Stationary states and time evolution

Relevant sections in text: §2.1–2.4, 2.6

Time independent Schrödinger equation

Now we will develop some of the technology we need to solve the Schrödinger equation for the state as a function of time for some simple physical situations. For simplicity, I will still focus on the system called "a particle moving in one dimension". You will recall that one can often solve linear partial differential equations by the method of *separation of variables*. Let us apply this method to the SE.

The SE describing the time evolution of the state of a particle of mass m moving in one dimension (x) under the influence of a potential energy function $V(x,t)$ is a partial differential equation for the wave function $\Psi(x,t)$ given by

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

The potential energy function is assumed to be known; it represents the influence of the particle's environment on the particle. Using the standard separation of variables strategy, let us suppose that the wavefunction can be written as a product of a function of t and a function of x,

$$\Psi(x,t) = \psi(x)f(t).$$

To see what equations ψ and f must satisfy, substitute into the SE to get (exercise)

$$i\hbar\psi\frac{df}{dt} = -\frac{\hbar^2}{2m}f\frac{d^2\psi}{dx^2} + V\psi f.$$

Away from values of x and t where Ψ vanishes, we can divide both sides of this equation by $\Psi = \psi f$ to find (exercise)

$$i\hbar\frac{1}{f}\frac{df}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V.$$

Now, if V depends upon t we are stuck; the separation of variables strategy just isn't viable in this case. There are other, approximate approaches which can be brought to bear for systems with time dependent potentials which we shall study much later. So let us henceforth *suppose that V doesn't depend upon time, $V = V(x)$*. Then the left hand side of the above equation only depends upon t, while the right hand side depends only upon x. This implies that both sides must equal a single constant, call it E. (To see this, consider the partial derivative of both sides of the equation with respect to x: you will find the right hand side is a constant. Similarly, by taking the partial with respect to t, you find the left hand side is a constant.)

Let's summarize what we have found so far. If $V = V(x)$ and we assume $\Psi(x,t) = \psi(x)f(t)$, then ψ and f solve a decoupled set of *ordinary differential equations*:

$$i\hbar\frac{df}{dt} = Ef,$$

and

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

The first of these equations is easy to solve for any value of E. We have

$$f(t) = Ce^{-\frac{i}{\hbar}Et},$$

where C is a constant (which may be complex). The second equation is known as the *time-independent Schrödinger equation*, which we shall abbreviate as TISE.

As is the case with the Schrödinger equation, the time-independent Schrödinger equation is a linear equation for ψ, so we can multiply solutions by constants to get other solutions, and we can add solutions to get other solutions. We shall soon see that the TISE also determines the possible values for the constant E. Unfortunately, there is no single formula for the set of solutions of the TISE valid for all choices of $V(x)$. Until we specify the potential $V(x)$ we cannot try to solve it; even then there may be no closed form for the solutions. We shall look at some simple potentials soon, which will give us a good feel of how the solution space typically looks.

We have found that the separation of variables solution to the SE is of the form

$$\Psi(x,t) = \psi(x)e^{-\frac{i}{\hbar}Et},$$

where ψ satisfies the TISE and we have absorbed the constant C into the definition of ψ (why can we do this?). If Ψ is to represent the state at time t it must be normalized, this means

$$1 = \int |\Psi(x,t)|^2\,dx = \int |\psi(x)|^2\,dx.$$

Thus the function $\psi(x)$ must in fact be a normalized wave function. You can see that it represents the state of the system at $t = 0$.

Keep in mind that the method of separation of variables is one way to get at solutions, but not all solutions need be of the separation of variables form. Indeed, the linearity of the SE means that linear combinations of separation of variables solutions will also be solutions and these combinations need not be of the separation of variables form. Under favorable circumstances (mathematically speaking), *every* solution will be expressible as a superposition — possibly infinite — of separation of variables solutions.

Stationary states

The separation of variable solutions we have constructed to the SE define a particular class of states of the system which are known as *stationary states*. To see where this name comes from, consider the expectation value of any observable $Q = Q(x, p)$. We get at time t (exercise)

$$\begin{aligned}\langle Q \rangle &= \int \Psi^*(x,t) Q(x, \frac{\hbar}{i}\frac{\partial}{\partial x}) \Psi(x,t)\, dx \\ &= \int e^{\frac{i}{\hbar}Et} \psi^*(x)\, Q(x, \frac{\hbar}{i}\frac{\partial}{\partial x})\, e^{-\frac{i}{\hbar}Et} \psi(x)\, dx. \\ &= \int \psi^*(x) Q(x, \frac{\hbar}{i}\frac{\partial}{\partial x}) \psi(x)\, dx.\end{aligned}$$

So, even though the wave function changes in time, the expectation values of observables are time-independent *provided the system is in a stationary state.** As mentioned earlier, all physical predictions of quantum mechanics can be made via expectation values of suitably chosen observables. Consequently, all observable characteristics of a physical system will not change in time when the system happens to be in a stationary state. Conversely, if some observable characteristic of a system is changing in time, then the system is not in a stationary state.** Probably the most famous stationary states in quantum mechanics are the energy levels of atoms. We shall see how to find them explicitly for the hydrogen atom a little later in the course.†

It is permissible to call either the separation of variables solution Ψ or its position-dependent factor ψ stationary states. Indeed, since all expectation values using Ψ or ψ give the same results, it turns out that both represent *the same state* physically (of course, they are different functions mathematically).

It is worth emphasizing this last point. Given a wave function $\psi(x)$, the wave function $e^{i\alpha}\psi(x)$, where α is independent of x, represents the same state. The complex number $e^{i\alpha}$ (α real) is called a *phase factor* and has an absolute value of unity. Any two wave functions differing by a phase factor correspond to the same state of the particle. Indeed, you can check that they are both normalized and each gives the same expectation value to any chosen observable as a consequence of the fact that observables are represented by *linear* operators. We see that the representation of states by complex functions is a little redundant. There are more sophisticated ways of mathematically representing states that do not have this redundancy, but it does no harm to keep things as they are. Indeed there are many advantages to our present (slightly redundant) description.

* Note that the factor-ordering ambiguity in the definition of Q does not affect this result.
** In this case the system is in a superposition of stationary states.
† Here is a puzzle for you: Consider the well-known phenomenon of "spontaneous emission" in which an atom in an excited energy state emits a photon and drops to a lower energy state. Now think about this: is an excited state of an atom *really* a stationary state?

The wave functions $\psi(x)$ solving the TISE have another very important physical property: they are states of "definite energy". This means the dispersion (that is, standard deviation, or variance) of the probability distribution for energy in the stationary state ψ is zero. To see this, we begin by recalling the Hamiltonian operator $\hat{H}$, which is defined by

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi.$$

This operator represents the total energy, which I will denote by H, so to compute the variance in energy we should calculate

$$\Delta H = \langle H^2\rangle - \langle H\rangle^2.$$

In terms of $\hat{H}$ we can write the TISE as

$$\hat{H}\psi = E\psi,$$

which is a type of *eigenvalue problem*, since $\hat{H}$ is a linear operator (akin to an infinite matrix). Let us suppose $\psi(x)$ solves the TISE for some value of E and compute the variance of the energy in this state. To begin, we easily compute

$$\langle H\rangle = \int \psi^*\hat{H}\psi\,dx = E\int \psi^*\psi\,dx = E.$$

Consequently the statistical average value of energy (which you obtain from many energy measurements of the particle always prepared in the state ψ) will be E. This gives a physical interpretation to the separation constant which appeared when we separated variables. Now we show that the standard deviation of the energy is zero, so in fact the state ψ corresponds to the energy E with probability one – with "certainty". We know that $\langle H\rangle^2 = E^2$. Now we compute:

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

Consequently,

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

Thus

$$\Delta H^2 = \langle H^2\rangle - \langle H\rangle^2 = E^2 - E^2 = 0.$$

We have arrived at a Big Idea: *If we have a particle in a stationary state characterized by the eigenvalue E, then we know that a measurement of energy will yield E with probability one.* Note that we could have just as well used the stationary state $\Psi(x,t)$ in the above

computations (exercise). Both Ψ and ψ satisfy the same TISE; they both represent the same state of definite energy.*

Assuming there is only one state for a given energy – we say the energy is *non-degenerate* – a measurement of the energy uniquely fixes the state of the particle to be the corresponding stationary state. This leads to a good strategy for preparing a system in a given state for the purpose of doing experiments. If one wants an ensemble of particles all in the same stationary state, one simply measures the energy of a collection of particles and then filters out all but those having the energy of the desired stationary state.

The two principal features of the stationary states are: (i) time independent physical properties and (ii) statistically certain value of energy. It may seem merely a coincidence that the stationary states have both these properties. But the notions of time and energy, have a universal duality in physics. You can see why in the present context by considering the Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi.$$

On the left hand side we have a term characterizing the time dependence of the state. This is equated to the action of the Hamiltonian – the energy operator – on the wave function.

Later we shall give a formal, systematic presentation of the laws of quantum mechanics. It is part of those laws that the "energy eigenvalues" E that arise when solving the TISE are the *only* possible values an energy measurement can return. Thus the possible values of E are sometimes called the *allowed energies* or the *energy spectrum* of the particle. We shall see that for bound systems, in contrast to the classical mechanical prediction, the energy spectrum does not form a continuum.

Since the stationary state solutions to the Schrödinger equation will at different times differ by a phase factor, they all represent the same state. In particular, since the initial state is a state of definite energy then it remains so for all time.† Put differently, if you know the initial energy E with probability one, you will find that same energy E with probability one at any other time. This is a form of the principle of conservation of energy. Note that we had to assume that $\frac{\partial V}{\partial t} = 0$ to get it, just as in classical mechanics.

Not having yet specified the potential energy function $V(x)$ we cannot say very much more about the precise nature of the energy spectrum. Soon we shall look at some specific examples where we will be able to compute the spectrum. One thing we *can* say in general is that the *allowed energies must be greater than the minimum of the potential energy.* This is a homework problem in your book.

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* Notice that the mathematical form of the linear operator $\hat{H}$ did not get used in getting this result. What we have here is an instance of a general rule: eigenfunctions of operators are states where the eigenvalue will be measured with certainty.

† This follows from the fact that solutions to the Schrödinger equation are uniquely determined by the wave function at any given time.

Problem 2.2 from Griffiths' text

Show that E must exceed the minimum value of $V(x)$ for every normalizable solution to the TISE.

To prove this, write the TISE as

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

To prove the result we will assume the contrary – we will suppose that E is *less than or equal* to the minimum V_{min} of $V(x)$ – and we will obtain a contradiction. Multiply both sides of this equation by ψ^* and integrate over all space:

$$\int_{-\infty}^{\infty} \psi^* \frac{d^2\psi}{dx^2}\, dx = \int_{-\infty}^{\infty} \frac{2m}{\hbar^2}[V(x) - E]\psi^*\psi\, dx.$$

Now, by our assumption, we have that $\frac{2m}{\hbar^2}(V(x) - E) \geq 0$. This means the integrand on the right hand side is non-negative. Consequently, if ψ satisfies the TISE then

$$\int_{-\infty}^{\infty} \psi^* \frac{d^2\psi}{dx^2}\, dx \geq 0.$$

Now, as a nice exercise, you should integrate by parts to get

$$-\int_{-\infty}^{\infty} |\frac{d\psi}{dx^2}|^2\, dx \geq 0,$$

where I dropped the boundary terms because

$$\lim_{x\to\pm\infty} \psi(x) = 0$$

since ψ is assumed normalizable. But this integral relation is impossible. To see why, first suppose that we have strict ($>$) inequality; this can't happen because the integral is positive (exercise) and the minus sign makes the left hand side negative. The only other possibility is that the left hand side vanishes. But since the integrand is positive, this means that the integrand must vanish everywhere. This means that ψ is constant everywhere, which is impossible if ψ is normalized (exercise). Thus we reach a contradiction from our original assumption ($E \leq V_{min}$) and it follows that $E > V_{min}$. □

This result, that we must have $E > V_{min}$, is similar to a prediction of classical mechanics (exercise), but with one important difference. In classical mechanics we have $E \geq V_{min}$; the possibility exists that the kinetic energy is zero and $E = V_{min}$. This is an equilibrium state of the classical system This is, apparently, not possible in quantum mechanics. The impossibility of $E = V_{min}$ in quantum mechanics can be attributed to the uncertainty principle. The classical state in which $E = V_{min}$ is one in which p vanishes and x is

fixed at the point where the potential is minimized, *i.e.,* this is the equilibrium state of fixed position and vanishing velocity. As we have discussed, it is impossible in quantum mechanics to have a state in which the position and velocity are both determined with probability one. If the particle is localized near the minimum of potential, this requires a corresponding non-zero variance in the momentum, which, in effect, allows the kinetic energy to be non-zero. This can be interpreted as a manifestation of "zero point energy", which we shall see again soon.

In a moment we will study some simple examples of stationary states. Let us give a preview of how they will feature in solutions to the Schrödinger equation. The TISE determines these stationary states and their associated *energy eigenvalues* E. Thus, there will be allowed energies E_n, $n = 1, 2, 3, \ldots$ and corresponding stationary states – also called "energy eigenstates" represented by "energy eigenfunctions":

$$\Psi_n(x,t) = \psi_n(x) e^{-\frac{i}{\hbar}E_n t}, \quad n = 1, 2, \ldots$$

for which the energy is known with certainty to be E_n. Each of the $\Psi_n(t)$ will solve the SE. Since the SE is linear, we can form a *superposition* of stationary states to get new, non-stationary states which solve the SE:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-\frac{i}{\hbar}E_n t}.$$

Here the c_n are complex constants; they are arbitrary up to a single constraint due to normalization. These constants can be determined by specifying the wave function at a single time, *e.g.,* $t = 0$. It will be a non-trivial fact that any solution of the SE can be obtained by making an appropriate choice of the c_n in the above expansion in stationary states; the expansion above represents the *general solution* to the SE. In this way, the key to finding solutions of the Schrödinger equation (for time independent potentials) is to find the associated energy eigenstates.

Particle in a box

As our first and simplest illustration of the ideas discussed above, we are now going to make a quantum mechanical model of a particle in a (1-dimensional) box. More precisely, we want to describe a particle which can move freely in a region, say $x \in (0, a)$, but is forbidden to go elsewhere by some "rigid walls". We model this situation by setting

$$\Psi(x,t) = 0, \quad \text{for } x \geq a,\ x \leq 0,$$

for all t, and solving the Schrödinger equation in the spatial region $x \in (0, a)$. In this way we guarantee that the probability for finding the particle outside the "box" is zero. If

you like, you can think of these boundary conditions as stemming from a potential well of infinite depth:

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & x < 0 \ \text{ or } \ x > a. \end{cases}$$

This way of formulating the problem will become more clear once we have studied the potential well of *finite* depth. Anyway, this is why this model is sometimes called a particle in an "infinite potential well". Clearly, a vanishing wave function solves the SE outside the box, so we simply have to find the rest of the solution, *i.e.,* what happens inside the box. We then match the interior solution to the exterior solution by demanding continuity of the probability distribution for position.

To find the possible states of the particle as a function of time we use our previous results and analyze the TISE. In the box the particle is to move freely so we set $V(x) = 0$ for $0 < x < a$ and we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \quad 0 < x < a.$$

This kind of differential equation should be familiar to you; the equation is easily solved to give

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

where A and B are constants and

$$k = \frac{\sqrt{2mE}}{\hbar}. \tag{1}$$

Now, at this point, A, B, and k (or E) are all arbitrary complex numbers which determine the state (m and $\hbar$ are fixed parameters). We still must impose boundary conditions, which will be that the probability density for position vanishes at the boundaries of the box. Setting

$$\psi(0)^*\psi(0) = 0$$

we find

$$|B|^2 = 0,$$

so that $B = 0$. Consequently, the condition

$$\psi(a)^*\psi(a) = 0$$

becomes

$$|A|^2 \sin^2(ka) = 0.$$

We can't pick $A = 0$ since the wave function would vanish – it wouldn't be normalizable! Hence we must have

$$k = \frac{\pi}{a}\, n, \quad n = 1, 2, \ldots. \tag{2}$$

I dropped $n = 0$ since this gives the solution $\psi = 0$, which is not normalizable. I also did not include the negative integers, which also solve the equation. The reason for this is that $A\sin(\frac{n\pi}{a}x)$ and $A\sin(\frac{-n\pi}{a}x)$ differ by a minus sign – a phase factor – and so do not represent distinct stationary states.

Using the result (2) for k along with the earlier relation (1), the boundary conditions fix the energy to take the discrete values:

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}\,n^2, \quad n = 1, 2, \ldots.$$

This result – quantization of energy – should impress you! Consider a classical particle in a (1-d) box. If we model the wall as perfectly rigid, we can suppose that the particle collides elastically with the wall and keeps the same speed before and after the bounce. (Of course the velocity changes direction.) The energy of the particle is purely kinetic and is constant throughout the motion. The value of the energy is fixed by the initial velocity; it can take any non-negative value, including zero. Thus the states of the classical particle can have any $E \geq 0$. On the other hand, the possible states of the quantum particle have an energy that can only take on a discrete set of values. One says that the energies have been "quantized". Moreover, the lowest possible energy is

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2} > 0,$$

so the lowest possible energy is non-zero, unlike the classical particle. We already knew this would happen. Recall our general discussion of stationary states where we proved that the allowed energies are strictly larger than the minimum of the potential energy (which is zero in our present example). This can be thought of as a manifestation of the uncertainty principle. Heuristically, the stationary states all vanish outside of the box, so the particle is localized to some extent in any of the states. Therefore the momentum uncertainty must be non-zero and we have some "zero point energy".

Finally, note that Planck's constant sets the scale of discreteness in energy via the combination $\frac{h^2}{ma^2}$. For a macroscopic box (sufficiently large a) or a macroscopic particle (sufficiently large mass) the discreteness is so small as to be negligible and a continuous model of energy is appropriate. But for microscopic systems the discreteness becomes significant. You can also see that the quantization of energy also becomes negligible when n is sufficiently large. Of course what "sufficiently large" means for n will depend upon the value of $\frac{h^2}{ma^2}$.

The stationary state associated with the energy E_n is given by

$$\Psi_n(x,t) = \psi_n(x)e^{-\frac{i}{\hbar}E_n t},$$

with E_n given by the formula above and

$$\psi_n(x) = \begin{cases} A \sin\left(\frac{\pi n}{a}\, x\right), & 0 \leq x \leq a, \\ 0, & x \geq a,\ x \leq 0. \end{cases}$$

The constant A is undetermined by the SE (or TISE), but this is a good thing since we still need to normalize the wave function. As a nice exercise, you can check that with

$$|A| = \sqrt{\frac{2}{a}},$$

the stationary state is normalized:

$$\begin{aligned} \int_{-\infty}^{\infty} |\Psi_n(x,t)|^2\, dx &= \int_0^a \frac{2}{a} \sin^2\left(\frac{\pi}{a}\, nx\right)\, dx \\ &= 1. \end{aligned}$$

There are a couple of things to notice regarding normalization issues. First, you can easily see that since the TISE is linear, we will always have a free multiplicative constant in any solution to the TISE with homogeneous (vanishing) boundary conditions. The absolute value of this constant is always fixed by normalization. This leaves a "phase factor" of the form $e^{i\alpha}$, α real, which cannot be determined. This is okay since we have already noted that states differing by a phase factor are physically equivalent. Usually, the simplest choice is to set $\alpha = 0$. In this case that means setting $A = \sqrt{\frac{2}{a}}$,

The state Ψ_1 is the state of lowest possible energy. It is called the *ground state*. The states with $n > 1$ are called *excited states*. The integer n is sometimes called a "quantum number". Note that a state with quantum number n has $n - 1$ zeroes, or *nodes* (not counting the zeroes at the boundaries). These are places where the probability density for finding the particle vanishes. This should impress you! In any excited state there are regions where the particle can be found that are connected by points at which the particle cannot be. This is impossible in classical mechanics and underscores the limitations of the classical notion of "particle" in the quantum realm. This raises the question of how classical motion can possibly emerge from stationary states in macroscopic circumstances. Let us spend a moment seeing how classical mechanics behavior can manage to emerge from quantum mechanics behavior.

Relation to classical motion

Here I will briefly discuss the correspondence of our quantum mechanical results for a particle in a box with those arising from classical mechanics. I will do this by comparing the probability distributions for position in states with a given energy. (We have already

considered the differences in the energy spectrum.) To do this, we must phrase the classical results in statistical terms. Classically a particle in a state with a given (kinetic) energy E bounces back and forth in the box at constant speed. The probability for finding the classical particle in a region of a given size can be defined as proportional to the amount of time the particle spends there, with the proportionality constant fixed by normalization. Since the particle moves with constant speed, the time spent in a region of size σ is proportional to σ. Consequently, the classical probability to be between a value x_0 and $x_0 + \sigma$ is simply

$$P(x_0, x_0 + \sigma) = \frac{\sigma}{a} \quad \text{(classical mechanics)}.$$

The quantum mechanical probability $P(x_0, x_0 + \sigma)$ is a little more complicated. We have (exercise)

$$\begin{aligned} P(x_0, x_0 + \sigma) &= \frac{2}{a} \int_{x_0}^{x_0+\sigma} \sin^2 \left(\frac{\pi}{a} nx \right) \, dx \\ &= \frac{\sigma}{a} + \frac{1}{2\pi n} \left[\sin(\frac{2\pi n}{a} x_0) - \sin(\frac{2\pi n}{a}(x_0 + \sigma)) \right]. \end{aligned}$$

(quantum mechanics)

You can check that, as a function of x_0, this probability distribution oscillates around the value σ/a with n maxima and minima. The amplitude of the oscillations is proportional to $\frac{1}{n}$. Consequently, for sufficiently large n, we have that

$$P(x, x + \sigma) \approx \frac{\sigma}{a},$$

which is the classical result. The classical result arises approximately for sufficiently excited states. Apparently, "macroscopic" behavior for the particle in a stationary state is associated with large quantum numbers, which in this case is associated with macroscopic energies. Note that we made no assumptions about the size of the box or the mass of the particle.

There is another perspective on the classical limit which is of physical interest. The wavelength of the stationary state wave function is given by

$$\lambda = \frac{2a}{n}.$$

The classical limit we just found ($n \to \infty$) is the condition that λ should be small compared to σ:

$$\frac{\lambda}{\sigma} << 1.$$

Consequently, we can interpret the appearance of classical behavior as corresponding to the wave aspect of the state being negligible on the scales at which we are making measurements. Using the formula for the energy spectrum, we can write the wavelength as

$$\lambda = \frac{2\pi\hbar}{\sqrt{2mE}}$$

and then write the condition for classical behavior in terms of energy to get

$$\frac{2\pi\hbar}{\sigma\sqrt{2mE}} << 1.$$

From this way of characterizing the "classical limit", we see that if σ, m, or E is sufficiently large – "macroscopic" – relative to $\hbar$, we get the classical behavior. We see that the smaller we take σ, the larger we must take the energy and/or the mass if we want the classical approximation to hold. The wavelength

$$\lambda = \frac{2\pi\hbar}{\sqrt{2mE}}$$

is called the "de Broglie wavelength", after Louis de Broglie who postulated that a wavelength $\frac{2\pi\hbar}{p}$ be associated to a particle with momentum p.* As a rule of thumb, quantum effects are important when the de Broglie wavelength of a particle is comparable to other important length scales in a problem. For macroscopic momenta, energies, masses, and length scales, the de Broglie wavelength is exceedingly small and quantum effects are negligible.

For particles in a system at non-zero temperature, the typical kinetic energy – and hence momentum and de Broglie wavelength – depend upon the temperature. In a homework problem you will see that in a typical solid the shared electrons are pretty much always quantum mechanical, while the nuclei are pretty much always classical. You will also see that helium atoms in an ideal gas at 1 atmosphere of pressure are quantum mechanical only at very low temperatures, while hydrogen atoms in outer space are pretty much always classical (as atoms - the electrons are quantum mechanical!).

Properties of the stationary states

Here we assemble some important mathematical properties of the stationary states for a particle in an infinite square well. These properties are (i) the stationary states are "orthonormal"; (ii) the stationary states are "complete". This discussion may seem a bit dry physics-wise, but it is important. These fundamental properties will turn out to apply in one form or another to stationary states for pretty much *any* potential energy function. For simplicity, we drop the phase factors $e^{-\frac{i}{\hbar}Et}$ from the states and work with the *energy eigenfunctions* ψ_n. You can easily check that if we had kept the phase factors they would drop out of all the main results.

The energy eigenfunctions form an *orthonormal set* in the following sense:

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\,dx = \delta_{mn}.$$

* Here we can identify $p = \sqrt{2mE}$.

Note that the range of integration could also be taken to be $x \in [0, a]$. The complex conjugate is clearly superfluous: the ψ_n are all real functions. However, we shall not always work with real functions (*e.g.,* if we had kept the phase factors $e^{-iEt/\hbar}$) and then the complex conjugate is mandatory. In particular, the complex conjugation guarantees that the result is independent of the possibility of multiplying the states by a phase factor to get a physically equivalent state. The symbol δ_{mn} is the *Kronecker delta* which takes the value one if $m = n$ and is zero otherwise. Later we shall discuss the sense in which the integral given above is like a scalar (or "dot") product, which will justify the terminology "orthonormal". For now, "ortho" means "orthogonal", and we are just seeing the usual orthogonality properties of the sine and cosine functions on an interval. "Normal" means normalized, which you already understand.

As a very good exercise you should check the orthonormality relationship, via integral tables or computer. An explicit proof appears in your text, and is easy to follow.

The energy eigenfunctions ψ_n are *complete*, that is, they form a *basis* for any normalizable function on the interval $[0, a]$. More precisely, given any normalizable function $f(x)$ on the interval $[0, a]$ and with boundary values $f(0) = f(a) = 0$, we can always find constants c_n, $n = 1, 2, \ldots$, such that we can express f as a superposition (possibly infinite) of energy eigenfunctions:†

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

In this expansion the choice of the expansion coefficients c_n fixes the function $f(x)$ and, conversely, the c_n are determined by a choice of $f(x)$. To prove this completely is an exercise in Fourier analysis, which we shall not go into. It *is* worth showing how the coefficients c_n are determined by $f(x)$. We have, using orthonormality,*

$$\begin{aligned}
\int_0^a f(x)\psi_m^*(x)\,dx &= \int_0^a \sum_{n=1}^{\infty} c_n \psi_n(x)\psi_m^*(x)\,dx \\
&= \sum_{n=1}^{\infty} c_n \int_0^a \psi_n(x)\psi_m^*(x)\,dx \\
&= \sum_{n=1}^{\infty} c_n \delta_{mn} \\
&= c_m.
\end{aligned}$$

† Technical note for the math types: The sum converges to $f(x)$ at each x only if f is infinitely differentiable, otherwise it converges to f relative to the integral norm, which implies it converges to f "almost everywhere".

* The interchange of integration and summation requires justification, but I won't provide it here lest this turn into a math class

Thus, given any (complex) function $f(x)$ which is zero outside the box we can find the expansion coefficients via

$$c_n = \int_0^a \psi_n^*(x) f(x)\, dx.$$

You can think of this result in terms of a very simple analogy with ordinary algebra of vectors in three dimension. As you know, if $\mathbf{v}$ is a vector, and $\mathbf{e}_i$, $i = 1, 2, 3, \ldots$ is an orthonormal basis (*e.g.,* the usual $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ in 3-d space),

$$\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij},$$

then the i^{th} component, v_i of $\mathbf{v}$ in this basis is simply

$$v_i = \mathbf{e}_i \cdot \mathbf{v}.$$

The components v_i are the expansion coefficients:

$$\mathbf{v} = v_1\mathbf{e}_1 + v_2\mathbf{e}_2 + \ldots = \sum_i v_i \mathbf{e}_i.$$

You can check this as follows:

$$\mathbf{e}_i \cdot \mathbf{v} = \mathbf{e}_i \cdot \sum_k v_k \mathbf{e}_k = \sum_k v_k \mathbf{e}_i \cdot \mathbf{e}_k = \sum_k v_k \delta_{ik} = v_i.$$

Similarly, think of the set consisting of all normalizable functions as a set of vectors. Think of the energy eigenfunctions ψ_n as an orthonormal basis relative to the "dot product" defined by the integral we discussed earlier. Think of the expansion coefficients c_n as components of a vector f in the basis ψ_n. Finally, our formula for the c_n in terms of the integral is just the dot product formula above.

General solution to Schrödinger equation

Since each stationary state

$$\Psi_n(x,t) = \psi_n(x) e^{-\frac{i}{\hbar}E_n t}, \quad n = 1, 2, \ldots, \quad 0 < x < a,$$

solves the SE, any *linear combination* of stationary states with constant (x and t independent) coefficients will also solve the SE (exercise):

$$\Psi(x,t) = \sum_n c_n \Psi_n(x,t) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right) \exp\left(-\frac{in^2\pi^2\hbar}{2ma^2}t\right).$$

Here the c_n are the complex coefficients. You can check, by explicit computation, that this wave function does indeed solve the SE and obeys the boundary conditions $\Psi(0,t) =$

$\Psi(a,t) = 0$. Keep in mind that the solution above is for the region $x \in [0,a]$; outside of this region we set $\Psi(x,t) = 0$. For arbitrary constants c_n this wave function $\Psi(x,t)$ is the *general solution* to the SE. This means that any given solution to the SE (with the given boundary conditions) can be written in this form for some choice of the coefficients c_n. It is not hard to see why, at least heuristically, that this is so. First, I have already mentioned that solutions to the SE are uniquely determined by a choice of initial conditions, $\Psi(x,0)$, (and boundary conditions – in our case $\Psi(0,t) = \Psi(a,t) = 0$).* Suppose we pick a function $f(x)$ and demand that $\Psi(x,0) = f(x)$. Setting $t = 0$ in the general solution to the SE we then have

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

As we discussed in the previous section, this determines the expansion coefficients c_n and thus determines the wave function for all time.

Let us look at a simple example (this is taken from Problem 2.7 in the text). Suppose the initial wave function is chosen to be

$$\Psi(x,0) = \begin{cases} Ax, & 0 \le x \le a/2 \\ A(a-x), & a/2 \le x \le a \end{cases}$$

where A is determined by normalization. What are the constants c_n in the expansion in the basis of energy eigenfunctions? We have

$$\begin{aligned} c_n &= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)\, dx \\ &= \int_0^{a/2} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) Ax\, dx + \int_{a/2}^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) A(a-x)\, dx. \end{aligned}$$

We have

$$\int_0^{a/2} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) Ax\, dx = \frac{Aa^{3/2}}{\pi^2 n^2}\left[\sin\left(\frac{n\pi}{2}\right) - \frac{1}{2}n\pi\cos\left(\frac{n\pi}{2}\right)\right],$$

and

$$\int_{a/2}^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) A(a-x)\, dx = \frac{Aa^{3/2}}{\pi^2 n^2}\left[\sin\left(\frac{n\pi}{2}\right) + \frac{1}{2}n\pi\cos\left(\frac{n\pi}{2}\right)\right],$$

* You can easily see why. Suppose you have two solutions with the same initial conditions. Then the difference of these two solutions will be a solution and it will have *vanishing* initial conditions. This means in particular that the integral of $\Psi^*\Psi$ vanishes at the initial time. But this integral does not change in time if Ψ satisfies the Schrödinger equation. This means $\Psi^*\Psi$ must vanish at any subsequent time and hence Ψ will vanish for all time. This means the two solutions we started with must be the same!

Therefore:

$$c_n = \frac{2Aa^{3/2}}{\pi^2 n^2}\sin\left(\frac{n\pi}{2}\right) = \begin{cases} \frac{2Aa^{3/2}}{\pi^2 n^2}, & n = 1, 5, 9, \ldots \\ -\frac{2Aa^{3/2}}{\pi^2 n^2}, & n = 3, 7, 11, \ldots \\ 0 & n \text{ even.} \end{cases}$$

Tiime evolution of the wave function

Given that the general solution of the Schrödinger equation (for the particle in a box) is of the form

$$\Psi(x,t) = \sum_n c_n \Psi_n(x,t) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right) \exp\left(-\frac{in^2\pi^2\hbar}{2ma^2}t\right).$$

You can see that if the initial state is an energy eigenfunction then all the c_n but one – the one corresponding to the initial energy eigenstate – will vanish, and the wave function will represent a stationary state. If the initial state is not an energy eigenfunction – as in the example in the last section – then at least two of the c_n will be non-vanishing and the time dependence of the wave function cannot be factored out as an overall phase. This means that time evolution of the state necessarily occurs, *i.e.,* some observable features will change in time. Let us have a closer look at this result.

Suppose that only two of the expansion coefficients are non-vanishing, e.g., $c_1 \neq 0$, $c_2 \neq 0$, $c_k = 0$, $k > 2$. The wave function at time t takes the form

$$\Psi(x,t) = \sqrt{\frac{2}{a}}\left(c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}\right).$$

We can factor out one of the phases, say, the first one as an irrelevant overall phase:

$$\Psi(x,t) = \sqrt{\frac{2}{a}}e^{-iE_1t/\hbar}\left(c_1\psi_1(x) + c_2\psi_2(x)e^{-i(E_2-E_1)t/\hbar}\right).$$

You can see that relevant part of the time evolution of the wave function is sinusoidal at frequency

$$\Omega = \frac{E_2 - E_1}{\hbar}.$$

This is the nature of the (physically relevant) time dependence of solutions of the Schrödinger equation. Notice that the frequency of the oscillation only depends upon the difference of the energies. This way the arbitrary zero point of the energy scale is not in play, physically speaking.

Probability distribution for energy

The general solution of the SE represents the state of the system at each time t. When we expand the general solution in the basis of stationary states the expansion coefficients have a fundamental physical significance. First of all, recall that the wave function must be normalized. The normalization condition is

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

which gives

$$\int_0^a \sum_{m,n=1}^{\infty} c_m^* c_n \psi_m^*(x) \psi_n(x) e^{-\frac{i}{\hbar}(E_n - E_m)t} \, dx.$$

Using the orthonormality of the stationary states,

$$\int_0^a \psi_m^* \psi_n \, dx = \delta_{mn},$$

we get (good exercise)*

$$\sum_{n=1}^{\infty} |c_n|^2 = 1.$$

Thus, the absolute-square integral of Ψ being unity is the same as the absolute-square sum of the expansion coefficients being unity. This result really just depended upon the completeness and orthonormality of the stationary states. Note that the expansion coefficients are determined by the state at $t = 0$, so the above summation condition is equivalent to saying that the initial state is normalized (exercise). This should not surprise you; we showed some time ago that if the wave function is normalized at a single time and it solves the Schrödinger equation then it remains normalized.

Recall that the normalization integral for a wave function is a statement that the probability for all outcomes of a position measurement add up to one. The normalization condition on the c_n has a similar interpretation. Recall that if the particle is in a stationary state, *i.e.,* all c_i vanish but one — say c_{17}, then the probability for measuring energy and getting E_{17} is one (and, of course, the probability for getting any other energy zero). In this case, this probability distribution can be identified with the fact that

$$|c_{17}|^2 = 1, \quad |c_i|^2 = 0, \quad \text{when } i \neq 17$$

* Note: this result requires interchanging the order of integration and the infinite summations in the original normalization condition. Strictly speaking, this requires mathematical justification. While we won't go there, it *is* justified.

for a particle in the stationary state labeled by $n = 17$. Next, note that the expectation value of the energy at any time is given by (exercise),

$$\begin{aligned}\langle H\rangle &= \int_0^a \Psi^* H \Psi \, dx \\ &= \int_0^a \sum_{n=1}^{\infty} c_m^* c_n \psi_m^*(x) E_n \psi_n(x) e^{\frac{i}{\hbar}(E_m - E_n)t} \, dx \\ &= \sum_n |c_n|^2 E_n.\end{aligned}$$

Here the orthonormality of the stationary states was used. In light of these results concerning the c's, one interprets $|c_n|^2$ as the probability of finding the energy E_n. Indeed, we have already pointed out that the expectation value of a quantity (*e.g.,* energy or position) can be computed by adding up all the possible values of the quantity with coefficients between 0 and 1 corresponding to the probabilities for getting that result. With the rule

$$\text{Probability of getting energy } E_n = |c_n|^2,$$

we reproduce this way of computing the expectation value. This interpretation of the expansion coefficients c_n in terms of the probability distribution for energy in the given state Ψ is one of the principal rules of quantum mechanics. Note that the probability of getting a given energy is time-independent even though the state of the system may be changing in time; this is the fundamental manifestation of energy conservation in quantum mechanics. Notice also that we are tacitly taking a vanishing probability for any energy which is not one of the energy eigenvalues ($\frac{\pi^2\hbar^2 n^2}{2ma^2}, n = 1, 2, \ldots$, in the present case).

Problem 2.38 in Griffiths' text

A particle of mass m is in the ground state of the infinite square well. Suddenly the well expands to twice its original size ($a \to 2a$) leaving the wave function undisturbed. The energy of the particle is now measured.

(a) What is the most probable result and what is its probability?

(b) What is the next most probable result and what is its probability?

(c) What is the expectation value of the energy?

Solution:

The idea here is that the walls of the box are moved sufficiently rapidly that we can view the state of the system as being unchanged by the process. This is an approximation, which is sometimes called the "sudden approximation". We now view the state of the system from the point of view of observables for a particle in a box of size $2a$.

(a) It is understood that the "energy" is that of a particle in a box of size $2a$. This is still just the kinetic energy $\hat{p}^2/2m$, but now the boundary conditions are different. The energy eigenfunctions and energy eigenvalues are

$$\psi_n(x) = \sqrt{\frac{2}{2a}} \sin\left(\frac{n\pi x}{2a}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}.$$

The wave function (in the sudden approximation) is the ground state of a particle in a box of size a:

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) & 0 < x < a \\ 0, & \text{otherwise.} \end{cases}$$

The probability $P(n)$ of getting the stationary state with quantum number n is

$$\begin{aligned} P(n) &= \left| \int_0^{2a} \left(\sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right) \right) \psi(x)\, dx \right|^2 \\ &= \left| \int_0^{a} \left(\sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right) \right) \left(\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \right) dx \right|^2 \end{aligned}$$

You should easily be able to see that the probability is $1/2$ when $n = 2$ since the integral is proportional to the normalization integral for a particle in a box of size a. The probability is zero when $n \neq 2$ is even, which follows from the orthogonality of stationary states of a particle in a box of size a. When n is odd we get:

$$P(n) = \frac{32}{\pi^2(n^2-4)^2}, \quad n \text{ odd.}$$

Therefore the probability is largest when $n = 2$, with $P(2) = 1/2$.

(b) The next most probable result is the ground state, $n = 1$, with probability $P(1) = 32/9\pi^2 \approx 0.36$.

(c) The easiest way to calculate the expectation value of energy is

$$\langle H \rangle = -\frac{\hbar^2}{2m} \int_0^{2a} \psi(x)\psi''(x)\, dx = \frac{\hbar^2\pi^2}{ma^3} \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{\hbar^2\pi^2}{2ma^2}$$

Notice that this is just the expectation value one would obtain before the walls were moved. The integral defining the expectation value has not changed. One can also consider summing the infinite series shown in the previous section, but I don't advise it. On the other hand, the result for part (c) ia clever way of deducing the result of that infinite sum.

Simple harmonic oscillator

The potential energy function,

$$V(x) = \frac{1}{2}kx^2,$$

is called the (simple) harmonic oscillator potential for obvious reasons — namely, it is the potential energy for displacement x from equilibrium of particle experiencing a Hooke's law restoring force oscillator. This potential energy is physically quite important since it can be used to give an exactly soluble approximation to more complicated potential functions. Recall that we can consider a Taylor series approximation of a general potential around a point x_0:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \ldots.$$

The idea of such an expansion is that, at least near x_0, we can approximate the function $V(x)$ by keeping only a few terms in the expansion. In particular, if x_0 is an *equilibrium point*, we have that

$$V'(x_0) = 0.$$

If we choose our origin at this equilibrium point, then we can write

$$V(x) \approx \frac{1}{2}kx^2,$$

where $k = V''(x_0)$, and we have dropped an irrelevant additive constant. Provided that $k > 0$, the equilibrium is stable and, at least classically, it is self-consistent to restrict attention to motion near to equilibrium using the quadratic (or harmonic) approximation to the potential.

Because we often study the dynamics of systems in the vicinity of equilibrium the harmonic oscillator approximation is ubiquitous throughout physics. Suitably generalized to more degrees of freedom, one can even use this approximation to understand things like phonons and photons! The oscillator is, mathematically speaking, a little more complicated than, say, the particle in a box. The importance of the oscillator to physics will (hopefully) justify a detailed look.

We now would like to see what physical behavior is associated to the harmonic oscillator potential energy function using quantum mechanics. In particular we want to solve the SE to find the time evolution of states. To do this we need to solve the TISE, which is useful in any case since it gives us the states of definite energy and the allowed energies. The TISE for a harmonic oscillator is

$$-\frac{\hbar^2}{2m}\psi''(x) + \frac{1}{2}kx^2\psi(x) = E\psi(x).$$

Our goal is to find all solutions of this ordinary differential equation and the corresponding allowed energies. The most straightforward (if tedious) way to solve this equation is by writing $\psi(x)$ as a power series in x and recursively solving for the coefficients in the power series. This is detailed in your text. We shall have to use this method later in the course (when we consider the Coulomb potential), so we will not try this method here. Instead we shall use a very quick – if overly clever – method due (I think) to the famous physicist Paul Dirac*.

To begin, we define linear operators

$$\hat{a}_\pm = \frac{1}{\sqrt{2m\hbar\omega}} \left(\mp i\hat{p} + m\omega\hat{x}\right),$$

where

$$\omega = \sqrt{\frac{k}{m}}$$

is the natural angular frequency of the oscillator. The idea is that, as an observable, $a_\pm$ is a fancy way of encoding the position and momentum observables via its real and imaginary parts. Given a function $\psi(x)$, the corresponding linear operator acts as

$$\hat{a}_\pm\psi = \frac{1}{\sqrt{2m\hbar\omega}} \left(\mp\hbar\frac{d\psi}{dx} + m\omega x\psi\right).$$

Note that here we have an instance of two linear operators, $\hat{a}_+$ and $\hat{a}_-$, which don't commute (exercise); we have

$$\hat{a}_-\hat{a}_+\psi - \hat{a}_+\hat{a}_-\psi = \psi.$$

We write this operator relationship in terms of the commutator:

$$[\hat{a}_-, \hat{a}_+] \equiv \hat{a}_-\hat{a}_+ - \hat{a}_+\hat{a}_- = \hat{1}.$$

With a little algebra, it is not hard to see that we can now write the TISE in either of two equivalent forms:

$$\hbar\omega(\hat{a}_+\hat{a}_- + \frac{1}{2}\hat{1})\psi = E\psi,$$

or

$$\hbar\omega(\hat{a}_-\hat{a}_+ - \frac{1}{2}\hat{1})\psi = E\psi,$$

For reasons to be seen soon, the operators $a_\pm$ are usually called *ladder operators* or *creation and annihilation operators*. These operators are very handy for solving the TISE for the harmonic oscillator (and *only* the harmonic oscillator). This is because of the following very important fact. If $\psi(x)$ solves the TISE for energy E, then $\hat{a}_\pm\psi$ will solve the TISE, with energy $E \pm \hbar\omega$. Let us prove this.

* Dirac was one of the principal architects of quantum mechanics as we know it today.

Assume that ψ solves

$$\hbar\omega(\hat{a}_+\hat{a}_- + \frac{1}{2}\hat{1})\psi = E\psi,$$

and/or

$$\hbar\omega(\hat{a}_-\hat{a}_+ - \frac{1}{2}\hat{1})\psi = E\psi,$$

for a given value E of the energy. Now consider the function $\hat{a}_+\psi$. We have

$$\begin{aligned}\hat{a}_+\hat{a}_-(\hat{a}_+\psi) &= \hat{a}_+(\hat{a}_-\hat{a}_+\psi) \\ &= \hat{a}_+[(E/\hbar\omega + \frac{1}{2})\psi] \\ &= (E/\hbar\omega + \frac{1}{2})\hat{a}_+\psi.\end{aligned}$$

Consequently,

$$\hbar\omega(\hat{a}_+\hat{a}_- + \frac{1}{2}\hat{1})\hat{a}_+\psi = (E + \hbar\omega)\hat{a}_+\psi.$$

Evidently, if ψ is an energy eigenfunction with eigenvalue E, then $\hat{a}_+\psi$ is proportional to an eigenfunction (not necessarily normalized) with energy $E + \hbar\omega$. As a good exercise you should check that $\hat{a}_-\psi$ solves the TISE with energy $E - \hbar\omega$ if ψ solves the TISE with energy E.

To summarize, $\hat{a}_+$ maps solutions of the TISE to new solutions with energy raised by $\hbar\omega$, and $\hat{a}_-$ maps solutions of the TISE to new solutions with energy lowered by $\hbar\omega$. For this reason, $\hat{a}_+$ and $\hat{a}_-$ are sometimes called "raising and lowering operators", or "ladder operators", or "creation and annihilation operators".

Using the ladder operators we see that the allowed energies for the harmonic oscillator include, at least, discrete energies differing by $\hbar\omega$. The lowering operator produces states of lower and lower energy. We showed earlier (using normalizability of wave functions and the TISE) that the lowest allowed energy is greater than the minimum value of the potential energy. Since $V(x) = \frac{1}{2}kx^2$, the minimum of the potential is zero. Consequently, we know the lowering operator cannot produce states with energy less than or equal to zero. What must happen is that as we repeatedly apply the lowering operator, we will eventually get a wave function ψ_0 of least energy E_0. If we apply $\hat{a}_-$ to ψ_0 we will get a function that is not normalizable. This can happen in two ways: either (i) the wave function $\hat{a}_-\psi_0$ vanishes, or (ii) the integral of its square must not exist. To see that the

latter cannot happen we compute

$$\begin{aligned}\int_{-\infty}^{\infty} |\hat{a}_-\psi_0(x)|^2\,dx &= \int_{-\infty}^{\infty} (\hat{a}_-\psi)^*(\hat{a}_-\psi) \\ &= \int_{-\infty}^{\infty} \frac{1}{2m\hbar\omega}\left(\hbar\frac{d\psi_0^*}{dx} + m\omega x\psi_0^*\right)\left(\hbar\frac{d\psi_0}{dx} + m\omega x\psi_0\right) \\ &= \int_{-\infty}^{\infty} \psi_0^*\frac{1}{2m\hbar\omega}\left(\hbar\frac{d}{dx} + m\omega x\right)\left(\hbar\frac{d\psi_0}{dx} + m\omega x\psi_0\right) \\ &= \int_{-\infty}^{\infty} \psi_0^*\hat{a}_+\hat{a}_-\psi_0 \\ &= (E_0/\hbar\omega - \frac{1}{2})\int_{-\infty}^{\infty} \psi_0^*\psi_0\,dx\end{aligned}$$

where I integrated by parts and used the fact that ψ_0 is normalizable and vanishes as $x \to \pm\infty$. Since the integral exists, it follows that $\hat{a}_-\psi_0$ is in fact normalizable and therefore the only option is (i), that $\hat{a}_-\psi_0 = 0$. From the integral just calculated above, this means that $(E_0/\hbar\omega - \frac{1}{2}) = 0$. We conclude that the state of lowest energy, represented by the *ground state* wave function ψ_0, must have energy $E_0 = \frac{1}{2}\hbar\omega$ and satisfies

$$\hat{a}_-\psi_0 = 0.$$

Let us determine the ground state wave function $\psi_0(x)$. It is an eigenfunction of the Hamiltonian with eigenvalue $E_0 = \frac{1}{2}\hbar\omega$:

$$-\frac{\hbar^2}{2m}\psi_0'' + \frac{1}{2}m\omega^2\psi_0 = \frac{1}{2}\hbar\omega\psi_0,$$

More importantly, we have just seen ψ_0 satisfies

$$\hat{a}_-\psi_0 = 0 \quad\Longleftrightarrow\quad \psi_0' + \frac{m\omega}{\hbar}x\,\psi_0 = 0.$$

This last equation is easily solved; we get a Gaussian:

$$\psi_0 = A\,\exp\left(-\frac{m\omega}{2\hbar}x^2\right),$$

where A is a constant fixed by normalization to be

$$A = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}.$$

You should check as an exercise that ψ_0 satisfies the TISE and is properly normalized.

We have found the wave function representing the stationary state of lowest energy. This ground state wave function is uniquely determined by the condition that $\hat{a}_-\psi_0 = 0$ (and normalization). Repeated application of the lowering operator to any excited state

must eventually lead to this ground state. Conversely, all excited states must be obtained by repeatedly applying the raising operator $\hat{a}_+$ to ψ_0. The energy eigenfunctions are thus given by (A_n is a normalization constant)

$$\psi_n = A_n(\hat{a}_+)^n \exp\left(-\frac{m\omega}{2\hbar}x^2\right), \quad n = 0, 1, 2, \ldots$$

with energies

$$E_n = (n + \frac{1}{2})\hbar\omega, \quad n = 0, 1, 2, \ldots.$$

It is straightforward, if a little painful, to show that the normalization constants are (up to a phase factor)

$$A_n = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \left(\frac{1}{n!(\hbar\omega)^n}\right)^{\frac{1}{2}}.$$

As usual, the stationary states which solve the Schrödinger equation are given by

$$\Psi(x, t) = e^{-\frac{i}{\hbar}E_n t}\psi_n(x).$$

Hermite polynomials

To describe the stationary states in more detail it is convenient to introduce a dimensionless position variable:

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x.$$

(Note that I am dividing x by the width of the ground state probability distribution in position.) The energy eigenfunctions can now be written as

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\frac{\xi^2}{2}},$$

where

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}.$$

$H_n(\xi)$ is an n^{th}-order polynomial in ξ. It is called the *Hermite polynomial* of order n. These polynomials show up in various places in mathematical physics and have been extensively studied. A few of them are

$$H_0(\xi) = 1$$
$$H_1(\xi) = 2\xi$$
$$H_2(\xi) = 4\xi^2 - 2.$$

As you can see from the above examples, if n is even (odd) then the polynomials are even (odd).

The most important property of the Hermite polynomials is that they determine an orthonormal basis for normalizable functions of one variable. The "orthonormality" of energy eigenfunctions means

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\,dx = \delta_{mn}.$$

Every normalizable (complex) function $f(x)$ can be expressed as

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

for some choice of the (complex) constants c_n. The Hermite polynomials determine a basis which is orthonormal with respect to a Gaussian "weight function". In particular, they satisfy

$$\int_{-\infty}^{\infty} H_m(\xi)H_n(\xi)e^{-\xi^2}\,d\xi = \sqrt{\pi}2^n n!\delta_{mn}.$$

The Hermite polynomials are an example of a *complete set of orthogonal polynomials* (with a Gaussian "weight function").

Main properties of the stationary states

The stationary states for the harmonic oscillator are labeled by non-negative integers. The states labeled by even (odd) integers are even (odd) in x. The ground state is labeled by $n = 0$ and is a Gaussian wave function. Up to the normalization constant, the state with index n is the ground state Gaussian wave function times an n^{th}-order polynomial in x. As it turns out, the integer n also indicates how many times the graph of the wave function passes through zero — it can be shown that the polynomial appearing at energy level n has n real roots. Thus the eigenfunctions look like oscillatory functions (though not sinusoidal) with a Gaussian "envelope". So, just as for the particle in a box, the probability density for position has regions where it is non-vanishing joined at points where the probability density vanishes.

The allowed energies are discrete and display the "zero point energy" phenomenon: the lowest energy is not zero, even though the minimum of the potential energy function is zero. This can be viewed as a manifestation of the uncertainty principle. To see this, let us consider the ground state. For the Gaussian ground state of the oscillator, the expectation values of position and momentum are zero, so the expectation values of the squared position and squared momentum must be non-zero to give the non-zero variances required by the uncertainty principle for position and momentum. In particular, *in the ground state*, the expectation value

$$\langle H\rangle = \frac{1}{2m}\langle p^2\rangle + \frac{1}{2}k\langle x^2\rangle = \frac{1}{2m}\Delta p^2 + \frac{1}{2}k\Delta x^2 = \frac{1}{2}\hbar\omega.$$

is non-zero (and positive) and determined by the variances. The ground state is a state of definite energy, that is, for this state $E = \frac{1}{2}\hbar\omega$ with probability one. This means that the expectation value of H is the energy of the stationary state. Therefore, we can say that the uncertainty principle is responsible for $\langle H \rangle > 0$ from which it follows $E_0 > 0$.

There are a couple of even more striking properties of these states of definite energy. When n is odd, because the wave function is odd in x, it necessarily vanishes at $x = 0$. Thus, for example, the probability density for finding the particle at the equilibrium point with energy $\frac{3}{2}\hbar\omega$ is zero! More bizarre still, you will note that the wave functions — and hence the position probability distributions – are non-zero in a neighborhood of *every* value of x. To see why I say this is bizarre, consider the classical result. A classical particle with energy E moving in the potential $V(x) = \frac{1}{2}kx^2$ will only have its position in a range bounded by the amplitude of the motion (exercise)

$$-\sqrt{\frac{2E}{k}} \leq x \leq \sqrt{\frac{2E}{k}}.$$

The quantum particle, on the other hand, has a non-zero probability of being found at arbitrarily large values of x! One way to easily see this is to simply note that the ground state probability density never vanishes. This is the first instance of the "tunneling" phenomenon predicted by quantum mechanics. Tunneling *is* observed in nature (*e.g.,* in alpha decay).

In order to reconcile this interesting quantum behavior with our macroscopic, classical world, begin by noting that the width of the Gaussian position probability distribution for the ground state is given by $\sqrt{\frac{\hbar}{m\omega}}$. The energy for this state is $\frac{1}{2}\hbar\omega$. The classical turning points for a particle with this energy are (exercise) $x = \pm\sqrt{\frac{\hbar}{m\omega}}$, so the particle is most likely to be found in the "classical region" where $E \geq V$. In particular, in the ground state, with macroscopic parameters chosen for m and ω, the width of the Gaussian is exceedingly small. So for a macroscopic oscillator the probability for finding the particle away from the classical equilibrium is virtually zero.

Problem 2.11(c) in Griffiths text

Compute the average kinetic energy and average potential energy for the states ψ_0 and ψ_1. Is their sum what you would expect?

Solution: These kinds of calculations are best done using the ladder operators which feature in

$$x = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-), \quad p = i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}_+ - \hat{a}_-).$$

We then have

$$T = \frac{p^2}{2m} = -\frac{1}{4}\hbar\omega(\hat{a}_+^2 - \hat{a}_+\hat{a}_- - \hat{a}_-\hat{a}_+ + \hat{a}_-^2) = -\frac{1}{4}\hbar\omega(\hat{a}_+^2 - 2\hat{a}_+\hat{a}_- + \hat{a}_-^2 - 1),$$

and

$$V = \frac{1}{2}m\omega^2 x^2 = \frac{1}{4}\hbar\omega(\hat{a}_+^2 + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-^2) = \frac{1}{4}\hbar\omega(\hat{a}_+^2 + 2\hat{a}_+\hat{a}_- + \hat{a}_-^2 + 1).$$

We then have, with $\psi = \psi_0$ or $\psi = \psi_1$.

$$\langle T\rangle = -\frac{1}{4}\hbar\omega\int_{-\infty}^{\infty}\psi^*(\hat{a}_+^2 - 2\hat{a}_+\hat{a}_- + \hat{a}_-^2 - 1)\psi dx.$$

The first and third terms with $\hat{a}_\pm^2$ will not contribute since they will add or subtract two energy quanta from ψ and the result will be orthogonal to ψ. The last term is easily evaluated since ψ is normalized. The operator $\hat{a}_+\hat{a}_-$ in the second term will yield zero when acting on ψ_0. For ψ_1 we have, using $[\hat{a}_-, \hat{a}_+] = \hat{1}$,

$$\hat{a}_+\hat{a}_-\psi_1 = \hat{a}_+\hat{a}_-(Na_+\psi_0) = N\hat{a}_+^2\hat{a}_-\psi_0 + N\hat{a}_+\psi_0 = N\hat{a}_+\psi_0 = \psi_1.$$

Here N is a normalization constant. We can thus use the fact that ψ_1 is normalized to evaluate the contribution of the a_+a_- terms. We thus get

$$\langle T\rangle = -\frac{1}{4}\hbar\omega(0+0+0-1) = \frac{1}{4}\hbar\omega, \text{ for } \psi_0$$

$$\langle T\rangle = -\frac{1}{4}\hbar\omega(0-2+0-1) = \frac{3}{4}\hbar m\omega, \text{ for } \psi_1$$

In the same way one gets

$$\langle V\rangle = \frac{1}{4}\hbar\omega, \text{ for } \psi_0$$

and

$$\langle V\rangle = \frac{3}{4}\hbar\omega, \text{ for } \psi_1.$$

Consequently

$$\langle T\rangle + \langle V\rangle = \langle H\rangle = \begin{cases} \frac{1}{2}\hbar\omega & \psi = \psi_0 \\ \frac{3}{2}\hbar\omega & \psi = \psi_1 \end{cases},$$

as expected for energy eigenfunctions with eigenvalues $\hbar\omega/2$ and $3\hbar\omega/2$, respectively. □

Classical limit of the stationary states

Just as we did for the particle in the box, we can consider the limiting case in which the particle behavior in a stationary state approaches the classical limit. But what *is* the classical limit for a harmonic oscillator? We need to figure out the probability for finding a

classical particle with energy E at position x (irrespective of initial conditions). As before, this probability for finding a classical particle in a region will be proportional to the time the particle spends in that region. It is a very nice exercise from classical mechanics to show that, away from a turning point, the time dt spent in a region of size dx about x is given by

$$dt = \sqrt{\frac{1}{\frac{2}{m}(E - \frac{1}{2}kx^2)}}\, dx.$$

This implies that, properly normalized, the probability density $\rho_{\text{classical}}(x)$ is given by

$$\rho_{\text{classical}}(x) = \frac{1}{\pi x_0} \frac{1}{\sqrt{1 - \frac{x^2}{x_0^2}}},$$

where $x = \pm x_0$ is the maximum displacement from equilibrium ($E = \frac{1}{2}kx_0^2$).

You should think of this distribution as follows. If repeatedly take a classical oscillator and prepare it so that it has maximum displacement $\pm x_0$ (via any choice of initial conditions compatible with energy $E = \frac{1}{2}kx_0^2$) and compute the classical probability $P(x, \sigma)$ that the particle is in a region between x and $x + \sigma$ you will find

$$P(x,\sigma) = \int_x^{x+\sigma} \frac{1}{\pi x_0} \frac{1}{\sqrt{1 - \frac{x^2}{x_0^2}}}\, dx = \frac{1}{\pi}\left[\sin^{-1}\left(\frac{x+\sigma}{x_0}\right) - \sin^{-1}\left(\frac{x}{x_0}\right)\right].$$

Of course, $\rho_{\text{classical}}(x)$ looks nothing like the quantum probability distribution obtained by squaring the stationary state wave functions. However, recalling our experience with the particle in a box, consider a state with $n >> 1$. In this case, the quantum probability distribution can be shown to be a very rapidly oscillating function that follows, in its average value, the classical distribution derived above inside the classical region, and decays very rapidly outside the classical region. The origin of the rapid oscillations is the fact that $n >> 1$ is the number of zeros of the distribution. Just as we found for the particle in the box, if we ask for the probability that the particle be in a given region, and take the state of interest to have sufficiently large energy, the quantum probability is the same as the classical result. What happens is that, if the energy is chosen so that many oscillations occur in the probability distribution across the region of interest, the probability is well-approximated by the average distribution, which is the classical one. Thus if we don't look too closely, and the energy is high enough, the quantum behavior occurs at too fine a scale for us to see it, and the classical behavior is all we can observe.

Time evolution of states

Having found the stationary states for the harmonic oscillator we can find the time evolution of any initial state. The technique has already been discussed for the particle in a box; but the ideas are quite important, so we present them again.

The Schrödinger equation gives the "equation of motion" for the wave function as a function of time. Its solution is denoted $\Psi(x,t)$. To uniquely determine which of the infinitely many solutions of the SE to use, we can specify the initial conditions, namely, $\Psi(x,0)$. We use the completeness of the energy eigenfunctions ψ_n to write

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

where the c_n are complex numbers and $\psi_n(x)$ is the eigenfunction with energy eigenvalue E_n we discussed earlier (polynomials times Gaussian). The constants c_n are determined by the integrals

$$c_n = \int_{-\infty}^{\infty} \psi_n^* \Psi(0,x)\, dx.$$

The wave function $\Psi(x,t)$ is obtained via

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n e^{-\frac{i}{\hbar}E_n t} \psi_n(x).$$

You can think of this formula as saying that, given the initial state is a sum of stationary states, the state at time t is just that same sum with the stationary states evolving in the usual way, that is, each via the phase factor $e^{-\frac{i}{\hbar}E_n t}$. Do not think that these phase factors are physically irrelevant. Only a single, overall factor of absolute value unity will drop out of expectation values and hence not alter the physical content of the wave function. The phase factors that appear in the general solution of the SE are different in each term, so while we could factor one of them out, we cannot eliminate the relative phase information that they contain.

For example, suppose that the initial state was of the form

$$\Psi(x,0) = \alpha\psi_0(x) + \beta\psi_1(x).$$

This is not a state of definite energy, but rather is a *superposition* of two stationary states. It is easy to see that this function is normalizable (exercise). Consider $|\Psi(x,0)|^2$, it involves $|\psi_0|^2$, $|\psi_1|^2$ and $\psi_0\psi_1$. The integral of the first two types of terms is finite via normalizability of the stationary states. The integral of the last type of term is zero via orthogonality of stationary states. The two complex constants $\alpha = c_0$ and $\beta = c_1$ are partially determined by normalization (exercise):

$$|\alpha|^2 + |\beta|^2 = 1.$$

But this is one condition on two constants, so some freedom remains in the choice of these two complex numbers. Different choices of α and β (consistent with the normalization)

corresponds to assigning different probabilities for finding a given energy at the initial time. Recall that the probability for finding E_n is given by $|c_n|^2$. For our example, $|\alpha|^2$ is the probability for finding $\frac{1}{2}\hbar\omega$ while $|\beta|^2$ is the probability for finding $\frac{3}{2}\hbar\omega$. Evidently, the probability for finding any other energy, *e.g.,* $\hbar\omega$ is zero. If oscillator is repeatedly prepared in the state $\alpha\psi_0(x) + \beta\psi_1(x)$ and the energy is measured, the average energy (after many repeats) is

$$\langle H\rangle = |\alpha|^2(\frac{1}{2}\hbar\omega) + |\beta|^2(\frac{3}{2}\hbar\omega).$$

These probabilities and averages are in fact independent of which time is used to take the measurements (exercise). This is a feature peculiar to energy measurements, and is a manifestation of the conservation of energy. Other observables will not be conserved in time, *e.g.,* position, and will manifest time dependent behavior in non-stationary states.

The free particle

Now we turn to the simplest dynamical system, the free particle. We make our quantum mechanical model of this system by allowing the wave function to be non-zero everywhere, and we set $V(x) = 0$ in the Schrödinger equation. We shall see that this system is a little more subtle in quantum mechanics than it is in classical mechanics.

We begin by solving the Schrödinger equation for the free particle in the usual way for time-independent potentials: first solve the TISE for the stationary states (and allowed energies) and then superimpose the stationary states to get the general solution of the SE. The TISE is (exercise)

$$-\frac{\hbar^2}{2m}\psi'' = E\psi.$$

This equation is easy to solve — indeed it is the same equation we found for the particle in a box. The difference here is that there are no boundary conditions. Consequently, it is convenient to use complex exponentials rather than sines and cosines to express the solutions. For *any* value of k, the general solution of the TISE is

$$\psi(x) = Ae^{ikx} + Be^{-ikx},$$

where

$$k = \frac{1}{\hbar}\sqrt{2mE}, \quad E = \frac{\hbar^2k^2}{2m}.$$

and A, B are complex constants. We assume k is real for reasons to be explained later. For now, just note that this makes the energy real and positive like its classical counterpart. Evidently, we can build all solutions of the TISE by superposition of complex waves

$$\psi_E^{\pm} = e^{\pm ikx}, \quad E = \frac{\hbar^2k^2}{2m}.$$

As usual, the wave number k is related to the wavelength of the wave by λ by $\lambda = 2\pi/k$. Notice that the two wave functions $\psi_E^{\pm}$ each correspond to the same energy E. We say the energy E is "degenerate" in the sense that more than one state manifests the same energy.

Evidently, the free particle is a case where (i) the energy is not "quantized" (it's continuous rather than discrete); (ii) the smallest allowed energy, $E = 0$, is *equal* to the minimum of the potential. Recall that this cannot happen for normalizable solutions, so the stationary states above will not be normalizable. You can easily check this from the fact that

$$|\psi_E^{\pm}(x)|^2 = 1.$$

We shall discuss this a bit more in a moment, but for now I emphasize that, because of their non-normalizability, strictly speaking *there are no states of definite energy for the free particle!* This is a bit disturbing, but seems to be a fact of life. It in no way conflicts with our experimental knowledge of the universe. You should think of the stationary "states" for a free particle (I will usually drop the quotes from now on) as a useful mathematical idealization which occurs when we do not put any boundary conditions on the wave function. Physically, there is no problem. One can always imagine that the particle is actually confined to a very large region – a particle in a very large box. Then the energy eigenfunctions are normalizable. The free particle is the idealization which occurs when the walls of the box are sufficiently far away that you can ignore their presence. Like all idealizations, this has its limitations. For now we put the mathematical subtleties on hold, and focus on properties of these idealized stationary states which are, more or less, independent of normalization issues.

We have solved the TISE, so now we can discuss time evolution by considering families of wave functions solving the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\psi'' = i\hbar\frac{\partial\psi}{\partial t}.$$

To begin, we consider the time evolution of the stationary state wave functions (obtained by separation of variables as usual). A stationary state of definite energy $E \geq 0$, at time t is given by

$$\Psi(x,t) = e^{\pm ikx - iEt/\hbar} = e^{\pm ikx - i\hbar k^2 t/2m} = e^{\pm ik(x \mp \hbar k t/2m)}, \quad k \geq 0.$$

This is really a family of stationary state solutions parametrized by the wave number k. If we agree to let k take on any real value (previously we kept it positive) we can obtain all the stationary state solutions with the slightly simpler formula:

$$\Psi_k(x,t) = e^{ik(x - \hbar k t/2m)}, \quad -\infty < k < \infty.$$

With this convention understood, k represents the wave *vector*.

You may recognize the stationary state wave function as that of a traveling wave. Recall that a traveling wave looks like a sinusoidal function of $(kx \mp \omega t)$, where – for k positive – the minus sign signifies waves traveling to the right at speed ω/k while the plus sign signifies waves traveling to the left with speed ω/k. The real and imaginary parts of Ψ_k are of this form, with

$$\omega = \frac{\hbar k^2}{2m}.$$

The wave defined by Ψ_k travels toward positive (negative) x when k is positive (negative). The velocity of the wave is given by (exercise)

$$v = \frac{\omega}{k} = \frac{\hbar k}{2m} = \pm\sqrt{\frac{E}{2m}}.$$

Notice that the velocity of the wave depends upon its wavelength (via the wave vector). This phenomena is known as *dispersion*; we shall see why below.

It is worth comparing the preceding results with the classical motion of a particle with energy E. A classical particle with energy E has velocity given by

$$v_{\text{classical}} = \pm\sqrt{\frac{2E}{m}}.$$

Evidently the classical speed is double the wave speed:

$$v_{\text{classical}} = 2v.$$

So, while it may be tempting to identify the wave speed of the stationary state solution of the SE with the particle velocity, this doesn't look too good from the point of view of the classical limit. The lesson here is that you should not think of the wave function as a material model for the particle. A better way to connect the quantum behavior of the particle with the classical velocity of the particle is via statistical properties of the momentum observable. Because the wave function is not normalizable, we cannot compute any probabilities, strictly speaking. But let us note that the stationary states obey

$$(\hat{p}\Psi)(x,t) = \hbar k \Psi(x,t).$$

So (aside from normalization issues) we see that the stationary states are acting like momentum eigenfunctions and so can be viewed as (idealizations of) states where the momentum is known with certainty to have momentum $\hbar k$. Using the relation between wave number and energy, we see that

$$\hbar k = m v_{\text{classical}}.$$

Here you see how the Schrödinger equation recovers the original ideas of de Broglie.

To give a physically correct description of the particle behavior, including a correspondence with the classical free particle motion, we will have to work with *bona fide* wave functions, that is, normalized solutions of the SE. These solutions will necessarily be built up from superpositions of the stationary states and so they will not be states of definite energy or momentum except approximately.

Wave packets

Even though the solutions of the TISE are not normalizable, they *are* complete and can be used to construct (via superposition) normalized solutions to the SE. Such solutions must be localized in space to some extent since they must vanish as $x \to \pm\infty$. Since such a wave function is some kind of wave with localized amplitude, it is called a *wave packet*. Let us show how to construct such a thing using Fourier analysis.

Every normalizable solution of the SE can be expressed as a superposition of the solutions of the TISE found above. Indeed, we can write

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m} t)}\, dk.$$

This is just a continuous energy version of our usual way of making the general solution by superimposing stationary states (exercise).

You can also understand the appearance of this formula as follows. It is a standard result of Fourier analysis that any normalizable function, such as $\Psi(x,t)$ at a fixed instant of time, can be written as

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \alpha(k,t) e^{ikx}\, dk.$$

Substitute this expression for $\Psi(x,t)$ into the SE and find (exercise)

$$\int_{-\infty}^{\infty} [i\hbar \frac{\partial \alpha(k,t)}{\partial t} - \frac{\hbar^2 k^2}{2m} \alpha(k,t)] e^{ikx}\, dk = 0.$$

Since the Fourier transform of the quantity in brackets vanishes, so does the quantity itself:

$$i\hbar \frac{\partial \alpha(k,t)}{\partial t} - \frac{\hbar^2 k^2}{2m} \alpha(k,t) = 0.$$

This equation is easily solved (exercise):

$$\alpha(k,t) = \phi(k) e^{-i\frac{\hbar k^2}{2m} t},$$

where $\phi(k)$ is an arbitrary complex-valued function.

The arbitrary function $\phi(k)$ in the general solution to the free particle SE, given above, is the continuous version of the expansion coefficients c_n that we used for the particle in a box and harmonic oscillator. Indeed, if the particle were confined to a region $x \in [0, a]$, then the boundary conditions restrict the wave number to be

$$k = \frac{\pi}{a} n, \quad n = 1, 2, \ldots.$$

For large enough a we can view k as a continuous variable and the expansion coefficients c_n in the general solution of the Schrödinger equation can be viewed as a function ϕ of the (approximately) continuous variable k. Just as in that case the function $\phi(k)$ is fixed by initial conditions. Thus, suppose that the state of the particle at $t = 0$ is known, call it $\Psi(x, 0)$. As we did above, we can consider its Fourier representation:

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx}\, dk.$$

We see that $\phi(k)$ is the *Fourier transform* of $\Psi(x, 0)$ (and that $\Psi(x, 0)$ is the Fourier transform of $\phi(k)$). We have a similar integral formula for the "expansion coefficients" in the Fourier representation of $\Psi(x, 0)$,

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, 0) e^{-ikx}\, dk,$$

in complete analogy with our previous examples. It is a fundamental result of Fourier analysis that the Fourier transform $\phi(k)$ of a normalizable function, *e.g.,* $\Psi(x, 0)$, is normalizable (as a function of k) and *vice versa*. Therefore, if we choose for $\phi(k)$ any normalized function, then we are guaranteed to get a normalized initial wave function. As we have noted many times, the solutions of the Schrödinger equation are normalized at any time if they are normalized at a single time. Thus we build normalized solutions to the Schrödinger equation. You can see that, while the stationary states for a free particle are not, strictly speaking, allowed states because their wave functions can't be normalized, they do form a nice "basis" for the normalizable wave functions representing *bona fide* states.

So what have we gained from all this? Well, we can now build *bona fide* time-dependent states, that is, normalizable solutions of the SE, which can be physically analyzed in detail. We can even build states which mimic – as far as possible – the classical motion of a free particle. We do this by making a judicious choice of the initial state, *i.e.,* the Fourier transform $\phi(k)$. I now want to show you that if $\phi(k)$ is strongly peaked about a specific value of k, then the position probability will be localized to some region of space and this region of non-negligible probability for particle position will move in time at the classical velocity. In this sense one can recover classical motion of a particle.

We have seen that the solutions of the SE corresponding to a fixed value of k move at speed

$$v = \frac{\omega}{k} = \frac{\hbar k}{2m}.$$

Let us consider a normalizable solution obtained by superimposing such waves via

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

where $|\phi(k)|$ is strongly peaked about some chosen value k_0. and we have defined

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

To have a concrete example in mind, suppose that $|\phi(k)|$ is a Gaussian, narrowly peaked around k_0. The resulting initial wave function will also be localized in space, *i.e.,* a wave packet. To see this explicitly, just note that the Fourier transform of a Gaussian function (of k) is a Gaussian function (of x):

$$\int_{-\infty}^{\infty} e^{ikx} e^{-a^2(k-k_0)^2}\, dk = \frac{\sqrt{\pi}}{a} e^{ik_0 x} e^{-\frac{1}{4}\frac{x^2}{a^2}}.$$

We can infer that the wave solving the Schrödinger equation will consist of an oscillatory part, approximately like the stationary state with $k = k_0$, but with an amplitude that is modulated by a Gaussian "envelope" that vanishes as $x \to \pm\infty$ (so the wave function is normalizable). Such a state is called a *wave packet*. If we choose a different profile for $\phi(k)$, the state will be a traveling wave modulated by an envelope of a different shape, but as long as ϕ is peaked around a single value the qualitative structure of the wave packet is the same. Since each of the constituent waves moves at a different speed, it turns out that this envelope will spread in time. But if $\phi(k)$ is very narrowly peaked the spreading will be negligible for a while since the dominant waves in the superposition will have wave numbers which are all close to k_0.

I will now show that in general the envelope of the wave packet will travel at the classical speed for a particle with kinetic energy $\frac{\hbar^2 k_0^2}{2m}$. Since $\phi(k)$ is presumed to be negligible away from $k = k_0$, expand $\omega(k)$ in a Taylor series about k_0:

$$\omega(k) \approx \omega(k_0) + \omega'(k_0)(k - k_0).$$

Putting this into the integral representation for $\Psi(x,t)$ we get

$$\begin{aligned}\Psi(x,t) &\approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i\{kx - [\omega(k_0) + \omega'(k_0)(k-k_0)]\, t\}}\, dk \\ &= \frac{1}{\sqrt{2\pi}} e^{-i[\omega(k_0) - ik_0\omega'(k_0)]t} \int_{-\infty}^{\infty} \phi(k) e^{i[k(x - \omega'(k_0)\, t)]}\, dk.\end{aligned}$$

Compare this integral with that which occurs at $t = 0$,

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx}\, dk.$$

Up to an overall phase factor, $\Psi(x,t)$ is of the same form but with x replaced by $x-\omega'(k_0)t$. We therefore get

$$\Psi(x,t) \approx e^{-i[\omega(k_0)-k_0\omega'(k_0)]t}\Psi(x-\omega'(k_0)t,0).$$

Since the phase factor is physically irrelevant, we see that the wave function is (in this approximation) describing the same localized position probability distribution as at $t=0$, but moved over by an amount $\omega'(k_0)t$. So, while the constituent waves of the wave packet move (approximately) at different phase velocities, depending upon k,

$$v_{phase} = \frac{\omega(k)}{k} = \frac{\hbar k}{2m},$$

the envelope of the wave packet moves (approximately!) at the *group velocity*

$$v_{group} = \omega'(k_0) = \frac{\hbar k_0}{m},$$

which is the classical velocity of a particle with energy

$$E = \frac{\hbar^2 k_0^2}{2m}.$$

Insofar as the most probable location of the particle is the principal observational feature, as it would be in a macroscopic situation, we see that the quantity $\hbar k_0$ characterizes the classical momentum of the wave packet type of state in which $\phi(k)$ is narrowly peaked about k_0. This is another way quantum mechanics justifies de Broglie's ideas.

A couple of additional comments should be made here. First of all, we had to make approximations to get our "classical" result. This is necessary since particles simply do not precisely behave as classical mechanics would have you believe. The initial state of our wave packet has a well-localized momentum spread (*e.g.,* it is a narrow Gaussian), but a somewhat spread out position distribution (*e.g.,* another Gaussian), as can be seen from the uncertainty principle applied to a Gaussian state. Moreover, because the waves making up the wave packet have different (phase) velocities, the wave packet will spread as time passes. This is the phenomenon of "dispersion", mentioned earlier. Provided we are dealing with a "macroscopic" particle, these "uncertainties" in position and momentum, spreading in time, etc., will be imperceptible. Note also that the state, while having its energy well-localized at $\frac{\hbar^2 k_0^2}{2m}$, still allows a non-zero probability for a measurement of energy to differ from this most probable value. Again, for macroscopic systems this small uncertainty in the energy is imperceptible. In this way we recover the classical motion of a macroscopic particle.*

* This is fine as far as it goes, but there must be more to the story since it is not clear why all macroscopic objects seem to be prepared in an appropriate wave packet kind of state. Considerations of this issue lead to ideas involving "decoherence", which you can read about.

Problem 2.21 in Griffiths' text

A free particle has the initial wave function

$$\Psi(x,0) = Ae^{-a|x|}, \quad A, a > 0.$$

(a) Normalize Ψ.

(b) Find $\phi(k)$.

(c) Find $\Psi(x,t)$.

(d) Discuss limiting cases for the parameter a.

This wave function is actually the bound state solution for a particle of mass m in a δ-function potential well of strength $\hbar^2 a/m$. Consequently it defines a stationary state solution for the Schrödinger equation appropriate to that potential well. Here we are just considering what happens when we evolve this initial state in time as a free particle would evolve. Of course it does not define a stationary state in this case.

(a) We have

$$1 = \int_{-\infty}^{\infty} |A|^2 e^{-2a|x|}\, dx = 2|A|^2 \int_0^{\infty} e^{-2ax} = \frac{|A|^2}{a},$$

so we can normalize the wave function by setting $A = \sqrt{a}$.

(b) We have

$$\begin{aligned}
\phi(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} \Psi(x,0)\, dx \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} \sqrt{a} e^{-a|x|})\, dx \\
&= \frac{2}{\sqrt{2\pi}} \int_0^{\infty} e^{-ikx} \sqrt{a} e^{-ax})\, dx + \frac{2}{\sqrt{2\pi}} \int_0^{\infty} e^{ikx} \sqrt{a} e^{-ax})\, dx \\
&= \sqrt{\frac{2a^3}{\pi}} \frac{1}{a^2 + k^2}
\end{aligned}$$

(c) With $\omega = \frac{\hbar k^2}{2m}$ we have

$$\begin{aligned}
\Psi(x,t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i(kx - \omega t)} \phi(k)\, dk \\
&= \frac{a^{3/2}}{\pi} \int_{-\infty}^{\infty} e^{i(kx - \frac{\hbar k^2}{2m} t)} \frac{1}{a^2 + k^2}\, dk.
\end{aligned}$$

(d) The wave function is peaked about $x = 0$ while its Fourier transform is peaked about $k = 0$. As a becomes small, the wave function is more spread out while the absolute value of the Fourier transform becomes more peaked about $k = 0$. Physically, the position of the particle is relatively uncertain while the dominant contribution to the wave function at time t is coming from $k = 0$. Recall that $\hbar k$ is the momentum contribution of the wave featuring in the Fourier transform. So the dominant contribution to the wave function is coming from small momentum. This is a quantum version of a particle at rest. As a becomes large the wave function is more localized about $x = 0$ and the absolute value of the Fourier transform becomes more spread out so that a variety of wave numbers contribute to the solution at time t. This is a quantum version of a particle localized at a single point; many momenta values feature in the wave function for this state. Notice that the wave function is not normalizable as $a \to 0$ and the Fourier transform develops a pole at $k = 0$. As $a \to \infty$ both the wave function and its Fourier transform approach zero. □

The square well

Our final one-dimensional example is the "square well". Here the potential energy is of the form

$$V(x) = \begin{cases} -V_0, & -a < x < a \\ 0, & |x| > a. \end{cases}$$

In the limit where V_0 is suitably large we expect this system to be well-described by our earlier, simpler "particle in a box".

Let me briefly review the classical mechanics description of such a system. Firstly, energy is conserved and the particle can have positive or negative energy. If the particle's energy is negative, then it must be in the region $-a < x < a$ (exercise), where it bounces back and forth with constant speed, just like a particle in a box. That the speed is constant (between bounces) can be seen from the fact that the potential energy is constant in this region; consequently there is no force and the kinetic energy must be constant. If the energy is positive, the particle is not bound to any region of space, the particle can be found anywhere (exercise). The motion of the particle is *not* that of a free particle, however. The potential is not constant over the whole x axis; the particle can be "scattered" off of the attractive potential. Of course, in a one-dimensional model the notion of "scattering" is pretty trivial. Still it is useful to picture what happens. Suppose a particle approaches the well from the left. As long as $x < a/2$ the velocity of the particle is constant (exercise). At the instant the particle crosses the well boundary at $x = -a/2$ the velocity of the particle increases (exercise: by how much?). This you can see easily by conservation of energy. The particle continues with this new, constant velocity until it passes the point $x = a/2$. At this point the particle jumps to its initial velocity, and keeps that velocity from then on.

Remark: If you try to see this increase/decrease in speed using Newton's second law, you will run into the problem that the potential energy is not differentiable at $x = \pm a/2$. For those of you who have experience with delta-functions, the force near $x = \pm a/2$ is a delta-function, which gives an impulsive change in the velocity of the particle, in agreement with conservation of energy. Don't let the discontinuous nature of the potential upset your mathematical sensibilities. For our purposes, the idealized "square" corners are analytically much easier and models very nicely a continuous potential that has some slight rounding of the corners.

Ponder this: suppose you are in the laboratory scattering particles off of this potential. You shoot particles with some given initial speed at the well and then detect the particles after their encounter with the well. Since the particles' velocity prior to encountering the well is the same as after the encounter, how would you "see" the effects of the well in your detector data?

The square well potential is a very simple — indeed, the simplest — model of an electron in an atom in the sense that there are "bound states" and "scattering states" (also called "ionized states"). Although the reasoning above was purely classical, we shall see that these two classes of states will also exist quantum mechanically. Of course, there will be a few interesting differences in the observable aspects of the system which are intrinsically quantum mechanical.

As usual, to solve the Schrödinger equation we first solve the TISE to find the stationary states and allowed energies. Our strategy is to solve the TISE separately in the regions $-a < x < a$ and $|x| > a$, and then adjust integration constants to make $\psi(x)$ and $\psi'(x)$ continuous for all x. The solutions of the TISE then allow us to find the general solution of the SE, as usual, via a superposition of the stationary state wave functions. From the general solution of the SE we can describe the evolution of the state of the system in time for any initial conditions.

When solving the TISE, we will find it helpful to distinguish the two cases $-V_0 < E < 0$ and $E > 0$ (remember the classical limit). The case $-V_0 < E < 0$ will admit normalizable solutions to the TISE, which represents the *bound states*. The solutions of the TISE corresponding to $E > 0$ will not be normalizable; so they do not represent *bona fide* states. This is the same subtlety that occurs with a free particle. As in that case, the stationary state solutions to the TISE can be used to form normalized states by superposition. The dynamical evolution of such states is a simple example of the behavior of *scattering states* in quantum mechanics.

Bound states

We begin with the case $E < 0$, which we shall see corresponds to *bound states*, that

is, states in which the probability for finding the particle arbitrarily far from the $x = 0$ is arbitrarily small.

Let us solve the TISE for $x > a$. Setting $E = -|E|$, the TISE is

$$-\frac{\hbar^2}{2m}\psi'' = -|E|\psi.$$

This is easy to solve. The solutions are growing or decaying exponentials (exercise). Growing exponentials will not allow for normalizable solutions, so we do not consider these solutions.* We get then (exercise)

$$\psi(x) = Fe^{-\kappa x}, \quad x > a,$$

where

$$\kappa = \frac{1}{\hbar}\sqrt{2m|E|}$$

and F is a constant of integration. When $x < -a$ we get a very similar situation and we have

$$\psi(x) = Be^{\kappa x}, \quad x < -a,$$

where B is another integration constant. Note that, as $x \to \pm\infty$ the solutions do not blow up, indeed, they vanish exponentially. This will permit the stationary states to be normalizable.

Now we solve the TISE for $-a < x < a$. We have

$$-\frac{\hbar^2}{2m}\psi'' - V_0\psi = -|E|\psi.$$

Since V_0 is just a constant, we can move it to the other side of the equation and solve as before. Because we are finding a solution in a bounded region, we need to keep both exponentials (which oscillate now). We can equally well use cosines and sines to express the solution. We get (exercise)

$$\psi(x) = C\sin(lx) + D\cos(lx),$$

where C and D are constants and

$$l = \frac{1}{\hbar}\sqrt{2m(V_0 - |E|)}.$$

We know that normalizable solutions of the TISE must have $E > -V_0$, which implies $E < V_0$, so the arguments of the sine and cosine are real. What will go wrong if $E \leq -V_0$? As an exercise you can check that it will not be possible to match the "inside the well"

* Here is another instance of how one uses boundary conditions to fix integration constants and/or energies when solving the TISE.

solution and its first derivative to the "outside the well" solutions which we picked, unless we put back in the growing exponentials and spoil the normalizability.

It simplifies life a little to use the fact that the potential energy is an even function of x, and so we can assume each of the stationary states is even or odd.* To see this, simply note that if $\psi(x)$ is a solution to the TISE with for some E then so is $\tilde{\psi}(x) = \psi(-x)$. Consequently, because the TISE is linear we can superimpose such solutions to get solutions (with the same value of E) and always work with solutions of the form

$$\psi_{\text{even}} = \psi(x) + \psi(-x), \quad \psi_{\text{odd}} = \psi(x) - \psi(-x).$$

Following the text, let us focus on even solutions:

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & \text{if } x > a, \\ D\cos(lx), & \text{if } -a < x < a, \\ Fe^{\kappa x}, & \text{if } x < -a. \end{cases}$$

Odd solutions are handled similarly and have a similar qualitative behavior. I will leave it to you to see how that goes. Given this form of the even solution, we have 3 constants to be determined (D, F, E). One condition on these constants is provided by normalization. The remaining conditions are continuity of $\psi(x)$ and $\psi'(x)$ at $x = a$. (The conditions at $x = -a$ are automatically satisfied since we focused on even solutions.) Along with normalization, these continuity conditions will completely determine the solution as well as the allowed energies. As usual, they will force the energy to be "quantized".

The boundary conditions (continuity of ψ and ψ') are (exercise)

$$Fe^{-\kappa a} = D\cos(la)$$

and

$$\kappa F e^{-\kappa a} = lD\sin(la).$$

These equations look like they determine both B and D, but actually they determine one of those and E. How to see this? Write the equations for D and F as a linear system:

$$\begin{pmatrix} \cos(la) & -e^{-\kappa a} \\ l\sin(la) & -\kappa e^{-\kappa a} \end{pmatrix} \begin{pmatrix} D \\ F \end{pmatrix} = 0.$$

As you know, this linear system will have a solution for D and F if and only if the determinant of the matrix vanishes, so that:

$$\kappa\cos(la) - l\sin(la) = 0,$$

* *Danger:* Do not make the mistake of thinking that the stationary states are *all* even, or all odd; both will occur.

or*

$$\kappa = l \tan(la).$$

This is a *transcendental equation* for the allowed energies E. The best way to solve it is numerically. To see how the solutions get determined, you can graph the left and right hand sides as functions of E and see where the graphs intersect. You will see that one gets a discrete set of allowed energies this way. You will also see that there are only a finite number of allowed energies!

It is perhaps worth emphasizing that the boundary conditions which enforce continuity of the wave function and its first derivative will arise whenever you break up the solution of the TISE into regions of space — even for the unbound scattering solutions, which will not be normalizable. The cause of the discreteness of energy for the bound states, mathematically speaking, is in the normalizability of the wave function. Since we already guaranteed that by choosing the decaying exponential solutions outside the well, the "quantization" of energies sneaks back in when we match the interior solutions to the exterior solutions.

Having found the allowed energies (if only numerically), you can substitute them one at a time into one of the continuity conditions displayed above to eliminate one of the constants D or F. The other constant is fixed by normalization. I will spare you the calculations since we won't be needing the results.

The result of all this is a discrete – and finite – set of energy eigenfunctions with corresponding allowed energies. The eigenfunctions are oscillatory in the well, but are decaying exponentials outside the well. Thus, qualitatively, we have a similar behavior in the well as with the particle in the box. On the other hand, unlike the case of an infinite well, there are only a finite number of energy eigenfunctions. Perhaps more impressive is the fact *there is a non-zero probability for finding the particle outside the well.* This is in sharp contrast to what happens in classical mechanics. We saw also saw this "tunneling" phenomenon with the harmonic oscillator. Note that the rate of decay of the exponential is fixed by the parameter κ. For macroscopic values of mass and energy, this parameter is very large (exercise). Thus the probability for a macroscopic system to "tunnel" out of the well is negligible.

Let us discuss the allowed energies in a little more detail. The most elegant method of finding them is to define dimensionless variables $z = la$ and $z_0 = \frac{a}{\hbar}\sqrt{2mV_0}$. In terms of them the transcendental equation takes the form

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}.$$

* One can get this condition as a necessary condition by taking the ratio of the two starting equations for F and D.

The idea is to solve this equation for $z \geq 0$ for a given z_0. You can experiment with the computer to see how to get at the roots of this equation. If you make graphs of the left and right hand sides of the equation you will see that, because the right hand side becomes imaginary at $z > z_0$ and becomes infinite at $z = 0$, there will only be a finite, discrete number of intersections, *i.e.,* solutions.

Now consider two interesting limiting cases. First, suppose that $z_0 >> 1$. This corresponds to a very deep well (and/or a very wide well), so we expect to approximately recover the particle in a box results. We do. In this approximation the transcendental equation for z says

$$\tan z >> 1.$$

The roots of this equation are in the approximation the values of z where the tangent blows up, that is, at $z = \frac{(2N+1)\pi}{2}$, $N = 0, 1, 2,$ Back in terms of our original parameters we get

$$E_n \approx \frac{(2N+1)^2\pi^2\hbar^2}{2m(2a)^2} - V_0, \quad N = 0, 1, 2, \ldots.$$

This is exactly what we expect. To compare with the infinite square well you must: (1) note that the current example has a well of width $2a$; (2) note that the particle in the box had the minimum potential at zero, here the minimum is $-V_0$, so the energy to be compared is the energy above the minimum in each case; (3) keep in mind that we only get half of all the energies since we restricted to the even solutions from the start. Also, keep in mind that there are really only a finite number of energies, in contrast to the particle in a box. Still, for a deep enough well, we can get as many energies as we want.

Another nice limit to consider is the case where $z_0 << 1$. This case corresponds to a very narrow and/or a very shallow well. As z_0 is reduced, the number of energy eigenfunctions decreases. For sufficiently small z there is only a single root to the transcendental equation. Thus, for a very shallow well, we have only a single allowed energy for a bound state! This is another manifestation of the uncertainty principle. Compare this with the classical description of such a limit.

Unbound, "scattering" states

We are now going to consider solutions of the TISE for the square well potential in which the energy is positive. As we shall see, such solutions will not be normalizable, just as in the free particle case. This does not mean we cannot do quantum mechanics in this case, but only that states of definite positive energy are not quite realizable. Normalizable unbound states will require superpositions of stationary states into wave packets. The logic of the situation is entirely the same as our wave packet discussion for the free particle.

For your convenience, let me remind you the behavior of the scattering states in the classical limit. Classically, the motion of a particle moving under the influence of the square well potential with positive energy is that of a free particle away from the boundaries of the well, but with a different (greater) velocity inside the well than outside. In particular, if a particle is sent from the left of the well, for example, then it will arrive at a point outside the well on the right side sooner than it would have if there were no potential. This is the "scattering" effect of a 1-d potential well.

It is easy to solve the TISE inside and outside the well for $E > 0$ to find (exercise)

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad x < -a,$$

$$\psi(x) = C\sin(lx) + D\cos(lx), \quad -a < x < a,$$

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}, \quad x > a.$$

Here

$$k = \frac{\sqrt{2mE}}{\hbar}, \quad l = \frac{\sqrt{2m(E+V_0)}}{\hbar}.$$

Note that our current convention keeps k and l as non-negative numbers. As usual, the constants A, B, C, D, E, F, G are to be fixed, as far as possible, by boundary conditions given by continuity of the wave function and its first derivative. For the bound states we had one more condition to impose: normalization. Here "normalization" is not a condition since the unbound energy eigenfunctions will not be normalizable. Of course, the *bona fide* wave functions will be normalizable superpositions of the un-normalizable stationary state wave functions, just as for the free particle.

To proceed, let us first consider the separation of variables solutions of the full SE outside the well. We saw, when studying the free particle, that the positive (negative) wave numbers k correspond to particle motion to the right (left). Here we get traveling waves moving to the left (the terms with coefficients B, and G) and to the right (the terms with coefficients A and F) on each side of the well. Focus on the left side of the well. We have an "incident" and "reflected" probability wave corresponding to the terms with A and B, respectively. Let us consider a scattering scenario where the particle comes in from the left side of the well and scatters off of the well. While there may be a reflected left-moving wave on the left side of the well, we assume in this scattering scenario that there is no left-moving particle on the right side of the well. We do all this mathematically by restricting attention to solutions with $G = 0$. To get a mental image to go with the math, you can think of the ratio of $|A|^2/|B|^2$ as giving the ratio of incident particle probability to reflected probability. The ratio $|F|^2/|A|^2$ is then the ratio of "transmitted" probability to incident probability. I will spell this out a little more carefully in a moment.

For our scattering scenario we have set $G = 0$. To determine the remaining coefficients A, B, C, D, F (and possibly the energy E) we use continuity of the wave function and its

first derivative, as before. We will get 4 conditions which fix A, B, C, D, F in terms of E. The energy is not determined; it can take any positive value. The fact that the energy E is not determined by the boundary conditions is completely analogous to the situation with the free particle. The energy can take any positive value. Keep in mind that the term "energy" is somewhat limited in the sense that there is no state of definite energy since the solutions are not normalizable.

The details of the continuity conditions are straightforward and can be found in your text. After a bit of algebra, we get the following relations among the integration constants:

$$B = i\frac{\sin(2la)}{2kl}(l^2 - k^2)F,$$

$$F = \frac{e^{-2ika}A}{\cos(2la) - i\frac{\sin(2la)}{2kl}(k^2 + l^2)}.$$

Given A and the energy E, we can find F and then B. There are also a couple of other similar equations that determine C and D in terms of A and E. We won't use them, so I won't bother to write them.

The bottom line is this: using the boundary conditions we can determine B, C, D, F, G as a function of the energy E and the coefficient A. To characterize the results, we define the *transmission coefficient* T and *reflection coefficient* R by

$$T = \frac{|F|^2}{|A|^2}, \quad R = \frac{|B|^2}{|A|^2}.$$

Using the formulas above, you can check that

$$T = \frac{1}{1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right)}$$

and

$$R = 1 - T.$$

How to interpret all of this? Well, again, the wave functions we are considering are not normalizable, so we cannot, strictly speaking, directly use probability notions to interpret the solutions of the TISE. Still, we can suppose that we have superimposed the solutions obtained above over a range of energies to make a normalizable wave function (just as we did for the free particle). Indeed, it can be shown, as usual, that any normalizable wave function can be written as a superposition of the solutions (with varying choices of A and E) of the TISE. For each energy E, we have formulas for how much of each of the corresponding waves in the superposition is transmitted by the barrier and how much is reflected. The transmission (reflection) coefficient as a function of E gives the

relative probability for transmission (reflection) of the component wave solving the TISE with energy E. Note that

$$R + T = 1,$$

which is consistent with this interpretation.

What could you do with this information in the real world? To use the relative probabilities, we repeatedly fire a particle from the left at the well. Imagine we have a beam of particles, characterized by some spread of energies. For each energy, the fraction of particles that are transmitted is T, and the fraction that are reflected is R. The net transmission and reflection will be an average over those for each energy. If you like, you can suppose that the wave function of the incoming particle has a strongly peaked dependence on a given energy so that, approximately, the particle has a well-defined energy. Then we can view the transmission and reflection coefficients computed above to approximately describe the scattering (insofar as the spread in energies is negligible).

Classically, all the particles are transmitted, *i.e.,* they pass "over" the well, and then move with their initial kinetic energy. Quantum mechanically you can see the same behavior for the transmitted particles. The solution of the TISE before and after the well is exactly that of a free particle with the given energy E. Probably the most interesting effect of quantum mechanics is that there is a non-zero probability for the particle to be reflected by the well. Classically this doesn't happen.

It is possible to shoot a particle at the well with just the right energy so that no reflection occurs. This energy is that which sets $T = 1$, and is given by (exercise)

$$E_{T=1} = \frac{n^2\pi^2\hbar^2}{2m(2a)^2} - V_0.$$

You will recognize that perfect transmission occurs when E is one of the allowed energies of the *infinite* square well! Any other energy will have the particle having a non-zero probability for reflection. Note that for macroscopic systems, the energies of the infinite square well are *very* closely spaced, since $\frac{\pi^2\hbar^2}{2m(2a)^2}$ will be a very small number in macroscopic units of energy. Consequently, for macroscopic systems one is always sufficiently near to one of these special energies so that the reflection phenomenon is negligible.

Degeneracy

We have seen that eigenfunctions of the Hamiltonian are states where the energy is known with certainty. If the energy of a system is known with certainty (*i.e.,* we measure it), can we immediately say what is the state? Usually, knowledge of a single observable is not enough to determine the state of a system completely. This is certainly the case in classical mechanics. Think about a particle moving in 1-d in some given force field

corresponding to a potential energy V. Recall that the state of the classical particle can be determined by its position and momentum (or velocity). Just knowing the energy tells you the value of $E = \frac{1}{2}mv^2 + V(x)$, but this does not necessarily pin down the values of x or v; many combinations of position and velocity – many different states – may give the same energy. In three dimensions this fact is even more pronounced. For example, if the (kinetic) energy of a free particle moving in 3-d is specified, there is a continuous infinity of possible positions and velocities the particle may have. If an observable is specified to have some value and more than one state is associated to this value we say that observable value is *degenerate*. If only one state of the system corresponds to that observable value we say the value is *non-degenerate*. For example, you can easily convince yourself that for a *classical* harmonic oscillator the value of energy $E = 0$ is non-degenerate while any value $E \neq 0$ is degenerate.

Let us focus on the energy and its possible degeneracy in quantum theory. Two wave functions represent the same state if they differ by a phase. Alternatively, two wave functions ψ_1 and ψ_2 define distinct states if they are *linearly independent*: there is no relation of the form $a\psi_1 + b\psi_2 = 0$ where a and b are constants. To see this, just divide both sides by a to get

$$\psi_1 = -\frac{b}{a}\psi_2.$$

Since both wave functions are normalized it follows that

$$\left|-\frac{b}{a}\right|^2 = 1 \quad \Longleftrightarrow \quad -\frac{b}{a} = e^{i\alpha},\ \alpha \text{ real}.$$

Thus two wave functions are linearly independent if and only if they do not differ by only a phase factor. The value of an observable, *e.g.,* an energy E, is *degenerate* if there is more than one linearly independent eigenfunction with the same eigenvalue E.

For a particle moving in one dimension I will now show that the energy eigenvalues (with *bona fide* normalized eigenfunctions*) are always non-degenerate. Contrast this with the situation in classical mechanics where, typically, there is some degeneracy for energy values. Why do you think this is?

Problem 2.45 in Griffifths

Prove: For a particle moving in one dimension, $-\infty < x < \infty$, there are no degenerate bound states

* For non-normalizable energy eigenstates, *e.g.,* for a free particle or for scattering states for a potential well, it is possible to have degeneracy – even in one dimension. For example, a free particle with a given energy will have to linearly independent energy eigenfunctions corresponding to left-directed momentum and right-directed momentum.

Suppose there are two bound state solutions to the time-independent Schrödinger equation, ψ_1 and ψ_2 for a given potential energy V with the same energy E. You may have encountered the *Wronskian* of two solutions in your study of differential equations. In this case it is given by

$$W = \psi_2\psi_1' - \psi_1\psi_2'.$$

Two functions are linearly independent (in some region) if and only if the Wronskian is non-zero in that region. We shall see that the Wronskian is in fact zero in the present context. Using the TISE, it follows that W is a constant:

$$W' = \psi_2\psi_1'' - \psi_1\psi_2'' = \psi_2\left(\frac{2mE}{\hbar} - V\right)\psi_1 - \psi_1\left(\frac{2mE}{\hbar} - V\right)\psi_2 = 0.$$

Now, assuming that ψ_1 and ψ_2 are normalized, they must vanish as $x \to \pm\infty$. Since ψ_1' and ψ_2' must be bounded (or else one cannot even define the TISE), it follows that $W = 0$. We thus have

$$\psi_2\psi_1' = \psi_1\psi_2'.$$

This implies, away from zeros of ψ_2,

$$\left(\frac{\psi_1}{\psi_2}\right)' = \frac{1}{\psi_2^2}(\psi_1'\psi_2 - \psi_2'\psi_1) = 0,$$

so that $\psi_2 = (const.)\psi_1$ away from zeros of ψ_2. One can interchange the roles of ψ_1 and ψ_2 and show the same result away from zeros of ψ_1. This suffices to establish the result everywhere. We conclude that any two bound state wave functions with a given energy are linearly dependent; there is only one bound state for each energy. □

For a particle moving in more than one dimension there are too many degrees of freedom for a single observable to completely characterize the state, in general. So, for higher dimensional examples, *e.g.,* atoms, there will be some degeneracy for the energy eigenvalues.