3.1: Schrodinger's Equation

Consider a dynamical system consisting of a single non-relativistic particle of mass m moving along the x-axis in some real potential $V(x)$. In quantum mechanics, the instantaneous state of the system is represented by a complex wavefunction $\psi(x,t)$. This wavefunction evolves in time according to Schrödinger's equation:

$$\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t} = -\frac{\hbar^{\,2}}{2\,m}\,\frac{\partial^{\,2}\psi}{\partial x^{\,2}} + V(x)\,\psi. \tag{3.1.1}$$

The wavefunction is interpreted as follows: $|\psi(x,t)|^{\,2}$ is the probability density of a measurement of the particle's displacement yielding the value x. Thus, the probability of a measurement of the displacement giving a result between a and b (where $a<b$) is

$$P_{x\,\in\,a:b}(t) = \int_a^b |\psi(x,t)|^{\,2}\,dx. \tag{3.1.2}$$

Note that this quantity is real and positive definite.

3.2: Normalization of the Wavefunction

Now, a probability is a real number lying between 0 and 1. An outcome of a measurement that has a probability 0 is an impossible outcome, whereas an outcome that has a probability 1 is a certain outcome. According to Equation ([e3.2]), the probability of a measurement of x yielding a result lying between $-\infty$ and $+\infty$ is

$$P_{x\,\in\,-\infty:\infty}(t) = \int_{-\infty}^{\infty}|\psi(x,t)|^{\,2}\,dx. \tag{3.2.1}$$

However, a measurement of x must yield a value lying between $-\infty$ and $+\infty$, because the particle has to be located somewhere. It follows that $P_{x\,\in\,-\infty:\infty} = 1$, or

$$\int_{-\infty}^{\infty}|\psi(x,t)|^{\,2}\,dx = 1, \tag{3.2.2}$$

which is generally known as the *normalization condition* for the wavefunction.

For example, suppose that we wish to normalize the wavefunction of a Gaussian wave-packet, centered on $x=x_0$, and of characteristic width σ (see Section [s2.9]): that is,

$$\psi(x) = \psi_0\,{\rm e}^{-(x-x_0)^{\,2}/(4\,\sigma^{\,2})}. \tag{3.2.3}$$

In order to determine the normalization constant ψ_0, we simply substitute Equation ([e3.5]) into Equation ([e3.4]) to obtain

$$|\psi_0|^{\,2}\int_{-\infty}^{\infty}{\rm e}^{-(x-x_0)^{\,2}/(2\,\sigma^{\,2})}\,dx = 1. \tag{3.2.4}$$

Changing the variable of integration to $y = (x-x_0)/(\sqrt{2}\,\sigma)$, we get

$$|\psi_0|^{\,2}\sqrt{2}\,\sigma\int_{-\infty}^{\infty}{\rm e}^{-y^{\,2}}\,dy = 1. \tag{3.2.5}$$

However ,

$$\int_{-\infty}^{\infty}{\rm e}^{-y^{\,2}}\,dy = \sqrt{\pi}, \tag{3.2.6}$$

which implies that

$$|\psi_0|^{\,2} = \frac{1}{(2\pi\,\sigma^{\,2})^{1/2}}. \tag{3.2.7}$$

Hence, a general normalized Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{\,i\,\varphi}}{(2\pi\,\sigma^2)^{1/4}}\,e^{-(x-x_0)^2/(4\,\sigma^2)}, \tag{3.2.8}$$

where φ is an arbitrary real phase-angle.

It is important to demonstrate that if a wavefunction is initially normalized then it stays normalized as it evolves in time according to Schrödinger's equation. If this is not the case then the probability interpretation of the wavefunction is untenable, because it does not make sense for the probability that a measurement of x yields any possible outcome (which is, manifestly, unity) to change in time. Hence, we require that

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi(x,t)|^{\,2}\,dx = 0, \tag{3.2.9}$$

for wavefunctions satisfying Schrödinger's equation. The previous equation gives

$$\frac{d}{dt}\int_{-\infty}^{\infty}\psi^\ast\,\psi\,dx = \int_{-\infty}^{\infty}\left(\frac{\partial\psi^\ast}{\partial t}\,\psi + \psi^\ast\,\frac{\partial\psi}{\partial t}\right)\,dx = 0. \tag{3.2.10}$$

Now, multiplying Schrödinger's equation by $\psi^\ast/({\rm i}\,\hbar)$, we obtain

$$\psi^*\,\frac{\partial\psi}{\partial t} = \frac{{\rm i}\,\hbar}{2\,m}\,\psi^*\,\frac{\partial^2\psi}{\partial x^2} - \frac{\rm i}{\hbar}\,V\,|\psi|^2. \tag{3.2.11}$$

The complex conjugate of this expression yields

$$\psi\,\frac{\partial\psi^*}{\partial t} = -\frac{{\rm i}\,\hbar}{2\,m}\,\psi\,\frac{\partial^2\psi^*}{\partial x^2} + \frac{i}{\hbar}\,V\,|\psi|^2 \tag{3.2.12}$$

[because $(A\,B)^* = A^*\,B^*$, $A^{**} = A$, and ${\rm i}^* = -{\rm i}$].

Summing the previous two equations, we get

$$\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t} = \frac{{\rm i}\hbar}{2\,m}\left(\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial t^2}\right) = \frac{{\rm i}\hbar}{2\,m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right). \tag{3.2.13}$$

Equations ([e3.12]) and ([e3.15]) can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^{\,2}\,dx = \frac{{\rm i}\,\hbar}{2\,m}\left[\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{3.2.14}$$

The previous equation is satisfied provided

$$|\psi| \rightarrow 0 \quad \text{as} \quad |x| \rightarrow \infty. \tag{3.2.15}$$

However, this is a necessary condition for the integral on the left-hand side of Equation ([e3.4]) to converge. Hence, we conclude that all wavefunctions that are *square-integrable* [i.e., are such that the integral in Equation ([e3.4]) converges] have the property that if the normalization condition ([e3.4]) is satisfied at one instant in time then it is satisfied at all subsequent times.

It is also possible to demonstrate, via very similar analysis to that just described, that

$$\frac{dP_{x\,\in\,a:b}}{dt} + j(b,t) - j(a,t) = 0, \tag{3.2.16}$$

where $P_{x\,\in\,a:b}$ is defined in Equation ([e3.2]), and

$$j(x,t) = \frac{{\rm i}\,\hbar}{2\,m}\left(\psi\,\frac{\partial\psi^*}{\partial x} - \psi^*\,\frac{\partial\psi}{\partial x}\right) \tag{3.2.17}$$

is known as the *probability current*. Note that j is real. Equation ([epc]) is a *probability conservation equation*. According to this equation, the probability of a measurement of x lying in the interval a to b evolves in time due to the difference between the flux of probability into the interval [i.e., $j(a,t)$], and that out of the interval [i.e., $j(b,t)$]. Here, we are interpreting $j(x,t)$ as the flux of probability in the $+x$-direction at position x and time t.

Note, finally, that not all wavefunctions can be normalized according to the scheme set out in Equation ([e3.4]). For instance, a plane-wave wavefunction

$$\psi(x,t) = \psi_0\,{\rm e}^{\,{\rm i}\,(k\,x-\omega\,t)} \tag{3.2.18}$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x\,\in\,a:b}(t) \propto \int_a^b |\psi(x,t)|^{\,2}\,dx. \tag{3.2.19}$$

In the following, all wavefunctions are assumed to be square-integrable and normalized, unless otherwise stated.

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3.3: Expectation Values (Averages) and Variances

We have seen that $|\psi(x,t)|^2$ is the probability density of a measurement of a particle's displacement yielding the value x at time t. Suppose that we make a large number of independent measurements of the displacement on an equally large number of identical quantum systems. In general, measurements made on different systems will yield different results. However, from the definition of probability (see Chapter [s2]), the mean of all these results is simply

$$\langle x\rangle = \int_{-\infty}^{\infty} x\,|\psi|^2\,dx. \tag{3.3.1}$$

Here, $\langle x\rangle$ is called the *expectation value* of x. (See Chapter [s2].) Similarly the expectation value of any function of x is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)\,|\psi|^2\,dx. \tag{3.3.2}$$

In general, the results of the various different measurements of x will be scattered around the expectation value, $\langle x\rangle$. The degree of scatter is parameterized by the quantity

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x-\langle x\rangle)^2\,|\psi|^2\,dx \equiv \langle x^2\rangle - \langle x\rangle^2, \tag{3.3.3}$$

which is known as the *variance* of x. (See Chapter [s2].) The square-root of this quantity, σ_x, is called the *standard deviation* of x. (See Chapter [s2].) We generally expect the results of measurements of x to lie within a few standard deviations of the expectation value.

For instance, consider the normalized Gaussian wave-packet [see Equation ([eng])]

$$\psi(x) = \frac{\mathrm{e}^{\mathrm{i}\varphi}}{(2\pi\,\sigma^2)^{1/4}}\,\mathrm{e}^{-(x-x_0)^2/(4\,\sigma^2)}. \tag{3.3.4}$$

The expectation value of x associated with this wavefunction is

$$\langle x\rangle = \frac{1}{\sqrt{2\pi\,\sigma^2}}\int_{-\infty}^{\infty} x\,\mathrm{e}^{-(x-x_0)^2/(2\,\sigma^2)}\,dx. \tag{3.3.5}$$

Let $y=(x-x_0)/(\sqrt{2}\,\sigma)$. It follows that

$$\langle x\rangle = \frac{x_0}{\sqrt{\pi}}\int_{-\infty}^{\infty}\mathrm{e}^{-y^2}\,dy + \frac{\sqrt{2}\,\sigma}{\sqrt{\pi}}\int_{-\infty}^{\infty} y\,\mathrm{e}^{-y^2}\,dy. \tag{3.3.6}$$

However, the second integral on the right-hand side is zero, by symmetry. Hence, making use of Equation ([e3.8]), we obtain

$$\langle x\rangle = x_0. \tag{3.3.7}$$

Evidently, the expectation value of x for a Gaussian wave-packet is equal to the most likely value of x (i.e., the value of x that maximizes $|\psi|^2$).

The variance of x associated with the Gaussian wave-packet ([e3.24]) is

$$\sigma_x^2 = \frac{1}{\sqrt{2\pi\,\sigma^2}}\int_{-\infty}^{\infty}(x-x_0)^2\,\mathrm{e}^{-(x-x_0)^2/(2\,\sigma^2)}\,dx. \tag{3.3.8}$$

Let $y=(x-x_0)/(\sqrt{2}\,\sigma)$. It follows that

$$\sigma_x^2 = \frac{2\,\sigma^2}{\sqrt{\pi}}\int_{-\infty}^{\infty} y^2\,\mathrm{e}^{-y^2}\,dy. \tag{3.3.9}$$

However,

$$\int_{-\infty}^{\infty} y^2\,\mathrm{e}^{-y^2}\,dy = \frac{\sqrt{\pi}}{2}, \tag{3.3.10}$$

giving

$$\sigma_x^2 = \sigma^2. \tag{3.3.11}$$

This result is consistent with our earlier interpretation of σ as a measure of the spatial extent of the wave-packet. (See Section [s2.9].) It follows that we can rewrite the Gaussian wave-packet ([e3.24]) in the convenient form

$$\psi(x) = \frac{\mathrm{e}^{\,\mathrm{i}\,\varphi}}{(2\pi\,\sigma_x^2)^{1/4}}\,\mathrm{e}^{-(x-\langle x\rangle)^2/(4\,\sigma_x^2)}. \tag{3.3.12}$$

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3.4: Ehrenfest's Theorem

A simple way to calculate the expectation value of momentum is to evaluate the time derivative of $\langle x\rangle$, and then multiply by the mass m: that is,

$$\langle p\rangle = m\,\frac{d\langle x\rangle}{dt} = m\,\frac{d}{dt}\int_{-\infty}^{\infty} x\,|\psi|^{\,2}\,dx = m\int_{-\infty}^{\infty} x\,\frac{\partial|\psi|^{\,2}}{\partial t}\,dx. \tag{3.4.1}$$

However, it is easily demonstrated that

$$\frac{\partial|\psi|^{\,2}}{\partial t} + \frac{\partial j}{\partial x} = 0 \tag{3.4.2}$$

[this is just the differential form of Equation ([epc])], where j is the probability current defined in Equation ([eprobc]). Thus,

$$\langle p\rangle = -m\int_{-\infty}^{\infty} x\,\frac{\partial j}{\partial x}\,dx = m\int_{-\infty}^{\infty} j\,dx, \tag{3.4.3}$$

where we have integrated by parts. It follows from Equation ([eprobc]) that

$$\langle p\rangle = -\frac{{\rm i}\,\hbar}{2}\int_{-\infty}^{\infty}\left(\psi^\ast\,\frac{\partial\psi}{\partial x} - \frac{\partial\psi^\ast}{\partial x}\,\psi\right)dx = -{\rm i}\,\hbar\int_{-\infty}^{\infty}\psi^\ast\,\frac{\partial\psi}{\partial x}\,dx, \tag{3.4.4}$$

where we have again integrated by parts. Hence, the expectation value of the momentum can be written

$$\langle p\rangle = m\,\frac{d\langle x\rangle}{dt} = -{\rm i}\,\hbar\int_{-\infty}^{\infty}\psi^\ast\,\frac{\partial\psi}{\partial x}\,dx. \tag{3.4.5}$$

It follows from the previous equation that

$$\frac{d\langle p\rangle}{dt} = -{\rm i}\,\hbar\int_{-\infty}^{\infty}\left(\frac{\partial\psi^\ast}{\partial t}\,\frac{\partial\psi}{\partial x} + \psi^\ast\,\frac{\partial^{\,2}\psi}{\partial t\,\partial x}\right)dx = \int_{-\infty}^{\infty}\left[\left({\rm i}\,\hbar\,\frac{\partial\psi}{\partial t}\right)^\ast\frac{\partial\psi}{\partial x} + \frac{\partial\psi^\ast}{\partial x}\left({\rm i}\,\hbar\,\frac{\partial\psi}{\partial t}\right)\right]dx,$$

where we have integrated by parts. Substituting from Schrödinger’s equation ([e3.1]), and simplifying, we obtain

$$\frac{d\langle p\rangle}{dt} = \int_{-\infty}^{\infty}\left[-\frac{\hbar^{\,2}}{2\,m}\,\frac{\partial}{\partial x}\!\left(\frac{\partial\psi^\ast}{\partial x}\,\frac{\partial\psi}{\partial x}\right) + V(x)\,\frac{\partial|\psi|^{\,2}}{\partial x}\right]dx = \int_{-\infty}^{\infty} V(x)\,\frac{\partial|\psi|^{\,2}}{\partial x}\,dx. \tag{3.4.6}$$

Integration by parts yields

$$\frac{d\langle p\rangle}{dt} = -\int_{-\infty}^{\infty}\frac{dV}{dx}\,|\psi|^{\,2}\,dx = -\left\langle\frac{dV}{dx}\right\rangle. \tag{3.4.7}$$

Hence, according to Equations ([e4.34x]) and ([e3.41]),

$$\begin{aligned} m\,\frac{d\langle x\rangle}{dt} &= \langle p\rangle,\\ \frac{d\langle p\rangle}{dt} &= -\left\langle\frac{dV}{dx}\right\rangle. \end{aligned}$$

Evidently, the expectation values of displacement and momentum obey time evolution equations that are analogous to those of classical mechanics. This result is known as *Ehrenfest’s theorem* .

Suppose that the potential $V(x)$ is slowly varying. In this case, we can expand dV/dx as a Taylor series about $\langle x\rangle$. Keeping terms up to second order, we obtain

$$\frac{dV(x)}{dx} = \frac{dV(\langle x\rangle)}{d\langle x\rangle} + \frac{dV^{\,2}(\langle x\rangle)}{d\langle x\rangle^{\,2}}\,(x-\langle x\rangle) + \frac{1}{2}\,\frac{dV^{\,3}(\langle x\rangle)}{d\langle x\rangle^3}\,(x-\langle x\rangle)^{\,2}. \tag{3.4.8}$$

Substitution of the previous expansion into Equation ([e3.43]) yields

$$\frac{d\langle p\rangle}{dt} = -\frac{dV(\langle x\rangle)}{d\langle x\rangle} - \frac{\sigma_x^2}{2}\,\frac{dV^{\,3}(\langle x\rangle)}{d\langle x\rangle^{\,3}}, \tag{3.4.9}$$

because $\langle 1\rangle = 1$, and $\langle x-\langle x\rangle\rangle = 0$, and $\langle (x-\langle x\rangle)^{\,2}\rangle = \sigma_x^2$. The final term on the right-hand side of the previous equation can be neglected when the spatial extent of the particle wavefunction, σ_x, is much smaller than the variation length-scale of the potential. In this case, Equations ([e3.42]) and ([e3.43]) reduce to

$$m\,\frac{d\langle x\rangle}{dt} = \langle p\rangle,$$
$$\frac{d\langle p\rangle}{dt} = -\frac{dV(\langle x\rangle)}{d\langle x\rangle}.$$

These equations are exactly equivalent to the equations of classical mechanics, with $\langle x\rangle$ playing the role of the particle displacement. Of course, if the spatial extent of the wavefunction is negligible then a measurement of x is almost certain to yield a result that lies very close to $\langle x\rangle$. Hence, we conclude that quantum mechanics corresponds to classical mechanics in the limit that the spatial extent of the wavefunction (which is typically of order the de Boglie wavelength) is negligible. This is an important result, because we know that classical mechanics gives the correct answer in this limit.

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3.5: Operators

An operator, O (say), is a mathematical entity that transforms one function into another: that is,

$$O(f(x)) \to g(x). \tag{3.5.1}$$

For instance, x is an operator, because $x\,f(x)$ is a different function to $f(x)$, and is fully specified once $f(x)$ is given. Furthermore, d/dx is also an operator, because $df(x)/dx$ is a different function to $f(x)$, and is fully specified once $f(x)$ is given. Now,

$$x\,\frac{df}{dx} \neq \frac{d}{dx}(x\,f)\,. \tag{3.5.2}$$

This can also be written

$$x\,\frac{d}{dx} \neq \frac{d}{dx}\,x, \tag{3.5.3}$$

where the operators are assumed to act on everything to their right, and a final $f(x)$ is understood [where $f(x)$ is a general function]. The previous expression illustrates an important point. Namely, in general, operators do not commute with one another. Of course, some operators do commute. For instance,

$$x\,x^{\,2} = x^{\,2}\,x. \tag{3.5.4}$$

Finally, an operator, O, is termed linear if

$$O(c\,f(x)) = c\,O(f(x)), \tag{3.5.5}$$

where f is a general function, and c a general complex number. All of the operators employed in quantum mechanics are linear.

Now, from Equations ([e3.22]) and ([e3.38]),

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

These expressions suggest a number of things. First, classical dynamical variables, such as x and p, are represented in quantum mechanics by linear operators that act on the wavefunction. Second, displacement is represented by the algebraic operator x, and momentum by the differential operator $-{\rm i}\,\hbar\,\partial/\partial x$: that is, \[\label{e3.54} p \equiv -{\rm i}\,\hbar\,\frac{\partial}{\partial x}.\]

Finally, the expectation value of some dynamical variable represented by the operator $O(x)$ is simply

$$\langle O\rangle = \int_{-\infty}^{\infty}\psi^\ast(x,t)\,O(x)\,\psi(x,t)\,dx. \tag{3.5.6}$$

Clearly, if an operator is to represent a dynamical variable that has physical significance then its expectation value must be real. In other words, if the operator O represents a physical variable then we require that $\langle O\rangle = \langle O\rangle^\ast$, or

$$\int_{-\infty}^{\infty}\psi^\ast\,(O\,\psi)\,dx = \int_{-\infty}^{\infty}(O\,\psi)^\ast\,\psi\,dx, \tag{3.5.7}$$

where $O^\ast$ is the complex conjugate of O. An operator that satisfies the previous constraint is called an *Hermitian* operator. It is easily demonstrated that x and p are both Hermitian. The *Hermitian conjugate*, $O^\dagger$, of a general operator, O, is defined as follows:

$$\int_{-\infty}^{\infty}\psi^\ast\,(O\,\psi)\,dx = \int_{-\infty}^{\infty}(O^\dagger\,\psi)^\ast\,\psi\,dx. \tag{3.5.8}$$

The Hermitian conjugate of an Hermitian operator is the same as the operator itself: that is, $p^\dagger = p$. For a non-Hermitian operator, O (say), it is easily demonstrated that $(O^\dagger)^\dagger = O$, and that the operator $O + O^\dagger$ is Hermitian. Finally, if A and B are two operators, then $(A\,B)^\dagger = B^\dagger\,A^\dagger$.

Suppose that we wish to find the operator that corresponds to the classical dynamical variable $x\,p$. In classical mechanics, there is no difference between $x\,p$ and $p\,x$. However, in quantum mechanics, we have already seen that $x\,p \neq p\,x$. So, should we choose

$x\,p$ or $p\,x$? Actually, neither of these combinations is Hermitian. However, $(1/2)\,[x\,p+(x\,p)^\dagger]$ is Hermitian. Moreover, $(1/2)\,[x\,p+(x\,p)^\dagger]=(1/2)\,(x\,p+p^\dagger\,x^\dagger)=(1/2)\,(x\,p+p\,x)$, which neatly resolves our problem of the order in which to place x and p.

It is a reasonable guess that the operator corresponding to energy (which is called the Hamiltonian, and conventionally denoted H) takes the form

$$H\equiv\frac{p^{\,2}}{2\,m}+V(x). \tag{3.5.9}$$

Note that H is Hermitian. Now, it follows from Equation ([e3.54]) that

$$H\equiv-\frac{\hbar^{\,2}}{2\,m}\,\frac{\partial^{\,2}}{\partial x^{\,2}}+V(x). \tag{3.5.10}$$

However, according to Schrödinger's equation, ([e3.1]), we have

$$-\frac{\hbar^{\,2}}{2\,m}\,\frac{\partial^{\,2}}{\partial x^{\,2}}+V(x)={\rm i}\,\hbar\,\frac{\partial}{\partial t}, \tag{3.5.11}$$

so

$$H\equiv{\rm i}\,\hbar\,\frac{\partial}{\partial t}. \tag{3.5.12}$$

Thus, the time-dependent Schrödinger equation can be written

$${\rm i}\,\hbar\,\frac{\partial\psi}{\partial t}=H\,\psi. \tag{3.5.13}$$

Finally, if $O(x,p,E)$ is a classical dynamical variable that is a function of displacement, momentum, and energy then a reasonable guess for the corresponding operator in quantum mechanics is $(1/2)\,[O(x,p,H)+O^\dagger(x,p,H)]$, where $p=-{\rm i}\,\hbar\,\partial/\partial x$, and $H={\rm i}\,\hbar\,\partial/\partial t$.

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3.6: Momentum Representation

Fourier's theorem (see Section [s2.9]), applied to one-dimensional wavefunctions, yields

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\bar{\psi}(k,t)\,\mathrm{e}^{+\mathrm{i}\,k\,x}\,dk,$$
$$\bar{\psi}(k,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\psi(x,t)\,\mathrm{e}^{-\mathrm{i}\,k\,x}\,dx,$$

where k represents wavenumber. However, $p = \hbar\,k$. Hence, we can also write

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\,\hbar}}\int_{-\infty}^{\infty}\phi(p,t)\,\mathrm{e}^{+\mathrm{i}\,p\,x/\hbar}\,dp,$$
$$\phi(p,t) = \frac{1}{\sqrt{2\pi\,\hbar}}\int_{-\infty}^{\infty}\psi(x,t)\,\mathrm{e}^{-\mathrm{i}\,p\,x/\hbar}\,dx,$$

where $\phi(p,t) = \bar{\psi}(k,t)/\sqrt{\hbar}$ is the momentum-space equivalent to the real-space wavefunction $\psi(x,t)$.

At this stage, it is convenient to introduce a useful function called the *Dirac delta-function* . This function, denoted $\delta(x)$, was first devised by Paul Dirac , and has the following rather unusual properties: $\delta(x)$ is zero for $x \neq 0$, and is infinite at $x = 0$. However, the singularity at $x = 0$ is such that

$$\int_{-\infty}^{\infty}\delta(x)\,dx = 1. \tag{3.6.1}$$

The delta-function is an example of what is known as a *generalized function*: that is, its value is not well defined at all x, but its integral is well defined. Consider the integral

$$\int_{-\infty}^{\infty}f(x)\,\delta(x)\,dx. \tag{3.6.2}$$

Because $\delta(x)$ is only non-zero infinitesimally close to $x = 0$, we can safely replace $f(x)$ by $f(0)$ in the previous integral (assuming $f(x)$ is well behaved at $x = 0$), to give

$$\int_{-\infty}^{\infty}f(x)\,\delta(x)\,dx = f(0)\int_{-\infty}^{\infty}\delta(x)\,dx = f(0), \tag{3.6.3}$$

where use has been made of Equation ([e3.64a]). A simple generalization of this result yields

$$\int_{-\infty}^{\infty}f(x)\,\delta(x-x_0)\,dx = f(x_0), \tag{3.6.4}$$

which can also be thought of as an alternative definition of a delta-function.

Suppose that $\psi(x) = \delta(x-x_0)$. It follows from Equations ([e3.65]) and ([e3.69]) that

$$\phi(p) = \frac{\mathrm{e}^{-ipx_0/\hbar}}{\sqrt{2\pi\hbar}} \tag{3.6.5}$$

Hence, Equation ([e3.64]) yields the important result

$$\delta(x-x_0) = \frac{1}{2\pi\,\hbar}\int_{-\infty}^{\infty}\mathrm{e}^{+\mathrm{i}\,p\,(x-x_0)/\hbar}\,dp. \tag{3.6.6}$$

Similarly,

$$\delta(p-p_0) = \frac{1}{2\pi\,\hbar}\int_{-\infty}^{\infty}\mathrm{e}^{+\mathrm{i}\,(p-p_0)\,x/\hbar}\,dx. \tag{3.6.7}$$

It turns out that we can just as easily formulate quantum mechanics using the momentum-space wavefunction, $\phi(p,t)$, as the real-space wavefunction, $\psi(x,t)$. The former scheme is known as the *momentum representation* of quantum mechanics. In the momentum representation, wavefunctions are the Fourier transforms of the equivalent real-space wavefunctions, and dynamical variables are represented by different operators. Furthermore, by analogy with Equation ([e3.55]), the expectation value of some operator $O(p)$ takes the form

$$\langle O\rangle = \int_{-\infty}^{\infty}\phi^*(p,t)\,O(p)\,\phi(p,t)\,dp. \tag{3.6.8}$$

Consider momentum. We can write

$$\begin{aligned}\langle p\rangle &= \int_{-\infty}^{\infty}\psi^*(x,t)\left(-\mathrm{i}\,\hbar\,\frac{\partial}{\partial x}\right)\psi(x,t)\,dx\\ &= \frac{1}{2\pi\,\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\phi^*(p',t)\,\phi(p,t)\,p\,\mathrm{e}^{+\mathrm{i}\,(p-p')\,x/\hbar}\,dx\,dp\,dp',\end{aligned}$$

where use has been made of Equation ([e3.64]). However, it follows from Equation ([e3.72]) that

$$\langle p\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\phi^*(p',t)\,\phi(p,t)\,p\,\delta(p-p')\,dp\,dp'. \tag{3.6.9}$$

Hence, using Equation ([e3.69]), we obtain

$$\langle p\rangle = \int_{-\infty}^{\infty}\phi^*(p,t)\,p\,\phi(p,t)\,dp = \int_{-\infty}^{\infty}p\,|\phi|^{\,2}\,dp. \tag{3.6.10}$$

Evidently, momentum is represented by the operator p in the momentum representation. The previous expression also strongly suggests [by comparison with Equation ([e3.22])] that $|\phi(p,t)|^{\,2}$ can be interpreted as the probability density of a measurement of momentum yielding the value p at time t. It follows that $\phi(p,t)$ must satisfy an analogous normalization condition to Equation ([e3.4]): that is,

$$\int_{-\infty}^{\infty}|\phi(p,t)|^{\,2}\,dp = 1. \tag{3.6.11}$$

Consider displacement. We can write

$$\begin{aligned}\langle x\rangle &= \int_{-\infty}^{\infty}\psi^*(x,t)\,x\,\psi(x,t)\,dx\\ &= \frac{1}{2\pi\,\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\phi^*(p',t)\,\phi(p,t)\left(-\mathrm{i}\,\hbar\,\frac{\partial}{\partial p}\right)\mathrm{e}^{+\mathrm{i}\,(p-p')\,x/\hbar}\,dx\,dp\,dp'.\end{aligned}$$

Integration by parts yields

$$\langle x\rangle = \frac{1}{2\pi\,\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\phi^*(p',t)\,\mathrm{e}^{+\mathrm{i}\,(p-p')\,x/\hbar}\left(\mathrm{i}\,\hbar\,\frac{\partial}{\partial p}\right)\phi(p,t)\,dx\,dp\,dp'. \tag{3.6.12}$$

Hence, making use of Equations ([e3.72]) and ([e3.69]), we obtain

$$\langle x\rangle = \frac{1}{2\pi\,\hbar}\int_{-\infty}^{\infty}\phi^*(p)\left(\mathrm{i}\,\hbar\,\frac{\partial}{\partial p}\right)\phi(p)\,dp. \tag{3.6.13}$$

Evidently, displacement is represented by the operator

$$x \equiv \mathrm{i}\,\hbar\,\frac{\partial}{\partial p} \tag{3.6.14}$$

in the momentum representation.

Finally, let us consider the normalization of the momentum-space wavefunction $\phi(p,t)$. We have

$$\int_{-\infty}^{\infty}\psi^*(x,t)\,\psi(x,t)\,dx = \frac{1}{2\pi\,\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\phi^*(p',t)\,\phi(p,t)\,\mathrm{e}^{+\mathrm{i}\,(p-p')\,x/\hbar}\,dx\,dp\,dp'. \tag{3.6.15}$$

Thus, it follows from Equations ([e3.69]) and ([e3.72]) that

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx = \int_{-\infty}^{\infty} |\phi(p,t)|^2 \, dp. \tag{3.6.16}$$

Hence, if $\psi(x,t)$ is properly normalized [see Equation ([e3.4])] then $\phi(p,t)$, as defined in Equation ([e3.65]), is also properly normalized [see Equation ([enormp])].

The existence of the momentum representation illustrates an important point. Namely, there are many different, but entirely equivalent, ways of mathematically formulating quantum mechanics. For instance, it is also possible to represent wavefunctions as row and column vectors, and dynamical variables as matrices that act upon these vectors.

Contributors and Attributions

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3.7: Heisenberg's Uncertainty Principle

Consider a real-space Hermitian operator, $O(x)$. A straightforward generalization of Equation ([e3.55a]) yields

$$\int_{-\infty}^{\infty}\psi_1^*\,(O\,\psi_2)\,dx = \int_{-\infty}^{\infty}(O\,\psi_1)^*\,\psi_2\,dx, \tag{3.7.1}$$

where $\psi_1(x)$ and $\psi_2(x)$ are general functions.

Let $f=(A-\langle A\rangle)\,\psi$, where $A(x)$ is an Hermitian operator, and $\psi(x)$ a general wavefunction. We have

$$\int_{-\infty}^{\infty}|f|^{\,2}\,dx = \int_{-\infty}^{\infty}f^*\,f\,dx = \int_{-\infty}^{\infty}[(A-\langle A\rangle)\,\psi]^{\,*}\,[(A-\langle A\rangle)\,\psi]\,dx. \tag{3.7.2}$$

Making use of Equation ([e3.84]), we obtain

$$\int_{-\infty}^{\infty}|f|^{\,2}\,dx = \int_{-\infty}^{\infty}\psi^*\,(A-\langle A\rangle)^{\,2}\,\psi\,dx = \sigma_A^{\,2}, \tag{3.7.3}$$

where $\sigma_A^{\,2}$ is the variance of A. [See Equation ([e3.24a]).] q4 Similarly, if $g=(B-\langle B\rangle)\,\psi$, where B is a second Hermitian operator, then

$$\int_{-\infty}^{\infty}|g|^{\,2}\,dx = \sigma_B^{\,2}, \tag{3.7.4}$$

Now, there is a standard result in mathematics, known as the *Schwartz inequality* , which states that

$$\left|\int_a^b f^*(x)\,g(x)\,dx\right|^{\,2} \leq \int_a^b|f(x)|^{\,2}\,dx\,\int_a^b|g(x)|^{\,2}\,dx, \tag{3.7.5}$$

where f and g are two general functions. Furthermore, if z is a complex number then

$$|z|^{\,2} = [\mathrm{Re}(z)]^{\,2}+[\mathrm{Im}(z)]^{\,2} \geq [\mathrm{Im}(z)]^{\,2} = \left[\frac{1}{2\,\mathrm{i}}\,(z-z^*)\right]^{\,2}. \tag{3.7.6}$$

Hence, if $z=\int_{-\infty}^{\infty}f^*\,g\,dx$ then Equations ([e3.86])–([e3.89]) yield

$$\sigma_A^{\,2}\,\sigma_B^{\,2} \geq \left[\frac{1}{2\,\mathrm{i}}\,(z-z^*)\right]^{\,2}. \tag{3.7.7}$$

However,

$$z = \int_{-\infty}^{\infty}[(A-\langle A\rangle)\,\psi]^{\,*}\,[(B-\langle B\rangle)\,\psi]\,dx = \int_{-\infty}^{\infty}\psi^*\,(A-\langle A\rangle)\,(B-\langle B\rangle)\,\psi\,dx, \tag{3.7.8}$$

where use has been made of Equation ([e3.84]). The previous equation reduces to

$$z = \int_{-\infty}^{\infty}\psi^*\,A\,B\,\psi\,dx - \langle A\rangle\,\langle B\rangle. \tag{3.7.9}$$

Furthermore, it is easily demonstrated that

$$z^* = \int_{-\infty}^{\infty}\psi^*\,B\,A\,\psi\,dx - \langle A\rangle\,\langle B\rangle. \tag{3.7.10}$$

Hence, Equation ([e3.90]) gives

$$\sigma_A^{\,2}\,\sigma_B^{\,2} \geq \left(\frac{1}{2\,\mathrm{i}}\langle[A,B]\rangle\right)^{\,2}, \tag{3.7.11}$$

where

$$[A,B] \equiv A\,B - B\,A. \tag{3.7.12}$$

Equation ([e3.94]) is the general form of *Heisenberg's uncertainty principle* in quantum mechanics. It states that if two dynamical variables are represented by the two Hermitian operators A and B, and these operators do not commute (i.e., $A\,B \neq B\,A$), then it is impossible to simultaneously (exactly) measure the two variables. Instead, the product of the variances in the measurements is always greater than some critical value, which depends on the extent to which the two operators do not commute.

For instance, displacement and momentum are represented (in real-space) by the operators x and $p \equiv -\mathrm{i}\,\hbar\,\partial/\partial x$, respectively. Now, it is easily demonstrated that

$$[x,p] = \mathrm{i}\,\hbar. \tag{3.7.13}$$

Thus,

$$\sigma_x\,\sigma_p \geq \frac{\hbar}{2}, \tag{3.7.14}$$

which can be recognized as the standard displacement-momentum uncertainty principle (see Section [sun]). It turns out that the minimum uncertainty (i.e., $\sigma_x\,\sigma_p = \hbar/2$) is only achieved by Gaussian wave-packets (see Section [s2.9]): that is,

$$\psi(x) = \frac{\mathrm{e}^{+ip_0 x/\hbar}}{\left(2\pi\sigma_x^2\right)^{1/4}}\,\mathrm{e}^{-(x-x_0)^2/4\sigma_x^2} \tag{3.7.15}$$

$$\phi(p) = \frac{\mathrm{e}^{-\mathrm{i}p x_0/\hbar}}{\left(2\pi\sigma_p^2\right)^{1/4}}\,\mathrm{e}^{-(p-p_0)^2/4\sigma_p^2} \tag{3.7.16}$$

where $\phi(p)$ is the momentum-space equivalent of $\psi(x)$.

Energy and time are represented by the operators $H \equiv \mathrm{i}\,\hbar\,\partial/\partial t$ and t, respectively. These operators do not commute, indicating that energy and time cannot be measured simultaneously. In fact,

$$[H,t] = \mathrm{i}\,\hbar, \tag{3.7.17}$$

so

$$\sigma_E\,\sigma_t \geq \frac{\hbar}{2}. \tag{3.7.18}$$

This can be written, somewhat less exactly, as

$\Delta E \Delta t \gtrsim \hbar$ are the uncertainties in energy and time, respectively. The previous expression is generally known as the *energy-time uncertainty principle*.

For instance, suppose that a particle passes some fixed point on the x-axis. Because the particle is, in reality, an extended wave-packet, it takes a certain amount of time, $\varDelta t$, for the particle to pass. Thus, there is an uncertainty, $\varDelta t$, in the arrival time of the particle. Moreover, because $E = \hbar\,\omega$, the only wavefunctions that have unique energies are those with unique frequencies: that is, plane-waves. Because a wave-packet of finite extent is made up of a combination of plane-waves of different wavenumbers, and, hence, different frequencies, there will be an uncertainty $\varDelta E$ in the particle's energy that is proportional to the range of frequencies of the plane-waves making up the wave-packet. The more compact the wave-packet (and, hence, the smaller $\varDelta t$), the larger the range of frequencies of the constituent plane-waves (and, hence, the large $\varDelta E$), and vice versa.

To be more exact, if $\psi(t)$ is the wavefunction measured at the fixed point as a function of time then we can write

$$\psi(t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\chi(E)\mathrm{e}^{-iEt/\hbar}\,dE \tag{3.7.19}$$

In other words, we can express $\psi(t)$ as a linear combination of plane-waves of definite energy E. Here, $\chi(E)$ is the complex amplitude of plane-waves of energy E in this combination.

By Fourier's theorem, we also have

$$\chi(E) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(t)\mathrm{e}^{+iEt/\hbar}\,dt \tag{3.7.20}$$

For instance, if $\psi(t)$ is a Gaussian then it is easily shown that $\chi(E)$ is also a Gaussian: that is,

$$\psi(t) = \frac{\mathrm{e}^{-i E_0 t/\hbar}}{\left(2\pi\sigma_t^2\right)^{1/4}} \mathrm{e}^{-(t-t_0)^2/4\sigma_t^2} \tag{3.7.21}$$

$$\chi(E) = \frac{\mathrm{e}^{+i E t_0/\hbar}}{\left(2\pi\sigma_E^2\right)^{1/4}} \mathrm{e}^{-(E-E_0)^2/4\sigma_E^2} \tag{3.7.22}$$

where $\sigma_E\,\sigma_t = \hbar/2$. As before, Gaussian wave-packets satisfy the minimum uncertainty principle $\sigma_E\,\sigma_t = \hbar/2$. Conversely, non-Gaussian wave-packets are characterized by $\sigma_E\,\sigma_t > \hbar/2$.

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3.8: Eigenstates and Eigenvalues

Consider a general real-space operator, $A(x)$. When this operator acts on a general wavefunction $\psi(x)$ the result is usually a wavefunction with a completely different shape. However, there are certain special wavefunctions which are such that when A acts on them the result is just a multiple of the original wavefunction. These special wavefunctions are called *eigenstates*, and the multiples are called *eigenvalues*. Thus, if

$$A\,\psi_a(x) = a\,\psi_a(x), \tag{3.8.1}$$

where a is a complex number, then ψ_a is called an eigenstate of A corresponding to the eigenvalue a.

Suppose that A is an Hermitian operator corresponding to some physical dynamical variable. Consider a particle whose wavefunction is ψ_a. The expectation of value A in this state is simply [see Equation ([e3.55])]

$$\langle A\rangle = \int_{-\infty}^{\infty}\psi_a^\ast\,A\,\psi_a\,dx = a\int_{-\infty}^{\infty}\psi_a^\ast\,\psi_a\,dx = a, \tag{3.8.2}$$

where use has been made of Equation ([e3.107]) and the normalization condition ([e3.4]). Moreover,

$$\langle A^2\rangle = \int_{-\infty}^{\infty}\psi_a^\ast\,A^2\,\psi_a\,dx = a\int_{-\infty}^{\infty}\psi_a^\ast\,A\,\psi_a\,dx = a^{\,2}\int_{-\infty}^{\infty}\psi_a^\ast\,\psi_a\,dx = a^{\,2}, \tag{3.8.3}$$

so the variance of A is [cf., Equation ([e3.24a])]

$$\sigma_A^{\,2} = \langle A^2\rangle - \langle A\rangle^2 = a^{\,2} - a^{\,2} = 0. \tag{3.8.4}$$

The fact that the variance is zero implies that every measurement of A is bound to yield the same result: namely, a. Thus, the eigenstate ψ_a is a state that is associated with a unique value of the dynamical variable corresponding to A. This unique value is simply the associated eigenvalue.

It is easily demonstrated that the eigenvalues of an Hermitian operator are all real. Recall [from Equation ([e3.84])] that an Hermitian operator satisfies

$$\int_{-\infty}^{\infty}\psi_1^\ast\,(A\,\psi_2)\,dx = \int_{-\infty}^{\infty}(A\,\psi_1)^\ast\,\psi_2\,dx. \tag{3.8.5}$$

Hence, if $\psi_1 = \psi_2 = \psi_a$ then

$$\int_{-\infty}^{\infty}\psi_a^\ast\,(A\,\psi_a)\,dx = \int_{-\infty}^{\infty}(A\,\psi_a)^\ast\,\psi_a\,dx, \tag{3.8.6}$$

which reduces to [see Equation ([e3.107])]

$$a = a^\ast, \tag{3.8.7}$$

assuming that ψ_a is properly normalized.

Two wavefunctions, $\psi_1(x)$ and $\psi_2(x)$, are said to be *orthogonal* if

$$\int_{-\infty}^{\infty}\psi_1^\ast\,\psi_2\,dx = 0. \tag{3.8.8}$$

Consider two eigenstates of A, ψ_a and $\psi_{a'}$, which correspond to the two different eigenvalues a and a', respectively. Thus,

$$A\,\psi_a = a\,\psi_a,$$
$$A\,\psi_{a'} = a'\,\psi_{a'}.$$

Multiplying the complex conjugate of the first equation by $\psi_{a'}$, and the second equation by $\psi_a^\ast$, and then integrating over all x, we obtain

$$\int_{-\infty}^{\infty}(A\,\psi_a)^*\,\psi_{a'}\,dx = a\int_{-\infty}^{\infty}\psi_a^*\,\psi_{a'}\,dx,$$

$$\int_{-\infty}^{\infty}\psi_a^*\,(A\,\psi_{a'})\,dx = a'\int_{-\infty}^{\infty}\psi_a^*\,\psi_{a'}\,dx.$$

However, from Equation ([e3.111]), the left-hand sides of the previous two equations are equal. Hence, we can write

$$(a-a')\int_{-\infty}^{\infty}\psi_a^*\,\psi_{a'}\,dx = 0. \tag{3.8.9}$$

By assumption, $a \neq a'$, yielding

$$\int_{-\infty}^{\infty}\psi_a^*\,\psi_{a'}\,dx = 0. \tag{3.8.10}$$

In other words, eigenstates of an Hermitian operator corresponding to different eigenvalues are automatically orthogonal.

Consider two eigenstates of A, ψ_a and ψ_a', that correspond to the same eigenvalue, a. Such eigenstates are termed *degenerate*. The previous proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that any linear combination of ψ_a and ψ_a' is also an eigenstate of A corresponding to the eigenvalue a. Thus, even if ψ_a and ψ_a' are not orthogonal, we can always choose two linear combinations of these eigenstates that are orthogonal. For instance, if ψ_a and ψ_a' are properly normalized, and

$$\int_{-\infty}^{\infty}\psi_a^*\,\psi_a'\,dx = c, \tag{3.8.11}$$

then it is easily demonstrated that

$$\psi_a'' = \frac{|c|}{\sqrt{1-|c|^2}}\left(\psi_a - c^{-1}\,\psi_a'\right) \tag{3.8.12}$$

is a properly normalized eigenstate of A, corresponding to the eigenvalue a, that is orthogonal to ψ_a. It is straightforward to generalize the previous argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of an Hermitian operator are, or can be chosen to be, mutually orthogonal.

It is also possible to demonstrate that the eigenstates of an Hermitian operator form a complete set : that is, any general wavefunction can be written as a linear combination of these eigenstates. However, the proof is quite difficult, and we shall not attempt it here.

In summary, given an Hermitian operator A, any general wavefunction, $\psi(x)$, can be written

$$\psi = \sum_i c_i\,\psi_i, \tag{3.8.13}$$

where the c_i are complex weights, and the ψ_i are the properly normalized (and mutually orthogonal) eigenstates of A: that is,

$$A\,\psi_i = a_i\,\psi_i, \tag{3.8.14}$$

where a_i is the eigenvalue corresponding to the eigenstate ψ_i, and

$$\int_{-\infty}^{\infty}\psi_i^*\,\psi_j\,dx = \delta_{ij}. \tag{3.8.15}$$

Here, δ_{ij} is called the *Kronecker delta-function* , and takes the value unity when its two indices are equal, and zero otherwise.

It follows from Equations ([e3.123]) and ([e3.125]) that

$$c_i = \int_{-\infty}^{\infty}\psi_i^*\,\psi\,dx. \tag{3.8.16}$$

Thus, the expansion coefficients in Equation ([e3.123]) are easily determined, given the wavefunction ψ and the eigenstates ψ_i. Moreover, if ψ is a properly normalized wavefunction then Equations ([e3.123]) and ([e3.125]) yield

$$\sum_i |c_i|^2 = 1. \tag{3.8.17}$$

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3.9: Measurement

Suppose that A is an Hermitian operator corresponding to some dynamical variable. By analogy with the discussion in Section [scoll], we expect that if a measurement of A yields the result a then the act of measurement will cause the wavefunction to collapse to a state in which a measurement of A is bound to give the result a. What sort of wavefunction, ψ, is such that a measurement of A is bound to yield a certain result, a? Well, expressing ψ as a linear combination of the eigenstates of A, we have

$$\psi=\sum_i c_i\,\psi_i, \tag{3.9.1}$$

where ψ_i is an eigenstate of A corresponding to the eigenvalue a_i. If a measurement of A is bound to yield the result a then

$$\langle A\rangle = a, \tag{3.9.2}$$

and

$$\sigma_A^{\,2} = \langle A^2\rangle-\langle A\rangle = 0. \tag{3.9.3}$$

Now, it is easily seen that

$$\langle A\rangle = \sum_i |c_i|^{\,2}\,a_i,$$
$$\langle A^2\rangle = \sum_i |c_i|^{\,2}\,a_i^{\,2}.$$

Thus, Equation ([e4.130]) gives

$$\sum_i a_i^{\,2}\,|c_i|^{\,2}-\left(\sum_i a_i\,|c_i|^{\,2}\right)^2 = 0. \tag{3.9.4}$$

Furthermore, the normalization condition yields

$$\sum_i |c_i|^{\,2} = 1. \tag{3.9.5}$$

For instance, suppose that there are only two eigenstates. The previous two equations then reduce to $|c_1|^{\,2}=x$, and $|c_2|^{\,2}=1-x$, where $0\leq x\leq 1$, and

$$(a_1-a_2)^2\,x\,(1-x)=0. \tag{3.9.6}$$

The only solutions are $x=0$ and $x=1$. This result can easily be generalized to the case where there are more than two eigenstates. It follows that a state associated with a definite value of A is one in which one of the $|c_i|^{\,2}$ is unity, and all of the others are zero. In other words, the only states associated with definite values of A are the eigenstates of A. It immediately follows that the result of a measurement of A must be one of the eigenvalues of A. Moreover, if a general wavefunction is expanded as a linear combination of the eigenstates of A, like in Equation ([e4.128]), then it is clear from Equation ([e4.131]), and the general definition of a mean, that the probability of a measurement of A yielding the eigenvalue a_i is simply $|c_i|^{\,2}$, where c_i is the coefficient in front of the ith eigenstate in the expansion. Note, from Equation ([e4.134]), that these probabilities are properly normalized: that is, the probability of a measurement of A resulting in any possible answer is unity. Finally, if a measurement of A results in the eigenvalue a_i then immediately after the measurement the system will be left in the eigenstate corresponding to a_i.

Consider two physical dynamical variables represented by the two Hermitian operators A and B. Under what circumstances is it possible to simultaneously measure these two variables (exactly)? Well, the possible results of measurements of A and B are the eigenvalues of A and B, respectively. Thus, to simultaneously measure A and B (exactly) there must exist states which are simultaneous eigenstates of A and B. In fact, in order for A and B to be simultaneously measurable under all circumstances, we need all of the eigenstates of A to also be eigenstates of B, and vice versa, so that all states associated with unique values of A are also associated with unique values of B, and vice versa.

Now, we have already seen, in Section 1.8, that if A and B do not commute (i.e., if $A\,B\neq B\,A$) then they cannot be simultaneously measured. This suggests that the condition for simultaneous measurement is that A and B should commute.

Suppose that this is the case, and that the ψ_i and a_i are the normalized eigenstates and eigenvalues of A, respectively. It follows that

$$(A\,B - B\,A)\,\psi_i = (A\,B - B\,a_i)\,\psi_i = (A - a_i)\,B\,\psi_i = 0, \tag{3.9.7}$$

or

$$A\,(B\,\psi_i) = a_i\,(B\,\psi_i). \tag{3.9.8}$$

Thus, $B\,\psi_i$ is an eigenstate of A corresponding to the eigenvalue a_i (though not necessarily a normalized one). In other words, $B\,\psi_i \propto \psi_i$, or

$$B\,\psi_i = b_i\,\psi_i, \tag{3.9.9}$$

where b_i is a constant of proportionality. Hence, ψ_i is an eigenstate of B, and, thus, a simultaneous eigenstate of A and B. We conclude that if A and B commute then they possess simultaneous eigenstates, and are thus simultaneously measurable (exactly).

Continuous Eigenvalues

In the previous two sections, it was tacitly assumed that we were dealing with operators possessing discrete eigenvalues and square-integrable eigenstates. Unfortunately, some operators—most notably, x and p—possess eigenvalues that lie in a continuous range and non-square-integrable eigenstates (in fact, these two properties go hand in hand). Let us, therefore, investigate the eigenstates and eigenvalues of the displacement and momentum operators.

Let $\psi_x(x,x')$ be the eigenstate of x corresponding to the eigenvalue x'. It follows that

$$x\,\psi_x(x,x') = x'\,\psi_x(x,x') \tag{3.9.10}$$

for all x. Consider the Dirac delta-function $\delta(x-x')$. We can write

$$x\,\delta(x-x') = x'\,\delta(x-x'), \tag{3.9.11}$$

because $\delta(x-x')$ is only non-zero infinitesimally close to $x = x'$. Evidently, $\psi_x(x,x')$ is proportional to $\delta(x-x')$. Let us make the constant of proportionality unity, so that

$$\psi_x(x,x') = \delta(x-x'). \tag{3.9.12}$$

It is easily demonstrated that

$$\int_{-\infty}^{\infty}\delta(x-x')\,\delta(x-x'')\,dx = \delta(x'-x''). \tag{3.9.13}$$

Hence, $\psi_x(x,x')$ satisfies the orthonormality condition

$$\int_{-\infty}^{\infty}\psi_x^\ast(x,x')\,\psi_x(x,x'')\,dx = \delta(x'-x''). \tag{3.9.14}$$

This condition is analogous to the orthonormality condition ([e3.125]) satisfied by square-integrable eigenstates. Now, by definition, $\delta(x-x')$ satisfies

$$\int_{-\infty}^{\infty}f(x)\,\delta(x-x')\,dx = f(x'), \tag{3.9.15}$$

where $f(x)$ is a general function. We can thus write

$$\psi(x) = \int_{-\infty}^{\infty}c(x')\,\psi_x(x,x')\,dx', \tag{3.9.16}$$

where $c(x') = \psi(x')$, or

$$c(x') = \int_{-\infty}^{\infty}\psi_x^\ast(x,x')\,\psi(x)\,dx. \tag{3.9.17}$$

In other words, we can expand a general wavefunction $\psi(x)$ as a linear combination of the eigenstates, $\psi_x(x,x')$, of the displacement operator. Equations ([e4.144]) and ([e4.145]) are analogous to Equations ([e3.123]) and ([e3.126]), respectively, for square-integrable eigenstates. Finally, by analogy with the results in Section 1.9, the probability density of a measurement of x yielding the value x' is $|c(x')|^2$, which is equivalent to the standard result $|\psi(x')|^2$. Moreover, these probabilities are properly normalized provided $\psi(x)$ is properly normalized [cf., Equation ([e3.127])]: that is,

$$\int_{-\infty}^{\infty} |c(x')|^2\, dx' = \int_{-\infty}^{\infty} |\psi(x')|^2\, dx' = 1. \tag{3.9.18}$$

Finally, if a measurement of x yields the value x' then the system is left in the corresponding displacement eigenstate, $\psi_x(x, x')$, immediately after the measurement. That is, the wavefunction collapses to a "spike-function", $\delta(x - x')$, as discussed in Section [scoll].

Now, an eigenstate of the momentum operator $p \equiv -i\,\hbar\,\partial/\partial x$ corresponding to the eigenvalue p' satisfies

$$-i\,\hbar\,\frac{\partial\psi_p(x, p')}{\partial x} = p'\,\psi_p(x, p'). \tag{3.9.19}$$

It is evident that

$$\psi_p(x, p') \propto e^{+i\,p'\,x/\hbar}. \tag{3.9.20}$$

We require $\psi_p(x, p')$ to satisfy an analogous orthonormality condition to Equation ([e4.143]): that is,

$$\int_{-\infty}^{\infty} \psi_p^*(x, p')\,\psi_p(x, p'')\,dx = \delta(p' - p''). \tag{3.9.21}$$

Thus, it follows from Equation ([e3.72]) that the constant of proportionality in Equation ([e4.148]) should be $(2\pi\,\hbar)^{-1/2}$: that is,

$$\psi_p(x, p') = \frac{e^{+i\,p'\,x/\hbar}}{(2\pi\,\hbar)^{1/2}}. \tag{3.9.22}$$

Furthermore, according to Equations ([e3.64]) and ([e3.65]),

$$\psi(x) = \int_{-\infty}^{\infty} c(p')\,\psi_p(x, p')\,dp', \tag{3.9.23}$$

where $c(p') = \phi(p')$ [see Equation ([e3.65])], or

$$c(p') = \int_{-\infty}^{\infty} \psi_p^*(x, p')\,\psi(x)\,dx. \tag{3.9.24}$$

In other words, we can expand a general wavefunction $\psi(x)$ as a linear combination of the eigenstates, $\psi_p(x, p')$, of the momentum operator. Equations ([e4.152]) and ([e4.153]) are again analogous to Equations ([e3.123]) and ([e3.126]), respectively, for square-integrable eigenstates. Likewise, the probability density of a measurement of p yielding the result p' is $|c(p')|^2$, which is equivalent to the standard result $|\phi(p')|^2$. The probabilities are also properly normalized provided $\psi(x)$ is properly normalized [cf., Equation ([e3.83])]: that is,

$$\int_{-\infty}^{\infty} |c(p')|^2\, dp' = \int_{-\infty}^{\infty} |\phi(p')|^2\, dp' = \int_{-\infty}^{\infty} |\psi(x')|^2\, dx' = 1. \tag{3.9.25}$$

Finally, if a mesurement of p yields the value p' then the system is left in the corresponding momentum eigenstate, $\psi_p(x, p')$, immediately after the measurement.

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3.10: Stationary States

An eigenstate of the energy operator $H \equiv \mathrm{i}\,\hbar\,\partial/\partial t$ corresponding to the eigenvalue E_i satisfies

$$\mathrm{i}\,\hbar\,\frac{\partial\psi_E(x,t,E_i)}{\partial t} = E_i\,\psi_E(x,t,E_i). \tag{3.10.1}$$

It is evident that this equation can be solved by writing

$$\psi_E(x,t,E_i) = \psi_i(x)\,\mathrm{e}^{-\mathrm{i}\,E_i\,t/\hbar}, \tag{3.10.2}$$

where $\psi_i(x)$ is a properly normalized stationary (i.e., non-time-varying) wavefunction. The wavefunction $\psi_E(x,t,E_i)$ corresponds to a so-called *stationary state*, because the probability density $|\psi_E|^2$ is non-time-varying. Note that a stationary state is associated with a unique value for the energy. Substitution of the previous expression into Schrödinger's equation ([e3.1]) yields the equation satisfied by the stationary wavefunction:

$$\frac{\hbar^2}{2\,m}\,\frac{d^2\psi_i}{dx^2} = [V(x) - E_i]\,\psi_i. \tag{3.10.3}$$

This is known as the *time-independent Schrödinger equation*. More generally, this equation takes the form

$$H\,\psi_i = E_i\,\psi_i, \tag{3.10.4}$$

where H is assumed not to be an explicit function of t. Of course, the ψ_i satisfy the usual orthonormality condition:

$$\int_{-\infty}^{\infty}\psi_i^\ast\,\psi_j\,dx = \delta_{ij}. \tag{3.10.5}$$

Moreover, we can express a general wavefunction as a linear combination of energy eigenstates:

$$\psi(x,t) = \sum_i c_i\,\psi_i(x)\,\mathrm{e}^{-\mathrm{i}\,E_i\,t/\hbar}, \tag{3.10.6}$$

where

$$c_i = \int_{-\infty}^{\infty}\psi_i^\ast(x)\,\psi(x,0)\,dx. \tag{3.10.7}$$

Here, $|c_i|^2$ is the probability that a measurement of the energy will yield the eigenvalue E_i. Furthermore, immediately after such a measurement, the system is left in the corresponding energy eigenstate. The generalization of the previous results to the case where H has continuous eigenvalues is straightforward.

If a dynamical variable is represented by some Hermitian operator A that commutes with H (so that it has simultaneous eigenstates with H), and contains no specific time dependence, then it is evident from Equations ([e4.157]) and ([e4.158]) that the expectation value and variance of A are time independent. In this sense, the dynamical variable in question is a constant of the motion.

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3.11: Exercises

1. Monochromatic light with a wavelength of $6000Å$ passes through a fast shutter that opens for 10^{-9} sec. What is the subsequent spread in wavelengths of the no longer monochromatic light?
2. Calculate $\langle x\rangle$, $\langle x^{2}\rangle$, and σ_x, as well as $\langle p\rangle$, $\langle p^{2}\rangle$, and σ_p, for the normalized wavefunction
$$\psi(x) = \sqrt{\frac{2\,a^{3}}{\pi}}\,\frac{1}{x^{2}+a^{2}}. \tag{3.11.1}$$
Use these to find $\sigma_x\,\sigma_p$. Note that $\int_{-\infty}^{\infty}dx/(x^{2}+a^{2}) = \pi/a$.
3. Classically, if a particle is not observed then the probability of finding it in a one-dimensional box of length L, which extends from $x=0$ to $x=L$, is a constant $1/L$ per unit length. Show that the classical expectation value of x is $L/2$, the expectation value of x^{2} is $L^2/3$, and the standard deviation of x is $L/\sqrt{12}$.
4. Demonstrate that if a particle in a one-dimensional stationary state is bound then the expectation value of its momentum must be zero.
5. Suppose that $V(x)$ is complex. Obtain an expression for $\partial P(x,t)/\partial t$ and $d/dt\int P(x,t)\,dx$ from Schrödinger's equation. What does this tell us about a complex $V(x)$?
6. $\psi_1(x)$ and $\psi_2(x)$ are normalized eigenfunctions corresponding to the same eigenvalue. If
$$\int_{-\infty}^{\infty}\psi_1^{*}\,\psi_2\,dx = c, \tag{3.11.2}$$
where c is real, find normalized linear combinations of ψ_1 and ψ_2 that are orthogonal to (a) ψ_1, (b) $\psi_1+\psi_2$.
7. Demonstrate that $p = -i\,\hbar\,\partial/\partial x$ is an Hermitian operator. Find the Hermitian conjugate of $a = x + i\,p$.
8. An operator A, corresponding to a physical quantity α, has two normalized eigenfunctions $\psi_1(x)$ and $\psi_2(x)$, with eigenvalues a_1 and a_2. An operator B, corresponding to another physical quantity β, has normalized eigenfunctions $\phi_1(x)$ and $\phi_2(x)$, with eigenvalues b_1 and b_2. The eigenfunctions are related via
$$\begin{aligned}\psi_1 &= (2\,\phi_1 + 3\,\phi_2)\,/\sqrt{13},\\ \psi_2 &= (3\,\phi_1 - 2\,\phi_2)\,/\sqrt{13}.\end{aligned}$$
α is measured and the value a_1 is obtained. If β is then measured and then α again, show that the probability of obtaining a_1 a second time is $97/169$.
9. Demonstrate that an operator that commutes with the Hamiltonian, and contains no explicit time dependence, has an expectation value that is constant in time.
10. For a certain system, the operator corresponding to the physical quantity A does not commute with the Hamiltonian. It has eigenvalues a_1 and a_2, corresponding to properly normalized eigenfunctions
$$\begin{aligned}\phi_1 &= (u_1 + u_2)\,/\sqrt{2},\\ \phi_2 &= (u_1 - u_2)\,/\sqrt{2},\end{aligned}$$
where u_1 and u_2 are properly normalized eigenfunctions of the Hamiltonian with eigenvalues E_1 and E_2. If the system is in the state $\psi = \phi_1$ at time $t=0$, show that the expectation value of A at time t is
$$\langle A\rangle = \left(\frac{a_1+a_2}{2}\right) + \left(\frac{a_1-a_2}{2}\right)\cos\left(\frac{[E_1-E_2]\,t}{\hbar}\right). \tag{3.11.3}$$

Contributors and Attributions

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CHAPTER OVERVIEW

4: One-Dimensional Potentials

In this chapter, we shall investigate the interaction of a non-relativistic particle of mass m and energy E with various one-dimensional potentials, $V(x)$. Because we are searching for stationary solutions with unique energies, we can write the wavefunction in the form (see Section [sstat])

$$\psi(x,t) = \psi(x)\,e^{-i\,E\,t/\hbar}, \tag{4.1}$$

where $\psi(x)$ satisfies the time-independent Schrödinger equation:

$$\frac{d^{\,2}\psi}{dx^{\,2}} = \frac{2\,m}{\hbar^{\,2}}\,[V(x)-E]\,\psi. \tag{4.2}$$

In general, the solution, $\psi(x)$, to the previous equation must be finite, otherwise the probability density $|\psi|^{\,2}$ would become infinite (which is unphysical). Likewise, the solution must be continuous, otherwise the probability current ([eprobc]) would become infinite (which is also unphysical).

- 4.1: Infinite Potential Well
- 4.2: Square Potential Barrier
- 4.3: WKB Approximation
- 4.4: Cold Emission
- 4.5: Alpha Decay
- 4.6: Square Potential Well
- 4.7: Simple Harmonic Oscillator
- 4.E: One-Dimensional Potentials (Exercises)

4.1: Infinite Potential Well

Consider a particle of mass m and energy E moving in the following simple potential:

$$V(x)=\begin{cases}0 & \text{for } 0\leq x\leq a\\ \infty & \text{otherwise}\end{cases}. \tag{4.1.1}$$

It follows from Equation ([e5.2]) that if $d^2\psi/dx^2$ (and, hence, ψ) is to remain finite then ψ must go to zero in regions where the potential is infinite. Hence, $\psi=0$ in the regions $x\leq 0$ and $x\geq a$. Evidently, the problem is equivalent to that of a particle trapped in a one-dimensional box of length a. The boundary conditions on ψ in the region $0<x<a$ are

$$\psi(0)=\psi(a)=0. \tag{4.1.2}$$

Furthermore, it follows from Equation ([e5.2]) that ψ satisfies

$$\frac{d^2\psi}{dx^2}=-k^2\,\psi \tag{4.1.3}$$

in this region, where

$$k^2=\frac{2\,m\,E}{\hbar^2}. \tag{4.1.4}$$

Here, we are assuming that $E>0$. It is easily demonstrated that there are no solutions with $E<0$ which are capable of satisfying the boundary conditions ([e5.4]).

The solution to Equation ([e5.5]), subject to the boundary conditions ([e5.4]), is

$$\psi_n(x)=A_n\,\sin(k_n\,x), \tag{4.1.5}$$

where the A_n are arbitrary (real) constants, and

$$k_n=\frac{n\,\pi}{a}, \tag{4.1.6}$$

for $n=1,2,3,\cdots$. Now, it can be seen from Equations ([e5.6]) and ([e5.8]) that the energy E is only allowed to take certain discrete values: that is,

$$E_n=\frac{n^2\,\pi^2\,\hbar^2}{2\,m\,a^2}. \tag{4.1.7}$$

In other words, the eigenvalues of the energy operator are discrete. This is a general feature of bounded solutions: that is, solutions for which $|\psi|\rightarrow 0$ as $|x|\rightarrow\infty$. According to the discussion in Section [sstat], we expect the stationary eigenfunctions $\psi_n(x)$ to satisfy the orthonormality constraint

$$\int_0^a\psi_n(x)\,\psi_m(x)\,dx=\delta_{nm}. \tag{4.1.8}$$

It is easily demonstrated that this is the case, provided $A_n=\sqrt{2/a}$. Hence,

$$\psi_n(x)=\sqrt{\frac{2}{a}}\,\sin\!\left(n\,\pi\,\frac{x}{a}\right) \tag{4.1.9}$$

for $n=1,2,3,\cdots$.

Finally, again from Section [sstat], the general time-dependent solution can be written as a linear superposition of stationary solutions:

$$\psi(x,t)=\sum_{n=0,\infty}c_n\,\psi_n(x)\,\mathrm{e}^{-\mathrm{i}\,E_n\,t/\hbar}, \tag{4.1.10}$$

where

$$c_n=\int_0^a\psi_n(x)\,\psi(x,0)\,dx. \tag{4.1.11}$$

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