

# Chapter 1

## Wave mechanics

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*In wave mechanics the wavefunction describes the physics of a particle moving in a potential. The wavefunction satisfies the Schrödinger equation, a linear partial differential equation that is first order in time derivatives. For a physical interpretation of the wavefunction we define the probability density and the probability current. When the potential is time independent, we find stationary states which represent states of fixed energy and are solutions of a time-independent version of the Schrödinger equation. We discuss the properties of the spectrum of one-dimensional potentials. We develop the variational method and derive the basic inequality that gives upper bounds for the ground state energy of a quantum system. Finally, we review the position and momentum representations of quantum mechanics.*

### 1.1 The Schrödinger equation

In classical mechanics the motion of a particle is described using the time-dependent position  $\vec{x}(t)$  as the dynamical variable. In wave mechanics the dynamical variable is a wavefunction. This wavefunction is a complex number that depends on position and on time. We will denote complex numbers by  $\mathbb{C}$  and real numbers by  $\mathbb{R}$ . When all three spatial dimensions are relevant we write the wavefunction as

$$\Psi(\vec{x}, t) \in \mathbb{C}. \quad (1.1.1)$$

When only one spatial dimension is relevant we write it as  $\Psi(x, t) \in \mathbb{C}$ . The wavefunction satisfies the Schrödinger equation. For one-dimensional space we write

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \Psi(x, t). \quad (1.1.2)$$

This is the equation for a (non-relativistic) particle of mass  $m$  moving along the  $x$  axis while acted on by the potential  $V(x, t) \in \mathbb{R}$ . It is clear from this equation that the wavefunction

must be complex: if it were real, the right-hand side of (1.1.2) would be real while the left-hand side would be imaginary, due to the explicit factor of  $i$ .

Let us make two important remarks:

1. The Schrödinger equation is a *first order* differential equation in time. This means that if we prescribe the wavefunction  $\Psi(x, t_0)$  for all of space at an arbitrary initial time  $t_0$ , the wavefunction is determined for all times.
2. The Schrödinger equation is a *linear* equation for  $\Psi$ : if  $\Psi_1$  and  $\Psi_2$  are solutions so is  $a_1\Psi_1 + a_2\Psi_2$  with  $a_1$  and  $a_2$  arbitrary *complex* numbers. This is the property of linear *superposition*.

Since the wavefunction contains all the information about the particle we sometimes call  $\Psi(x, t)$  the *state* of the particle. The Schrödinger equation (1.1.2) can be written more briefly as

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \hat{H} \Psi(x, t), \quad (1.1.3)$$

where we have introduced the **Hamiltonian** operator  $\hat{H}$ :

$$\hat{H} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t). \quad (1.1.4)$$

We call  $\hat{H}$  an operator because it acts on functions of  $x$  and  $t$  to give functions of  $x$  and  $t$ : it acts on the space of complex functions, a space that contains wavefunctions. Note that  $V(x, t)$  acts just by multiplication. This  $\hat{H}$  above is just one possible Hamiltonian. There are many other possible choices appropriate for different physical problems. Thus (1.1.3), with  $\hat{H}$  unspecified is the general form of the Schrödinger equation.

Since the Schrödinger equation uses complex numbers, we must review a few basic facts. Given a complex number  $z \in \mathbb{C}$ , we can write it as  $z = a + ib$ , with  $a, b \in \mathbb{R}$ . Its complex conjugate  $z^*$  is defined by  $z^* \equiv a - ib$ . Let  $|z|$  denote the norm or length of the complex number  $z$ . The norm is a positive number (thus real!) and it is given by

$$\text{Norm of } z = a + ib : |z| \equiv \sqrt{a^2 + b^2}. \quad (1.1.5)$$

If the norm of a complex number is zero, the complex number is zero. This is true because  $a^2 + b^2 = 0$ , with  $a$  and  $b$  real, imply that  $a = b = 0$ . You can quickly verify that

$$|z|^2 = zz^*. \quad (1.1.6)$$

For brevity, the complex conjugate  $(\Psi(x, t))^*$  of  $\Psi(x, t)$  is usually written as  $\Psi^*(x, t)$ .

We define the probability density  $P(x, t)$ , also denoted as  $\rho(x, t)$ , as the norm-squared of the wavefunction:

$$P(x, t) = \rho(x, t) \equiv \Psi^*(x, t)\Psi(x, t) = |\Psi(x, t)|^2. \quad (1.1.7)$$

This probability density so defined is positive. The physical interpretation of the wavefunction arises from the declaration that

$$P(x, t) dx \text{ is the probability of finding the particle in the interval } [x, x + dx] \text{ at time } t. \quad (1.1.8)$$

This interpretation requires a *normalized* wavefunction, which means that the wavefunction used above must satisfy, for all times,

$$\int_{-\infty}^{\infty} dx P(x, t) = \int_{-\infty}^{\infty} dx |\Psi(x, t)|^2 = 1, \quad \forall t. \quad (1.1.9)$$

By integrating over space, we are adding up the probabilities that the particle be found in all of the tiny intervals  $dx$  that comprise the real line. Since the particle must be found somewhere this sum must be equal to one.

Suppose you are handed a wavefunction that is normalized at time  $t_0$ :

$$\int_{-\infty}^{\infty} dx |\Psi(x, t_0)|^2 = 1, \quad \forall t. \quad (1.1.10)$$

As mentioned above, knowledge of the wavefunction at one time implies, via the Schrödinger equation, knowledge of the wavefunction for all times. The Schrödinger equation must guarantee that the wavefunction remains normalized for all times. Proving this is a good exercise:

**Exercise 1.** Show that the Schrödinger equation implies that the norm of the wavefunction does not change in time:

$$\frac{d}{dt} \int_{-\infty}^{\infty} dx |\Psi(x, t)|^2 = 0. \quad (1.1.11)$$

You will have to use both the Schrödinger equation and its complex-conjugate version. Moreover you will have to use  $\Psi(x, t) \rightarrow 0$  as  $|x| \rightarrow \infty$ , which is true, as no normalizable wavefunction can take a non-zero value as  $|x| \rightarrow \infty$ . While generally the derivative  $\frac{\partial}{\partial x} \Psi$  also goes to zero as  $|x| \rightarrow \infty$  you only need to assume that it remains bounded.

Associated with the probability density  $\rho(x, t) = \Psi^* \Psi$  there is a probability **current**  $J(x, t)$  that characterizes the flow of probability in the  $x$  direction and is given by

$$J(x, t) = \frac{\hbar}{m} \text{Im} \left( \Psi^* \frac{\partial \Psi}{\partial x} \right). \quad (1.1.12)$$

The analogy in electromagnetism is informative. There we have a current density vector  $\mathbf{J}$  and a charge density  $\rho$ . The statement of charge conservation is the differential relation

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0. \quad (1.1.13)$$

This equation applied to a fixed volume  $V$  implies that the rate of change of the enclosed charge  $Q_V(t)$  is only due to the flux of  $\mathbf{J}$  across the surface  $S$  that bounds the volume:

$$\frac{dQ_V}{dt}(t) = - \oint_S \mathbf{J} \cdot d\mathbf{a}. \quad (1.1.14)$$

Make sure you know how to get this equation from (1.1.13). While the probability current in more than one spatial dimension is also a vector, in our one-dimensional case it has just one component, the component along  $x$ . While we could write this current with an  $x$  subscript to emphasize this, we usually don't (see (1.1.12)). The conservation equation is the analog of (1.1.13):

$$\frac{\partial J}{\partial x} + \frac{\partial \rho}{\partial t} = 0. \quad (1.1.15)$$

You can check that this equation holds using the above formula for  $J(x, t)$ , the formula for  $\rho(x, t)$ , and the Schrödinger equation. The integral version is formulated by first defining the probability  $P_{ab}(t)$  of finding the particle in the interval  $x \in [a, b]$

$$P_{ab}(t) \equiv \int_a^b dx |\Psi(x, t)|^2 = \int_a^b dx \rho(x, t). \quad (1.1.16)$$

You can then quickly show that

$$\frac{dP_{ab}}{dt}(t) = J(a, t) - J(b, t). \quad (1.1.17)$$

Here  $J(a, t)$  denotes the rate at which probability flows into the interval at the left boundary, while  $J(b, t)$  denotes the rate at which probability flows out of the interval at the right boundary. The current has units of  $(\text{time})^{-1}$ .

It is sometimes easier to work with wavefunctions that are not normalized. The normalization can be performed if and when it is needed. We will thus refer to wavefunctions in general without assuming normalization, otherwise we will call them *normalized* wavefunctions. In this spirit, two wavefunctions  $\Psi_1$  and  $\Psi_2$  that solve the Schrödinger equation are *declared* to be physically equivalent if they differ by multiplication by a complex *number*. Using the symbol  $\sim$  for equivalence, we write

$$\Psi_1 \sim \Psi_2 \iff \Psi_1(x, t) = \alpha \Psi_2(x, t), \quad \alpha \in \mathbb{C}. \quad (1.1.18)$$

If the wavefunctions  $\Psi_1$  and  $\Psi_2$  are normalized they are equivalent if they differ by an overall *constant* phase:

$$\text{Normalized wavefunctions: } \Psi_1 \sim \Psi_2 \iff \Psi_1(x, t) = e^{i\theta} \Psi_2(x, t), \quad \theta \in \mathbb{R}. \quad (1.1.19)$$

## 1.2 Stationary States

In a large class of problems the Schrödinger potential  $V(x, t)$  has no time dependence and it is simply a function  $V(x)$  of position. We focus on that case now. The Schrödinger equation is then

$$i\hbar \frac{\partial \Psi}{\partial t}(x, t) = \hat{H} \Psi(x, t), \quad \text{with} \quad \hat{H} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x). \quad (1.2.1)$$

Note that the operator  $\hat{H}$  is time independent – it does not involve time at all. In this situation there are very useful solutions of the Schrödinger equation: stationary states.

A **stationary** state of energy  $E \in \mathbb{R}$  is a solution  $\Psi(x, t)$  of the Schrödinger equation that takes the form

$$\Psi(x, t) = e^{-iEt/\hbar} \psi(x). \quad (1.2.2)$$

Here  $\psi(x) \in \mathbb{C}$  is a function of  $x$  only (no time!) that solves an equation that will be discussed below. All the time dependence of the stationary state is carried by the exponential prefactor. Such a state is called stationary because physical observables of the state are actually time independent. Consider, for example, the norm of the state. We see that the time dependence drops out

$$P(x, t) = \Psi^*(x, t) \Psi(x, t) = e^{+iEt/\hbar} \psi^*(x) e^{-iEt/\hbar} \psi(x) = \psi^*(x) \psi(x) = |\psi(x)|^2. \quad (1.2.3)$$

Had the energy  $E$  been a complex number  $E = E_0 - i\Gamma$ , with  $E_0$  and  $\Gamma$  real, the time dependence would not have dropped out:

$$\begin{aligned} P(x, t) &= \Psi^*(x, t) \Psi(x, t) = e^{+iE^*t/\hbar} \psi^*(x) e^{-iEt/\hbar} \psi(x) \\ &= e^{i(E^* - E)t/\hbar} \psi^*(x) \psi(x) = e^{-2\Gamma t/\hbar} |\psi(x)|^2. \end{aligned} \quad (1.2.4)$$

This kind of solution is not acceptable because the normalization of the wavefunction is not preserved in time.

Let us find out the equation that  $\psi(x)$  must satisfy. Plugging (1.2.2) into (1.1.3) we have

$$i\hbar \frac{\partial}{\partial t} e^{-iEt/\hbar} \psi(x) = \hat{H} e^{-iEt/\hbar} \psi(x), \quad (1.2.5)$$

The time derivative on the left-hand side acts only on the exponential, and the  $\hat{H}$  operator on the right-hand side can be moved through the exponential (it commutes with it!). We thus get

$$i\hbar \left( \frac{\partial}{\partial t} e^{-iEt/\hbar} \right) \psi(x) = e^{-iEt/\hbar} \hat{H} \psi(x). \quad (1.2.6)$$

Taking the derivative and canceling the exponentials we get

$$i\hbar \left( -i \frac{E}{\hbar} \right) \psi(x) = \hat{H} \psi(x), \quad (1.2.7)$$

which we write as

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

(1.2.8)

Recalling the expression for the Hamiltonian we have

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

(1.2.9)

Note that the partial derivatives along  $x$  are now written as ordinary derivatives since they act on functions that have no other argument except  $x$ . Using primes to denote derivatives with respect to the argument, the above equation is

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x). \quad (1.2.10)$$

This is the equation for  $\psi$  that makes  $\Psi(x, t) = e^{-iEt/\hbar}\psi(x)$  a stationary state of energy  $E$ . Any of the three boxed equations above is referred to as the **time-independent** Schrödinger equation. The state  $\Psi(x, t)$  is normalized if  $\psi(x)$  is normalized:

$$\int_{-\infty}^{\infty} dx |\psi(x)|^2 = 1. \quad (1.2.11)$$

Since the time-independent Schrödinger equation is a second-order differential equation in  $x$ , a solution is completely fixed by the value of  $\psi$  and  $\psi'$  at any point  $x_0$  ( $\neq \infty$ ). This does not mean, of course, that it is easily calculated from these values. A weaker, but still useful version of this property is that if we know  $\psi(x)$  for *any* interval on the  $x$  axis, the full solution is fully determined. If  $V(x)$  is nowhere infinite,  $\psi = \psi' = 0$  at any point implies  $\psi = 0$  everywhere.

A full solution of the time-independent Schrödinger equation means finding all the values  $E$  for which acceptable solutions  $\psi(x)$  exist and, of course, finding those solutions for each  $E$ . While normalizable solutions are particularly useful, we also consider un-normalizable solutions, which have applications as well.

A solution  $\psi(x)$  associated with an energy  $E$  satisfies  $\hat{H}\psi(x) = E\psi(x)$  so it is technically an eigenstate of the Hamiltonian with eigenvalue  $E$ . We speak of the Hamiltonian as the **energy operator** and  $\psi(x)$  is called an **energy eigenstate** of energy  $E$ . The set of all allowed values of  $E$  is called the **spectrum** of the Hamiltonian  $\hat{H}$ . A **degeneracy** in the spectrum occurs when there is more than one solution  $\psi(x)$  for a given value of the energy.

The solutions  $\psi(x)$  of the time-independent Schrödinger equation depend on the properties of the potential  $V(x)$ . It is hard to make general statements about the wavefunction unless we restrict the types of potentials. We consider potentials that are not continuous but are piece-wise continuous, like the finite square well. Our potentials can easily fail to be bounded, like the potential for the harmonic oscillator. We allow delta functions in one-dimensional potentials but do not explore powers or derivatives of delta functions. We allow for potentials that become plus infinity beyond certain points. These points represent hard walls and they occur, for example, in the infinite square-well.

For such potentials, we can impose the following regularity conditions on the wavefunction:

$$\psi(x) \text{ is continuous and bounded and its derivative } \psi'(x) \text{ is bounded.} \quad (1.2.12)$$

A bounded (complex) function is one that is never infinite. We do not impose the requirement that  $\psi(x)$  be normalizable. This would be too restrictive. There are energy eigenstates that are not normalizable. Momentum eigenstates of a free particle are also not normalizable. Solutions for which  $\psi$  is not normalizable do not have a direct physical interpretation, but are very useful: suitable superpositions of them give normalizable solutions that can represent a particle.

In the spectrum of a Hamiltonian, localized energy eigenstates are particularly important. This motivates the definition:

An energy eigenstate  $\psi(x)$  is a **bound** state if  $\psi(x) \rightarrow 0$  when  $|x| \rightarrow \infty$ .

(1.2.13)

For the classes of potentials discussed, a wavefunction that vanishes as  $|x| \rightarrow \infty$  is normalizable. Thus a bound state is a normalizable energy eigenstate.

The eigenstates of  $\hat{H}$  provide a useful set of functions. For simplicity, we consider here the case when the spectrum is discrete. We can then denote the possible energies by  $E_n$  with  $n = 1, 2, \dots$ , ordered as follows

$$E_1 \leq E_2 \leq E_3 \leq \dots \quad (1.2.14)$$

and let the corresponding eigenstates be  $\psi_n(x)$ , with

$$\hat{H}\psi_n(x) = E_n \psi_n(x), \quad n \geq 1. \quad (1.2.15)$$

In general a potential  $V(x)$  can result in a spectrum that contains a discrete part and a continuous part. The discrete part is denumerable but the continuous part is not. The formulae we will write below require some modification when there spectrum contains a continuous part. The eigenstates in the continuous spectrum are not normalizable. We have used the  $\leq$  symbol to order the energies to take into account the possibility of degeneracies.

A property of differential equations ensures that for rather general potentials the  $\hat{H}$  eigenstates  $\psi_n(x)$  can be chosen to be orthonormal, namely, orthogonal to each other and normalizable. What does it mean for two functions to be orthogonal? Orthogonal vectors have a vanishing dot product, where the dot product is a clever way to obtain a single number from two vectors. For two functions  $f_1$  and  $f_2$  an *inner* product can be defined by integrating the product function  $f_1 f_2$  over all  $x$ , thus giving us a number. Since our functions are complex valued, a small modification is needed: the inner product of  $f_1$  and  $f_2$  is taken to be  $\int dx f_1^*(x) f_2(x)$ . The functions  $f_1$  and  $f_2$  are orthogonal if this integral vanishes. An orthonormal set of functions is one in which each function is orthogonal to all others, while its inner product with itself gives one. As a result, orthonormality means that

Orthonormality:  $\int_{-\infty}^{\infty} dx \psi_m^*(x) \psi_n(x) = \delta_{m,n}.$

(1.2.16)

Recall that the Kronecker delta  $\delta_{m,n}$  is defined to be zero if  $m \neq n$  and is equal to one otherwise.

The energy eigenstates are also *complete* in the sense that any reasonable (see (1.2.12)) wavefunction  $\psi(x)$  can be expanded as a superposition of energy eigenstates. This means that there exist complex numbers  $b_n$  such that

$$\psi(x) = \sum_{n=1}^{\infty} b_n \psi_n(x), \quad b_n \in \mathbb{C}. \quad (1.2.17)$$

If this wavefunction is normalized then we have

$$\int_{-\infty}^{\infty} dx \psi^*(x) \psi(x) = 1 \quad \rightarrow \quad \sum_{n=1}^{\infty} |b_n|^2 = 1. \quad (1.2.18)$$

The property of completeness is very powerful. As we will demonstrate now, if the energy eigenstates are known, the general solution of the Schrödinger equation is known. Indeed, assume that the wavefunction at time equal zero is the  $\psi(x)$  above. Then we have

$$\Psi(x, t=0) = \psi(x) = \sum_{n=1}^{\infty} b_n \psi_n(x). \quad (1.2.19)$$

We now claim that the wavefunction at all times can be written down immediately by multiplying each term in the above sum by a time-dependent exponential:

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

(1.2.20)

To prove that this is the solution we must check two things: that it satisfies the Schrödinger equation and that it reduces to the correct value at  $t = 0$ . The first follows by linearity because each term in the above sum is a stationary state solution of the Schrödinger equation. The second is clear by inspection: at  $t = 0$  all exponentials become equal to one and the solution reduces to  $\Psi(x, t=0)$  in (1.2.19). The uniqueness of the solution is guaranteed by the first remark below (1.1.2).

It should be emphasized that the superposition of stationary states of different energies is *not* a stationary state. Thus  $\Psi(x, t)$  in (1.2.20) is not a stationary state: you can't write  $\Psi(x, t)$  as the product of a single time-dependent exponential times a spatial function.

The expansion coefficients  $b_n$  used above can be calculated explicitly if we know the energy eigenstates. Indeed using (1.2.16) and (1.2.17) a one-line computation (do it!) gives

$$b_n = \int_{-\infty}^{\infty} dx \psi_n^*(x) \psi(x). \quad (1.2.21)$$

A curious identity can be derived by substituting this result back into (1.2.17):

$$\psi(x) = \sum_{n=1}^{\infty} \left( \int_{-\infty}^{\infty} dx' \psi_n^*(x') \psi(x') \right) \psi_n(x) = \int_{-\infty}^{\infty} dx' \left( \sum_{n=1}^{\infty} \psi_n^*(x') \psi_n(x) \right) \psi(x'), \quad (1.2.22)$$



where we interchanged the order of integration and summation (a safe operation in most cases!). The above equation is of the form

$$f(x) = \int_{-\infty}^{\infty} dx' K(x', x) f(x'), \quad (1.2.23)$$

and is supposed to hold for any function  $f(x)$ . It is intuitively clear that that  $K(x', x)$  must vanish for  $x' \neq x$  for otherwise we could cook up a contradiction by choosing a peculiar function  $f(x)$ . Taking  $f(x) = \delta(x - x_0)$  the equation gives

$$\delta(x - x_0) = \int dx' K(x', x) \delta(x' - x_0) = K(x_0, x). \quad (1.2.24)$$

We therefore conclude that  $K(x', x) = \delta(x - x')$  (recall that  $\delta(x) = \delta(-x)$ ). Back in (1.2.22) we thus find

Completeness:  $\sum_{n=1}^{\infty} \psi_n^*(x') \psi_n(x) = \delta(x - x').$

(1.2.25)

Let us compare the completeness relation above with the orthonormality relation (1.2.16). In the completeness relation we set equal the labels of the eigenfunctions and sum over them while keeping the two position arguments fixed. In the orthogonality relation we set equal the position arguments of the eigenfunctions and integrate (sum) over them while keeping the two labels fixed. On the right-hand sides we find “delta functions”: a Kronecker delta setting equal the two labels in the orthonormality relation and a true delta function setting equal the two positions in the completeness relation. The two relations are obtained from each other by exchange of labels: position labels and energy labels. This is a neat duality!

It is fun to calculate the expectation value of the Hamiltonian in the solution  $\Psi(x, t)$  in (1.2.20). For arbitrary operators  $\hat{A}$  we can define the **expectation value**  $\langle \hat{A} \rangle_{\Psi}$  on a normalized state  $\Psi(x, t)$  by the following formula:

$$\langle \hat{A} \rangle_{\Psi}(t) \equiv \int_{-\infty}^{\infty} dx \Psi^*(x, t) (\hat{A} \Psi(x, t)). \quad (1.2.26)$$

Generally this expectation value is time dependent, and that’s why we displayed the argument  $t$  on the left-hand side. Even if  $\hat{A}$  is a time-independent operator, the expectation value can still be time dependent. What happens when we take the operator to be our time-independent Hamiltonian  $\hat{H}$ ? Using (1.2.20) twice, we get

$$\begin{aligned} \langle \hat{H} \rangle_{\Psi}(t) &= \int_{-\infty}^{\infty} dx \Psi^*(x, t) (\hat{H} \Psi(x, t)) \\ &= \sum_{n, n'} \int_{-\infty}^{\infty} dx b_n^* e^{iE_n t/\hbar} \psi_n^*(x) b_{n'} e^{-iE_{n'} t/\hbar} \hat{H} \psi_{n'}(x) \\ &= \sum_{n, n'} b_n^* b_{n'} E_{n'} e^{i(E_n - E_{n'}) t/\hbar} \int_{-\infty}^{\infty} dx \psi_n^*(x) \psi_{n'}(x) \\ &= \sum_{n, n'} b_n^* b_{n'} E_{n'} e^{i(E_n - E_{n'}) t/\hbar} \delta_{n, n'}, \end{aligned} \quad (1.2.27)$$

so that we get

$$\langle \hat{H} \rangle_{\Psi}(t) = \sum_{n=1}^{\infty} |b_n|^2 E_n. \quad (1.2.28)$$

The expectation value of the Hamiltonian is actually time-independent! This is the quantum version of energy conservation. This is the expected value of the energy: a weighted sum of the possible energies with weights the norm-squared of the expansion coefficients.

Another operator often used to explore the physics of states is the momentum operator  $\hat{p}$ . Acting on wavefunctions that depend on a coordinate  $x$  it is a differential operator:

$$\hat{p} \equiv \frac{\hbar}{i} \frac{\partial}{\partial x}. \quad (1.2.29)$$

We will sometimes calculate the expectation value of the momentum operator.

If the wavefunction  $\Psi(x, t)$  is not normalized but is normalizable, then the wavefunction

$$\frac{\Psi(x, t)}{\sqrt{\int dx \Psi^* \Psi}} \quad (1.2.30)$$

is normalized and physically equivalent to  $\Psi(x, t)$ . Note that the denominator in the above expression is just a constant. We use the normalized representative of  $\Psi(x, t)$  in the definition on  $\langle \hat{A} \rangle$  to find the expectation value is given by

$$\langle \hat{A} \rangle_{\Psi}(t) \equiv \frac{\int_{-\infty}^{\infty} dx \Psi^*(x, t) (\hat{A} \Psi(x, t))}{\int dx \Psi^*(x, t) \Psi(x, t)}. \quad (1.2.31)$$

This formula can be used for any normalizable  $\Psi$ . If  $\Psi$  is normalized the formula reduces to the earlier expression for  $\langle \hat{A} \rangle$ .

### 1.3 Properties of energy eigenstates

In order to simplify our notation we rewrite the time-independent Schrödinger equation (1.2.9) as follows

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - V(x)) \psi = 0. \quad (1.3.1)$$

We then define energy-like quantities  $\mathcal{E}$  and  $\mathcal{V}$  using a common rescaling factor:

$$\mathcal{E} \equiv \frac{2m}{\hbar^2} E, \quad \mathcal{V}(x) \equiv \frac{2m}{\hbar^2} V(x). \quad (1.3.2)$$

With this the Schrödinger equation (1.3.1) becomes

$$\psi'' + (\mathcal{E} - \mathcal{V}(x)) \psi = 0.$$

(1.3.3)

We are now ready to consider a very useful result: in a one-dimensional potential there cannot be two or more bound states with the same energy. This is the content of our first theorem:

**Theorem 1.** There is no degeneracy for bound states in one-dimensional potentials.

**Proof.** Suppose there is such degeneracy so that there are  $\psi_1(x)$  and  $\psi_2(x)$ , different from each other and both corresponding to the same energy  $E$ , thus same value of  $\mathcal{E}$ . If so, we have that the following equations hold

$$\begin{aligned}\psi_1'' + (\mathcal{E} - \mathcal{V}(x))\psi_1 &= 0, \\ \psi_2'' + (\mathcal{E} - \mathcal{V}(x))\psi_2 &= 0.\end{aligned}\tag{1.3.4}$$

Multiplying the top equation by  $\psi_2$  and the bottom one by  $\psi_1$  and subtracting them we find

$$\psi_2\psi_1'' - \psi_1\psi_2'' = 0.\tag{1.3.5}$$

The left-hand side is actually a derivative

$$(\psi_2\psi_1' - \psi_1\psi_2')' = 0.\tag{1.3.6}$$

It follows from this that the expression inside the parenthesis must be a constant  $c$ :

$$\psi_2\psi_1' - \psi_1\psi_2' = c.\tag{1.3.7}$$

The constant can be evaluated by examining the left-hand side for  $|x| \rightarrow \infty$ . We then have that  $\psi_1 \rightarrow 0$  and  $\psi_2 \rightarrow 0$ , since they are bound states, while the derivatives are bounded, as assumed in (1.2.12). It follows that the left-hand side vanishes as  $|x| \rightarrow \infty$  and therefore  $c = 0$ . We thus have

$$\psi_2\psi_1' = \psi_1\psi_2' \quad \rightarrow \quad \frac{\psi_1'}{\psi_1} = \frac{\psi_2'}{\psi_2} \quad \rightarrow \quad \frac{d}{dx}(\ln \psi_1 - \ln \psi_2) = 0.\tag{1.3.8}$$

This implies that we have for some constant  $c'$

$$\ln \psi_1 = \ln \psi_2 + \ln c' \quad \rightarrow \quad \psi_1(x) = c'\psi_2(x).\tag{1.3.9}$$

We have thus shown that the wavefunctions  $\psi_1$  and  $\psi_2$  are equivalent. In contradiction with the initial assumption, they are the same energy eigenstate. This concludes the proof.  $\square$

For our second theorem we show that the reality of  $\mathcal{V}$  allows us to work with real wavefunctions  $\psi(x)$ . This is to say that even though there are complex solutions, we can choose real ones without loss of generality.

**Theorem 2.** The energy eigenstates  $\psi(x)$  can be chosen to be real.

**Proof.** Consider our main equation for the complex wavefunction  $\psi(x)$ :

$$\psi'' + (\mathcal{E} - \mathcal{V}(x))\psi = 0.\tag{1.3.10}$$

Since  $(\psi'')^* = (\psi^*)''$  the complex conjugation of the above equation gives

$$(\psi^*)'' + (\mathcal{E} - \mathcal{V}(x))\psi^* = 0. \quad (1.3.11)$$

We see that  $\psi^*(x)$  is another solution of the Schrödinger equation with the same energy. The solution  $\psi^*(x)$  is different from  $\psi(x)$  if there is no constant  $c$  such that  $\psi^* = c\psi$ . In that case  $\psi^*$  and  $\psi$  represent two degenerate solutions and, by superposition, we can obtain two *real* degenerate solutions:

$$\psi_r \equiv \frac{1}{2}(\psi + \psi^*), \quad \psi_{im} \equiv \frac{1}{2i}(\psi - \psi^*). \quad (1.3.12)$$

These are, of course, the real and imaginary parts of  $\psi$ . If  $\psi^* = c\psi$  the real and imaginary parts yield the same real solution. In either case we can work with a real solution.  $\square$

If we are dealing with bound states of one-dimensional potentials more can be said: it is not that we can choose to work with real solutions but rather that any solution is, to begin with, essentially real.

**Corollary 1.** Any bound state  $\psi(x)$  of a one-dimensional potential is, up to an overall constant phase, real.

**Proof.** Recall that bound states are by definition energy eigenstates and by Theorem 1, they are never degenerate. This means that the two real solutions  $\psi_r$  and  $\psi_{im}$  considered above must be equal up to a constant that can only be real:

$$\psi_{im} = c\psi_r, \quad \text{with } c \in \mathbb{R} \quad (1.3.13)$$

It then follows that  $\psi = \psi_r + i\psi_{im} = (1 + ic)\psi_r$ . Writing  $1 + ic = \sqrt{1 + c^2}e^{i\beta}$  with real  $\beta$ , shows that  $\psi$  is, up to a constant phase  $\beta$ , equal to a real solution.

Our next result shows that for a potential that is a symmetric function of  $x$ , we can work with energy eigenstates that are either symmetric or antisymmetric functions of  $x$ .

**Theorem 3.** If  $V(-x) = V(x)$ , the energy eigenstates can be chosen to be even or odd under  $x \rightarrow -x$ .

**Proof.** Again, we begin with our main equation

$$\psi''(x) + (\mathcal{E} - \mathcal{V}(x))\psi(x) = 0. \quad (1.3.14)$$

Recall that primes denote here derivative with respect to the argument, so  $\psi''(x)$  means the function “second-derivative-of- $\psi$ ” evaluated at  $x$ . Similarly  $\psi''(-x)$  means the function “second-derivative-of- $\psi$ ” evaluated at  $-x$ . Thus we can change  $x$  for  $-x$  with impunity in the above equation getting

$$\psi''(-x) + (\mathcal{E} - \mathcal{V}(x))\psi(-x) = 0, \quad (1.3.15)$$

where we used that  $V$ , and thus  $\mathcal{V}$ , is even. We now want to make clear that the above equation implies that  $\psi(-x)$  is another solution of the Schrödinger equation with the same energy. For this let us define

$$\varphi(x) \equiv \psi(-x) \quad \rightarrow \quad \frac{d}{dx}\varphi(x) = \psi'(-x) \cdot (-1). \quad (1.3.16)$$

Taking a second derivative and using (6.6.70)

$$\frac{d^2}{dx^2}\varphi(x) = \psi''(-x) = -(\mathcal{E} - \mathcal{V}(x))\varphi(x), \quad (1.3.17)$$

so that indeed  $\varphi(x) = \psi(-x)$  provides a degenerate solution to the Schrödinger equation:

$$\frac{d^2}{dx^2}\varphi(x) + (\mathcal{E} - \mathcal{V}(x))\varphi(x) = 0. \quad (1.3.18)$$

Equipped with the degenerate solutions  $\psi(x)$  and  $\psi(-x)$  we can now form symmetric (s) and antisymmetric (a) combinations that are, respectively, even and odd under  $x \rightarrow -x$ :

$$\psi_s(x) \equiv \frac{1}{2}(\psi(x) + \psi(-x)), \quad \psi_a(x) \equiv \frac{1}{2}(\psi(x) - \psi(-x)). \quad (1.3.19)$$

These are the solutions claimed to exist in Theorem 3.  $\square$

Again, if we focus on bound states of one-dimensional potentials the absence of degeneracy has a stronger implication: the solutions are automatically even or odd.

**Corollary 2.** Any bound state  $\psi(x)$  of a one-dimensional even potential is either even or odd under  $x \rightarrow -x$ .

**Proof:** The absence of degeneracy implies that the solutions  $\psi(x)$  and  $\psi(-x)$  must be the same solution. Because of corollary 1, we can choose  $\psi(x)$  to be real and thus we must have

$$\psi(-x) = c\psi(x), \quad \text{with } c \in \mathbb{R}. \quad (1.3.20)$$

Letting  $x \rightarrow -x$  in the above equation we get  $\psi(x) = c\psi(-x) = c^2\psi(x)$  from which we learn that  $c^2 = 1$ . The only possibilities are  $c = \pm 1$ . So  $\psi(x)$  is *automatically* even or odd under  $x \rightarrow -x$ .  $\square$

## 1.4 Energy spectrum for one-dimensional potentials

Consider the time-independent Schrödinger equation (1.2.10) written as

$$\psi'' = -\frac{2m}{\hbar^2}(E - V(x))\psi. \quad (1.4.1)$$

We must have a continuous  $\psi(x)$ . If  $\psi$  is discontinuous then  $\psi'$  contains delta-functions and  $\psi''$  in the above left-hand side contains derivatives of delta functions. This would require

the right-hand side to have derivatives of delta functions, and those would have to appear in the potential. Since we have declared that our potentials contain no derivatives of delta functions we must indeed have a continuous  $\psi$ .

Consider now four possibilities concerning the potential:

1.  $V(x)$  is continuous. In this case the continuity of  $\psi(x)$  and (1.4.1) imply  $\psi''$  is also continuous. This requires  $\psi'$  continuous.
2.  $V(x)$  has finite discontinuities. In this case  $\psi''$  has finite discontinuities: it includes the product of a continuous  $\psi$  against a discontinuous  $V$ . But then  $\psi'$  must be continuous, with non-continuous derivative.
3.  $V(x)$  contains delta functions. In this case  $\psi''$  also contains delta functions: it includes the product of a continuous  $\psi$  and a delta function in  $V$ . Thus  $\psi'$  has finite discontinuities.
4.  $V(x)$  contains a hard wall. A potential that is finite immediately to the left of  $x = a$  and becomes infinite for  $x > a$  is said to have a hard wall at  $x = a$ . In such a case, the wavefunction will vanish for  $x \geq a$ . The slope  $\psi'$  will be finite as  $x \rightarrow a$  from the left, and will vanish for  $x > a$ . Thus  $\psi'$  is discontinuous at the wall.

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

Both $\psi$ and $\psi'$ are continuous unless the potential has delta functions or hard walls in which cases $\psi'$ may have finite discontinuities.	(1.4.2)
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The origin of the discrete and continuous spectrum can be seen from simple examples. We have three situations to discuss, as shown in Figure 1.1 as (a), (b), and (c). We will consider the number of parameters needed to write a solution  $\psi(x)$  and the number of constraints due to boundary conditions. Without loss of generality we can consider real solutions, and therefore the parameters will be real.

- (a) Here the energy  $E$  is below the potential far to the left and far to the right, but not in the middle. On the left the solution must be a decaying exponential  $\alpha_1 \exp(-\kappa|x|)$ , where  $\alpha_1$  is a constant to be determined and  $\kappa$  is known if the energy  $E$  is known. So thus far we get one unknown constant  $\alpha_1$ . In the middle region where  $E > V$  the solution is oscillatory  $\alpha_2 \cos kx + \alpha_3 \sin kx$ , with two unknown constants  $\alpha_2$  and  $\alpha_3$ , and  $k$  determined if  $E$  is known. Finally to the right we have a solution  $\alpha_4 \exp(-\kappa x)$  since the wavefunction must vanish as  $x \rightarrow \infty$ . So we have four (real) unknown constants  $\alpha_i$ ,  $i = 1, 2, 3, 4$ . Since  $\psi$  and  $c\psi$  are the same solution we can scale the solution to set, for example,  $\alpha_1 = 1$ . Therefore, we only have three constants to determine. There are, however, four constraints from boundary conditions: the continuity of  $\psi$  and  $\psi'$  at each of the two interfaces. With three unknowns and four conditions we cannot

guarantee the existence of a solution. If we view the energy  $E$ , however, as unknown, then we have four unknowns and four conditions. Indeed solutions exist for discrete values of the energy. We get a discrete spectrum.

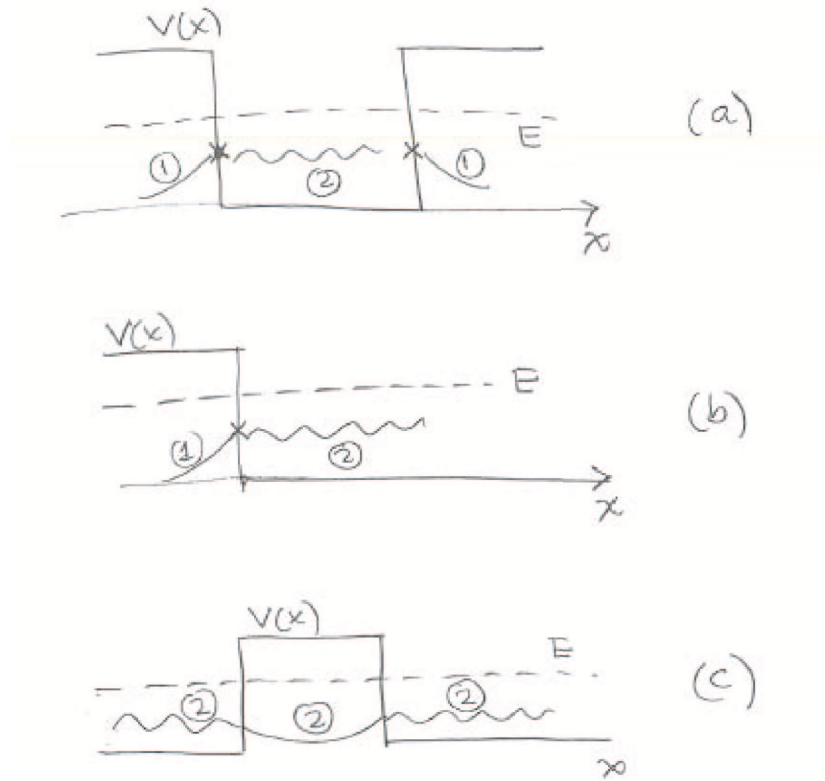


Figure 1.1: Discussing the number of constants needed to specify a solution. (a) Energy is smaller than the potential for  $x \rightarrow \pm\infty$ . (b) Energy is smaller than the potential for  $x \rightarrow -\infty$  and larger than the potential for  $x \rightarrow \infty$ . (c) Energy is larger than the potential for  $x \rightarrow \pm\infty$ .

- (b) Here we have one unknown constant for the solution to the left of the interface (multiplying a decaying exponential) and two unknown constants for the oscillatory solution to the right of the interface, for a total of three unknowns, or just two unknowns once the overall scale freedom is accounted in. We also have two boundary conditions at the interface. So we can expect a solution. Indeed there should be a solution for each value of the energy. The spectrum here is continuous and non-degenerate.
- (c) Two constants are needed here in each of the three regions: they multiply sines and

cosines to the left and to the right, and multiply the two exponentials in the middle. Thus six constants and due to scaling just five unknowns. We still have four boundary conditions so there should be solutions. In fact, there are two solutions for each energy. We can understand this as follows. Think of using just one coefficient to the far left, say the coefficient multiplying the sine function. With one less coefficient we have the same number of unknowns as constraints so we should get one solution (for any  $E$ ). We get another solution if we use the cosine function to the far left. So we have two solutions for each energy. The spectrum is continuous and doubly degenerate.

Figure 1.2 illustrates the spectrum of the Hamiltonian for a rather generic type of potential. Here  $V_+$  is the top asymptote of the potential,  $V_-$  is the bottom asymptote of the potential, and  $V_0$  is the lowest value of the potential. In the figure we indicate the type of spectrum for energies in each interval:  $E > V_+$ , then  $V_- < E < V_+$ , then  $V_0 < E < V_-$  and finally  $E < V_0$ .

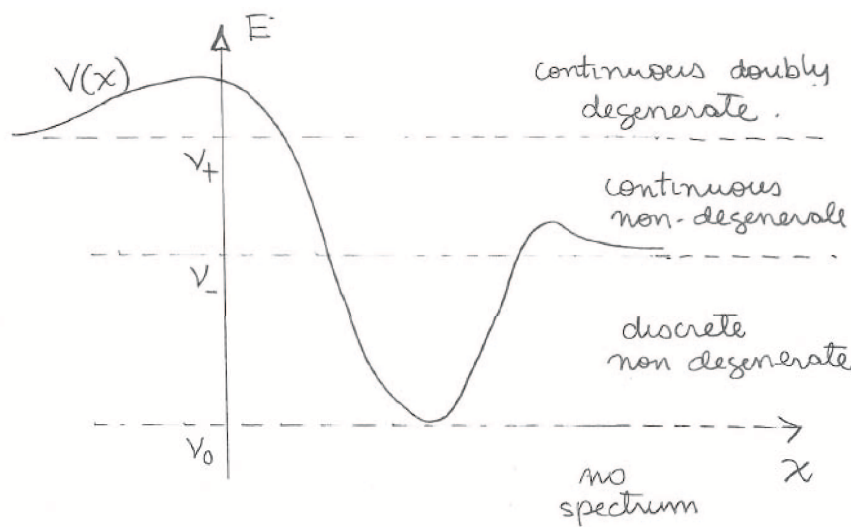


Figure 1.2: A generic potential and the type of spectrum for various energy ranges.

There are useful results about the number and positions of points where a wavefunction can vanish. A **zero** of a wavefunction  $\psi(x)$  is a point  $x_0$  in the domain of the wavefunction where  $\psi(x_0) = 0$ . If you have a hard wall at a point  $x_0$ ,  $\psi$  must vanish there and  $x_0$  is a zero. When  $x \in (-\infty, \infty)$  a bound state will have zeroes at  $\pm\infty$  where  $\psi$  vanishes and in fact  $\psi'$  vanishes. A **node** in a wavefunction is a zero in the *interior* of the domain of the wavefunction. Thus zeroes at  $x = \pm\infty$  do not qualify as nodes, nor do zeroes at hard walls, whose position in fact define a boundary of the domain. Note that at a node  $x_0$  we must have  $\psi'(x_0) \neq 0$ , otherwise, by regularity the wavefunction would have to vanish everywhere.



**Theorem 4** For the discrete bound-state spectrum of a one-dimensional potential let the allowed energies be  $E_1 < E_2 < E_3 < \dots$  with  $E_1$  the ground state energy. Let the associated energy eigenstates be  $\psi_1, \psi_2, \psi_3, \dots$ . The wavefunction  $\psi_1$  has no nodes,  $\psi_2$  has one node, and each consecutive wavefunction has one additional node. In conclusion  $\psi_n$  has  $n - 1$  nodes.

The most famous part of the above theorem is that the ground state has no nodes! We will not prove this theorem here. In fact you will show in the homework that  $\psi_{k+1}$  has at least one node between two consecutive zeroes of  $\psi_k$ . This implies that  $\psi_{k+1}$  has at least one more node than  $\psi_k$ . This can be illustrated in Figure 1.3 that shows a bound state  $\psi_4(x)$  with three nodes at  $x_1, x_2$ , and  $x_3$  and extra zeroes at  $x = -\infty$  and  $x = \infty$ . For  $\psi_5$  there must be a node  $w_1$  in  $(-\infty, x_1)$ , a node  $w_2 \in (x_1, x_2)$  and so on until a last node  $w_4 \in (x_3, \infty)$ .

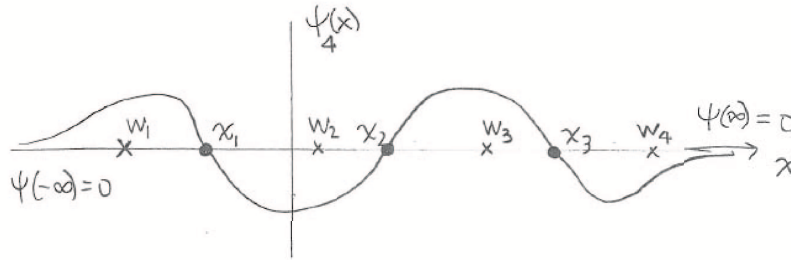


Figure 1.3: A wavefunction  $\psi_4$  with three nodes  $(x_1, x_2, x_3)$  and two extra zeroes at  $x = \pm\infty$ . The next wavefunction  $\psi_5$  must have four nodes, with positions indicated by  $w_1, w_2, w_3$  and  $w_4$ .

**Example: Potential with five delta functions.** We will discuss the bound states of the Schrödinger equation with potential

$$V(x) = -V_0 a \sum_{n=-2}^2 \delta(x - na). \quad (1.4.3)$$

This potential has delta functions at  $x$  equal to  $-2a, -a, 0, a$ , and  $2a$ , as shown in Figure 1.4.

We first examine the effect of the delta functions on the eigenstates. We will see that they produce discontinuities in  $\psi'$  at the position of the delta functions. We begin with the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x), \quad (1.4.4)$$

and integrate this equation from  $a - \epsilon$  to  $a + \epsilon$ , where  $\epsilon$  is a small value that we will take down to zero. By doing this we will get one out of the five delta functions to fire. We find

$$-\frac{\hbar^2}{2m} \int_{a-\epsilon}^{a+\epsilon} dx \frac{d^2\psi}{dx^2} + \int_{a-\epsilon}^{a+\epsilon} dx V(x)\psi(x) = E \int_{a-\epsilon}^{a+\epsilon} dx \psi(x). \quad (1.4.5)$$

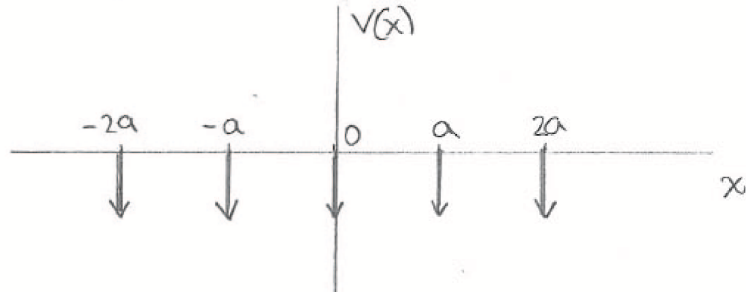


Figure 1.4: A potential  $V(x)$  with five downwards pointing delta-functions.

The first term involves a total derivative, the second term just picks up the delta function at  $x = a$ , and the right hand side is evaluated by noting that since  $\psi$  is continuous its value at  $x = a$  gives the leading contribution:

$$-\frac{\hbar^2}{2m} \frac{d\psi}{dx} \Big|_{a-\epsilon}^{a+\epsilon} - V_0 a \int_{a-\epsilon}^{a+\epsilon} dx \delta(x-a) \psi(x) = E(2\epsilon) \psi(a) + \mathcal{O}(\epsilon^2). \quad (1.4.6)$$

In the limit as  $\epsilon \rightarrow 0$  we will denote  $a + \epsilon$  as  $a^+$  and  $a - \epsilon$  as  $a^-$ . These labels are needed since  $\psi'$  has to be discontinuous at  $x$ . Indeed, we get

$$-\frac{\hbar^2}{2m} (\psi'(a^+) - \psi'(a^-)) - V_0 a \psi(a) = 0. \quad (1.4.7)$$

This implies that the discontinuity  $\Delta\psi'$  of  $\psi'$  is given by

$$\boxed{\Delta\psi'(a) \equiv \psi'(a^+) - \psi'(a^-) = \frac{2m}{\hbar^2} (-V_0 a) \psi(a).} \quad (1.4.8)$$

The discontinuity of  $\psi'$  at the position of the delta function is proportional to the value of  $\psi$  at this point. The constant of proportionality is linear on the strength  $V_0 a$  of the delta function. It follows that if the delta function of the potential is at a point where  $\psi$  vanishes then both  $\psi$  and  $\psi'$  are continuous and the delta function has no effect.

Let us now focus on bound states. These will be states with  $E < 0$ . The Schrödinger equation away from the delta functions is just

$$\psi'' = -\frac{2mE}{\hbar^2} \psi = \kappa^2 \psi, \quad \text{with} \quad \kappa^2 \equiv -\frac{2mE}{\hbar^2} > 0. \quad (1.4.9)$$

The solutions are therefore the linear combinations

$$\psi(x) = ae^{-\kappa x} + be^{\kappa x}, \quad (1.4.10)$$

with  $a$  and  $b$  real constants to be determined (recall the wavefunction can be taken to be real). In Figure 1.5 we show these functions for  $a > b > 0$ . Note the the curves intersect just once. It follows that the wavefunction will never have a zero if  $a$  and  $b$  have the same sign and it will have exactly one zero if  $a$  and  $b$  have opposite signs.

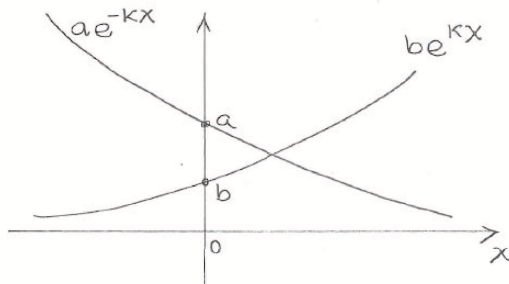


Figure 1.5: Plots of  $ae^{-\kappa x}$  and  $be^{\kappa x}$  with  $a, b > 0$ . This can be used to show that any linear superposition of these two functions can at most have one zero.

Let us then make the following remarks:

1. *The wavefunction has no nodes for  $x \geq 2a$  (nor for  $x \leq -2a$ ).* For  $x \geq 2a$  the solution, if non vanishing, must be of the form  $ce^{-\kappa x}$ . This can only vanish if  $c = 0$ . In this case the wavefunction would vanish identically for  $x \geq 2a$ . This does not look good and we can explain why. Since  $\psi(2a) = 0$  then  $\psi'$  is not discontinuous and, by continuity, a bit to the left of  $2a$  both  $\psi$  and  $\psi'$  vanish. This is enough to make the solution vanish over the next interval  $x \in (a, 2a)$ . Continuing in this way we find that the solution for  $\psi$  would have to be zero everywhere. This is not acceptable.
2. *There is at most one node in between each pair of contiguous  $\delta$ -functions.* This follows because the solution must take the form (1.4.10) and we argued that such function can at most have one zero.
3. A node appears at  $x = 0$  for all the antisymmetric bound states. In those cases, there cannot be another node in the interval  $[-a, a]$ . Nodes may appear at  $x = \pm a$ , but this is presumably not generic.
4. There are at most five bound states because the maximum number of nodes is four; one in between each delta function. All these five bound states exist if the delta functions are strong enough. The ground state is even, has no nodes and presumably looks like the one drawn in Figure 1.6.

*Exercise.* Sketch the expected shapes of the four excited bound states of the potential.

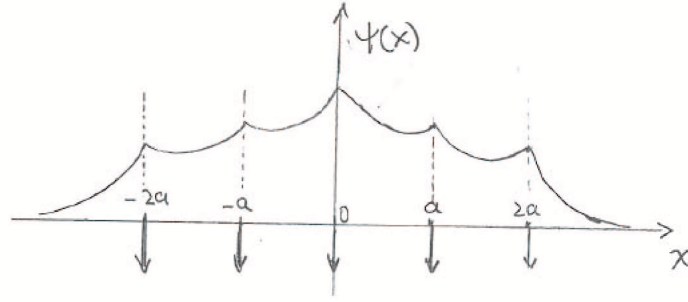


Figure 1.6: A sketch of the ground state wavefunction.

## 1.5 Variational Principle

Consider a system with Hamiltonian  $\hat{H}$  and focus on the time-independent Schrödinger equation:

$$\hat{H}\psi(\vec{x}) = E\psi(\vec{x}). \quad (1.5.11)$$

Let us assume that the system has a collection of normalizable energy eigenstates, including a ground state with ground state energy  $E_{gs}$ . Note the use of  $\vec{x}$ : our discussion applies to quantum systems in any number of spatial dimensions. Our first goal is to learn something about the ground state energy without solving the Schrödinger equation nor trying to figure out the ground state wavefunction.

For this purpose, consider an *arbitrary* normalized wavefunction  $\psi(\vec{x})$ :

$$\int d\vec{x} \psi^*(\vec{x})\psi(\vec{x}) = 1. \quad (1.5.12)$$

By arbitrary we mean a wavefunction that need not satisfy the time-independent Schrödinger equation, that is, a wavefunction that need not be an energy eigenstate. This is called a **trial** wavefunction; it is a wavefunction that we simply choose as we wish. Then we claim the ground state energy  $E_{gs}$  of the Hamiltonian is smaller or equal than the expectation value of  $\hat{H}$  in this arbitrary normalized trial wavefunction  $\psi$ , namely,

$$E_{gs} \leq \langle \hat{H} \rangle_{\psi} \equiv \int d\vec{x} \psi^*(\vec{x}) \hat{H} \psi(\vec{x}), \quad \text{Normalized } \psi. \quad (1.5.13)$$

When the right-hand side of the above inequality is evaluated we get an energy and learn that the ground state energy must be smaller or equal to the value we get. Thus any trial wavefunction provides an *upper bound* for the ground state energy. Better and better trial wavefunctions will produce lower and lower upper bounds. Note that if the trial wavefunction is set equal to the (unknown) ground-state wavefunction, the expectation value of  $\hat{H}$  becomes exactly  $E_{gs}$  and the inequality is saturated.

Let us prove (1.5.13). For simplicity, we will consider here the case where the energy eigenstates  $\psi_n(\vec{x})$  of  $\hat{H}$  are denumerable and their corresponding energies  $E_n$  are ordered as

$$E_{gs} = E_1 \leq E_2 \leq E_3 \leq \dots \quad (1.5.14)$$

Of course  $\hat{H}\psi_n = E_n\psi_n$ . Since the energy eigenstates are complete, any trial wavefunction can be expanded in terms of them (see (1.2.19)):

$$\psi(\vec{x}) = \sum_{n=1}^{\infty} b_n \psi_n(\vec{x}). \quad (1.5.15)$$

The normalization condition (1.5.12) gives us,

$$\sum_{n=1}^{\infty} |b_n|^2 = 1. \quad (1.5.16)$$

The evaluation of the right-hand side in (1.5.13) was done before in (1.2.28) so we have

$$\langle \hat{H} \rangle_{\psi} = \int d\vec{x} \psi^*(\vec{x}) \hat{H} \psi(\vec{x}) = \sum_{n=1}^{\infty} |b_n|^2 E_n. \quad (1.5.17)$$

Since  $E_n \geq E_1$  for all  $n$ , we can replace the  $E_n$  on the above right-hand side for  $E_1$  getting a smaller or equal value:

$$\langle \hat{H} \rangle_{\psi} = \sum_{n=1}^{\infty} |b_n|^2 E_n \geq \sum_{n=1}^{\infty} |b_n|^2 E_1 = E_1 \sum_{n=1}^{\infty} |b_n|^2 = E_1 = E_{gs}, \quad (1.5.18)$$

where we used (1.5.16). This is in fact the claim in (1.5.13).

It is generally more convenient not to worry about the normalization of the trial wavefunctions. Given a trial wavefunction  $\psi$  that is not normalized, the wavefunction

$$\frac{\psi(x)}{\sqrt{N}} \quad \text{with} \quad N = \int d\vec{x} \psi^*(\vec{x}) \psi(\vec{x}), \quad (1.5.19)$$

is normalized and can be used in (1.5.13). We therefore find that

$$\boxed{E_{gs} \leq \frac{\int d\vec{x} \psi^*(\vec{x}) \hat{H} \psi(\vec{x})}{\int d\vec{x} \psi^*(\vec{x}) \psi(\vec{x})} \equiv \mathcal{F}[\psi].} \quad (1.5.20)$$

This formula can be used for trial wavefunctions that are not normalized. We also introduced the definition of the functional  $\mathcal{F}[\psi]$ . A functional is a machine that given a function, in this case  $\psi(\vec{x})$ , gives us a number. Our result states that the ground state energy arises as the minimum value that the functional  $\mathcal{F}$  can take. The inequality in (1.5.20) is our main result from the variational principle.

The above inequality can be used to find good upper bounds for the ground state energy of quantum systems that are not exactly solvable. For this purpose it is useful to construct trial wavefunctions

$$\psi(\vec{x}; \beta_1, \beta_2, \dots, \beta_m)$$

that depend on a set of parameters  $\beta_i$ , with  $i = 1, \dots, m$ . One then computes the expectation value  $\langle \hat{H} \rangle_\psi$  which, of course, is a function of the parameters. Any random values for the parameters will give an upper bound for the ground state energy, but by minimizing  $\langle \hat{H} \rangle_\psi$  over the parameter space we get the lowest possible upper bound consistent with the chosen form for the trial wavefunction.

**Example.** Consider a one-dimensional problem with the delta function potential

$$V(x) = -\alpha \delta(x), \quad \alpha > 0. \quad (1.5.21)$$

In this problem the ground state energy is calculable exactly and one has

$$E_{gs} = -\frac{m\alpha^2}{2\hbar^2}. \quad (1.5.22)$$

So this exercise is just an illustration of the method. Consider an unnormalized gaussian trial wavefunction, with a real parameter  $\beta$ :

$$\psi(x) = e^{-\frac{1}{2}\beta^2 x^2}, \quad \int_{-\infty}^{\infty} dx \psi^2 = \frac{\sqrt{\pi}}{\beta}. \quad (1.5.23)$$

The functional  $\mathcal{F}$  in (1.5.20) is then<sup>1</sup>

$$\begin{aligned} \frac{\int dx \psi^*(x) \hat{H} \psi(x)}{\int dx \psi^*(x) \psi(x)} &= \frac{\beta}{\sqrt{\pi}} \int dx e^{-\frac{1}{2}\beta^2 x^2} \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \alpha \delta(x) \right) e^{-\frac{1}{2}\beta^2 x^2} \\ &= \frac{\beta}{\sqrt{\pi}} \frac{\hbar^2}{2m} \int dx \left[ \frac{d}{dx} e^{-\frac{1}{2}\beta^2 x^2} \right]^2 - \frac{\beta}{\sqrt{\pi}} \alpha \\ &= \frac{\beta}{\sqrt{\pi}} \frac{\hbar^2}{2m} \frac{\beta \sqrt{\pi}}{2} - \frac{\beta}{\sqrt{\pi}} \alpha \\ &= \frac{\beta^2 \hbar^2}{4m} - \frac{\beta}{\sqrt{\pi}} \alpha. \end{aligned} \quad (1.5.24)$$

The first term on the last right-hand side is the kinetic energy and the second term is the potential energy. For any value of  $\beta$  the final expression above provides an upper bound for the ground state energy, and the best upper bound is the lowest one. We thus have that the ground state energy satisfies

$$E_{gs} \leq \text{Min}_\beta \left( \frac{\beta^2 \hbar^2}{4m} - \frac{\beta}{\sqrt{\pi}} \alpha \right). \quad (1.5.25)$$

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<sup>1</sup>We use the integrals  $\int du e^{-u^2} = \sqrt{\pi}$  and  $\int du u^2 e^{-u^2} = \frac{1}{2}\sqrt{\pi}$ . A very useful step is to integrate by parts the second derivatives, as we do in here.

The minimum is easily found

$$\beta = \frac{2m\alpha}{\hbar^2\sqrt{\pi}} \quad \rightarrow \quad E_{gs} \leq -\frac{m\alpha^2}{\pi\hbar^2} = \frac{2}{\pi} \left( -\frac{m\alpha^2}{2\hbar^2} \right). \quad (1.5.26)$$

Comparing with (1.5.22) we see that the bound we found is in fact  $\frac{2}{\pi}E_{gs} \simeq 0.64E_{gs}$ . The trial wavefunction brought us to about 64% of the correct value.

In the exercises you will develop the following results:

1. Restricted to trial wavefunctions orthogonal to the ground state, the functional  $\mathcal{F}$  gives upper bounds for the energy of the first excited state.
2. Consider an attractive one-dimensional potential defined as a nowhere positive potential that approaches zero at infinity. The ground state for this potential is a bound state, namely, a state with energy less than zero.
3. We have shown that the functional  $\mathcal{F}[\psi]$  has a minimum when  $\psi$  is the ground state wavefunction.  $\mathcal{F}[\psi]$  is actually stationary at each and every energy eigenstate. For eigenstates of energies higher than the ground state  $\mathcal{F}$  has a saddle point.

## 1.6 Position, momentum, and matrices

In quantum mechanics the position operator  $\hat{x}$  and the momentum operator  $\hat{p}$  do not commute. They satisfy the commutation relation

$$[\hat{x}, \hat{p}] = i\hbar. \quad (1.6.27)$$

When we speak about the state of a particle and describe it with the wavefunction  $\Psi(x, t)$  we are using the “position” representation of the state. Since the time dependence is irrelevant to the present discussion, we will simply consider wavefunctions  $\psi(x)$ . All of our results apply to  $\Psi(x, t)$ . The position operator  $\hat{x}$  then acts on  $\psi(x)$  in a simple way. We define

$$\hat{x}\psi(x) \equiv x\psi(x). \quad (1.6.28)$$

In words the position operator acting on an  $x$ -dependent wavefunction simply multiplies the wavefunction by  $x$ . The momentum operator in the position representation is given by

$$\hat{p} \equiv \frac{\hbar}{i} \frac{\partial}{\partial x} \quad (1.6.29)$$

This is to say that acting on a wavefunction  $\psi(x)$  we have

$$\hat{p}\psi(x) = \frac{\hbar}{i} \frac{d\psi}{dx}. \quad (1.6.30)$$

Note that the commutation relation (1.6.27) is satisfied by the above definitions, as we can check acting on any wavefunction:

$$\begin{aligned}
 [\hat{x}, \hat{p}]\psi(x) &= (\hat{x}\hat{p} - \hat{p}\hat{x})\psi(x) \\
 &= \hat{x}\hat{p}\psi(x) - \hat{p}\hat{x}\psi(x) \\
 &= \hat{x}\frac{\hbar}{i}\frac{d\psi}{dx} - \hat{p}x\psi(x) \\
 &= \frac{\hbar}{i}x\frac{d\psi}{dx} - \frac{\hbar}{i}\frac{d}{dx}(x\psi) \\
 &= \frac{\hbar}{i}x\frac{d\psi}{dx} - \frac{\hbar}{i}\psi - \frac{\hbar}{i}x\frac{d\psi}{dx} \\
 &= i\hbar\psi(x).
 \end{aligned} \tag{1.6.31}$$

Since the wavefunction is arbitrary, we have verified that our explicit representation of the operators  $\hat{x}$  (by multiplication) and  $\hat{p}$  (by differentiation) satisfies the commutation relation  $[\hat{x}, \hat{p}] = i\hbar$ .

In quantum mechanics it is useful to think of states as vectors and operators as matrices. A wavefunction for a particle on the box  $0 \leq x \leq a$ , for example can be thought as vector with many components, each one giving the value of the function at a specific point. To make this concrete one discretizes the space into small intervals of size  $\epsilon$  such that  $N\epsilon = a$ . In that case we can represent the information in  $\psi(x)$  in a large column vector

$$\psi(x) \longleftrightarrow \begin{pmatrix} \psi(0) \\ \psi(\epsilon) \\ \psi(2\epsilon) \\ \vdots \\ \psi(N\epsilon) \end{pmatrix}. \tag{1.6.32}$$

The  $N + 1$  component column vector summarizes the values of the wavefunction at equally separated points.  $N$  is some kind of regulator: a precise description requires  $N \rightarrow \infty$  or  $\epsilon \rightarrow 0$ . Associated with the description (1.6.32) the operator  $\hat{x}$  can be viewed as the  $(N + 1) \times (N + 1)$  diagonal matrix

$$\hat{x} \longleftrightarrow \begin{pmatrix} 0 & 0 & 0 & \dots & 0 \\ 0 & \epsilon & 0 & \dots & 0 \\ 0 & 0 & 2\epsilon & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & N\epsilon \end{pmatrix}. \tag{1.6.33}$$



You can see that the action of the matrix  $\hat{x}$  on the vector (1.6.32) gives the vector

$$\begin{pmatrix} 0 \cdot \psi(0) \\ \epsilon \cdot \psi(\epsilon) \\ 2\epsilon \cdot \psi(2\epsilon) \\ \vdots \\ N\epsilon \cdot \psi(N\epsilon) \end{pmatrix}, \quad (1.6.34)$$

which is indeed the representation of  $x\psi(x)$ . Given our definition of the action of  $\hat{x}$ , expectation values in normalized states are naturally defined by

$$\langle \hat{x} \rangle \equiv \int dx' \psi^*(x') (x' \psi(x')). \quad (1.6.35)$$

There are also matrix representations of the momentum operator and they will be discussed in exercises.

Are there eigenstates of the  $\hat{x}$  operator? Yes, but their are not normalizable. An eigenstate of  $\hat{x}$  must be a localized state, and the obvious candidate is a delta function. Defining

$$\psi_{x_0}(x) \equiv \delta(x - x_0), \quad (1.6.36)$$

we verify that

$$\hat{x}\psi_{x_0}(x) = x\psi_{x_0}(x) = x\delta(x - x_0) = x_0\delta(x - x_0) = x_0\psi_{x_0}(x), \quad (1.6.37)$$

confirming that  $\psi_{x_0}(x)$  is an eigenstate of  $\hat{x}$  with eigenvalue  $x_0$ . A delta function cannot be normalized, so the position eigenstates are not normalizable.

Eigenstates of the momentum operator also exist and are also not normalizable. Defining

$$\psi_p(x) \equiv \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}, \quad (1.6.38)$$

we readily confirm that

$$\hat{p}\psi_p(x) = \frac{\hbar}{i} \frac{\partial}{\partial x} \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} = p \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} = p\psi_p(x). \quad (1.6.39)$$

So  $\psi_p(x)$  is a momentum eigenstate with momentum eigenvalue  $p$ . It is a plane wave.

The so-called momentum representation is mathematically described by Fourier transforms. The Fourier transform  $\tilde{\psi}(p)$  of  $\psi(x)$  is defined by

$$\tilde{\psi}(p) \equiv \int_{-\infty}^{\infty} dx \frac{e^{-ipx/\hbar}}{\sqrt{2\pi\hbar}} \psi(x). \quad (1.6.40)$$

The function  $\tilde{\psi}(p)$  encodes the same of information as  $\psi(x)$ . We call  $\tilde{\psi}(p)$  the momentum space representation of the state. Clearly for each value of  $p$ ,  $\tilde{\psi}$  is a linear superposition of

values of  $\psi(x)$  for all  $x$ . We can view the Fourier transformation as a linear transformation, the action of a matrix that depends on  $p$  on the vector that represents  $\psi(x)$ . The inverse Fourier transform is written as

$$\psi(x) = \int_{-\infty}^{\infty} dp \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} \tilde{\psi}(p). \quad (1.6.41)$$

We can view this formula as an expansion of  $\psi(x)$  in a basis of momentum eigenstates, with  $\tilde{\psi}(p)$  the expansion coefficients.

We have seen that  $\psi(x)$  and  $\tilde{\psi}(p)$  are just two different representations of the same state:

$$\psi(x) \longleftrightarrow \tilde{\psi}(p). \quad (1.6.42)$$

The arrow above is implemented by Fourier Transformation. Calculate now the action of  $\frac{\hbar}{i} \frac{d}{dx}$  on (1.6.41)

$$\begin{aligned} \frac{\hbar}{i} \frac{d}{dx} \psi(x) &= \frac{\hbar}{i} \frac{d}{dx} \int_{-\infty}^{\infty} dp \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} \tilde{\psi}(p) = \int_{-\infty}^{\infty} dp \left( \frac{\hbar}{i} \frac{d}{dx} e^{ipx/\hbar} \right) \frac{1}{\sqrt{2\pi\hbar}} \tilde{\psi}(p) \\ &= \int_{-\infty}^{\infty} dp \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} p \tilde{\psi}(p). \end{aligned} \quad (1.6.43)$$

In the language of (1.6.42) we write this as

$$\frac{\hbar}{i} \frac{d}{dx} \psi(x) \longleftrightarrow p \tilde{\psi}(p). \quad (1.6.44)$$

We see that the momentum operator, viewed as the action of  $\frac{\hbar}{i} \frac{d}{dx}$  in position space, is simply multiplication by  $p$  on momentum space wavefunctions  $\tilde{\psi}$ :

$$\hat{p} \tilde{\psi}(p) = p \tilde{\psi}(p). \quad (1.6.45)$$

This is, of course, perfectly analogous to the way that  $\hat{x}$  acts on position space wavefunctions.

**Exercise.** Verify that acting on momentum space wavefunctions the  $\hat{x}$  operator is represented by

$$\text{Momentum representation :} \quad \hat{x} \equiv i\hbar \frac{d}{dp}. \quad (1.6.46)$$

You can do this in two ways. Working with Fourier transforms, or by verifying (as in (1.6.31)) that it is consistent with  $[\hat{x}, \hat{p}] = i\hbar$  acting on momentum space wavefunctions.