1 Stationary States

Consider the Schrödinger equation for the wavefunction $\Psi(x,t)$ with the assumption that the potential energy $V$ is time independent:

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

(1.1)

where we displayed the form of the Hamiltonian operator $\hat{H}$ with the time independent potential $V(x)$. Stationary states are a very useful class of solutions of this differential equation. The signature property of a stationary state is that the position and the time dependence of the wavefunction factorize. Namely,

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

(1.2)

for some functions $g$ and $\psi$. For such a separable solution to exist we need the potential to be time independent, as we will see below. The solution $\Psi(x,t)$ is time-dependent but it is called stationary because of a property of observables. The expectation value of observables with no explicit time dependence in arbitrary states has time dependence. On a stationary state they do not have time dependence, as we will demonstrate.

Let us use the ansatz (1.2) for $\Psi$ in the Schrödinger equation. We then find

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

(1.3)

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

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

(1.4)

The left side is a function of only $t$, while the right side is a function of only $x$ (a time dependent potential would have spoiled this). 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 because $\hat{H}$ has units of energy. We therefore get two separate equations. The first reads

$$i\hbar \frac{dg}{dt} = Eg.$$  

(1.5)

This is solved by

\[ g(t) = e^{-iEt/\hbar}, \]  

and the most general solution is simply a constant times the above right-hand side. From the \( x \)-dependent side of the equality we get

\[ \hat{H}\psi(x) = E\psi(x). \]  

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

\[ \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right) \psi(x) = E\psi(x), \]  

Note that this equation does not determine the overall normalization of \( \psi \). Therefore we can write the full solution without loss of generality using the \( g(t) \) given above:

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

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

\[ \hat{H}\Psi(x,t) = E\Psi(x,t), \]  

since the time dependent function in \( \Psi \) cancels out.

We have noted that the energy \( E \) must be real. If it was not we would also have trouble normalizing the stationary state consistently. The normalization condition for \( \Psi \), if \( E \) is not real, would give

\[ 1 = \int dx \Psi^*(x,t)\Psi(x,t) = \int dx e^{iE* t/\hbar} e^{-iEt/\hbar} \psi^*(x)\psi(x) \]

\[ = e^{i(E^* - E)t/\hbar} \int dx \psi^*(x)\psi(x) = e^{2\text{Im}(E)t/\hbar} \int dx \psi^*(x)\psi(x). \]  

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

\[ \int_{-\infty}^{\infty} dx \psi^*(x)\psi(x) = 1. \]  

How do we interpret the eigenvalue \( E \)? Using (1.10) we see that the expectation value of \( \hat{H} \) on the state \( \Psi \) is indeed the energy

\[ \langle \hat{H} \rangle_\Psi = \int dx \Psi^*(x,t)\hat{H}\Psi(x,t) = \int dx \Psi^*(x,t)E\Psi(x,t) = E \int dx \Psi^*(x,t)\Psi(x,t) = E, \]  

Since the stationary state is an eigenstate of \( \hat{H} \), the uncertainty \( \Delta\hat{H} \) of the Hamiltonian in a stationary state is zero.

There are two important observations on stationary states:
1. The expectation value of any time-independent operator $\hat{Q}$ on a stationary state $\Psi$ is time-independent:

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

(1.14)

since the last expectation value is manifestly time independent.

2. The superposition of stationary states with different energies is not stationary. This is clear because a stationary state requires a factorized solution of the Schrödinger equation: if we add two factorized solutions with different energies they will have different time dependence and the total state cannot be factorized. We now show that that a time-independent observable $\hat{Q}$ may have a time-dependent expectation values in such a state. Consider a superposition

\[
\Psi(x,t) = c_1 e^{-iE_1t/\hbar}\psi_1(x) + c_2 e^{-iE_2t/\hbar}\psi_2(x),
\]

(1.15)

where $\psi_1$ and $\psi_2$ are $\hat{H}$ eigenstates with energies $E_1$ and $E_2$, respectively. Consider a Hermitian operator $\hat{Q}$. With the system in state (1.15), its expectation value is

\[
\langle Q \rangle_{\Psi} = \int_{-\infty}^{\infty} dx \Psi^*(x,t)\hat{Q}\Psi(x,t)
\]

\[
= \int_{-\infty}^{\infty} dx \left(c_1^* e^{iE_1t/\hbar}\psi_1^*(x) + c_2^* e^{iE_2t/\hbar}\psi_2^*(x)\right)\left(c_1 e^{-iE_1t/\hbar}\hat{Q}\psi_1(x) + c_2 e^{-iE_2t/\hbar}\hat{Q}\psi_2(x)\right)
\]

\[
= \int_{-\infty}^{\infty} dx \left(|c_1|^2\psi_1^*\hat{Q}\psi_1 + |c_2|^2\psi_2^*\hat{Q}\psi_2 + c_1^* c_2 e^{i(E_1-E_2)t/\hbar}\psi_1^*\hat{Q}\psi_2 + c_2^* c_1 e^{-i(E_1-E_2)t/\hbar}\psi_2^*\hat{Q}\psi_1\right)
\]

(1.16)

We now see the possible time dependence arising from the cross terms. The first two terms are simple time-independent expectation values. Using the hermiticity of $\hat{Q}$ in the last term we then get

\[
\langle Q \rangle_{\Psi} = |c_1|^2\langle Q \rangle_{\psi_1} + |c_2|^2\langle Q \rangle_{\psi_2}
\]

\[
+ c_1^* c_2 e^{i(E_1-E_2)t/\hbar}\int_{-\infty}^{\infty} dx \psi_1^*\hat{Q}\psi_2 + c_2^* c_1 e^{-i(E_1-E_2)t/\hbar}\int_{-\infty}^{\infty} dx \psi_1(\hat{Q}\psi_2)^*
\]

(1.17)

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

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

(1.18)

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

2 Solving for Energy Eigenstates

We will now study solutions to the time-independent Schrödinger equation

\[
\hat{H}\psi(x) = E\psi(x).
\]

(2.19)
For a given Hamiltonian $\hat{H}$ we are interested in finding the eigenstates $\psi$ and the eigenvalues $E$, which happen to be the corresponding energies. Perhaps the most interesting feature of the above equation is that generally the value of $E$ cannot be arbitrary. 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 also allowed and sometimes important. There are indeed many solutions for any given potential. Assuming for convenience that the eigenstates and their energies can be counted we write

$$
\begin{align*}
\psi_1(x), & \quad E_1 \\
\psi_2(x), & \quad E_2 \\
\vdots & \quad \vdots
\end{align*}
$$

(2.20)

Our earlier discussion of Hermitian operators applies here. The energy eigenstates can be organized to form a complete set of orthonormal functions:

$$
\int \psi_i^*(x)\psi_j(x) = \delta_{ij}.
$$

(2.21)

Consider the time-independent Schrödinger equation written as

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

(2.22)

The solutions $\psi(x)$ depend on the properties of the potential $V(x)$. It is hard 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. 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.

We want to understand general properties of $\psi$ and the behavior of $\psi$ at points where the potential $V(x)$ may have discontinuities or other singularities. We claim: we must have a continuous wavefunction. If $\psi$ is discontinuous then $\psi'$ contains delta-functions and $\psi''$ in the above left-hand side 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 we have declared that our potentials contain no derivatives of delta functions we must indeed have a continuous $\psi$.

Consider now four possibilities concerning the potential:

1. $V(x)$ is continuous. In this case the continuity of $\psi(x)$ and (2.22) imply $\psi''$ is also continuous. This requires $\psi'$ continuous.

2. $V(x)$ has finite discontinuities. In this case $\psi''$ has finite discontinuities: it includes the product of a continuous $\psi$ against a discontinuous $V$. But then $\psi'$ must be continuous, with non-continuous derivative.

3. $V(x)$ contains delta functions. In this case $\psi''$ also contains delta functions: it is proportional to the product of a continuous $\psi$ and a delta function in $V$. Thus $\psi'$ 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 \( \psi' \) will be finite as \( x \to a \) from the left, and will vanish for \( x > a \). Thus \( \psi' \) is discontinuous at the wall.

In the first two cases \( \psi' \) is continuous, and in the second two it can have a finite discontinuity. In conclusion

| Both \( \psi \) and \( \psi' \) are continuous unless the potential has delta functions or hard walls in which cases \( \psi' \) may have finite discontinuities. |

(2.23)

Let us give a slightly different argument for the continuity of \( \psi \) and \( \frac{d\psi}{dx} \) in the case of a potential with a finite discontinuity, such as the step shown in Fig. 1.

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

(2.24)

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

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

(2.25)

By definition, the discontinuity in the derivative of \( \psi \) at \( x = a \) is the limit as \( \epsilon \to 0 \) of the left-hand side:

\[ \Delta_a \left( \frac{d\psi}{dx} \right) = \lim_{\epsilon \to 0} \left( \frac{d\psi}{dx} \bigg|_{a+\epsilon} - \frac{d\psi}{dx} \bigg|_{a-\epsilon} \right). \]  

(2.26)

Back in (2.25) we then have

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

(2.27)

The potential \( V \) is discontinuous but not infinite around \( x = a \), nor is \( \psi \) infinite around \( x = a \) and, of course, \( E \) is assumed finite. As the integral range becomes vanishingly small about \( x = a \) the integrand remains finite and the integral goes to zero. We thus have

\[ \Delta_a \left( \frac{d\psi}{dx} \right) = 0. \]  

(2.28)
There is no discontinuity in $\frac{d\psi}{dx}$. This gives us one of our boundary conditions.

To learn about the continuity of $\psi$ we reconsider the first integral of the differential equation. The integration that led to (2.25) now applied to the range from $x_0 < a$ to $x$ yields

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

(2.29)

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

$$\psi(a + \epsilon) - \psi(a - \epsilon) = 2\epsilon \frac{d\psi}{dx} \bigg|_{x_0} - \frac{2m}{\hbar} \int_{a-\epsilon}^{a+\epsilon} dx \int_{x_0}^{x} (E - V(x')).$$

(2.30)

Taking the $\epsilon \to 0$ limit, the first term on the right-hand side clearly vanishes and the second term goes to zero because $\int_{x_0}^{x} (E - V(x'))$ is a bounded function of $x$. As a result we have

$$\Delta_a \psi = 0,$$

(2.31)

showing that the wavefunction is continuous at $x = a$. This is our second boundary condition.

3 Free particle on a circle.

Consider now the problem of a particle confined to a circle of circumference $L$. The coordinate along the circle is called $x$ and we can view the circle as the interval $x \in [0, L]$ with the endpoints identified. It is perhaps clearer mathematically to think of the circle as the full real line $x$ with the identification

$$x \sim x + L,$$

(3.1)

which means that two points whose coordinates are related in this way are to be considered the same point. If follows that we have the periodicity condition

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

(3.2)

From this it follows that not only $\psi$ is periodic but all of its derivatives are also periodic.

The particle is assumed to be free and therefore $V(x) = 0$. The time-independent Schrödinger equation is then

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

(3.3)

Before we solve this, let us show 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 $\psi$ is normalized we get

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

(3.4)

The integrand on the left hand side can be rewritten as

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

(3.5)
and the total derivative can be integrated
\[-\frac{\hbar^2}{2m} \left[ (\psi^* \frac{d\psi}{dx}) |_{x=L} - (\psi^* \frac{d\psi}{dx}) |_{x=0} \right] + \frac{\hbar^2}{2m} \int_0^L \left| \frac{d\psi}{dx} \right|^2 dx = E. \tag{3.6}\]

Since \(\psi(x)\) and its derivatives are periodic, the contributions from \(x = L\) and \(x = 0\) cancel out and we are left with
\[E = \frac{\hbar^2}{2m} \int_0^L \left| \frac{d\psi}{dx} \right|^2 dx \geq 0, \tag{3.7}\]
which establishes our claim. We also see that \(E = 0\) requires \(\psi\) constant (and nonzero!).

Having shown that all solutions must have \(E \geq 0\) let us go back to the Schrödinger equation, which can be rewritten as
\[
\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi. \tag{3.8}
\]
We can then define \(k\) via
\[k^2 \equiv \frac{2mE}{\hbar} \geq 0. \tag{3.9}\]
Since \(E \geq 0\), the constant \(k\) is real. Note that this definition is very natural, since it makes
\[E = \frac{\hbar^2 k^2}{2m}, \tag{3.10}\]
which means that, as usual, \(p = \hbar k\). Using \(k^2\) the differential equation becomes the familiar
\[
\frac{d^2\psi}{dx^2} = -k^2 \psi. \tag{3.11}\]
We could write the general solution in terms of sines and cosines of \(kx\), but let’s use complex exponentials:
\[\psi(x) \sim e^{ikx}. \tag{3.12}\]
This solves the differential equation and, moreover, it is a momentum eigenstate. The periodicity condition (3.2) requires
\[e^{ik(x+L)} = e^{ikx} \rightarrow e^{ikL} = 1 \rightarrow kL = 2\pi n, \quad n \in \mathbb{Z}. \tag{3.13}\]
We see that momentum is quantized because the wavenumber is quantized! The wavenumber has discrete possible values
\[k_n \equiv \frac{2\pi n}{L}, \quad n \in \mathbb{Z}. \tag{3.14}\]
All integers positive and negative are allowed and are in fact necessary because they all correspond to \textit{different} values of the momentum \(p_n = \hbar k_n\). The solutions to the Schrödinger equation can then be indexed by the integer \(n\):
\[\psi_n(x) = N e^{ik_n x}, \tag{3.15}\]
where \(N\) is a real normalization constant. Its value is determined from
\[1 = \int_0^L \psi_n^*(x)\psi_n(x)dx = \int_0^L N^2dx = N^2L \rightarrow N = \frac{1}{\sqrt{L}}, \tag{3.16}\]
so we have

\[
\psi_n(x) = \frac{1}{\sqrt{L}} e^{ik_n x} = \frac{1}{\sqrt{L}} e^{\frac{2\pi i n x}{L}}. \tag{3.17}
\]

The associated energies are

\[
E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 4\pi^2 n^2}{2m L^2} = \frac{2\pi^2 \hbar^2 n^2}{m L^2}. \tag{3.18}
\]

There are infinitely many energy eigenstates. We have degenerate states because \(E_n\) is just a function of \(|n|\) and thus the same for \(n\) and \(-n\). Indeed \(\psi_n\) and \(\psi_{-n}\) both have energy \(E_n\). The only nondegenerate eigenstate is \(\psi_0 = \frac{1}{\sqrt{L}}\), which is a constant wavefunction with zero energy.

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 states can be distinguished by their momentum: \(\psi_n\) has momentum \(2\pi n\) and \(\psi_{-n}\) has momentum \((-2\pi n\frac{L}{L})\).

Given two degenerate energy eigenstates, any linear combination of these states is an eigenstate with the same energy. Indeed if

\[
\hat{H} \psi_1 = E \psi_1, \quad \hat{H} \psi_2 = E \psi_2, \tag{3.19}
\]

then

\[
\hat{H}(a \psi_1 + b \psi_2) = a \hat{H} \psi_1 + b \hat{H} \psi_2 = a E \psi_1 + b E \psi_2 = E(a \psi_1 + b \psi_2). \tag{3.20}
\]

We can therefore form two linear combinations of the degenerate eigenstates \(\psi_n\) and \(\psi_{-n}\) to obtain another description of the energy eigenstates:

\[
\psi_n + \psi_{-n} \sim \cos(k_n x), \quad \psi_n - \psi_{-n} \sim \sin(k_n x). \tag{3.21}
\]

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

The energy eigenstates \(\psi_n\) are automatically orthonormal since they are \(\hat{p}\) eigenstates with no degeneracies (and as you recall eigenstates of a hermitian operator with different eigenvalues are automatically orthogonal):

\[
\int_0^L \psi_n^*(x) \psi_m(x) dx = \frac{1}{L} \int_0^L e^{\frac{2\pi i (m-n) x}{L}} dx = \delta_{mn}. \tag{3.22}
\]

They are also complete: we can then 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

\[
\Psi(x,0) = \sum_{n \in \mathbb{Z}} a_n \psi_n(x), \tag{3.23}
\]

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

\[
a_n = \int_0^L dx \psi_n^*(x) \Psi(x,0). \tag{3.24}
\]

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

\[
\Psi(x,t) = \sum_{n \in \mathbb{Z}} a_n \psi_n(x) e^{-iE_n t}. \tag{3.25}
\]

Andrew Turner transcribed Zwiebach’s handwritten notes to create the first LaTeX version of this document.