

Chapter 10

Stationary states

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Stationary states are separable solutions of the Schrödinger equation that have a simple time dependence and represent energy eigenstates obtained by solving the time-independent equation $\hat{H}\psi = E\psi$. The expectation value of any time-independent Hermitian operator on a stationary state is time independent. When solving for energy eigenstates of a particle in a potential we assume that ψ and its spatial derivative ψ' are continuous unless the potential has delta functions or hard walls in which cases ψ' is discontinuous. We study the energy and momentum eigenstates of a free particle moving on a circle.

10.1 Stationary states

Stationary states are class of simple and useful solutions of the Schrödinger equation. They give us intuition and help us build such general solutions of this equation. Stationary states have time dependence, but this dependence is so simple that in such states observables are in fact time-independent. For the case of a particle moving in a potential, stationary states exist if the potential is time independent.

Let us therefore consider the Schrödinger equation for the wavefunction $\Psi(x, t)$ with the assumption that the potential energy is time independent and thus written as $V(x)$:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \Psi(x, t). \quad (10.1.1)$$

The signature property of a stationary state is that the position and the time dependence of the wavefunction factorize, which means that

$$\Psi(x, t) = g(t) \psi(x), \quad (10.1.2)$$

for some function g depending only on time and a function ψ depending only on position. To see if this ansatz for Ψ is possible we substitute it in the Schrödinger equation. We then

find

$$\left(i\hbar \frac{dg(t)}{dt}\right) \psi(x) = g(t) \hat{H} \psi(x), \quad (10.1.3)$$

because $g(t)$ can be moved across \hat{H} . We can then divide this equation by $\Psi(x, t) = g(t)\psi(x)$ to obtain

$$i\hbar \frac{1}{g(t)} \frac{dg(t)}{dt} = \frac{1}{\psi(x)} \hat{H} \psi(x). \quad (10.1.4)$$

The left-hand side is manifestly a function of t only, while the right-hand side is a function of x only because \hat{H} contains no time dependent potential. Moreover each side has units of energy: the left-hand side because it has units of \hbar over time, and the right-hand side because it has the units of \hat{H} . The only way the two sides can equal each other for all values of t and x is for both sides to be equal to a *constant* E with units of energy. We therefore get two separate equations. The first equation, from the left-hand side, reads

$$i\hbar \frac{dg}{dt} = E g. \quad (10.1.5)$$

This is solved by

$$g(t) = e^{-iEt/\hbar}, \quad (10.1.6)$$

and the most general solution is simply a constant times the above right-hand side. The second equation, from the x -dependent side of the equality is

$$\boxed{\hat{H} \psi(x) = E \psi(x).} \quad (10.1.7)$$

This equation is an eigenvalue equation for the Hermitian operator \hat{H} . We showed that the eigenvalues of Hermitian operators must be real, thus the constant E **must be real**. The equation above is called the **time-independent Schrödinger equation**. More explicitly it reads

$$\boxed{\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right) \psi(x) = E \psi(x),} \quad (10.1.8)$$

Note that this equation does not determine the overall normalization of ψ : if some ψ is a solution, so is $a\psi$ with a a constant. Therefore we can write the full solution without loss of generality using the $g(t)$ given above:

$$\boxed{\text{Stationary state: } \Psi(x, t) = e^{-iEt/\hbar} \psi(x), \quad \text{with } E \in \mathbb{R} \text{ and } \hat{H} \psi = E \psi.} \quad (10.1.9)$$

It is interesting to note that not only is $\psi(x)$ an eigenstate of the Hamiltonian operator \hat{H} , the full stationary state is also an \hat{H} eigenstate

$$\hat{H} \Psi(x, t) = E \Psi(x, t), \quad (10.1.10)$$

since the time dependent function in Ψ cancels out.

We have noted that the energy E must be real. If it was not, we would not be able to normalize the stationary state consistently. The normalization condition for Ψ , if E is not real, would give

$$\begin{aligned} 1 &= \int dx \Psi^*(x, t) \Psi(x, t) = \int dx e^{iE^*t/\hbar} e^{-iEt/\hbar} \psi^*(x) \psi(x) \\ &= e^{i(E^*-E)t/\hbar} \int dx \psi^*(x) \psi(x) = e^{2\text{Im}(E)t/\hbar} \int dx \psi^*(x) \psi(x). \end{aligned} \quad (10.1.11)$$

The final expression has a time dependence due to the exponential. On the other hand the normalization condition states that this expression must be equal to one. It follows that the exponent must be zero, i.e., E is real. Given this, we also see that the normalization condition yields

$$\boxed{\int_{-\infty}^{\infty} dx \psi^*(x) \psi(x) = 1.} \quad (10.1.12)$$

The energy eigenvalue E is in fact the expectation value of \hat{H} on the state Ψ :

$$\begin{aligned} \langle \hat{H} \rangle_{\Psi} &= \int dx \Psi^*(x, t) \hat{H} \Psi(x, t) \\ &= \int dx \Psi^*(x, t) E \Psi(x, t) = E \int dx \Psi^*(x, t) \Psi(x, t) = E. \end{aligned} \quad (10.1.13)$$

Since the stationary state is an eigenstate of \hat{H} , the uncertainty $\Delta \hat{H}$ of the Hamiltonian in a stationary state is zero (recall (9.3.14)). If we measure the energy of a stationary state the result is always the energy eigenvalue E . Stationary states are energy eigenstates.

There are two important observations on stationary states:

- (1) The expectation value of any time-independent operator \hat{Q} on a stationary state Ψ is time-independent:

$$\langle \hat{Q} \rangle_{\Psi(x, t)} = \int dx \Psi^*(x, t) \hat{Q} \Psi(x, t) = \int dx e^{iEt/\hbar} \psi^*(x) \hat{Q} e^{-iEt/\hbar} \psi(x). \quad (10.1.14)$$

Since any time-dependent function can be moved across \hat{Q} , the two time-dependent exponentials now cancel and we find

$$\langle \hat{Q} \rangle_{\Psi(x, t)} = \int dx \psi^*(x) \hat{Q} \psi(x) = \langle \hat{Q} \rangle_{\psi(x)}, \quad (10.1.15)$$

which is manifestly time independent.

- (2) The superposition of stationary states with different energies is not stationary. This is clear because a stationary state is a product of a function of time and a function of position: two such states with different energies have different functions of time and the sum state cannot be written as a product of a function of time and a function of position. We now show that a time-independent observable \hat{Q} may have a time-dependent expectation value in such a state. Consider a superposition

$$\Psi(x, t) = c_1 e^{-iE_1 t/\hbar} \psi_1(x) + c_2 e^{-iE_2 t/\hbar} \psi_2(x), \quad (10.1.16)$$

where ψ_1 and ψ_2 are \hat{H} eigenstates with energies E_1 and E_2 , respectively. Consider a Hermitian operator \hat{Q} . With the system in state (10.1.16), its expectation value is

$$\begin{aligned} \langle \hat{Q} \rangle_\Psi &= \int_{-\infty}^{\infty} dx \Psi^*(x, t) \hat{Q} \Psi(x, t) \\ &= \int_{-\infty}^{\infty} dx (c_1^* e^{iE_1 t/\hbar} \psi_1^*(x) + c_2^* e^{iE_2 t/\hbar} \psi_2^*(x)) \\ &\quad (c_1 e^{-iE_1 t/\hbar} \hat{Q} \psi_1(x) + c_2 e^{-iE_2 t/\hbar} \hat{Q} \psi_2(x)) \\ &= \int_{-\infty}^{\infty} dx \left(|c_1|^2 \psi_1^* \hat{Q} \psi_1 + |c_2|^2 \psi_2^* \hat{Q} \psi_2 \right. \\ &\quad \left. + c_1^* c_2 e^{i(E_1 - E_2)t/\hbar} \psi_1^* \hat{Q} \psi_2 + c_2^* c_1 e^{-i(E_1 - E_2)t/\hbar} \psi_2^* \hat{Q} \psi_1 \right). \end{aligned} \quad (10.1.17)$$

The first two terms on the last right-hand side are time-independent expectation values; the time dependence arises from the last two terms. Using the hermiticity of \hat{Q} in the last term we then get

$$\begin{aligned} \langle Q \rangle_\Psi &= |c_1|^2 \langle Q \rangle_{\psi_1} + |c_2|^2 \langle Q \rangle_{\psi_2} \\ &\quad + c_1^* c_2 e^{i(E_1 - E_2)t/\hbar} \int_{-\infty}^{\infty} dx \psi_1^* \hat{Q} \psi_2 + c_1 c_2^* e^{-i(E_1 - E_2)t/\hbar} \int_{-\infty}^{\infty} dx \psi_1 (\hat{Q} \psi_2)^*. \end{aligned} \quad (10.1.18)$$

The last two terms are complex conjugates of each other and therefore

$$\langle Q \rangle_\Psi = |c_1|^2 \langle Q \rangle_{\psi_1} + |c_2|^2 \langle Q \rangle_{\psi_2} + 2 \operatorname{Re} \left[c_1^* c_2 e^{i(E_1 - E_2)t/\hbar} \int_{-\infty}^{\infty} dx \psi_1^* \hat{Q} \psi_2 \right]. \quad (10.1.19)$$

This expectation value is indeed time-dependent if $E_1 \neq E_2$ and $(\psi_1, \hat{Q} \psi_2)$ is nonzero. The expectation value $\langle Q \rangle_\Psi$ is real, as it must be for any Hermitian operator.

10.2 Solving for energy eigenstates

The time dependence of a stationary state, or energy eigenstate, is always a simple $e^{-iEt/\hbar}$, where E is the value of the energy. The the space dependence is harder to obtain and it is constrained by the time-independent Schrödinger equation

$$\hat{H} \psi(x) = E \psi(x). \quad (10.2.1)$$

For a given Hamiltonian \hat{H} we are interested in finding the eigenstates ψ and the eigenvalues E , which are corresponding energies. Perhaps the most interesting feature of the above equation is that it determines the allowed values of E . Just like finite-size matrices have a set of eigenvalues, the above, time-independent Schrödinger equation may have a discrete set of possible energies. A continuous set of possible energies is often allowed as well. Indeed, for any given potential there are many solutions of the above equation.

The set of energies that are solutions of the time-independent Schrödinger equation is called the **energy spectrum** of the theory. The name ‘spectrum’ is appropriate, as an energy eigenstate is associated to a time-dependent exponential with frequency $\omega = E/\hbar$. (More generally, one speaks of the ‘spectrum’ of any Hermitian operator as the set of its eigenvalues.) Assuming for convenience that the eigenstates and their energies can be counted we write

$$\begin{array}{ll} \psi_1(x), & E_1 \\ \psi_2(x), & E_2 \\ \vdots & \vdots \end{array} \quad (10.2.2)$$

Our discussion of Hermitian operators applies here. In particular, the energy eigenstates can be organized to form a *complete set of orthonormal functions*:

$$\int_{-\infty}^{\infty} dx \psi_i^*(x) \psi_j(x) = \delta_{ij}. \quad (10.2.3)$$

We now wish to understand some general features of the spatial dependence $\psi(x)$ of energy eigenstates. For this consider the time-independent Schrödinger equation written as

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(E - V(x))\psi. \quad (10.2.4)$$

The solutions $\psi(x)$ depend on the properties of the potential $V(x)$. It is difficult to make general statements about the wavefunction unless we restrict the types of potentials. We will certainly consider continuous potentials. We also consider potentials that are not continuous but are piece-wise continuous, that is, they have a number of discontinuities. Our potentials can easily fail to be bounded, as is the case for the harmonic oscillator potential $V(x) \sim x^2$, which becomes infinite as $|x| \rightarrow \infty$. We allow delta functions in one-dimensional potentials but do not consider powers or derivatives of delta functions. We allow for potentials that become plus infinity beyond certain points. These points represent hard walls because no finite amount of kinetic energy allows a particle to enter a region of infinite potential energy.

To make our discussion a bit more precise we define finite discontinuities. We say that a function $f(x)$ has a discontinuity at $x = a$ if the quantity $\Delta_a f(x)$ defined below is a finite, non-zero number:

$$\Delta_a f(x) \equiv \lim_{\epsilon \rightarrow 0} (f|_{a+\epsilon} - f|_{a-\epsilon}). \quad (10.2.5)$$

Here $f|_c$ denotes $f(c)$. This is intuitively clear: a function is discontinuous at $x = a$ if it reaches different values as the point $x = a$ is approached from the right and from the

left. It is also true that the product of continuous functions is continuous. The product of a continuous function with a finitely discontinuous function is a finitely discontinuous function.

Claim: The wavefunction must be continuous at all points. If ψ is not continuous it must be discontinuous. Assume ψ has finite discontinuities. Then ψ' contains delta-functions and ψ'' in the left-hand of (10.2.4) contains derivatives of delta functions. This would require the right-hand side to have derivatives of delta functions, and those would have to appear in the potential since ψ is at worst finitely discontinuous. Having declared that our potentials contain no derivatives of delta functions we reach the conclusion that ψ cannot contain finite discontinuities. Worse discontinuities would lead to similar problems. We must indeed have a continuous ψ . The precise mathematical definition of continuity implies that a function fails to be continuous at points where it takes infinite value. In fact, we find it physically consistent to assume that *our wavefunctions take finite values at all points.*

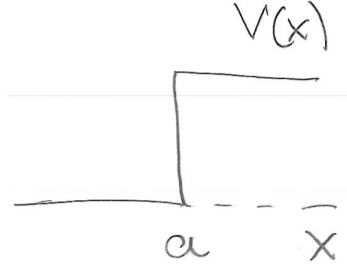
Consider now four possibilities concerning the potential:

- (1) $V(x)$ is continuous. In this case the continuity of $\psi(x)$ implies that ψ'' , given by the right-hand side of (10.2.4), is also continuous. If ψ'' is continuous, ψ' must also be continuous.
- (2) $V(x)$ has finite discontinuities. In this case ψ'' has finite discontinuities because, by (10.2.4) it includes the product of a continuous ψ against a finitely discontinuous V . But then $\psi' \sim \int \psi''$ must be continuous, because the integral of a function with finite discontinuities is continuous.
- (3) $V(x)$ contains delta functions. In this case ψ'' also contains delta functions as it includes the product of a continuous ψ and a delta function in V . With ψ'' having delta functions, $\psi' \sim \int \psi''$ must have finite discontinuities because the integral of a function that includes delta functions has finite discontinuities.
- (4) $V(x)$ contains a hard wall. A potential that is finite immediately to the left of $x = a$ and becomes infinite for $x > a$ is said to have a hard wall at $x = a$. In such a case, the wavefunction will vanish for $x \geq a$. The slope ψ' will be finite as $x \rightarrow a$ from the left, and will vanish for $x > a$. Thus ψ' is discontinuous at the wall.

In the first two cases ψ' is continuous, and in the second two it can have a finite discontinuity. In conclusion, we have obtained the following conditions

Both ψ and ψ' are continuous unless the potential has delta functions or hard walls in which cases ψ' may have finite discontinuities.	(10.2.6)
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Let us give a slightly different argument for the continuity of ψ and $\frac{d\psi}{dx}$ in the case of a potential with a finite discontinuity, such as the step potential shown in Fig. 10.1. For this

Figure 10.1: A potential $V(x)$ with a finite discontinuity at $x = a$.

purpose integrate both sides of (10.2.4) from $a - \epsilon$ to $a + \epsilon$ to find

$$\int_{a-\epsilon}^{a+\epsilon} dx \frac{d}{dx} \left(\frac{d\psi}{dx} \right) = -\frac{2m}{\hbar^2} \int_{a-\epsilon}^{a+\epsilon} dx (E - V(x))\psi(x). \quad (10.2.7)$$

The left-hand side integrand is a total derivative so we have

$$\left. \frac{d\psi}{dx} \right|_{a+\epsilon} - \left. \frac{d\psi}{dx} \right|_{a-\epsilon} = -\frac{2m}{\hbar^2} \int_{a-\epsilon}^{a+\epsilon} dx (E - V(x))\psi(x). \quad (10.2.8)$$

Taking now the limit as ϵ goes to zero, the left-hand side becomes the discontinuity in the derivative of ψ at $x = a$ so that we get

$$\Delta_a \left(\frac{d\psi}{dx} \right) = -\lim_{\epsilon \rightarrow 0} \frac{2m}{\hbar^2} \int_{a-\epsilon}^{a+\epsilon} dx (E - V(x))\psi(x). \quad (10.2.9)$$

The potential V is discontinuous but bounded about $x = a$, the wavefunction ψ is also bounded and, of course, E is assumed finite. As the integral range becomes vanishingly small about $x = a$ the integrand remains finite and therefore the integral goes to zero. We thus have

$$\Delta_a \left(\frac{d\psi}{dx} \right) = 0. \quad (10.2.10)$$

There is no discontinuity in $d\psi/dx$. This is as stated in (10.2.6).

To learn about the behavior of ψ we reconsider the integration that led to (10.2.8) but now applied to the range from $x_0 < a$ to $x > a$ yields

$$\frac{d\psi(x)}{dx} = \left. \frac{d\psi}{dx} \right|_{x_0} - \frac{2m}{\hbar} \int_{x_0}^x (E - V(x'))\psi(x')dx'. \quad (10.2.11)$$

Note that the integral on the right-hand side

$$h(x) \equiv \int_{x_0}^x (E - V(x'))\psi(x')dx', \quad (10.2.12)$$

is a bounded function of x . We now integrate (10.2.11) from $a - \epsilon$ to $a + \epsilon$. Since the first term on the right-hand side is a constant we find

$$\psi(a + \epsilon) - \psi(a - \epsilon) = 2\epsilon \left. \frac{d\psi}{dx} \right|_{x_0} - \frac{2m}{\hbar} \int_{a-\epsilon}^{a+\epsilon} dx h(x). \quad (10.2.13)$$

Taking the $\epsilon \rightarrow 0$ limit, the first term on the right-hand side clearly vanishes and the second term goes to zero because $h(x)$ is a bounded function of x . As a result we have

$$\Delta_a \psi = 0, \quad (10.2.14)$$

showing that, as expected, the wavefunction is continuous at $x = a$.

10.3 Free particle on a circle; a second look

Consider again the problem of a particle confined to a circle of circumference L . The coordinate along the circle is called x and, as discussed before, we can view the circle as the full real line x with the identification

$$x \sim x + L. \quad (10.3.1)$$

This means that two points whose coordinates are related in this way are to be considered **the same point**. The energy eigenstates must satisfy the periodicity condition

$$\psi(x + L) = \psi(x). \quad (10.3.2)$$

From this it follows that not only $\psi(x)$ is periodic but all of its derivatives are also periodic. The periodicity of an energy eigenstate $\psi(x)$ implies that its time-dependent version, obtained by multiplication by $\exp(-iEt/\hbar)$, with E its energy, is also periodic in x .

Let us consider the case when there is no potential on the circle, $V(x) = 0$, and the particle is thus free. The time-independent Schrödinger equation is then

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi(x). \quad (10.3.3)$$

We want to find the allowed values of E and the corresponding wavefunctions. The ground state energy is the lowest value of E for which we can find a solution. Let us first demonstrate, without solving the equation, that any solution must have $E \geq 0$. For this multiply the above equation by $\psi^*(x)$ and integrate over the circle $x \in [0, L)$. Since ψ is normalized we get

$$-\frac{\hbar^2}{2m} \int_0^L \psi^*(x) \frac{d^2\psi}{dx^2} dx = E \int \psi^*(x) \psi(x) dx = E. \quad (10.3.4)$$

A rewriting of the left-hand side gives the equation

$$-\frac{\hbar^2}{2m} \int_0^L \left[\frac{d}{dx} \left(\psi^* \frac{d\psi}{dx} \right) - \frac{d\psi^*}{dx} \frac{d\psi}{dx} \right] dx = E. \quad (10.3.5)$$

The total derivative can be integrated and we find

$$-\frac{\hbar^2}{2m} \left[\left(\psi^* \frac{d\psi}{dx} \right) \Big|_{x=L} - \left(\psi^* \frac{d\psi}{dx} \right) \Big|_{x=0} \right] + \frac{\hbar^2}{2m} \int_0^L \left| \frac{d\psi}{dx} \right|^2 dx = E. \quad (10.3.6)$$

Since $\psi(x)$ and its derivatives are periodic, the contributions from $x = L$ and $x = 0$ cancel out and we are left with

$$E = \frac{\hbar^2}{2m} \int_0^L \left| \frac{d\psi}{dx} \right|^2 dx \geq 0, \quad (10.3.7)$$

which establishes our claim. We also see that the lowest possible energy is $E = 0$ and requires a vanishing integrand and therefore a wavefunction with zero derivative all along the circle. Such wavefunction is a constant that cannot be zero, because a zero solution represents no particle and is inconsistent. Thus a constant non-zero wavefunction represents the ground state of the particle on the circle!

Having shown that all solutions must have $E \geq 0$ let us go back to the Schrödinger equation, which can be rewritten as

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi. \quad (10.3.8)$$

We can then define k via

$$k^2 \equiv \frac{2mE}{\hbar^2} \geq 0. \quad (10.3.9)$$

Since $E \geq 0$, the constant k is real and $k \in (-\infty, \infty)$. Note that this definition is very natural, since it makes

$$E = \frac{\hbar^2 k^2}{2m}, \quad (10.3.10)$$

which means that, as usual, $p = \hbar k$. Using k instead of E the differential equation takes the familiar form

$$\frac{d^2\psi}{dx^2} = -k^2 \psi. \quad (10.3.11)$$

Each solution of this equation is an energy eigenstate. We can write the general solution in terms of sines and cosines of kx , or complex exponentials of kx . Let's consider a solution defined by a complex exponential:

$$\psi(x) \sim e^{ikx}. \quad (10.3.12)$$

This solves the differential equation and therefore it is an energy eigenstate, but it is also a momentum eigenstate! In fact, it has momentum $\hbar k$. Since (10.3.11) is a second order differential equation we have two solutions, e^{ikx} and e^{-ikx} . It is convenient, however, to consider them separately, since each is a momentum eigenstate, but any superposition of them is not.

The periodicity condition (10.3.2) applied to the above $\psi(x)$ requires

$$e^{ik(x+L)} = e^{ikx} \quad \rightarrow \quad e^{ikL} = 1 \quad \rightarrow \quad kL = 2\pi n, \quad n \in \mathbb{Z}. \quad (10.3.13)$$

The wavenumber is quantized and therefore momentum is quantized! The wavenumber has discrete values

$$k_n \equiv \frac{2\pi n}{L}, \quad n \in \mathbb{Z}. \quad (10.3.14)$$

All integers, positive, negative, and zero, are allowed and are in fact necessary because they all correspond to *different* values of the momentum $p_n = \hbar k_n$. The solutions to the Schrödinger equation can then be indexed by the integer n :

$$\psi_n(x) = N e^{ik_n x}, \quad (10.3.15)$$

where N is a real normalization constant whose value is determined from

$$1 = \int_0^L \psi_n^*(x) \psi_n(x) dx = \int_0^L N^2 dx = N^2 L \rightarrow N = \frac{1}{\sqrt{L}}. \quad (10.3.16)$$

Our normalized energy *and* momentum eigenstates thus take the form

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{L}} e^{ik_n x} = \frac{1}{\sqrt{L}} e^{\frac{2\pi i n x}{L}}, \quad n \in \mathbb{Z}.} \quad (10.3.17)$$

The associated energies and momenta are

$$\begin{aligned} E_n &= \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 4\pi^2 n^2}{2mL^2} = 2\pi^2 n^2 \frac{\hbar^2}{mL^2}, \\ p_n &= \hbar k_n = 2\pi n \frac{\hbar}{L}. \end{aligned} \quad (10.3.18)$$

The ground state is obtained for $n = 0$ and, as anticipated, $\psi_0 = 1/\sqrt{L}$ is just a constant. The ground state has zero energy and zero momentum. There are infinitely many energy eigenstates. The energy spectrum has degeneracies because E_n is just a function of n^2 and thus both ψ_n and ψ_{-n} have energy E_n . The only nondegenerate eigenstate is the ground state ψ_0 .

Whenever we find degenerate energy eigenstates we must wonder what makes those states different, given that they have the same energy. To answer this one must find an observable that takes different values on the states. Happily, in our case we know the answer. Our degenerate energy eigenstates can be distinguished by their momentum: ψ_n has momentum $2\pi n\hbar/L$ and ψ_{-n} has momentum $(-2\pi n\hbar/L)$. Note that the spectrum of the Hermitian operator \hat{p} is non-degenerate: there is one and only one state for each possible momentum eigenvalue.

We noted when discussing stationary states that the superposition of energy eigenstates with different energies is not an energy eigenstate. The situation changes if we have degenerate eigenstates. Given two degenerate energy eigenstates, *any* linear combination of these states is an eigenstate with the same energy. Indeed if ψ_1 and ψ_2 are degenerate

$$\hat{H}\psi_1 = E\psi_1, \quad \hat{H}\psi_2 = E\psi_2, \quad (10.3.19)$$

then $a\psi_1 + b\psi_2$, with a and b arbitrary complex constants, is also a state of energy E :

$$\hat{H}(a\psi_1 + b\psi_2) = a\hat{H}\psi_1 + b\hat{H}\psi_2 = aE\psi_1 + bE\psi_2 = E(a\psi_1 + b\psi_2). \quad (10.3.20)$$

We can therefore form two linear combinations of the degenerate eigenstates ψ_n and ψ_{-n} to obtain another description of the normalized energy eigenstates for $n \neq 0$:

$$\begin{aligned} \frac{1}{\sqrt{2}}(\psi_n + \psi_{-n}) &= \sqrt{\frac{2}{L}} \cos(k_n x), \\ \frac{1}{i\sqrt{2}}(\psi_n - \psi_{-n}) &= \sqrt{\frac{2}{L}} \sin(k_n x). \end{aligned} \quad (10.3.21)$$

While these energy eigenstates are real functions on the circle, they are not momentum eigenstates. Only our exponentials are simultaneous eigenstates of both \hat{H} and \hat{p} .

We have learned that eigenstates of Hermitian operators with different eigenvalues are orthogonal. The energy eigenstates ψ_n are *orthonormal* since they are all normalized and they are eigenstates of the Hermitian operator \hat{p} with no degeneracies. Indeed, we easily verify that:

$$\int_0^L \psi_n^*(x) \psi_m(x) dx = \frac{1}{L} \int_0^L e^{\frac{2\pi i(m-n)x}{L}} dx = \delta_{mn}. \quad (10.3.22)$$

The energy eigenstates are also complete: we can construct a general wavefunction as a superposition that is in fact a Fourier series! For any $\Psi(x, 0)$ that satisfies the periodicity condition, we can write

$$\Psi(x, 0) = \sum_{n \in \mathbb{Z}} a_n \psi_n(x), \quad (10.3.23)$$

where, as you should check, the coefficients a_n are determined by the integrals

$$a_n = \int_0^L dx \psi_n^*(x) \Psi(x, 0). \quad (10.3.24)$$

The initial state $\Psi(x, 0)$ is then easily evolved in time:

$$\Psi(x, t) = \sum_{n \in \mathbb{Z}} a_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}}. \quad (10.3.25)$$

Let us discuss an interesting subtlety of the problem of a particle on a circle. We have dealt with the momentum operator \hat{p} and its eigenstates. How about the position operator \hat{x} ? Perhaps surprisingly, the position operator is not well defined! The problem arises because of the identification $x \sim x + L$ that defines the circle. The coordinate of each point on the circle is ambiguous up to additive multiples of L . If we try to fix this ambiguity by declaring that the coordinate on the circle is $x \in [0, L]$ then the result is a discontinuity in

the coordinate as we reach $x = L$, which is equivalent to $x = 0$. Alternatively, if we tried to define the operator \hat{x} via

$$\hat{x}\psi(x) \equiv x\psi(x)? \quad (10.3.26)$$

we still have problems: while $\psi(x)$ is assumed to be periodic to be well-defined on the circle, $x\psi(x)$ is not periodic. The \hat{x} operator acting on any legal state does not give a legal state. All is not lost, however. We can define a series of operators \hat{Q}_n

$$\hat{Q}_n \equiv \exp\left(\frac{2\pi i n \hat{x}}{L}\right), \quad (10.3.27)$$

that are well defined because they are unchanged under the replacement $\hat{x} \rightarrow \hat{x} + L$. Acting on wavefunctions

$$\hat{Q}_n \psi(x) = e^{2\pi i n x/L} \psi(x), \quad (10.3.28)$$

we do not spoil the periodicity condition and thus have a well-defined action. The famous commutator $[\hat{x}, \hat{p}] = i\hbar$ that we derived for quantum mechanics on the full real line, does not hold anymore, since \hat{x} is not a well defined operator on the circle.