Time-Independent Schrödinger Equation

1. Stationary States

In the Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi, \tag{1}$$

we assume that the potential $V(x)$ is time-independent, i.e., $V = V(x)$, in which case the wave function $\Psi(x,t)$ can be separated into two parts:

$$\Psi(x,t) = \psi(x)\varphi(t). \tag{2}$$

For separated wave functions, we have

$$\begin{aligned}\frac{\partial\Psi}{\partial t} &= \psi\frac{\partial\varphi}{\partial t},\\ \frac{\partial^2\Psi}{\partial x^2} &= \frac{\partial^2\psi}{\partial x^2}\varphi,\end{aligned} \tag{3}$$

thus the Schrödinger equation becomes

$$i\hbar\psi\frac{\partial\varphi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}\varphi + V\psi\varphi. \tag{4}$$

Dividing both sides by $\psi\varphi$, we get

$$i\hbar\frac{1}{\varphi}\frac{\mathrm{d}\varphi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V. \tag{5}$$

Since the left-hand side of the equation depends only on t and the right-hand side depends only on x, both sides must be equal to a constant, which we denote by E:

$$i\hbar\frac{1}{\varphi}\frac{\mathrm{d}\varphi}{\mathrm{d}t} = E, \tag{6}$$

or,

$$\frac{\mathrm{d}\varphi}{\mathrm{d}t} = -\frac{iE}{\hbar}\varphi, \tag{7}$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V = E, \tag{8}$$

or

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi. \tag{9}$$

Then we have turned the Schrödinger equation, a partial differential equation, into two ordinary differential equations, (7) and (9).
The solution to (7) is

$$\varphi(t) = e^{-\frac{iEt}{\hbar}}, \tag{10}$$

as we care only about the product $\Psi(x,t) = \psi(x)\varphi(t)$. The equation (9) is called the time-independent Schrödinger equation.
There are three important properties of the solutions to the time-independent Schrödinger equation:

1. They are stationary states. Although the wave function itself,

$$\Psi(x,t) = \psi(x)e^{-\frac{iEt}{\hbar}}, \tag{11}$$

   oscillates in time, the probability density

$$\begin{aligned} |\Psi(x,t)|^2 &= \Psi^*\Psi \\ &= \psi^* e^{\frac{iEt}{\hbar}}\psi e^{-\frac{iEt}{\hbar}} \\ &= |\psi(x)|^2, \end{aligned} \tag{12}$$

   is time-independent. The same thing happens when calculating the expectation value of any dynamical variable,

$$\begin{aligned} \langle Q(x,p)\rangle &= \int \Psi^*\left[Q\left(x, -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)\right]\Psi\,\mathrm{d}x \\ &= \int \psi^*\left[Q\left(x, -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)\right]\psi\,\mathrm{d}x \end{aligned} \tag{13}$$

   is constant in time. In particular, $\langle x\rangle$ is constant in time, hence $\langle p\rangle = m\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = 0$.

2. They are states of definite energy. In classical mechanics, the total energy (kinetic plus potential) is called the Hamiltonian:

$$H(x,p) = \frac{p^2}{2m} + V(x), \tag{14}$$

which is corresponded to the Hamiltonian operator, by replacing p with $-i\hbar\frac{\partial}{\partial x}$:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{15}$$

Using Hamiltonian operator, the time-independent Schrödinger equation (equation (9)) can be written as:

$$\hat{H}\psi = E\psi. \tag{16}$$

The expectation value of the total energy is

$$\begin{aligned}\langle H\rangle &= \int \Psi^* \hat{H} \Psi \, \mathrm{d}x \\ &= \int \psi^* \hat{H} \psi \, \mathrm{d}x \\ &= \int \psi^* E \psi \, \mathrm{d}x \\ &= E \int |\psi|^2 \, \mathrm{d}x \\ &= E, \end{aligned} \tag{17}$$

and

$$\begin{aligned}\langle H^2\rangle &= \int \Psi^* \hat{H}^2 \Psi \, \mathrm{d}x \\ &= \int \psi^* \hat{H}^2 \psi \, \mathrm{d}x \\ &= \int \psi^* E^2 \psi \, \mathrm{d}x \\ &= E^2 \int |\psi|^2 \, \mathrm{d}x \\ &= E^2. \end{aligned} \tag{18}$$

So the variance of H is

$$\sigma_H^2 = \langle H^2\rangle - \langle H\rangle^2 = E^2 - E^2 = 0, \tag{19}$$

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

3. The general solution is a linear combination of separated solutions (stationary states). The time-independent Schrödinger equation (equation (9)) yields an infinite collection of solutions, $\{\psi_n(x)\}$, each with its associated separation constant, $\{E_n\}$; thus there is a different wave function for each allowed energy:

$$\Psi_n(x,t) = \psi_n(x) e^{-i\frac{E_n t}{\hbar}}. \tag{20}$$

The general solution is a linear combination of these solutions:

$$\begin{aligned}\Psi(x,t) &= \sum_{n=1}^{\infty} c_n \Psi_n(x,t) \\ &= \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\frac{E_n t}{\hbar}},\end{aligned} \tag{21}$$

where the coefficients $\{c_n\}$ can be chosen to satisfy the initial conditions:

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x). \tag{22}$$

$|c_n|^2$ is the probability that a measurement of the energy would return to the value E_n. Thus of course,

$$\sum_{n=1}^{\infty} |c_n|^2 = 1, \tag{23}$$

and the expectation value of the energy is

$$\langle E \rangle = \sum_{n=1}^{\infty} |c_n|^2 \ E_n. \tag{24}$$

2. The Infinite Square Well

The infinite square well potential is defined as

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases} \tag{25}$$

Outside the well, $\psi(x) = 0$. Inside the well, the time-independent Schrödinger equation (equation (9)) becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi, \tag{26}$$

or

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi, \quad k = \frac{\sqrt{2mE}}{\hbar}. \tag{27}$$

The general solution to (27) is

$$\psi(x) = A\sin(kx) + B\cos(kx). \tag{28}$$

Continuity of $\psi(x)$ requires that

$$\psi(0) = 0, \tag{29}$$

which means $B = 0$, and

$$\psi(a) = 0, \tag{30}$$

which means

$$ka = 0, \pm\pi, \pm 2\pi, ... \tag{31}$$

But $k = 0$ is trivial and the negative solutions give nothing new, so the distinct solutions are

$$k_n = \frac{n\pi}{a}, \quad n = 1, 2, 3, ... \tag{32}$$

Hence the possible values of E are

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}. \tag{33}$$

To find A, we normalize $\psi(x)$:

$$\begin{aligned} 1 &= \int_0^a |\psi(x)|^2 \,\mathrm{d}x \\ &= |A|^2 \int_0^a \sin^2(kx) \,\mathrm{d}x \\ &= |A|^2 \,\frac{a}{2}, \end{aligned} \tag{34}$$

which means $A = \sqrt{\frac{2}{a}}$. Then the solutions are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right). \tag{35}$$

As a collection, the functions $\{\psi_n(x)\}$ have some interesting and important properties:

1. They are alternately even and odd: $\psi_1(x)$ is odd, $\psi_2(x)$ is even, $\psi_3(x)$ is odd, and so on.
2. As n increases, each successive state has one more node: $\psi_1(x)$ has none, $\psi_2(x)$ has one, $\psi_3(x)$ has two, and so on.
3. They are mutually orthonormal, in the sense that

$$\int \psi_m(x)^* \psi_n(x) \,\mathrm{d}x = \delta_{nm}, \tag{36}$$

   where δ_{nm} is the Kronecker delta.
4. They are complete, in the sense that any function $f(x)$ can be expressed as a linear combination of them:

$$\begin{aligned} f(x) &= \sum_{n=1}^{\infty} c_n \psi_{n(x)} \\ &= \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right), \end{aligned} \tag{37}$$

where c_n can be evaluated by

$$\begin{aligned}\int \psi_m(x)^* f(x)\,\mathrm{d}x &= \int \psi_m^*(x)\left(\sum_{n=1}^{\infty} c_n \psi_n(x)\right)\mathrm{d}x \\ &= \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\,\mathrm{d}x \\ &= \sum c_n \delta_{mn} \\ &= c_m. \end{aligned} \tag{38}$$

Actually, the first is true whenever $V(x)$ is symmetric; the second is true for any $V(x)$; the third and fourth are true for any $V(x)$.
The stationary states(equation (11)) of the infinite square well are

$$\begin{aligned}\Psi_n(x,t) &= \psi_n(x) e^{-i\frac{E_n t}{\hbar}} \\ &= \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i\left(\frac{n^2\pi^2\hbar}{2ma^2}\right)t}. \end{aligned} \tag{39}$$

Then the general solution(equation (21)) is

$$\begin{aligned}\Psi(x,t) &= \sum_{n=1}^{\infty} c_n \Psi_n(x,t) \\ &= \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i\left(\frac{n^2\pi^2\hbar}{2ma^2}\right)t}. \end{aligned} \tag{40}$$

The coefficients $\{c_n\}$ can be determined by the initial condition $\Psi(x,0)$, using (38).

3. The Harmonic Oscillator

The potential energy of a classical harmonic oscillator is

$$V(x) = \frac{1}{2}kx^2, \tag{41}$$

with the solution $x(t) = A\sin(\omega t) + B\cos(\omega t)$, where $\omega = \sqrt{\frac{k}{m}}$.
The quantum problem is to solve the Schrödinger equation for the potential

$$V(x) = \frac{1}{2}m\omega^2 x^2. \tag{42}$$

The time-independent Schrödinger equation (equation (9)) becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi. \tag{43}$$

3.1. Algebraic Method

Using the momentum operator $\hat{p} = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$, equation (43) can be written as

$$\frac{1}{2m}\left[\hat{p}^2+(m\omega x)^2\right]\psi=E\psi. \tag{44}$$

The basic idea is to factor the Hamiltonian,

$$\hat{H}=\frac{1}{2m}\left[\hat{p}^2+(m\omega x)^2\right], \tag{45}$$

with two ladder operators,

$$\hat{a}_\pm=\frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p}+m\omega x). \tag{46}$$

The commutator of two operators $\hat{A}$ and $\hat{B}$ is

$$\left[\hat{A},\hat{B}\right]=\hat{A}\hat{B}-\hat{B}\hat{A}. \tag{47}$$

The commutator of $\hat{x}=x$ and $\hat{p}=-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$ can be calculated as

$$\begin{aligned}
[\hat{x},\hat{p}]f(x)&=\hat{x}\hat{p}f(x)-\hat{p}\hat{x}f(x)\\
&=x\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}f(x)\right)-\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)(xf(x))\\
&=-i\hbar\left[x\frac{\mathrm{d}f(x)}{\mathrm{d}x}-x\frac{\mathrm{d}f(x)}{\mathrm{d}x}-f(x)\right]\\
&=i\hbar f(x),
\end{aligned} \tag{48}$$

which means $[\hat{x},\hat{p}]=i\hbar$.
The product $\hat{a}_-\hat{a}_+$ is

$$\begin{aligned}
\hat{a}_-\hat{a}_+&=\frac{1}{2\hbar m\omega}(i\hat{p}+m\omega x)(-i\hat{p}+m\omega x)\\
&=\frac{1}{2\hbar m\omega}\left(\hat{p}^2+(m\omega x)^2-im\omega(x\hat{p}-\hat{p}x)\right)\\
&=\frac{1}{2\hbar m\omega}\left(\hat{p}^2+(m\omega x)^2-im\omega[\hat{x},\hat{p}]\right)\\
&=\frac{1}{2\hbar m\omega}\left(\hat{p}^2+(m\omega x)^2+\hbar m\omega\right)\\
&=\frac{1}{\hbar\omega}\hat{H}+\frac{1}{2},
\end{aligned} \tag{49}$$

thus $\hat{H}=\hbar\omega\left(\hat{a}_-\hat{a}_+-\frac{1}{2}\right)$.
Similarly, the product $\hat{a}_+\hat{a}_-$ is

$$\hat{a}_+\hat{a}_-=\frac{1}{\hbar\omega}\hat{H}-\frac{1}{2}, \tag{50}$$

thus $\hat{H}=\hbar\omega\left(\hat{a}_+\hat{a}_-+\frac{1}{2}\right)$.
In terms of $\hat{a}_\pm$, the Schrödinger equation becomes

$$\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi. \tag{51}$$

Theorem 3.1 If ψ satisfies the Schrödinger equation with energy E, i.e.,

$$\hat{H}\psi = E\psi, \tag{52}$$

then $\hat{a}_\pm\psi$ satisfies the Schrödinger equation with energy $E \pm \hbar\omega$, i.e.,

$$\hat{H}\hat{a}_\pm\psi = (E \pm \hbar\omega)\hat{a}_\pm\psi. \tag{53}$$

Proof.

$$\begin{aligned}
\hat{H}\hat{a}_\pm\psi &= \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\hat{a}_\pm\psi \\
&= \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp\hat{a}_\pm \pm \frac{1}{2}\hat{a}_\pm\right)\psi \\
&= \hbar\omega\hat{a}_\pm\left(\hat{a}_\mp\hat{a}_\pm \pm \frac{1}{2}\right)\psi \\
&= \hat{a}_\pm\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm 1 \pm \frac{1}{2}\right)\psi \\
&= \hat{a}_\pm\left(\hat{H} \pm \hbar\omega\right)\psi \\
&= (E \pm \hbar\omega)\hat{a}_\pm\psi.
\end{aligned} \tag{54}$$

□

That's why $\hat{a}_+$ is called the raising operator and $\hat{a}_-$ is called the lowering operator. The ground state of the harmonic oscillator is the state annihilated by $\hat{a}_-$:

$$\hat{a}_-\psi_0 = 0. \tag{55}$$

Substituting $\hat{a}_-$ with its expression, we get

$$\begin{aligned}
\frac{1}{\sqrt{2\hbar m\omega}}(i\hat{p} + m\omega x)\psi_0 &= 0 \\
\left(\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right)\psi_0 &= 0 \\
\frac{\mathrm{d}\psi_0}{\mathrm{d}x} &= -\frac{m\omega}{\hbar}x\psi_0,
\end{aligned} \tag{56}$$

which is a first-order differential equation. The solution is

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}. \tag{57}$$

The normalization condition is

$$1 = \int_{-\infty}^{\infty} |\psi_0(x)|^2\,\mathrm{d}x \tag{58}$$

$$
\begin{aligned}
&= |A|^2 \int_{-\infty}^{\infty} e^{-\frac{m\omega}{\hbar}x^2}\,\mathrm{d}x \\
&= |A|^2 \sqrt{\frac{\pi\hbar}{m\omega}},
\end{aligned} \tag{58}
$$

which means $A = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$, and hence

$$
\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}. \tag{59}
$$

To determine the energy of the ground state, we plug it into the Schrödinger equation (equation (51)) and note that $\hat{a}_-\psi_0 = 0$:

$$
\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi_0 = E_0\psi_0, \tag{60}
$$

thus $E_0 = \frac{1}{2}\hbar\omega$.
Then the excited states can be obtained by applying the raising operator to the ground state, increasing the energy by $\hbar\omega$ each time:

$$
\psi_n = A_n(\hat{a}_+)^n\psi_0, \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \tag{61}
$$

where A_n is the normalization constant.
We know that $\hat{a}_\pm\psi_n$ is proportional to $\psi_{n\pm1}$,

$$
\hat{a}_+\psi_n = c_n\psi_{n+1}, \quad \hat{a}_-\psi_n = d_n\psi_{n-1}. \tag{62}
$$

Theorem 3.2 For "any" functions $f(x)$ and $g(x)$,

$$
\int_{-\infty}^{\infty} f^*(\hat{a}_\pm g)\,\mathrm{d}x = \int_{-\infty}^{\infty} (\hat{a}_\mp f)^* g\,\mathrm{d}x. \tag{63}
$$

Proof.

$$
\begin{aligned}
\int_{-\infty}^{\infty} f^*(\hat{a}_\pm g)\,\mathrm{d}x &= \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} f^*\left(\mp\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right) g\,\mathrm{d}x \\
&= \frac{1}{\sqrt{2\hbar m\omega}}\left[\mp\hbar f^* g \,\big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\left[\left(\pm\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right) f\right]^* g\,\mathrm{d}x\right] \\
&= \int_{-\infty}^{\infty} (\hat{a}_\mp f)^* g\,\mathrm{d}x.
\end{aligned} \tag{64}
$$

□

In particular,

$$
\int_{-\infty}^{\infty} (\hat{a}_\pm\psi_n)^*(\hat{a}_\pm\psi_n)\,\mathrm{d}x = \int_{-\infty}^{\infty} (\hat{a}_\mp\hat{a}_\pm\psi_n)^*\psi_n\,\mathrm{d}x. \tag{65}
$$

From equations (51) and (61), we have

$$\begin{aligned}\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi_n &= E_n\psi_n \\ &= \hbar\omega\left(n+\frac{1}{2}\right)\psi_n,\end{aligned} \tag{66}$$

which means

$$\hat{a}_+\hat{a}_-\psi_n = n\psi_n, \quad \hat{a}_-\hat{a}_+\psi_n = (n+1)\psi_n, \tag{67}$$

thus,

$$\begin{aligned}\int_{-\infty}^{\infty} (\hat{a}_+\psi_n)^* (\hat{a}_+\psi_n)\,\mathrm{d}x &= |c_n|^2 \int_{-\infty}^{\infty} \psi_{n+1}^*\psi_{n+1}\,\mathrm{d}x \\ &= (n+1)\int_{-\infty}^{\infty} \psi_n^*\psi_n\,\mathrm{d}x,\end{aligned} \tag{68}$$

so $|c_n|^2 = n+1$.
Similarly, we can get $|d_n|^2 = n$.
Hence,

$$\hat{a}_+\psi_n = \sqrt{n+1}\psi_{n+1}, \quad \hat{a}_-\psi_n = \sqrt{n}\psi_{n-1}. \tag{69}$$

Using mathematical induction, we have

$$\psi_n = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0. \tag{70}$$

As in the case of the infinite square well, the stationary states of the harmonic oscillator are orthonormal:

$$\int_{-\infty}^{\infty} \psi_m^*\psi_n\,\mathrm{d}x = \delta_{mn}. \tag{71}$$

Proof.

$$\begin{aligned}n\int_{-\infty}^{\infty} \psi_m^*\psi_n\,\mathrm{d}x &= \int_{-\infty}^{\infty} \psi_m^*\hat{a}_+\hat{a}_-\psi_n\,\mathrm{d}x \\ &= \int_{-\infty}^{\infty} (\hat{a}_+\hat{a}_-\psi_m)^*\psi_n\,\mathrm{d}x \\ &= m\int_{-\infty}^{\infty} \psi_m^*\psi_n\,\mathrm{d}x.\end{aligned} \tag{72}$$

Unless $m = n$, $\int_{-\infty}^{\infty} \psi_m^*\psi_n\,\mathrm{d}x = 0$. □

Orthonormality means we can again use

$$c_n = \int \psi_n^*\Psi(x,0)\,\mathrm{d}x \tag{73}$$

to determine the coefficients $\{c_n\}$. $|c_n|^2$ is the probability of measuring the energy to obtain the value E_n.
Using the definition (equation (46)), it is convenient to express x and $\hat{p}$ in terms of ladder operators:

$$x = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-),$$
$$\hat{p} = i\sqrt{\hbar m\frac{\omega}{2}}(\hat{a}_+ - \hat{a}_-). \tag{74}$$

3.2. Analytic Method

By introducing the dimensionless variable $\xi = \sqrt{m\frac{\omega}{\hbar}}x$, equation (43) becomes

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = (\xi^2 - K)\psi, \tag{75}$$

where

$$K = \frac{2E}{\hbar\omega} \tag{76}$$

is the dimensionless energy.
At very large ξ, the energy K is negligible, and the solution is

$$\psi(\xi) \sim e^{-\frac{\xi^2}{2}}, \tag{77}$$

which suggests that the solution can be separated into two parts:

$$\psi(\xi) = h(\xi)e^{-\frac{\xi^2}{2}}. \tag{78}$$

Differentiating equation (78) twice, we get

$$\frac{\mathrm{d}\psi}{\mathrm{d}\xi} = \left(\frac{\mathrm{d}h}{\mathrm{d}\xi} - \xi h\right)e^{-\frac{\xi^2}{2}},$$
$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = \left(\frac{\mathrm{d}^2h}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}h}{\mathrm{d}\xi} + (\xi^2 - 1)h\right)e^{-\frac{\xi^2}{2}}. \tag{79}$$

Substituting these into equation (75), we get

$$\frac{\mathrm{d}^2h}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}h}{\mathrm{d}\xi} + (K - 1)h = 0. \tag{80}$$

Rewrite $h(\xi)$ as a power series:

$$h(\xi) = \sum_{n=0}^{\infty} a_n\xi^n, \tag{81}$$

whose derivatives are

$$\begin{aligned}\frac{\mathrm{d}h}{\mathrm{d}\xi} &= \sum_{n=0}^{\infty} n a_n \xi^{n-1}, \\ \frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} &= \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2} \\ &= \sum_{n=0}^{\infty} (n+2)(n+1) a_{n+2} \xi^n. \end{aligned} \tag{82}$$

Substituting these into equation (80), we get

$$\sum_{n=0}^{\infty} [(n+2)(n+1)a_{n+2} - 2na_n + (K-1)a_n]\xi^n = 0. \tag{83}$$

Since ξ is arbitrary, the coefficient of each power of ξ must vanish:

$$(n+2)(n+1)a_{n+2} - 2na_n + (K-1)a_n = 0, \tag{84}$$

or

$$a_{n+2} = \frac{2n-K+1}{(n+1)(n+2)} a_n. \tag{85}$$

Starting with a_0, it generates all the even-numbered coefficients,

$$\begin{aligned} a_2 &= \frac{1-K}{2} a_0, \\ a_4 &= \frac{5-K}{12} a_2 = \frac{(5-K)(1-K)}{24} a_0, \\ &\ldots \end{aligned} \tag{86}$$

and starting with a_1, it generates all the odd-numbered coefficients,

$$\begin{aligned} a_3 &= \frac{3-K}{6} a_1, \\ a_5 &= \frac{7-K}{20} a_3 = \frac{(7-K)(3-K)}{120} a_1, \\ &\ldots \end{aligned} \tag{87}$$

We write the complete solution as

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi), \tag{88}$$

where

$$h_{\text{even}}(\xi) = a_0 + a_2\xi^2 + a_4\xi^4 + \ldots \tag{89}$$

is an even function of ξ, built on a_0, and

$$h_{\text{odd}}(\xi) = a_1\xi + a_3\xi^3 + a_5\xi^5 + \ldots \tag{90}$$

is an odd function of ξ, built on a_1.

However, not all solutions so obtained are normalizable. For normalizable solutions, the power series must terminate. There must occur some highest j, say n. From equation (85), this means that the numerator must vanish for some n:

$$2n - K + 1 = 0 \quad \Rightarrow \quad K = 2n + 1, \tag{91}$$

which leads to the quantization condition for the energy(equation (76)):

$$E = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, ... \tag{92}$$

For allowed values of K, the recursion formula (equation (85)) reads

$$\begin{aligned} a_{j+2} &= \frac{2j - (2n+1) + 1}{(j+1)(j+2)} a_j \\ &= \frac{-2(n-j)}{(j+1)(j+2)} a_j. \end{aligned} \tag{93}$$

If $n = 0$, there is only one coefficient, a_0. This gives the ground state wave function:

$$h(\xi) = a_0, \tag{94}$$

and hence

$$\psi_0(\xi) = a_0 e^{-\frac{\xi^2}{2}}. \tag{95}$$

If $n = 1$, we take $a_0 = 0$, which gives the first excited state:

$$h(\xi) = a_1 \xi, \tag{96}$$

and hence

$$\psi_1(\xi) = a_1 \xi e^{-\frac{\xi^2}{2}}. \tag{97}$$

If $n = 2$, $a_2 = -2a_0$, which gives the second excited state:

$$\begin{aligned} h(\xi) &= a_0 + a_2 \xi^2 \\ &= a_0(1 - 2\xi^2), \end{aligned} \tag{98}$$

and hence

$$\psi_2(\xi) = a_0(1 - 2\xi^2) e^{-\frac{\xi^2}{2}}. \tag{99}$$

In conclusion, the normalized stationary states of the harmonic oscillator are given by

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\frac{\xi^2}{2}}, \tag{100}$$

where $H_n(\xi)$ is the n-th order Hermite polynomial.
The quantum harmonic oscillator is strikingly different from its classical counterpart– not only are the energies quantized, but the position distributions have some bizarre features. For instance, the probability of finding the particle outside the classically

allowed region (i.e., $|x| > A$, where $A = \sqrt{\frac{2E}{m\omega^2}}$) is nonzero. And in all odd states, the probability of finding the particle at $x = 0$ is zero, even though the classical oscillator spends most of its time near $x = 0$.

4. The Free Particle

We turn next to the free particle, which is described by the potential $V(x) = 0$.
Classically this would be motion at constant velocity, but in quantum mechanics the problem is surprisingly subtle. The time-independent Schrödinger equation (equation (9)) becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi, \tag{101}$$

or

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi, \quad k = \frac{\sqrt{2mE}}{\hbar}. \tag{102}$$

So far, it's the same as the infinite square well(equation (27)), but the boundary conditions are different.
The general solution in exponential form is given by

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \tag{103}$$

Unlike the infinite square well, we have no boundary conditions to restrict the values of k (and hence E); the free particle can have any (positive) energy. Tacking on the time dependence, $e^{-\frac{iEt}{\hbar}}$, we have

$$\begin{aligned}\Psi(x,t) &= Ae^{ikx}e^{-\frac{iEt}{\hbar}} + Be^{-ikx}e^{-\frac{iEt}{\hbar}} \\ &= Ae^{ik\left(x-\frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x+\frac{\hbar k}{2m}t\right)},\end{aligned} \tag{104}$$

or

$$\Psi_{k(x,t)} = Ae^{i\left(kx-\frac{\hbar k^2}{2m}t\right)}, \tag{105}$$

where

$$k = \pm\frac{\sqrt{2mE}}{\hbar}, \quad \begin{cases} k > 0 \Rightarrow & \text{traveling to the right} \\ k < 0 \Rightarrow & \text{traveling to the left.} \end{cases} \tag{106}$$

The "stationary states" of the free particle are propagating waves, with wave length $\lambda = \frac{2\pi}{|k|}$, and, according to the de Broglie relation, momentum $p = \hbar k$, which is not normalizable:

$$\int_{-\infty}^{\infty} \Psi_k^* \Psi_k \,\mathrm{d}x = |A|^2 \int_{-\infty}^{\infty} \mathrm{d}x. \tag{107}$$

This means that a free particle cannot exist in a stationary state, or have a definite energy.

But the general solution is still a linear combination of these solutions, but now an integral instead of a sum:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} \, \mathrm{d}k, \tag{108}$$

which can be normalized for appropriate $\phi(k)$, necessarily carrying a range of ks, hence a range of energies and speeds, called a **wave packet**.
For a free particle the solution takes the form of (108), we need to determine $\phi(k)$ as to match the initial wave function:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} \, \mathrm{d}k, \tag{109}$$

which means, according to the Fourier transform, that

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} \, \mathrm{d}x. \tag{110}$$

The speed of these waves is

$$\begin{aligned} v_{\text{quantum}} &= \frac{\hbar|k|}{2m} \\ &= \sqrt{\frac{E}{2m}}. \end{aligned} \tag{111}$$

On the other hand, the classical speed of a free particle with energy $E = \frac{1}{2}mv^2$ is

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}}, \tag{112}$$

which is twice the quantum speed.
In fact, v_{quantum} in (111) is the phase velocity of the wave, and the group velocity is twice the phase velocity—just right to match the classical speed.
The problem is to determine the group velocity of the wave packet with the generic form

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \omega t)} \, \mathrm{d}k, \tag{113}$$

where in our case $\omega = \frac{\hbar k^2}{2m}$.
Assume that $\psi(k)$ is narrowly peaked about k_0, so that we can expand ω in a Taylor series about k_0, keeping only the first two terms:

$$\omega(k) \approx \omega(k_0) + \omega_0'(k - k_0), \tag{114}$$

where $\omega_0' = \frac{\mathrm{d}\omega}{\mathrm{d}k}\big|_{k=k_0}$.
Changing variables from k to $s = k - k_0$, we have

$$\Psi(x,t) \approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(s + k_0) e^{i[(k_0+s)x - (\omega_0 + \omega_0' s)t]} \, \mathrm{d}s \tag{115}$$

$$= \frac{1}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{\infty} \phi(s + k_0) e^{is(x - \omega_0' t)} \, \mathrm{d}s. \tag{115}$$

The term in front is a sinusoidal (the "ripples"), traveling with the phase velocity $v_{\text{phase}} = \frac{\omega_0}{k_0}$, the integral(the "envelope") propagates with the group velocity $v_{\text{group}} = \omega_0'$. Thus,

$$\begin{aligned} v_{\text{phase}} &= \frac{\omega}{k}, \\ v_{\text{group}} &= \frac{\mathrm{d}\omega}{\mathrm{d}k}. \end{aligned} \tag{116}$$

In our case, $\omega = \frac{\hbar k^2}{2m}$, so

$$\begin{aligned} v_{\text{phase}} &= \frac{\hbar k}{2m}, \\ v_{\text{group}} &= \frac{\hbar k}{m} = 2 v_{\text{phase}}. \end{aligned} \tag{117}$$

5. The Delta-Function Potential

5.1. Bound States and Scattering States

For the infinite square well and the harmonic oscillator, the solutions to the time-independent Schrödinger equation are normalizable, and labeled by a discrete index n; for the free particle, the solutions are not normalizable, and labeled by a continuous variable k. The former represent physically realizable states in their own right, the latter do not; but in both cases, the general solution is a linear combination of stationary states—for the first type the combination is a sum over n, for the second type an integral over k.

In classical mechanics, a one-dimensional time-independent potential $V(x)$ can give rise to two different kinds of motion: **bound states**, in which the potential $V(x)$ rises higher than the particle's total energy E on either side, it cannot escape; and **scattering states**, in which the potential $V(x)$ is lower than the particle's total energy E on one side (or both), it can escape.

The two kinds of solutions to the time-independent Schrödinger equation correspond precisely to these two kinds of motion. The distinction is even cleaner in quantum domain, because the phenomenon of **tunneling** allows the particle to "leak" through any finite potential barrier, so the only thing that matters is the potential at infinity:

$$\begin{cases} E < V(-\infty) \text{ and } V(+\infty) \Rightarrow \text{bound state} \\ E > V(-\infty) \text{ or } V(+\infty) \Rightarrow \text{scattering state} \end{cases} \tag{118}$$

In real life most potentials go to zero at infinity, in which case the criterion simplifies even further:

$$\begin{cases} E < 0 \Rightarrow \text{bound state} \\ E > 0 \Rightarrow \text{scattering state} \end{cases} \tag{119}$$

Because the infinite square well and the harmonic oscillator potentials go to infinity as $x \to \pm\infty$, they admit bound states only; because the free particle potential is zero everywhere, it only allows scattering states. From this section we shall explore potentials that allow both kinds of states.

5.2. The Delta-Function Well

The **Dirac delta function** is an infinitely narrow, infinitesimally narrow spike at the origin, with area 1:

$$\delta(x) \equiv \begin{cases} 0 & \text{if } x \neq 0 \\ \infty & \text{if } x = 0 \end{cases}, \quad \text{with} \int_{-\infty}^{\infty} \delta(x)\,\mathrm{d}x = 1. \tag{120}$$

Technically, it isn't a function at all, since it is not finite at $x = 0$(mathematically, it is a **distribution** or a **generalized function**).

Notice that $\delta(x-a)$ would be a spike of area 1 at $x = a$. Integrating a function $f(x)$ against the delta function, we have

$$\begin{aligned}\int_{-\infty}^{\infty} f(x)\delta(x-a)\,\mathrm{d}x &= \int_{-\infty}^{\infty} f(a)\delta(x-a)\,\mathrm{d}x \\ &= f(a)\int_{-\infty}^{\infty} \delta(x-a)\,\mathrm{d}x \\ &= f(a). \end{aligned} \tag{121}$$

In fact, the integral need not go from $-\infty$ to ∞; it can go from $a-\varepsilon$ to $a+\varepsilon$, for any $\varepsilon > 0$:

$$\int_{a-\varepsilon}^{a+\varepsilon} f(x)\delta(x-a)\,\mathrm{d}x = f(a). \tag{122}$$

Let's consider a potential of the form

$$V(x) = -\alpha\delta(x), \tag{123}$$

where α is a positive constant. The time-independent Schrödinger equation (equation (9)) becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \alpha\delta(x)\psi = E\psi; \tag{124}$$

it yields both bound states ($E < 0$) and scattering states ($E > 0$).

First, we consider the bound states. In the region $x < 0, V(x) = 0$, so

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi, \tag{125}$$

where $\kappa = \frac{\sqrt{-2mE}}{\hbar}$ is real and positive. The general solution is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}, \tag{126}$$

but the first term diverges as $x \to -\infty$, so $A = 0$:

$$\psi(x) = Be^{\kappa x}, \quad (x < 0). \tag{127}$$

In the region $x > 0, V(x) = 0$, too, so the general solution is of the same form, but now the second term diverges as $x \to +\infty$, so $B = 0$:

$$\psi(x) = Fe^{-\kappa x}, \quad (x > 0). \tag{128}$$

It remains only to stitch the two solutions together at $x = 0$. The standard boundary condition for ψ tells
1. ψ is always continuous;
2. $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ is discontinuous except at points where $V(x)$ is infinite.

In this case, the first condition gives

$$B = F = \psi(0), \tag{129}$$

then

$$\psi(x) = \begin{cases} Be^{\kappa x}, & (x < 0) \\ Be^{-\kappa x}, & (x > 0) \end{cases} \tag{130}$$

The delta function determines the discontinuity in the derivative of ψ at $x = 0$. Intergrating the time-independent Schrödinger equation (Equation (9)) from $-\varepsilon$ to $+\varepsilon$, we have:

$$\begin{aligned} -\frac{\hbar^2}{2m}\int_{-\varepsilon}^{+\varepsilon} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x + \int_{-\varepsilon}^{+\varepsilon} V(x)\psi(x)\,\mathrm{d}x &= E\int_{-\varepsilon}^{+\varepsilon} \psi(x)\,\mathrm{d}x \\ -\frac{\hbar^2}{2m}\frac{\mathrm{d}\psi}{\mathrm{d}x}\bigg|_{-\varepsilon}^{+\varepsilon} + \int_{-\varepsilon}^{+\varepsilon} V(x)\psi(x)\,\mathrm{d}x &= E\int_{-\varepsilon}^{+\varepsilon} \psi(x)\,\mathrm{d}x, \end{aligned} \tag{131}$$

and taking the limit $\varepsilon \to 0$, we get

$$\begin{aligned} -\frac{\hbar^2}{2m}\lim_{\varepsilon\to 0}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\bigg|_{-\varepsilon}^{+\varepsilon}\right) + \int_{-\varepsilon}^{+\varepsilon} V(x)\psi(x)\,\mathrm{d}x = 0& \\ \lim_{\varepsilon\to 0}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\bigg|_{-\varepsilon}^{+\varepsilon}\right) = \frac{2m}{\hbar^2}\int_{-\varepsilon}^{+\varepsilon} V(x)\psi(x)\,\mathrm{d}x,& \end{aligned} \tag{132}$$

where if $V(x)$ is finite, the second term vanishes, then $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ is discontinuous.
When $V(x) = -\alpha\delta(x)$, we have

$$\begin{aligned} \lim_{\varepsilon\to 0}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\bigg|_{-\varepsilon}^{+\varepsilon}\right) &= -\frac{2m\alpha}{\hbar^2}\int_{-\varepsilon}^{+\varepsilon} \delta(x)\psi(x)\,\mathrm{d}x \\ (-B\kappa) - (+B\kappa) &= -\frac{2m\alpha}{\hbar^2}\psi(0) \\ 2B\kappa &= \frac{2m\alpha}{\hbar^2}B \end{aligned} \tag{133}$$

$$\kappa = \frac{m\alpha}{\hbar^2}, \tag{133}$$

and the allowed energy is

$$\begin{aligned} E &= -\frac{\hbar^2\kappa^2}{2m} \\ &= -\frac{m\alpha^2}{2\hbar^2}. \end{aligned} \tag{134}$$

Fincally, we normalize ψ:

$$\begin{aligned} 1 &= \int_{-\infty}^{+\infty} |\psi(x)|^2 \, \mathrm{d}x \\ &= 2B^2 \int_0^{+\infty} e^{-2\kappa x} \, \mathrm{d}x \\ &= \frac{B^2}{\kappa}, \end{aligned} \tag{135}$$

which gives

$$\begin{aligned} B &= \sqrt{\kappa} \\ &= \frac{\sqrt{m\alpha}}{\hbar}. \end{aligned} \tag{136}$$

Evidently, the delta-function well, regardless of its "strength" α, has only one bound state:

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-\frac{m\alpha|x|}{\hbar^2}} \quad E = -\frac{m\alpha^2}{2\hbar^2}. \tag{137}$$

Next, we consider the scattering states, with $E > 0$. In the region $x < 0, V(x) = 0$, the Schrödinger equation reads

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi, \tag{138}$$

where$k = \frac{\sqrt{2mE}}{\hbar}$ is real and positive. The general solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \tag{139}$$

Similarly, for $x > 0$,

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}. \tag{140}$$

The continuity of $\psi(x)$ at $x = 0$ requires

$$A + B = F + G = \psi(0). \tag{141}$$

The second boundary condition (equation (132)) gives

$$\lim_{\varepsilon\to 0}\left(\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-\varepsilon}^{+\varepsilon}\right) = \frac{2m}{\hbar^2}\int_{-\varepsilon}^{+\varepsilon} V(x)\psi(x)\,\mathrm{d}x$$

$$ik(F-G) - ik(A-B) = -\frac{2m\alpha}{\hbar^2}\psi(0)$$

$$ik(F-G-A+B) = -\frac{2m\alpha}{\hbar^2}(A+B), \tag{142}$$

or, more compactly,

$$F - G = A(1+2i\beta) - B(1-2i\beta), \quad \text{where } \beta \equiv \frac{m\alpha}{\hbar^2 k}. \tag{143}$$

Having imposed both boundary conditions, we are left with two equations (Equations (141) and (143)) in four unknowns (A, B, F, and G). Normalization won't help, because the scattering states are not normalizable.

As we know, e^{ikx} gives a wave traveling to the right, and e^{-ikx} gives a wave traveling to the left. Thus, Ae^{ikx} is a wave coming in from the left, and Be^{-ikx} is a wave returning to the left; Ge^{-ikx} is a wave coming in from the right, and Fe^{ikx} is a wave returning to the right. In a typical scattering experiment particles are fired from one direction, say from the left, then the amplitude of the wave coming in from the right is zero, $G = 0$. A is the amplitude of the **incident wave**; B is the amplitude of the **reflected wave**; F is the amplitude of the **transmitted wave**. Solving Equations (141) and (143) for B and F, we have

$$B = \frac{i\beta}{1-i\beta}A,$$

$$F = \frac{1}{1-i\beta}A. \tag{144}$$

(In scattering from the right, $A = 0$, G is the incident amplitude, F is the reflected amplitude, and B is the transmitted amplitude.)

The *relative* probability that an incident particle will be reflected back, **refelction coefficient**, is

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1+\beta^2}$$

$$= \frac{1}{1+\frac{2\hbar^2 E}{m\alpha^2}}. \tag{145}$$

The *relative* probability that an incident particle will continue on through, **transmission coefficient**, is

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1+\beta^2}$$

$$= \frac{1}{1+\frac{m\alpha^2}{2\hbar^2 E}} \tag{146}$$

Of course, $R+T=1$, as it should be. On the other hand, the higher the energy E, the greater the probability of transmission, and the lower the probability of reflection.
For a delta-function *barrier*, $V(x)=+\alpha\delta(x)$, which kills the bound state, the reflection and transmission coefficients, depending only on α^2, are unchanged. Strange to say, the particle is just as likely to pass through the barrier as to cross over the well! Unlike classical mechanics, where the particle is reflected back if $E<V_{\max}$ or transmitted if $E>V_{\max}$, in quantum mechanics the particle can be transmitted even if $E<V_{\max}$, this is called **tunneling**.

6. The Finite Square Well

Consider the finite square well

$$V(x)=\begin{cases}-V_0 & -a\le x\le a\\ 0 & |x|>a\end{cases}, \tag{147}$$

where V_0 is a (positive) constant. Like the delta-function well, this potential admits both bound states (with $E<0$) and scattering states (with $E>0$).
First, we consider the bound states. In the region $x<-a, V(x)=0$, so

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=\kappa^2\psi, \tag{148}$$

where

$$\kappa=\frac{\sqrt{-2mE}}{\hbar} \tag{149}$$

is real and positive. The general solution is

$$\psi(x)=Ae^{-\kappa x}+Be^{\kappa x}, \tag{150}$$

but the first term diverges as $x\to-\infty$, so $A=0$:

$$\psi(x)=Be^{\kappa x},\quad (x<-a). \tag{151}$$

In the region $-a<x<a, V(x)=-V_0$, so

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=-l^2\psi, \tag{152}$$

where

$$l=\frac{\sqrt{2m(E+V_0)}}{\hbar} \tag{153}$$

is real and positive. The general solution is

$$\psi(x)=C\sin(lx)+D\cos(lx),\quad (-a<x<a). \tag{154}$$

In the region $x>a, V(x)=0$,

$$\psi(x)=Fe^{-\kappa x}+Ge^{\kappa x}, \tag{155}$$

but the second term diverges as $x \to +\infty$, so $G = 0$:

$$\psi(x) = Fe^{-\kappa x}, \quad (x > a). \tag{156}$$

Since the potential is even, the wave function must be even or odd.

1. The even solution is

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & (x > a) \\ D\cos(lx), & (0 < x < a) \\ \psi(-x), & (x < 0) \end{cases} \tag{157}$$

The continuity of $\psi(x)$ at $x = a$ gives

$$Fe^{-\kappa a} = D\cos(la), \tag{158}$$

and the continuity of $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ at $x = a$ gives

$$-\kappa Fe^{-\kappa a} = -lD\sin(la), \tag{159}$$

deviding by (158), we have

$$\kappa = l\tan(la), \tag{160}$$

which is a formula for the allowed energies, since κ and l are functions of E. To solve for E, Let

$$z \equiv la, \tag{161}$$

and

$$z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}. \tag{162}$$

By (149) and (153), we have

$$\kappa^2 + l^2 = \frac{2mV_0}{\hbar^2}, \tag{163}$$

so

$$\kappa a = \sqrt{z_0^2 - z^2}. \tag{164}$$

Then (160) becomes

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}. \tag{165}$$

2. The odd solution is

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & (x > a) \\ C\sin(lx), & (0 < x < a) \\ -\psi(-x), & (x < 0) \end{cases} \tag{166}$$

The continuity of $\psi(x)$ at $x = a$ gives

$$Fe^{-\kappa a} = C \sin(la), \tag{167}$$

and the continuity of $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ at $x = a$ gives

$$-\kappa F e^{-\kappa a} = lC \cos(la), \tag{168}$$

deviding by (167), we have

$$\kappa = -l \cot(la). \tag{169}$$

Similarly, we have

$$-\cot z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}. \tag{170}$$

Two limiting cases are of special interest:

1. **Wide, deep well** If z_0 is very large,

$$\begin{aligned} \tan z &= \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \approx \infty \\ z &= \frac{n\pi}{2}, \quad n = 1, 3, 5, ... \end{aligned} \tag{171}$$

and

$$\begin{aligned} -\cot z &= \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \approx \infty \\ z &= n\pi, \quad n = 1, 2, 3, ... \end{aligned} \tag{172}$$

Then in summary,

$$z = \frac{n\pi}{2}, \quad n = 1, 2, 3, ... \tag{173}$$

It follows that

$$\begin{aligned} E_n + V_0 &= \frac{z^2\hbar^2}{2ma^2} \\ &= \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \end{aligned} \tag{174}$$

which is precisely the energy of a particle in an infinite square well of width $2a$.

2. **Narrow, shallow well** As z_0 decreases, there are fewer and fewer bound states, until finally, for $z_0 < \frac{\pi}{2}$, only one remains. However, there is always one bound state, no matter how "weak" the well is.

Then we consider the scattering states, with $E > 0$. In the region $x < -a, V(x) = 0$, we have

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{175}$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{176}$$

Inside the well, $-a < x < a, V(x) = -V_0$,

$$\psi(x) = C\sin(lx) + D\cos(lx), \tag{177}$$

where

$$l \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar}. \tag{178}$$

In the region $x > a, V(x) = 0$,

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}, \tag{179}$$

or assuming there is no incoming wave from the right, $G = 0$:

$$\psi(x) = Fe^{ikx}. \tag{180}$$

Here A is the incident amplitude, B is the reflected amplitude, and F is the transmitted amplitude.
The continuity of $\psi(x)$ at $x = -a$ gives

$$Ae^{-ika} + Be^{ika} = -C\sin(la) + D\cos(la), \tag{181}$$

and the continuity of $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ at $x = -a$ gives

$$ik[Ae^{-ika} - Be^{ika}] = -l[C\cos(la) + D\sin(la)], \tag{182}$$

the continuity of $\psi(x)$ at $x = a$ gives

$$C\sin(la) + D\cos(la) = Fe^{ika}, \tag{183}$$

and the continuity of $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ at $x = a$ gives

$$l[C\cos(la) - D\sin(la)] = ikFe^{ika}. \tag{184}$$

Eliminating C and D from these four equations, we have

$$\begin{aligned} B &= i\frac{\sin(2la)}{2kl}(l^2 - k^2)F, \\ F &= \frac{e^{2ika}A}{\cos(2la) - i\frac{k^2+l^2}{2kl}\sin(2la)}. \end{aligned} \tag{185}$$

The transmission coefficient is

$$T^{-1} = 1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right). \tag{186}$$

Notice that when

$$\frac{2a}{\hbar}\sqrt{2m(E+V_0)} = n\pi, \quad n = 1, 2, 3, ... \tag{187}$$

the transmission coefficient $T = 1$. The energies for perfect transmission are

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \tag{188}$$

which happen to be the energy of a particle in an infinite square well of width $2a$.