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15 Schrodinger Equation

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Recommended Citation

Torre, Charles G., "15 Schrodinger Equation" (2014). *Foundations of Wave Phenomena*. 8.

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15. The Schrödinger Equation.

An important feature of the wave equation is that its solutions $q(\vec{r}, t)$ are uniquely determined once the initial values $q(\vec{r}, 0)$ and $\partial q(\vec{r}, 0)/\partial t$ are specified. As was mentioned before, if we view the wave equation as describing a continuum limit of a network of coupled oscillators, then this result is very reasonable since one must specify the initial position and velocity of an oscillator to uniquely determine its motion. It is possible to write down other “equations of motion” that exhibit wave phenomena but which only require the initial values of the dynamical variable — not its time derivative — to specify a solution. This is physically appropriate in a number of situations, the most significant of which is in quantum mechanics where the wave equation is called the *Schrödinger equation*. This equation describes the time development of the observable attributes of a particle via the *wave function* (or probability amplitude) ψ . In quantum mechanics, the complete specification of the initial conditions of the particle’s motion is embodied in the initial value of ψ . The price paid for this change in the allowed initial data while asking for a linear wave equation is the introduction of complex numbers into the equation for the wave. Indeed, the values taken by ψ are complex numbers. In what follows we shall explore some of the elementary features of the wave phenomena associated with the Schrödinger equation.

15.1 One-Dimensional Schrödinger equation

Let us begin again in one spatial dimension, labeled by x . We consider a *complex-valued function* ψ . This is a function that associates a complex number $\psi(x, t)$ to each point x of space and instant t of time. In other words, at each (x, t) , $\psi(x, t)$, is a complex number. Consequently, we can — if desired — break ψ into its real and imaginary parts:

$$\psi(x, t) = f(x, t) + ig(x, t), \quad (15.1)$$

where f and g are real functions. We can also use a polar representation:

$$\psi(x, t) = R(x, t)e^{i\Theta(x, t)}, \quad R \geq 0. \quad (15.2)$$

See §1.3 for a review of complex variable notation.

The complex-valued function ψ is called the *wave function* — you’ll see why shortly. The wave function ψ is required to satisfy the *Schrödinger equation*:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t}. \quad (15.3)$$

Here $V = V(x, t)$ is some given real-valued function of space and time representing the potential energy function of the particle, \hbar is Planck’s constant (h) divided by 2π , and

m is a parameter representing the mass of the particle. The Schrödinger equation is a complex, linear, homogeneous, partial differential equation with variable coefficients (thanks to $V(x, t)$). It is equivalent to a pair of real, coupled, linear differential equations for the real and imaginary parts of ψ as you can see by using the fact that equality of complex numbers means separate equality of their real and imaginary parts (*exercise*).

The Schrödinger equation specifies the time evolution of a quantum mechanical particle,* thus it plays a role in quantum mechanics roughly akin to the role played by the famous $\vec{F} = m\vec{a}$ in Newtonian mechanics. While we often speak of *the* Schrödinger equation, strictly speaking there is no single differential equation valid for all situations. Rather, each potential energy function defines a Schrödinger equation appropriate to the physical system. This is also true with $\vec{F} = m\vec{a}$ in Newtonian mechanics; one uses different forms for \vec{F} depending upon the physical situation. We also note that in some applications of the Schrödinger equation it is useful to allow the potential energy function V to be complex valued. Such potentials can be used to model processes involving particle decay. For simplicity we shall assume that the potential energy function is real. (See the Problems and also §15.4 for hints as to what happens when we let V be complex-valued.)

While I certainly won't be offering a course in quantum mechanics in this text, it is worth commenting on the physical meaning of solutions to (15.3). The simplest use of the wave function ψ is via the rule that $\psi^*(x, t)\psi(x, t) dx$ is the probability that a measurement of the particle's position at time t will find the particle in the region between x and $x + dx$. Put differently, the probability $P_t(x \in [a, b])$ for finding the particle at location $x \in [a, b]$ at time t is given by

$$P_t(x \in [a, b]) = \int_a^b dx |\psi(x, t)|^2.$$

More complicated expressions involving ψ are used to give the probability distributions for other particle observables besides position. You will have a chance to get used to such ideas in a later course in quantum mechanics. Suffice it to say that the probability distribution for any observable can be calculated from the wave function.

Fortunately, we do not really need to understand much of quantum mechanics in order to see the basic wave phenomena embodied in the Schrödinger equation. Still, from time to time it will be appropriate to make a few remarks concerning the physical interpretation of some of our results.

15.2 Free Particle Solution of the Schrödinger Equation

Let us now try to understand the sense in which (15.3) is a wave equation. This is most easily done by considering the special case $V(x, t) = 0$, which physically corresponds to

* There is also a Schrödinger equation for systems of particles, not to mention even more exotic dynamical systems. But we will stick to the simplest case of a single particle.

the motion of a free particle.† Although you can probably guess solutions to this equation, let us apply some of the techniques we have developed.

We begin with separation of variables; we try a solution of the form

$$\psi(x, t) = X(x)T(t), \quad (15.4)$$

and substitute to find (*exercise*):

$$-\frac{\hbar^2}{2m} \frac{X''}{X} = i\hbar \frac{T'}{T}. \quad (15.5)$$

As usual, we conclude that

$$-\frac{\hbar^2}{2m} X'' = \alpha X, \quad (15.6)$$

and

$$i\hbar T' = \alpha T,$$

where α is some constant.* These equations are easily solved:

$$X(x) = Ae^{ikx}, \quad T(t) = Be^{-i\omega(k)t}, \quad (15.7)$$

where k is any constant and

$$\omega(k) = \frac{\hbar k^2}{2m}. \quad (15.8)$$

Note that we could have written $X(x) = Ae^{\pm ikx}$, but we can get both choices of sign by choosing k positive or negative, so for simplicity we drop the \pm . Keep in mind, though, that for a given ω there are two independent solutions for $X(x)$, namely $e^{\pm i|k|x}$.

Since ψ is complex-valued, there is no obvious *a priori* restriction on whether k is real or not. As it happens, physical considerations in conjunction with the principles of quantum mechanics end up requiring k to be real in this example, so we'll only consider that case. The solution

$$\psi(x, t) = Ce^{i(kx - \omega(k)t)} \quad (15.9)$$

is then a complex form of a traveling wave (*i.e.*, its real and imaginary parts are traveling waves). We do not need to take the real part of ψ , however, since the wave function is allowed to be complex. Like the wave equation, the Schrödinger equation is linear and homogeneous. This means that one can take linear combinations of solutions (with complex coefficients) to get new solutions — a fact that has far-reaching physical consequences in quantum mechanics.

† One could also set $V(x, t) = \text{const.}$; this will be explored in the problems.

* Physically, α is identified with the energy of the stationary state we are constructing.

The *general solution* of the free particle ($V(x, t) = 0$) Schrödinger equation is a familiar superposition of traveling waves:

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} C(k) e^{i(kx - \omega(k)t)} dk. \quad (15.10)$$

This looks a lot like a Fourier representation of solutions to the wave equation from previous sections. As a homework problem you will derive this form of the solution to the Schrödinger equation using Fourier transform methods.

Let us make a few comments regarding the physical meaning of (15.9) and (15.10). Physically, the wave function (15.9) represents a free particle with momentum $p = \hbar k$ and energy $E = \hbar\omega = \frac{\hbar^2 k^2}{2m}$. Recall that $\psi^*(x)\psi(x)dx$ is interpreted as the probability for finding the particle between x and $x+dx$. This probability is the same throughout all space for a particle described by (15.9) because $\psi^*\psi = \text{constant}$, independent of x (*exercise*). Thus the particle in a state described by (15.9) has an equal chance to be found anywhere in space. By contrast, the momentum of the particle in this state is known with certainty to have the value $\hbar k$. This state of affairs is an extreme manifestation of the position-momentum *uncertainty principle*: the statistical uncertainty in the position is inversely proportional to that of the momentum. Thus, in particular, if the momentum is “known” precisely (vanishing statistical uncertainty) then the position takes all values with equal probability. The general solution (15.10) of the free particle Schrödinger equation, being a superposition over plane waves, corresponds to a superposition of momenta and energies. Because of this superposition, neither the energy nor the momentum of a free particle described by (15.10) has a precise value in the sense that there is a probability distribution describing the range of possible outcomes of a measurement of these observables.

Equation (15.8) defines the relation between frequency and wave number (equivalently, wavelength) for the free particle Schrödinger equation; it is the dispersion relation for this equation. Compare the dispersion relation for the Schrödinger equation with the dispersion relation (8.71) for the wave equation in one dimension. The latter exhibits a linear relation between frequency and wave number while the former exhibits a quadratic relation. To understand the implications of these different dispersion relations let us recall that, in general, sinusoidal waves of the form $A \sin(kx - \omega t)$ travel with speed given by ω/k . For the wave equation, (8.71) tells us that the speed is just the constant v which appears in the wave equation, $\omega/k = v$, *i.e.*, the waves travel with speed v irrespective of the frequency (or wavelength) of the wave. For the Schrödinger equation, (15.8) tells us that

$$\frac{\omega}{k} = \frac{\hbar k}{2m}, \quad (15.11)$$

which implies that the speed of the sinusoidal wave depends upon the wavelength.* The shorter wavelengths have the higher speeds (*exercise*). At any given time we can Fourier

* Note that this result says the sinusoidal wave speed is *one half* the momentum $\hbar k$ of

analyze any solution of the free particle Schrödinger equation into a superposition of sinusoidal waves with varying wavelengths (see (15.10)). Since each of these waves travels with a different speed, the Fourier superposition will change in time. The principal consequence of this being that the shape of the wave will not be preserved in time as it is in the case of the wave equation — the Schrödinger wave will in fact “disperse” as the shorter wavelengths “outrun” the longer wavelengths (see fig. 21 below). This is the origin of the term “dispersion relation” for formulas such as (8.71) and (15.8).

The difference in dispersion relations for the 1-d wave equation and the 1-d Schrödinger equation can be used to understand why there is no simple formula like $q(x, t) = f(x+vt) = g(x - vt)$ for the solutions to the Schrödinger equation. Since, for the wave equation, the wave propagation speed is the same (v) for all wavelengths, the Fourier superposition defining the left moving (f) and the right moving (g) parts of the wave is preserved in time. This means that the left and right moving parts of the wave maintain their integrity and, in particular, we always get the same shape for the left moving and right moving components of the wave. This cannot happen for the (free particle) Schrödinger waves since the dispersion relation means the Fourier superposition will change in time. The Fourier form of the solution is still available, of course, but there can be nothing like a d’Alembert formula.

In contrast to the one-dimensional wave equation for a complex-valued function, whose general solution involves two complex functions of one variable, the general solution to the Schrödinger equation involves only one undetermined complex function of one variable. We see this explicitly in the free particle case (15.10), where the undetermined function is represented by $C(k)$. This reflects the fact that only the initial value of the wave function $\psi(x, 0)$ is needed to uniquely fix the solution. Thus suppose $\psi(x, 0) = f(x)$, where $f(x)$ is some given function. Then $C(k)$ is the Fourier transform of $f(x)$ (*exercise*). In this way the initial condition determines the solution.

According to the rules of quantum mechanics, $C(k)$ defines the probability amplitude for momentum, that is, $C^*(k)C(k)dk$ is the probability for finding the particle to have momentum with values between $\hbar k$ and $\hbar k + \hbar dk$. Alternatively, the probability $P_t(p \in [u, w])$ for the particle to have momentum $p \in [u, w]$ at time t is given by*

$$P_t(p \in [u, w]) = \int_u^w dk |C(k)|^2 .$$

Let us illustrate this with an example which we have already explored mathematically.

the particle divided by the mass! So one cannot literally interpret the free particle wave function motion as particle motion. The slogan “particles are waves” has to be handled with care.

* Notice that this probability distribution is independent of time – what is the physical meaning of this?

Consider an initial condition in the form of a Gaussian

$$\psi(x, 0) = Ae^{-x^2/a^2}, \quad (15.12)$$

where the height A and width a are constants. Physically, this corresponds to a particle which is most likely found at the origin, but which has a non-vanishing probability to be found anywhere on the x -axis. The likelihood for finding the particle away from the origin grows as the parameter a is increased, *i.e.*, as the width of the Gaussian increases. Conversely, for sufficiently small a we can say that the particle is “known” to be near $x = 0$. From our previous work with the Gaussian profile, you can check that its Fourier transform is (*exercise*)

$$C(k) = \frac{1}{2\sqrt{2}}Aae^{-k^2a^2/4}. \quad (15.13)$$

We see that $C(k)$ (and hence $|C(k)|^2$) is also a Gaussian. Evidently, the momentum is most likely to be zero in this state, but the likelihood for finding a non-zero momentum increases as the parameter a decreases. The probability distribution in position has its width increasing with increasing a , while the probability distribution in momentum, has its width decreasing with increasing a . If we know the particle is at $x = 0$ with certainty, then the momentum value is very uncertain, statistically speaking. This is a good example of the uncertainty principle for position and momentum: as the probability distribution in position (momentum) becomes more tightly localized around a given value the probability distribution in momentum (position) becomes more de-localized. Speaking more loosely, as the position of the particle becomes more (less) uncertain the momentum of the particle becomes less (more) uncertain.

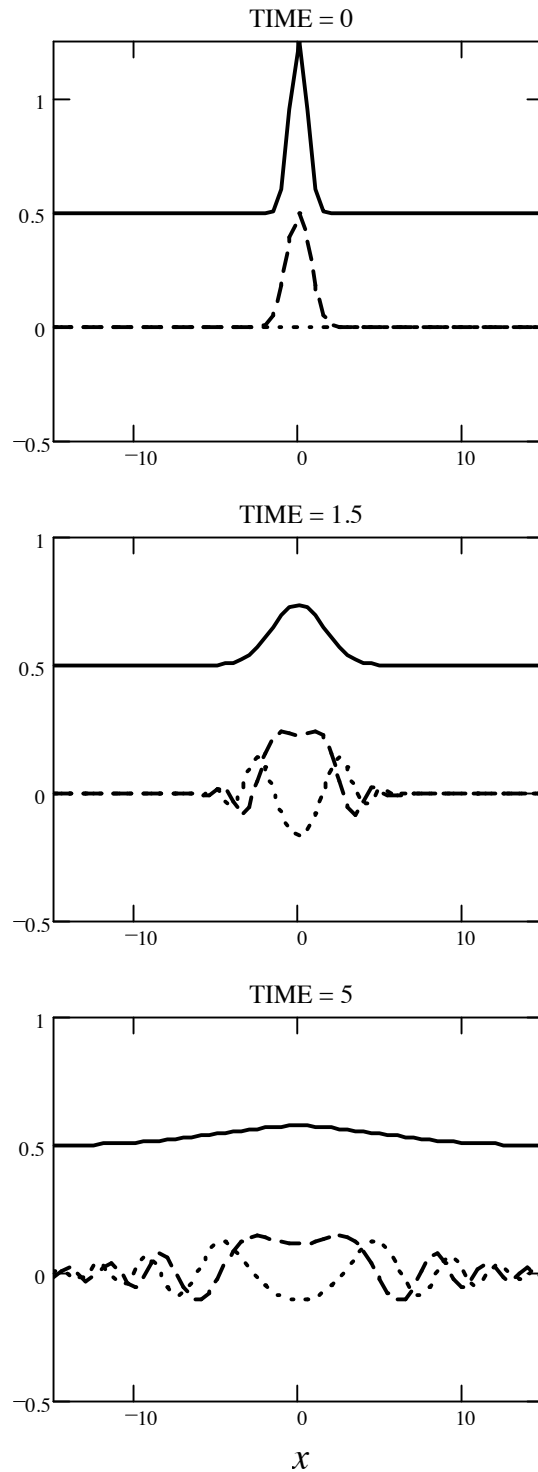


Figure 21. Time dependence of the Gaussian wave-packet solution to the Schrödinger equation. In each graph $\text{Re}(\psi)$ is the dashed line, $\text{Im}(\psi)$ is the dotted line, and $\psi^* \psi$ is the solid line. Note that the time dependence is different than for the wave equation.

15.3 The 3-Dimensional Schrödinger Equation

The Schrödinger equation for a particle moving in three dimensions involves the Laplacian:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r}, t)\psi = i\hbar\frac{\partial\psi}{\partial t}. \quad (15.14)$$

Now, of course, the wave function depends on the position in three-dimensional space, $\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}$ and the time t , $\psi = \psi(\vec{r}, t)$. You can easily see that this equation reduces to (15.3) if the y and z dependence of ψ and V are eliminated. The meaning of the wave function is a simple extension of the 1-d result: $|\psi(\vec{r}, t)|^2 d^3x$ is the probability that the particle is found in a volume element d^3x at the point \vec{r} at time t . The free particle case ($V = 0$) is easily treated by separation of variables and/or Fourier methods, as you will explore in a homework problem.

15.4 Conservation of Probability, Normalization

The Schrödinger equation admits a very important conservation law, which provides a nice example of the continuity equation formalism we discussed earlier. To derive the conservation law, we need both the Schrödinger equation (15.14) and its complex conjugate

$$-\frac{\hbar^2}{2m}\nabla^2\psi^* + V(\vec{r}, t)\psi^* = -i\hbar\frac{\partial\psi^*}{\partial t}. \quad (15.15)$$

(*Note:* Here we have used the assumption that the potential energy is a real function.) We can construct a continuity equation as follows. Multiply the Schrödinger equation (15.14) by ψ^* and multiply the complex conjugate equation (15.15) by ψ . Take the difference of the two resulting equations to get (*exercise*)

$$-\frac{\hbar^2}{2m}\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right) = i\hbar\left(\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right), \quad (15.16)$$

or

$$i\hbar\left(\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right) + \frac{\hbar^2}{2m}\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right) = 0. \quad (15.17)$$

Thus, if ψ satisfies (15.14) (with V real), then it also satisfies (15.17). Next, we recall the identity (10.3). Let us apply (10.3) to the vector field $\psi\nabla\psi^*$:

$$\nabla \cdot (\psi\nabla\psi^*) = \nabla\psi \cdot \nabla\psi^* + \psi\nabla^2\psi^*. \quad (15.18)$$

Similarly

$$\nabla \cdot (\psi^*\nabla\psi) = \nabla\psi^* \cdot \nabla\psi + \psi^*\nabla^2\psi. \quad (15.19)$$

Subtracting these two results and using the fact that the dot product is commutative ($A \cdot B = B \cdot A$) we get (*exercise*)

$$\nabla \cdot [\psi\nabla\psi^* - \psi^*\nabla\psi] = \psi\nabla^2\psi^* - \psi^*\nabla^2\psi. \quad (15.20)$$

Thus the second term in parenthesis in (15.17), involving the Laplacian, can be expressed as the divergence of a vector field. It is straightforward to check that the first term in parenthesis in (15.17), involving the time derivative, can be expressed as a time derivative (*exercise*):

$$\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} = \frac{\partial}{\partial t}(\psi^* \psi). \quad (15.21)$$

From these manipulations we see that the result (15.17) can be expressed as a continuity equation (*exercise*)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0 \quad (15.22)$$

where

$$\rho = \psi^* \psi \quad (15.23)$$

$$\vec{j} = \frac{i\hbar}{2m}(\psi \nabla \psi^* - \psi^* \nabla \psi). \quad (15.24)$$

Note that the reality of the function V was crucial for this result. If we used a complex potential energy this continuity equation would not arise (see problems).

We can now use our previous experience with continuity equations to derive a conservation law. Recall that a continuity equation such as (15.22) implies that the time rate of change of the volume integral of ρ over a given volume, denoted by R , will be controlled by the flux of \vec{j} through the boundary S of R . Thus,

$$N(t) = \int_R d^3x \psi^*(\vec{r}, t) \psi(\vec{r}, t) \quad (15.25)$$

satisfies

$$\frac{dN(t)}{dt} = \int_S dS \vec{j} \cdot \hat{n}, \quad (15.26)$$

provided, of course, that ψ satisfies the Schrödinger equation (15.14). In particular, *with boundary conditions chosen so that the flux of \vec{j} through S vanishes*, the probability for finding the particle in the region R will be time-independent. One says that “probability is conserved”.

This conservation law allows us to *normalize* the solutions to the Schrödinger equation. Recall that $\rho(\vec{r}, t) d^3x$ is the probability that the particle is located in an infinitesimal neighborhood d^3x of \vec{r} at time t . Suppose that the particle is restricted to a region R of space (which may in fact be all of space). The total probability for finding the particle anywhere in R at any given time should be unity. Thus we should demand that at any time t

$$\int_R \psi^*(\vec{r}, t) \psi(\vec{r}, t) d^3x = 1. \quad (15.27)$$

One says that the wave function is “normalized” (to unity); this normalization is crucial for the physical interpretation of the wave function in terms of probabilities. In particular, the initial (say, $t = 0$) wave function should be normalized:

$$\int_R \psi^*(\vec{r}, 0)\psi(\vec{r}, 0) d^3x = 1. \quad (15.28)$$

In fact, it is enough specify initial/boundary conditions such that (15.28) holds and the wave function is guaranteed to be normalized for all time if it satisfies the Schrödinger equation. Indeed, if (15.28) is satisfied, then with boundary conditions chosen such that the flux of \vec{j} through the boundary of R vanishes, (15.26) guarantees that (15.27) is satisfied (*exercise*). This result is quite important since the solutions to the Schrödinger equation are uniquely determined by the initial (normalized) wave function. If the wave function at later times were not normalized, then the probability interpretation of quantum mechanics would not work.

15.5 Boundary Conditions, Particle in a Box

Our argument that took us from the continuity equation for conservation of probability to the ability to normalize the wave function relied upon using appropriate boundary conditions. Appropriate boundary conditions are such that the flux of \vec{j} through the boundary of the region of interest should vanish. If this region is all of space, this is accomplished by using solutions to the Schrödinger equation such that $\psi \rightarrow 0$ (at a fast enough rate) as $r \rightarrow \infty$. Physically, this corresponds to requiring that the particle never escapes to infinity (at any finite time).

It is often physically appropriate to limit the spatial domain of the particle. A common model system used in quantum mechanics is a “particle in a box”. This is a model which describes a particle that is confined to some finite region in space, but is otherwise “free”. For example, a spherical box would be the points $r < a$, $a = \text{constant}$, and we would demand that $\psi = 0$ when $r \geq a$. This means that the particle is never outside the spherical box. From the formula for the probability current density, you can easily see that the flux of probability through the boundary of a region will vanish if the wave function vanishes on the boundary. Thus probability for being in the box will be constant in time. Let us explore a simplified model of a particle in a box in a little more detail.

We again restrict our attention to one spatial dimension for simplicity. We consider a free particle moving in a box in which $0 < x < L$. We look for a solution of the free particle Schrödinger equation that is non-zero in the box, but is zero outside the box. Since the zero function always satisfies the Schrödinger equation, we have already solved the Schrödinger equation outside the box (*exercise*). We will restrict our attention to interior solutions which continuously “join” this exterior solution, *i.e.*, the solutions must

continuously vanish at the walls of the box:

$$\psi(0, t) = \psi(L, t) = 0. \quad (15.29)$$

For example, a simple set of functions which vanish at the boundaries $x = 0$ and $x = L$ is given by

$$f(x) = N \sin\left(\frac{n\pi}{L}x\right), \quad n = 1, 2, 3, \dots \quad (15.30)$$

where N is a constant (determined by normalization). We require the particle to be *somewhere*, so it won't do to let $\psi = 0$ everywhere. Thus we restrict attention to $n \neq 0$. We could have also let $n = -1, -2, \dots$, but these functions are just constant multiples of the functions we have chosen and so do not lead to anything new in this context.* Let us choose one of these sine functions to represent the initial wave function for the particle in the box:

$$\psi(x, 0) = \begin{cases} N \sin\left(\frac{n\pi}{L}x\right), & \text{if } -L \leq x \leq L; \\ 0, & \text{if } |x| \geq L. \end{cases} \quad (15.31)$$

The constant N is determined by normalization:

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1.$$

As an *exercise* you should do this integral and show that this fixes N to be of the form

$$N = \sqrt{\frac{2}{L}} e^{i\alpha}, \quad (15.32)$$

where α is any real number. We shall set $\alpha = 0$ in what follows.

We suppose that (15.31) is the initial wave function. To find the solution at time t with this initial condition we can use Fourier analysis, but let us take the following shortcut. We already have a very simple class of solutions obtained using the separation of variables technique (see (15.7)). The solutions shown there do not satisfy the boundary conditions (15.29) because the function $X(x)$ shown there does not satisfy the boundary conditions. However both the Schrödinger equation as well as the ordinary differential equations satisfied by X and T are linear so we can build new solutions by taking linear combinations. And it is easy to take appropriate linear combinations to get solutions which *do* satisfy (15.29) (*exercise*). You can easily check (*exercise*) that with

$$\psi(x, t) = X(x)T(t), \quad (15.33)$$

where

$$X(x) = \sqrt{\frac{2}{L}} \sin kx, \quad T(t) = e^{-i\omega(k)t}, \quad (15.34)$$

* In quantum mechanics only linearly independent wave functions represent distinct states of the system.

and

$$k = \frac{n\pi}{L}, \quad \omega(k) = \frac{\hbar k^2}{2m} \quad (15.35)$$

we get a solution to the free particle Schrödinger equation that is always normalized, satisfies the boundary conditions $\psi(0, t) = 0 = \psi(L, t)$, and agrees with the initial condition (15.31).

Physically, the wave function (15.33)—(15.35) represents a particle with energy

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2,$$

moving in the region $0 < x < L$. While the energy of the particle is uniquely determined, the momentum of the particle is not uniquely determined; it has non-zero statistical uncertainty. This is a consequence of the uncertainty principle (*exercise*).

Because of the boundary conditions we have chosen, the flux of the energy current density vanishes at the boundaries of the box. Consequently, we know that the integral of $\psi^* \psi$ over the box should not change in time. We can easily check this explicitly:

$$\int_0^L dx \psi^*(x, t) \psi(x, t) = \int_0^L dx \frac{2}{L} \sin^2\left(\frac{n\pi}{L}x\right) = 1.$$