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1 Quantum Mechanics

According to quantum mechanics, at a given moment in time t, a system of particles is described by a probability amplitude function, a complex-valued function $\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots; t)$ of the (point) particle positions. The probability amplitude, which is also referred to as the wave function, has the significance that its absolute square $|\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots; t)|^2$ at the time in question determines the probability for the event: *particles at the specified positions*. The description in terms of the wave function is complete, i.e. the dynamics of the particles is determined by a differential equation that is first order in time. The rate of change in time of the wave function is specified in terms of the wave function at the time in question and an operator, the Schrödinger equation,

$$i\hbar \frac{\partial \psi(\mathbf{x}_1, \mathbf{x}_2, \ldots; t)}{\partial t} = \hat{H}\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots; t). \tag{1.1}$$

The linear operator $\hat{H}$ is called the Hamiltonian and is ultimately determined by experimental knowledge. The symbol $\hbar$ is a constant of nature, and as such also empirically determined. A “hat” has been introduced to signify that a quantity is an operator, i.e. it operates on a function, thereby turning it into another function, and standard notation for the result of an operator operating on a function has been used, $\hat{H}\psi(\mathbf{x}, t) \equiv (\hat{H}\psi)(\mathbf{x}, t)$. As an example, for a free particle of mass m, the Hamiltonian is the spatial differential operator

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{x}^2}, \tag{1.2}$$

where

$$\frac{\partial^2}{\partial \mathbf{x}^2} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{1.3}$$

Various notations for the Laplacian or Laplace operator will be employed:

$$\frac{\partial^2}{\partial \mathbf{x}^2} = \nabla_{\mathbf{x}}^2 = \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}} = \Delta_{\mathbf{x}}, \qquad \nabla_{\mathbf{x}} \equiv \frac{\partial}{\partial \mathbf{x}}. \tag{1.4}$$

In accordance with its probabilistic interpretation, at any moment in time, a proper wave function satisfies the normalization condition

$$\int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \, |\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N; t)|^2 = 1, \tag{1.5}$$

since the particles are assumed with certainty to be somewhere in space.

The free particle Schrödinger equation is analogous to a linear wave equation, and has the plane wave solutions

$$\psi_{\mathbf{k}}(\mathbf{x}, t) = A\, e^{i\mathbf{k}\cdot\mathbf{x} - i(\hbar\mathbf{k}^2/2m)t} \tag{1.6}$$

specified in terms of a wave vector **k**. These are unnormalized solutions from which normalized solutions, i.e. wave packets, can be obtained by superposing solutions of different wave vectors (as constructed in Chapter 2).

We could at this point get right on with solving the Schrödinger equation for the physical problems of interest, having the Hamiltonian handed to us through the knowledge obtained by our forefathers.[1] A reader inclined to such a "tell me like it is" approach can jump directly to Chapter 2 and use the Schrödinger equation to study quantum tunneling or to the following chapters studying the properties of metals and semiconductors. However, such an "I believe in the Schrödinger equation and all its consequences" approach does not present the quantum mechanical concepts in the most instructive way. Our intuition is built on our direct experience with large objects, and there is no way in which we can directly experience quantum behavior by our senses. In fact, quantum mechanics is at odds with common sense, and unintelligible in terms of the way the macroscopic world behaves as we perceive directly with our senses and understand by the empirically confirmed laws of classical physics. Foremost, we note that, in quantum mechanics, probability has entered in a fundamental way, i.e. *chance* is a feature of how the world works. In general, for given identical circumstances, it is impossible to predict what will happen in the future: quantum mechanics is probabilistic in nature. Quantum mechanics only provides the odds for different outcomes. We also observe the strange feature that, in contrast to any physical statement, a description in terms of *complex* numbers is demanded. For the interested reader, it is shown in Appendix A that the Schrödinger equation can be arrived at from a few basic principles.

1.1 Hamiltonian

Consider the Schrödinger equation for a single particle of mass m in a potential,

$$i\hbar \frac{\partial \psi(\mathbf{x}, t)}{\partial t} = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}^2} + V(\mathbf{x}, t) \right) \psi(\mathbf{x}, t). \tag{1.7}$$

The Hamiltonian, specifying the Schrödinger equation, then consists of the Laplacian and a multiplication operator, the space- and time-dependent potential, $V(\mathbf{x}, t)$, multiplying the wave function,

$$\hat{H} \equiv \hat{H}(t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}^2} + V(\mathbf{x}, t). \tag{1.8}$$

The real scalar potential, $V(\mathbf{x}, t)$, describes the fact that the particle is not free, but at different locations experiences different environments, which in addition can be changing

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[1] In the same vein, you have probably solved Newton's equation having the expression for the gravitational force being *handed* to you.

in time. As shown in Appendix A, the potential is the potential energy the particle has according to classical mechanics, and the gradient of the potential equals the classical force, $\mathbf{F}(\mathbf{x},t) = -\nabla V(\mathbf{x},t)$.

That normalization at one instant of time,

$$\int d\mathbf{x}\, |\psi(\mathbf{x},t)|^2 = 1, \tag{1.9}$$

guarantees it at all times is a defining property of a Hamiltonian. If a function is normalized, it vanishes spatially at infinity in order for the normalization integral to be finite. For arbitrary normalized functions $\psi(\mathbf{x},t)$ and $\phi(\mathbf{x},t)$, two partial integrations, where the boundary terms at infinity vanish, transfer the Laplacian to the other function,

$$\int d\mathbf{x}\, \phi^*(\mathbf{x}) \left(\frac{\partial^2 \psi(\mathbf{x})}{\partial \mathbf{x}^2} \right) = \int d\mathbf{x}\, \psi(\mathbf{x}) \left(\frac{\partial^2 \phi(\mathbf{x})}{\partial \mathbf{x}^2} \right)^*, \tag{1.10}$$

and we have used that differentiation and complex conjugation are interchangeable operations. Since the potential is a real function, it can trivially be moved as a factor under the complex conjugation, and the Hamiltonian, Eq. (1.8), is seen to have the property

$$\int d\mathbf{x}\, \phi^*(\mathbf{x},t)\, \hat{H}\psi(\mathbf{x},t) = \int d\mathbf{x}\, \psi(\mathbf{x},t)(\hat{H}\phi(\mathbf{x},t))^*. \tag{1.11}$$

An operator having the property (1.11) is called a hermitian operator.

If $\psi(\mathbf{x},t)$ is a solution of the Schrödinger equation (1.7), then it follows that

$$\begin{aligned} \frac{d}{dt} \int d\mathbf{x}\, |\psi(\mathbf{x},t)|^2 &= \int d\mathbf{x} \left(\psi^*(\mathbf{x},t)\, \frac{\partial \psi(\mathbf{x},t)}{\partial t} + \psi(\mathbf{x},t)\, \frac{\partial \psi^*(\mathbf{x},t)}{\partial t} \right) \\ &= \frac{1}{i\hbar} \left(\int d\mathbf{x}\, \psi^*(\mathbf{x},t)\, \hat{H}\psi(\mathbf{x},t) - \int d\mathbf{x}\, \psi(\mathbf{x},t)\hat{H}^*\psi^*(\mathbf{x},t) \right) \\ &= 0, \end{aligned} \tag{1.12}$$

the last equality following from Eq. (1.11).[2] Therefore, if at one instant the wave function is normalized, the Schrödinger dynamics guarantees that it stays normalized at all times as a consequence of the Hamiltonian being hermitian.

1.2 Free Propagator

The fundamental solution of a Schrödinger equation, the propagator of the particle, is the solution that specifies the time evolution of an arbitrary wave function. The expression for

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[2] For the considered case of a scalar potential, the Hamiltonian is real, $\hat{H}^* = \hat{H}$. For the case of a vector potential, this property is lost, but the Hamiltonian is still hermitian as discussed in Exercise A.2 on page 345.

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the propagator for a free particle will be obtained here by solving the Schrödinger equation. For this we employ Fourier transformation (discussed in Appendix C).

Consider first, for simplicity, the one-dimensional case. Given a wave function, $\psi(x,t)$, the Fourier-transformed function with respect to the spatial variable is

$$\psi(k,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, e^{-ixk}\psi(x,t) \tag{1.13}$$

and the inverse Fourier transformation is

$$\psi(x,t) = \int_{-\infty}^{\infty} dk\, e^{ikx}\psi(k,t). \tag{1.14}$$

Inserting the Fourier expansion of the wave function, Eq. (1.14), into the free particle Schrödinger equation,

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2}, \tag{1.15}$$

gives the equation

$$\int_{-\infty}^{\infty} dk\, e^{ixk}\left(i\hbar\frac{\partial\psi(k,t)}{\partial t} - \frac{\hbar^2k^2}{2m}\psi(k,t)\right) = 0. \tag{1.16}$$

The Fourier representation is unique (the Fourier transform of the zero function is the zero function), and the Fourier transform of the wave function thus satisfies the first-order differential equation

$$i\hbar\frac{\partial\psi(k,t)}{\partial t} = \frac{\hbar^2k^2}{2m}\psi(k,t). \tag{1.17}$$

The task of solving Eq. (1.17) thus amounts to finding the function that, when differentiated with respect to time once, gives back the same function multiplied by a number, here the imaginary number $-i\hbar k^2/2m$. This is the defining mark of the exponential function, and the solution of Eq. (1.17) is

$$\psi(k,t) = a_k\, e^{-i(\hbar k^2/2m)t}, \tag{1.18}$$

where a_k according to Eq. (1.13) is determined by

$$a_k = e^{i(\hbar k^2/2m)t}\psi(k,t) = e^{i(\hbar k^2/2m)t}\frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, e^{-ixk}\psi(x,t), \tag{1.19}$$

the formula being valid for arbitrary time t.

The general solution of the free particle Schrödinger equation, Eq. (1.14), is thus a superposition of the functions given by Eq. (1.6), the plane wave solutions themselves corresponding to the choice $a_k = A\delta(k-k_0)$.

Assuming the wave function at time t', $\psi(x,t')$, is known, the Fourier transform, $\psi(k,t')$, at the same instant is known, and thereby the prefactor

$$a_k = e^{i(\hbar k^2/2m)t'}\psi(k,t'). \tag{1.20}$$

Inserting this expression into Eq. (1.18), the Fourier transform is then specified at all times by

$$\psi(k,t) = \psi(k,t')\, e^{-i(\hbar k^2/2m)(t-t')}, \tag{1.21}$$

where

$$\psi(k,t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\; e^{-ixk}\psi(x,t'). \tag{1.22}$$

The Fourier transform of a free particle wave function, Eq. (1.21), thus has a simple time dependence: an exponential with a phase varying linearly in time.

Inserting the expression (1.21) into Eq. (1.14) gives

$$\begin{aligned}\psi(x,t) &= \int_{-\infty}^{\infty} dk\; e^{ikx}\psi(k,t')\, e^{-i(\hbar k^2/2m)(t-t')}\\ &= \int_{-\infty}^{\infty} dk\; e^{ikx} e^{-i(\hbar k^2/2m)(t-t')}\frac{1}{2\pi}\int_{-\infty}^{\infty} dx'\; e^{-ix'k}\psi(x',t'),\end{aligned} \tag{1.23}$$

the last equality following from Eq. (1.22). Interchanging the order of the integrations gives

$$\psi(x,t) = \int_{-\infty}^{\infty} dx'\; K_0(x,t;x',t')\,\psi(x',t'), \tag{1.24}$$

where

$$K_0(x,t;x',t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\; e^{ik(x-x')-i(\hbar k^2/2m)(t-t')}. \tag{1.25}$$

Since $\psi(x,t)$ is a solution of the free particle Schrödinger equation, so is the kernel, K_0, according to Eq. (1.24). The Gaussian integral, Eq. (1.24), is performed by completing the square (see Appendix B), giving the expression

$$K_0(x,t;x',t') = \sqrt{\frac{m}{2\pi i\hbar(t-t')}}\; \exp\left(\frac{i}{\hbar}\,\frac{m(x-x')^2}{2(t-t')}\right). \tag{1.26}$$

According to Eq. (1.24), the kernel, K_0, propagates the arbitrary initial state, and is therefore called the propagator; here for the case of a free particle, it is the free propagator. Free quantum dynamics, initially described by the Schrödinger *differential* equation, has thus been inverted to be described by an integral equation.[3]

In three spatial dimensions, we simply have to do three-fold exactly the same calculation as above due to the multiplicative character of Fourier transformation:

$$\exp(-i\mathbf{x}\cdot\mathbf{k}) = \exp(-ik_1x - ik_2y - ik_3z) = \exp(-ik_1x)\exp(-ik_2y)\exp(-ik_3z).$$

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[3] Propagation of a wave function by a kernel is generally valid: the fundamental equation of quantum dynamics arrived at in Appendix A, Eq. (A.12). The propagator is the basic quantum mechanical quantity, the quantum concept surviving even in relativistic quantum theory.

The general expression for the free particle propagator is therefore (here specified for d spatial dimensions)

$$K_0(\mathbf{x},t;\mathbf{x}',t') = \left(\frac{m}{2\pi\hbar i(t-t')}\right)^{d/2} \exp\left(\frac{im}{2\hbar}\frac{(\mathbf{x}-\mathbf{x}')^2}{t-t'}\right). \tag{1.27}$$

Exercise 1.1 Show by explicit differentiation that the free propagator $K_0(x,t;x',t')$ satisfies the free particle Schrödinger equation.

Exercise 1.2 Show that the plane wave solutions of the free particle Schrödinger equation (1.6), though non-normalized, are propagated by the free propagator, Eq. (1.27), i.e.

$$e^{i\mathbf{k}\cdot\mathbf{x}-i(\hbar\mathbf{k}^2/2m)t} = \int_{-\infty}^{\infty} d\mathbf{x}'\; K_0(\mathbf{x},t;\mathbf{x}',0)\, e^{i\mathbf{k}\cdot\mathbf{x}'}. \tag{1.28}$$

Exercise 1.3 Consider the free evolution of the Gaussian wave packet (consider the one-dimensional case for simplicity) which at time $t=0$ is centered around position $x=0$ and has a width δx (the parameters δx and p are real numbers),

$$\psi_{0p}(x,t=0) = \left(\frac{1}{2\pi\delta x^2}\right)^{1/4} \exp\left(-\frac{x^2}{4\delta x^2} + \frac{i}{\hbar}px\right). \tag{1.29}$$

Show that this initial state is normalized. Obtain, by using Eq. (1.24), the wave function and probability density at times $t>0$.

Solution

The integration to be performed is Gaussian and obtained by completing the square

$$\begin{aligned}\psi_{0p}(x,t) &= \int_{-\infty}^{\infty} dx'\; K_0(x,t;x',0)\,\psi_{0p}(x',0)\\ &= \left(\frac{\delta x^2}{2\pi\delta x_t^4}\right)^{1/4} \exp\left(\frac{im}{2\hbar t}x^2\right) \exp\left(-\frac{im\delta x^2}{2\hbar t}\frac{(x-x_0(t))^2}{\delta x_t^2}\right),\end{aligned} \tag{1.30}$$

where

$$\delta x_t^2 = \delta x^2\left(1+\frac{i\hbar t}{2m\delta x^2}\right), \qquad x_0(t) = \frac{p}{m}t. \tag{1.31}$$

The probability density at time t then becomes

$$P_{0p}(x,t) = |\psi_{0p}(x,t)|^2 = \sqrt{\frac{1}{2\pi\Delta x_t^2}}\exp\left(-\frac{(x-x_0(t))^2}{2\Delta x_t^2}\right), \tag{1.32}$$

where

$$\Delta x_t^2 = \frac{|\delta x_t^2|^2}{\delta x^2} = \delta x^2\left(1+\left(\frac{\hbar t}{2m\delta x^2}\right)^2\right). \tag{1.33}$$

As time goes by, the probability density keeps its Gaussian shape, but the profile does not propagate rigidly in space, instead experiencing wave packet spreading: its height decreasing and width increasing in concordance with the constraint of normalization of the probability distribution. The center of the Gaussian wave packet, $x_0(t) = pt/m$, moves with the constant velocity, p/m, the velocity with which a free particle of mass m and momentum p moves according to Newton's equation. Knowing the free propagator, we could turn to a discussion of the concept of *momentum*, or equivalently velocity, in quantum mechanics. However, this is postponed until needed, the details being relegated to Appendix G.

1.3 Probability Current

In view of the conservation of probability, Eq. (1.12), a diminishing probability in time in some region of space means that probability has streamed out of that volume. The Schrödinger equation identifies the probability current density describing this dynamics. The time derivative of the probability density, $P(\mathbf{x},t) = |\psi(\mathbf{x},t)|^2 = \psi(\mathbf{x},t)\,\psi^*(\mathbf{x},t)$, where $*$ denotes complex conjugation,

$$\frac{\partial P(\mathbf{x},t)}{\partial t} = \psi^*(\mathbf{x},t)\,\frac{\partial \psi(\mathbf{x},t)}{\partial t} + \psi(\mathbf{x},t)\,\frac{\partial \psi^*(\mathbf{x},t)}{\partial t} \tag{1.34}$$

becomes, according to the Schrödinger equation,

$$\frac{\partial P(\mathbf{x},t)}{\partial t} = \frac{1}{i\hbar}[\psi^*(\mathbf{x},t)\hat{H}(t)\psi(\mathbf{x},t) - \psi(\mathbf{x},t)(\hat{H}(t))^*\psi^*(\mathbf{x},t)]. \tag{1.35}$$

Consider the case of a particle in a scalar potential, i.e. described by the Hamiltonian in Eq. (1.8). The two terms in Eq. (1.35) containing the potential cancel each other, leaving

$$\begin{aligned}\frac{\partial P(\mathbf{x},t)}{\partial t} &= \frac{i\hbar}{2m}(\psi^*(\mathbf{x},t)\,\Delta_{\mathbf{x}}\psi(\mathbf{x},t) - \psi(\mathbf{x},t)\Delta_{\mathbf{x}}\psi^*(\mathbf{x},t))\\ &= -\frac{\hbar}{2im}\nabla_{\mathbf{x}}\cdot(\psi^*(\mathbf{x},t)\nabla_{\mathbf{x}}\psi(\mathbf{x},t) - \psi(\mathbf{x},t)\nabla_{\mathbf{x}}\psi^*(\mathbf{x},t)),\end{aligned} \tag{1.36}$$

where the last equality is a trivial rewriting, in terms of the *divergence*, as the additional two generated terms cancel each other. Introducing the vector field (which we note is real, $\mathbf{S}^* = \mathbf{S}$)

$$\begin{aligned}\mathbf{S}(\mathbf{x},t) &= \frac{\hbar}{2im}(\psi^*(\mathbf{x},t)\,\nabla_{\mathbf{x}}\psi(\mathbf{x},t) - \psi(\mathbf{x},t)\nabla_{\mathbf{x}}\psi^*(\mathbf{x},t))\\ &= \frac{\hbar}{2im}\,\psi^*(\mathbf{x},t)\nabla_{\mathbf{x}}\psi(\mathbf{x},t) + \text{c.c.}\end{aligned} \tag{1.37}$$

for a particle in the state described by the wave function $\psi(\mathbf{x},t)$, Eq. (1.36) takes the form of a continuity equation,

$$\frac{\partial P(\mathbf{x},t)}{\partial t} + \nabla_{\mathbf{x}} \cdot \mathbf{S}(\mathbf{x},t) = 0. \tag{1.38}$$

Integrating Eq. (1.38) over volume Ω, and using Gauss's theorem from vector calculus turns the divergence term into a surface integral[4]

$$\frac{d}{dt}\int_{\Omega} d\mathbf{x}\, P(\mathbf{x},t) = \int_{\Omega} d\mathbf{x}\, \frac{\partial P(\mathbf{x},t)}{\partial t} = -\int_{\Omega} d\mathbf{x}\, \nabla \cdot \mathbf{S}(\mathbf{x},t) = -\int_{S} d\mathbf{s} \cdot \mathbf{S}(\mathbf{x},t), \tag{1.39}$$

where S is the surface enclosing the volume Ω, and $d\mathbf{s} = ds\,\mathbf{n}$ is the directed surface element, where $\mathbf{n}$ is a unit vector normal to the surface area element, ds, directed outward from the enclosed volume. Equation (1.39) expresses the fact that the change in time of the probability for the particle to be in volume Ω at the time in question is expressed in terms of the net flow of the vector field $\mathbf{S}(\mathbf{x},t)$ through the surface enclosing the volume. The vector field $\mathbf{S}(\mathbf{x},t)$ therefore has the meaning of a probability current density or flux, i.e. $\Delta s\,\mathbf{n} \cdot \mathbf{S}(\mathbf{x},t)$ is the probability per unit time that the particle at time t will pass through the small surface at position $\mathbf{x}$ with area Δs. If $\mathbf{n} \cdot \mathbf{S}$ is positive, the flow is in the direction specified by $\mathbf{n}$, and if negative the flow is opposite, i.e. out- or in-flow. Since $|\psi(\mathbf{x},t)|^2$ is a probability, $\mathbf{S}(\mathbf{x},t)$ is also an average quantity, the average particle current density. According to Eq. (1.36), the probability current density is generated by the kinetic energy part of the Hamiltonian, the potential only entering implicitly through the wave function, a solution of the Schrödinger equation where the potential is present.[5] The probability current density is a measurable quantity. Just as the probability statements of the wave function are obtainable by repeated measurements, so is the probability current density by measuring the particle flux in terms of, for example, the blackening of photographic emulsions constituting the surface elements of interest.

Even for non-normalizable wave functions, such as the plane wave equation (1.6) corresponding to a state of a free particle, Eq. (1.39) renders $|\psi|^2$ a measure of the relative probability density for bounded spatial regions.

Writing the wave function in terms of its modulus and phase, two real functions, $\psi = |\psi| e^{i\Lambda}$, the expression in Eq. (1.37) becomes

$$\mathbf{S}(\mathbf{x},t) = \frac{\hbar}{m}\, |\psi(\mathbf{x},t)|^2\, \nabla_{\mathbf{x}} \Lambda(\mathbf{x},t). \tag{1.40}$$

1.4 Stationary States and Energy

For an isolated system, the Hamiltonian being time-independent, the Schrödinger equation is now shown to have solutions describing situations where all physical properties are

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[4] If unfamiliar with Gauss's theorem, then first do the calculation in one spatial dimension where the boundary terms appear immediately by the fundamental theorem of integration. Then the three-dimensional case where Ω is a box corresponds to doing the partial integration three times.

[5] In the case of a vector potential, its influence will in addition enter explicitly in the probability current density as discussed in Exercise A.2 on page 345.

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independent of time, a stationary state of the system. In particular, the probability density is time-independent in a stationary state, and, for a single particle $|\psi(\mathbf{x},t)|^2 = P(\mathbf{x})$, nothing happens in the whereabouts of the particle as time passes. A stationary state of the particle must thus be described by a function whose time dependence can only occur in the phase,

$$\psi(\mathbf{x},t) = \sqrt{P(\mathbf{x})}\, e^{i\Lambda(\mathbf{x},t)}, \tag{1.41}$$

where so far Λ can be an arbitrary but real function. The probability current density in a stationary state is, according to Eq. (1.40),

$$\mathbf{S}(\mathbf{x},t) = \frac{\hbar}{m} P(\mathbf{x}) \nabla_{\mathbf{x}} \Lambda(\mathbf{x},t). \tag{1.42}$$

For a stationary state where no physical properties are to change in time, the probability current density must also be time-independent, which then requires that the gradient of $\Lambda(\mathbf{x},t)$ be independent of time, and $\Lambda(\mathbf{x},t)$ therefore has the form (the minus sign just for convenience)

$$\Lambda(\mathbf{x},t) = \varphi(\mathbf{x}) - f(t), \tag{1.43}$$

where φ and f are real functions in view of Λ being real.[6] The wave function of a stationary state is thus the product of independent spatial and temporal parts,

$$\psi(\mathbf{x},t) = \sqrt{P(\mathbf{x})}\, e^{i\varphi(\mathbf{x})} e^{-if(t)}. \tag{1.44}$$

The time derivative is

$$i\hbar \frac{\partial \psi(\mathbf{x},t)}{\partial t} = \hbar \dot{f}(t)\, \psi(\mathbf{x},t) \tag{1.45}$$

and a stationary state function is a solution of the Schrödinger equation only if (dividing out the overall factor $e^{if(t)}$)

$$\hbar \dot{f}(t) \sqrt{P(\mathbf{x})}\, e^{i\varphi(\mathbf{x})} = \hat{H} \sqrt{P(\mathbf{x})}\, e^{i\varphi(\mathbf{x})}. \tag{1.46}$$

Since the right-hand side of the equation is independent of time, the time derivative of $f(t)$ must be a constant, and therefore

$$f(t) = r_1 t + r_2, \tag{1.47}$$

where r_1 and r_2 are real numbers. According to Eq. (1.46), a stationary state is thus described by a wave function of the form[7]

$$\psi_E(\mathbf{x},t) = \psi_E(\mathbf{x})\, e^{-(i/\hbar)Et}, \tag{1.48}$$

where E is a real number, $E \equiv r_1 \hbar$, and $\psi_E(\mathbf{x}) = \sqrt{P(\mathbf{x})}\, e^{i\varphi(\mathbf{x})}$ is determined by

$$\hat{H}\psi_E(\,\mathbf{x}) = E\psi_E(\mathbf{x}). \tag{1.49}$$

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[6] The other option, $\Lambda(\mathbf{x},t) = -f(t)g(\mathbf{x}) + \varphi(\mathbf{x})$, $\nabla_{\mathbf{x}}\, g(\mathbf{x}) = \mathbf{0}$, reduces to the former case as the constraint on $g(\mathbf{x})$ demands it to be constant in space, $g(\mathbf{x}) = c$.

[7] In view of its physical interpretation, a wave function is not uniquely defined, but can always be subjected to a phase factor change, $\psi \to \psi\, e^{i\varphi}$, where the phase, φ, can be any real number. The state of a physical system is thus properly represented by a so-called ray, the (equivalence) class of wave functions $e^{i\varphi}\psi$, differing only by an overall phase factor of modulus one (with respect to which the observable quantities, $|\psi|^2$ and $\mathbf{S}$, are invariant).

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The spatial part of the wave function for a stationary state is a solution of the so-called time-independent Schrödinger equation, an eigenfunction of the Hamiltonian corresponding to an eigenvalue E.

The real number E determines the time dependence of the stationary state at all times. Stationary states are the only solutions of the Schrödinger equation whose time dependence is a phase factor with a phase linear in time and characterized by a single real number, and we shall call this conserved quantity, or constant of motion, the *energy* of the particle in the stationary state in question. A particle in a stationary state would, if isolated, stay in this state of definite energy forever.

The energy eigenfunctions and eigenvalues for a free particle were already encountered in Eq. (1.6). The kinetic energy is related to the wave vector, $\mathbf{k}$, according to $E = \hbar^2\mathbf{k}^2/2m$. We note that, if momentum $\mathbf{p} = \hbar\mathbf{k}$ (the de Broglie relation) is associated with the wave vector of a plane wave, the energy dispersion is identical to that of a classical particle, $E = \mathbf{p}^2/2m$.

For a stationary state, the probability density is constant in time, and since then $\nabla\cdot\mathbf{S} = 0$, the net flow into any volume vanishes, i.e. in-flow equals out-flow. For the stationary free particle state, Eq. (1.6), the probability current density at each point in space equals

$$\mathbf{S} = \frac{\hbar\mathbf{k}}{m}|A|^2 = \frac{1}{\hbar}\frac{\partial E(\mathbf{k})}{\partial\mathbf{k}}|A|^2 = \frac{\partial E(\mathbf{p})}{\partial\mathbf{p}}|A|^2. \tag{1.50}$$

A solution of a time-independent Schrödinger equation that is real (up to the usual overall phase factor) has in the corresponding stationary state, according to Eq. (1.40) or (1.37), a probability current density that vanishes everywhere.

Shifting a Hamiltonian by a real constant V_0, $\hat{H} \rightarrow \hat{H} + V_0$, has no physical consequences as it is equivalent to subjecting the wave function to the phase transformation $\psi(x,t) \rightarrow \psi(x,t)\exp(-iV_0t/\hbar)$. If $\psi(x,t)$ is a solution to the Schrödinger equation described by the Hamiltonian $\hat{H}$, then $\psi(x,t)\exp(-iV_0t/\hbar)$ is a solution to the Schrödinger equation described by the Hamiltonian $\hat{H} + V_0$. The physical observables, the probability density and current density, are identical for either of the wave functions, as the two wave functions describe the same physical situation. For a stationary state, the change corresponds to shifting the energy values by the amount V_0, i.e. shifting the zero level from which energy is measured. The energy value of a quantum state is thus only defined modulo a constant, i.e. only an energy *difference* has physical significance in quantum mechanics.

Exercise 1.4 Show that, as a consequence of the Hamiltonian being a hermitian operator, the energy eigenvalue in Eq. (1.49) must be real.

Exercise 1.5 Show that, for a particle in a bounded potential, $V(\mathbf{x}) \geq V_{\min}$, the energy spectrum is bounded from below, $E \geq V_{\min}$.

Exercise 1.6 Show that $\nabla \cdot S = 0$ for a stationary state also follows directly from the time-independent Schrödinger equation.