

Quantum mechanics

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The Wave Function

1.1 The Schrödinger Equation

In classical mechanics, the total energy E of a particle can be written as

$$E = \frac{1}{2}mv^2 + V(x) = \frac{p^2}{2m} + V(x). \quad (1.1)$$

Since we know that all particles are actually waves of frequency ω and wavenumber \mathbf{k} , so eq. (1.1) becomes

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V(x). \quad (1.2)$$

We now introduce the wave function of a particle Ψ as

$$\Psi(\mathbf{r}, t) = Ae^{i(\mathbf{k}\mathbf{r} - \omega t)}. \quad (1.3)$$

In one-dimensional case, eq. (1.3) reduces to

$$\Psi(x, t) = Ae^{i(kx - \omega t)}. \quad (1.4)$$

where $|\Psi(x, t)|^2 dx$ is the probability of finding the particle between x and $x + dx$ at time t (so Ψ is actually a probability density function) and A is chosen such that Ψ is normalized, *i.e.*,

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1. \quad (1.5)$$

Noting that $\partial\Psi/\partial t = -i\omega\Psi$ and $\partial^2\Psi/\partial x^2 = -k^2\Psi$, Ψ times eq. (1.2) becomes

$$\Psi\hbar\omega = \Psi\left(\frac{\hbar^2 k^2}{2m} + V(x)\right) = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi \quad (1.6)$$

Rearranging, we obtain the Schrödinger equation¹

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi. \quad (1.7)$$

The Schrödinger equation in quantum mechanics plays a similar role to Newton's second law in classical mechanics. Given suitable initial conditions (typically, $\Psi(x, 0)$), the Schrödinger equation determines $\Psi(x, t)$ for all future time, just as Newton's second law determines $x(t)$ for all future time.

Example: Wave Function Remains Normalized.

Question: Show that once the wave function is normalized at $t = 0$, it remains normalized for any later time.

Solution: Consider

$$\frac{\partial}{\partial t} |\Psi|^2 = \frac{\partial}{\partial t} (\Psi^* \Psi) = \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}, \quad (1.8)$$

since $\partial \Psi / \partial t$ is given in the Schrödinger equation (eq. (1.7)), while $\partial \Psi^* / \partial t$ can be found by taking the complex conjugate of the Schrödinger equation (by changing the sign of the exponential in eq. (1.3)), we have

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + V\Psi^*. \quad (1.9)$$

Therefore

$$\begin{aligned} \frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx &= \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx \\ &= \int_{-\infty}^{\infty} (\Psi^* (\frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V\Psi^*) + \Psi (-\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V\Psi^*)) dx \\ &= \int_{-\infty}^{\infty} \frac{i\hbar}{2m} (\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^*}{\partial x^2}) dx \\ &= \frac{i\hbar}{2m} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) dx \\ &= \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \Big|_{-\infty}^{+\infty} = 0. \end{aligned} \quad (1.10)$$

where in the last equality we invoked the fact that Ψ and Ψ^* must go to zero as x goes to ∞ otherwise the wave function will not be normalizable.

Therefore, since $\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 0$, it implies that $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx$ is a constant. But we know that $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx$ at $t = 0$ is 1. Therefore the wave function remains normalized all the time.

¹Some call this the time-dependent Schrödinger equation, in contrast with the time-independent Schrödinger equation that we will encounter later (in which case the term on the LHS is replaced by $E\psi$), but in most cases we will refer both simply by Schrödinger equation, as the distinction is clear.

Example: Effect to the Wave Function by adding a Constant Potential.

Question: Show that the effect of adding a constant potential V_0 introduce an extra phase $V_0 t/\hbar$ to the wave function.

Solution: By substituting $\Psi_0 = \Psi e^{-iV_0 t/\hbar}$ into the Schrödinger equation with potential $V + V_0$, where Ψ satisfies the normal Schrödinger equation with potential V , we can verify that Ψ_0 indeed satisfies the modified Schrödinger equation:

$$\begin{aligned} i\hbar \frac{\partial \Psi_0}{\partial t} &= i\hbar \frac{\partial \Psi}{\partial t} e^{-iV_0 t/\hbar} + i\hbar \Psi \left(-\frac{iV_0}{\hbar} \right) e^{-iV_0 t/\hbar} \\ &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \right] e^{-iV_0 t/\hbar} + V_0 \Psi e^{-iV_0 t/\hbar} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_0}{\partial x^2} + (V + V_0) \Psi_0. \end{aligned} \quad (1.11)$$

This, however has no effect on the average value of other dynamical variables such as momentum as the extra phase is independent of x , so it vanishes after the absolute value of the wave function is taken.

Example: Potential for a Wave Function.

Question: Consider the wave function $\Psi = Ae^{-a(mx^2/\hbar)+it}$. Find $V(x)$ such that this is a solution to Schrödinger equation. Then confirm the uncertainty principle by calculating σ_x and σ_p .

Solution: From the wave function given, we obtain

$$\frac{\partial \Psi}{\partial t} = -ia\Psi, \quad \frac{\partial \Psi}{\partial x} = -\frac{2amx}{\hbar}\Psi \quad (1.12)$$

and

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{2am}{\hbar}(\Psi + x \frac{\partial \Psi}{\partial x}) = -\frac{2am}{\hbar}(1 - \frac{2amx^2}{\hbar})\Psi. \quad (1.13)$$

From the Schrödinger equation, we have

$$V\Psi = i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar(-ia\Psi) + \frac{\hbar^2}{2m}(-\frac{2am}{\hbar})(1 - \frac{2amx^2}{\hbar})\Psi = 2a^2mx^2\Psi. \quad (1.14)$$

So $V(x) = 2ma^2x^2$.

To obtain σ_x and σ_p , we have to first normalize the function by requiring

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = |A|^2 \int_{-\infty}^{\infty} e^{-\frac{2amx^2}{\hbar}} dx = |A|^2 \sqrt{\frac{\pi\hbar}{2am}} \quad (1.15)$$

since the absolute value of $Aee^{i\theta}$ is simply A . So $A = (2am/\pi\hbar)^{\frac{1}{4}}$.

Now $\langle x \rangle, \langle x^2 \rangle, \langle p \rangle$ and $\langle p^2 \rangle$ can be straightforwardly calculated from integrations to get $\langle x \rangle = \langle p \rangle = 0$ as expected, $\langle x^2 \rangle = \hbar/4am$ and $\langle p^2 \rangle = am\hbar$.

Therefore

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{\hbar}{4am}}, \quad \sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{am\hbar} \implies \sigma_x \sigma_p = \frac{\hbar}{2}, \quad (1.16)$$

which is just consistent with the uncertainty principle.

1.2 The Copenhagen interpretation

In this set of notes, we adopt the Copenhagen interpretation of quantum mechanics, as it is the most widely recognized view in today's physics's landscape.

According to this view, as long as nothing tries to interact with the particle, it is on every possible position allowed by its wave function each with the probability $|\Psi(x, t)|^2 dx$ for position located between x and $x + dx$. Upon measurement, however, the wave function collapses.

Here, we have to be very careful with the term “measurement” and “collapses”. A “measurement” is broadly defined as any interaction with the wave function that eliminate some possibilities of its possible location. “Collapses” thus implies some possible positions of electrons are eliminated.

In ideal case, the wave function is localized at a point in space and becomes a dirac delta function. Soon, however, it spreads out according to the Schrödinger equation. In other cases, however, the wave function **partially collapses** and we are only certain that the particle is located at a certain range of positions but also not located at a certain range of positions.

This idea is best illustrated by the double slit experiment:

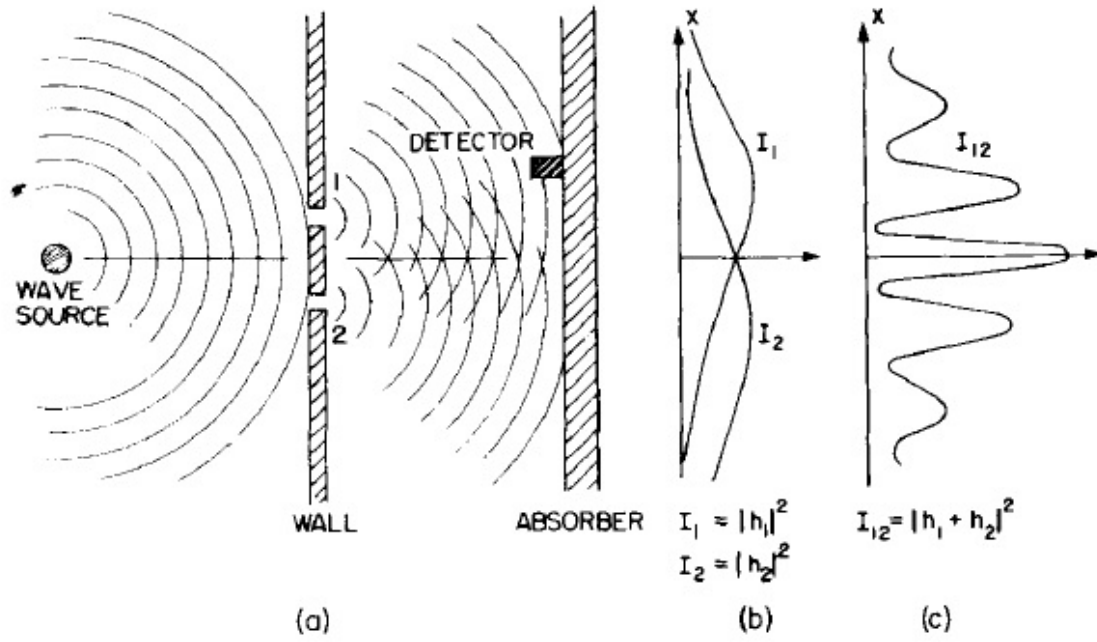


Figure 1.1

Consider one electron² that is emitted by the source. When its wave function reaches the slits, the wave function evolves as shown in fig. 1.1. If we probe the intermediate screen (where the slits are located), the wave function will collapse to either state:

1. a state where the particle hits the intermediate screen and we see a spot on the intermediate screen, or
2. a state where the electron passes through the slits.

In the latter state, however, we still have no idea which slit the electron has passed through, therefore the electron is still simultaneously passing through both slits. Then, from the Huygen's principle we can regard the wave function as two secondary waves with origin located at the slits. These two waves superpose each other and thus at the screen, the wave function looks like an diffraction plus an interference pattern (Ψ in this case is analogous to E in optic's interference). If the electron random picks a position according to this probability distribution function, then as the number of electrons emitted becomes sufficiently large, an interference pattern will be shown on the screen.

However, by measuring which slit the electron goes through, the wave function of the electron becomes only one secondary wave with origin located at one of the slit. And the resulting wave function at the screen for the electron will be reminiscent of the diffraction pattern in ordinary optics without interference. As the number of electrons becomes sufficiently large, then an overlapping pattern (superposition) of diffraction from the two slits will be shown on screen.

From a mathematical standpoint, the discrepancy arise from the fact that $|\Psi_1 + \Psi_2|^2 \neq |\Psi_1|^2 + |\Psi_2|^2$. In optics, this is analogous to the fact that the last term in $I_{12} = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos(\phi_2 - \phi_1)$ doesn't exist when there is no interference.

²Here electron is just a replacement of photon just to illustrates the fact that any particle is a wave.

From a philosophical standpoint, this result has profound impact on how observation correlates to reality. This quantum effect begs to answer the famous philosophical question “If a tree falls in a forest and no one is around to hear it, does it make a sound?”. And the answer seems to be that as long as we are not certain that something happen (upon measurement), every possibilities remain possible. During the flight of the electron, it must have collided with some air particles in its way that forces it to localize at a point. However, as long as we don’t probe the air particles, we don’t know whether that have been collided with the electron and thus the electron remains in all possible paths.

1.3 Momentum and Hamiltonian Operators

The expected value of momentum $\langle p \rangle$ can be defined identically as in classical mechanics as $\langle p \rangle = m\langle v \rangle = m d\langle x \rangle / dt$, where $d\langle x \rangle / dt$ can be computed straightforwardly as

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \int_{-\infty}^{\infty} \frac{\partial}{\partial t} x |\Psi|^2 dx = \frac{i\hbar}{2m} \int_{-\infty}^{\infty} x \frac{\partial}{\partial x} (\Psi^* \frac{d\Psi}{dx}) dx \\ &= -\frac{i\hbar}{2m} \int_{-\infty}^{\infty} (\Psi^* \frac{d\Psi}{dx} - \Psi \frac{d\Psi^*}{dx}) dx = -\frac{i\hbar}{m} \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx, \end{aligned} \quad (1.17)$$

where we used the result in eq. (1.10) in the second equality and have performed integration by part twice at the end.

Therefore,

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \left[-i\hbar \frac{\partial}{\partial x} \right] \Psi dx. \quad (1.18)$$

and $[i\hbar \partial / \partial x]$ is called the momentum operator.

Together with the position operator (which is simply x) that calculates the expected position of the particle, for any quantity $Q(x, p)$ that is a function of the position and the momentum, such as angular momentum and kinetic energy, the expected value or the average value can be simply calculated by

$$\langle Q(x, p) \rangle = \int_{-\infty}^{\infty} \Psi^* \left[\hat{Q} \left(x, -i\hbar \frac{\partial}{\partial x} \right) \right] \Psi dx, \quad (1.19)$$

where \hat{Q} is the corresponding operator, which is just Q but with momentum p replaced by the momentum operator $-i\hbar \partial / \partial x$.

For example, the total energy (or the Hamiltonian) of a particle with momentum p at position x is given by $H(x, p) = p^2 / 2m + V(x)$, so the corresponding Hamiltonian operator is $\hat{H} = -(\hbar^2 / 2m) \partial^2 / \partial x^2 + V(x)$ and the expected value of the total energy is

$$\langle H(x, p) \rangle = \int \psi^* \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi dx. \quad (1.20)$$

Example: Ehrenfest's Theorem.**Question:** Calculate $\partial\langle p\rangle/\partial t$.**Solution:** Since

$$\begin{aligned}
\frac{\partial}{\partial t} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) &= \frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial}{\partial x} \left(\frac{\partial \Psi}{\partial t} \right) \\
&= \left[-\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^* \right] \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi \right] \quad (1.21) \\
&= \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial^3 \Psi}{\partial x^3} - \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} \right] + \frac{i}{\hbar} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x} (V \Psi) \right],
\end{aligned}$$

Therefore

$$\begin{aligned}
\frac{\partial \langle p \rangle}{\partial t} &= -i\hbar \int_{-\infty}^{\infty} \frac{\partial}{\partial t} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx \\
&= -i\hbar \int_{-\infty}^{\infty} \left(\frac{i\hbar}{2m} \left[\Psi^* \frac{\partial^3 \Psi}{\partial x^3} - \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} \right] + \frac{i}{\hbar} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x} (V \Psi) \right] \right) dx \\
&= (-i\hbar) \left(\frac{i\hbar}{2m} \right) \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} \Big|_{-\infty}^{+\infty} - \left(\frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{\infty} \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} dx \right) \right. \\
&\quad \left. - \int_{-\infty}^{\infty} \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} dx \right) + (-i\hbar) \left(\frac{i}{\hbar} \right) \int_{-\infty}^{\infty} \left(V \Psi^* \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial V}{\partial x} \right) dx \\
&= 0 + \int_{-\infty}^{\infty} -\Psi \Psi^* \frac{\partial V}{\partial x} dx = \left\langle -\frac{\partial V}{\partial x} \right\rangle. \quad (1.22)
\end{aligned}$$

which is almost identical to the classical result that predicts

$$\frac{\partial \langle p \rangle}{\partial t} = -\frac{\partial}{\partial x} V(\langle x \rangle) \quad (1.23)$$

according to Ehrenfest's theorem.

Example: Classical Formalism of Quantum Mechanics.

Question: In this question, we try to model the behaviour of wave function with classical formalism. Consider a classical particle with energy E in a potential well $V(x)$ of the case of simple harmonic oscillator where $V(x) = \frac{1}{2}kx^2$ and find $\rho(x), \rho(p), \langle x^2 \rangle, \langle p^2 \rangle, \sigma_x$ and σ_p , where $\rho(x)dx$ and $\rho(p)dp$ are the probability of the particle located at x and have the a momentum p if we choose a random instant.

Solution: The speed of the particle is

$$V(x) = \sqrt{\frac{2}{m}(E - V(x))} = \sqrt{\frac{2}{m}(E - \frac{1}{2}kx^2)}. \quad (1.24)$$

The period of the particle is $T = 2\pi\sqrt{m/k}$.

So the probability density function $\rho(x)$ can be found by

$$\rho(x)dx = \frac{dt}{\frac{T}{2}} = \frac{2dx}{v(x)T} \quad (1.25)$$

If we let $-a$ and a to be the end points of the particle, then $E = ka^2/2$ and

$$\rho(x) = \frac{2}{T} \frac{1}{\sqrt{\frac{2}{m}(E - \frac{1}{2}kx^2)}} = \frac{1}{\pi\sqrt{a^2 - x^2}}. \quad (1.26)$$

So

$$\langle x^2 \rangle = 2 \int_0^a \frac{x^2 dx}{\pi\sqrt{a^2 - x^2}} = \frac{E}{k} \quad (1.27)$$

and

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\langle x^2 \rangle} = \sqrt{\frac{E}{k}}. \quad (1.28)$$

For the probability density function of with respect to momentum $\rho(p)$,

$$\rho(p)dp = \frac{dt}{T} = \frac{dx}{v(x)T}. \quad (1.29)$$

Quantum entanglement is not “affect”, since it is based on conservation law, if one up the other must be down, but state of anyone of them not known before-hand.

Separation of Variables

2.1 The General Approach

To solve for the wave function of a particle, we look for the solution in the form of

$$\Psi(x, t) = \psi(x)\varphi(t). \quad (2.1)$$

Substituting into the Schrödinger equation and divide through $\Psi = \psi\varphi$, we have

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V. \quad (2.2)$$

Since the LHS and RHS of the above equation is a function of t and x alone, respectively, they must a constant of t and x , which we call it E (for it is actually the energy of the particle). We thus have

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = E \implies \varphi(t) = e^{-\frac{iEt}{\hbar}} \quad (2.3)$$

for the t dependence and for the x dependence we have to solve for $\psi(x)$ in the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = \hat{H}\psi = E\psi, \quad (2.4)$$

where \hat{H} is the Hamiltonian operator defined in eq. (1.20).

There are a few properties of separable solutions that make them special. Firstly, the probability density of the position

$$|\Psi(x, t)|^2 = \Psi^* \Psi = \psi^* e^{+\frac{iEt}{\hbar}} \psi e^{-\frac{iEt}{\hbar}} = |\psi(x)|^2 \quad (2.5)$$

is independent of time, and so does any expected values which are functions of position and momentum from eq. (1.19).

Secondly, the total energy is definite. With eq. (2.4) in hand, the expected value of the total energy is

$$\langle H \rangle = \int \psi^* \hat{H} \psi dx = E \int |\psi|^2 dx = E \int |\Psi|^2 dx = E. \quad (2.6)$$

By computing the expected value of H^2 , which is $\langle H^2 \rangle = E^2$, one can conclude that the variance of H

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0, \quad (2.7)$$

which means that every measurement of the total energy is certain to return the value E .

Lastly, the general solution of $\Psi(x, t)$ is a linear combination of the separable solutions, each with its own allowed energy E_n

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}}, \quad (2.8)$$

where the linearity coefficients c_n have the significance that $|c_n|^2$ is the probability that a measurement of the energy would return the value E_n .¹

Therefore we have

$$\begin{aligned} 1 &= \int |\Psi(x, 0)|^2 dx = \int \left(\sum_{m=1}^{\infty} c_m \psi_m(x) \right)^* \left(\sum_{n=1}^{\infty} c_n \psi_n(x) \right) dx \\ &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \int \psi_m(x)^* \psi_n(x) dx \\ &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_m^* c_n \delta_{mn} = \sum_{n=1}^{\infty} |c_n|^2, \end{aligned} \quad (2.9)$$

and also

$$\begin{aligned} \langle H \rangle &= \int \Psi^* \hat{H} \Psi dx = \int \left(\sum_{m=1}^{\infty} c_m \psi_m \right)^* \hat{H} \left(\sum_{n=1}^{\infty} c_n \psi_n \right) dx \\ &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_m^* c_n E_n \int \psi_m^* \psi_n dx = \sum_{n=1}^{\infty} |c_n|^2 E_n. \end{aligned} \quad (2.10)$$

¹It is incorrect to say that $|c_n|^2$ is the probability that the particle is in the n^{th} stationary state, since the particle is in state Ψ , but not Ψ_n , so you never find the particle to be in a particular state, you only measure some observable quantities such as the energy of the particle, a number, but not a wave function.

2.2 Infinite Square Well

Suppose we have the potential

$$V(x) = \begin{cases} 0, & 0 \leq x \leq a, \\ \infty, & \text{otherwise.} \end{cases} \quad (2.11)$$

Outside the well, $\psi(x) = 0$. Inside the well, eq. (2.4) reads

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad k \equiv \frac{\sqrt{2mE}}{\hbar}, \quad (2.12)$$

where we have subtly assumed that $E \geq 0$.

Together with the boundary conditions $\psi(0) = \psi(a) = 0$, the solution is

$$\psi_n(x) = A \sin(k_n x), \quad k_n = \frac{n\pi}{a}, \quad n = 1, 2, 3, \dots \quad (2.13)$$

Curiously, the boundary condition at $x = a$ does not determine the constant A , but rather the constant k , and hence the possible values of $E_n = n^2\pi^2\hbar^2/2ma^2$.

To find A , we normalize Ψ (or ψ)

$$\int_0^a |A|^2 \sin^2(kx) dx = |A|^2 \frac{a}{2} = 1 \implies A = \sqrt{\frac{2}{a}}. \quad (2.14)$$

The coefficients c_n in eq. (2.8) can be calculated via the Fourier's trick, as

$$c_n = \int \Psi_n(x, 0)^* \Psi(x, 0) dx, \quad (2.15)$$

since the functions $\Psi_n(x, 0)$ are orthogonal and complete.

2.3 Harmonic Oscillator

Suppose the potential is now

$$V(x) = \frac{1}{2}m\omega^2 x^2. \quad (2.16)$$

From eq. (2.4) we now have

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi. \quad (2.17)$$

There are two ways which we can solve this Schrödinger equation, as we will show below

2.3.1 Algebraic Method

Before we start solving the Schrödinger equation, we introduce the commutator

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}, \quad (2.18)$$

which measures how badly the operators \hat{A} and \hat{B} fail to commute.

For the pair of operators x and \hat{p} , we have

$$(x\hat{p} - \hat{p}x)f(x) = x(-i\hbar)\frac{df}{dx} - (i\hbar)\frac{d}{dx}(xf) = i\hbar f(x) \implies [x, \hat{p}] = i\hbar, \quad (2.19)$$

which is known as the canonical commutation relation.

To solve the Schrödinger equation, we first rewrite eq. (2.17) as

$$\frac{1}{2m} [\hat{p}^2 + (m\omega x)^2] \psi = \hat{H}\psi = E\psi. \quad (2.20)$$

The idea now is to factorize the Hamiltonian, by introducing the operators

$$\hat{a}_{\pm} \equiv \frac{1}{\sqrt{2\hbar m\omega}} (\pm i\hat{p} + m\omega x),^2 \quad (2.21)$$

whose product is

$$\hat{a}_- \hat{a}_+ = \frac{1}{2\hbar m\omega} (\hat{p}^2 + (m\omega x)^2) - \frac{i}{2\hbar} [x, \hat{p}] = \frac{1}{\hbar\omega} \hat{H} + \frac{1}{2}. \quad (2.22)$$

So the Schrödinger equation becomes

$$\hbar\omega \left(\hat{a}_{\pm} \hat{a}_{\mp} \pm \frac{1}{2} \right) \psi = E\psi. \quad (2.23)$$

Writing the Schrödinger equation in this form, we can see that if ψ satisfies the Schrödinger equation with energy E , then $\hat{a}_{\pm}\psi$ satisfies the Schrödinger equation with energy $E \pm \hbar\omega$, since

$$\begin{aligned} \hat{H}(\hat{a}_{\pm}\psi) &= \hbar\omega \left(\hat{a}_{\pm} \hat{a}_{\mp} + \frac{1}{2} \right) (\hat{a}_{\pm}\psi) = \hbar\omega \left(\hat{a}_{\pm} \hat{a}_{\mp} \hat{a}_{\pm} + \frac{1}{2} \hat{a}_{\pm} \right) \psi \\ &= \hbar\omega \hat{a}_{\pm} \left(\hat{a}_{\mp} \hat{a}_{\pm} + \frac{1}{2} \right) \psi = \hat{a}_{\pm} \left(\hbar\omega \left(\hat{a}_{\pm} \hat{a}_{\mp} + 1 + \frac{1}{2} \right) \psi \right) \\ &= \hat{a}_{\pm} (\hat{H} + \hbar\omega) \psi = \hat{a}_{\pm} (E + \hbar\omega) \psi = (E + \hbar\omega) (\hat{a}_{\pm}\psi), \end{aligned} \quad (2.24)$$

²The motivation is that $u^2 + v^2 = (iu + v)(-iu - v)$ can be easily factorized, but now we extend this to operators.

where in the last equality of the second line we used that fact that $\hat{a}_\mp \hat{a}_\pm = \hat{a}_\pm \hat{a}_\mp + 1$, since $[\hat{a}_-, \hat{a}_+] = 1$.

This means that as long as we find one solution, we can find all the solutions using the ladder operators \hat{a}_\pm . Of course, we will not be able to apply the lowering operator \hat{a}_- repeatedly to reach a state with energy less than zero. There occurs a lowest energy state (called the ground state) ψ_0 such that

$$\hat{a}_- \psi_0 = 0 \implies \psi_0 = A e^{-\frac{m\omega}{2\hbar} x^2} = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar} x^2}, \quad (2.25)$$

which corresponds the state with energy $E_0 = \hbar\omega/2$, and we would only get $\psi = 0$ no matter how many times we apply the lowering operator \hat{a}_- to ψ_0 .

With our foot now planted on the ground state, the solution of the Schrödinger equation is now clear as

$$\psi_n(x) = A_n (\hat{a}_+)^n \psi_0(x), \quad E_n = \left(n + \frac{1}{2} \right) \hbar\omega. \quad (2.26)$$

To find A_n , we first note that

Formalism of Quantum Mechanics

3.1 Hilbert Space

The vector space (called the Hilbert space)¹, which contain all wave functions, is the set of all square integrable functions, *i.e.*, all functions $f(x)$ such that

$$\int_a^b |f(x)|^2 dx \leq \infty \quad (3.1)$$

The inner product of two functions in the Hilbert space is defined as

$$\langle f|g \rangle \equiv \int_a^b f(x)^* g(x) dx. \quad (3.2)$$

To represent a possible physical state, however, the wave function Ψ must be normalized by

$$\langle \Psi|\Psi \rangle = \int_a^b |\Psi|^2 dx = 1, \quad (3.3)$$

which is similar to how we almost always only refer to the normalized eigenvector as “the eigenvector” of a matrix.

The main difference between Hilbert space and ordinary vector space is that Hilbert space has infinite dimension while ordinary vector space has finite dimension. Consequently, a matrix can be hardly defined in Hilbert Space. Instead, a linear transformation is represented by an operator.

¹Mathematically, a Hilbert space is a complete inner product space, and the collection of square-integrable functions is only one example of a Hilbert space.

3.2 Observables

3.2.1 Hermitian Operators

The expectation value of an observable $Q(x, p)$ can be obtained by acting the corresponding operator \hat{Q} on Ψ as

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi dx = \langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle, \quad (3.4)$$

where we did not need to take the complex conjugate when switching the order of the inner product since observables must be real.

An operator \hat{Q} satisfying such condition is called an hermitian operator, and it can be proved that hermitian operators satisfy an even more general condition

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle. \quad (3.5)$$

For example, the momentum operator is hermitian since

$$\langle f | \hat{p} g \rangle = \int_{-\infty}^{\infty} f^* \left(-i\hbar \frac{dg}{dx} \right) dx = -i\hbar f^* g \Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \left(-i\hbar \frac{df}{dx} \right)^* g dx = \langle \hat{p} f | g \rangle, \quad (3.6)$$

where we threw away the boundary term because if $f(x)$ and $g(x)$ are square integrable, they must go to zero at $\pm\infty$.

Analogously, we call a matrix A hermitian if $\langle \mathbf{u}, A\mathbf{v} \rangle = \mathbf{u}^\dagger A\mathbf{v} = (A^\dagger \mathbf{u})^\dagger \mathbf{v} = \langle A\mathbf{u}, \mathbf{v} \rangle$.

3.2.2 Determinate States

A state represented by the wave function Ψ is a determinate state for the observable Q if every measurement of Q is certain to return the same value. This is equivalent to saying that the standard deviation of Q is zero

$$\sigma_Q^2 = \langle (Q - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - \langle Q \rangle)^2 \Psi \rangle = \langle (\hat{Q} - \langle Q \rangle) \Psi | (\hat{Q} - \langle Q \rangle) \Psi \rangle = 0, \quad (3.7)$$

where we used eq. (3.4) in the second equality, and the property of the hermitian operator $\hat{Q} - \langle Q \rangle$ in the second to last equality.

But the only vector whose inner product with itself vanishes is 0, so

$$\hat{Q} \Psi = \langle Q \rangle \Psi. \quad (3.8)$$

This is the eigenvalue equation for the operator \hat{Q} , where $\langle Q \rangle$ is the corresponding eigenvalue and Ψ is an eigenfunction of \hat{Q} . The collection of all the eigenvalues (there are infinite the same way a $n \times n$ matrix has n eigenvalues, but now $n \rightarrow \infty$) is called the spectrum of the eigenfunction.

3.3 Eigenfunctions of a Hermitian Operator

3.3.1 Discrete Spectra

The Spectrum of an operator is discrete if the eigenvalues are separated from one another, *e.g.*, integers. If this is the case, the eigenfunctions lie in Hilbert space and constitute physically realizable states.

3.4 Generalized Statistical Interpretation

If you measure an observable $Q(x, p)$ on a particle in the state $\Psi(x, t)$, you are certain to get one of the eigenvalues of the hermitian operator $\hat{Q}(x, -i\hbar d/dx)$.² If the spectrum of \hat{Q} is discrete, the probability of getting the particular eigenvalue q_n associated with the eigenfunction $f_n(x)$ is

$$p_n = |c_n|^2, \quad c_n = \langle f_n | \Psi \rangle. \quad (3.9)$$

If the spectrum is continuous, with real eigenvalues $q(z)$ and eigenfunctions $f_z(x)$, then the probability of getting a result in the range dz is

$$p_n = |c(z)|^2 dz, \quad c_z = \langle f_z | \Psi \rangle. \quad (3.10)$$

Upon measurement, the wave function collapses to the coresponding eigenstate.³

²If Q involves, say, the product xp , we need other consideration to determine whether we should write $\hat{x}\hat{p}$ or $\hat{p}\hat{x}$.

³In the case of continuous spectra the collapse is to a narrow range about the measured value, depending on the precision of the measuring device.