Chapter 2

Time-Independent Schrödinger Equation

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1 Stationary States

In the Schrödinger equation,

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

we assume that the potential energy V 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

$$\frac{\partial \Psi}{\partial t} = \psi\frac{\mathrm{d}\varphi}{\mathrm{d}t}, \tag{3}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\varphi, \tag{4}$$

and the Schrödinger equation becomes

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

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

$$i\hbar\frac{1}{\varphi}\frac{\mathrm{d}\varphi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V. \tag{6}$$

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

$$i\hbar\frac{1}{\varphi}\frac{\mathrm{d}\varphi}{\mathrm{d}t} = E, \tag{7}$$

or

$$\frac{\mathrm{d}\varphi}{\mathrm{d}t} = -\frac{iE}{\hbar}\varphi, \tag{8}$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V = E, \tag{9}$$

or

$$\boxed{-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi.} \tag{10}$$

Then we have turned the Schrödinger equation, a partial differential equation, into two ordinary differential equations, equation (8) and equation (10).
The solution to equation (8) is

$$\varphi(t) = e^{-iEt/\hbar}, \tag{11}$$

as we care only about the product $\psi(x)\varphi(t)$.
The equation (10) is the time-independent Schrödinger equation.
There are three important properties of the solutions to equation (10):

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

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}, \tag{12}$$

oscillates in time, the probability density,

$$\begin{aligned} |\Psi(x,t)|^2 &= \Psi^*\Psi & (13)\\ &= \psi^* e^{iEt/\hbar}\psi e^{-iEt/\hbar} & (14)\\ &= |\psi(x)|^2, & (15) \end{aligned}$$

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

$$\begin{aligned} \langle Q(x,p)\rangle &= \int \Psi^* \left[Q(x, -i\hbar\frac{\mathrm{d}}{\mathrm{d}x})\right]\Psi dx & (16)\\ &= \int \psi^* \left[Q(x, -i\hbar\frac{\mathrm{d}}{\mathrm{d}x})\right]\psi dx & (17) \end{aligned}$$

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

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

$$H(x,p) = \frac{p^2}{2m} + V(x), \tag{18}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{19}$$

Using Hamiltonian operator, the time-independent Schrödinger equation (equation (10)) can be written as

$$\hat{H}\psi = E\psi. \tag{20}$$

The expectation value of the total energy is

$$\begin{aligned} \langle H\rangle &= \int \Psi^*\hat{H}\Psi\ \mathrm{d}x & (21)\\ &= \int \psi^*\hat{H}\psi\ \mathrm{d}x & (22)\\ &= \int \psi^* E\psi\ \mathrm{d}x & (23)\\ &= E\int |\psi|^2\ \mathrm{d}x & (24)\\ &= E, & (25) \end{aligned}$$

and

$$\begin{aligned} \langle H^2\rangle &= \int \Psi^*\hat{H}^2\Psi\ \mathrm{d}x & (26)\\ &= \int \psi^*\hat{H}^2\psi\ \mathrm{d}x & (27) \end{aligned}$$

$$= \int \psi^* E^2 \psi \, \mathrm{d}x \tag{28}$$

$$= E^2 \int |\psi|^2 \, \mathrm{d}x \tag{29}$$

$$= E^2. \tag{30}$$

So the variance of H is

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0, \tag{31}$$

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 (10)) 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:

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}. \tag{32}$$

The general solution is a linear combination of these solutions:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t) \tag{33}$$

$$= \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}, \tag{34}$$

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

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x). \tag{35}$$

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

$$\sum_{n=1}^{\infty} |c_n|^2 = 1, \tag{36}$$

and the expectation value of the energy is

$$\langle E \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n. \tag{37}$$

2 The Infinite Square Well

The infinite square well potential is defined as

$$V(x) = \begin{cases} 0, & 0 \le x \le a, \\ \infty, & \text{otherwise.} \end{cases} \tag{38}$$

Outside the well, $\psi(x) = 0$. Inside the well, the time-independent Schrödinger equation (equation (10)) becomes

$$-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi, \tag{39}$$

or

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi, \tag{40}$$

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

$$\psi(x) = A\sin kx + B\cos kx. \tag{41}$$

Continuity of $\psi(x)$ requires that

$$\psi(0) = 0, \tag{42}$$

which means $B = 0$, and

$$\psi(a) = 0, \tag{43}$$

which means

$$ka = 0, \pm\pi, \pm 2\pi, \cdots \tag{44}$$

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

$$k_n = \frac{n\pi}{a}, \quad n = 1, 2, 3, \cdots \tag{45}$$

Hence the possible values of E are

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}.} \tag{46}$$

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

$$\begin{aligned} 1 &= \int_0^a |\psi(x)|^2 \, \mathrm{d}x && (47) \\ &= |A|^2 \int_0^a \sin^2 kx \, \mathrm{d}x && (48) \\ &= |A|^2 \frac{a}{2}, && (49) \end{aligned}$$

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

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right). \tag{50}$$

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

$$\int \psi_m(x)^* \psi_n(x) \, \mathrm{d}x = \delta_{nm}, \tag{51}$$

   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:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{52}$$
$$= \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right), \tag{53}$$

where c_n can be evaluated by

$$\int \psi_m(x)^* f(x) \, \mathrm{d}x = \int \psi_m(x)^* \left(\sum_{n=1}^{\infty} c_n \psi_n(x)\right) \mathrm{d}x \tag{54}$$
$$= \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x) \, \mathrm{d}x \tag{55}$$
$$= \sum c_n \delta_{mn} \tag{56}$$
$$= c_m. \tag{57}$$

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 (12)) of the infinite square well are

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar} \tag{58}$$
$$= \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \tag{59}$$

Then the general solution (equation (33)) is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t) \tag{60}$$
$$= \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \tag{61}$$

The coefficients $\{c_n\}$ can be determined by the initial condition $\Psi(x,0)$, using equation (54) to (57).

3 The Harmonic Oscillator

The potential energy of a classical harmonic oscillator is

$$V(x) = \frac{1}{2}kx^2, \tag{62}$$

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

$$V(x) = \frac{1}{2}m\omega^2 x^2. \tag{63}$$

The time-independent Schrödinger equation (equation (10)) becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi. \tag{64}$$

3.1 Algebraic Method

Using the momentum operator $\hat{p} = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$, equation (64) can be written as

$$\frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right]\psi = E\psi. \tag{65}$$

The basic idea is to factor the Hamiltonian,

$$\hat{H} = \frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right], \tag{66}$$

with two ladder operators,

$$\hat{a}_\pm = \frac{1}{\sqrt{2\hbar m\omega}}\left(\mp i\hat{p} + m\omega x\right). \tag{67}$$

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

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{68}$$

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

$$[\hat{x}, \hat{p}]f(x) = \hat{x}\hat{p}f(x) - \hat{p}\hat{x}f(x) \tag{69}$$

$$= x\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}f(x)\right) - \left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)(xf(x)) \tag{70}$$

$$= -i\hbar\left[x\frac{\mathrm{d}f(x)}{\mathrm{d}x} - x\frac{\mathrm{d}f(x)}{\mathrm{d}x} - f(x)\right] \tag{71}$$

$$= i\hbar f(x), \tag{72}$$

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

$$\hat{a}_-\hat{a}_+ = \frac{1}{2\hbar m\omega}\left(i\hat{p} + m\omega x\right)\left(-i\hat{p} + m\omega x\right) \tag{73}$$

$$= \frac{1}{2\hbar m\omega}\left(\hat{p}^2 + (m\omega x)^2 - im\omega(x\hat{p} - \hat{p}x)\right) \tag{74}$$

$$= \frac{1}{2\hbar m\omega}\left(\hat{p}^2 + (m\omega x)^2 - im\omega[\hat{x}, \hat{p}]\right) \tag{75}$$

$$= \frac{1}{2\hbar m\omega}\left(\hat{p}^2 + (m\omega x)^2 + \hbar m\omega\right) \tag{76}$$

$$= \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2}, \tag{77}$$

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

$$\hat{a}_+\hat{a}_- = \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2}, \tag{78}$$

thus $\hat{H} = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)$.
In terms of $\hat{a}_\pm$, the Schrödinger equation (equation (64)) becomes

$$\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi. \tag{79}$$

Theorem 1. If ψ satisfies the Schrödinger equation with energy E, i.e.,

$$\hat{H}\psi = E\psi, \tag{80}$$

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

$$\hat{H}\hat{a}_\pm\psi = (E \pm \hbar\omega)\hat{a}_\pm\psi. \tag{81}$$

Proof:

$$\begin{aligned}
\hat{H}\hat{a}_\pm\psi &= \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\hat{a}_\pm\psi && (82)\\
&= \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp\hat{a}_\pm \pm \frac{1}{2}\hat{a}_\pm\right)\psi && (83)\\
&= \hbar\omega\hat{a}_\pm\left(\hat{a}_\mp\hat{a}_\pm \pm \frac{1}{2}\right)\psi && (84)\\
&= \hat{a}_\pm\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm 1 \pm \frac{1}{2}\right)\psi && (85)\\
&= \hat{a}_\pm(\hat{H} \pm \hbar\omega)\psi && (86)\\
&= (E \pm \hbar\omega)\hat{a}_\pm\psi. && (87)
\end{aligned}$$

□

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 $\hat{a}_-$:

$$\hat{a}_-\psi_0 = 0. \tag{88}$$

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

$$\begin{aligned}
\frac{1}{\sqrt{2\hbar m\omega}}\left(i\hat{p} + m\omega x\right)\psi_0 = 0 && (89)\\
\left(\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right)\psi_0 = 0 && (90)\\
\frac{\mathrm{d}\psi_0}{\mathrm{d}x} = -\frac{m\omega}{\hbar}x\psi_0, && (91)
\end{aligned}$$

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

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}. \tag{92}$$

The normalization condition is

$$\begin{aligned}
1 &= \int_{-\infty}^{+\infty} |\psi_0(x)|^2 \,\mathrm{d}x && (93)\\
&= |A|^2\int_{-\infty}^{+\infty} e^{-\frac{m\omega}{\hbar}x^2}\,\mathrm{d}x && (94)\\
&= |A|^2\sqrt{\frac{\pi\hbar}{m\omega}}, && (95)
\end{aligned}$$

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

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}. \tag{96}$$

To determine the energy of the ground state, we plug it into the Schrödinger equation (equation (79)) and note that $\hat{a}_+\psi_0 = 0$:

$$\hbar\omega\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\right)\psi_0 = E_0\psi_0, \tag{97}$$

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:

$$\psi_n = A_n(\hat{a}_+)^n\psi_0, \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \tag{98}$$

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

$$\hat{a}_+\psi_n = c_n\psi_{n+1}, \quad \hat{a}_-\psi_n = d_n\psi_{n-1}. \tag{99}$$

Theorem 2. For "any" functions $f(x)$ and $g(x)$,

$$\int_{-\infty}^{\infty} f^*(\hat{a}_\pm g)\ \mathrm{d}x = \int_{-\infty}^{\infty} (\hat{a}_\mp f)^* g\ \mathrm{d}x. \tag{100}$$

Proof:

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

□

In particular,

$$\int_{-\infty}^{\infty}(\hat{a}_\pm\psi_n)^*(\hat{a}_\pm\psi_n)\ \mathrm{d}x = \int_{-\infty}^{\infty}(\hat{a}_\mp\hat{a}_\pm\psi_n)^*\psi_n\ \mathrm{d}x. \tag{101}$$

From equation (79) and equation (98), we have

$$\begin{aligned}
\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi_n &= E_n\psi_n && (102)\\
&= \hbar\omega\left(n + \frac{1}{2}\right)\psi_n, && (103)
\end{aligned}$$

which means

$$\hat{a}_+\hat{a}_-\psi_n = n\psi_n, \quad \hat{a}_-\hat{a}_+\psi_n = (n+1)\psi_n, \tag{104}$$

so,

$$\int_{-\infty}^{\infty} (\hat{a}_+\psi_n)^*(\hat{a}_+\psi_n)\ \mathrm{d}x = |c_n|^2 \int_{-\infty}^{\infty} \psi_{n+1}^*\psi_{n+1}\ \mathrm{d}x \tag{105}$$

$$= (n+1) \int_{-\infty}^{\infty} \psi_n^*\psi_n\ \mathrm{d}x, \tag{106}$$

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

$$\hat{a}_+\psi_n = \sqrt{n+1}\psi_{n+1}, \quad \hat{a}_-\psi_n = \sqrt{n}\psi_{n-1}. \tag{107}$$

Using mathematical induction, we have

$$\psi_n = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0. \tag{108}$$

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

$$\int_{-\infty}^{\infty} \psi_m^*\psi_n\ \mathrm{d}x = \delta_{mn}. \tag{109}$$

Proof:

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

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

Orthonormality means that we can again use

$$c_n = \int \psi_n^*\Psi(x,0)\ \mathrm{d}x \tag{110}$$

to determine the coefficients $\{c_n\}$. $|c_n|^2$ is the probability that a measurement of the energy would return to the value E_n.
Using the definition (equation 67), it is convenient to express x and $\hat{p}$ in terms of the ladder operators:

$$x = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-), \tag{111}$$

$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}_+ - \hat{a}_-). \tag{112}$$

3.2 Analytic Method

By introducing the dimensionless variable $\xi = \sqrt{\frac{m\omega}{\hbar}}x$, equation (64) becomes

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = (\xi^2 - K)\psi, \tag{113}$$

where

$$K = \frac{2E}{\hbar\omega} \tag{114}$$

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

$$\psi(\xi) \sim e^{-\xi^2/2}, \tag{115}$$

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

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}. \tag{116}$$

Differentiating equation (116) twice, we get

$$\frac{\mathrm{d}\psi}{\mathrm{d}\xi} = \left(\frac{\mathrm{d}h}{\mathrm{d}\xi} - \xi h\right) e^{-\xi^2/2}, \tag{117}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = \left(\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}h}{\mathrm{d}\xi} + (\xi^2 - 1)h\right) e^{-\xi^2/2}. \tag{118}$$

Substituting these into equation (113), we get

$$\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}h}{\mathrm{d}\xi} + (K-1)h = 0. \tag{119}$$

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

$$h(\xi) = \sum_{n=0}^{\infty} a_n \xi^n, \tag{120}$$

whose derivatives are

$$\frac{\mathrm{d}h}{\mathrm{d}\xi} = \sum_{n=0}^{\infty} n a_n \xi^{n-1}, \tag{121}$$

$$\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} = \sum_{n=0}^{\infty} n(n-1)a_n \xi^{n-2} \tag{122}$$

$$= \sum_{n=0}^{\infty}(n+2)(n+1)a_{n+2}\xi^n. \tag{123}$$

Substituting these into equation (119), we get

$$\sum_{n=0}^{\infty} \left[(n+2)(n+1)a_{n+2} - 2na_n + (K-1)a_n\right] \xi^n = 0. \tag{124}$$

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

$$(n+2)(n+1)a_{n+2} - 2na_n + (K-1)a_n = 0, \tag{125}$$

or

$$a_{n+2} = \frac{2n - K + 1}{(n+1)(n+2)} a_n. \tag{126}$$

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

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

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

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

We write the complete solution as

$$h(\xi) = h_{even}(\xi) + h_{odd}(\xi), \tag{127}$$

where

$$h_{even}(\xi) = a_0 + a_2\xi^2 + a_4\xi^4 + \cdots$$

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

$$h_{odd}(\xi) = a_1\xi + a_3\xi^3 + a_5\xi^5 + \cdots$$

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 (126), this means that the numerator must vanish for some n:

$$2n - K + 1 = 0 \quad \Rightarrow \quad K = 2n + 1, \tag{128}$$

which leads to the quantization condition for the energy(equation (114)):

$$E = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots \tag{129}$$

For allowed values of K, the recursion formula (equation (126)) reads

$$a_{j+2} = \frac{2j - (2n+1) + 1}{(j+1)(j+2)}a_j \tag{130}$$

$$= \frac{-2(n-j)}{(j+1)(j+2)}a_j. \tag{131}$$

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

$$h(\xi) = a_0,$$

and hence

$$\psi_0(\xi) = a_0 e^{-\xi^2/2}.$$

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

$$h(\xi) = a_1 \xi,$$

and hence

$$\psi_1(\xi) = a_1 \xi e^{-\xi^2/2}.$$

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

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

and hence

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

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

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}, \tag{132}$$

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 $x = 0$.

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