The state of a particle (in one dimension) in a potential $V(x)$ is specified by the wave function $\psi(x,t)$

Equation governs $\psi(x,t)$ is the Schrodinger equation

The Schrödinger equation

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial^2 x^2}(x,t) + V(x)\Psi(x,t)} \tag{10-1}$$

The Schrödinger equation governs the motion of a particle in one dimension in a potential $V(x)$.

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t) \tag{10-2}$$

The term in parentheses can be interpreted as an operator acting on the wavefunction called the **Hamiltonian**.

$$\hat{H} = -\frac{\hbar^2}{2m}\underbrace{\frac{\partial^2}{\partial x^2}}_{\substack{\text{kinetic energy}\\ \text{is associated}\\ \text{with curvature}\\ \text{of wavefunction}}} + V(x) \tag{10-3}$$

corresponds to classical energy

$$E = \frac{p^2}{2m} + V(x). \tag{10-4}$$

Note. ˆ indicates operator

The Schrödinger equation (SE) can be written as

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t)} \tag{10-5}$$

Properties of the SE

Unlike the wave equation for EM fields in vacuum,

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{E} = 0, \tag{10-6}$$

or Newton's equation

$$m\ddot{x} = F(x), \tag{10-7}$$

the SE is first-order in time.

- It is sufficient to specify $\Psi(x, t = 0)$ to calculate $\Psi(x, t)$ at all later times t. For second-order equations we need to specify both the function and its derivative, or equivalently, position and momentum at $t = 0$ to determine the solution at later times.

- The particle position and the particle momentum are simultaneously encoded in the wave function $\Psi(x, t)$. This property is associated with the fact that $\Psi(x, t)$ is complex.

- The wavefunction $\Psi(x, t)$ is complex, the SE describes how the complex wavefunction propagates in space and time.

- The SE is non-relativistic.

- The SE is linear, i.e. if ψ_1, ψ_2 are solutions, so is $\psi = c_1\psi_1 + c_2\psi_2$, where c_1,c_2 are arbitrary complex numbers: **superposition priniciple** for waves.

Physical interpretation of $\psi(x,t)$.

$\psi(x,t)$ is an inherently complex function

Physical observables are all real.

$\psi^*(x,t)\,\psi(x,t)\,dx = P(x,t)\,dx$

$\uparrow$ proportional to the probability of finding the particle at a location between x and $x+dx$

$\int_{-\infty}^{\infty} \psi^*(x,t)\,\psi(x,t)\,dx = 1$ normalization

Meaning of • $\psi^*(x,t)\,\psi(x,t)$

$\psi(x,t) = R(x,t) + i\,I(x,t)$

$\psi^*(x,t) = R(x,t) - i\,I(x,t)$

$\psi^*(x,t)\,\psi(x,t) = [R(x,t)]^2 + [I(x,t)]^2$

≥ 0 (not only real but also positive, this is important because the probability density $P(x,t)$ must be positive)

Probability current density

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V\psi=i\hbar\frac{\partial\psi}{\partial t} \qquad \mid \psi^*$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2}+V^*\psi^*=-i\hbar\frac{\partial\psi^*}{\partial t} \qquad \mid \psi$$

Assume $V=V^*$ (real potential)

$$-\frac{\hbar^2}{2m}\left(\psi^*\frac{\partial^2\psi}{\partial x^2}-\psi\frac{\partial^2\psi^*}{\partial x^2}\right)=i\hbar\left(\psi^*\frac{\partial\psi}{\partial t}+\psi\frac{\partial\psi^*}{\partial t}\right)$$

$$\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x^2}-\psi\frac{\partial^2\psi^*}{\partial x^2}\right)=\psi^*\frac{\partial\psi}{\partial t}+\psi\frac{\partial\psi^*}{\partial t}$$

$$\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x^2}\right)=\psi^*\frac{\partial^2\psi}{\partial x^2}+\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x}$$
$$-\frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x}-\psi\frac{\partial^2\psi^*}{\partial x}$$

$$\frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)\right]=\frac{\partial}{\partial t}(\psi^*\psi)$$

Continuity equation

$\nabla\cdot\vec{J}+\frac{\partial\rho}{\partial t}=0$ $\quad$ $\vec{J}$ = current density $\quad$ ρ = charge density

One dimension

$$\frac{\partial}{\partial x}J_x=-\frac{\partial\rho}{\partial t}$$

$$\Rightarrow \underset{\substack{\uparrow\\ \text{probability flux}}}{S}(x,t)=-\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)$$

$S(x,t)$ is real

$$S^*(x,t)=+\frac{i\hbar}{2m}\left(\psi\frac{\partial\psi^*}{\partial x}-\psi^*\frac{\partial\psi}{\partial x}\right)$$
$$=S(x,t)\Rightarrow S(x,t)\text{ is real}$$

$S(x,t)$ = probability per unit time that the particle associated with the wave function $\psi(x,t)$ will cross the point x, in the direction of increasing value of x

$\frac{\partial}{\partial x}S(x,t)+\frac{\partial\rho}{\partial t}=0$ $\quad$ conservation of probability density

While this interpretation of S is suggestive, it must be realized that $S(x,t)$ is not susceptible to direct measurement in the sense $P(x,t)$ is. It would be misleading, for example, to say $S(x,t)$ is the measured particle flux at point x and time t, for a measurement of position and velocity (which is equivalent to momentum) and is therefore inconsistent with the uncertainty relation. Nevertheless, it is sometimes helpful to think of S as current, especially when it depends only slightly or not all on x, so that an accurate velocity determination can be made without impairing the usefulness of the concept of current.

Classical continuity equation in one dimension

$$\frac{\partial}{\partial x}(\rho v_x) = -\frac{\partial \rho}{\partial t}$$

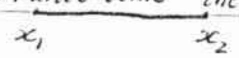
$$\int_{x_1}^{x_2} \frac{\partial}{\partial x}(\rho v_x) = -\frac{\partial}{\partial t}\int_{x_1}^{x_2} \rho\, dx$$

$$(\rho v_x)_{x_2} - (\rho v_x)_{x_1} = -\frac{\partial}{\partial t}\int_{x_1}^{x_2} \rho\, dx$$

⇓ The amount of charge density leaving the region / unit time

⇓ The amount of charge density entering the region / unit time

⇓ The amount of charge density loss / unit time.



Therefore if no charge is destroyed or created in this region then the continuity equation must be satisfied.

Expectation values.

With $\psi(\vec{x}, t)$ normalized

$P(x, t) = \psi^*(x, t)\, \psi(x, t)\, dx$

↑
probability of finding the particle between x and $x + dx$ at instant.

Average number in throwing a dice:

$$1 \cdot \frac{1}{6} + 2 \cdot \frac{1}{6} + 3 \cdot \frac{1}{6} + 4 \cdot \frac{1}{6} + 5 \cdot \frac{1}{6} + 6 \cdot \frac{1}{6}$$

$$= \frac{21}{6}$$

Generalize this idea

$$\langle x \rangle = \int_{-\infty}^{\infty} x\, P(x, t)\, dx$$

↑
expectation value of the x coordinate of the particle at time t

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x, t)\, x\, \psi(x, t)\, dx$$

Clearly the expectation value of $f(x)$ at instant t is given by

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t)\, f(x)\, \psi(x, t)\, dx$$

In particular,

$$\langle V(x, t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t)\, V(x, t)\, \psi(x, t)\, dx.$$

Now we want to ask what is the expectation value of energy and momentum

Try to generalize the idea.

Start with $\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, p\, \psi(x,t)\, dx$

But P is not a function of x, t, we have to find other ways.

Going back to the free particle wave

$$\psi_f = e^{i(Kx-\omega t)}$$

$$-i\hbar \frac{\partial}{\partial x}\psi_f = -i\hbar(iK)\psi_f = p_x \psi_f(x,t)$$

Suggest $p_x \rightarrow -i\hbar\frac{\partial}{\partial x}$ (operator)

$$\langle E \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, E\, \psi(x,t)\, dx$$

$$i\hbar\frac{\partial}{\partial t}\psi_f = +i\hbar(-i\omega)\psi_f = E\,\psi_f(x,t)$$

Suggest $E \rightarrow i\hbar\frac{\partial}{\partial t}$ (operator)

Further justification from Schrodinger equation

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

$$\int_{-\infty}^{\infty}\psi^*(x,t)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x,t)\psi(x,t)\right]dx$$

$$= \int \psi^*(x,t)\, i\hbar\frac{\partial}{\partial t}\,\psi(\vec{x},t)\, dx$$

With the identification suggested above, the Schrodinger equation leads to the desired conservation law in expectation value form,

$$\left\langle \frac{p^2}{2m}\right\rangle + \langle V \rangle = \langle E \rangle$$

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x,t)\, dx$$

$i\hbar \frac{\partial}{\partial x}$ is an operator, the location is of great importance

Three possible locations

(i) It is located at the position we have given above.

(ii) $\int_{-\infty}^{\infty} \psi^*(x,t)\, \psi(x,t) \left(-i\hbar \frac{\partial}{\partial x}\right) dx$ has no meaning.

(iii) $\int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial}{\partial x}\right) \psi^*(x,t)\, \psi(x,t)\, dx$

$$= -i\hbar \;\; \psi^*(x,t)\, \psi(x,t) \Big|_{-\infty}^{\infty}.$$

$\int_{-\infty}^{\infty} \psi^*(x,t)\, \psi(x,t)\, dx = 1 \;\Rightarrow\; |\psi(x,t)|^2 \to 0$ faster than $\frac{1}{|x|}$ as $|x| \to \infty$

$$\Rightarrow \quad \psi^*(x,t)\, \psi(x,t) \Big|_{-\infty}^{\infty} = 0$$

Furthermore, the expression is imaginary.

Therefore, (i) is the only acceptible definition of $\langle p \rangle$

Exercise: Prove $\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x,t)\, dx$

and $\langle E \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial t}\right) \psi(x,t)\, dx$

are real.

Exercise: Given $\psi(x,t) = N e^{-(x-x_0)^2/2K^2}\, e^{-i\omega t}$

(i) Find the normalization N

(ii) Find $\langle x \rangle$, $\langle x^2 \rangle$ and $\langle p \rangle$

Ehrenfest's theorem

$$\frac{d}{dt}\langle x \rangle = \frac{d}{dt} \int_{-\infty}^{\infty} \psi^*(x,t)\, x\, \psi(x,t)\, dx$$

$$= \int_{-\infty}^{\infty} \left\{ \left[\frac{\partial}{\partial t} \psi^*(x,t)\right] x\, \psi(x,t) + \psi^*(x,t)\, x \frac{\partial}{\partial t} \psi(x,t) \right\} dx$$

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

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

$$\frac{d}{dt}\langle x \rangle = \int_{-\infty}^{\infty} \left\{ \frac{i}{\hbar} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi^* + V\psi^*\right] x\, \psi(x,t) - \frac{i}{\hbar} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi \right.\right.$$

$$\left.\left. + V\psi\right] x\, \psi^*(x,t) \right\} dx$$

$$= \frac{i\hbar}{2m} \int_{-\infty}^{\infty} \left\{ \psi^*(x,t)\, x \frac{\partial^2}{\partial x^2} \psi(x,t) - \left[\frac{\partial^2}{\partial x^2} \psi^*(x,t)\right] x\, \psi(x,t) \right\} dx.$$

Lemma $\int_{-\infty}^{\infty} \underbrace{x\psi}_{u} \underbrace{\frac{\partial^2}{\partial x^2} \psi^* dx}_{d v} = \overset{\overset{0}{\parallel}}{\left[\underbrace{x\psi}_{u} \underbrace{\frac{\partial \psi^*}{\partial x}}_{v} \right]_{-\infty}^{\infty}} - \int_{-\infty}^{\infty} \underset{v}{\frac{\partial \psi^*}{\partial x}} \underset{du}{\frac{\partial (x\psi)}{\partial x}}\, dx$

$$= -\int_{-\infty}^{\infty} \underset{u}{\frac{\partial (x\psi)}{\partial x}} \underset{dv}{\frac{\partial \psi^*}{\partial x}}\, dx$$

$$= -\left[\frac{\partial(x\psi)}{\partial x}\psi^*\right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\psi^*\frac{\partial^2}{\partial x^2}(x\psi)\,dx$$

$$\frac{d}{dt}\langle x\rangle = \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\psi^*\left(x\frac{\partial^2}{\partial x^2}\psi - \frac{\partial^2}{\partial x^2}(x\psi)\right)dx$$

$$x\frac{\partial^2}{\partial x^2}\psi - \frac{\partial^2}{\partial x^2}(x\psi)$$

$$= x\frac{\partial^2}{\partial x^2}\psi - \frac{\partial}{\partial x}\left(x\frac{\partial\psi}{\partial x} + \psi\right)$$

$$= x\frac{\partial^2}{\partial x^2}\psi - x\frac{\partial^2}{\partial x}\psi - \frac{\partial\psi}{\partial x} - \frac{\partial\psi}{\partial x}$$

$$= -2\frac{\partial\psi}{\partial x}$$

$$\frac{d}{dt}\langle x\rangle = \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\psi^*\left(-2\frac{\partial}{\partial x}\right)\psi\,dx$$

$$= \frac{1}{m}\int_{-\infty}^{\infty}\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,dx$$

$$= \frac{\langle p\rangle}{m}$$

$$\langle p\rangle = m\frac{d\langle x\rangle}{dt}$$

Similarily, $\frac{d\langle p\rangle}{dt} = -\frac{\partial\langle V(x\ t)\rangle}{\partial x}$

$$\frac{d}{dt}\langle p\rangle = \frac{d}{dt}\int_{-\infty}^{\infty}\psi^*\left(-i\hbar\frac{\partial}{\partial x}\psi\right)dx$$

$$= -i\hbar\int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\frac{\partial\psi}{\partial x} + \psi^*\frac{\partial^2\psi}{\partial x\partial t}\right)dx$$

$$= \int_{-\infty}^{\infty}\left\{\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + V\psi^*\right)\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial}{\partial x}\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi\right]\right\}dx$$

$$= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left\{\frac{\partial^2\psi^*}{\partial x^2}\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial^3\psi}{\partial x^3}\right\}dx$$

$$+ \int_{-\infty}^{\infty}\left\{V\psi^*\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial(V\psi)}{\partial x}\right\}dx$$

$$\frac{\partial}{\partial x}\left(\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial^2\psi}{\partial x^2}\right)$$

$$= \frac{\partial^2\psi^*}{\partial x^2}\frac{\partial\psi}{\partial x} + \frac{\partial\psi^*}{\partial x}\frac{\partial^2\psi}{\partial x^2} - \frac{\partial\psi^*}{\partial x}\frac{\partial^2\psi}{\partial x^2} - \psi^*\frac{\partial^3\psi}{\partial x^3}$$

$$\frac{d}{dt}\langle p\rangle = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\frac{\partial}{\partial x}\left(\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial^2\psi}{\partial x^2}\right)dx$$

$$+ \int_{-\infty}^{\infty}\left(\psi^*V\frac{\partial\psi}{\partial x} - \psi^*V\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial V}{\partial x}\psi\right)dx$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial^2\psi}{\partial x^2}\right)\Big|_{-\infty}^{\infty}$$

$$- \int_{-\infty}^{\infty}\left(\psi^*\frac{\partial V}{\partial x}\psi\right)dx$$

$$= -\int_{-\infty}^{\infty}\psi^*\frac{\partial V}{\partial x}\psi\,dx$$

$$= -\left\langle\frac{\partial V}{\partial x}\right\rangle$$

Uncertainty in x

$$\Delta x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$$ $x - \langle x \rangle$ = deviation

$$= \sqrt{\langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle}$$

$$= \sqrt{\langle x^2 \rangle - 2\langle x \rangle^2 + \langle x \rangle^2}$$

$$= \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

Similarily, we can define Δp.

In the limit in which the distances and momenta involved in describing the motion of the particle are very large compared with the uncertainties of these quantities, then it is no longer necessary to distinguish between x and $\langle x \rangle$, p and $\langle p \rangle$, or $\frac{\partial V}{\partial x}$ and $\langle \frac{\partial V}{\partial x} \rangle$. Then the equations we have derived from the theory of quantum mechanics becomes completely identical with the laws of Newtonian mechanics. Quantum mechanics does indeed agree with Newtonian mechanics in the limit in which the uncertainty principle is not important.

Time independent Schrodinger equation

If the potential is independent of t, then the Schrodinger equation becomes

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

A standard technique in solving such problem is to write

$$\psi(x,t)=\varphi(x)\phi(t)$$

Substitute back into the Schrodinger equation

$$-\frac{\hbar^2}{2m}\phi(t)\frac{d^2}{dx^2}\varphi(x)+V(x)\varphi(x)\phi(t)=i\hbar\varphi(x)\frac{\partial}{\partial t}\phi(t)$$

Divide through by $\varphi(x)\phi(t)$

$$-\frac{\hbar^2}{2m}\frac{1}{\varphi(x)}\frac{d^2}{dx^2}\varphi(x)+V(x)=i\hbar\frac{1}{\phi(t)}\frac{\partial}{\partial t}\phi(t)$$

Both side must depend on a seperation constant

$$-\frac{\hbar^2}{2m}\frac{1}{\varphi(x)}\frac{d^2}{dx^2}\varphi(x)+V(x)=c$$

$$i\hbar\frac{1}{\phi(t)}\frac{d}{dt}\phi(t)=c \qquad \frac{d}{dt}\phi(t)=-\frac{i}{\hbar}c\phi(t)\Rightarrow\phi(t)=e^{-\frac{i}{\hbar}ct}$$

$$\begin{aligned}\langle E\rangle &=\int\psi^*(x,t)\left(i\hbar\frac{\partial}{\partial t}\right)\psi(x,t)\,dx\\ &=\int\psi^*(x,t)\left(i\hbar\frac{-i}{\hbar}c\right)\psi(x,t)\,dx\\ &=\int\psi^*(x,t)\,E\,\psi(x,t)\,dx\end{aligned}$$

$$\Rightarrow\quad c=E$$

Therefore

$$\phi(t)=e^{-i\frac{Et}{\hbar}}$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\varphi(x)+V(x)\varphi(x)=E\varphi(x)$$

This is known as the time-independent Schrodinger equation.

The solutions of this equation are not necessary complex.

Energy quantization in the Schrodinger theory.

Energy quantization arises because, in solving the time independent Schrodinger equation, one finds that <u>acceptable</u> solutions exist only for certain values of the total energy E.

Those values of E, for which acceptable solution can be found, is known as eigenvalues

The solution accociated with it is known as eigenfunctions.

Requirements for acceptible solutions,

(i) $\varphi(x)$ is square integrable

(ii) (a) $\varphi(x)$ must be finite

(b) $\varphi(x)$ must be continous

(c) $\frac{d\varphi(x)}{dx}$ must be finite

(d) $\frac{d\varphi(x)}{dx}$ must be continous

→ (a), (c) follows from the requirement that $P(x,t)$, $S(x,t)$ are well defined.

→ Requirement (c) ⇒ requirement (b)

→ From time independent equation

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

$$\frac{d^2}{dx^2}\varphi(x) = \frac{2m}{\hbar}[V(x) - E]\varphi(x)$$

For finite $V(x)$, E, and $\varphi(x)$, it follows that $\frac{d^2}{dx^2}\varphi(x)$ ⇒ requirement (d)

If $\varphi_n(x) \longleftrightarrow E_n$ are solution of the time independent Schrodinger equation. then

$$\psi_n(x,t) = \varphi_n(x)\, e^{-\frac{E_n t}{\hbar}}$$

is a solution of the time dependent Schrodinger equation

The general solution is

$$\psi(x,t) = \sum_n a_n \varphi_n(x)\, e^{-iE_n t/\hbar}$$

a_n are determined by the initial condition.

e.g. $\psi(x,\underset{\substack{\downarrow \\ t=0}}{0})$

$$\psi(x,0) = \sum_n a_n \varphi_n(x)$$

a_n can be found, given $\psi(x,0)$ and $\varphi_n(x)$

Interpretation of the wave function $\Psi(x,t)$

If we perform a measurement of the particle's position at time t, the probability of finding the particle between x and $x+dx$ is given by $|\Psi(x,t)|^2dx$. The SE is a partial differential equation (contains both $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial t}$). Since $V(x)$ is independent of time, it can be simplified into two ordinary differential equations.

ansatz. $\boxed{\Psi(x,t) = T(t)\psi(x)}$

The SE becomes

$$i\hbar\psi(x)\frac{dT}{dt}(t) = T(t)\left\{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right\} \tag{10-13}$$

Dividing by $T(t)\psi(x)$ where $T(t)\psi(x) \neq 0$ yields

$$ih\frac{1}{T}\frac{dT}{dt}(t) = \left\{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right\}\frac{1}{\psi(x)} \tag{10-14}$$

Since the two sides depend on different variables, they must be constants. Call this constant E, it will be the total energy of the system

$$i\hbar\frac{dT}{dt}(t) = ET(t) \Longrightarrow \boxed{T(t) = Ce^{-iEt/\hbar}} \tag{10-15}$$

The time dependence is simply a phase factor that evolves in time at angular frequency $\frac{E}{\hbar}$. The equation for $\psi(x)$ is

$$\left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right\}\psi(x) = E\psi(x) \Longrightarrow \text{ time-independent} \tag{10-16}$$

$$\boxed{\hat{H}\psi(x) = E\psi(x)} \Longrightarrow \textbf{time-independent Schrödinger equation} \tag{10-17}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{10-18}$$

$$\boxed{i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t)} \tag{10-19}$$

is called the **time-dependent Schrödinger equation**. The time-independent SE: $\hat{H}\psi(x) = E\psi(x)$ is an eigenvalue equation (operator acting on wavefunction yields the same wavefunction, multiplied by a constant E). This is reminiscent of matrices, eigenvectors, eigenvalues → Heisenberg's matrix formulation of **QM** in 8.05. We call a solution $\psi_n(x)$ of the time-independent SE $\hat{H}\psi_n = E_n\psi_n(x)$ an eigenstate of the system, with eigenvalue E_n. The time-evolution of an eigenstate $\psi_n(x)$ is then simply given by

$$\Psi_n(x,t) = e^{-iE_nt/\hbar}\psi_n(x). \tag{10-20}$$

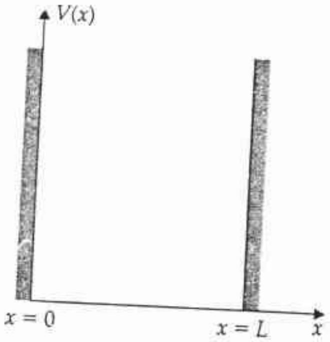
Our task is to find all eigenstates $\psi_n(x)$ and corresponding eigenvalues E_n. Then, as we will show later, the problem is solved completely: An arbitrary state that solves the SE can be written as an superposition of eigenstates. The eigenvalues E_n may be discrete values (as in the Bohr atom), or they may form a continuum (e.g., energies of a free particle). More generally, a solution $\psi_E(x)$ of the SE $\hat{H}\psi_E(x) = E\psi_E(x)$ for energy E is called an **energy eigenstate** or **energy eigenfunction** of the system. We will encounter other eigenvalues equations, e.g. for momentum, position, angular momentum etc. For now, thinks of $\psi_E(x)$ as a solution of the differential equation.

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi_E(x)}{\partial x^2} + V(x)\psi_E(x) = E\psi_E(x)} \tag{10-21}$$

with energy E as a parameter. Let us work out a particularly simple example.

Example. The infinite well. (See the textbook)

$$V(x) = \begin{cases} \infty & \text{for } x > L \\ 0 & \text{for } 0 < x < L \\ \infty & \text{for } x < 0 \end{cases}$$



The infinite-well potential has infinitely high potential-energy "walls" that confine a particle under its influence to the region $0 < x < L$. It is convenient to choose the bottom of the well to correspond to zero potential energy.

In the region $0 < x < L$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}u(x) = E\,u(x)$$

Boundary condition

$$u(0) = u(L) = 0$$

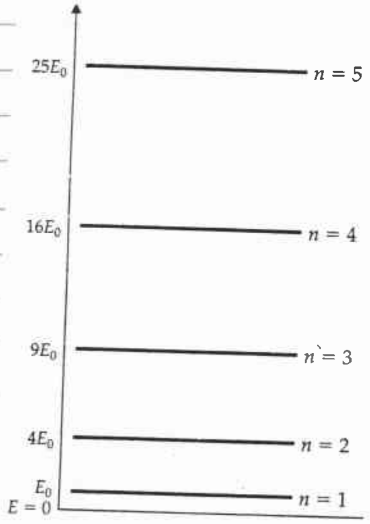
$$u(x) = A \sin kx \qquad (u = 0 \text{ at } x = 0)$$

$$\underline{kL = n\pi} \qquad n = 1, 2, \cdots$$

$$\downarrow$$

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

$$\Rightarrow \quad E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2} \qquad n = 1, 2, \cdots$$



The energy spectrum (i.e., the allowed, or possible, energy values) for a particle of mass m in the infinite well of •Fig. 6–5. The ground-state energy is $E_0 = \dfrac{\hbar^2\pi^2}{2mL^2}$.

Normalization

$$|A|^2 \int_0^L \sin^2 kx \, dx = 1$$

$$\Rightarrow \quad A = \frac{\sqrt{2}}{L}\underset{\substack{\downarrow \\ \text{does not appear} \\ \text{in physical probabilities}}}{e^{i\varphi}}$$

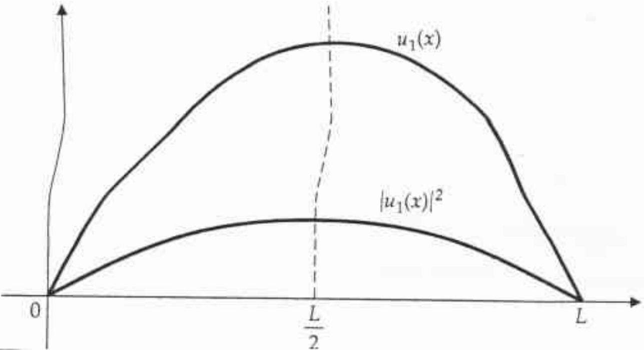
$$\int \psi^* \underset{\substack{\downarrow \\ \text{linear operator}}}{L} \psi \, dx$$

$\swarrow$

the result is independent of φ

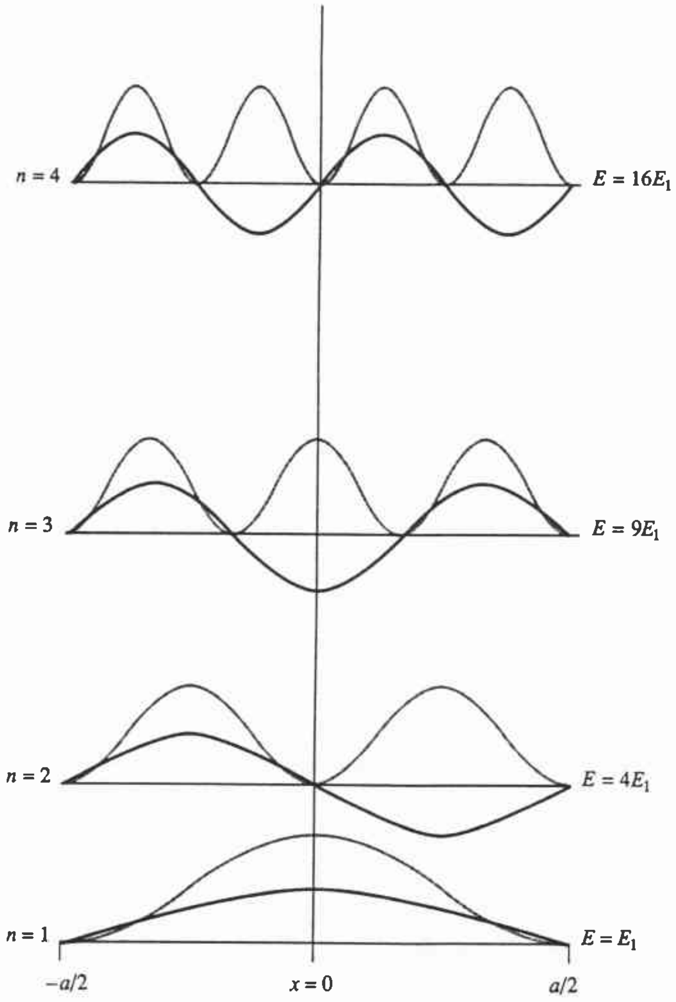
Ground state wave function

$$u_1(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L}$$



The ground-state wave function $u_1(x)$, as well as the associated probability distribution $|u_1(x)|^2$, for the infinite well is symmetric about

分類：
編號： 6-9
總號：



The wave functions (solid color) and probability densities (light color) for the ground state ($n = 1$) and first three excited states ($n = 2$, 3, and 4) of a particle confined to an infinite one-dimensional potential well of width a. Note that the wave functions are either odd or even functions of x.

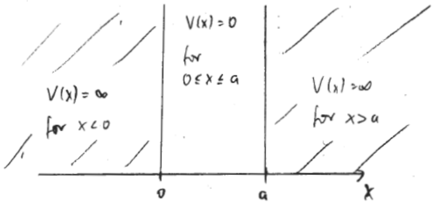


Figure IV: Infinite well.

Particle in a box with infinite walls

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V(x)\psi(x) = E\psi(x) \tag{10-22}$$

implies that $\psi(x) = 0$ where $V \to \infty$ (otherwise E or curvature have to by infinite)$\Longrightarrow$ $\psi(x) = 0$ for $x < 0$ or $x > a$ For $0 \leq x \leq a$ we have,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi(x) \tag{10-23}$$

or

$$\psi'' = -\frac{2mE}{\hbar^2}\psi(x) \tag{10-24}$$

If $E < 0$, the solutions are of the form $e^{\pm kx}$ with $k^2 = \frac{2m|E|^2}{\hbar^2}$. We require the wavefunction $\psi(x)$ to be continuous (no steps), otherwise $\frac{\partial\psi}{\partial x}$ becomes infinite. To make $\psi(0) = 0$ for $\psi = Ae^{kx} + Be^{-kx}$, we need $A = -B$, but then $\psi(a) \neq 0$, and ψ is not continuous. $\Longrightarrow$ *There are no solutions for negative eigenvalues* E.

For $E > 0$, the solutions are of the form $e^{\pm ikx}$ with $k^2 = \frac{2mE}{\hbar^2}$ (or $\sin kx$, $\cos kx$). The allowed values of E or k are determined by the boundary conditions. Writing $\psi(x) = Ae^{ikx} + Be^{-ikx}$, we need $A = -B$ for $\psi(0) = A + B = 0$. Then for $\psi = 0$ we need $Ae^{ika} - Ae^{-ika} = \frac{2Ai}{2i}(e^{ika} - e^{-ikaa}) = 2iA\sin ka = 0$. This is fulfilled only if $ka = n\pi$ or $k_n = n\frac{\pi}{a}$, $n = 1, 2, 3, \ldots$ ($n = 0$, $\psi = 0$). Therefore the eigenvalues are

$\boxed{E_n = \frac{\hbar^2 {k_n}^2}{2m} = \frac{\hbar^2\pi^2}{2ma^2}n^2}$, $n = 1, 2, 3, ...$ energy eigenvalues

with corresponding eigenfunctions

$\boxed{\psi_n(x) = C_n \sin k_n x = C_n \sin\left(n\pi\frac{x}{a}\right)}$

where C_n is some complex constant. The above is a general feature of **QM**. *The boundary conditions on the wave function force the quantization of energy levels, i.e. allow only discrete energy values.*

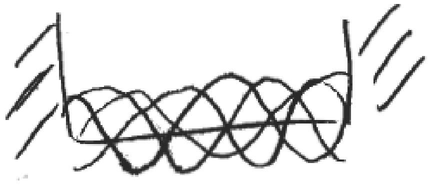


Figure V: Most de Broglie wavelengths lead to destructive interference.

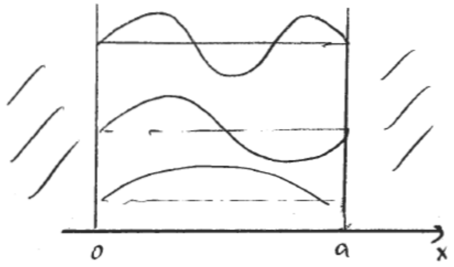


Figure VI: Eigenstates of box with infinite walls.

Reason. Constructive interference, stationary phase after one round trip, for other energies ψ interferes away. In order to interpret $|\psi_n(x)|^2$ as a probability we need to normalize it so the probability to find the particle anywhere in space is unity

$$\boxed{\int_{-\infty}^{\infty} dx |\psi(x)|^2 = 1} \quad \text{Normalization of wavefunction} \tag{10-25}$$

Here $\int_{-\infty}^{\infty} dx |\psi_n(x)|^2 = |C_n|^2 \int_0^a dx \sin^2\left(n\pi\frac{x}{a}\right) = \frac{1}{2}a|C_n|^2 = 1$

An overall global phase of the wavefunction has no physical consequences so we choose C_n real. We obtain

$$\boxed{u_n = \sqrt{\frac{2}{a}} \sin\left(n\pi\frac{x}{a}\right)}$$

normalized eigenstates of the square well $n = 1, 2, 3, \ldots$ ($0 \leq x \leq a$, $u_n = 0$, otherwise)

Note. The minimum energy of the particle in the box is not zero, but given by the ground-state energy $E_1 = \frac{\hbar^2\pi^2}{2ma^2}$. This is sometimes called the **zero-point energy**.

Since $V(x) = 0$ in the region where the particle can be found, the zero-point energy must be purely kinetic in this case. We could have estimated it using the Heisenberg uncertainty relation: Confining the particle to a region $\Delta x = a$ introduces a momentum uncertainty $\Delta p \sim \frac{\hbar}{\Delta x} = \frac{\hbar}{a}$, and a kinetic energy $\frac{(\Delta p)^2}{2m} \sim \frac{\hbar^2}{2ma^2}$. Since $V(x) = 0$ for $x \leq x \leq a$, and $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$ in this region, and $E = \frac{p^2}{2m}$ in **CM**, it appears that momentum is associated with the derivative $\frac{\partial}{\partial x}$ of the wavefunction, and kinetic energy with the curvature $\frac{\partial^2}{\partial x^2}$.

The eigenfunctions have the property that

$$\int_{-\infty}^{\infty} dx u_n^*(x) u_m(x) = \int_0^a dx \frac{2}{a} \sin\left(n\pi\frac{x}{a}\right) \sin\left(m\pi\frac{x}{a}\right) \tag{11-1}$$

$$= \frac{1}{a}\int_0^a dx \left\{\cos\left((n-m)\pi\frac{x}{a}\right) - \cos\left((n+m)\pi\frac{x}{a}\right)\right\} \tag{11-2}$$

$$= \frac{\sin((n-m)\pi)}{(n-m)\pi} - \frac{\sin((n+m)\pi)}{(n+m)\pi} \tag{11-3}$$

$$= \begin{cases} 0 & \text{for } n \neq m, \\ 1 & \text{for } n = m. \end{cases} \tag{11-4}$$

$$= \delta_{nm} \tag{11-5}$$

$$\boxed{\delta_{nm} = \begin{cases} 0 & \text{for } n \neq m, \\ 1 & \text{for } n = m. \end{cases}} \rightarrow \text{Kronecker delta} \tag{11-6}$$

This is a general property, not particular to this example: Eigenfunctions belonging to different eigenvalues are **orthogonal**, if the eigenfunctions are normalized we call them **orthonormal**.

$$\boxed{\int_{-\infty}^{\infty} dx u_n^*(x) u_m(x) = \delta_{mn}} \quad \text{orthonormality condition} \tag{11-7}$$

Complex conjugate not necessary for box potential, where eigenfunctions are real, but necessary in general.

$$\int u_n^* u_n dx = \int |u_n|^2 dx = 1 \quad \text{normalization} \tag{11-8}$$

Eigenfunctions as basis

Why is knowing the eigenfunctions important? Consider box potential: Fourier's theorem states that any function $\psi(x)$ that satisfies that boundary conditions $\psi(0) = 0 = \psi(a)$ can be written as a sum of $\sin\left(n\pi\frac{x}{a}\right)$.

Note. $\cos\left(n\pi\frac{x}{a}\right)$ terms do not appear since they do not satisfy the boundary conditions.

Since $u_n \propto \sin\left(n\pi\frac{x}{a}\right)$, we can also write

$$\boxed{\psi(x) = \sum_{n=0}^{\infty} c_n u_n(x)} \quad \text{expansion of arbitrary } \psi(x) \text{ into eigenfunctions} \tag{11-9}$$

In order to calculate the expansion coefficients c_n, we use the orthonormality property of the eigenfunctions.

$$\int_{-\infty}^{\infty} dx u_m^* \psi(x) = \int_0^a dx u_m^*(x) \left(\sum_{n=0}^{\infty} c_n u_n(x)\right) \tag{11-10}$$

$$= \sum_{n=0}^{\infty} c_n \int_0^a dx u_m^* u_n(x) = \sum_{n=0}^{\infty} c_n \delta_{mn} \tag{11-11}$$

$$= c_m \tag{11-12}$$

Thus the expansion coefficient can be calculated as the integral

$$\boxed{c_m = \int_{-\infty}^{\infty} dx u_m^*(x)\psi(x)} \quad \text{expansion coefficients} \tag{11-13}$$

Again we do not need the complex conjugate here, since u_m is real, but we have written it in the correct general form. We call the set of functions $\{u_n(x)\}$ **complete** if an arbitrary function $\psi(x)$ can be written as a superposition of functions of the set. A complete, orthonormal set of functions is called a **basis**. The above properties, derived for the particles in the box, are true in general in **QM**:

1. The energy eigenfunctions u_n of a Hamiltonian

   $$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{11-14}$$

   form a basis, an arbitrary wavefunction $\psi(x)$ can be expanded as superposition of eigenstates

   $$\boxed{\psi(x) = \sum_n c_n u_n(x)} \tag{11-15}$$

   with complex coefficients c_n. If the spectrum of eigenvalues, or part of the spectrum of eigenvalues is continuous, the expansion contains an integral $\psi(x) = \sum_n c_n u_n(x) + \int dE c(E) u_E(x)$.

2. The expansion coefficients c_n are given by

$$\boxed{c_n = \int_{-\infty}^{\infty} dx u_n^*(x)\psi(x)}, \tag{11-16}$$

i.e., they can be calculated once the eigenfunctions u_n are known explicitly.

Analogy to vector analysis

Consider an n-dimensional vector space. A set of n mutually orthogonal unit vectors $\{\hat{e}_i\}_{i=1,\ldots,n}$ forms a basis, i.e. an arbitrary vector $\mathbf{v}$ can be expanded into unit vectors:

$$\mathbf{v} = \sum_{i=1}^{n} \underbrace{c_i}_{\text{complex number}} \underbrace{\hat{e}_i}_{\text{basis vector}} \tag{11-17}$$

with suitably chosen coefficients c_i. The c_i are uniquely determined, and given by

$$c_i = \hat{e}_i \cdot \mathbf{v}. \tag{11-18}$$

In vector analysis terms, the wavefunctions $\psi(x)$ form a vector space, called the **Hilbert space**, the energy eigenfunctions $u_n(x)$ form a basis. The dimension of the Hilbert space is the number of independent energy eigenfunctions; if that number is infinite, the Hilbert space is infinite-dimensional.

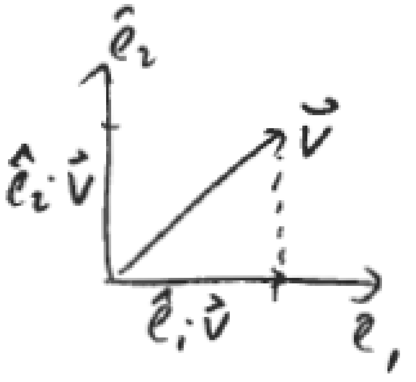


Figure I: projection of $\mathbf{v}$ onto $\hat{e}_i$

We have the following correspondences:

QM	**vector analysis**
wavefunction: $\psi(x)$	vector: $\mathbf{v}$
energy eigenfunction: $u_i(x)$	basis vector: $\hat{e}_i$
# of independent $u_i(x)$	dimension of vector space
$\int_{-\infty}^{\infty} dx u_i^*(x)\psi(x)$	dot product: $\hat{e}_i \cdot \mathbf{v}$
$\int_{-\infty}^{\infty} dx \psi_1^*(x)\psi_2^*(x)$	dot product: $\mathbf{v_1} \cdot \mathbf{v_2}$
$\int_{-\infty}^{\infty} dx u_i^*(x)u_j^*(x) = \delta_{ij}$	orthonormality: $\hat{e}_i \cdot \hat{e}_j = \delta_{ij}$
$\psi(x) = \sum_i c_i u_i(x)$ for any $\psi(x)$	Completeness: $\mathbf{v} = \sum_i c_i \hat{e}_i$ for any $\mathbf{v}$
Eigenvalue equation: $\hat{H}\psi_E(x) = E\psi_E(x)$	Eigenvalue equation: $\hat{M}\mathbf{v} = m\mathbf{v}$
Set of eigenfunction of certain type of operators (Hermitian operators) forms basis. Hamiltonian is such an operator.	Set of eigenfunctions of certain types of matrices forms basis. (self-adjoint matrices $M^\dagger = M$.)

Physical interpretation of expansion coefficients

Assume that we have prepared some arbitrary wavefunction $\psi(x)$ (that is consistent with the coundary conditions) inside the box.

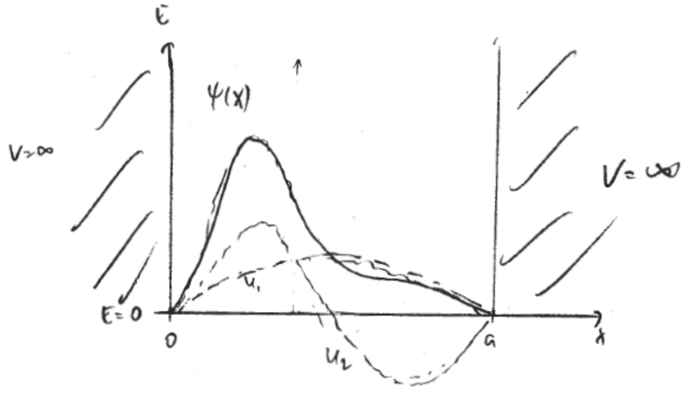


Figure II: Pictorial expansion of wavefunction in a box in terms of eigenfunctions.

- Expansion into eigenfunctions:

$$\psi(x) = \sum_{i=1}^{\infty} c_i u_i(x) \tag{11-19}$$

$$= c_1 u_1(x) + c_2 u_2(x) + \dots \tag{11-20}$$

- phase (sign) of c_i important, detemines whether more amplitude on left/right etc.
- The larger $|c_i|$, the more the wavefunction $\psi(x)$ is "like" $u_i(x)$, (the larger the projection of $\psi(x)$ onto u_i, given by (analogy to $\hat{e}_i \cdot \mathbf{v}$) $c_i = \int dx u_i^*(x)\psi(x)$).
- Calculate $\sum_{i=1}^{\infty} |c_i|^2$:

$$\sum_{i=1}^{\infty} |c_i|^2 = \sum_{i=1}^{\infty} c_i^* c_i \tag{11-21}$$

$$= \sum_{i=1}^{\infty} c_i^* \int dx u_i^*(x)\psi(x) \tag{11-22}$$

$$= \int dx \psi(x) \sum_{i=1}^{\infty} c_i^* u_i^*(x) \tag{11-23}$$

$$= \int dx \psi(x) \left(\sum_{i=1}^{\infty} c_i u_i(x) \right)^* \tag{11-24}$$

$$= \int dx \psi(x) \psi^*(x) \tag{11-25}$$

$$= \int dx |\psi(x)|^2 \tag{11-26}$$

$$= 1 \tag{11-27}$$

Since $\sum_{i=1}^{\infty} |c_i|^2 = 1$, the quantity $|c_i|^2$ can be interpreted as the probability to find the particle in the state i, if a measurement of the particle's energy eigenstate is made, given that the particle has been initially prepared in a state characterized by an arbitrary wavefunction $\psi(x)$. How is a measurement of the energy eigenstate of the particle made? $\Longrightarrow$ Measure energy of particle.
$E_n = \epsilon n^2$, $\epsilon = E_1 = \frac{\hbar^2 \pi^2}{2ma^2}$

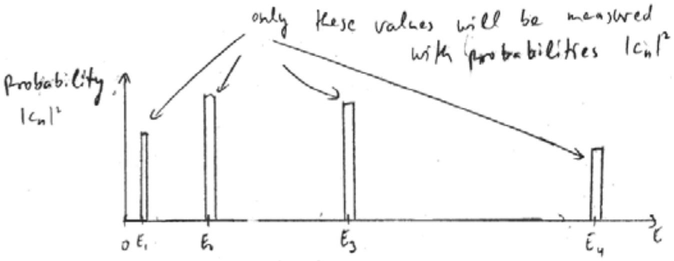


Figure III: Measurement of particle energy in state Ψ that is not an energy eigenstates can yield different values E_i with probabilities $|c_i|^2$.

After the energy measurement

After the energy measurement with outcome E_i, the particle will be in the energy eigenstate u_i, and all subsequent energy measurements will yield the energy E_i.

What is the energy before measurement is made?

If $\psi(x)$ is not an eigenstate, the energy is "uncertain". A measurement can yield different energy values, only probabilities can be predicted. However, an average value of the energy can be calculated:

$$\boxed{\langle E\rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n} \quad \rightarrow \quad \text{generally valid} \tag{12-1}$$

Using the definition of the expansion coefficients c_n, we can also write this as

$$\begin{aligned}
\langle E\rangle &= \sum_{n=1}^{\infty} |c_n|^2 E_n \\
&= \sum_{n=1}^{\infty} c_n \left(\int dx u_n^*(x)\psi(x)\right)^* E_n \\
&= \sum c_n \int dx \psi^*(x) E_n u_n(x) \\
&= \sum c_n \int dx \psi^*(x) \hat{H} u_n(x) \\
&= \int dx \psi^*(x) \hat{H} \left(\sum_n c_n u_n(x)\right) \\
&= \int dx \psi^*(x) \hat{H} \psi(x)
\end{aligned}$$

Expectation value of energy in state $\psi(x)$:

$$\boxed{\langle E\rangle = \int dx \psi^*(x)\hat{H}\psi(x)} \quad \rightarrow \quad \text{valid for any potential, not only box potential} \tag{12-2}$$

Hamiltonian operator and energy

If we postulate that a particle of momentum p is associated with a deBroglie wavelength $\lambda_{\mathrm{dB}} = \frac{h}{p}$, then it is represented by a plane wave e^{ikx} with a wavevector

$k = \frac{2\pi}{\lambda_{dB}} = \frac{2\pi p}{h} = \frac{p}{\hbar}$, or $p = \hbar k$. Then, since the Fourier transform $\phi(k)$ of $\psi(x)$ gives the probability amplitude for the plane wave with wavevector $k \rightarrow$

$$\left(\psi(x) = \frac{1}{\sqrt{2\pi}} \int dk \phi(k) e^{ikx} \right), \tag{12-3}$$

the expectation value of momentum is given by

$$\langle p \rangle = \int dk \hbar k |\phi(k)|^2 \tag{12-4}$$

$$\langle p^2 \rangle = \int dk (\hbar k)^2 |\phi(k)|^2 \tag{12-5}$$

Note. In PS5 you show using the properties of Fourier transforms that these expectation values can also be expressed as

$$\langle p \rangle = \int dx \psi^*(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x) \tag{12-6}$$

$$\langle p^2 \rangle = \int dx \psi^*(x) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \psi(x) \tag{12-7}$$

It follows that the expectation value of the KE is

$$\langle T \rangle = \left\langle \frac{p^2}{2m} \right\rangle = \int dx \psi^*(x) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \psi(x) \tag{12-8}$$

How large is the expectation value of the potential energy?

Potential $V(x)$ should be weighted by probability to find particle between x and $x + dx$, hence

$$\langle V \rangle = \int dx V(x) |\psi(x)|^2 = \int dx \psi^*(x) V(x) \psi(x) \tag{12-9}$$

Since $\langle E \rangle = \langle V \rangle + \langle T \rangle$ it follows that

$$\langle E \rangle = \int dx \psi^*(x) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) \tag{12-10}$$

$$= \int dx \psi^*(x) \hat{H} \psi(x) \tag{12-11}$$

This is the so-called "sandwich form" for calculating the mean value (expectation value) of the energy. If $\psi(x)$ is an energy eigenfunction with eigenvalue E_0, i.e. if

$\hat{H}\psi_{E_0}(x) = E_0\psi_{E_0}(x)$, then

$$\begin{aligned}\langle E\rangle &= \int dx \psi^*_{E_0}(x)\hat{H}\psi_{E_0}(x)\\ &= \int dx \psi^*_{E_0}(x)E_0\psi_{E_0}(x)\\ &= E_0\int dx|\psi_{E_0}(x)|^2\\ &= E_0,\end{aligned} \tag{12-12}$$

where we have used the fact that the wavefunction is normalized. This shows that the constant E_0 appearing when we make the product ansatz $\Psi(x,t) = T(t)\psi(x)$ to solve the SE is really the energy of the system. We define the expectation value $\left\langle \hat{O}\right\rangle$ of an operator $\hat{O}$ acting on a wavefunction $\psi(x)$ via the sandwich form

$$\boxed{\left\langle \hat{O}\right\rangle = \int dx \psi^*(x)\hat{O}\psi(x)} \tag{12-13}$$

Then we have

$$\langle E\rangle = \left\langle \hat{H}\right\rangle = \int dx \psi^*(x)\hat{H}\psi(x) \tag{12-14}$$

The mean energy of the state described by the wave-function $\psi(x)$ is the expectation value of the Hamiltonian operator $\hat{H}$. We say that the Hamiltonian $\hat{H}$ is the operator associated with the measurable quantity energy. The operator $\hat{T}$ associated with the kinetic energy is

$$\boxed{\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}} \tag{12-15}$$

with $\langle T\rangle = \left\langle \hat{T}\right\rangle = \int dx\psi^*(x)\hat{T}\psi(x)$, while the operator $\hat{V}$ for the potential energy is simply a multiplicative factor

$$\boxed{\hat{V} = V(x)} \tag{12-16}$$

with $\langle V\rangle = \left\langle \hat{V}\right\rangle = \int dx\psi^*(x)\hat{V}\psi(x)$

Why is potential energy associated with a simple multiplicative factor while kinetic energy is associated with a second derivative?

Because we are working with wavefunctions in real space $\psi(x)$. *We say that we are working with wavefunctions in position space or in the position representation.*

Another possibility is to work in momentum space (the momentum representation). Then the wavefunction should be the probability amplitude in momentum space, which is just the Fourier transform $\phi(p)$ of $\psi(x)$. Then to calculate the KE we have to weigh $\frac{p^2}{2m}$ for each p with the probability to find the particle momentum between p and $p + dp$:

$$\left\langle \frac{p^2}{2m} \right\rangle = \int dp \frac{p^2}{2m} |\phi(p)|^2 \tag{12-17}$$

$$= \int dp \phi^*(p) \frac{p^2}{2m} \phi(p) \tag{12-18}$$

We see that in momentum space the KE operator is simply a multiplicative factor

$$\boxed{\hat{T} = \frac{\hat{p}^2}{2m} = \frac{p^2}{2m}} \quad \rightarrow \quad \text{in momentum space} \tag{12-19}$$

How to calculate the potential energy $V(x)$ in terms of the wavefunctions in momentum space $\phi(p)$?

Note. In PS5, you have shown that

$$\langle x \rangle = \int dp \phi^*(p) \left(i\hbar \frac{\partial}{\partial p} \right) \phi(p) \tag{12-20}$$

$$\langle x^n \rangle = \int dp \phi^*(p) \left(i\hbar \frac{\partial}{\partial p} \right)^n \phi(p) \tag{12-21}$$

Consequently, for any potential function

$$V(x) = \sum_{n=0}^{\infty} a_n x^n \tag{12-22}$$

we can calculate the expectation value $\langle V \rangle$ as

$$\langle V \rangle = \int dp \phi^*(p) V \left(i\hbar \frac{\partial}{\partial p} \right) \phi(p)$$

$$= \int dp \phi^*(p) \hat{V} \phi(p) \tag{12-23}$$

Consequently, the representation of the operator for the PE in momentum space is

$$\boxed{\hat{V} = V \left(i\hbar \frac{\partial}{\partial p} \right)}, \tag{12-24}$$

where a function V of an operator is defined in terms of its Taylor expansion, Eq. (12-22). It follows that the Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V} \tag{12-25}$$

$$= \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + V(x) \qquad \text{in position space} \tag{12-26}$$

$$= \frac{p^2}{2m} + V\left(i\hbar\frac{\partial}{\partial p}\right) \qquad \text{in momentum space} \tag{12-27}$$

The SE equation is always the same:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t) \qquad \text{time-dependent SE} \tag{12-28}$$

$$i\hbar\frac{\partial}{\partial t}\Phi(p,t) = \hat{H}\Phi(p,t) \qquad \text{time-dependent SE} \tag{12-29}$$

$$\hat{H}\psi(x) = E\psi(x) \qquad \text{time-independent SE} \tag{12-30}$$

$$\hat{H}\phi(p) = E\phi(p) \qquad \text{time-independent SE} \tag{12-31}$$

Example. For the harmonic oscillator, the SE (in appropriately chosen units) looks the same in position and momentum space:

1. linear potential $V(x) = Ax$

$$-\frac{\hbar^2}{2m}\psi''(x) + Ax\psi(x) = E\psi(x) \qquad \text{in position space} \tag{12-32}$$

$$\frac{p^2}{2m}\phi(p) + i\hbar A\phi'(p) = E\phi(p) \qquad \text{simpler equation in momentum space} \tag{12-33}$$

2. harmonic oscillator: $V(x) = \frac{1}{2}m\omega^2x^2$

$$-\frac{\hbar^2}{2m}\psi''(x) + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x) \tag{12-34}$$

$$\frac{p^2}{2m}\phi(p) - \frac{1}{2}\hbar^2m\omega^2\phi''(p) = E\phi(p) \tag{12-35}$$

If we know the solutions in one space, we know the solutions in the other. The HO is symmetric in position and momentum.

Time evolution of the wave function

Consider a particle in the infinite box with a wavefunction at $t = 0$, $\Psi(x, t = 0)$. Expansion into eigenstates $\Psi(x, t = 0) = c_1 u_1(x) + c_2 u_2(x) + \cdots = \sum_{n=1}^{\infty} c_n u_n(x)$. Since each eigenstate $u_n(x, t)$ evolves at a rate given by its eigenenergy E_n,

$$\begin{aligned} u_n(x,t) &= u_n(x, t=0) e^{-iE_n t/\hbar} && \text{(12-36)} \\ &= u_n(x) e^{-iE_n t/\hbar} && \text{(12-37)} \end{aligned}$$

the wavefunction $\Psi(x, t)$ at later time t is simply given by the linear superposition

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n u_n(x) e^{-iE_n t/\hbar}} \tag{12-38}$$

where the expansion coefficients c_n are calculated at $t = 0$:

$$\boxed{c_n = \int_{-\infty}^{\infty} dx u_n^*(x) \Psi(x, t=0)} \tag{12-39}$$

Hence the importance of energy eigenstates and eigenvalues: The eigenvalues represent not only the only possible outcomes of individual energy measurements, but the combination of eigenstates and eigenvalues allows one to write down the time evolution of an arbitrary initial state.

How does a particle move?

Example. $\Psi(x, t = 0) = \frac{1}{\sqrt{2}}(u_1(x) + u_2(x))$. Particle in equal superposition of ground and first excited state.

$$\begin{aligned} \Psi(x,t) &= \frac{1}{\sqrt{2}} \left[u_1(x) e^{-iE_1 t/\hbar} + u_2(x) e^{-iE_2 t/\hbar} \right] && \text{(12-40)} \\ &= \frac{1}{\sqrt{2}} e^{-iE_1 t/\hbar} \left[u_1(x) + u_2(x) e^{i(E_2 - E_1)t/\hbar} \right] && \text{(12-41)} \\ |\Psi(x,t)|^2 &= \frac{1}{2} |u_1(x) + u_2(x) e^{-i(E_2 - E_1)t/\hbar}|^2 && \text{(12-42)} \end{aligned}$$

At any fixed position, interference term between u_1 and u_2 oscillates from constructive to destructive interference with angular frequency

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} \tag{12-43}$$

The energy difference determines the oscillation of the particle between the halves of the box.

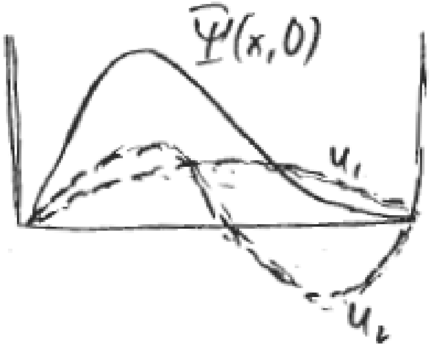


Figure I: A particle in a superposition of the ground state an the first excited state oscillates from left to right at the frequency corresponding to the energy difference between the two states.

Note. If $\Psi(x, t = 0)$ is an eigenstate, $\Psi(x, t = 0) = u_n(x)$, then $|\Psi(x,t)|^2 = |\Psi(x, 0)|^2$, i.e. the probability density does not change in time: Bohr's **stationary states** are **energy eigenstates**.

An oscillating electron (particle) is in a superposition of at least two energy eigenstates. An electron in a Bohr atom that emits a Lyman α photon is in a superposition of the ground (E_1) and the first excited state (E_2). It oscillates in space at the frequency $\frac{E_2-E_1}{\hbar}$, exactly the frequency of the emitted Lyman α photon.

Our box example also shows: The more localized the initial spatial distribution $\Psi(x, 0)$, the more eigenstates are involved, and the more complicated the time evolution will be (there will be interference terms oscillating at $(E_2 - E_1)/\hbar$, $(E_3 - E_1)/\hbar$, $(E_3 - E_2)/\hbar$, $\ldots$) All motion of particles involves oscillating interference.

What is the relation between the SE and CM

QM should reproduce CM as limiting case

- **CM** $p = mv = m\frac{dx}{dt}$

- We expect this (and other) classical equation(s) to hold for the **QM** expectation values (average position, momentum), at least in some limiting case.

- Calculate $m\left\langle\frac{dx}{dt}\right\rangle$: the only time variation arises from the time variation of wave function, x is coordinate, not particle position in the **SE**.

$$m\left\langle \frac{dx}{dt}\right\rangle = m\frac{d}{dt}\langle x\rangle \tag{12-44}$$

$$= m\frac{d}{dt}\int dx\Psi^*(x,t)x\Psi(x,t) \tag{12-45}$$

$$= m\int dx\left\{\frac{\partial\Psi^*}{\partial t}x\Psi + \Psi^* x\frac{\partial\Psi}{\partial t}\right\} \tag{12-46}$$

$$= m\int dx\left[\frac{1}{-i\hbar}\left\{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + V(x)\Psi^*\right\}x\Psi + \Psi^* x\frac{1}{i\hbar}\left\{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi\right\}\right] \tag{12-47}$$

$$= \frac{\hbar}{2i}\int_{-\infty}^{\infty} dx\left[\frac{\partial^2\Psi}{\partial x^2}x\Psi - \Psi^* x\frac{\partial^2\Psi}{\partial x^2}\right] - \frac{1}{ih}\int dx\left[\Psi^* V(x)x\Psi - \Psi^* xV(x)\Psi\right] \tag{12-48}$$

The second term is zero, the first term can be integrated by parts:

$$\begin{aligned}\frac{\partial^2\Psi^*}{\partial x^2}x\Psi &= \frac{\partial}{\partial x}\left(\frac{\partial\Psi^*}{\partial x}x\Psi\right) - \frac{\partial\Psi^*}{\partial x}\frac{\partial}{\partial x}(x\Psi)\\ &= \frac{\partial}{\partial x}\left(\frac{\partial\Psi^*}{\partial x}x\Psi\right) - \frac{\partial\Psi^*}{\partial x}\Psi - \frac{\partial\Psi^*}{\partial x}x\frac{\partial\Psi}{\partial x}\end{aligned} \tag{12-49}$$

Similarly,

$$\Psi^* x\frac{\partial^2\Psi}{\partial x^2} = \left(\frac{\partial^2\Psi^*}{\partial x^2}x\Psi\right)^* \tag{12-50}$$

$$A = \frac{\partial}{\partial x}\left[\frac{\partial\Psi^*}{\partial x}\Psi - \Psi^* x\frac{\partial\Psi}{\partial x}\right] - \frac{\partial\Psi^*}{\partial x}\Psi + \Psi^*\frac{\partial\Psi}{\partial x} \tag{12-51}$$

$$= \frac{\partial}{\partial x}\left[\frac{\partial\psi^*}{\partial x}x\psi - \Psi^* x\frac{\partial\Psi}{\partial x}\right] - \frac{\partial}{\partial x}(\Psi^*\Psi) + 2\Psi^*\frac{\partial\Psi}{\partial x} \tag{12-52}$$

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi} \rightarrow \text{ SE} \tag{12-53}$$

For the wavefunction to be normalizable, it has to vanish at ±∞ faster than $\frac{1}{\sqrt{x}}$. Consequently, the integral over the first two terms in A yields zero and we are left with

$$m\frac{d}{dt}\langle x\rangle = \frac{\hbar}{2i}\int_{-\infty}^{\infty} dx 2\Psi^* \frac{\partial \Psi}{\partial x} \tag{12-54}$$

$$= \int_{-\infty}^{\infty} dx \Psi^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t) \tag{12-55}$$

$$= \int_{-\infty}^{\infty} dx \Psi^*(x,t)\hat{p}\Psi(x,t) = \langle p\rangle \tag{12-56}$$

So it follows from the SE that the expectation value of momentum is equal to the particle mass times the rate of change of the expectation value of particle position:

$$m\frac{d}{dt}\langle x\rangle = \langle p\rangle \tag{12-57}$$

This equation follows from the SE in combination with the position representation of the momentum operator $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$. Does the appearance of $\frac{1}{i}$ mean that momentum is complex (imaginary)? Let us calculate the complex conjugate $\langle p\rangle^*$ of the expectation values of $\langle p\rangle$ in some arbitrary state $\Psi(x,t)$ . . .

$$\langle p\rangle^* = \langle \hat{p}\rangle \tag{13-1}$$

$$= \left(\int dx \Psi^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\right)^* \tag{13-2}$$

$$= \int dx \Psi \left(-\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi^* \tag{13-3}$$

$$= -\frac{\hbar}{i}\int_{-\infty}^{\infty} dx \left[\frac{\partial}{\partial x}\left(\Psi\Psi^*\right) - \Psi^*\frac{\partial}{\partial x}\Psi\right] \tag{13-4}$$

$$= \int dx \Psi^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi \tag{13-5}$$

$$= \langle p\rangle\,, \tag{13-6}$$

where again we have used integration by parts and the fact that Ψ vanishes at $\pm\infty$. Consequently, $\langle p\rangle = \langle p\rangle^*$, i.e. all expectation values of $\hat{p}$ are real. Since an eigenvalue is the expectation value for the corresponding stationary state, all eigenvalues of the momentum operator must be real. An operator whose eigenvaluse are real (or equivalently, whose expectation value for all admissible wavefunctions is real) is called a **Hermitian operator**.

$$\boxed{\text{Physically measurable quantities are represented by Hermitian operators.}}$$

Similarly, one can show that $\langle E\rangle^* = \langle E\rangle$ for any state, so all energy eigenvalue are real: The Hamiltonian operator $\hat{H}$ is a Hermitian operator.

Can we "derive" Newton's $F = ma$ from the SE?

CM: $F = -\frac{dV}{dx} = ma = \frac{dp}{dt}$ Let us calculate the expectation value of $\frac{dp}{dt}$:

$$\left\langle \frac{dp}{dt}\right\rangle = \frac{d}{dt}\langle p\rangle \tag{13-7}$$

$$= \frac{d}{dt}\int dx \Psi^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t) \tag{13-8}$$

$$= \frac{\hbar}{i}\int dx \left(\frac{\partial \Psi^*}{\partial t}\frac{\partial \Psi}{\partial x} + \Psi^*\frac{\partial}{\partial x}\frac{\partial}{\partial t}\right) \tag{13-9}$$

$$= \int dx \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial \psi}{\partial x} + V\Psi^*\frac{\partial \Psi}{\partial x} - \Psi^*\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\psi\right)\right]}_{A} \tag{13-10}$$

The integrand is

$$\begin{aligned} A = &-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x} + \cancel{V\Psi^*\frac{\partial\Psi}{\partial x}} + \frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2}\right) \\ &-\frac{\hbar^2}{2m}\frac{\partial\Psi^*}{\partial x}\frac{\partial^2\Psi}{\partial x^2} - \Psi^*\left(\frac{\partial V}{\partial x}\right)\Psi - \cancel{\Psi^* V\frac{\partial\Psi}{\partial x}} && \text{(13-11)} \\ = &\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\frac{\partial\Psi}{\partial x}\right] - \Psi^*\left(\frac{\partial V}{\partial x}\right)\Psi && \text{(13-12)} \end{aligned}$$

Again the integral over the first term vanishes since $\Psi \to 0$ for $x \to \pm\infty$, and we are left with

$$\left\langle \frac{dp}{dt} \right\rangle = \int dx \Psi^*(x,t)\left(-\frac{\partial V}{\partial x}(x)\right)\Psi(x,t) = \left\langle -\frac{dV}{dx} \right\rangle \qquad \text{(13-13)}$$

or

$$\boxed{\frac{d}{dt}\langle p \rangle = -\left\langle \frac{dV}{dx} \right\rangle} \qquad \text{(13-14)}$$

It follows from the SE that **the expectation values obey the classical equations of motion**.

$$\begin{aligned} m\frac{d}{dt}\langle x \rangle &= \langle p \rangle && \text{(13-15)} \\ \frac{d}{dt}\langle p \rangle &= -\left\langle \frac{dV}{dx} \right\rangle && \text{(13-16)} \end{aligned}$$

Average momentum changes due to average force

$$-\left\langle \frac{dV}{dx} \right\rangle = -\int dx \Psi^*\left(\frac{\partial V}{\partial x}\right)\Psi = \int dx F(x)|\Psi(x,t)|^2, \qquad \text{(13-17)}$$

i.e. position-dependent force $F(x)$ is weighted by probability density $|\Psi(x,t)|^2$ for finding the particle at position x at time t. Note, however, that $\left\langle \frac{dV}{dx} \right\rangle \neq \frac{d}{d\langle x \rangle}V(\langle x \rangle)$

Example 1. Double-peaked distribution. The probability to find the particle at the average position $\langle x \rangle$ is small, so the force there cannot be of much consequence for the particle's motion.

Example 2. Force varying quickly on wavepacket scale. Classical calculation $-\frac{d}{d\langle x \rangle}V(\langle x \rangle)$ would predict very large (and quickly varying force as $\langle x \rangle$ changes), actual **QM** force

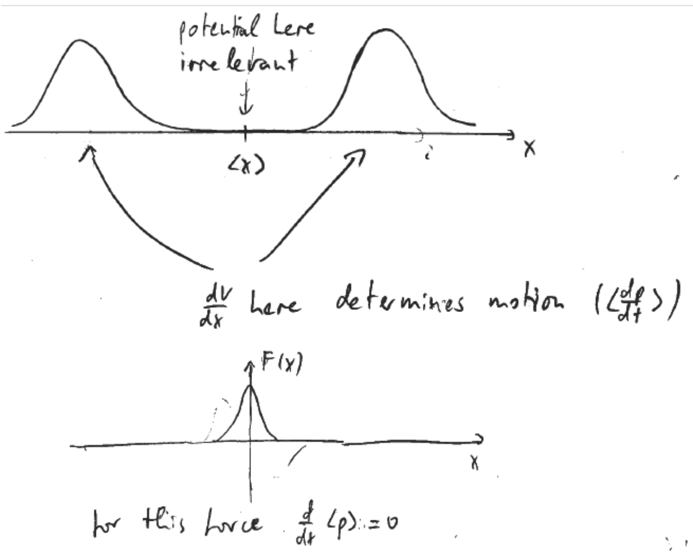


Figure I: Double-peaked particle distribution with vanishing probability to find particle at average position.

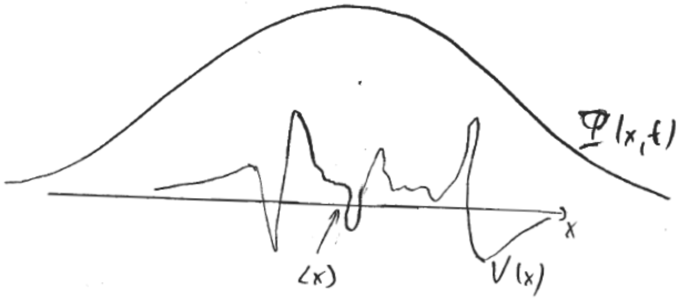


Figure II: Particle wavepacket large compared to spatial variation of the force. The time evolution of the wavepacket will depend on the value of the force averaged over the wavepacket, not just on the force at the average particle location.

$\left\langle -\frac{dV}{dx} \right\rangle$ experienced by particle is much smaller. However, if the force varies slowly compared to the size of a single wavepacket, then

$$\left\langle -\frac{dV}{dx} \right\rangle = \langle F(x) \rangle \approx F(\langle x \rangle) = -\frac{d}{d\langle x \rangle} V(\langle x \rangle) \qquad \text{(13-18)}$$

This is the reason why we can treat particles in macroscopic potential usually as classical particles.

$$\boxed{\frac{d}{dt}\langle p \rangle = -\left\langle \frac{dV}{dx} \right\rangle} \quad \rightarrow \quad \text{always true} \qquad \text{(13-19)}$$

$$\boxed{\frac{d}{dt}\left\langle p\right\rangle \approx -\frac{d}{d\left\langle x\right\rangle}V(\left\langle x\right\rangle)} \quad \rightarrow \quad \textbf{Ehrenfest's theorem} \text{ for slowly varying potentials} \tag{13-20}$$

Eigenfunctions of the momentum operator

What are the eigenfunctions u_p of the momentum operator, i.e. the eigenfunctions satisfying

$$\hat{p}u_p = pu_p, \tag{13-21}$$

where p is some (fixed) particular eigenvalue of $\hat{p}$. We know that the operator $\hat{p}$ is Hermitian, so all eigenvalues p are real. In position space, we have $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ and $\frac{\hbar}{i}\frac{\partial}{\partial x}u_p(x) = pu_p(x)$, $u_p(x) = Ae^{ipx/\hbar}$. The momentum eigenfunctions are (of course) just the plane waves. Let us check the orthonormality condition for eigenstates:

$$\int_{-\infty}^{\infty} dx u_p{}^*(x)u_p(x) = A_{p'}{}^*A_p\int dx e^{-ip'x/\hbar}e^{ipx/\hbar} \tag{13-22}$$

$$= A_{p'}{}^*A_p\int dx e^{i(p-p')x/\hbar} \tag{13-23}$$

$$= \hbar A_p{}^*A_p\int dy e^{i(p-p')y} \tag{13-24}$$

$$= \hbar A_{p'}{}^*A_p\delta(p-p')2\pi \tag{13-25}$$

$$= \hbar 2\pi A_{p'}{}^*A_p\delta(p-p') \tag{13-26}$$

The momentum eigenfunction are orthogonal for $p \neq p'$, but we have a normalization problem for $p = p'$: The Dirac delta function diverfes, or equivalently, the integral

$$\int dx|u_p(x)|^2 = |A_P|^2\int_{-\infty}^{\infty} dx\,\underbrace{|e^{ipx/\hbar}|^2}_{=1} \tag{13-27}$$

diverges. Before looking at possibilities to deal with normalization problem, let us calculate the expansion coefficients $c(p)$

$$c(p) = \int dx A_p{}^*e^{-ipx/\hbar}\psi(x) = A_p{}^*\underbrace{\int dx\psi(x)e^{-ipx\hbar}}_{\sqrt{2\pi\hbar}\phi(p)} \tag{13-28}$$

We see that if we make the normalization choice $A_p = \frac{1}{\sqrt{2\pi\hbar}}$, then the expansion coefficients $c(p)$ into momentum eigenstates are just given by the Fourier transform

$$u_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \quad \rightarrow \quad \text{"normalized" momentum eigenstates} \tag{13-29}$$

$$\psi(x) = \underbrace{\int_{-\infty}^{\infty} dp \phi(p) u_p(x)}_{\text{expansion into momentum eigenstates}} \tag{13-30}$$

$$= \underbrace{\frac{1}{\sqrt{2\pi\hbar}} \int dp \phi(p) e^{ipx/\hbar}}_{\text{Fourier transformation}} \tag{13-31}$$

The expansion into momentum eigenstates and Fourier tranformation are one and the same. Since $\psi(x)$ and $\phi(p)$ contain the same information about the particle, we can use either one to characterize the position and motion of the particle. A more fundamental motion is the **state of the particle** (a state is a vector in Hilbert space), the state can be expressed (written down) in various representations (like position representation $\psi(x)$, momentum representation $\phi(p)$, energy representation c_E) associated with Hermitian operators (position $\hat{x}$, momentum $\hat{p}$, energy $\hat{H}$). We call $\phi(p)$ the **momentum representation** of a particular state, and interpret it as the **wavefunction in momentum space**. The SE governs the time evolution of the wavefunction, or equivalently, the time evolution of the state of the particle in Hilbert space.

For one particle in one (three) dimensions, the Hilbert space is one- (three-) dimensional, but for N particles in three dimensions the Hilbert space is $3N$-dimensional. In general, it cannot be factored into a tensor product of N three-dimensional vector space $V_{\text{system}} \neq V_1 \otimes V_2 \otimes \cdots \otimes V_N$, or equivalently, the wavefunction for N particles does not factor into a product of wavefunctions for each particle,

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_1}, t) \neq \Psi_1(\mathbf{r_1})\Psi_2(\mathbf{r_2}) \ldots \Psi_N(\mathbf{r_N}) \tag{13-32}$$

In this case, when the wavefunction for an N-particle system cannot be written as a product of wavefunctions for the individual particles, i.e. when the particles do not evolve independently, we speak of an **entangled state**. Because of this possibility a quantum system of N particles is vastly (exponentially in N) richer than an classical system of N particles. However, in most cases we lose track of the particle-particle correlations associated with entanglement, and the system behaves quasi-classically. A quantum system that could preserve the correlations, and that could be manipulated externally, would constitute a quantum computer. A quantum computer could solve certain computation problems (only a handful have been discovered so far) exponentially faster than a classical computer. Because of the enormous size of the

Hilbert space, certain quantum mechanical problems involving many-particle correlations (e.g. high temperature superconductivity that involves correlated motion of many electrons) are very difficult to solve or simulate on a classical computer. Now back to a single particle in one dimension . . .

Normalization of wavefunctions in free space

The momentum eigenstates in the position representation, $u_p(x)$ defined by

$$\hat{p}u_p(x) = \frac{\hbar}{i}\frac{\partial}{\partial x}u_p(x) = pu_p(x), \tag{14-1}$$

and given by

$$u_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \tag{14-2}$$

cannot be normalized in free space to be interpreted as a probability density since $|u_p(x)|^2 = \frac{1}{2\pi\hbar}$, and $\int_{-\infty}^{\infty} dx|u_p(x)|^2$ diverges. However, they do satisfy the **continuum orthonormality condition**

$$\boxed{\int_{-\infty}^{\infty} dx u_p{}^*(x)u_{p'}(x) = \delta(p-p')}. \tag{14-3}$$

This normalization corresponds to a uniform particle density (particle per meter) given by $|u_p(x)|^2 = \frac{1}{2\pi\hbar}$. Let us calculate the **probability current** (particles moving past a point x per second), defined by

$$\boxed{j(x) = \frac{\hbar}{2im}\left[\psi^*(x)\frac{\partial\psi}{\partial x}(x) - \left(\frac{\partial\psi^*}{\partial x}(x)\right)\psi(x)\right]} \rightarrow \text{see PS} \tag{14-4}$$

For $\psi(x) = u_p(x)$ we find

$$j(x) = \frac{\hbar}{2im}\frac{1}{2\pi\hbar}\left[\frac{ip}{\hbar} - \left(-\frac{ip}{\hbar}\right)\right] \tag{14-5}$$

$$= \frac{1}{2\pi\hbar}\frac{p}{m}, \tag{14-6}$$

which is exactly what we expect for a uniform particle density $|u_p(x)|^2 = \frac{1}{2\pi\hbar}$ moving at velocity $v = \frac{p}{m}$.

In general, choosing a wavefunction $\psi(x) = Ce^{ipx}$ corresponds to particles moving at velocity $\frac{p}{m}$, a particle density $|psi(x)|^2 = |C|^2$, and a particle current $j(x) = |C|^2\frac{p}{m}$. Alternatives to deal with the normalization problem (wavefunction not square-integrable) for momentum states are:

1. Wavepackets
   A superposition of a finite number of momentum eigenstates is not normalizable, but a wavepacket consisting of an infinite number of momentum eigenstates (Fourier components) is.

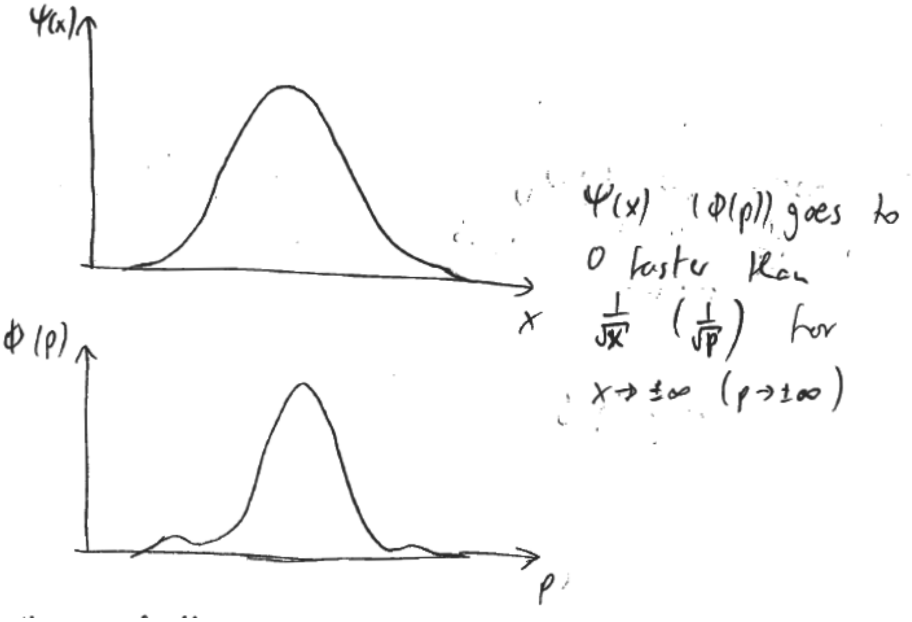


Figure I: A wavepacket $\psi(x)$ in position space or $\phi(k)$ in momentum space whose wavefunction for large x (or k) falls off faster than $x^{-1/2}$ ($k^{-1/2}$) can be directly normalized.

2. Periodic boundary conditions
   Assume box of finite length L, require periodic boundary conditions

$$\psi(0) = \psi(L) \tag{14-7}$$

For plane waves $e^{ipx/\hbar}$ this implies that $e^{ipL/\hbar} = 1$ or $\frac{pL}{\hbar} = kL = n2\pi$, n integer, i.e. momentum is quantized, $p_n = n\hbar k_o$ with $k_0 = \frac{2\pi}{L}$. The corresponding momentum states are normalizable in the interval $[0, L]$,

$$\int_0^L dx |Ce^{ipx/\hbar}|^2 = L|C|^2 = 1 \tag{14-8}$$

$$\boxed{u_{p_n}(x) = \frac{1}{\sqrt{L}} e^{ip_n x/\hbar}} \tag{14-9}$$

→ **normalized momentum eigenstates** in box of size L with $p_n = n\hbar k_o$

$$\int_0^L dx u_{p_n}{}^*(x) u_{p_m}(x) = \delta_{nm} \quad \rightarrow \quad \text{orthonormality condition in box} \tag{14-10}$$

We perform all calculations for fixed size box, then take the limit $L \to \infty$ (i.e. $k_0 \to 0$, momentum spectrum becomes continuous). All physically sensible

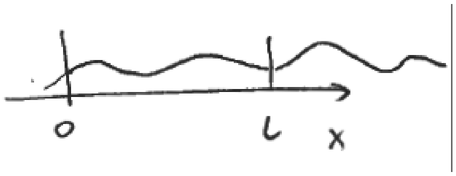


Figure II: Wavefunction in box of length L with periodic boundary conditions.

results will be independent of the initially chosen box size L as long as L is large compared to distances of interest.

Time evolution of free-particle wavepackets

In free space we often work with **normalized Gaussian wavepackets**

$$\Psi(x,t=0)=\frac{1}{(2\pi)^{1/4}{w_0}^{1/2}}e^{-\frac{x^2}{4{w_0}^2}} \tag{14-11}$$

Written in this form we have

- $|\Psi(x,0)|^2=\frac{1}{(2\pi)^{1/2}w_0}e^{-\frac{x^2}{2{w_0}^2}}$
- $\int dx|\Psi(x,0)|^2=1$
- $\langle x\rangle=0$
- $\langle x^2\rangle={w_0}^2$
- $(\delta x)^2=\langle x^2\rangle-\langle x\rangle^2={w_0}^2$

$\Delta x=w_0$ is the uncertainty or rms width (root-mean-square width) of the wavepacket. Why do we prefer this Gaussian form of wavepacket?

1. Particularly simple and symmetric, the **Fourier transform is also a Gaussian** wavepacket:

   $$\phi(k)=\frac{1}{(2\pi)^{1/4}{k_0}^{1/2}}e^{-\frac{k^2}{4{k_0}^2}} \tag{14-12}$$

   with $k_0=\frac{1}{2w_0}$. $(\Delta k)^2=\langle k^2\rangle-\langle k\rangle={k_0}^2$

2. This is a wavepacket with the **minimum uncertainty** $\Delta x\Delta k=\frac{1}{2}$ $(\Delta x\Delta p=\frac{\hbar}{2})$ allowed by **QM**

3. Physical system after give rise to Gaussian broadening in momentum or position, e.g., thermal distribution of atomic momenta in a gas is a Gaussian distribution.

How do we make a wavepacket move at velocity v_1?

We displace the distribution in momentum space from $\langle p\rangle = \langle \hbar k\rangle = 0$ to $\langle p\rangle = \langle \hbar k\rangle = \hbar k_1 = mv_1$ (see Fig. III).

$$\phi(k) = \frac{1}{(2\pi)^{1/4}{k_0}^{1/2}} e^{-\frac{(k-k_1)^2}{4{k_0}^2}}. \tag{14-13}$$

The inverse Fourier transform, i.e., the spatial wavefunction

$$\Psi(x, t=0) = \frac{1}{(2\pi)^{1/4}{w_0}^{1/2}} e^{-\frac{x^2}{4{w_o}^2}} e^{ik_1 x} \tag{14-14}$$

is still a Gaussian, but now with a phase variation e^{ik_1x}, rather than a constant phase over the wavepacket (compare Eq. (14-11). This phase variation e^{ik_1x} in position space "encodes" the motion of the wavepacket at velocity $v_1 = \frac{\hbar k_1}{m}$: The dominant de Broglie wavelength in the wavepacket corresponds to a wavevector k_1, or a momentum $\hbar k_1$.

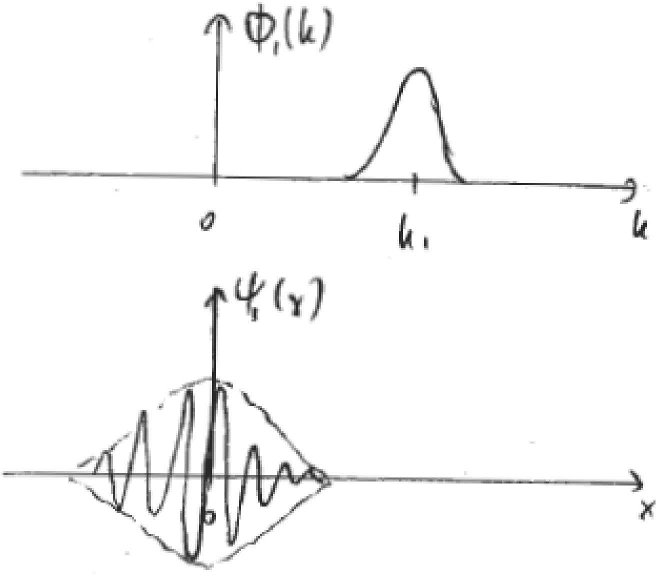


Figure III: Moving Gaussian wavepacket with average velocity $v_1 = \hbar k_1/m$ and spatial wavefunction $\psi_1(x) = \frac{1}{(2\pi)^{1/4}w_0^{1/2}} e^{-\frac{x^2}{4w_0^2}e^{ik_1x}}$.

How does a free-space Gaussian wave packet evolve in time?

In general, we expand a wavefunction $\Psi(x,0)$ into energy eigenfunctions $u_E(x)$, and then evolve the energy eigenfunctions as $e^{-iEt/\hbar}$.

In free space, there is only KE. Then the momentum eigenstates $u_p(x)$ are **simultaneous eigenstates of energy**:

$$\hat{H}u_p(x) = \frac{\hat{p}^2}{2m}u_p(x) \tag{14-15}$$

$$= \frac{1}{2m}\left(\hbar i\frac{\partial}{\partial x}\right)^2 \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \tag{14-16}$$

$$= \frac{p^2}{2m}u_p(x) \tag{14-17}$$

or

$$\hat{H}u_p(x) = \frac{p^2}{2m}u_p(x) \tag{14-18}$$

$$= E_p u_p(x) \tag{14-19}$$

in free space. The energy eigenstates are said to be **doubly degenerate**: For each eigenvalue of energy $E > 0$ there are two different momentum states (namely $u_{\pm p}(x)$ with $p = \sqrt{2m\hbar}$) that have the same energy. It follows that a momentum eigenstate with eigenvalue p evolves in time as $e^{-iE_pt/\hbar}$, so that the wavefunction in momentum space evolves in time as

$$\Phi(p,t) = \Phi(p,0)e^{-i\frac{p^2}{2m}t/\hbar} \tag{14-20}$$

→ **time evolution of momentum eigenfunctions in free space**. The wavefunction in real space is given by the inverse Fourier transform $\Psi(x,t)$, or equivalently, as the superposition of energy eigenfunctions with their corresponding phase evolution factors $e^{-iE_pt/\hbar}$:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int dp\Phi(p,t)e^{ipx/\hbar} \tag{14-21}$$

$$(= \int dp\Phi(p,t)u_p(x)) \tag{14-22}$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\int dp\Phi(p,0)e^{ipx/\hbar}e^{-\frac{p^2}{2m}t/\hbar} \tag{14-23}$$

$$= \int dp\Phi(p,0)U_p(x,t) \tag{14-24}$$

$$= \int dp\Phi(p,t)u_p(x) \tag{14-25}$$

where $U_p(x,t) = u_p(x)e^{-\frac{p^2}{2m}t/\hbar} = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}e^{-i\frac{p^2}{2m}t/\hbar}$ are the time-dependent momentum eigenfunctions in free space. The above equation shows that the phases of different Fourier components $u_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}$ evolve in time at different speeds, the "running out of phase" of different Fourier components leads to a spreading of the wavepacket in position space. In the problem sets you will show that the rms width $\Delta x(t) = w(t)$ of the wavepacket grows in time as

$$w(t) = w_0\sqrt{1 + \frac{\hbar^2 k^2}{m^2 {w_0}^2}} \tag{14-26}$$

Since a wavepacket contains different momentum components, it changes in time in free space even though there are non external forces acting. For long times $t \gg t_0 = \frac{m{w_o}^2}{\hbar}$ the wavepacket spreads as $w(t) \approx \frac{\hbar}{mw_0}t$, i.e. at a speed $v_0 = \frac{\hbar}{mw_0}$ that is inversely proportional to its initial size. That speed is negligible for macroscopic wavepacket size, but can be appreciable for initially well-localized microscopic objects. The spreading of a wavepacket in free space was early evidence that the wavepacket size cannot be identified with the particle size. The spreading is due to the quadratic (i.e. not linear) dependence of the energy, and hence the phase evolution rate, on momentum. Note that the wavepacket of a massless particle, e.g. a photon, with $E = pc$ would not spread. (The SE is non-relativistic and does not apply to photons.)

Motion of wave packets, group velocity, and stationary phase

Why is it that a wavefunction

$$\Psi(x,0) = \frac{1}{(2\pi)^{1/4}{w_0}^{1/2}}e^{-\frac{x^2}{4{w_0}^2}}e^{ik_1x} \tag{14-27}$$

represents a particle moving at velocity $v_1 = \frac{\hbar k_1}{m}$? Since a crest of a single momentum component $u_{k_1}(x,t) = \frac{1}{\sqrt{2\pi}}e^{-k_1x}e^{-i\frac{\hbar k^2}{2m}t}$ moves forward a distance $\lambda = \frac{2\pi}{k_1}$ in a time $T = \frac{2\pi}{\omega_1}$ (remember that $\omega_1 = \frac{\hbar {k_1}^2}{2m}$ and $e^{-iE_1t/\hbar} = e^{-i\omega_1 t}$), the velocity of the crest is $v_{\text{ph}} = \frac{\lambda}{T} = \frac{2\pi}{k_1}\frac{\omega}{2\pi} = \frac{\omega_1}{k_1} = \frac{\hbar k_1}{2m}$

$$\boxed{v_{\text{ph}} = \frac{\omega_1}{k_1} = \frac{\hbar k_1}{2m} = \frac{p_1}{2m}} \tag{14-28}$$

This is the **phase velocity of a momentum component**.

The particle does **not** move at the phase velocity $v_{\text{ph}} = \frac{\omega_1}{k_1}$ at which the plane wave associated with a single momentum moves forward. At what velocity then?

- Look at exponent and write:
  $E_1 = E_1(k_1) = \hbar\omega_1 = \hbar\omega(k_1) = \frac{\hbar {k_1}^2}{2m}$
- $e^{\left(-\frac{x^2}{4{w_0}^2}+ik_1x-i\omega(k_1)t\right)}$

Remember Fermat's principle of stationary phase: path is defined by region of space where phasors point mostly in one direction, i.e. where the phase $\phi(k) = -\frac{x^2}{4{w_o}^2} + ikx + i\omega(k_1)t$ does not vary between different momentum components k to lowest order

$$0 = \frac{\partial\phi}{\partial k} = ix - i\left(\frac{\partial\omega}{\partial k}\right)t = i\left(x - \left(\frac{\partial\omega}{\partial x}t\right)\right), \tag{14-29}$$

or

$$x(t) = \left(\frac{\partial\omega}{\partial k}\right)t. \tag{14-30}$$

Fermat's principle leads us to the concept of group velocity

$$\boxed{v_{\text{gr}} = \frac{\partial\omega}{\partial k}(k_1) = \frac{\hbar k_1}{m} = \frac{p_1}{m}} \tag{14-31}$$

Group velocity of the wavepacket at which the wavepacket, i.e. the region of constructive interference, propagates. The difference between group and phase velocity is due to the fact the $\frac{\partial\omega}{\partial k} \neq \frac{\omega}{k}$, or $\frac{\partial E}{\partial p} = \frac{\partial(\hbar\omega)}{\partial(\hbar k)} \neq \frac{E}{p}$, i.e. the quadratic dependence of KE on momentum in free space. This is in contrast to photons with a linear dispersion relation $\frac{\partial\omega}{\partial k} = \frac{\omega}{k} = c$ in vacuum, where group and phase velocity are the same.

Example: Simple harmonic oscillator

$$V(x) = \frac{1}{2} k x^2$$

(See Griffiths' "Introduction to Quantum Mechanics" P. 37 to 43 ; and the textbook P. 143-144)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi = E\psi$$

$$m\omega^2 = k$$

Let $\xi = \sqrt{\frac{m\omega}{\hbar}}\, x$ (changing variable to simplify the equation)

$$\Rightarrow \frac{d^2\psi}{d^2\xi} = (\xi^2 - K)\psi \qquad K = \frac{2E}{\hbar\omega}$$

For large ξ

$$\Rightarrow \frac{d^2\psi}{d\xi^2} \cong \xi^2\psi$$

$\Rightarrow$ approximate solution $\psi(\xi) \simeq A e^{-\xi^2/2} + \underset{\substack{\downarrow \\ \text{not normalizable}}}{B e^{+\xi^2/2}}$

$$\psi(\xi) = h(\xi)\, e^{-\xi^2/2}$$

(hoping $h(\xi)$ has simpler functional form than $\psi(x)$)

$$\Rightarrow \frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K-1)h = 0$$

Solve the equation using the series expansion method

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j \xi^j$$

Task is to find $a_0, a_1, \cdots$

$$\frac{dh}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + \cdots = \sum_{j=0}^{\infty} j a_j \xi^{j-1}$$

$$\frac{d^2h}{d\xi^2} = 2a_2 + 2\cdot 3 a_3\xi + 3\cdot 4 a_4 \xi^2 + \cdots = \sum_{j=0}^{\infty} (j+1)(j+2) a_{j+2}\xi^j$$

Put back into the differential equation

$$\sum_{j=0}^{\infty} [\, (j+1)(j+2) a_{j+2} - 2j a_j + (K-1) a_j]\xi^j = 0$$

$$\Rightarrow (j+1)(j+2) a_{j+2} - 2j a_j + (K-1) a_j = 0$$

$$\Rightarrow a_{j+2} = \underbrace{\frac{(2j+1-K)}{(j+1)(j+2)}}_{\text{recursion relation}} a_j$$

$a_0 \Rightarrow a_2, a_4, \cdots$ can be calculated
$a_1 \Rightarrow a_1, a_2, \cdots$ can be calculated

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

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

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

However, not all the solutions so obtained are normalizable

For large j, $\quad a_{j+2} \simeq \frac{2}{j} a_j$

$$\downarrow$$

$$a_j \sim \frac{C}{(j/2)!}$$

$$h(\xi) \simeq C \sum \frac{1}{(j/2)!}\xi^j \simeq C \sum \frac{1}{k!}\xi^{2k} \simeq Ce^{\xi^2/2}$$

$$\downarrow$$

not acceptible

Therefore, the series must be terminate

$\downarrow$

There must occur some "highest" j (call it n)

$$K = 2n+1$$

$$\Downarrow$$

$$E_n = (n+\tfrac{1}{2})\hbar\omega \qquad n = 0, 1, 2, \cdots$$

$$\updownarrow$$

$$\psi_n(x) = \underbrace{\left(\frac{m\omega}{n\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}}}_{\text{normalization constant}} \underbrace{H_n(\xi)}_{\text{Hermite polynomial}} e^{-\xi^2/2}$$

We return now to the Schrödinger equation for the harmonic oscillator (Equation 2.39):

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

Things look a little cleaner if we introduce the dimensionless variable

$$\xi\equiv\sqrt{\frac{m\omega}{\hbar}}x; \qquad [2.55]$$

in terms of ξ, the Schrödinger equation reads

$$\frac{d^2\psi}{d\xi^2}=(\xi^2-K)\psi, \qquad [2.56]$$

where K is the energy, in units of $(1/2)\hbar\omega$:

$$K\equiv\frac{2E}{\hbar\omega}. \qquad [2.57]$$

Our problem is to solve Equation 2.56, and in the process obtain the "allowed" values of K (and hence of E).

To begin with, note that at very large ξ (which is to say, at very large x), ξ^2 completely dominates over the constant K, so in this regime

$$\frac{d^2\psi}{d\xi^2}\approx\xi^2\psi, \qquad [2.58]$$

which has the approximate solution (check it!)

$$\psi(\xi)\approx Ae^{-\xi^2/2}+Be^{+\xi^2/2}. \qquad [2.59]$$

The B term is clearly not normalizable (it blows up as $|x|\to\infty$); the physically acceptable solutions, then, have the asymptotic form

$$\psi(\xi)\to(\quad)e^{-\xi^2/2}, \quad \text{at large } \xi. \qquad [2.60]$$

This suggests that we "peel off" the exponential part,

$$\psi(\xi)=h(\xi)e^{-\xi^2/2}, \qquad [2.61]$$

in hopes that what remains $[h(\xi)]$ has a simpler functional form than $\psi(\xi)$ itself.[14] Differentiating Equation 2.61, we have

$$\frac{d\psi}{d\xi}=\left(\frac{dh}{d\xi}-\xi h\right)e^{-\xi^2/2}$$

and

$$\frac{d^2\psi}{d\xi^2}=\left(\frac{d^2h}{d\xi^2}-2\xi\frac{dh}{d\xi}+(\xi^2-1)h\right)e^{-\xi^2/2},$$

so the Schrödinger equation (Equation 2.56) becomes

$$\frac{d^2h}{d\xi^2}-2\xi\frac{dh}{d\xi}+(K-1)h=0. \qquad [2.62]$$

I propose to look for a solution to Equation 2.62 in the form of a power series in ξ[15]:

$$h(\xi)=a_0+a_1\xi+a_2\xi^2+\cdots=\sum_{j=0}^{\infty}a_j\xi^j. \qquad [2.63]$$

---

[14] Note that although we invoked some approximations to *motivate* Equation 2.61, what follows is *exact*. The device of stripping off the asymptotic behavior is the standard first step in the power series method for solving differential equations—see, for example, Boas (cited in footnote 8), Chapter 12.

[15] According to Taylor's theorem, any reasonably well-behaved function can be expressed as a power series, so Equation 2.63 involves no real loss of generality. For conditions on the applicability of the series method, see Boas (cited in footnote 8) or George Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Orlando, FL: Academic Press, 1985), Section 8.5.

Differentiating the series term by term,

$$\frac{dh}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + \cdots = \sum_{j=0}^{\infty} j a_j \xi^{j-1},$$

and

$$\frac{d^2h}{d\xi^2} = 2a_2 + 2\cdot 3a_3\xi + 3\cdot 4a_4\xi^2 + \cdots = \sum_{j=0}^{\infty}(j+1)(j+2)a_{j+2}\xi^j.$$

Putting these into Equation 2.62, we find

$$\sum_{j=0}^{\infty}\left[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j\right]\xi^j = 0. \qquad [2.64]$$

It follows (from the uniqueness of power series expansions[16]) that the coefficient of *each power* of ξ must vanish,

$$(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j = 0,$$

and hence that

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)}a_j. \qquad [2.65]$$

This **recursion formula** is entirely equivalent to the Schrödinger equation itself. Given a_0 it enables us (in principle) to generate $a_2, a_4, a_6, \ldots$, and given a_1 it generates $a_3, a_5, a_7, \ldots$. Let us write

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi), \qquad [2.66]$$

where

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

is an *even* function of ξ (since it involves only even powers), built on a_0, and

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

is an *odd* function, built on a_1. Thus Equation 2.65 determines $h(\xi)$ in terms of two arbitrary constants (a_0 and a_1)—which is just what we would expect, for a second-order differential equation.

However, not all the solutions so obtained are normalizable. For at very large j, the recursion formula becomes (approximately)

$$a_{j+2} \approx \frac{2}{j}a_j,$$

---

[16] See, for example, Arfken (footnote 15), Section 5.7.

with the (approximate) solution

$$a_j \approx \frac{C}{(j/2)!},$$

for some constant C, and this yields (at large ξ, where the higher powers dominate)

$$h(\xi) \approx C \sum \frac{1}{(j/2)!}\xi^j \approx C \sum \frac{1}{k!}\xi^{2k} \approx Ce^{\xi^2}.$$

Now, if h goes like $\exp(\xi^2)$, then ψ (remember ψ?—that's what we're trying to calculate) goes like $\exp(\xi^2/2)$ (Equation 2.61), which is precisely the asymptotic behavior we *don't* want.[17] There is only one way to wiggle out of this: For normalizable solutions *the power series must terminate*. There must occur some "highest" j (call it n) such that the recursion formula spits out $a_{n+2} = 0$ (this will truncate *either* the series h_{even} *or* the series h_{odd}; the *other* one must be zero from the start). For physically acceptable solutions, then, we must have

$$K = 2n + 1,$$

for some positive integer n, which is to say (referring to Equation 2.57) that the *energy* must be of the form

$$E_n = (n + \frac{1}{2})\hbar\omega, \quad \text{for } n = 0, 1, 2, \ldots. \qquad [2.67]$$

Thus we recover, by a completely different method, the fundamental quantization condition we found algebraically in Equation 2.50.

For the allowed values of K, the recursion formula reads

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)}a_j. \qquad [2.68]$$

If $n = 0$, there is only one term in the series (we must pick $a_1 = 0$ to kill h_{odd}, and $j = 0$ in Equation 2.68 yields $a_2 = 0$):

$$h_0(\xi) = a_0,$$

and hence

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

(which reproduces Equation 2.48). For $n = 1$ we pick $a_0 = 0$,[18] and Equation 2.68 with $j = 1$ yields $a_3 = 0$, so

$$h_1(\xi) = a_1\xi,$$

---

[17] It's no surprise that the ill-behaved solutions are still contained in Equation 2.65; this recursion relation is equivalent to the Schrödinger equation, so it's got to include both the asymptotic forms we found in Equation 2.59.

[18] Note that there is a completely different set of coefficients a_j for each value of n.

and hence

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

(confirming Equation 2.51). For $n = 2$, $j = 0$ yields $a_2 = -2a_0$, and $j = 2$ gives $a_4 = 0$, so

$$h_2(\xi) = a_0(1 - 2\xi^2)$$

and

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

and so on. (Compare Problem 2.13, where the same result was obtained by algebraic means.)

In general, $h_n(\xi)$ will be a polynomial of degree n in ξ, involving even powers only, if n is an even integer, and odd powers only, if n is an odd integer. Apart from the overall factor (a_0 or a_1) they are the so-called **Hermite polynomials**, $H_n(\xi)$.[19] The first few of them are listed in Table 2.1. By tradition, the arbitrary multiplicative factor is chosen so that the coefficient of the highest power of ξ is 2^n. With this convention, the normalized[20] stationary states for the harmonic oscillator are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}. \qquad [2.69]$$

They are identical (of course) to the ones we obtained algebraically in Equation 2.50. In Figure 2.5a I have plotted $\psi_n(x)$ for the first few n's.

The quantum 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 range (that is, with x greater than the classical amplitude for the energy in question) is *not* zero (see Problem 2.15), and in all odd states the probability of finding the particle at the center of the potential well is zero. Only at relatively large n do we begin to see some resemblance to the classical case. In Figure 2.5b I have superimposed the classical position distribution on the quantum one (for $n = 100$); if you smoothed out the bumps in the latter, the two would fit pretty well (however, in the classical case we are talking about the distribution of positions over *time* for *one* oscillator, whereas in the quantum case we are talking about the distribution over an *ensemble* of identically-prepared systems).[21]

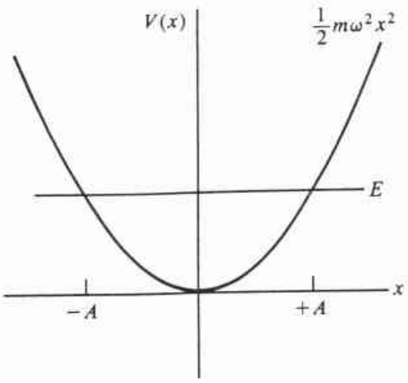
Table 2.1: The first few Hermite polynomials, $H_n(x)$.

$H_0 = 1,$
$H_1 = 2x,$
$H_2 = 4x^2 - 2,$
$H_3 = 8x^3 - 12x,$
$H_4 = 16x^4 - 48x^2 + 12,$
$H_5 = 32x^5 - 160x^3 + 120x.$

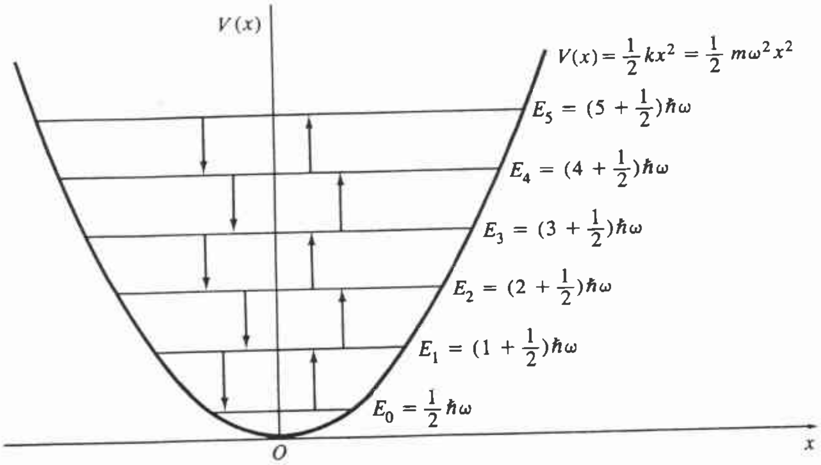
---

[19] The Hermite polynomials have been studied extensively in the mathematical literature, and there are many tools and tricks for working with them. A few of these are explored in Problem 2.18.

[20] I shall not work out the normalization constant here; if you are interested in knowing how it is done, see, for example, Leonard Schiff, *Quantum Mechanics*, 3rd ed. (New York: McGraw-Hill, 1968), Section 13.

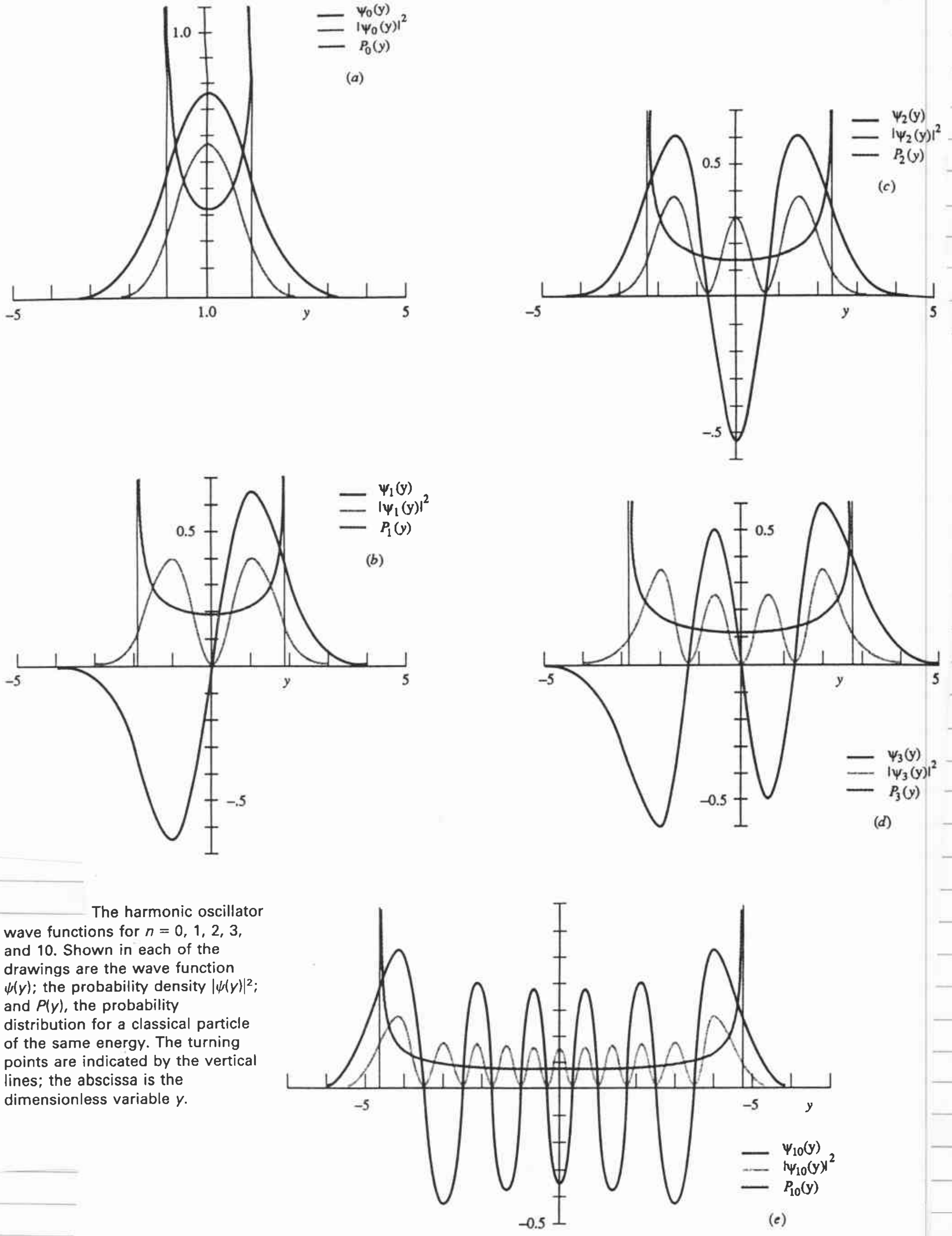


The potential function $V(x)$ of a one-dimensional harmonic oscillator. Classically, a particle of energy E oscillates between the turning points at $x = \pm A$.

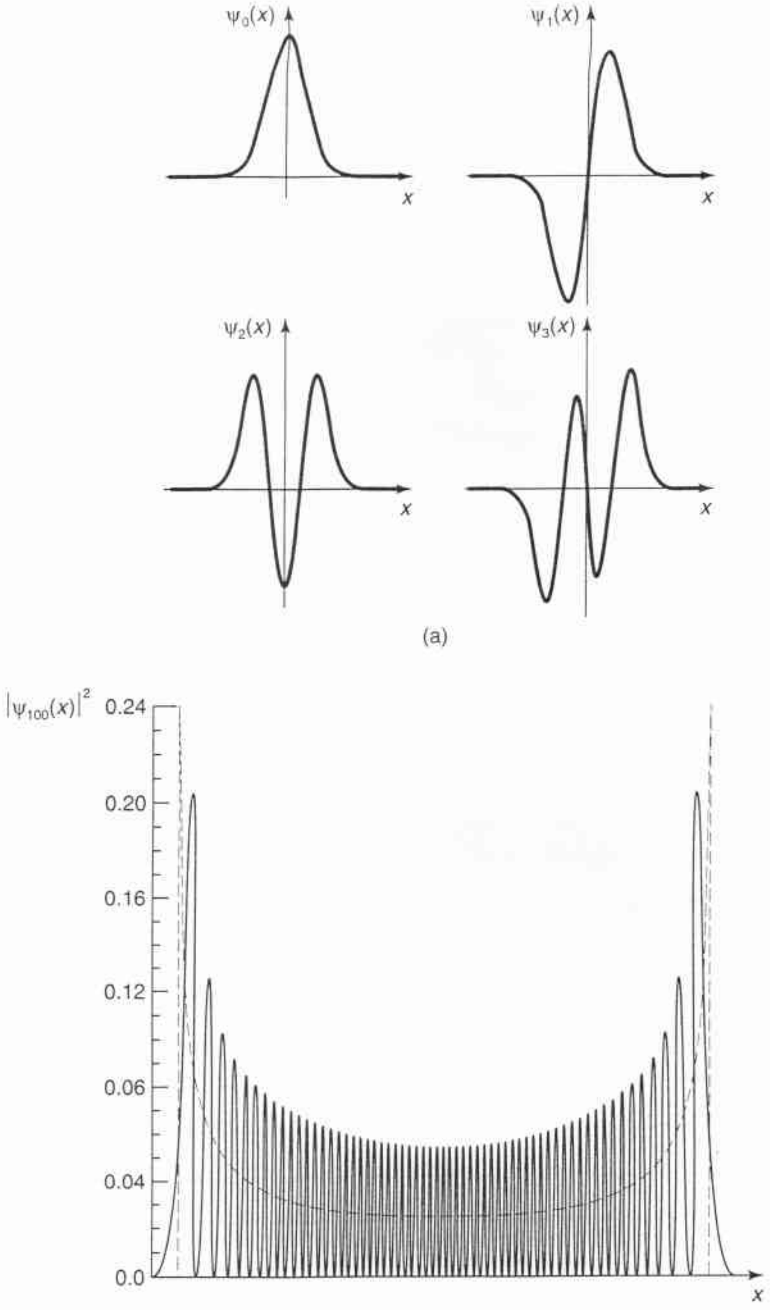


The energy levels of the harmonic oscillator. Note that the difference between adjacent energy levels is independent of n and equal to $\Delta E = \hbar\omega_0$. Transitions corresponding to $\Delta n = \pm 1$ are indicated by arrows.

分類：
編號： 6-17
總號：



The harmonic oscillator wave functions for $n = 0, 1, 2, 3,$ and 10. Shown in each of the drawings are the wave function $\psi(y)$; the probability density $|\psi(y)|^2$; and $P(y)$, the probability distribution for a classical particle of the same energy. The turning points are indicated by the vertical lines; the abscissa is the dimensionless variable y.



(a) The first four stationary states of the harmonic oscillator.
(b) Graph of $|\psi_{100}|^2$, with the classical distribution (dashed curve) superimposed.

Appendix

THE HARMONIC OSCILLATOR

§ 5.1 Classical Theory

According to classical theory a harmonic oscillator is a particle, mass m, moving under the action of a force

$$F = -m\omega^2 x. \tag{5.1}$$

The equation of motion is then

$$\frac{d^2x}{dt^2}+\omega^2 x = 0, \tag{5.2}$$

with solution

$$x = a\cos\omega t, \tag{5.3}$$

which represents an oscillatory motion of angular frequency ω, and amplitude a. The potential is related to the force by

$$F = -\frac{\partial V}{\partial x},$$

so that

$$V(x) = \tfrac{1}{2}m\omega^2 x^2. \tag{5.4}$$

The energy of the oscillation (5.3) is the potential energy when the particle is at an extreme position. Therefore

$$E = \tfrac{1}{2}ma^2\omega^2. \tag{5.5}$$

§ 5.2 Quantum Theory: The Eigenvalues

We now consider the quantum theory of such a system. Since the classical motion is bound for all values, the entire quantum energy spectrum should consist of discrete values. The energy eigenvalue equation is (3.16) with

$$\hat{H} = \frac{\hat{p}^2}{2m}+\tfrac{1}{2}m\omega^2\hat{x}^2. \tag{5.6}$$

In the Schrödinger representation this is

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{m\omega^2}{2}x^2\right]u_n(x) = E_n u_n(x). \tag{5.7}$$

A2

If this is multiplied by $2/\hbar\omega$ we get

$$\left[\frac{-\hbar}{m\omega}\frac{\partial^2}{\partial x^2}+\frac{m\omega}{\hbar}x^2\right]u_n(x) = \frac{2E_n}{\hbar\omega}u_n(x). \tag{5.8}$$

Introducing the variables

$$y = \left(\frac{m\omega}{\hbar}\right)^{1/2}x, \tag{5.9}$$

$$\epsilon_n = E_n/\hbar\omega, \tag{5.10}$$

the equation becomes

$$\left(\frac{\partial^2}{\partial y^2}-y^2\right)u_n(y) = -2\epsilon_n u_n(y). \tag{5.11}$$

This equation may be solved by the standard techniques, which are employed below for angular momentum and the hydrogen atom. Instead, we use the factorization method, which is particularly elegant for this problem and brings to the fore a new type of operator, which in the long run plays a very important role in the theory.

Since

$$\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)u_n(y) \equiv \left(\frac{\partial^2}{\partial y^2}-y^2-1\right)u_n(y),$$

(5.11) may be re-written

$$\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)u_n(y) = [-2\epsilon_n-1]u_n(y). \tag{5.11a}$$

Alternatively, it may be written

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)u_n(y) = [-2\epsilon_n+1]u_n(y). \tag{5.11b}$$

Multiply (5.11a) by $(\partial/\partial y-y)$, then

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)u_n(y) = [-2\epsilon_n-1]\left(\frac{\partial}{\partial y}-y\right)u_n(y). \tag{5.12}$$

Then, either

$$\left(\frac{\partial}{\partial y}-y\right)u_n(y) = 0; \tag{5.13}$$

or

$$\left(\frac{\partial}{\partial y}-y\right)u_n(y) = u_{n+1}(y), \text{ say,} \tag{5.14}$$

A 3

and (5.12) can be written

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)u_{n+1}(y) = [-2(\epsilon_n+1)+1]\,u_{n+1}(y). \tag{5.15}$$

This is (5.11b) for u_{n+1}, provided

$$\epsilon_n+1 = \epsilon_{n+1}. \tag{5.16}$$

The only solution to (5.13) is

$$u(y) = e^{+(1/2)y^2}.$$

This diverges for large y and is therefore not a possible state. Thus given any solution $u_n(y)$, eigenvalue ϵ_n, it is always possible to generate a new state $u_{n+1}(y)$ by (5.14) with eigenvalue ϵ_n+1.

Similarly, multiplying (5.11b) by $(\partial/\partial y+y)$,

$$\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)u_n(y) = [-2\epsilon_n+1]\left(\frac{\partial}{\partial y}+y\right)u_n(y). \tag{5.17}$$

Now either

$$\left(\frac{\partial}{\partial y}+y\right)u_n(y) = 0; \tag{5.18}$$

or

$$\left(\frac{\partial}{\partial y}+y\right)u_n(y) = u_{n-1}(y),\ \text{say}, \tag{5.19}$$

In the latter case (5.17) can be written

$$\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)u_{n-1}(y) = [-2(\epsilon_n-1)-1]\,u_{n-1}(y), \tag{5.20}$$

which is (5.11a) for u_{n-1} provided

$$\epsilon_{n-1} = \epsilon_n-1. \tag{5.21}$$

Thus given any solution u_n, eigenvalue ϵ_n, it is possible to generate a new state of lower energy, $u_{n-1}(y)$, determined by (5.19) with eigenvalue (ϵ_n-1), unless u_n is the ground state, u_0. In this case it must satisfy (5.18);

$$\left(\frac{\partial}{\partial y}+y\right)u_0(y) = 0. \tag{5.22}$$

This determines the ground state eigenfunction to be

$$u_0(y) = e^{-(1/2)y^2}. \tag{5.23}$$

Further, by (5.22) and (5.11b), the ground state energy is

$$2\epsilon_0-1 = 0. \tag{5.24}$$

A-4

Combining these results, (5.24) and (5.16), the eigenvalues are

$$\epsilon_0 = \tfrac{1}{2}, \qquad \epsilon_1 = 1+\tfrac{1}{2}, \ldots \qquad \epsilon_n = n+\tfrac{1}{2}, \ldots$$

So that

$$E_n = (\tfrac{1}{2}+n)\hbar\omega, \qquad n = 0, 1, 2, \ldots, \tag{5.25}$$

a discrete set for all energies, in accordance with the general argument given above.

The expression for the energy levels is one of the most important in quantum mechanics. It justifies Planck's explanation of the interaction of radiation with matter, provided matter can be regarded as a collection of oscillators, each one emitting or absorbing radiation of its own frequency. The energy exchange is then restricted by the oscillator eigenvalues to take place in units of $\hbar\omega$, which is just Planck's hypothesis.

§ 5.3 The Eigenfunctions: Annihilation and Creation Operators

The successive eigenfunctions can be generated from $u_0(x)$ by repeated application of (5.14), so that, for example,

$$\begin{aligned} u_1(y) &= \left(\frac{\partial}{\partial y} - y\right) u_0(y), \\ &= \left(\frac{\partial}{\partial y} - y\right) e^{-(1/2)y^2}, \\ &= -2y\, e^{-(1/2)y^2}. \end{aligned} \tag{5.26}$$

The ground state is an even function of y with no nodes; the first excited state is an odd function with one node. It is easy to verify by repeated applications of (5.14), that the other successive eigenfunctions have the general features derived in the previous chapter. The functions so generated are known as Hermite polynomials.

The ground state eigenfunction is in fact a Gaussian hump of the form considered in the discussion of the uncertainty principle, of width, according to (5.23) and (5.9),

$$\Delta_x = \left(\frac{\hbar}{m\omega}\right)^{1/2}. \tag{5.27}$$

According to (5.5), this is just the amplitude of the classical oscillation of the same energy as the ground state.

The operators

$$\left(\frac{\partial}{\partial y} - y\right), \quad \left(\frac{\partial}{\partial y} + y\right), \tag{5.28}$$

Appendix A

Hermite Polynomials

From P. 6-10, we find

$$\frac{d^2H}{d\xi^2} - 2\xi\frac{dH}{d\xi} + (K-1)H = 0$$

$$(h \to H)$$

Acceptable solutions can be found only if

$$K = 2n+1 \qquad n = 0, 1, 2, \cdots$$

$$\Rightarrow \quad \frac{d^2H_n}{d\xi^2} - 2\xi\frac{dH_n(\xi)}{d\xi} + 2n\,H_n(\xi) = 0$$

$\downarrow$

this is defining differential equation

Generating function and recursive relations

$\downarrow$

$$S(\xi,s) = e^{\xi^2-(s-\xi)^2} = e^{-s^2+2s\xi} = \sum_{n=0}^{\infty}\frac{H_n(\xi)}{n!}s^n$$

Expanding the exponential function in terms of powers of s and ξ, we see that the coefficients of the powers s^n are polynomials in terms of ξ – the Hermite polynomials. This can be shown as follows: we have

$$\frac{\partial S}{\partial \xi} = 2s\,e^{-s^2+2s\xi} = \sum_{n=0}^{\infty}\frac{2s^{n+1}}{n!}H_n(\xi)$$
$$= \sum_{n=0}^{\infty}\frac{s^n}{n!}\frac{\partial H_n(\xi)}{\partial \xi} \quad ,$$

$$\frac{\partial S}{\partial s} = (-2s+2\xi)\,e^{-s^2+2s\xi} = \sum_{n=0}^{\infty}\frac{(-2s+2\xi)s^n}{n!}H_n(\xi)$$
$$= \sum_{n=0}^{\infty}\frac{s^{n-1}}{(n-1)!}H_n(\xi) \quad . \tag{5}$$

Equating equal powers of s in the sums of these two equations, we obtain

$$\frac{\partial H_n(\xi)}{\partial \xi} = 2nH_{n-1}(\xi) \quad ,$$
$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \quad . \tag{6}$$

Therefore it follows that

$$\frac{\partial H_n(\xi)}{\partial \xi} = 2\xi H_n(\xi) - H_{n+1}(\xi) \quad , \tag{7}$$

and hence

$$\frac{\partial^2 H_n(\xi)}{\partial \xi^2} = 2H_n(\xi) + 2\xi\frac{\partial H_n(\xi)}{\partial \xi} - \frac{\partial H_{n+1}(\xi)}{\partial \xi}$$
$$= 2\xi\frac{\partial H_n(\xi)}{\partial \xi} + 2H_n(\xi) - (2n+2)H_n(\xi)$$

$$= 2\xi \frac{\partial H_n(\xi)}{\partial \xi} - 2nH_n(\xi) \quad . \tag{8}$$

This is exactly differential equation (3), proving that the $H_n(\xi)$ appearing in the generating function (4) are indeed Hermite polynomials.

The recurrence formulas (6) may be used to calculate the H_n and their derivatives. Another explicit expression directly obtainable from the generating function is quite useful; let us now establish this important relation. From (4) it follows instantly that

$$\left.\frac{\partial^n S(\xi, s)}{\partial s^n}\right|_{s=0} = H_n(\xi) \quad . \tag{9}$$

Now, for an arbitrary function $f(s - \xi)$, it also holds that

$$\frac{\partial f}{\partial s} = -\frac{\partial f}{\partial \xi} \quad . \tag{10}$$

Thus

$$\begin{aligned}\frac{\partial^n S}{\partial s^n} &= e^{\xi^2} \frac{\partial^n e^{-(s-\xi)^2}}{\partial s^n} \\ &= (-1)^n e^{\xi^2} \frac{\partial^n}{\partial \xi^n} e^{-(s-\xi)^2} \quad .\end{aligned} \tag{11}$$

Comparing (11) with (9) yields the very useful formula,

$$H_n(\xi) = (-1)^n = e^{\xi^2} \frac{\partial^n}{\partial \xi^n} e^{-\xi^2} \quad . \tag{12}$$

$$\lambda = \sqrt{\frac{m\omega}{\hbar}}$$

The $H_n(\xi)$ are polynomials of nth degree in ξ with the dominant term $2^n\xi^n$. The first five $H_n(\xi)$ calculated from (7.22) or (12) of the foregoing example are:

$$\begin{aligned}&H_0(\xi) = 1 \quad , \qquad H_1(\xi) = 2\xi \quad , \\ &H_2(\xi) = 4\xi^2 - 2 \quad , \quad H_3(\xi) = 8\xi^3 - 12\xi \quad , \quad H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \quad .\end{aligned} \tag{7.23}$$

The eigenfunctions (7.21) were combined by introducing the abbreviation $\xi = \sqrt{\lambda}x$ and using the Hermite polynomials in a way that holds for both even and odd n, i.e.

$$\psi_n(x) = N_n e^{(-1/2)\xi^2} H_n(\xi) \quad , \quad \xi = \sqrt{\lambda}x \quad . \tag{7.24}$$

The constant N_n, which depends on the index n, is determined by the normalization condition

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1 \quad , \tag{7.25}$$

since we require the position probability to be 1 for the particle in the entire configuration space. Thus

$$n=0:\psi_0(x)=\sqrt[4]{\frac{\lambda}{\pi}}\exp\left(-\frac{1}{2}\lambda x^2\right)\quad,$$

$$n=1:\psi_1(x)=2\sqrt{\frac{1}{2}\sqrt{\frac{\lambda}{\pi}}}\exp\left(-\frac{1}{2}\lambda x^2\right)\sqrt{\lambda}x\quad,$$

$$n=2:\psi_2(x)=\sqrt{\frac{1}{8}\sqrt{\frac{\lambda}{\pi}}}\exp\left(-\frac{1}{2}\lambda x^2\right)(4\lambda x^2-2)\quad. \tag{7.33}$$

From (7.24) and (7.30) it follows that, for space reflection, the eigenfunctions have the symmetry property

$$\psi_n(-x)=(-1)^n\psi_n(x)\quad. \tag{7.34}$$

This means

n even: $\psi(-x)=\psi(x)\rightarrow$ parity $+1$
n odd: $\psi(-x)=-\psi(x)\rightarrow$ parity -1 .

For the lowest H_n, it can easily be shown that they possess precisely n different real zeros and $n-1$ extremal values (see Fig. 7.1). With respect to (12) in Example 7.2, we have

$$H_{nk+1}=-e^{\xi^2}\frac{d}{d\xi}(e^{-\xi^2}H_n)\quad. \tag{7.35}$$

On the assumption that H_n possesses $n+1$ real extremal values, we can conclude the existence of $n+1$ extremal values for $e^{-\xi^2}H_n$ (since $e^{-\xi^2}\rightarrow 0$ for $\xi\rightarrow\infty$). The extremal values are identical with the zeros of the derivative $d/d\xi$; therefore H_{n+1} has precisely $n+1$ real zeros. This conclusion shows that the Hermite polynomials $H_n(\xi)$ – and, in consequence, the wave functions $\psi_n(\xi)$ – possess n different real zeros. This is a special case of a universally valid theorem which states that the principal quantum number of an eigenfunction is identical with the number of zeros.

In Fig. 7.1, some of the ψ_n are plotted together with an energy diagram. The energy eigenvalues are represented as horizontal lines with the quantum segments $E_n=(n+\frac{1}{2})\hbar\omega$. For each of the lines there is a corresponding eigenfunction $\psi_n(x)$ drawn on an arbitrary scale.

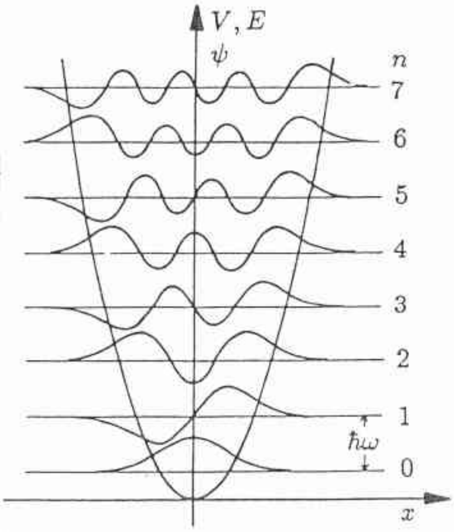


Fig. 7.1. Oscillator potential, energy levels and corresponding wavefunctions

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2\,dx = \frac{1}{\sqrt{\lambda}} N_n^2 \int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi)^2\,d\xi = 1 \quad . \tag{7.26}$$

Using relation (12) of Example 7.2 to express one of the Hermite polynomials that appears in the integrand of the normalization integral, the evaluation of this integral becomes simply

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2\,dx = (-1)^n \frac{N_n^2}{\sqrt{\lambda}} \int_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} e^{-\xi^2}\,d\xi \quad . \tag{7.27}$$

By partial integration we obtain

$$\begin{aligned} &\int_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} e^{-\xi^2}\,d\xi \\ &\quad = \left[\left(\frac{d^{n-1}}{d\xi^{n-1}} e^{-\xi^2}\right) H_n(\xi)\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{dH_n}{d\xi} \frac{d^{n-1}}{d\xi^{n-1}} e^{-\xi^2}\,d\xi \quad . \end{aligned} \tag{7.28}$$

The first term is, because of (12) in Example 7.2, equal to $(-1)^{n-1} e^{-\xi^2} H_{n-1}(\xi) H_n(\xi)$. It vanishes at infinity, due to the exponential function.

Having carried out partial integration n times, we are left with

$$\int_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} e^{-\xi^2}\,d\xi = (-1)^n \int_{-\infty}^{\infty} \frac{d^n H_n}{d\xi^n} e^{-\xi^2}\,d\xi \quad . \tag{7.29}$$

Since $H_n(\xi)$ is a polynomial of nth order with the dominant term $2^n \xi^n$, for the nth derivative,

$$\frac{d^n}{d\xi^n} H_n(\xi) = 2^n n! \tag{7.30}$$

holds.

From this we find that

$$\int_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} e^{-\xi^2}\,d\xi = (-1)^n (2^n) n! \int_{-\infty}^{\infty} e^{-\xi^2}\,d\xi = (-1)^n (2^n) n! \sqrt{\pi} \quad , \tag{7.31}$$

and for the normalization constant,

$$N_n = \sqrt{\sqrt{\frac{\lambda}{\pi}} \frac{1}{2^n n!}} \quad .$$

The stationary states of the harmonic oscillator in quantum mechanics are therefore

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!} \sqrt{\frac{\lambda}{\pi}}} \exp\left(-\frac{1}{2}\lambda x^2\right) H_n(\sqrt{\lambda} x) \quad . \tag{7.32}$$

Here we have suppressed the phase factor $(-1)^n$, since it is not essential. To discuss the solution, we take a look at the first three eigenfunctions of the linear harmonic oscillator (see Fig. 7.1):

2. ⓐ Raising and Lowering Operator

The Hamiltonian of a particle of mass m which oscillates with frequency ω under the influence of a one-dimensional harmonic potential is

$$\hat{H} = \frac{\hat{P}^2}{2m} + \frac{1}{2} m\omega^2 \hat{X}^2. \qquad (4.108)$$

The problem is how to find the energy eigenvalues and eigenstates of this Hamiltonian. This problem can be studied by two separate methods. The first consists of solving the time-independent Schrödinger equation (TISE) for the Hamiltonian (4.108). The second method, called the *ladder method*, does not deal with solving the Schrödinger equation, it deals instead with operator algebra involving operators known as the *creation* and *annihilation* operators; this method is an essence a matrix formulation, because it expresses the various quantities in terms of matrices. We adopt here the second method, for it is more straightforward, more elegant and much simpler than solving the Schrödinger equation. Unlike the examples seen up to now, solving the Schrödinger equation for the potential $V(x) = \frac{1}{2} m\omega x^2$ is no easy job.[3]

Let us rewrite the Hamiltonian (4.108) in terms of the two dimensionless operators $\hat{p} = \hat{P}/\sqrt{m\hbar\omega}$ and $\hat{q} = \hat{X}\sqrt{m\omega/\hbar}$:

$$\hat{H} = \frac{\hbar\omega}{2}(\hat{p}^2 + \hat{q}^2), \qquad (4.109)$$

and then introduce two non-Hermitian operators

$$\hat{a} = \frac{1}{\sqrt{2}}(\hat{q} + i\hat{p}), \qquad \hat{a}^\dagger = \frac{1}{\sqrt{2}}(\hat{q} - i\hat{p}). \qquad (4.110)$$

The physical meaning of the operators $\hat{a}$ and $\hat{a}^\dagger$ will be examined later. Note that

$$\hat{a}^\dagger \hat{a} = \frac{1}{2}(\hat{q} - i\hat{p})(\hat{q} + i\hat{p}) = \frac{1}{2}(\hat{q}^2 + \hat{p}^2 + i\hat{q}\hat{p} - i\hat{p}\hat{q}) = \frac{1}{2}(\hat{q}^2 + \hat{p}^2) + \frac{i}{2}[\hat{q},\ \hat{p}], \quad (4.111)$$

where, using $[\hat{X}, \hat{P}] = i\hbar$, we can verify that the commutator between $\hat{q}$ and $\hat{p}$ is

$$[\hat{q},\ \hat{p}] = \left[\sqrt{\frac{m\omega}{\hbar}}\hat{X},\ \frac{1}{\sqrt{\hbar m\omega}}\hat{P}\right] = \frac{1}{\hbar}\left[\hat{X}, \hat{P}\right] = i, \qquad (4.112)$$

hence

$$\hat{a}^\dagger \hat{a} = \frac{1}{2}(\hat{q}^2 + \hat{p}^2) - \frac{1}{2}, \qquad (4.113)$$

or

$$\frac{1}{2}(\hat{q}^2 + \hat{p}^2) = \hat{a}^\dagger \hat{a} + \frac{1}{2}. \qquad (4.114)$$

Inserting (4.114) into (4.109) we obtain

$$\boxed{\hat{H} = \hbar\omega\left(\hat{a}^\dagger \hat{a} + \frac{1}{2}\right) = \hbar\omega\left(\hat{N} + \frac{1}{2}\right) \qquad \text{with} \qquad \hat{N} = \hat{a}^\dagger \hat{a},} \qquad (4.115)$$

where $\hat{N}$ is known as the *number operator or occupation number* operator, which is clearly Hermitian.

---

[3] See, for example, B. H. Bransden, and C. J. Joachain, *Introduction to Quantum Mechanics*, Longman Scientific and Technical, London, 1994, Section 4.8, and R. W. Robinett, *Quantum Mechanics: Classical Results, Modern Systems, and Visualized Examples*, Oxford University Press, New York, 1997, Chapter 10.

Simple Harmonic Oscillator
Zettili

Let us now derive the commutator $\left[\hat{a}, \hat{a}^{\dagger}\right]$. Since $[\hat{X}, \hat{P}] = i\hbar$ we have $[\hat{q}, \hat{p}] = \frac{1}{\hbar}[\hat{X}, \hat{P}] = i$, hence

$$\left[\hat{a}, \hat{a}^{\dagger}\right] = \frac{1}{2}\left[\hat{q} + i\hat{p}, \hat{q} - i\hat{p}\right] = -i\left[\hat{q}, \hat{p}\right] = 1, \tag{4.116}$$

or

$$\boxed{\left[\hat{a}, \hat{a}^{\dagger}\right] = 1.} \tag{4.117}$$

4.8.1 Energy Eigenvalues

Note that $\hat{H}$ as given by (4.115) commutes with $\hat{N}$, since $\hat{H}$ is linear in $\hat{N}$. Thus, $\hat{H}$ and $\hat{N}$ can have a set of joint eigenstates, to be denoted by $\mid n\rangle$

$$\hat{N} \mid n\rangle = n \mid n\rangle, \tag{4.118}$$

and

$$\hat{H} \mid n\rangle = E_n \mid n\rangle; \tag{4.119}$$

the states $\mid n\rangle$ are called energy eigenstates. Combining (4.115) and (4.119), we obtain the energy eigenvalues at once:

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega.} \tag{4.120}$$

We will show later that n is a *positive integer*.

The physical meaning of the operators $\hat{a}$, $\hat{a}^{\dagger}$, and $\hat{N}$ can now be clarified. First, we need the following two commutators that can be extracted from (4.117) and (4.115):

$$\boxed{[\hat{a}, \hat{H}] = \hbar\omega\hat{a}, \qquad [\hat{a}^{\dagger}, \hat{H}] = -\hbar\omega\hat{a}^{\dagger}.} \tag{4.121}$$

These commutation relations along with (4.119) lead to

$$\hat{H}\left(\hat{a} \mid n\rangle\right) = (\hat{a}\hat{H} - \hbar\omega\hat{a}) \mid n\rangle = (E_n - \hbar\omega)\left(\hat{a} \mid n\rangle\right), \tag{4.122}$$

$$\hat{H}\left(\hat{a}^{\dagger} \mid n\rangle\right) = (\hat{a}^{\dagger}\hat{H} + \hbar\omega\hat{a}^{\dagger}) \mid n\rangle = (E_n + \hbar\omega)(\hat{a}^{\dagger} \mid n\rangle). \tag{4.123}$$

Thus, $\hat{a} \mid n\rangle$ and $\hat{a}^{\dagger} \mid n\rangle$ are eigenstates of $\hat{H}$ with eigenvalues $(E_n - \hbar\omega)$ and $(E_n + \hbar\omega)$, respectively. So the respective actions of $\hat{a}$ and $\hat{a}^{\dagger}$ on $\mid n\rangle$ generate new energy states that are lower and higher by one unit of $\hbar\omega$. As a result, $\hat{a}$ and $\hat{a}^{\dagger}$ are respectively known as the *lowering* and *raising* operators, or the *annihilation* and *creation* operators; they are also known as the *ladder operators*.

Let us now determine how the operators $\hat{a}$ and $\hat{a}^{\dagger}$ act on the energy eigenstates $\mid n\rangle$. Since $\hat{a}$ and $\hat{a}^{\dagger}$ do not commute with $\hat{N}$, the states $\mid n\rangle$ are eigenstates neither to $\hat{a}$ nor to $\hat{a}^{\dagger}$. Using (4.117) along with $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$, we can show that

$$\boxed{[\hat{N}, \hat{a}] = -\hat{a}, \qquad [\hat{N}, \hat{a}^{\dagger}] = \hat{a}^{\dagger},} \tag{4.124}$$

hence $\hat{N}\hat{a} = \hat{a}(\hat{N}-1)$ and $\hat{N}\hat{a}^\dagger = \hat{a}^\dagger(\hat{N}+1)$. Combining these relations with (4.118), we obtain

$$\hat{N}\left(\hat{a} \mid n\rangle\right) = \hat{a}(\hat{N}-1) \mid n\rangle = (n-1)\left(\hat{a} \mid n\rangle\right), \tag{4.125}$$

$$\hat{N}\left(\hat{a}^\dagger \mid n\rangle\right) = \hat{a}^\dagger(\hat{N}+1) \mid n\rangle = (n+1)(\hat{a}^\dagger \mid n\rangle). \tag{4.126}$$

These relations reveal that $\hat{a} \mid n\rangle$ and $\hat{a}^\dagger \mid n\rangle$ are eigenstates of $\hat{N}$ with eigenvalues $(n-1)$ and $(n+1)$, respectively. This implies that when $\hat{a}$ and $\hat{a}^\dagger$ operate on $\mid n\rangle$, respectively, they decrease and increase n by one unit. That is, while the action of $\hat{a}$ on $\mid n\rangle$ generates a new state $\mid n-1\rangle$, (i.e., $\hat{a} \mid n\rangle \sim \mid n-1\rangle$), the action of $\hat{a}^\dagger$ on $\mid n\rangle$ generates $\mid n+1\rangle$. Hence from (4.125) we can write

$$\hat{a} \mid n\rangle = c_n \mid n-1\rangle, \tag{4.127}$$

where c_n is a constant to be determined from the requirement that the states $\mid n\rangle$ be normalized for all values of n. On the one hand, (4.127) yields

$$\left(\langle n \mid \hat{a}^\dagger\right) \cdot \left(\hat{a} \mid n\rangle\right) = \langle n \mid \hat{a}^\dagger\hat{a} \mid n\rangle = |c_n|^2 \langle n-1 \mid n-1\rangle = |c_n|^2, \tag{4.128}$$

and on the other hand, (4.118) gives

$$\left(\langle n \mid \hat{a}^\dagger\right) \cdot \left(\hat{a} \mid n\rangle\right) = \langle n \mid \hat{a}^\dagger\hat{a} \mid n\rangle = n\langle n \mid n\rangle = n. \tag{4.129}$$

When combined, the last two equations yield

$$|c_n|^2 = n. \tag{4.130}$$

This implies that n, which is equal to the norm of $\hat{a} \mid n\rangle$ (see (4.129)), *cannot be negative*, $n \geq 0$, since the norm is a positive quantity. Substituting (4.130) into (4.127) we end up with

$$\boxed{\hat{a} \mid n\rangle = \sqrt{n} \mid n-1\rangle.} \tag{4.131}$$

This equation shows that repeated applications of the operator $\hat{a}$ on $\mid n\rangle$ generate a sequence of eigenvectors $\mid n-1\rangle,\ \mid n-2\rangle,\ \mid n-3\rangle,\ \ldots$. Since $n \geq 0$ and since $\hat{a} \mid 0\rangle = 0$, this sequence has to terminate at $n = 0$; this is true if we start with an integer value of n. But if we start with a noninteger n, the sequence will not terminate, hence it leads to eigenvectors with negative values of n. But as shown above, since n cannot be negative, we conclude that n has to be a *nonnegative integer*.

Now, we can easily show, as we did for (4.131), that

$$\boxed{\hat{a}^\dagger \mid n\rangle = \sqrt{n+1} \mid n+1\rangle.} \tag{4.132}$$

This implies that repeated applications of $\hat{a}^\dagger$ on $\mid n\rangle$ generate an infinite sequence of eigenvectors $\mid n+1\rangle,\ \mid n+2\rangle,\ \mid n+3\rangle,\ \ldots$. Since n is a positive integer, the energy spectrum of a harmonic oscillator as specified by (4.120) is therefore *discrete*:

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad (n = 0, 1, 2, 3, \ldots).} \tag{4.133}$$

As expected for bound states of one-dimensional potentials, the energy spectrum is both discrete and nondegenerate. As in the case of the infinite square well potential, the lowest energy eigenvalue of the oscillator is not zero but equal to $E_0 = \hbar\omega/2$. It is called the *zero-point energy* . The zero-point energy of bound state systems cannot be zero, for it would violate the uncertainty principle.

4.8.2 Energy Eigenstates

The operator method can also be used to determine the energy eigenvectors. First, using (4.132), we see that the various eigenvectors can be written in terms of the ground state $| 0\rangle$ as follows:

$$| 1\rangle = \hat{a}^\dagger | 0\rangle, \tag{4.134}$$

$$| 2\rangle = \frac{1}{\sqrt{2}}\hat{a}^\dagger | 1\rangle = \frac{1}{\sqrt{2!}}\left(\hat{a}^\dagger\right)^2 | 0\rangle, \tag{4.135}$$

$$| 3\rangle = \frac{1}{\sqrt{3}}\hat{a}^\dagger | 2\rangle = \frac{1}{\sqrt{3!}}\left(\hat{a}^\dagger\right)^3 | 0\rangle, \tag{4.136}$$

$$\vdots$$

$$| n\rangle = \frac{1}{\sqrt{n}}\hat{a}^\dagger | n-1\rangle = \frac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n | 0\rangle. \tag{4.137}$$

So, to find any excited eigenstate $| n\rangle$, we need simply to operate $\hat{a}^\dagger$ on $| 0\rangle$ n successive times.

Note that any set of kets $| n\rangle$ and $|n'\rangle$, corresponding to different eigenvalues, must be orthogonal, $\langle n' \mid n\rangle \sim \delta_{n',n}$, since none of the eigenstates of $\hat{H}$ is degenerate. Moreover, the states $| 0\rangle, | 1\rangle, | 2\rangle, | 3\rangle, \ldots, | n\rangle, \ldots$ are *simultaneous eigenstates* of $\hat{H}$ and $\hat{N}$; the set $\{| n\rangle\}$ constitutes an orthonormal and complete basis:

$$\langle n' \mid n\rangle = \delta_{n',n}, \qquad \sum_{n=0}^{+\infty} | n\rangle\langle n | = 1. \tag{4.138}$$

4.8.3 Energy Eigenstates in Position Space

Let us now determine the harmonic oscillator wave function in the position representation.

Equations (4.134) to (4.137) show that, knowing the ground state wave function, we can determine any other eigenstate by successive applications of the operator $a^\dagger$ on the ground state. So let us first determine the ground state wave function in the position representation.

The operator $\hat{p}$, defined by $\hat{p} = \hat{P}/\sqrt{m\hbar\omega}$, is given in the position space by

$$\hat{p} = -\frac{i\hbar}{\sqrt{m\hbar\omega}}\frac{d}{dx} = -ix_0\frac{d}{dx}, \tag{4.139}$$

where $x_0 = \sqrt{\hbar/(m\omega)}$ is a constant that has the dimensions of length; it sets the length scale of the oscillator. We can easily show that the annihilation and creation operators $\hat{a}$ and $\hat{a}^\dagger$, defined in (4.110), can be written in the position representation as

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\frac{\hat{X}}{x_0} + x_0\frac{d}{dx}\right) = \frac{1}{\sqrt{2}x_0}\left(\hat{X} + x_0^2\frac{d}{dx}\right), \tag{4.140}$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(\frac{\hat{X}}{x_0} - x_0\frac{d}{dx}\right) = \frac{1}{\sqrt{2}x_0}\left(\hat{X} - x_0^2\frac{d}{dx}\right). \tag{4.141}$$

Using (4.140) we can write the equation $\hat{a} \mid 0\rangle = 0$ in the position space as

$$\langle x|\hat{a} \mid 0\rangle = \frac{1}{\sqrt{2}x_0}\langle x|\hat{X} + x_0^2\frac{d}{dx} \mid 0\rangle = \frac{1}{\sqrt{2}x_0}\left(x\psi_0(x) + x_0^2\frac{d\psi_0(x)}{dx}\right) = 0, \tag{4.142}$$

hence

$$\frac{d\psi_0(x)}{dx} = -\frac{x}{x_0^2}\psi_0(x). \tag{4.143}$$

where $\psi_0(x) = \langle x \mid 0\rangle$ represents the ground state wave function. The solution of this differential equation is

$$\psi_0(x) = A\exp\left(-\frac{x^2}{2x_0^2}\right), \tag{4.144}$$

where A is a constant that can be determined from the normalization condition

$$1 = \int_{-\infty}^{+\infty} dx\, |\psi_0(x)|^2 = A^2\int_{-\infty}^{+\infty} dx\exp\left(-\frac{x^2}{x_0^2}\right) = A^2\sqrt{\pi}x_0, \tag{4.145}$$

hence $A = (m\omega/(\pi\hbar))^{1/4} = 1/\sqrt{\sqrt{\pi}x_0}$. The normalized ground state wave function is then given by

$$\boxed{\psi_0(x) = \frac{1}{\sqrt{\sqrt{\pi}x_0}}\exp\left(-\frac{x^2}{2x_0^2}\right).} \tag{4.146}$$

This is a Gaussian function.

We can then obtain the wave function of any excited state by a series of applications of $\hat{a}^\dagger$ on the ground state. For instance, the first excited state is obtained by one application of the operator $\hat{a}^\dagger$ of (4.141) on the ground state:

$$\begin{aligned}\langle x \mid 1\rangle &= \langle x|\hat{a}^\dagger \mid 0\rangle = \frac{1}{\sqrt{2}x_0}\left(x - x_0^2\frac{d}{dx}\right)\langle x \mid 0\rangle \\ &= \frac{1}{\sqrt{2}x_0}\left(x - x_0^2\left(-\frac{x}{x_0^2}\right)\right)\psi_0(x) = \frac{\sqrt{2}}{x_0}x\psi_0(x),\end{aligned} \tag{4.147}$$

or

$$\psi_1(x) = \frac{\sqrt{2}}{x_0}x\psi_0(x) = \sqrt{\frac{2}{\sqrt{\pi}x_0^3}}\,x\exp\left(-\frac{x^2}{2x_0^2}\right). \tag{4.148}$$

As for the eigenstates of the second and third excited states, we can obtain them by applying $\hat{a}^\dagger$ on the ground state twice and three times, respectively:

$$\langle x \mid 2\rangle = \frac{1}{\sqrt{2!}}\langle x|\left(a^\dagger\right)^2 \mid 0\rangle = \frac{1}{\sqrt{2!}}\left(\frac{1}{\sqrt{2!}x_0}\right)^2\left(x - x_0^2\frac{d}{dx}\right)^2\psi_0(x), \tag{4.149}$$

$$\langle x \mid 3\rangle = \frac{1}{\sqrt{3!}}\langle x|\left(a^\dagger\right)^3 \mid 0\rangle = \frac{1}{\sqrt{3!}}\left(\frac{1}{\sqrt{2}x_0}\right)^3\left(x - x_0^2\frac{d}{dx}\right)^3\psi_0(x). \tag{4.150}$$

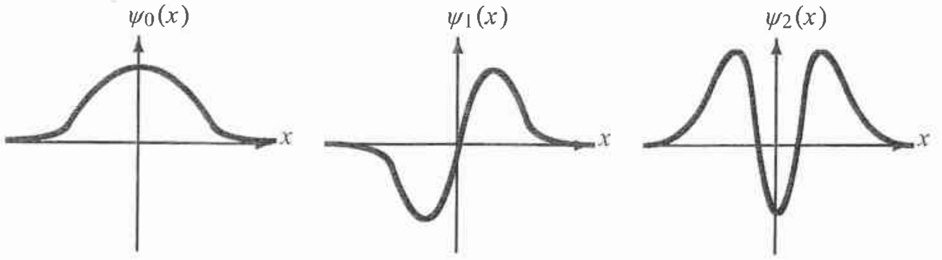


Figure 4.9 Shapes of the first three wave functions of the harmonic oscillator.

Similarly, using (4.137), (4.141) and (4.146), we can easily infer the energy eigenstate for the nth excited state:

$$\langle x \mid n\rangle = \frac{1}{\sqrt{n!}}\langle x|\left(a^{\dagger}\right)^n \mid 0\rangle = \frac{1}{\sqrt{n!}}\left(\frac{1}{\sqrt{2}x_0}\right)^n \left(x - x_0^2\frac{d}{dx}\right)^n \psi_0(x), \tag{4.151}$$

which in turn can be rewritten as

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{\sqrt{\pi}2^n n!}}\frac{1}{x_0^{n+1/2}}\left(x - x_0^2\frac{d}{dx}\right)^n \exp\left(-\frac{x^2}{2x_0^2}\right).} \tag{4.152}$$

In summary, by successive applications of $\hat{a}^{\dagger} = (\hat{X} - x_0^2 d/dx)/(\sqrt{2}x_0)$ on $\psi_0(x)$, we can find the wave function of any excited state $\psi_n(x)$. Figure 4.9 displays the shapes of the first few wave functions.

Oscillator wave functions and the Hermite polynomials

In what follows, let us express $\psi_n(x)$ in terms of the well-known Hermite polynomials. Using the operator identity

$$e^{-x^2/2}\left(x - \frac{x}{dx}\right)e^{x^2/2} = -\frac{d}{dx}, \tag{4.153}$$

we can prove that

$$\left(x - x_0^2\frac{d}{dx}\right)^n e^{-x^2/2x_0^2} = (-1)^n x_0^n e^{x^2/2x_0^2}\frac{d^n}{dx^n}e^{-x^2/x_0^2} = e^{-x^2/2x_0^2}H_n\left(\frac{x}{x_0}\right), \tag{4.154}$$

where $H_n(y)$ is an nth order polynomial called a *Hermite polynomial*:

$$H_n(y) = (-1)^n e^{y^2}\frac{d^n}{dy^n}e^{-y^2}. \tag{4.155}$$

From this relation it is easy to calculate the first few polynomials:

$$\begin{aligned} &H_0(y) = 1, && H_1(y) = 2y, \\ &H_2(y) = 4y^2 - 2, && H_3(y) = 8y^3 - 12y, \\ &H_4(y) = 16y^4 - 48y^2 + 12, && H_5(y) = 32y^5 - 160y^3 + 120y. \end{aligned} \tag{4.156}$$

Note that the polynomials $H_{2n}(y)$ are even and $H_{2n+1}(y)$ are odd, since $H_n(-y) = (-1)^n H_n(y)$. Combining (4.152) and (4.154) we can write the oscillator wave function in terms of the Hermite polynomials as follows:

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{\sqrt{\pi}\,2^n n! x_0}} e^{-x^2/2x_0^2} H_n\left(\frac{x}{x_0}\right).} \tag{4.157}$$

This wave function is either even or odd depending on n; in fact, $\psi_{2n}(x)$ is even and $\psi_{2n+1}(x)$ is odd since $H_{2n}(x)$ is even and $H_{2n+1}(x)$ is odd. This is expected because, as mentioned in Section 4.2.4, the wave functions of even one-dimensional potentials have definite parity.

4.8.4 The Matrix Representation of Various Operators

Here we look at the matrix representation of several operators in the N-space. In particular, we focus on the representation of the operators $\hat{a}$, $\hat{a}^\dagger$, $\hat{X}$, and $\hat{P}$. First, since the states $|\,n\rangle$ are joint orthonormal eigenstates of $\hat{H}$ and $\hat{N}$, it is easy to see from (4.118) and (4.119) that $\hat{H}$ and $\hat{N}$ are represented within the $\{|\,n\rangle\}$ basis by infinite diagonal matrices:

$$\hat{N} = \begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 2 & 0 & \cdots \\ 0 & 0 & 3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \qquad \hat{H} = \frac{\hbar\omega}{2}\begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 3 & 0 & \cdots \\ 0 & 0 & 5 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{4.158}$$

As for the operators $\hat{a}$, $\hat{a}^\dagger$, $\hat{X}$, $\hat{P}$, none of them are diagonal in the N-representation, since they do not commute with $\hat{N}$. The matrix elements of $\hat{a}$ and $\hat{a}^\dagger$ can be obtained from (4.131) and (4.132):

$$\hat{a} = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \qquad \hat{a}^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{4.159}$$

Now, let us find the N-representation of the position and momentum operators, $\hat{X}$ and $\hat{P}$. From (4.110) we can show that $\hat{X}$ and $\hat{P}$ are given in terms of $\hat{a}$ and $\hat{a}^\dagger$ as follows:

$$\hat{X} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a} + \hat{a}^\dagger\right), \qquad \hat{P} = i\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}^\dagger - \hat{a}\right). \tag{4.160}$$

Their matrix elements are given by:

$$\langle n'|\hat{X}\,|\,n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\delta_{n',n-1} + \sqrt{n+1}\delta_{n',n+1}\right), \tag{4.161}$$

$$\langle n'|\hat{P}\,|\,n\rangle = i\sqrt{\frac{m\hbar\omega}{2}}\left(-\sqrt{n}\delta_{n',n-1} + \sqrt{n+1}\delta_{n',n+1}\right), \tag{4.162}$$

in particular

$$\langle n\,|\,\hat{X}\,|\,n\rangle = \langle n\,|\,\hat{P}\,|\,n\rangle = 0. \tag{4.163}$$

The matrices corresponding to $\hat{X}$ and $\hat{P}$ are thus given by

$$\hat{X} = \sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \tag{4.164}$$

$$\hat{P} = i\sqrt{\frac{m\hbar\omega}{2}} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & \cdots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{4.165}$$

As mentioned in Chapter 2, the momentum operator is Hermitian, but not equal to its own complex conjugate: (4.165) shows that $\hat{P}^\dagger = \hat{P}$ and $\hat{P}^* = -\hat{P}$. As for $\hat{X}$, however, it is both Hermitian and equal to its complex conjugate: from (4.164) we have that $\hat{X}^\dagger = \hat{X}^* = \hat{X}$.

4.8.5 Expectation Values of Various Operators

Let us evaluate the expectation values for $\hat{X}^2$ and $\hat{P}^2$ in the N-representation,

$$\hat{X}^2 = \frac{\hbar}{2m\omega}\left(\hat{a}^2 + \hat{a}^{\dagger 2} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\right) = \frac{\hbar}{2m\omega}\left(\hat{a}^2 + \hat{a}^{\dagger 2} + 2\hat{a}^\dagger\hat{a} + 1\right), \tag{4.166}$$

$$\hat{P}^2 = -\frac{m\hbar\omega}{2}\left(\hat{a}^2 + \hat{a}^{\dagger 2} - \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}\right) = -\frac{m\hbar\omega}{2}\left(\hat{a}^2 + \hat{a}^{\dagger 2} - 2\hat{a}^\dagger\hat{a} + 1\right), \tag{4.167}$$

where we have used the fact that $\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} = 2\hat{a}^\dagger\hat{a} + 1$. Since the expectation values of $\hat{a}^2$ and $\hat{a}^{\dagger 2}$ are zero, $\langle n \mid \hat{a}^2 \mid n\rangle = \langle n \mid \hat{a}^{\dagger 2} \mid n\rangle = 0$, and $\langle n \mid \hat{a}^\dagger\hat{a} \mid n\rangle = n$, we have

$$\langle n \mid \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} \mid n\rangle = \langle n \mid 2\hat{a}^\dagger\hat{a} + 1 \mid n\rangle = 2n + 1, \tag{4.168}$$

hence

$$\langle n \mid \hat{X}^2 \mid n\rangle = \frac{\hbar}{2m\omega}\langle n \mid \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} \mid n\rangle = \frac{\hbar}{2m\omega}(2n+1), \tag{4.169}$$

$$\langle n \mid \hat{P}^2 \mid n\rangle = \frac{m\hbar\omega}{2}\langle n \mid \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} \mid n\rangle = \frac{m\hbar\omega}{2}(2n+1). \tag{4.170}$$

Comparing (4.169) and (4.170) we see that the expectation values of the potential and kinetic energies are equal and are also equal to half the total energy:

$$\boxed{\frac{m\omega^2}{2}\langle n \mid \hat{X}^2 \mid n\rangle = \frac{1}{2m}\langle n \mid \hat{P}^2 \mid n\rangle = \frac{1}{2}\langle n \mid \hat{H} \mid n\rangle.} \tag{4.171}$$

This result is known as the *virial theorem.*

We can now easily calculate the product $\Delta x \Delta p$ from (4.169) and (4.170). Since $\langle \hat{X}\rangle = \langle \hat{P}\rangle = 0$ we have

$$\Delta x = \sqrt{\langle \hat{X}^2\rangle - \langle \hat{X}\rangle^2} = \sqrt{\langle \hat{X}^2\rangle} = \sqrt{\frac{\hbar}{2m\omega}(2n+1)}, \tag{4.172}$$

$$\Delta p = \sqrt{\langle \hat{P}^2\rangle - \langle \hat{P}\rangle^2} = \sqrt{\langle \hat{P}^2\rangle} = \sqrt{\frac{m\hbar\omega}{2}(2n+1)}, \tag{4.173}$$

hence

$$\Delta x \Delta p = \left(n + \frac{1}{2}\right)\hbar \quad \Longrightarrow \quad \Delta x \Delta p \geq \frac{\hbar}{2}, \tag{4.174}$$

since $n \geq 0$; this is the Heisenberg uncertainty principle.

Chapter 8 Wave Functions

Let us go back to the simple harmonic oscillator case

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

$\downarrow$

Hamiltonian

$$\psi(x,t) = \psi(x)\, e^{-iEt/\hbar} \Leftarrow \underset{\text{time-dependent Schrodinger equation}}{H\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t)}$$

$$\underset{\text{time-independent Schrodinger equation}}{H\psi(x) = E\,\psi(x)}$$

$$H\,\psi_n(x) = E_n\,\psi_n(x)$$

$$\psi_n(x) = \underbrace{\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\frac{1}{\sqrt{2^n n!}}}_{\text{normalization}}\underbrace{H_n(\xi)}_{\text{Hermite polynomials}}\, e^{-\xi^2/2}$$

A short review on Hermite polynomials are given in Appendix A

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2\, dx = 1$$

$$\xi = \sqrt{\frac{m\omega}{\hbar}}\, x \qquad\qquad \omega = \sqrt{\frac{k}{m}}$$

$\psi_n(x)$ is the eigenfunction of the time-independent Schrodinger equation corresponds to eigenvalues $(n+\frac{1}{2})\hbar\omega$ respectively

$$\psi_\ell^* \qquad \frac{-\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + V\psi_n = E_n\psi_n \qquad\qquad H\psi_n = E_n\psi_n$$

$$\psi_n \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi_\ell^*}{dx^2} + V\psi_\ell^* = E_\ell\psi_\ell^*$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\psi_\ell^*\frac{d^2\psi_n}{dx} - \psi_n\frac{d^2\psi_\ell^*}{dx}\right) = (E_n - E_\ell)\psi_n\psi_\ell^*$$

$$\frac{2m}{\hbar^2}(E_\ell - E_n)\int_{-\infty}^{\infty}\psi_\ell^*\psi_n\, dx = \int_{-\infty}^{\infty}\frac{d}{dx}\left(\psi_\ell^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_\ell^*}{dx}\right)dx$$

$$= \left[\psi_\ell^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_\ell^*}{dx}\right]\Big|_{-\infty}^{\infty}$$

$$\underbrace{\int_{-\infty}^{\infty}\psi_n^*\psi_n\, dx < \infty}_{\text{normalization requirement.}} \Rightarrow \psi_n(x) \to 0 \text{ faster than } \frac{1}{\sqrt{x}}$$

$$\Rightarrow \frac{2m}{\hbar^2}(E_\ell - E_n)\int_{-\infty}^{\infty}\psi_\ell^*\psi_n\, dx = 0$$

$$E_\ell \neq E_n$$

$$\Rightarrow \int \psi_\ell^*(x)\psi_n(x)\, dx = 0$$

If $E_n = E_\ell$, then the eigenfunctions are said to be degenerate.

If $\psi_\ell'(x)$, $\psi_n'(x)$ are eigenfunctions , i.e., are solutions of the time independent Schrodinger equation , with the same eigenvalue $E_n = E_\ell$

Then. $\psi_a = \psi_\ell' + \alpha \psi_n'$ is also an eigenfunction.

$$\int \psi_n'^* \psi_a \, dx = \int \psi_n'^* \psi_\ell' \, dx + \alpha \int \psi_n'^* \psi_n \, dx$$

If we choose $\alpha = - \dfrac{\int \psi_n'^* \psi_\ell \, dx}{\int \psi_n'^* \psi_n \, dx}$, then ψ_n' , ψ_a are orthogonal

Choose $\psi_n = \psi_n'$, $\psi_\ell = \psi_a$, then ψ_n , ψ_ℓ will be orthogonal.

The idea can clearly be extended to cases where there are more than two independent eigenfunctions having the same energy

This is known as Schmidt orthogonalization procedure.

$\{\psi_n(x)\}$ forms a orthonormal set

$$\Rightarrow \int \psi_n^*(x) \, \psi_\ell(x) \, dx = \delta_{n\ell}$$

Expand $\Psi(x,t)$ in terms of above orthonormal set

$$\Psi(x,t) = \underbrace{\sum_{n=1}^{\infty}}_{\text{completeness}} a_n \psi_n(x,t)$$

$E_n \neq E_m$, we have $\int_{-\infty}^{\infty} \psi_m^*(x)\,\psi_n(x)\,dx = 0$

the wave function being normalized

$$\Rightarrow \int_{-\infty}^{\infty} \psi_m^*(x)\,\underset{\downarrow}{\,}\psi_n(x)\,dx = \delta_{mn}$$

orthonormality condition

$\{\psi_n(x)\}$ forms an orthonormal set of functions

$$\psi_n(x)\,e^{-iE_nt/\hbar} = \psi_n(x)\,e^{-i(n+\frac{1}{2})\omega t}$$

is a solution of the time-dependent Schrodinger equation.

The Schrodinger equation is linear

$$\psi(x,t) = \sum_{n=0}^{\infty} a_n\,\psi_n(x)\,e^{-iE_nt/\hbar}$$

is again a solution of the time-dependent Schrodinger equation

a_n can be determined by specifying the initial wave function $\psi(x,0)$

$$\psi(x,0) = \sum_n a_n\,\psi_n(x) \qquad \int \psi^*(x,0)\,\psi(x,0)\,dx = \sum_{n=0}^{\infty}|a_n|^2 = 1$$

$$\int_{-\infty}^{\infty} \psi_m^*(x)\,\psi(x,0)\,dx = \sum_n \int \psi_m^*(x)\,a_n\,\psi_n(x)$$

$$= \sum_n a_n\,\delta_{mn} = a_m$$

We have solved the Schrodinger equation, i.e., given the Hamiltonian H and the initial condition $\psi(x,0)$, $\psi(x,t)$ can be found.

If $\psi(x,t)$ is found, then

$$\langle E\rangle_t = \langle H\rangle_t = \int_{-\infty}^{\infty} \psi^*(x,t)\,H\,\psi(x,t)\,dx$$

$$= \int_{-\infty}^{\infty} \sum_n a_n^*\,\psi_n^*(x)\,e^{+iE_nt/\hbar} \sum_m E_m\,\psi_m(x)\,e^{-iE_mt/\hbar}\,dx$$

$$= \sum_n \sum_m a_n^* a_m E_m\,e^{i(E_n-E_m)t/\hbar}\,\delta_{nm} = \sum_m E_m\,|a_m|^2$$

$$a_m = \int_{-\infty}^{\infty} \psi_m^*(x)\,\psi(x,0)\,dx$$

Normalization condition

$$\int \Psi^*(x,t)\,\Psi(x,t)\,dx = 1$$

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\,\Psi(x,t)\,dx = \sum_n a_n a_n^* \overset{\overset{1}{\|}}{\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx}$$

$$+ \sum_\ell \sum_n a_\ell^* a_n\, e^{-i(E_n-E_\ell)t/\hbar} \underset{\underset{0}{\|}}{\int_{-\infty}^{\infty} \psi_\ell^*(x)\,\psi_n(x)\,dx}$$

$$= \sum_n a_n a_n^* = 1$$

The normalization condition is independent of time
⇒ if we normalize the wave function at time $t = t_0$ then it will remain normalized.

If $\Psi(x,0)$ is given ⇒ $\underset{\hookrightarrow}{\Psi(x,t)} = \sum_n a_n \Psi_n(x,t)$

specified if a_n, $\psi_n(x)$, E_n are given

$$\Psi(x,0) = \sum_{n=1}^{\infty} a_n \psi_n(x)$$

$$\int_{-\infty}^{\infty} \psi_\ell^*(x)\,\Psi(x,0)\,dx = \sum_{n=1}^{\infty} a_n \int_{-\infty}^{\infty} \psi_\ell^*(x)\,\psi_n(x)\,dx$$

$$= a_\ell$$

$$\Rightarrow \quad a_n = \int_{-\infty}^{\infty} \psi_n^*(x')\,\Psi(x',0)\,dx'$$

$$\Rightarrow \quad \Psi(x,t) = \sum_n \left\{ \int_{-\infty}^{\infty} \psi_n^*(x')\,\Psi(x',0)\,dx' \right\} e^{-iE_n t/\hbar}\,\psi_n(x)$$

$\psi(x,t)$ can be obtained:

(i) H is specified

(ii) $H\psi_n \underset{\downarrow}{=} E_n\psi_n$ is solved

time-independent Schrodinger equation is solved.

(iii) Initial condition is known.

Now if $\psi_n(x,0) = \psi_n(x)$

↓

eigenfunction of time independent Schrodinger equation for simple harmonic oscillator with eigenvalues $(n+\frac{1}{2})\hbar\omega$

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

↓

this wave function satisfies the time dependent Schrodinger equation and the initial condition

$$\langle A \rangle_t = \int_{-\infty}^{\infty} \psi_n^*(x)\, A\, \psi_n(x)\, dx = \int_{-\infty}^{\infty} \psi_n^*(x,t)\, A\, \psi_n(x,t)\, dx$$

independent of t.

$$\psi_n(x) = A_n \underset{\downarrow}{H_n(\xi)}\, e^{-\xi^2/2}$$

Hermite polynomial

$$\xi = \sqrt{\frac{m\omega}{\hbar}}\, x \quad , \quad \omega = \sqrt{\frac{k}{\omega}}$$
$$= \sqrt{\lambda}\, x$$

Normalization

$$\int_{-\infty}^{\infty} \psi_n^*(x)\, \psi_n(x)\, dx = 1$$
$$\parallel$$
$$\int_{-\infty}^{\infty} |A_n|^2 [H_n(\xi)]^2 e^{-\xi^2} dx = 1$$

$$\Rightarrow \quad A_n = \left[\frac{1}{2^n n!}\left(\frac{\lambda}{\pi}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

See the derivation in A-4 of Appendix A

Now we shall calculate the expectation values

(i) $\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\, x\, \psi_n(x)\, dx = 0$

↓

the integrand is an odd function of x

(ii) $\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\, x^2\, \psi_n(x)\, dx$

$$= |A_n|^2 \int_{-\infty}^{\infty} [H_n(\xi)]^2 x^2 e^{-\xi^2} dx$$

分類： 6-24
編號： 8-6
總號：

$y \to \xi$, $\xi = \sqrt{\lambda}\, x$ $dx \to \frac{d\xi}{\sqrt{\lambda}}$ $\lambda \to \alpha$

$$\langle x^2 \rangle = |A_n|^2 \frac{1}{\alpha} \int_{-\infty}^{\infty} [H_n(\xi)]^2 \, e^{-\xi^2} \xi^2 \, dx$$

$$\updownarrow$$

$$\frac{A_n^2}{\alpha} \int_{-\infty}^{\infty} e^{-y^2} [H_n(y)]^2 y^2 \, dx$$

分類： 6-25
編號： 8-7
總號：

$y H_n(y) = \frac{1}{2}[H_{n+1}(y) + 2n H_{n-1}(y)]$ Equation (6) of Appendix A

$$y^2 H_n(y) = \frac{1}{2}[y H_{n+1}(y) + 2ny H_{n-1}(y)]$$

$$= \frac{1}{2}[\frac{1}{2} H_{n+2}(y) + (n+\frac{1}{2}) H_n(y) + 2n\frac{1}{2} H_n(y) + \frac{1}{2} 2n\, 2(n-1) H_{n-2}(y)]$$

$$= \frac{1}{4} H_{n+2}(y) + (n+\frac{1}{2}) H_n(y) + n(n-1) H_{n-2}(y)$$

$$\langle x^2 \rangle = \frac{n+\frac{1}{2}}{\alpha} \underbrace{A_n^2 \int_{-\infty}^{\infty} e^{-y^2} [H_n(y)]^2 dy}_{=1}$$

normalization condition

$$= \frac{n+\frac{1}{2}}{\alpha}$$

(iii) $\langle p_x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \frac{\hbar}{i}\frac{d}{dx} \psi_n(x)\, dx$

$$= \frac{\hbar}{i} A_n^2 \sqrt{\alpha} \int_{-\infty}^{\infty} e^{-y^2/2} H_n(y) \frac{d}{dy}(e^{-y^2/2} H_n(y)) dx$$

$$\frac{d}{dy} e^{-y^2/2} H_n(y) = e^{-y^2/2} \frac{dH_n(y)}{dy} - y H_n(y) e^{-y^2/2}$$

$$= e^{-y^2/2}[2n H_{n-1}(y) - \frac{1}{2} H_{n+1}(y) - \frac{1}{2} 2n H_{n-1}(y)]$$

$$= e^{-y^2/2}[n H_{n-1}(y) - \frac{1}{2} H_{n+1}(y)]$$

Clearly, $\langle p_x \rangle = 0$

(iv) $\langle p_x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) (\frac{\hbar}{i}\frac{d}{dx})^2 \psi_n(x)\, dx$

$$= -\alpha\hbar^2 A_n^2 \int_{-\infty}^{\infty} e^{-y^2/2} H_n(y) \frac{d^2}{dy^2} e^{-y^2/2} H_n(y) dx$$

$$\frac{d^2}{dy^2} e^{-y^2/2} H_n(y) = \frac{d}{dy}\{e^{-y^2/2}[n H_{n-1}(y) - \frac{1}{2} H_{n+1}(y)]\}$$

$$= e^{-y^2/2}[n \frac{dH_{n-1}(y)}{dy} - \frac{1}{2}\frac{dH_{n+1}(y)}{dy}]\Big)$$ Equation (7) of Appendix (A)

$$- e^{-y^2/2}[ny H_{n-1}(y) - \frac{1}{2} y H_{n+1}(y)]$$

$$= e^{-y^2/2}[n \cdot 2(n-1) H_{n-2}(y) - \frac{1}{2} 2(n+1) H_n(y)$$
$$- n\frac{1}{2} H_n(y) - n\frac{1}{2} 2(n-1) H_{n-2}(y)$$
$$+ \frac{1}{2}\cdot\frac{1}{2} H_{n+2} + \frac{1}{2}\cdot\frac{1}{2}2(n+1) H_n(y)]$$

$$= e^{-y^2/2}[n(n-1) H_{n-2}(y) - (n+\frac{1}{2}) H_n(y) + \frac{1}{4} H_{n+1}(y)]$$

$$\langle p_x^2 \rangle = -\alpha\hbar^2 A_n^2 \int_{-\infty}^{\infty} e^{-y^2} \{-(n+\frac{1}{2})\} [H_n(y)]^2 dx = (n+\frac{1}{2})\alpha\hbar^2$$

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{\alpha}(n+\tfrac{1}{2})$$

$$(\Delta p_x)^2 = \langle p_x^2\rangle - \langle p_x\rangle^2 = (n+\tfrac{1}{2})\,\alpha\hbar^2$$

$$\Rightarrow \quad \Delta x\, \Delta p_x = (n+\tfrac{1}{2})\hbar$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$$

For ground state $n=0$, $H_0(\xi)=1$, only Gaussian integrals are needed

Expectation values of some observables for mixed states

$$\psi(x,0) = \frac{1}{\sqrt{2}}\Big(\underbrace{A_0 e^{-y^2/2}}_{\psi_0(x)} H_0(y) + \underbrace{A_1 e^{-y^2/2}}_{\psi_1(x)} H_1(y)\Big)$$

$\psi_0(x)$, $\psi_1(x)$ are properly normalized.

$$\psi(x,t) = \frac{1}{\sqrt{2}}\left[A_0 e^{-y^2/2} H_0(y)\, e^{-i\omega t/2} + A_1 e^{-y^2/2} H_1(y)\, e^{-3i\omega t/2}\right]$$

Remember $E_n = (n+\frac{1}{2})\hbar\omega$

$$\langle E\rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\left(i\hbar\frac{\partial}{\partial t}\right)\psi(x,t)\,dx$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\left(\psi_0^*(x)\, e^{i\omega t/2} + \psi_1^*(x)\, e^{i3\omega t/2}\right)\left(\hbar\frac{\omega}{2}\psi_0(x) e^{-i\omega t/2} + \hbar\frac{3\omega}{2}\psi_1(x)\right.$$

$$\left.\cdot\, e^{-i3\omega t/2}\right]dx$$

$$= \frac{1}{2}\hbar\omega\left(\frac{1}{2}+\frac{3}{2}\right) = \hbar\omega$$

$$\langle x\rangle = \int_{-\infty}^{\infty}\psi^*(x,t)\, x\, \psi(x,t)\,dx$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\left(\psi_0^*(x)\, e^{i\omega t/2} + \psi_1^*(x)\, e^{i3\omega t/2}\right) x \left(\psi_0(x)\, e^{-i\omega t/2} + \psi_1(x)\, e^{-i3\omega t/2}\right)dx$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\left[\psi_0^*(x)\, x\, \psi_0(x) + \psi_1^*(x)\, x\, \psi_1(x) + \psi_0^*(x)\, x\, \psi_1(x)\, e^{-i\omega t}\right.$$
$$\left. + \psi_1^*(x)\, x\, \psi_0(x)\, e^{i\omega t}\right]dx$$

$$= \left[\int_{-\infty}^{\infty}\psi_0^*(x)\, x\, \psi_1(x)\,dx\right]\cos\omega t$$

$$\int_{-\infty}^{\infty}\psi_0^*(x)\, x\, \psi_1(x)\,dx$$

$$= \frac{1}{\alpha}\int_{-\infty}^{\infty} A_0 A_1\, e^{-y^2} H_0(y)\, H_1(y)\, y\, dy$$

$\frac{1}{\sqrt{\alpha}}$ from $x \to y$, $\frac{1}{\sqrt{\alpha}}$ from $dx \to dy$

$$y H_1(y) = \frac{1}{2}H_2(y) + \frac{1}{2}\,2\cdot 1\, H_0(y) \quad \text{from recursive relation}$$

$$\int_{-\infty}^{\infty}\psi_0^*(x)\, x\, \psi_1(x) = \frac{1}{\alpha} A_0 A_1 \underbrace{\int_{-\infty}^{\infty} e^{-y^2}dy} = \frac{1}{\alpha}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left(\frac{1}{2}\right)^{\frac{1}{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\sqrt{\pi} = \frac{1}{\sqrt{2\alpha}}$$

$\Rightarrow \quad \langle x \rangle = \frac{1}{\sqrt{2\alpha}} \cos \omega t$

Similarily $\quad \langle p_x \rangle = -\sqrt{\frac{\alpha}{2}}\, \hbar \sin \omega t$

(Can be obtained through Ehrenfest theorem) ...

If $\quad \psi(x,0) = \frac{1}{\sqrt{2}} \left[e^{i\delta_0} \psi_0(x) + e^{i\delta_1} \psi_1(x) \right]$

then $\quad \psi(x,t) = e^{i\delta_0} \frac{1}{\sqrt{2}} \left[\psi_0(x)\, e^{-i\omega t/2} + e^{i(\delta_1-\delta_0)} \psi_1(x)\, e^{-i3\omega t/2} \right]$

$\Rightarrow \quad \langle x \rangle = \frac{1}{\sqrt{2\alpha}} \cos\left[\omega t + (\delta_1 - \delta_0) \right]$

$\langle p_x \rangle = -\sqrt{\frac{\alpha}{2}}\, \hbar \sin\left[\omega t + (\delta_1 - \delta_0) \right]$

The relative phase $\delta_1 - \delta_0$ is observable , δ_0 is unimportant.

Appendix A

Hermite Polynomials

From P. 6-10, we find

$$\frac{d^2H}{d\xi^2} - 2\xi\frac{dH}{d\xi} + (K-1)H = 0$$

$$(h \to H)$$

Acceptable solutions can be found only if

$$K = 2n+1 \qquad n = 0, 1, 2, \cdots$$

$$\Rightarrow \quad \frac{d^2H_n}{d\xi^2} - 2\xi\frac{dH_n(\xi)}{d\xi} + 2n\,H_n(\xi) = 0$$

$\downarrow$

this is defining differential equation

Generating function and recursive relations

$\downarrow$

$$S(\xi, s) = e^{\xi^2-(s-\xi)^2} = e^{-s^2+2s\xi} = \sum_{n=0}^{\infty}\frac{H_n(\xi)}{n!}s^n$$

Expanding the exponential function in terms of powers of s and ξ, we see that the coefficients of the powers s^n are polynomials in terms of ξ – the Hermite polynomials. This can be shown as follows: we have

$$\frac{\partial S}{\partial \xi} = 2s\,\mathrm{e}^{-s^2+2s\xi} = \sum_{n=0}^{\infty}\frac{2s^{n+1}}{n!}H_n(\xi)$$

$$= \sum_{n=0}^{\infty}\frac{s^n}{n!}\frac{\partial H_n(\xi)}{\partial \xi} \quad ,$$

$$\frac{\partial S}{\partial s} = (-2s+2\xi)\,\mathrm{e}^{-s^2+2s\xi} = \sum_{n=0}^{\infty}\frac{(-2s+2\xi)s^n}{n!}H_n(\xi)$$

$$= \sum_{n=0}^{\infty}\frac{s^{n-1}}{(n-1)!}H_n(\xi) \quad . \tag{5}$$

Equating equal powers of s in the sums of these two equations, we obtain

$$\frac{\partial H_n(\xi)}{\partial \xi} = 2nH_{n-1}(\xi) \quad ,$$

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \quad . \tag{6}$$

Therefore it follows that

$$\frac{\partial H_n(\xi)}{\partial \xi} = 2\xi H_n(\xi) - H_{n+1}(\xi) \quad , \tag{7}$$

and hence

$$\frac{\partial^2 H_n(\xi)}{\partial \xi^2} = 2H_n(\xi) + 2\xi\frac{\partial H_n(\xi)}{\partial \xi} - \frac{\partial H_{n+1}(\xi)}{\partial \xi}$$

$$= 2\xi\frac{\partial H_n(\xi)}{\partial \xi} + 2H_n(\xi) - (2n+2)H_n(\xi)$$

$$= 2\xi \frac{\partial H_n(\xi)}{\partial \xi} - 2nH_n(\xi) \quad . \tag{8}$$

This is exactly differential equation (3), proving that the $H_n(\xi)$ appearing in the generating function (4) are indeed Hermite polynomials.

The recurrence formulas (6) may be used to calculate the H_n and their derivatives. Another explicit expression directly obtainable from the generating function is quite useful; let us now establish this important relation. From (4) it follows instantly that

$$\left. \frac{\partial^n S(\xi, s)}{\partial s^n} \right|_{s=0} = H_n(\xi) \quad . \tag{9}$$

Now, for an arbitrary function $f(s - \xi)$, it also holds that

$$\frac{\partial f}{\partial s} = -\frac{\partial f}{\partial \xi} \quad . \tag{10}$$

Thus

$$\begin{aligned} \frac{\partial^n S}{\partial s^n} &= e^{\xi^2} \frac{\partial^n e^{-(s-\xi)^2}}{\partial s^n} \\ &= (-1)^n e^{\xi^2} \frac{\partial^n}{\partial \xi^n} e^{-(s-\xi)^2} \quad . \end{aligned} \tag{11}$$

Comparing (11) with (9) yields the very useful formula,

$$H_n(\xi) = (-1)^n = e^{\xi^2} \frac{\partial^n}{\partial \xi^n} e^{-\xi^2} \quad . \tag{12}$$

$$\lambda = \sqrt{\frac{m\omega}{\hbar}}$$

The $H_n(\xi)$ are polynomials of nth degree in ξ with the dominant term $2^n\xi^n$. The first five $H_n(\xi)$ calculated from (7.22) or (12) of the foregoing example are:

$$\begin{aligned} &H_0(\xi) = 1 \quad , \qquad H_1(\xi) = 2\xi \quad , \\ &H_2(\xi) = 4\xi^2 - 2 \quad , \quad H_3(\xi) = 8\xi^3 - 12\xi \quad , \quad H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \quad . \end{aligned} \tag{7.23}$$

The eigenfunctions (7.21) were combined by introducing the abbreviation $\xi = \sqrt{\lambda}x$ and using the Hermite polynomials in a way that holds for both even and odd n, i.e.

$$\psi_n(x) = N_n e^{(-1/2)\xi^2} H_n(\xi) \quad , \quad \xi = \sqrt{\lambda}x \quad . \tag{7.24}$$

The constant N_n, which depends on the index n, is determined by the normalization condition

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1 \quad , \tag{7.25}$$

since we require the position probability to be 1 for the particle in the entire configuration space. Thus

$$n=0:\ \psi_0(x)=\sqrt[4]{\frac{\lambda}{\pi}}\exp\left(-\frac{1}{2}\lambda x^2\right)\quad,$$

$$n=1:\ \psi_1(x)=2\sqrt{\frac{1}{2}\sqrt{\frac{\lambda}{\pi}}}\exp\left(-\frac{1}{2}\lambda x^2\right)\sqrt{\lambda}x\quad,$$

$$n=2:\ \psi_2(x)=\sqrt{\frac{1}{8}\sqrt{\frac{\lambda}{\pi}}}\exp\left(-\frac{1}{2}\lambda x^2\right)(4\lambda x^2-2)\quad. \tag{7.33}$$

From (7.24) and (7.30) it follows that, for space reflection, the eigenfunctions have the symmetry property

$$\psi_n(-x)=(-1)^n\psi_n(x)\quad. \tag{7.34}$$

This means

n even: $\psi(-x)=\psi(x)\rightarrow$ parity $+1$

n odd: $\psi(-x)=-\psi(x)\rightarrow$ parity -1 .

For the lowest H_n, it can easily be shown that they possess precisely n different real zeros and $n-1$ extremal values (see Fig. 7.1). With respect to (12) in Example 7.2, we have

$$H_{nk+1}=-e^{\xi^2}\frac{d}{d\xi}(e^{-\xi^2}H_n)\quad. \tag{7.35}$$

On the assumption that H_n possesses $n+1$ real extremal values, we can conclude the existence of $n+1$ extremal values for $e^{-\xi^2}H_n$ (since $e^{-\xi^2}\rightarrow 0$ for $\xi\rightarrow\infty$). The extremal values are identical with the zeros of the derivative $d/d\xi$; therefore H_{n+1} has precisely $n+1$ real zeros. This conclusion shows that the Hermite polynomials $H_n(\xi)$ – and, in consequence, the wave functions $\psi_n(\xi)$ – possess n different real zeros. This is a special case of a universally valid theorem which states that the principal quantum number of an eigenfunction is identical with the number of zeros.

In Fig. 7.1, some of the ψ_n are plotted together with an energy diagram. The energy eigenvalues are represented as horizontal lines with the quantum segments $E_n=\left(n+\frac{1}{2}\right)\hbar\omega$. For each of the lines there is a corresponding eigenfunction $\psi_n(x)$ drawn on an arbitrary scale.

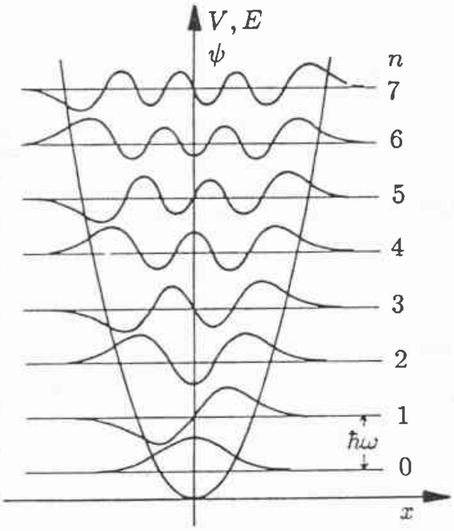


Fig. 7.1. Oscillator potential, energy levels and corresponding wavefunctions

$$\int\limits_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = \frac{1}{\sqrt{\lambda}} N_n^2 \int\limits_{-\infty}^{\infty} \mathrm{e}^{-\xi^2} H_n(\xi)^2 \, d\xi = 1 \quad . \tag{7.26}$$

Using relation (12) of Example 7.2 to express one of the Hermite polynomials that appears in the integrand of the normalization integral, the evaluation of this integral becomes simply

$$\int\limits_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = (-1)^n \frac{N_n^2}{\sqrt{\lambda}} \int\limits_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} \mathrm{e}^{-\xi^2} \, d\xi \quad . \tag{7.27}$$

By partial integration we obtain

$$\begin{aligned} &\int\limits_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} \mathrm{e}^{-\xi^2} \, d\xi \\ &= \left[\left(\frac{d^{n-1}}{d\xi^{n-1}} \mathrm{e}^{-\xi^2} \right) H_n(\xi) \right]_{-\infty}^{\infty} - \int\limits_{-\infty}^{\infty} \frac{dH_n}{d\xi} \frac{d^{n-1}}{d\xi^{n-1}} \mathrm{e}^{-\xi^2} \, d\xi \quad . \end{aligned} \tag{7.28}$$

The first term is, because of (12) in Example 7.2, equal to $(-1)^{n-1} \mathrm{e}^{-\xi^2} H_{n-1}(\xi) H_n(\xi)$. It vanishes at infinity, due to the exponential function.

Having carried out partial integration n times, we are left with

$$\int\limits_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} \mathrm{e}^{-\xi^2} \, d\xi = (-1)^n \int\limits_{-\infty}^{\infty} \frac{d^n H_n}{d\xi^n} \mathrm{e}^{-\xi^2} \, d\xi \quad . \tag{7.29}$$

Since $H_n(\xi)$ is a polynomial of nth order with the dominant term $2^n \xi^n$, for the nth derivative,

$$\frac{d^n}{d\xi^n} H_n(\xi) = 2^n n! \tag{7.30}$$

holds.

From this we find that

$$\int\limits_{-\infty}^{\infty} H_n(\xi) \frac{d^n}{d\xi^n} \mathrm{e}^{-\xi^2} \, d\xi = (-1)^n (2^n) n! \int\limits_{-\infty}^{\infty} \mathrm{e}^{-\xi^2} \, d\xi = (-1)^n (2^n) n! \sqrt{\pi} \quad , \tag{7.31}$$

and for the normalization constant,

$$N_n = \sqrt{\sqrt{\frac{\lambda}{\pi}} \frac{1}{2^n n!}} \quad .$$

The stationary states of the harmonic oscillator in quantum mechanics are therefore

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!} \sqrt{\frac{\lambda}{\pi}}} \exp\left(-\frac{1}{2} \lambda x^2 \right) H_n(\sqrt{\lambda} x) \quad . \tag{7.32}$$

Here we have suppressed the phase factor $(-1)^n$, since it is not essential. To discuss the solution, we take a look at the first three eigenfunctions of the linear harmonic oscillator (see Fig. 7.1):

multiplied by $u_0(y) = e^{-\frac{1}{2}y^2}$ at infinity. Consequently, we need the series to terminate, which requires $\epsilon_m = 2m + 1$ for some m. Thus,

$$\boxed{E_n = \frac{\hbar\omega}{2}\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right)} \quad \rightarrow \quad \text{HO energy levels} \tag{18-1}$$

Quantized energy levels of a harmonic oscillator. The ground state (zero-point) energy is $E_0 = \frac{1}{2}\hbar\omega$, the energy levels are equidistant.

Note. This feature allows us to identify the HO not only with a particle in potential $V(x) = \frac{1}{2}m\omega^2x^2$, but also with a **system of noninteracting (bosonic) particles**. Therefore, a mode of an electromagnetic field of frequency ω can be viewed as a HO with frequency ω; n photons in that mode correspond to the n-th occupied state of the HO. The uncertainty in x and p of the HO ground state corresponds to the "vacuum fluctuations" of the electromagnetic field $\langle x\rangle = 0$, $\langle x^2\rangle \neq 0$ corresponds to $\langle \mathbf{E}\rangle = 0$, $\langle \mathbf{E}^2\rangle \neq 0$ etc.

For given $\epsilon = 2n + 1$, the recursion relation $(*)$

$$(m + 1)(m + 2)c_{m+2} = (2m - \epsilon_n + 1)c_m = (2m - 2n)c_m \tag{18-2}$$

yields

- $c_2 = -\frac{2n}{1\cdot2}c_0$
- $c_4 = \frac{4-2n}{3\cdot4}c_2 = \frac{(4-2n)(0-2n)}{1\cdot2\cdot3\cdot4}c_0$

and in general

$$c_{2k} = (-2)^k\frac{n(n-2)\cdots(n-2k+4)(n-2k+2)}{(2k)!}c_0, \qquad 0 \leq 2k \leq n,\ n \text{ even} \tag{18-3}$$

for the even coefficients.

For the odd coefficients we have

- $c_3 = \frac{(2-2n)}{2\cdot3}c_1 = (-2)\frac{n-1}{2\cdot3}c_1$
- $c_5 = \frac{6-2n}{4\cdot5}c_3 = (-2)\frac{n-3}{4\cdot5}c_3 = (-2)^2\frac{(n-3)(n-1)}{1\cdot2\cdot3\cdot4\cdot5}c_1$

and in general

$$c_{2k+1} = (-2)^k\frac{(n-1)(n-3)\cdot(n-2k+3)(n-2k+1)}{(2k+1)!}c_1, \qquad 0 \leq 2k+1 \leq n,\ n \text{ odd.} \tag{18-4}$$

The eigenfunction $u_n(x)$ for energy level n with energy $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ is given by

$$u_n(y) = e^{-\frac{1}{2}y} \sum_{n=0}^{n/2} c_{2k} y^{2k} \qquad \text{for even } n, \tag{18-5}$$

$$u_n(y) = e^{-\frac{1}{2}y} \sum_{n=0}^{(n-1)/2} c_{2k+1} y^{2k+1} \qquad \text{for odd } n, \tag{18-6}$$

The coefficient c_0 or c_1 has to be chosen such that the wavefunction is normalized, and y is related to the position coordinate x via $y = \sqrt{\frac{m\omega}{\hbar}}x$. The quantity $\sqrt{\frac{\hbar}{m\omega}}$ has units of length and defines the natural quantum length scale for the harmonic oscillator. Apart from the normalization, the polynomials

$$h_n(y) = \sum_{k=0}^{n/2} c_{2k} y^{2k} \tag{18-7}$$

$$h_n(y) = \sum_{k=0}^{(n+1)/2} c_{2k+1} y^{2k+1} \tag{18-8}$$

are the **Hermite polynomials** $H_n(y)$. The Hermite polynomials obey the following relations:

$$H_n{}''(y) - 2yH_n{}'(y) + 2nH_n(y) = 0 \quad \rightarrow \quad \text{(defining equation)} \tag{18-9}$$

$$H_{n+1}(y) - 2yH_n(y) + 2nH_{n-1}(y) = 0 \tag{18-10}$$

$$H_{n+1}(y) - H_n{}'(y) + 2yH_n(y) = 0 \tag{18-11}$$

$$\sum_{n=0}^{\infty} H_n(y) \frac{z^n}{n!} = e^{2zy - z^2} \tag{18-12}$$

$$H_n(y) = (-1)^n e^{y^2} \left(\frac{d}{dy}\right)^2 e^{-y^2} \quad \rightarrow \quad \left(\begin{array}{c}\text{alternative definition} \\ \text{of Hermite polynomials}\end{array}\right) \tag{18-13}$$

Since the wavefunction belonging to level n is $u_n(y) = Ce^{-\frac{1}{2}^2}H_n(y)$, in order to normalize it, we need to calculate

$$\int_{-\infty}^{\infty} dy |u_n(y)|^2 = \int_{-\infty}^{\infty} dy |C|^2 e^{-y^2} H_n{}^2(y) \tag{18-14}$$

The Hermite polynomials are real. One can show that

$$\boxed{\int_{-\infty}^{\infty} dy e^{-y^2} H_n{}^2(y) = 2^n n! \sqrt{\pi}} \tag{18-15}$$

Normalization actually requires $\int_{-\infty}^{\infty} dx|u_n(x)|^2 = 1$, but since x and $y = \sqrt{\frac{m\omega}{\hbar}}x$ are related by a constant factor, $\int_{-\infty}^{\infty} dx|u_n(x)|^2 = \sqrt{\frac{\hbar}{m\omega}} \int_{-\infty}^{\infty} dy|u_n(y)|^2$.

$$H_0(y) = 1 \tag{18-16}$$
$$H_1(y) = 2y \tag{18-17}$$
$$H_2(y) = 4y^2 - 2 \tag{18-18}$$
$$H_3(y) = 8y^3 - 12y \tag{18-19}$$
$$H_4(y) = 16y^4 - 48y^2 + 12 \tag{18-20}$$
$$H_5(y) = 32y^5 - 160y^3 + 120y \tag{18-21}$$

Consequently, the lowest eigenfunctions look like (Fig. I). The eigenfunctions of the HO look the same in momentum space, since the Hamiltonian is symmetric in x and p, and

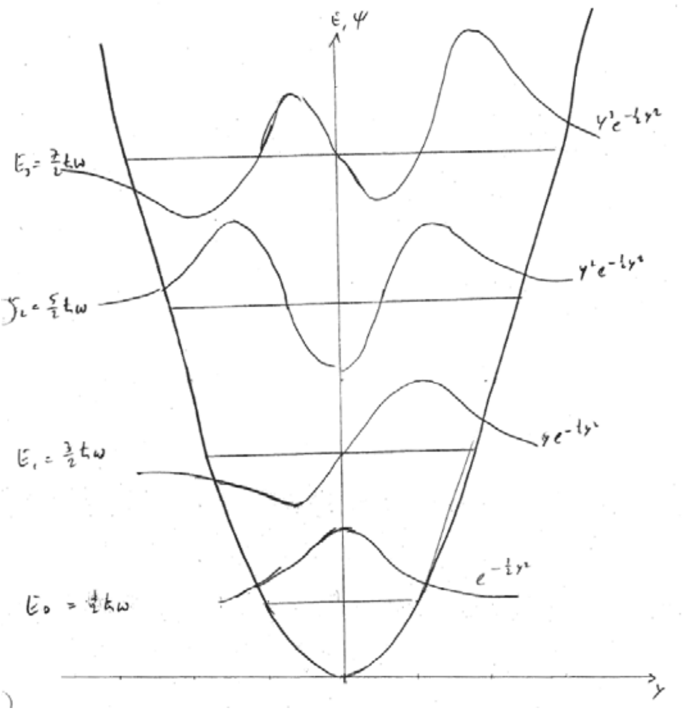


Figure I: HO eigenfunctions.

$$\hat{x} = x, \qquad \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad \text{in position space } \psi(x) \tag{18-22}$$
$$\hat{x} = i\hbar\frac{\partial}{\partial p}, \qquad \hat{p} = p \qquad \text{in momentum space } \phi(p) \tag{18-23}$$

The harmonic oscillator ground state, being a Gaussian function with no spatial dependence of the complex phase, has minimum uncertainty allowed by the Heisenberg relation:

$$\Delta x \Delta p = \frac{\hbar}{2} \qquad \text{for the ground state} \tag{18-24}$$

$$\Delta x \Delta p > \frac{\hbar}{2} \qquad \text{for any excited state} \tag{18-25}$$

- Show Bose-Einstein condensate expansion
- Thermal cloud
- isotropic expansion for anistropic trap
  $(\frac{p^2}{2m} = \frac{1}{2}kT)$
- condensate:
  $\frac{p^2}{2m} \propto \frac{1}{{x_0}^2} \propto \frac{m\omega}{\hbar} \longrightarrow$ anisotropic expansion

HO: operator method

There is an elegant and instructive way to derive the HO eigenstates without directly solving the SE. Instead, we use commutation relation between operators. We start by writing the Hamiltonian in dimensionless form

$$H = \hbar\omega \left[\frac{p^2}{2m\hbar\omega} + \frac{m\omega}{2\hbar} x^2 \right] \tag{18-26}$$

$$= \hbar\omega \left[\left(\frac{p}{\sqrt{2m\hbar\omega}} \right)^2 + \left(\frac{x}{\sqrt{2\hbar/m\omega}} \right)^2 \right] \tag{18-27}$$

$$= \hbar\omega \left[\left(\frac{p}{p_0} \right)^2 + \left(\frac{x}{x_0} \right)^2 \right] \tag{18-28}$$

with ${p_0}^2 = 2m\hbar\omega$, ${x_0}^2 = \frac{2\hbar}{m\omega}$. Classically we can write,

$$H_{cl} = \hbar\omega \left(\frac{x}{x_0} - i\frac{p}{p_0} \right) \left(\frac{x}{x_0} + i\frac{p}{p_0} \right), \tag{18-29}$$

however, since in **QM** $\hat{p}$ and $\hat{x}$ do not commute, we have

$$\left(\frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0} \right) \left(\frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0} \right) = \left(\frac{\hat{x}}{x_0} \right)^2 + \left(\frac{\hat{p}}{p_0} \right)^2 \tag{18-30}$$

$$= \left(\frac{\hat{x}}{x_0} \right)^2 + \left(\frac{\hat{p}}{p_0} \right)^2 + \frac{i}{x_0 p_0} \left[\hat{x}, \hat{p} \right]. \tag{18-31}$$

Using the commutator $[\hat{x}, \hat{p}] = i\hbar \frac{\partial}{\partial p} p - p i\hbar \frac{\partial}{\partial p} = i\hbar$ and $\frac{1}{\lambda_0 p_0} = \sqrt{\frac{m\omega}{2\hbar}} \frac{1}{\sqrt{2m\hbar\omega}} = \frac{1}{2\hbar}$ we have

$$\hat{H} = \hbar\omega \left(\left(\frac{x}{x_0} \right)^2 + \left(\frac{\hat{p}}{p_0} \right)^2 \right) \tag{18-32}$$

$$= \hbar\omega \left(\left(\frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0} \right) \left(\frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0} \right) - i\frac{1}{x_0 p_0} [\hat{x}, \hat{p}] \right) \tag{18-33}$$

$$= \hbar\omega \left(\left(\frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0} \right) \left(\frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0} \right) + \frac{1}{2} \right) \tag{18-34}$$

We can define a new, non-Hermitian operator by

$$\hat{a} := \frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0} \tag{18-35}$$

Consequently, the Hermitian conjugate operator is

$$\hat{a}^\dagger = \left(\frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0} \right)^\dagger = \frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0} \tag{18-36}$$

since $\hat{p}^\dagger = \hat{p}$, $\hat{x}^\dagger = \hat{x}$

Note. The Hermitian conjugate operator $O^\dagger$ of any operator is defined by the relation

$$\int_{-\infty}^{\infty} dx \psi_2{}^*(x) O^\dagger \psi_1(x) = \int_{-\infty}^{\infty} dx \left(O\psi_2(x) \right)^* \psi_1(x) \tag{18-37}$$

for any well-behaved wavefunctions $\psi_1(x)$, $\psi_2(x)$.

Consequently, for any operator $\hat{O} = c_1\hat{O}_1 + c_2\hat{O}_2$, where c_1 and c_2 are complex numbers,

$$\hat{O}^\dagger = \left(c_1\hat{O}_1 + c_2\hat{O}_2 \right)^\dagger = c_1{}^*\hat{O}_1^\dagger + c_2{}^*\hat{O}_2^\dagger \tag{18-38}$$

and for any operator $\hat{O} = \hat{O}_1\hat{O}_2^\dagger$ we have $\hat{O}^\dagger = \left(\hat{O}_1\hat{O}_2 \right)^\dagger = \hat{O}_2^\dagger\hat{O}_1^\dagger$

Proof. See problem set. □

Using the operators $\hat{a}$,$\hat{a}^\dagger$, we can write the Hamiltonian for the HO in the particularly simple form

$$\boxed{\hat{H} = \hbar\omega \left(\hat{a}^\dagger\hat{a} + \frac{1}{2} \right)} \tag{18-39}$$

Rather than being explicitly defined in terms of $\hat{x}$, $\hat{p}$, $\ldots$, and operator can be defined through its commutation relations with other operators. Let us look at $\hat{a}$, $\hat{a}^\dagger$:

$$\begin{aligned}
\left[\hat{a}, \hat{a}^\dagger\right] &= \left[\frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0}, \frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0}\right] && \text{(18-40)}\\
&= i\left[\frac{\hat{p}}{p_0}, \frac{\hat{x}}{x_0}\right] - i\left[\frac{\hat{x}}{x_0}, \frac{\hat{p}}{p_0}\right] && \text{(18-41)}\\
&= \frac{i}{p_0 x_0}\left([\hat{p}, \hat{x}] - [\hat{x}, \hat{p}]\right) && \text{(18-42)}\\
&= \frac{i}{2\hbar} 2\,[\hat{p}, \hat{x}] && \text{(18-43)}\\
&= \frac{i}{\hbar}\frac{\hbar}{i} && \text{(18-44)}\\
&= 1, && \text{(18-45)}
\end{aligned}$$

where we have used $[\hat{x}, \hat{x}] = 0 = [\hat{p}, \hat{p}]$. So we have

$$\begin{aligned}
\left[\hat{a}, \hat{a}^\dagger\right] &= 1 && \text{(18-46)}\\
[\hat{a}, \hat{a}] = \left[\hat{a}^\dagger, a^\dagger\right] &= 0 && \text{(18-47)}
\end{aligned}$$

As will be elaborated on in *8.06*, this defines a commutation relation for bosonic (quasi)-particles, i.e. particles whose wavefunction is symmetric under the exchange of two particles. For the commutators with the Hamiltonian, we have

$$\begin{aligned}
\left[\hat{H}, \hat{a}\right] &= \hbar\omega\left[\hat{a}^\dagger \hat{a}, \hat{a}\right] && \text{(18-48)}\\
&= \hbar\omega\left(\hat{a}^\dagger \hat{a}\hat{a} - \hat{a}\hat{a}^\dagger \hat{a}\right) && \text{(18-49)}\\
&= \hbar\omega\left(\hat{a}^\dagger \hat{a}\hat{a} - \left(1 + \hat{a}^\dagger \hat{a}\right)\hat{a}\right) && \text{(18-50)}\\
&= -\hbar\omega\hat{a} && \text{(18-51)}
\end{aligned}$$

and

$$\begin{aligned}
\left[\hat{H}, \hat{a}^\dagger\right] &= \hbar\omega\left[\hat{a}^\dagger \hat{a}, \hat{a}^\dagger\right] && \text{(18-52)}\\
&= \hbar\omega\left(\hat{a}^\dagger \hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a}^\dagger \hat{a}\right) && \text{(18-53)}\\
&= \hbar\omega\left(\hat{a}^\dagger \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\left(\hat{a}\hat{a}^\dagger - 1\right)\right) && \text{(18-54)}\\
&= \hbar\omega\hat{a}^\dagger && \text{(18-55)}
\end{aligned}$$

We are now in the situation to calculate the spectrum of eigenenergies of the HO simply using those commutation relations. Let us first note that since $\hat{H}$ is quadratic in x and p, all eigenvalues must be positive:

$$\begin{aligned}
\langle E\rangle = \left\langle \hat{H}\right\rangle &= \langle T\rangle + \langle V\rangle && \text{(18-56)}\\
&= \frac{1}{2m}\int dp\phi^*(p)p^2\phi(p) + \frac{1}{2}m\omega^2\int dx\psi^*(x)x^2\psi(x) > 0 && \text{(18-57)}
\end{aligned}$$

for any wavefunction $\psi(x)$ and its Fourier transform $\phi(p)$. Before determining the eigenspectrum, let us define a convenient notation.

State vector notation (Dirac notation)

We have already argued that a physical state, (i.e., a physical system whose initial conditions have been prepared to the maximum extent allowed by **QM**), is described by a vector in an abstract vector space (Hilbert space), and that a wavefunction in position space is only one possible representation of the state. Alternatively, the state can be described in the momentum representation (wavefunction in momentum space), or by specifying the expansion coefficients when expanding the basis of energy eigenstates. Using a notation introduced by Paul Dirac, one of the creators of **QM**, we write the state as

$$|\psi\rangle \tag{18-58}$$

and define

$$\langle\phi|\psi\rangle := \int dx\phi^*(x)\psi(x) \tag{18-59}$$

for any two states $|\psi\rangle$, $|\phi\rangle$ whose wavefunctions are by $\psi(x)$, $\phi(x)$. Dirac introduced

$$\underbrace{\langle\phi}_{\text{bra}}\underbrace{|}_{\text{-c-}}\underbrace{\psi\rangle}_{\text{ket}} \tag{18-60}$$

So $|\psi\rangle$ is called a "ket", and $\langle\phi|$ a "bra". You can think of the "bra" as the transpose of the "ket" vector

$$\begin{pmatrix} v_1 & v_2 & \cdots \end{pmatrix} \cdot \begin{pmatrix} w_1 \\ w_2 \\ \vdots \end{pmatrix} = \text{c-number (complex number)}, \tag{18-61}$$

but possibly for infinite-dimensional vectors. In this sandwich or Dirac notation, the expectation value of any operator $\hat{A}$ is given by

$$\left\langle \hat{A} \right\rangle = \left\langle \psi|\hat{A}|\psi \right\rangle = \int dx\psi^*(x)\hat{A}\psi(x). \tag{18-62}$$

In Dirac notation,

$$\langle\psi|\phi\rangle = \int dx\psi^*(x)\phi(x) = \left(\int dx\phi^*(x)\psi(x)\right)^* = \langle\phi|\psi\rangle^* \tag{18-63}$$

An operator $\hat{A}$ acting on a state produces another state, symbolically

$$\hat{A}\,|\psi\rangle = \left|\hat{A}\psi\right\rangle \tag{18-64}$$

Consequently,

$$\left\langle \phi|\hat{A}|\psi \right\rangle = \left\langle \phi|\hat{A}\psi \right\rangle = \int dx \phi^*(x) \left(\hat{A}\psi(x)\right) = \int dx \phi^*(x)\hat{A}\psi(x) \tag{18-65}$$

The Hermitian conjugate operator $\hat{A}^\dagger$ is defined by

$$\left\langle \phi|\hat{A}^\dagger|\psi \right\rangle = \int dx \left(A\phi(x)\right)^* \psi(x) = \left(\left(\int dx \psi^*(x) \left(A\phi(x)\right)\right)\right)^* \tag{18-66}$$

$$= \langle \psi|A\phi\rangle^* \tag{18-67}$$

$$= \langle A\phi|\psi\rangle \tag{18-68}$$

In Dirac notation, the orthonormality condition for eigenstates $|n\rangle$, $|m\rangle$ reads

$$\langle n|m\rangle = \int dx u_n{}^*(x) u_m(x) = \delta_{nm}, \tag{18-69}$$

where the expansion coefficients are

$$c_n = \int dx u_n{}^* \psi(x) = \langle n|\psi\rangle \,. \tag{18-70}$$

A bracket like $\langle a|b\rangle$ is a complex number, but a ketbra like $|b\rangle\langle a|$ is an operator since acting on a state it produces another state

$$\underbrace{|b\rangle}_{\text{state}} \underbrace{\langle a|\psi\rangle}_{\text{c-number}} \,. \tag{18-71}$$

One can show that the sum over all eigenstates $\sum_n |n\rangle\langle n|$ of a Hermitian operator is the unity operator

$$\sum_n |n\rangle\langle n| = \hat{1}, \tag{18-72}$$

and

$$|\psi\rangle = \hat{1}\,|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle = \sum c_n\,|n\rangle \quad \rightarrow \quad \begin{pmatrix} \text{expansion into} \\ \text{eigenstates} \end{pmatrix} \tag{18-73}$$

Back to the operator treatment of the HO: Let us assume that we have found an energy eigenstate with eigenenergy E and let us denote that state by $|E\rangle$. Let us define a new state $|\psi\rangle$ by having the operator $\hat{a}$ act on $|E\rangle$, $|\psi\rangle := \hat{a}\,|E\rangle$. What happens if we act with the Hamiltonian $|\psi\rangle$?

$$\hat{H}\,|\psi\rangle = \hat{H}\hat{a}\,|E\rangle \tag{18-74}$$

$$= \left(\left[\hat{H}, \hat{a}\right] + \hat{a}\hat{H}\right)|E\rangle \tag{18-75}$$

$$= \left(-\hbar\omega\hat{a} + \hat{a}E\right)|E\rangle \tag{18-76}$$

$$= \left(E - \hbar\omega\right)\hat{a}\,|E\rangle \tag{18-77}$$

$$= \left(E - \hbar\omega\right)|\psi\rangle \tag{18-78}$$

Here we have used the previously calculated result $\left[\hat{H}, \hat{a}\right] = -\hbar\omega\hat{a}$ for the commutator, and the fact that complex (here real) numbers commute with everything. The above formula signifies that $|\psi\rangle$ is also an energy eigenstate, but with lower energy $E = -\hbar\omega$. Since starting from any eigenstate $|E\rangle$ we can repeat the procedure any number of times,

$$\hat{a}^n |E\rangle = |E - n\hbar\omega\rangle , \tag{18-79}$$

and the eigenenergy has to remain positive, (we have shown $\left\langle \psi|\hat{H}|\psi \right\rangle > 0$ for any state), there must exist a state $|0\rangle$ such that

$$\hat{a} |0\rangle = 0 \tag{18-80}$$

i.e., a state whose energy cannot be lowered further.

Note. It is important to distinguish between $|0\rangle$ (lowest energy eigenstate, vector in Hilbert space) and 0 (zero of the Hilbert space, vector of zero length).

Note. Nothing implies that the state $|0\rangle$ has zero energy. in fact,

$$\hat{H} |0\rangle = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) |0\rangle \underset{\hat{a}|0\rangle=0}{=} \frac{1}{2}\hbar\omega |0\rangle , \tag{18-81}$$

so the ground state has eigenenergy $E_0 = \frac{1}{2}\hbar\omega$, this is the zero-point energy. In the context of identifying a HO at frequency ω with an electromagnetic mode at frequency ω, the ground state $|0\rangle$ is also called the vacuum (ground state has no excitations, photon number is zero): the vacuum has finite vacuum energy $E_0 = \frac{1}{2}\hbar\omega_0$.

What happens if $\hat{a}^\dagger$ acts on ground state? Let us define

$$\left|\tilde{1}\right\rangle := \hat{a}^\dagger |0\rangle . \tag{18-82}$$

The tilde $\sim$ is there to remind us that this state is not necessarily normalized, even if $|0\rangle$ is chosen to be normalized.

We then have

$$\hat{H}|\tilde{1}\rangle = \hat{H}\hat{a}^\dagger|0\rangle \tag{19-1}$$

$$= \left([\hat{H}, \hat{a}^\dagger] + \hat{a}^\dagger\hat{H}\right)|0\rangle \tag{19-2}$$

$$= \left(\hbar\omega\hat{a}^\dagger + \hat{a}^\dagger\frac{1}{2}\hbar\omega_0\right)|0\rangle \tag{19-3}$$

$$= \frac{3}{2}\hbar\omega\hat{a}^\dagger|0\rangle \tag{19-4}$$

$$= \frac{3}{2}\hbar\omega|\tilde{1}\rangle, \tag{19-5}$$

i.e., $|\tilde{1}\rangle = \hat{a}^\dagger|0\rangle$ is also an energy eigenstate, but with eigenenergy $\frac{3}{2}\hbar\omega$ instead of $\frac{1}{2}\hbar\omega$ for $|0\rangle$. Similarly, we can show that $|\tilde{2}\rangle = \hat{a}^\dagger|\tilde{1}\rangle$ is also an energy eigenstate, but with energy $\frac{5}{2}\hbar\omega$ etc. Consequently, we can construct a ladder of (yet to be normalized) energy eigenstates $|\tilde{n}\rangle$ by

$$|\tilde{n}\rangle = \left(\hat{a}^\dagger\right)^n|0\rangle \tag{19-6}$$

with

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega. \tag{19-7}$$

$\hat{a}$ ($\hat{a}^\dagger$) is called the lowering (raising) operator, it lowers (raises) the energy by $\hbar\omega$.

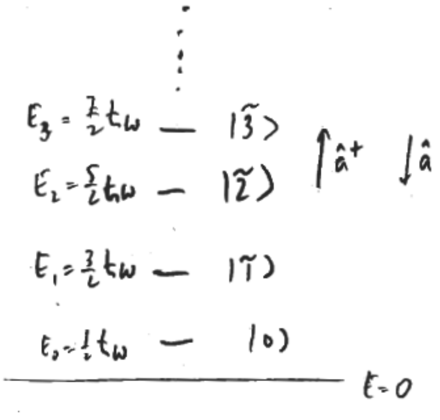


Figure I: $\hat{a}$, $\hat{a}^\dagger$ are sometimes called "ladder operators" since they take us up and down the ladder of energy eigenstates.

When describing a monochromatic electromagnetic field quantum mechanically, we can associate the frequency ω with a harmonic oscillator of that frequency. For non-interacting particles (such as photons) a state with n photons can be associated with the n-th eigenstate of the HO with n. The ground state then corresponds to an empty mode (no photons, $n = 0$), however there is still a finite energy $\frac{1}{2}\hbar\omega$ that we associate with vacuum fluctuations of the electromagnetic field. In this context, $\hat{a}^\dagger$ and $\hat{a}$ are called **creation** and **annihilation** operators, respectively, since they create and annihilate photons, or more generally, arbitrary non-interacting bosonic particles.

Normalization of HO energy eigenstates

Let us assume that the ground state $|0\rangle$ is already chosen to be properly normalized: $\langle 0|0\rangle = 1$.

Note. Remember that $\langle 0|0\rangle$ denotes $\langle 0|0\rangle = \int dx u_0^*(x) u_0(x)$.

How long is the state $|\tilde{1}\rangle = \hat{a}^\dagger|0\rangle$?

$$\begin{aligned}
\langle 1|1\rangle &= \langle \hat{a}^\dagger 0|\hat{a}^\dagger 0\rangle && (19\text{-}8)\\
&= \langle 0|\hat{a}|\hat{a}^\dagger 0\rangle && (19\text{-}9)\\
&= \langle 0|\hat{a}\hat{a}^\dagger|0\rangle && (19\text{-}10)\\
&= \langle 0|\left[\hat{a}, \hat{a}^\dagger\right] + \hat{a}^\dagger\hat{a}|0\rangle && (19\text{-}11)\\
&= \langle 0|1 + \hat{a}^\dagger\hat{a}|0\rangle \quad \rightarrow \quad \big(\hat{a}|0\rangle = 0\big) && (19\text{-}12)\\
&= 1 && (19\text{-}13)
\end{aligned}$$

The state $|\tilde{1}\rangle$ is already normalized, so we can write:

$$|1\rangle = \hat{a}^\dagger|0\rangle \quad \rightarrow \quad \text{normalized eigenstate} \qquad (19\text{-}14)$$

What about $|\tilde{2}\rangle = \hat{a}^\dagger|\tilde{1}\rangle = \hat{a}^\dagger|1\rangle$?

$$\begin{aligned}
\langle \tilde{2}|\tilde{2}\rangle &= \langle \hat{a}^\dagger 1|\hat{a}^\dagger 1\rangle && (19\text{-}15)\\
&= \langle 1|\hat{a}\hat{a}^\dagger|1\rangle && (19\text{-}16)\\
&= \langle 1|\big(\hat{a}^\dagger\hat{a} + 1\big)|1\rangle && (19\text{-}17)\\
&= \langle 1|\hat{a}^\dagger|0\rangle + 1 \quad \rightarrow \quad \big(\hat{a}|1\rangle = |0\rangle\big) && (19\text{-}18)\\
&= \langle 1|1\rangle + 1 && (19\text{-}19)\\
&= 2 && (19\text{-}20)
\end{aligned}$$

Then the properly normalized second excited state is

$$|2\rangle = \frac{1}{\sqrt{2}}|\tilde{2}\rangle = \frac{1}{\sqrt{2}}\left(\hat{a}^\dagger\right)^2|0\rangle. \tag{19-21}$$

We can show, in general, (see PS) that the length squared of the state $|\tilde{n}\rangle = \left(\hat{a}^\dagger\right)^n|0\rangle$ is $\langle\tilde{n}|\tilde{n}\rangle = n!$. Consequently, the n-th normalized eigenstate is

$$\boxed{|n\rangle := \frac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n|0\rangle}. \tag{19-22}$$

We can also show (see PS) that

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \tag{19-23}$$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{19-24}$$

From operators back to spatial wavefunctions

The condition on the ground state $|0\rangle$, $\hat{a}|0\rangle = 0$, reads in position space using our definition of the annihilation operator,

$$\hat{a} = \frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2\hbar m\omega}}\hat{p}, \tag{19-25}$$

$$\hat{a}u_0(x) = \left(\sqrt{\frac{m\omega}{2\hbar}}x + \frac{i}{\sqrt{2\hbar m\omega}}\frac{\hbar}{i}\frac{\partial}{\partial x}\right)u_0(x) = 0 \tag{19-26}$$

$$\left(m\omega x + \hbar\frac{\partial}{\partial x}\right)u_0(x) = 0. \tag{19-27}$$

The simple DE has the solution $u_0(x) = ce^{-\frac{m\omega}{2\hbar}x^2}$ with normalization $1 = c^2\frac{\pi\hbar}{m\omega}$. Consequently, the normalized ground-state wavefunction is

$$u_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}. \tag{19-28}$$

The normalized n-th eigenstate can be obtained from

$$|n\rangle = \frac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n|0\rangle \tag{19-29}$$

or

$$u_n(x) = \frac{1}{\sqrt{n!}}\left(\sqrt{\frac{m\omega}{2\hbar}}x - \frac{i}{\sqrt{2\hbar m\omega}}\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^n u_0(x). \tag{19-30}$$

Commutators, Heisenberg uncertainty, and simultaneous eigenfunctions

The fact that $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ in the position representation (or $\hat{x} = i\hbar\frac{\partial}{\partial p}$ in the momentum representation) implies

$$\hat{p}\hat{x}\psi(x) = \hat{p}\big(x\psi(x)\big) \neq \hat{x}\hat{p}\psi(x) = x\big(\hat{p}\psi(x)\big), \tag{19-31}$$

i.e., $\hat{x}$ and $\hat{p}$ do not commute. Define the difference between $\hat{p}\hat{x}$ and $\hat{x}\hat{p}$ as the **commutator**

$$\big[\hat{p}, \hat{x}\big] = \hat{p}\hat{x} - \hat{x}\hat{p}. \tag{19-32}$$

Here:

$$\big[\hat{p}, \hat{x}\big] = \frac{\hbar}{i} \quad \rightarrow \quad \text{(c-number)} \tag{19-33}$$

In general, $\big[\hat{A}, \hat{B}\big] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is an operator. The commutator is linear.

$$\big[c_1\hat{A}_1 + c_2\hat{A}_2, \hat{B}\big] = c_1\big[\hat{A}_1, \hat{B}\big] + c_2\big[\hat{A}_2, \hat{B}\big] \tag{19-34}$$

Other useful relations

$$\big[\hat{B}, \hat{A}\big] = -\big[\hat{A}, \hat{B}\big] \tag{19-35}$$

$$\big[\hat{A}\hat{B}, \hat{C}\big] = \hat{A}\big[\hat{B}, \hat{C}\big] + \big[\hat{A}, \hat{C}\big]\hat{B} \tag{19-36}$$

Simultaneous eigenfunctions

Consider a free particle. The plane waves $\psi(x) = e^{\pm ikx}$ are simultaneous eigenfunctions of energy with eigenvalue $\frac{\hbar^2k^2}{2m}$,

$$\hat{H}e^{\pm ikx} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}e^{\pm ikx} = \frac{\hbar^2k^2}{2m}e^{\pm ikx}, \tag{19-37}$$

and of momentum with eigenvalue $\pm\hbar k$,

$$\hat{p}e^{\pm ikx} = \frac{\hbar}{i}\frac{\partial}{\partial x}e^{\pm ikx} = \pm\hbar k e^{\pm ikx}. \tag{19-38}$$

Note. If we had chosen $\cos(kx)$, $\sin(kx)$, these would have also been energy eigenfunctions with eigenvalue $\frac{\hbar^2k^2}{2m}$, but not momentum eigenfunctions.

However, since $\cos(kx)$ and $\sin(kx)$ are degenerate (i.e., have the same energy eigenvalue), it is possible to choose linear combinations of degenerate eigenstates $e^{\pm ikx} = \cos(kx) \pm i\sin(kx)$ that are simultaneous eigenstates of momentum. In the potential well, on the other hand, the energy eigenstates were not simultaneous eigenstates of momentum. In general, we have:

Theorem 19.1. *Two Hermitian operators $\hat{A}$, $\hat{B}$ have a set of simultaneous eigenfunctions if and only if they commute.*

Proof. "⇒" Assume a complete set $\{u_{ab}\}$ of simultaneous eigenfunctions is found, i.e.,

$$\hat{A}u_{ab} = au_{ab} \tag{19-39}$$

$$\hat{B}u_{ab} = au_{ab} \tag{19-40}$$

a, b, eigenvalues. Then $[\hat{A}, \hat{B}]u_{ab} = (ab - ba)u_{ab} = 0$ for all eigenfunctions → $[\hat{A}, \hat{B}] = 0$.

"⇐" See *Gasiorowicz, 5-4.* ☐

Since only an eigenstate of $\hat{A}$ will have a definite outcome when a measurement of $\hat{A}$ is made, this means that ΔA and ΔB can always be simultaneously made zero only when $\hat{A}$ and $\hat{B}$ commute.

Theorem 19.2. *One can prove that in any chosen state ψ,*

$$(\Delta A)^2_\psi (\Delta B)^2_\psi \geq \langle i[\hat{A}, \hat{B}]\rangle^2_\psi \tag{19-41}$$

for any two Hermitian operators $\hat{A}$, $\hat{B}$.

Proof. see *Gasiorowicz*, online supplement SA. ☐

For $\hat{x}$, $\hat{p}$, we have

$$(\Delta x)^2_\psi (\Delta p)^2_\psi \geq \frac{1}{4}\langle i i\hbar\rangle^2_\psi = \frac{\hbar^2}{4}, \tag{19-42}$$

where the RHS does not depend on the state ψ. This is another derivation of the Heisenberg uncertainty relation $\Delta x \Delta p \geq \frac{\hbar}{2}$.

The Schrödinger equation in three dimensions

$$\boxed{\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})} \quad \rightarrow \quad \text{SE in 3D} \tag{19-43}$$

with

$$\hat{\mathbf{p}}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 \tag{19-44}$$

$$\hat{\mathbf{p}} = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}\right) \quad \rightarrow \quad \text{in the position representation} \tag{19-45}$$

The SE then reads $\left(\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$,

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = W\psi(\mathbf{r})} \quad \rightarrow \quad \text{SE in 3D} \tag{19-46}$$

Spherically symmetric potential

If the potential is spherically symmetric, $V(\mathbf{r}) = V(r)$, then it is convenient to work in spherical coordinates, where we can write

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right) \tag{19-47}$$

We define an operator via

$$\hat{\mathbf{L}}^2 = -\hbar^2\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right). \tag{19-48}$$

$\hat{\mathbf{L}}$ will be the operator associated with angular momentum.

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\hat{\mathbf{L}}^2}{\hbar^2 r^2} \tag{19-49}$$

Since $V(r)$ does not depend on θ, ϕ, we try an

ansatz.

$$\psi(\mathbf{r}) = R(r)Y(\theta,\phi) \tag{19-50}$$

Then,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}\frac{2}{r}\frac{\partial}{\partial r}\right) + V(r)\right]R(r)Y(\theta,\phi) \tag{19-51}$$

$$+\frac{L^2}{2mr^2}R(r)Y(\theta,\phi) \tag{19-52}$$

$$= ER(r)Y(\theta,\phi) \tag{19-53}$$

As before, when deriving the time-indepenedent SE, we divide by $R(r)Y(\theta,\phi) \neq 0$.

$$\cdots = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + V(r)\right]R(r) + \frac{1}{Y(\theta,\phi)}\frac{L^2}{2mr^2}R(r)Y(\theta,\phi) \tag{19-54}$$

$$= E \tag{19-55}$$

The LHS can only be a constant for all θ, ϕ if the second term does not depend on θ, ϕ. We arrive at two equations:

$$\frac{\hat{\mathbf{L}}^2}{2mr^2}Y(\theta,\phi) = \frac{\text{const}}{2mr^2}Y(\theta,\phi) = E_L(r)Y(\theta,\phi) \tag{19-56}$$

$$\frac{1}{R(r)}\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + V(r)\right]R(r) + \frac{\text{const}}{2mr^2} = E \tag{19-57}$$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + V(r) + \frac{\text{const}}{2mr^2}\right]R(r) = ER(r) \tag{19-58}$$

where $E_L = \frac{\text{const}}{2mr^2}$ is the energy associated with the angular dependence of the wavefunction.