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 given by

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

Here I am using the capital letter Ψ to denote the state as a function of time, per the notation in the text. The potential energy function is assumed to be known. 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 approaches to 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 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.)

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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* (exercise):

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

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 (exercise)

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

where C is a constant. The second equation is known as the *time-independent Schrödinger equation*, which we shall abbreviate as TISE. The constant E is to be determined in the course of solving the TISE.

The TISE 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 equation also determines the constant E. There is no general solution known for all choices of $V(x)$. Until we specify the potential $V(x)$ we cannot try to solve it. We shall look at some simple potentials soon.

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 (exercise: 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 $t = 0$.

Stationary states

The separation of variable solutions we have constructed to the SE 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)

$$\langle Q \rangle = \int \Psi^*(x, t)Q(x, \frac{\hbar}{i}\frac{\partial}{\partial x})\Psi(x, t)\, dx$$
$$= \int \psi^*(x)Q(x, \frac{\hbar}{i}\frac{\partial}{\partial x})\psi(x)\, dx.$$

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Thus, 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.

Exercise: 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?

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 any constant, 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. 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.

The wave functions $\psi(x)$ solving the TISE have a very important 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 $\hat{H}$, where

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

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* 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..

This operator represents the total energy, 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 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 $\Psi(x,t)$ in the above computations (exercise). Both Ψ and ψ satisfy the same TISE; they both represent the same state of definite energy.

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 wave functions at different times all differ by a phase factor, they all represent the same state. In particular, if the initial state of a system 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 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 – Problem 2.2.) To prove this, write the TISE as

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

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, the function $\frac{2m}{\hbar^2}(V(x) - E)$ is, by assumption, always greater than or equal to the constant $c^2 \equiv \frac{2m}{\hbar^2}(V_{min} - E)$. This constant is positive or zero. Consequently, if ψ satisfies the TISE then

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

where we used the fact that ψ is normalized. Note that, because ψ is normalizable, we must have

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

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

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

But this 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 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, 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 what will happen. We shall find that the TISE determines these 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":

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

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 solving 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. 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.

Particle in a box

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

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

and solving the Schrödinger equation in the region $x \in (0, a)$ These conditions are chosen to 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 will become clearer once we have studied the potential well of *finite* depth

This is why this model is sometimes called the "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 states as a function of time we use our previous results and study the TISE. In the box the particle is to move freely so we set $V(x) = 0$ and we have

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

This equation is easily solved (exercise) to give

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

where A and B are constants and

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

Now, at this point, A, B, and k (or E) are all arbitrary complex numbers. We still must impose boundary conditions. Setting

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

we find (exercise) that $B = 0$ and

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

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. Thus 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 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

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

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 via the combination $\frac{h^2}{ma^2}$. For a macroscopic box or particle 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 "sufficiently large" 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

$$\psi_n(x) = A\sin\left(\frac{\pi}{a}nx\right), \quad 0 \le x \le a,$$

$$\psi_n(x) = 0, \quad x \ge a, \ x \le 0.$$

The constant A is undetermined by the SE (or TISE), but this is a good thing; 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:

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

A couple of things to notice about 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 (exercise) 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 $\alpha = 0$.

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 the stationary states are either even or odd functions of x, depending upon whether n is odd or even, respectively. Note also 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 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.

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. (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 within $(0, a)$ of size σ 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 is simply

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

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

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

You can check that, as a function of x, this probability distribution oscillates in x around the value σ/a with n maxima and n zeros. 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 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 angle 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 $(n \to \infty)$ 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 is negligible on the scales at which we are making measurements. Phrasing this in terms of energy we have (exercise)

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

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.

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 apply to *any* stationary states. For simplicity, we drop the phase factors $e^{-\frac{i}{\hbar}Et}$ from the states and work with the *energy eigenfunctions* ψ_n.

First, we point out that these functions form an *orthonormal set* in the following sense:

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

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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 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 orthogonality relationship, via integral tables or computer. An explicit proof appears in your text, and is easy to follow.

Second we point out that the stationary states ψ_n are *complete*, that is, they form a *basis* for any normalizable function on the interval $[a, b]$. In particular, we can represent any normalizable function $f(x)$ on the interval $[0, a]$ and with boundary values $f(0) = f(a) = 0$ by an infinite series expansion:

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

(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".)

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. However, it is something you must keep in mind. It *is* worth showing how the coefficients c_n are determined by $f(x)$. We have, using orthonormality* (exercise)

$$\int_0^a f(x)\psi_m^*(x)\, dx = \int_0^a \sum_{n=1}^{\infty} c_n \psi_n(x)\psi_m^*(x)\, dx$$

$$= \sum_{n=1}^{\infty} c_n \delta_{mn}$$

$$= c_m.$$

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

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

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

You can think of this result in terms of a very simple analogy. 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 ith component, v_i of $\mathbf{v}$ in this basis is simply

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

The components v_i are the expansion coefficients:

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

Similarly, think of the set of (normalizable) functions as a set of vectors. Think of the energy eigenfunctions ϕ_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

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

solves the SE, any *linear combination* will also solve the SE (exercise):

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

Here the c_n are complex constants (time independent). You can check, by explicit computation, that this wave function does indeed solve the SE and obeys the BC $\Psi(0, t) = \Psi(a, t) = 0$. 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 solution to the SE (with the given boundary conditions) can be written in this form. 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

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* 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!

$\Psi(x,0) = f(x)$. We then have

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

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

Normalization of the general solution

The general solution of the SE represents the state of the system at each time t. Consequently, this wavefunction must be normalized, which has an important consequence for the physical interpretation of the expansion coefficients c_n. The normalization condition is (this is problem 2.10 in the text)

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

which gives (exercise)

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

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 is a statement that the probability for all outcomes of a position measurement add up to one. The normalization condition on the c_n

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* 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.

has a similar interpretation. Recall that if the particle is in a stationary state, *i.e.*, all c_i vanish but one — say c_k, then the probability for measuring energy and getting E_k is one (and, of course, all others zero). In this case, this probability distribution can be identified with the fact that

$$|c_k|^2 = 1, \quad |c_i|^2 = 0, \quad if \ i \neq k$$

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

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

Here the orthonormality of the stationary states was used. In light of these results concerning the c's, one interprets $|c_i|^2$ as the probability of finding the energy E_i. 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; this is a manifestation of energy conservation in quantum mechanics.

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 of an oscillator from equilibrium at $x = 0$). 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 of a general potential around a point x_0:

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

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 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

$$a_\pm = \frac{1}{\sqrt{2m\hbar\omega}}\left(\mp\hbar\frac{d}{dx} + m\omega x\right),$$

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

where
$$\omega = \sqrt{\frac{k}{m}}$$
is the natural angular frequency of the oscillator. Given a function $f(x)$, we have
$$a_{\pm} f = \frac{1}{\sqrt{2m\hbar\omega}}\left(\mp\hbar\frac{df}{dx} + m\omega x f\right).$$

Note that here we have an instance of linear operators that don't commute (exercise); we have
$$a_- a_+ \psi - a_+ a_- \psi = \psi.$$

We write this operator relationship in terms of the commutator:
$$[a_-, a_+] \equiv a_- a_+ - a_+ a_- = 1.$$

With a little algebra, it is not hard to see that we can now write the TISE in either of two equivalent forms:
$$\hbar\omega(a_+ a_- + \frac{1}{2})\psi = E\psi,$$
or
$$\hbar\omega(a_- a_+ - \frac{1}{2})\psi = E\psi,$$

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 $a_{\pm}\psi$ will solve the TISE, with energy $E \pm \hbar\omega$. Let us prove this.

Assume that ψ solves
$$\hbar\omega(a_+ a_- + \frac{1}{2})\psi = E\psi,$$
and
$$\hbar\omega(a_- a_+ - \frac{1}{2})\psi = E\psi,$$
for a given value E of the energy. Now consider the function $a_+\psi$. We have
$$a_+ a_-(a_+\psi) = a_+(a_- a_+\psi)$$
$$= a_+[(E/\hbar\omega + \frac{1}{2})\psi]$$
$$= (E/\hbar\omega + \frac{1}{2})a_+\psi.$$

Consequently,
$$\hbar\omega(a_+ a_+ + \frac{1}{2})a_+\psi = (E + \hbar\omega)a_+\psi.$$

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Evidently, $a_+\psi$ is proportional to a stationary state (not necessarily normalized) with energy $E + \hbar\omega$. As a good exercise you should check that $a_-\psi$ solves the TISE with energy $E - \hbar\omega$ if ψ solves the TISE with energy E.

To summarize, a_+ maps solutions of the TISE to new solutions with energy raised by $\hbar\omega$, and a_- maps solutions of the TISE to new solutions with energy lowered by $\hbar\omega$. For this reason, a_+ and 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. If we apply a_- to ψ_0 we will get a function that is not normalizable. This can happen in two ways, either the wave function $a_-\psi_0$ vanishes, or the integral of its square must not exist. To see that the latter cannot happen we compute

$$\int_{-\infty}^{\infty} |a_-\psi(x)|^2 \, dx = \int_{-\infty}^{\infty} (a_-\psi)^*(a_-\psi) = \int_{-\infty}^{\infty} \psi^* a_+ a_- \psi = (E/\hbar\omega - \frac{1}{2})$$

This is not infinite, so the integral will exist. The only option is that a_- takes the lowest energy wave function and maps it to the zero function. Thus (exercise) the state of lowest energy, the *ground state* ψ_0, must have energy $\frac{1}{2}\hbar\omega$ and

$$a_-\psi_0 = 0.$$

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

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

More importantly, it satisfies

$$a_-\psi_0 = 0 \quad \Longleftrightarrow \quad \psi_0' + \frac{m\omega}{\hbar}x\psi_0 = 0.$$

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

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

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where A is a constant fixed by normalization to be (exercise)

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

You should check as an exercise that ψ_0 satisfies the TISE.

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 $a_-\psi_0 = 0$. 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 a_+ to ψ_0. The energy eigenfunctions are thus given by (A_n is a normalization constant)

$$\psi_n = A_n (a_+)^n \exp\left(-\frac{m\omega}{2\hbar}x^2\right),$$

with energies (exercise)

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

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 we introduce a dimensionless position variable:

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

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

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

where

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

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$H_n(\xi)$ is an nth-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 properties of the Hermite polynomials is that they form an orthonormal basis for normalizable functions of one variable. The "orthonormality" means

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

Note the integral defining the orthonormality uses a Gaussian "weight function". The Hermite polynomials form a basis – the are "complete" – in the sense that 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 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. Up to the normalization constant, the state with index n is the ground state Gaussian wave function times an nth-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.

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 is, essentially, a manifestation of the uncertainty principle. Recall that, for a Gaussian position distribution, the product of the variances of the position and momentum distributions is bounded from below by a non-zero constant. As the position "uncertainty" is increased the momentum "uncertainty" must eventually decrease, and *vice versa*. For the Gaussian ground state of the oscillator, the expectation values of position and momentum

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are zero, so the expectation values of the squared position and squared momentum must be non-zero to give the non-zero variances. In particular, the expectation value

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

is non-zero (and positive) in the ground state. 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 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)

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

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 $E \ge V$. 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.

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 $n \gg 1$. 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 $n \gg 1$ 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.

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

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

where the c_n are complex numbers and the $\psi_n(x)$ are the solutions with energy E_n (polynomials times Gaussians) we discussed earlier. 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

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

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.

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, at least mathematically, 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. It is convenient to use complex exponentials to write the solution. For *any* value of k, the general solution of the TISE is (exercise)

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

where

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{or} \quad k = \pm\frac{1}{\hbar}\sqrt{2mE}$$

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, 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 are not normalizable. You can easily see this from the fact that

$$|\psi_E(x)|^2 = \text{constant}.$$

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 (we 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 you study features which do not depend upon the size of the box. 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. To begin, we consider the time evolution of the stationary state wave functions, obtained by separation of variables as usual. We note that any non-negative energy is allowed, just as in the classical analysis. A "state" of definite energy, at time t, solves the SE

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

and is given by (exercise*)

$$\Psi(x,t) = Ae^{-ik(x-\frac{\hbar k}{2m})t} + Be^{ik(x+\frac{\hbar k}{2m})t}.$$

Since k can take any real value, the solution we wrote above is a bit redundant, it can be represented as a superposition of still simpler solutions. These solutions are (exercise)

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

We will work with this most basic stationary state solution. Actually, this is a family of solutions parametrized by the wave vector k.

You will recognize this wave function as that of a traveling wave. Recall that a traveling wave looks like a sinusoidal function of $(kx - \omega t)$. The real and imaginary parts of Ψ_k are of this form, with

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

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

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

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* You can get these by separation of variables, as usual.

Notice that the speed of the wave depends upon its wavelength. This phenomena is known as *disperson* for reasons to be seen.

It is worth comparing this with the classical velocity of a particle with energy E

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

So, while it may be tempting to identify the 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. One lesson here is that you should not think of the wave function as a material model for the particle. A better way to connect with the classical velocity of the particle is via the momentum. 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 $\hbar k = m v_{\text{classical}}$. 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 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.

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. Just as in those examples, $\phi(k)$ 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*. Thus, while the stationary states for a free particle are not, strictly speaking, allowed states, they do form a nice "basis" for the allowed states. This result is just the standard result of Fourier analysis.

So what have we gained from all this? Well, we can now build *bona fide* states (that is normalizable solutions of the SE) that can be physically analyzed in detail using quantum

mechanics. 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 $\phi(k)$. We now show 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.

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 $k = k_0$. 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. Such a wave function will be localized in space, *i.e.,* a wave packet. To see this, just note that the Fourier transform of a Gaussian function (of k) is a Gaussian function (of x):

$$\int_{-\infty}^{\infty} e^{-ikx} e^{-a^2 x^2} \, dx = \frac{\sqrt{\pi}}{a} e^{-\frac{1}{4}\frac{k^2}{a^2}}, \quad \int_{-\infty}^{\infty} e^{ikx} e^{-b^2 k^2} \, dk = \frac{\sqrt{\pi}}{b} e^{-\frac{1}{4}\frac{x^2}{b^2}}.$$

Using these formulas, 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 $x \to \pm\infty$ (since 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, 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:

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

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

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

$$= \frac{1}{\sqrt{2\pi}}e^{-i[\omega(k_0)-ik_0\omega'(k_0)]t} \int_{-\infty}^{\infty} \phi(k)e^{i[k(x-\omega'(k_0)\,t)]}\,dk.$$

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 $\omega'(k_0)t$. Thus 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 at the *group velocity*

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

which is the classical velocity of a particle with energy

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

Since the group velocity controls the motion of the most probable location of the particle, we see the classical motion emerging from the quantum state provided the wave function is strongly peaked about this most probably position. We see that the quantity $\hbar k_0$ characterizes the classical momentum of a 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

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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. 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 if it is prepared in an appropriate state.

The square well

Our final one-dimensional example is the "square well". Here the potential energy is of the form
$$V(x) = \left\{ \begin{array}{cc} -V_0, & -a < x < a \\ 0, & |x| > a. \end{array} \right.$$
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 (exercise). 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. Our square well is just a mathematical model of a potential well which may, in fact, have rounded corners. 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.

From our classical analysis, we see that this potential is a very simple model of an electron in an atom (there are "bound states" and "scattering states" or "ionized states"). We shall see that these two classes of states will also exist quantum mechanically, but there will be a few interesting differences in the observable aspects of the system.

As usual, 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 $\psi(x)$ continuous for all x. Assuming the solutions to the TISE are normalizable, we get the allowed stationary states and corresponding energies. Normalizable or not, the solutions of the TISE allow us to find the general solution of the SE, via our separation of variables-superposition discussion. Of course, from the general solution of the TISE we can describe the evolution of the state of the system in time for any initial conditions.

When solving the TISE, we will find that the two cases $-V_0 < E < 0$ and $E > 0$ will be rather different (remember the classical limit). The case $-V_0 < E < 0$ will admit normalizable solutions to the TISE and 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 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. As you know by now, we can choose F to be real with no loss of generality (exercise). When $x < a$ we get a very similar situation (exercise)

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

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 allow normalizability of the stationary states.

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

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

We know that normalizable solutions of the TISE must have $E > -V_0$, so the argument of the sine and cosine is positive. 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" 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 is an even function, 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 then so is $\tilde{\psi}(x) = \psi(-x)$. Consequently, because the TISE is linear we can superimpose such solutions and always work with solutions of the form

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

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* Here is another instance of how one uses boundary conditions to fix integration constants and/or energies when solving the TISE.
* *Danger:* Do not make the mistake of thinking that the stationary states are *all* even, or all odd, both will occur.

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Following the text, let us focus on even solutions:

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

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, B, E). One condition is normalization. The remaining conditions are continuity of $\psi(x)$ and $\psi'(x)$ at $x = a$. 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".

It is worth emphasizing that such boundary conditions will arise whenever you break up the solution of the TISE into regions of space. As we shall see, they will force the energies to be discrete. But the real root of the discreteness, 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. We will see that when $E > 0$, the solutions of the TISE are not normalizable, and the "energies" are not quantized, that is, they form a continuum.

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

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

and

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

These equations look like they determine both B and D, but actually they determine one of those and E. To determine the energy eigenvalue E you can divide the two equations to get

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

Remember that $\kappa = \frac{1}{\hbar}\sqrt{2m|E|}$ and $l = \frac{1}{\hbar}\sqrt{2m(V_0 - |E|)}$, so 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! Having found the allowed energies, you can substitute them one at a time into the continuity conditions to eliminate one of the constants of integration. The other constant is fixed by normalization. I will spare you the calculation.

The result of all this is a discrete – and finite – set of stationary states with corresponding allowed energies. The wave functions 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, *there is a non-zero probability for finding the particle outside the well.* This is sharply in 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 $z_0 = \frac{a}{\hbar}\sqrt{2mV_0}$. Then the transcendental equation is (exercise)

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

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 or very wide well, so we expect to approximately recover the particle in a box results. We do. In this approximation we have

$$\tan z >> 1.$$

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

$$E_n \approx \frac{n^2\pi^2\hbar^2}{8ma^2} - V_0.$$

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, or very shallow well. In fact, once $z_0 < \pi$ then there is only a single root (exercise). 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. The logic of the situation is entirely the same as our wave packet discussion for the free particle.

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

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

As usual, the constants A, B, C, D, E, F, G are to be fixed, as far as possible, by boundary conditions. Usually we also have one more condition to impose: normalization. Here "normalization" is not a condition since these solutions are not normalizable (exercise). 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 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. We saw, when studying the free particle, that the positive (negative) wave numbers k correspond to particle motion to the right (left). Let us consider the case where the particle comes in from the left side of the well and scatters off of the well. In particular, we assume that the particle does not come from the right. We do 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 the ratio of "transmitted" probability to incident probability. I will spell this out a little more carefully in a moment.

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To determine the coefficients A, B, C, D, F and the energy E we use continuity of the wave function and its first derivative, as before. For details, see the text. We get 4 conditions which determine 4 integration constants in terms of one of the others. 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 a bit of a fake: there is no state of definite energy since the solutions are not normalizable.

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

The bottom line is this. Given a choice of A and E, we can determine all the other coefficients (as a function of the energy and 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 gives the relative probability for transmission (reflection). Indeed, you see that

$$R + T = 1,$$

which is consistent with this interpretation (exercise).

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 describe the scattering.

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.