
Quantum Mechanics

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Chapter 1

The wave function

1.1 The Schrodinger equation

Imagine a particle of mass m , constrained to move along the x -axis, subject to some specified force $F(x, t)$. The program of *classical* mechanics is to determine the position of the particle at any given time: $x(t)$. Once we know that, we can figure out the velocity ($v = dx/dt$), the momentum ($p = mv$), the kinetic energy ($T = (1/2)mv^2$), or any other dynamical variable of interest. And how do we go about determining $x(t)$? We apply Newton's second law: $F = ma$. (For *conservative* systems—the only kinds we shall consider, and, fortunately, the only kinds that *occur* at the microscopic level—the force can be expressed as the derivative of a potential energy function¹, $F = -\partial V/\partial x$, and Newton's law reads $m d^2x/dt^2 = -\partial V/\partial x$) This, together with appropriate initial conditions (typically the position and velocity at $t = 0$), determines $x(t)$.

Quantum mechanics approaches this same problem quite differently. In this case what we're looking for is the particle's **wave function**, $\Psi(x, t)$, and we get it by solving the **Schrodinger equation**:

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi} \quad (1.1) \quad \text{Schrodinger equation}$$

This equation plays a role logically analogous to Newton's second law: Given suitable initial conditions (typically, $\Psi(x, 0)$), the Schrodinger equation determines $\Psi(x, t)$ for all future time, just as, in classical mechanics, Newton's law determines $x(t)$ for all future time.

1.2 The statistical interpretation

What exactly is this "wave function"? Born's **statistical interpretation** of the wave function, says that $|\Psi(x, t)|^2$ gives the **probability** of finding the particle at point x , at time t , or more precisely

$$\boxed{\int_a^b |\Psi(x, t)|^2 dx = \text{probability of finding the particle between } a \text{ and } b, \text{ at time } t} \quad (1.2) \quad \text{Statistical interpretation}$$

¹Magnetic forces are an exception, but let's not worry about them just yet. By the way, we shall assume for the moment that the motion is nonrelativistic ($v \ll c$)

Probability is the *area* under the graph of $|\Psi(x, t)|^2$

The statistical interpretation introduces a kind of **indeterminacy** into quantum mechanics, for even if you know everything the theory has to tell you about the particle /to wit: its wave function, still you cannot predict with certainty the outcome of a simple experiment to measure its position– all quantum mechanics has to offer is *statistical* information about the *possible* results.

We say that the wave function **collapses**, upon measurement, to spike some point. There are, then, two entirely distinct kinds of physical processes: "ordinary" ones, in which the wave function evolves in a leisurely fashion under the Schrodinger equation, and "measurements", in which Ψ suddenly and discontinuously collapses ².

1.3 Probability

I will give some definitions. The total number is

$$N = \sum_{j=0}^{\infty} N(j) \quad (1.3)$$

The probability of getting j is

$$P(j) = \frac{N(j)}{N} \quad (1.4)$$

In particular, the sum of all the probabilities is 1:

$$\sum_{j=0}^{\infty} P(j) = 1 \quad (1.5)$$

In general, the average value of some *function* of j es given by

$$\boxed{\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j)P(j)} \quad (1.6) \quad \text{Average value of a function}$$

In quantum mechanics the average is usually the quantity of interest; in that context it has come to be called the **expectation value**.

Now we need a numerical measure of the amount of "spread" in a distribution, with respect to the average. The most obvious way to do this would be to find out how far each individual deviates from the average,

$$\Delta j = j - \langle j \rangle \quad (1.7)$$

and compute the average of Δj . Trouble is, of course, that you get zero, by the nature of the average, Δj is as often negative as positive. To avoid this irritating problem you might decide

²The role of measurement in quantum mechanics is so critical and so bizarre that you may well be wondering what precisely constitutes a measurement. Does it have to do with the interaction between a microscopic (quantum) system and a macroscopic (classical) measuring apparatus (as Bohr insisted), or is it intervention of a conscious "observer" (as Wigner proposed)? For the moment let's take the naive view: A measurement is the kind of thing that a scientist does in the laboratory, with rules, stopwatches, and so on

to average the *absolute value* of Δj . But absolute values are nasty to work with; instead, we get around the sign problem by *squaring* before averaging:

$$\sigma^2 \equiv \langle (\Delta j)^2 \rangle \quad (1.8) \quad \text{Variance}$$

This quantity is known as the **variance** of the distribution; σ itself is called the **standard deviation**.

There is a useful little theorem on variances:

$$\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2} \quad (1.9)$$

1.4 Continuous variables

I have assumed that we are dealing with a *discrete* variable—that is, one that can take on only isolated values. But it is simple enough to generalize to *continuous* distributions. If the interval is sufficiently short, this probability is *proportional to the length of the interval*. This

$$\text{probability that an individual lies between } x \text{ and } (x + dx) = \rho(x)dx \quad (1.10) \quad \text{Probability density}$$

The proportionality factor $\rho(x)$, is often loosely called "the probability of getting x ", but is sloppy language; a better term is **probability density**. The probability that x lies between a and b (a finite interval) is given by the integral of $\rho(x)$:

$$P_{ab} = \int_a^b \rho(x)dx \quad (1.11)$$

and the rules we deduced for discrete distributions translate in the obvious way:

$$1 = \int_{-\infty}^{+\infty} \rho(x)dx \quad (1.12)$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} x\rho(x)dx \quad (1.13)$$

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x)\rho(x)dx \quad (1.14)$$

$$\sigma^2 \equiv \langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \quad (1.15)$$

1.5 Normalization

We return now to the statistical interpretation of the wave function (1.2), which says that $|\Psi(x, t)|^2$ is the probability density for finding the particle at point x , at time t . It follows (1.5) that the integral of $|\Psi|^2$ must be 1 (the particle's got to be *somewhere*):

$$\boxed{\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1} \quad (1.16)$$

If $\Psi(x, t)$ is a solution of the Schrodinger equation, so too is $A\Psi(x, t)$, where A is any (complex) constant. What we must do, then, is pick this undetermined multiplicative factor so as to ensure that (1.16) is satisfied. This process is called **normalizing** the wave function. For some solutions to the Schrodinger equation the integral is *infinite*; in that case *no* multiplicative factor is going to make it 1. The same goes for the trivial solution $\Psi = 0$. Such **non-normalizable** solutions cannot represent particles, and must be rejected. Physically realizable states correspond to the **square-integrable** solutions to Schrodinger equation.³

Fortunately, the Schrodinger equation has the remarkable property that it automatically preserves the normalization of the wave function.

1.6 Momentum

For a particle in state Ψ , the expectation value of x is

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx \quad (1.17) \quad \text{Expectation value of } x$$

What exactly does this mean? It emphatically does not mean that if you measure the position of one particle over and over, $\int x |\Psi|^2 dx$ is the average of the results you'll get. Rather, $\langle x \rangle$ is the average of measurements, performed on particles *all in the state* Ψ , which means that either you must find some way to returning the particle to its original state after each measurement, or else you have to prepare a whole **ensemble** of particles, each in the same state Ψ , and measure the positions of all of them: $\langle x \rangle$ is the average of *these* results.

Now, as time goes on, $\langle x \rangle$ will change (because of the time dependence of Ψ), and we might be interested in knowing how fast it moves. We see that

$$\frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} dx \quad (1.18)$$

The *expectations value of the velocity is equal to the time derivative of the expectation value of position*:

$$\langle v \rangle = \frac{d\langle x \rangle}{dt} \quad (1.19)$$

(1.18) tell us, then, how to calculate $\langle v \rangle$ directly from Ψ .

Actually, it is customary to work with **momentum** ($p = mv$), rather than velocity:

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = -i\hbar \int \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx \quad (1.20) \quad \text{Momentum}$$

Let me write the expressions for $\langle x \rangle$ and $\langle p \rangle$ in a more suggestive way:

$$\langle x \rangle = \int \Psi^*(x) \Psi dx \quad (1.21)$$

$$\langle p \rangle = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx \quad (1.22)$$

³Evidently $\Psi(x, t)$ must go to zero faster than $1/\sqrt{|x|}$, as $|x| \rightarrow \infty$. Incidentally, normalization only fixed the *modulus* of A : the phase remains undetermined. However, as we shall, the latter carries no physical significance anyway.

We say that the **operator** x "represents" position, and the operator $(\hbar/i)(\partial/\partial x)$ "represents" momentum, in quantum mechanics; to calculate expectation values we "sandwich" the appropriate operator between Ψ^* and Ψ , and integrate.

What about other quantities? The fact is, all classical dynamics variables can be expressed in terms of position and momentum.

To calculate the expectation value of any such quantity, $Q(x, p)$, we simply replace every p by $(\hbar/i)(\partial/\partial x)$, insert the resulting operator between Ψ^* and Ψ , and integrate:

$$\langle Q(x, p) \rangle = \int \Psi^* Q \left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx \quad (1.23)$$

1.7 The uncertainty principle

The wavelength of Ψ is related to the *momentum* of the particle by the **de Broglie formula**:

$$p = \frac{\hbar}{\lambda} = \frac{2\pi\hbar}{\lambda} \quad (1.24) \quad \text{deBroglie formula}$$

Thus a spread in *wavelength* corresponds to a spread in *momentum*, and our general observation now says that the more precisely determined a particle's position is, the less precisely is its momentum. Quantitatively.

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \quad (1.25) \quad \text{Uncertainty principle}$$

where σ_x is the standard deviation in x , and σ_p is the standard deviation in p .

Please understand what the uncertainty principle means: Like position measurements, momentum measurements yield precise answers—the "spread" here refers to the fact that measurements on identically prepared systems do not yield identical results. You can, if you want, construct a state such the repeated position measurements will be very close together (by making Ψ a localized "spike"), but you still pay a price: Momentum measurements on this state will be widely scattered. Or you can prepare a state with a reproducible momentum (by making Ψ a long sinusoidal wave), but in that case, position measurements will be widely scattered.

Chapter 2

Time-independent Schrodinger equation

2.1 Stationary states

We talked a lot about the wave function, and how you use it to calculate various quantities of interest. But, how do you get $\Psi(x, t)$ in the first place? We need to solve the Schrodinger equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (2.1)$$

for a specified potential¹ $V(x, t)$. In this chapter (and most of this book) I shall assume that V is *independent* of t . In that case the Schrodinger equation can be solved by the method of **separation of variables**: We look for solutions that are simple *products*,

$$\Psi(x, t) = \psi(x)\varphi(t) \quad (2.2)$$

where ψ is a function of x alone, and φ is a function of t alone.

For separable solutions we have

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\varphi}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} \varphi$$

(ordinary derivatives, now), and Schrodinger equation reads

$$i\hbar \frac{d\varphi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} \varphi + V\psi\varphi \quad (2.3)$$

Or, dividing through by $\psi\varphi$:

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V \quad (2.4)$$

Now, the left side is a function of t alone, and the right side is a function of x alone². The only way this can possibly be true is if both sides are in fact *constant* – otherwise, by varying

¹It is tiresome to keep saying "potential energy function", so most people just call V the "potential", even though this invites occasional confusion with electric potential, which is actually potential energy per unit charge.

²Note that this would not be true if V were a function of t as well as x .

t , I could change the left side without touching the right side, and the two would no longer equal. For reasons that will appear in a moment, we shall call the separation constant E . Then

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = E$$

or

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar} \varphi$$

and

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V = E \quad (2.5)$$

or

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi} \quad (2.6) \quad \text{Time-independent Schrodinger equation}$$

Separation of variables has turned a *partial* differential equation into *two ordinary* differential equations (2.1) and (2.6). The first, (2.1) is easy to solve (just multiply through by dt and integrate); the general solution is $C \exp(-iEt/\hbar)$, but we might as well absorb the constant C into ψ (since the quantity of interest is the product $\psi\varphi$). Then

$$\varphi(t) = e^{-iEt/\hbar} \quad (2.7)$$

The second equation (2.6) is called the *time-independent Schrodinger equation* we can go further with it until the potential $V(x)$ is specified.

The rest of this chapter will be devoted to solving the time-independent Schrodinger equation, for a variety of simple potentials. But before I get to that you have every right ask: What's so great about separable solutions? After all, most solutions to the (time dependent) Schrodinger equation do not take the form $\psi(x)\varphi(t)$. I offer three answers—two of them physical, and one mathematical:

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

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \quad (2.8)$$

does (obviously) depend on t , the *probability density*,

$$|\Psi(x, t)|^2 = \Psi^* \Psi = \psi^* e^{+iEt/\hbar} \psi e^{-iEt/\hbar} = |\psi(x)|^2 \quad (2.9)$$

does not—the time-dependence cancels out³. The same thing happens in calculating the expectation value of any dynamical variable; (1.23) reduces to

$$\langle Q(x, p) \rangle = \int \psi^* Q \left(x, \frac{\hbar}{i} \frac{d}{dx} \right) \psi dx \quad (2.10)$$

Every expectation value is constant in time; we might as well drop the factor $\varphi(t)$ altogether, and simply use ψ in place of Ψ . In particular, $\langle x \rangle$ is constant, and hence $\langle p \rangle = 0$ (See (1.20)). Nothing ever happens in a stationary state.

³For normalizable solutions, E must be real

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

$$H(x, p) = \frac{p^2}{2m} + V(x) \quad (2.11)$$

The corresponding Hamiltonian *operator*, obtained by the canonical substitution $p \rightarrow (\hbar/i)(\partial/\partial x)$, is therefore⁴

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (2.12)$$

Thus the time-independent Schrodinger equation (2.6) can be written

$$\hat{H}\psi = E\psi \quad (2.13)$$

and the expectation value of the total energy is

$$\langle H \rangle = \int \psi^* \hat{H} \psi dx = E \int |\psi|^2 dx = E \int |\Psi|^2 dx = E \quad (2.14)$$

(Notice that the normalization of Ψ entails the normalization of ψ .) Moreover,

$$\hat{H}^2 \psi = \hat{H}(\hat{H}\psi) = \hat{H}(E\psi) = E(\hat{H}\psi) = E^2 \psi$$

and hence

$$\langle H^2 \rangle = \int \psi^* \hat{H}^2 \psi dx = E^2 \int |\psi|^2 dx = E^2$$

So the variance of H is

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0 \quad (2.15)$$

But remember, if $\sigma = 0$, then every member of the sample must share the same value (the distribution has zero spread). *Conclusion*: A separable solution has the property that *every measurement of the total energy is certain to return the value E* .

3. The general solution is a **linear combination** of separable solutions. As we're about to discover, the time-independent Schrodinger equation (2.6) yields an infinite collection of solution $(\psi_1(x), \psi_2(x), \dots)$, each with its associated value of the separation constant (E_1, E_2, \dots) ; thus there is a different wave function for each **allowed energy**:

$$\Psi_1(x, t) = \psi_1(x)e^{-iE_1t/\hbar}, \quad \Psi_2(x, t) = \psi_2(x)e^{-iE_2t/\hbar}, \dots$$

Now the time-dependent Schrodinger equation (2.1) has the property that any linear combination⁵ of solutions is itself a solution. Once we have found the separable solutions, then, we can immediately construct a much more general solution, on the form

⁴Whenever confusion might arise. I'll put a "hat" on the operator, to distinguish it from the dynamical variable it represents.

⁵A **linear combination** of the functions $f_1(z), f_2(z), \dots$ is an expression of the form

$$f(z) = c_1 f_1(z) + c_2 f_2(z) + \dots$$

where c_1, c_2, \dots are any (complex) constants.

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \quad (2.16)$$

It so happens that *every* solution to the (time-dependent) Schrodinger equation can be written in this form –it is simply a matter of finding the right constants (c_1, c_2, \dots) so as to fit the initial conditions for the problem at hand.

Let me recapitulate, from a somewhat different perspective. Here's the generic problem: You're given a (time-independent) potential $V(x)$ and the starting wave function $\Psi(x, 0)$; your job is to find the wave function, $\Psi(x, t)$, for any subsequent time t . To do this you must solve the (time-dependent) Schrodinger equation (2.1); this yields, in general, an infinite set of solutions ($\psi_1(x), \psi_2(x), \dots$), each with its own associated energy (E_1, E_2, \dots). To fit $\Psi(x, 0)$ you write down the general linear combination of these solutions:

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \quad (2.17)$$

the miracle is that you can *always* match the specified initial state by appropriate choice of the constants c_1, c_2, \dots . To construct $\Psi(x, t)$ you simply tack onto each term its characteristic time dependence, $\exp(-iE_n t/\hbar)$:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} = \sum_{n=1}^{\infty} c_n \Psi_n(x, t) \quad (2.18)$$

The separable solutions themselves,

$$\Psi_n(x, t) = \psi_n(x) e^{-iE_n t/\hbar} \quad (2.19)$$

are *stationary* states, in the sense that all probabilities and expectation values are independent of time, but this property is emphatically *not* shared by the general solution (2.18); the energies are different, for different stationary states, and the exponentials do not cancel, when you calculate $|\Psi|^2$.

2.2 The infinite square well

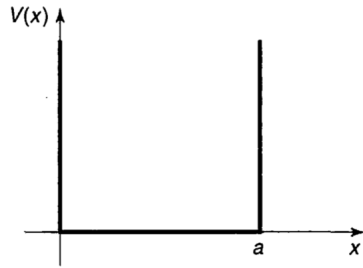


Figure 2.1: The infinite square well potential (2.20)

Suppose

$$V(x) = \begin{cases} 0 & , 0 \leq x \leq a \\ \infty & , \text{otherwise} \end{cases} \quad (2.20)$$

Fig. (2.1). A particle in this potential is completely free, except at two ends ($x = 0$ and $x = a$), where an infinite force prevents it from escaping.

Outside the well, $\psi(x) = 0$ (the probability of finding the particle there is zero) Inside the well, where $V = 0$, the time-independent Schrodinger equation (2.6) reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (2.21)$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (2.22)$$

(By writing it in this way, I have tacitly assumed that $E \geq 0$.) Equation (2.22) is the classical **simple harmonic oscillator** equation; the general solution is

$$\psi(x) = A \sin kx + B \cos kx \quad (2.23)$$

where A and B are arbitrary constants. Typically, these constants are fixed by the **boundary conditions** of the problem. What are the appropriate boundary conditions for $\psi(x)$? Ordinarily, both ψ and $d\psi/dx$ are continuous, but where the potential goes to infinity only the first of these applies.

Continuity of $\psi(x)$ requires that

$$\psi(0) = \psi(a) = 0 \quad (2.24)$$

so as to join onto the solution outside the well. What does this tell us about A and B ? Well,

$$\psi(0) = A \sin 0 + B \cos 0 = B$$

so $B = 0$, and hence

$$\psi(x) = A \sin kx \quad (2.25)$$

Then $\psi(a) = A \sin ka$, so either $A = 0$ (in which case we're left with the trivial –non-normalizable–solution $\psi(x) = 0$), or else $\sin ka = 0$, which means that

$$ka = 0, \pm\pi, \pm2\pi, \pm3\pi, \dots \quad (2.26)$$

But $k = 0$ is no good (again, that would imply $\psi(x) = 0$), and the negative solutions give nothing new, since $\sin(-\theta) = -\sin(\theta)$ and we can absorb the minus sign into A . So the *distinct* solutions are

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1, 2, 3, \dots \quad (2.27)$$

Curiously, the boundary condition at $x = a$ does not determine the constant A , but rather the constant k , and hence the possible values of E :

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}} \quad (2.28) \quad \begin{array}{l} \text{Possible values} \\ \text{of } E \end{array}$$

In radical contrast to the classical case, a quantum particle in the infinite square well cannot have just any old energy—it has to be one of these special **allowed** values⁶. To find A we normalize ψ :

$$\int_a^a |A|^2 \sin^2(kx) dx = |A|^2 \frac{a}{2} = 1, \quad \text{so } |A|^2 = \frac{2}{a}$$

This only determines the magnitude of A , but it is simpler to pick the positive real root: $A = \sqrt{2/a}$ (the phase of A carries no physical significance anyway). Inside the well, the solutions are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad (2.29)$$

As a collection, the functions $\psi_n(x)$ have some interesting and important properties:

1. They are alternately **even** and **odd**, with respect to the center of the well: ψ_1 is even, ψ_2 is odd, ψ_3 is even, and so on.
2. As you go up in energy, each successive state has one more **node** (zero-crossing): ψ_1 has one (the end points don't count), ψ_4 has one, ψ_3 has two, and so on.
3. They are mutually **orthogonal**, in the sense that

$$\int \psi_m(x)^* \psi_n(x) dx = 0 \quad (2.30)$$

whenever $m \neq n$. We can combine orthogonality and normalization into a single statement⁷:

$$\int \psi_m(x)^* \psi_n(x) dx = \delta_{mn} \quad (2.31)$$

We say that the ψ 's are **orthonormal**.

4. They are **complete**, in the sense that any other function, $f(x)$, can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right) \quad (2.32)$$

(2.32) is nothing but the **Fourier series** for $f(x)$, and the fact that any function can be expanded in this way is sometimes called **Dirichlet's theorem**. The coefficients c_n can be evaluated—for a given $f(x)$ —by a method I call **Fourier's trick**, which beautifully exploits the orthonormality of $\{\psi_n\}$: Multiply both sides of (2.32) by $\psi_m(x)^*$, and integrate

$$\psi_m(x)^* f(x) dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x) dx = \sum_{n=1}^{\infty} c_n \delta_{nm} = c_m \quad (2.33)$$

⁶Notice that the quantization of energy emerged as a rather technical consequence of the boundary conditions on solutions to the time-independent Schrödinger equation

⁷In this case the ψ 's are real, so the $*$ on ψ_m is unnecessary, but for future purposes it's a good idea to get the habit of putting it there.

Thus the n th coefficient in the expansion of $f(x)$ is

$$c_n = \int \psi_n(x)^* f(x) dx \quad (2.34)$$

Completeness holds for all the potentials you are likely to encounter, but the proofs tend to be nasty and laborious.

The stationary states (2.19) of the infinite square well are evidently

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t} \quad (2.35)$$

I claimed (2.18) that the most general solution to the (time-dependent) Schrodinger equation is a linear combinations of stationary states:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t} \quad (2.36)$$

It remains only for me to demonstrate that I can fit any prescribed initial wave function, $\Psi(x, 0)$, by appropriate choice of the coefficients c_n :

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

The completeness of the ψ 's guarantees that I can always express $\Psi(x, 0)$ in this way, and their orthonormality licenses the use of Fourier's trick to determine the actual coefficients:

$$c_n = \sqrt{\frac{2}{a}} \int_a^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0) dx \quad (2.37)$$

That does it: Given the initial wave function, $\Psi(x, 0)$, we first compute the expansion coefficients c_n using (2.37), and then plug these into (2.36) to obtain $\Psi(x, t)$.