications. To briefly discuss this basic concept of quantum mechanics, we first define the operator commutator. Assume that there are two operators  $\hat{A}$  and  $\hat{B}$ , we define the operator commutator as the difference between the two different orderings,

$$[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A}.$$

We say that the two operators commute only if the commutator is zero. To better understand this, we now present some examples.

---

**Example 1.1** Let  $\hat{A}$  be a position operator and  $\hat{B}$  be a momentum operator:

$$\hat{A} = \hat{x} = x \quad \text{and} \quad \hat{B} = \hat{p}_x = -i\hbar \frac{\partial}{\partial x}.$$

We can find that

$$[\hat{x}, \hat{p}_x]\psi = x \left( -i\hbar \frac{\partial}{\partial x} \right) \psi - \left( -i\hbar \frac{\partial}{\partial x} \right) (x\psi) = -i\hbar x \frac{\partial \psi}{\partial x} + i\hbar x \frac{\partial \psi}{\partial x} + i\hbar \psi = i\hbar \psi, \quad (1.28)$$

which means that the position operator  $\hat{x}$  does not commute with the momentum operator  $\hat{p}_x$ , and based on the calculation,

$$[\hat{x}, \hat{p}_x] = i\hbar. \quad (1.29)$$

However, if we consider  $\hat{A} = \hat{x}$  but  $\hat{B} = \hat{p}_y$ , one may verify that

$$[\hat{x}, \hat{p}_y]\psi = x \left( -i\hbar \frac{\partial}{\partial y} \right) \psi - \left( -i\hbar \frac{\partial}{\partial y} \right) (x\psi) = 0, \quad \rightarrow \quad [\hat{x}, \hat{p}_y] = 0,$$

that is,  $\hat{x}$  and  $\hat{p}_y$  commute.

---

Note that any wave function  $\psi$  in a complex Hilbert space may be viewed as a vector in a vector space, which may be expressed in terms of eigenfunction expansion. So, a more rigorous way to write Eq. (1.28) is

$$[\hat{x}, \hat{p}_x]|\psi\rangle = i\hbar|\psi\rangle.$$

A profound consequence of  $[\hat{x}, \hat{p}_x] = i\hbar$  is the Heisenberg uncertainty principle, which is expressed in the following famous mathematical expression in quantum physics,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}, \quad (1.30)$$

where

$$\sigma_x := \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2} \quad \text{and} \quad \sigma_p := \sqrt{\langle \hat{p}_x^2 \rangle - \langle \hat{p}_x \rangle^2}.$$

We note that, in statistics  $\sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}$  is called as the standard deviation of operator  $\hat{A}$ . If  $\hat{A}$  is measurable,  $\sigma_A$  represents the accuracy of the measurement. We note that for an operator both  $\langle \hat{A}^2 \rangle$  and  $\langle \hat{A} \rangle^2$  are real numbers, because

$$\langle \hat{A} \rangle = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle} \quad \text{and} \quad \langle \hat{A}^2 \rangle = \frac{\langle \hat{A} \psi | \hat{A} \psi \rangle}{\langle \psi | \psi \rangle}$$

if we assume that  $\hat{A}$  is self-adjoint and, if the wave function is normalized, we may drop the denominator.

When we say an operator is self-adjoint, what we mean is that

$$\langle \hat{A} \psi_1 | \psi_2 \rangle = \langle \psi_1 | \hat{A} \psi_2 \rangle \quad \text{or} \quad \int_{\mathbf{R}} \hat{A}^* \psi_1^*(x) \psi_2(x) dx = \int_{\mathbf{R}} \psi_1^*(x) \hat{A} \psi_2(x) dx. \tag{1.31}$$

Most operators in quantum mechanics are self-adjoint, for instance, the Hamiltonian operator,

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}).$$

In fact, Eq. (1.31) is the definition of symmetric operator. Based on the Hellinger–Toeplitz theorem, a everywhere-defined symmetric operator in the Hilbert space is bounded and self-adjoint, and we call the self-adjoint operators in the Hilbert space as the Hermitian operator. In quantum mechanics, we are mainly dealing with Hermitian operators.

Now, by using Eq. (1.29), we prove Eq. (1.30). We first show that

$$\sigma_A^2 \sigma_B^2 \geq \left( \frac{1}{2} \langle \{\hat{A}, \hat{B}\} \rangle - \langle \hat{A} \rangle \langle \hat{B} \rangle \right)^2 + \left( \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2, \tag{1.32}$$

where

$$\{\hat{A}, \hat{B}\} := \hat{A} \hat{B} + \hat{B} \hat{A}$$

is called the anticommutator.

Assume that both  $\hat{A}$  and  $\hat{B}$  are Hermitian. The corresponding standard deviation can be written as

$$\begin{aligned} \sigma_A^2 &= \langle (\hat{A} - \langle \hat{A} \rangle) \Psi | (\hat{A} - \langle \hat{A} \rangle) \Psi \rangle = \langle f | f \rangle, \\ &\text{where } |f\rangle = |(\hat{A} - \langle \hat{A} \rangle) \Psi\rangle \\ \sigma_B^2 &= \langle (\hat{B} - \langle \hat{B} \rangle) \Psi | (\hat{B} - \langle \hat{B} \rangle) \Psi \rangle = \langle g | g \rangle, \\ &\text{where } |g\rangle = |(\hat{B} - \langle \hat{B} \rangle) \Psi\rangle \end{aligned}$$

and, by the complex version of the Cauchy–Schwartz inequality,

$$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq \langle f | g \rangle^2.$$

Note that  $\langle f | f \rangle$  and  $\langle g | g \rangle$  are real numbers, but  $\langle f | g \rangle$  may be a complex number in general, and can be shown that

$$|\langle f | g \rangle|^2 = \left( \frac{\langle f | g \rangle + \langle g | f \rangle}{2} \right)^2 + \left( \frac{\langle f | g \rangle - \langle g | f \rangle}{2i} \right)^2 \tag{1.33}$$

and

$$\langle f|g \rangle = \langle \Psi | (\hat{A} - \langle \hat{A} \rangle) (\hat{B} - \langle \hat{B} \rangle) | \Psi \rangle = \langle \hat{A} \hat{B} \rangle - \langle \hat{A} \rangle \langle \hat{B} \rangle \quad (1.34)$$

and

$$\langle g|f \rangle = \langle \Psi | (\hat{B} - \langle \hat{B} \rangle) (\hat{A} - \langle \hat{A} \rangle) | \Psi \rangle = \langle \hat{B} \hat{A} \rangle - \langle \hat{B} \rangle \langle \hat{A} \rangle. \quad (1.35)$$

Substituting Eqs. (1.34) and (1.35) into Eq. (1.33) yields the desired result:

$$\sigma_A^2 \sigma_B^2 \geq \langle f|g \rangle^2 = \left( \frac{1}{2} \langle \{\hat{A}, \hat{B}\} \rangle - \langle \hat{A} \rangle \langle \hat{B} \rangle \right)^2 + \left( \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2.$$

For the case  $\hat{A} = \hat{x}$  and  $\hat{B} = \hat{p}_x$ , we have

$$\sigma_x^2 \sigma_{p_x}^2 \geq \left( \frac{1}{2i} \langle [\hat{x}, \hat{p}_x] \rangle \right)^2 \rightarrow \sigma_x \sigma_{p_x} \geq \left| \frac{1}{2i} \langle [\hat{x}, \hat{p}_x] \rangle \right| = \left| \frac{1}{2i} \langle i\hbar \rangle \right| = \frac{\hbar}{2}.$$

This is the complete proof of the uncertainty principle.

### 1.3.9 Hydrogen Atom

Now we consider a 3D example – an electron in hydrogen atom that is floating in free space, and hence, in this case, the potential energy between the electron and nucleus is  $V(r) = -Ze^2/(4\pi\epsilon_0 r)$ , or in atomic unit  $-e^2/r$ , where  $r = |\mathbf{r}|$ . The Schrödinger equation for this problem is

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

By symmetry, the problem is being solved in spherical coordinates, and the Schrödinger equation may be cast into the following form:

$$-\frac{\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \psi(\mathbf{r}) + (V(r) - E)\psi(\mathbf{r}) = 0, \quad (1.36)$$

where  $r$  is the radial distance,  $\theta$  is the azimuthal angle (longitude),  $\phi$  is the zenith angle (colatitude), and  $\mu = m_e m_u / (m_e + m_u)$ .

We often write the quantum angular Laplacian operator as

$$\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right], \rightarrow \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2}.$$

The Schrödinger equation can then be written as

$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}), \rightarrow -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi(\mathbf{r})}{\partial r} \right) + \frac{\hat{L}^2}{2\mu r^2} \psi(\mathbf{r}) - \frac{Ze^2}{4\pi\epsilon_0 r} \psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

Equation (1.36) can be solved by successive separation of variables. In the first separation of variables, we let  $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$ . After separating  $r$ -function part from  $\theta, \phi$ -part, we have

$$\begin{aligned} & -\frac{\hbar^2}{2\mu} \frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + r^2(V(r) - E) \\ & = \frac{\hbar^2}{2\mu} \left[ \frac{1}{Y \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] \\ & = \text{const.} = -\frac{\ell(\ell + 1)\hbar^2}{2\mu}. \end{aligned} \quad (1.37)$$

The solution of the above equations will correspond to some particular constants (eigenvalues), for reasons which will be discussed later, we choose the constant as  $-\ell(\ell + 1)\hbar^2/2\mu$ , where  $\ell$  is a constant integer. The radial part of Eq. (1.37) is

$$-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\ell(\ell + 1)\hbar^2}{2\mu r^2} R - \frac{Ze^2}{4\pi\epsilon_0 r} R = ER \quad (1.38)$$

and the circumference part of Eq. (1.37) is

$$\hat{L}Y(\theta, \phi) = \ell(\ell + 1)\hbar^2. \quad (1.39)$$

In the second separation of variables, we can further factor  $Y(\theta, \phi) = P(\theta)u(\phi)$ . With this form of the solution, we can further separate the second equation of Eq. (1.39) into another two equations,

$$-\frac{1}{u} \frac{d^2 u}{d\phi^2} = \frac{\sin \theta}{P} \frac{d}{d\theta} \left( \sin \theta \frac{dP}{d\theta} \right) + \ell(\ell + 1) \sin^2 \theta = \text{const.} = m^2. \quad (1.40)$$

Again, the two equations in Eq. (1.37) equal to a same constant, which for a good reason we may denote it as  $m^2$ , and  $m$  is a constant.

The separation of variables leads to the following three (eigenvalue) ordinary differential equations,

$$r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} + \frac{2Mr^2}{\hbar^2} (E - V(r)) - \ell(\ell + 1) = 0, \quad (1.41)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dP}{d\theta} \right) + \ell(\ell + 1)P - \frac{m^2}{\sin^2 \theta} P = 0, \quad (1.42)$$

$$\frac{d^2 u}{d\phi^2} = -m^2 u. \quad (1.43)$$

The solution of Eq. (1.41) is

$$R_{n\ell}(r) = \exp(-r/na_0) \left( \frac{r}{na_0} \right)^\ell L_{n-\ell-1}^{2\ell+1} \left( \frac{2r}{na_0} \right),$$

where  $L_{n-\ell-1}^{2\ell+1}$  are the associated Laguerre polynomials, and  $a_0 = 1$  in atomic units.

The solutions of Eqs. (1.42) and (1.43) are spherical harmonics and exponential functions, which can be expressed as follows:

$$P_{\ell m} = P_{\ell}^m(\cos \theta) \quad \text{and} \quad u_m = \exp(im\phi),$$

where  $P_{\ell m}(\cos \theta)$  are the associated Legendre polynomials, and the first few associated Legendre polynomials are

$$\begin{aligned} P_0^0(x) &= 1, \quad P_1^0(x) = x, \quad P_1^1(x) = -(1-x^2)^{1/2}, \\ P_2^0(x) &= \frac{1}{2}(3x^2-1), \quad P_2^1(x) = -3x(1-x^2)^{1/2}, \dots \end{aligned}$$

and the total stationary wave function solution for a hydrogen atom is

$$\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi).$$

### 1.3.10 Spin

An electron has three basic properties: mass, charge, and spin. To understand what electron spin is, we may imagine that an electron is a charged sphere rotating around the axis of the sphere, which we usually call the  $Z$ -axis. According to classical electromagnetics, such a rotating sphere would have an angular momentum  $S$  associated with its rotational motion about the  $Z$ -axis. Moreover, since the sphere is charged, the rotating charge will give rise to a current loop. According to the classical electromagnetism, such tiny current loop will generate a magnetic dipole, and we denote its magnetic moment as  $\mu_S$ .

In quantum mechanics, spin angular momentum  $S$  can take only certain directions and discrete magnitude. In solving the Schrodinger equation for the hydrogen atom, it is found that the orbital angular momentum is quantized according to the relationship

$$L^2 = \ell(\ell + 1)\hbar^2$$

and, hence, the magnitude of the angular momentum in terms of the orbital quantum number is of the form

$$L = \sqrt{\ell(\ell + 1)}\hbar$$

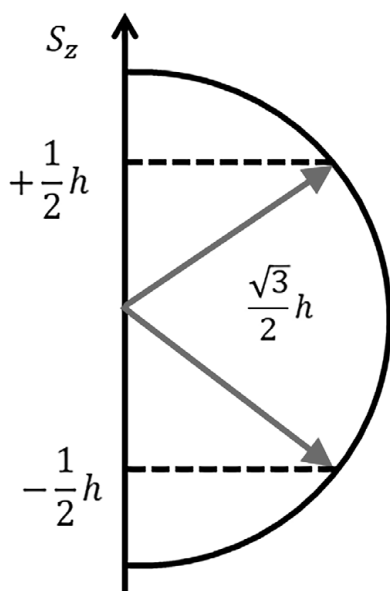
and that the  $z$ -component of the angular momentum in terms of the magnetic quantum number takes the form:

$$L_z = m_{\ell}\hbar.$$

The spin angular momentum follows the formula. The magnitude of spin angular momentum  $S$  is given by

$$S = \sqrt{s(s + 1)}\hbar,$$





**Figure 1.8**  $m_s = 1/2$ : “spin up” and  $m_s = -1/2$ : “spin down”

where  $s$  is the spin quantum number that equals to  $1/2$ . The spin direction is specified by the component of  $S$  along a  $Z$ -axis as shown in Fig. 1.8. The projection of the spin vector to the  $Z$ -axis has two possibilities:

$$S_Z = m_s \hbar = \pm \frac{1}{2} \hbar.$$

The associated magnetic moment is

$$\mu_z = \pm \frac{1}{2} g \mu_B,$$

where  $g$  is called the gyromagnetic ratio, and the electron spin  $g$ -factor has the value  $g = 2.00232$ . The electron spin can be predicted by the Dirac equation. In 1928, Paul Dirac derived a wave equation for describing the relativistic quantum wave equation of electrons. The Dirac equation is consistent with both the principles of quantum mechanics and the theory of special relativity, and the wave function is in (at least) four-dimensional (4D) space. The additional dimension provides the accommodation for spin and antimatter.

We can then introduce the spin Hermitian operator and its eigenvalues for electron spin as an analog of the orbital angular momentum operator. We denote the spin operator as  $\hat{S}$ , spin eigenfunction as  $\chi_{s,m}$ , and two spin quantum numbers as  $s$  and  $m_s$ , they are

$$\hat{S} = \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}$$

and

$$\hat{S}_x \chi_{s,m} = m_s \hbar \chi_{s,m} = \pm \frac{1}{2} \hbar \chi_{s,m_s}; \quad \hat{S}^2 \chi_{s,m} = s(s+1) \hbar^2 \chi_{s,m_s}.$$

Note that the spin wave functions  $\chi_{s,m_s}$  do not depend on the electron spatial coordinates  $r, \theta, \phi$ . They represent a purely internal degree of freedom, and we have two choices,

$$\chi_{1/2,1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_{1/2,-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

## 1.4 Interpretations of Quantum Mechanics

### 1.4.1 Uncertainty Principle

The uncertainty principle, which is also called Heisenberg's uncertainty principle, was first put forward by Werner Heisenberg (see Heisenberg (1985)) in the following expression:

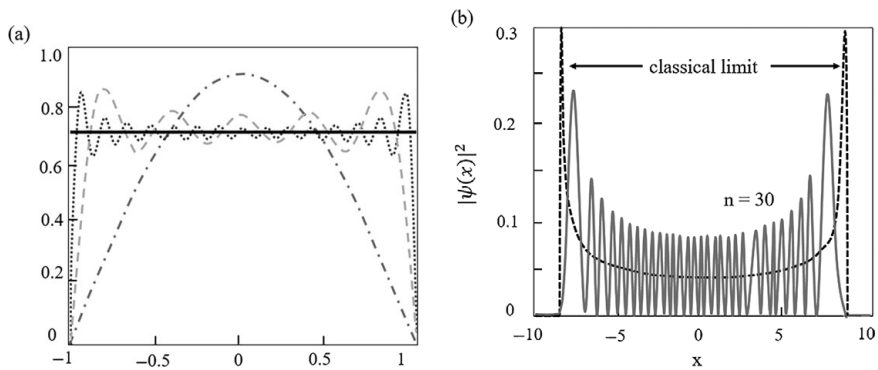
$$\sigma_r \sigma_p \geq \frac{\hbar}{2}.$$

According to Heisenberg's explanation, it indicates that in a quantum system, the more precisely the position of a particle is being measured, the less precisely can one measure its momentum and vice versa. However, from the current understanding, Heisenberg's explanation of the uncertainty principle may be a little bit misleading because it improperly emphasizes the importance of measurement interference and measurement technology. In fact, the uncertainty principle is not about measurement technology, and it is independent from technology; it is a quantum mechanics statement on correlation condition between two observables. The uncertainty principle elucidates the relation of wave-particle duality in clear mathematical terms, it also articulates the necessity of a statistical approach to the study of subatomic particles and, remarkably, it provides an explicit expression on scale transition from determinacy to indeterminacy.

The uncertainty principle provides a lower bound of the position and momentum correlation. However, that is the direct estimate. To make an estimate uncertainty relation, Niels Bohr gave a derivation of the uncertainty relations between position and momentum and between time and energy. Consider

$$E = h\nu \quad \text{and} \quad p = h/\lambda,$$

which connects the energy  $E$  and momentum  $p$  from the particle picture with those of frequency  $\nu$  and wavelength  $\lambda$  from the wave picture. Denoting the spatial and temporal extensions of the wave packet by  $\Delta x$  and  $\Delta t$ , and the extensions in the wave



**Figure 1.9** Comparison between classical probability density and amplitudes of wave functions: (a) particle in an infinite depth potential well and (b) harmonic oscillator

number and frequency by  $\Delta k$  and  $\Delta \nu$ , it then follows from Fourier analysis that, in the most favorable case,  $\Delta x \Delta k \approx \Delta t \Delta \nu \approx 1$  and one obtains the relations

$$\Delta p = h \Delta k, \quad \Delta E = h \Delta \nu \quad \rightarrow \quad \Delta t \Delta E \approx \Delta x \Delta p \approx h.$$

Note that  $\Delta x$ ,  $\Delta p$  are not the standard deviations, but unspecified measures of the size of a wave packet.

## 1.4.2 Correspondence Principle

In quantum physics, the correspondence principle (Bohr) states that the behavior of systems described by the theory of quantum mechanics reproduces classical physics in the limit of large quantum numbers. In other words, it states that, for large orbits and for large energies, quantum calculations must agree with classical calculations.

This can be demonstrated by the previous two examples, i.e., a particle in an infinite well and the quantum harmonic oscillator. From Fig. 1.9, one can find that, as the energy level increases, the profile of amplitudes of the wave function approaches the classical limit. This confirms the correspondence principle. However, for the quantum problems in which particle energy levels does not increase monotonically, how to link the microscale wave function description to the macroscale physical response is often a critical point of quantum mechanics for both theory and applications.

## 1.4.3 Pauli's Exclusion Principle

For a many-body quantum mechanical system, interchanging two particles occupying two different states should not change the probability density,  $|\Psi|^2$ , of the system. Consider a two noninteracting identical particle system. The probability density of the

two-particle wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  must be identical to that of the the wave function  $\Psi(\mathbf{r}_2, \mathbf{r}_1)$ , where the particles have been interchanged, i.e.,

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)| = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|.$$

There are two ways that this can be achieved:

1. Symmetric WF :  $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$ ;
2. Antisymmetric WF :  $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$ .

It turns out that particles whose wave functions are symmetric under particle interchange have integral or zero intrinsic spin and are termed “bosons.” Particles whose wave functions are antisymmetric under particle interchange have half-integral intrinsic spin and are termed “fermions.” Experimentation and quantum theory place electrons in the fermion category. That is the reason why we say that electrons are spin  $-1/2$  particles and are described by the antisymmetric wave function:

$$\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N).$$

Consider a two-particle noninteracting fermion system. The “noninteracting” qualifier implies the two-particle wave function can be written as the product of two single-particle wave functions. These can be written as either

$$\Psi_I(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \text{ or } \Psi_{II}(\mathbf{r}_2, \mathbf{r}_1) = \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1).$$

where  $a$  and  $b$  label two different single-particle states. Because we cannot distinguish between the particles, we cannot know which of  $\Psi_I$  or  $\Psi_{II}$ , describes the system. Consequently, we have to consider the system as being in some linear combination, or superposition of  $\Psi_I$  and  $\Psi_{II}$ . There are only two correctly normalized combinations possible:

1. Symmetric WF (bosons):  $\Psi = \frac{1}{\sqrt{2}}(\Psi_I + \Psi_{II})$ ;
2. Antisymmetric WF (fermions):  $\Psi = \frac{1}{\sqrt{2}}(\Psi_I - \Psi_{II})$ .

In the case of fermions, if  $a = b$ , then  $\Psi = 0$ , which implies that no two fermions can occupy the same state. By considering the form of wave function for a system of identical particles, we have illustrated Pauli’s exclusion principle.

#### 1.4.4 Copenhagen Interpretation

The “Copenhagen Interpretation” of quantum physics refers to the following set of statements for explanation of the meanings of quantum mechanics:

- A system is completely described by a wave function, representing the state of the system, which evolves smoothly in time, except when a measurement is made, at which point it instantaneously collapses to an eigenstate of the observable measured.

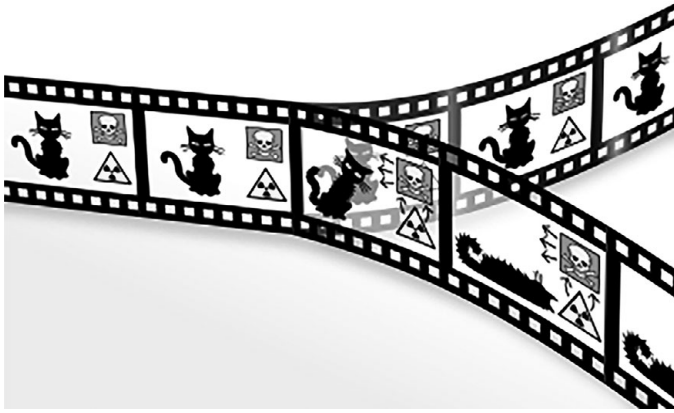
- The description of nature is essentially probabilistic, with the probability of a given outcome of a measurement given by the square of the amplitude of the wave function (Born rule, named after Max Born).
- It is not possible to know the value of all the properties of the system at the same time; those properties that are not known exactly must be described by probabilities (Heisenberg's uncertainty principle).
- Matter exhibits a wave–particle duality. An experiment can show the particle-like or wave-like properties of matter. In some experiments, both of these complementary viewpoints must be invoked to explain the results, according to the complementarity principle of Niels Bohr.
- Measuring devices are essentially classical devices and measure only classical properties such as position and momentum.
- The quantum mechanical description of large systems will closely approximate the classical description. This is the correspondence principle of Bohr and Heisenberg.

### 1.4.5 Schrödinger's Cat and Parallel Universe

The many-worlds interpretation is an interpretation of quantum mechanics that asserts the objective reality of the universal wave function and denies the actuality of wave function collapse. “Many-worlds” implies that all possible alternative histories and futures are real, each representing an actual “world” (or “universe”).

Schrödinger's cat is a thought experiment and sometimes it is described as a paradox. It was devised by Erwin Schrödinger in 1935. It illustrates what he saw as the problem of the Copenhagen interpretation of quantum mechanics when applied to everyday objects, resulting in a contradiction with common sense. The scenario presents a cat that might be alive or dead, depending on a previous random event.

One may even set up quite absurd but revealing cases where quantum mechanics, or at least the interpretation of quantum mechanics, conflicts with common sense. For example, we may consider an imaginary experiment where a cat is contained in a closed steel cage, along with a special device, in which there is a Geiger counter with a tiny amount of a radioactive substance. The amount of this radioactive substance is so small that, in the course of one hour, only one of the atoms may decay, but also with the equal probability that no atoms may decay. If the decay happens, a radiation detector will trigger the release of a hammer that will smash a glass container thereby releasing some form of poisonous gas, for instance hydrocyanic acid, killing the cat instantly. Thus, if one has left this entire system to itself for an hour, one may find that the cat may still be alive, if meanwhile no atom has decayed. On the other hand, one may also find the cat is dead, because there is an equal probability that an atom has decayed, and if there is only an atom decay, it would trigger the radioactive device and killed the cat. Therefore, the thought experiment cleverly translates a microscale quantum event described by a wave function into a macroscale event of the life-and-death experience



**Figure 1.10** Parallel universe interpretation based on Schödinger's cat paradox (Photograph courtesy of Christian Schirm and Wikipedia.org)

of a poor cat. The essence of this thought experiment is that it establishes a direct correlation between a microscale wave function (atom decay or not decay) with a macroscale state of a cat (dead or alive). Since at microscale, there is a superposed state of wave functions, accordingly it will link to a macroscale state of cat, in which both the living and the dead cat are mixed in equal parts. Such a superposed reality at macroscale may be interpreted as the superposition of two events happening in two parallel universes as shown in Fig. 1.10.

## 1.5 Homework Problems

**Problem 1.1** Consider a particle in an one-dimensional (1D) finite depth well, which obeys the Schrödinger equation,

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

where the potential energy is given as

$$V(x) = \begin{cases} V_0 & x \leq -\frac{L}{2} \\ 0 & |x| < \frac{L}{2} \\ V_0 & x \geq \frac{L}{2} \end{cases} .$$

Find all the eigenvalues (energy levels) and eigenfunctions of the solution. Discuss the solution when  $V_0 \rightarrow \infty$ .

**Problem 1.2** Consider the following time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = -\left( \frac{\hbar^2}{2m} \right) \nabla^2 \Psi + V_{eff} \Psi.$$

Make the following polar decomposition or variable separation,

$$\Psi(\mathbf{x}, t) = R(\mathbf{x}, t) \exp\left[i \frac{S(\mathbf{x}, t)}{\hbar}\right].$$

Show that the time-dependent Schrödinger equation is equivalent to the following quantum hydrodynamic system,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (1.44)$$

$$\frac{\partial S}{\partial t} + \frac{1}{2m} |\nabla S|^2 + V^{eff} + V^{qu} = 0 \quad (1.45)$$

where

$$\rho := R^2 \quad (1.46)$$

$$\mathbf{v} := \nabla \left( \frac{S}{m} \right) \quad (1.47)$$

$$\begin{aligned} V^{qu} &:= -\left( \frac{\hbar^2}{2m} \right) \frac{\nabla^2 R}{R} \\ &= -\left( \frac{\hbar^2}{2m} \right) \left( \nabla^2 \log R + |\nabla \log R|^2 \right) \end{aligned} \quad (1.48)$$

or, in terms of  $\rho$ ,

$$V^{qu} = \left( -\frac{\hbar^2}{4m\rho} \right) \left[ \nabla^2 \rho - \frac{1}{2\rho} (\nabla \rho) \cdot (\nabla \rho) \right]. \quad (1.49)$$

Equation (1.44) is an analog of conventional mass conservation law of continuum fluid dynamics.

**Problem 1.3** Consider a particle in a box (1D), which obeys the following Schrödinger equation,

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right) \Psi(x, t) = -\hbar \frac{\partial}{\partial t} \Psi(x, t)$$

with the time-independent part,

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

where

$$V(x) = \begin{cases} \infty, & x \leq -\frac{L}{2} \\ 0, & |x| < \frac{L}{2} \\ \infty, & x \geq \frac{L}{2} \end{cases}.$$

Assume that the initial condition of the wave function is,

$$\Psi(x, 0) = A \sin\left(\frac{2\pi x}{L}\right), \quad A \text{ is given.}$$

Find

$$\langle x \rangle, \quad \langle p_x \rangle, \quad \text{and} \quad \langle H \rangle?$$

**Problem 1.4** Consider the angular momentum operator,  $\hat{\mathbf{L}} = -i\hbar \mathbf{r} \times \nabla$ :

$$\hat{L}_x = -i\hbar \left[ y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right], \quad \hat{L}_y = -i\hbar \left[ z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right], \quad \text{and} \quad \hat{L}_z = -i\hbar \left[ x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right].$$

Calculate the operator commutator,

$$[\hat{L}_x, \hat{L}_y] = ?$$

**Problem 1.5** Define the standard deviation of two Hermitian operators,  $\hat{A}$  and  $\hat{B}$ , as:

$$\sigma_A = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2} \quad \text{and} \quad \sigma_B = \sqrt{\langle \hat{B}^2 \rangle - \langle \hat{B} \rangle^2}.$$

Show that

$$\sigma_A^2 = \langle (\hat{A} - \langle \hat{A} \rangle) \Psi | (\hat{A} - \langle \hat{A} \rangle) \Psi \rangle = \langle f | f \rangle,$$

$$\text{where } |f\rangle := |(\hat{A} - \langle \hat{A} \rangle) \Psi\rangle$$

$$\sigma_B^2 = \langle (\hat{B} - \langle \hat{B} \rangle) \Psi | (\hat{B} - \langle \hat{B} \rangle) \Psi \rangle = \langle g | g \rangle,$$

$$\text{where } |g\rangle := |(\hat{B} - \langle \hat{B} \rangle) \Psi\rangle$$

and

$$\langle f | g \rangle = \langle \hat{A} \hat{B} \rangle - \langle \hat{A} \rangle \langle \hat{B} \rangle$$

$$\langle g | f \rangle = \langle \hat{B} \hat{A} \rangle - \langle \hat{B} \rangle \langle \hat{A} \rangle. \quad (1.50)$$

Let  $\hat{A} = \hat{x}$  and  $\hat{B} = \hat{p}_x$  and use the Cauchy–Schwartz inequality to show that

$$\sigma_x \sigma_{p_x} \geq \frac{\hbar}{2},$$

considering the fact that, for the complex number  $\langle f | g \rangle$ ,

$$|\langle f | g \rangle|^2 = \left( \frac{\langle f | g \rangle + \langle g | f \rangle}{2} \right)^2 + \left( \frac{\langle f | g \rangle - \langle g | f \rangle}{2i} \right)^2.$$