WAVE MECHANICS

B. Zwiebach

September 13, 2013

Contents

1 The Schrödinger equation

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

$$\Psi(\vec{x}, t) \in \mathbb{C}. \tag{1.1}$$

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

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t}(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \Psi(x, t).} \tag{1.2}$$

This is the equation for a (non-relativistic) particle of mass m moving along the x axis while acted 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 (1.2) 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 Ψ: if Ψ_1 and Ψ_2 are solutions so is $a_1\Psi_1 + a_2\Psi_2$ with a_1 and a_2 arbitrary *complex numbers*.

Given a complex number $z = a + ib$, $a, b \in \mathbb{R}$, its complex conjugate is $z^* = a - ib$. 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 $|z| = \sqrt{a^2 + b^2}$. If the norm of a complex number is zero, the complex number is zero. You can quickly verify that

$$|z|^2 = zz^*. \tag{1.3}$$

For a wavefunction $\Psi(x, t)$ its complex conjugate $(\Psi(x, t))^*$ will be 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:

$$P(x, t) = \rho(x, t) \equiv \Psi^*(x, t)\Psi(x, t) = |\Psi(x, t)|^2. \tag{1.4}$$

This probability density so defined is positive. The physical interpretation of the wavefunction arises because we declare that

$$\boxed{P(x, t)\, dx \text{ is the probability to find the particle in the interval } [x, x + dx] \text{ at time } t.}$$
$$\tag{1.5}$$

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

$$\int_{-\infty}^{\infty} dx\, |\Psi(x, t)|^2 = 1, \quad \forall\, t. \tag{1.6}$$

By integrating over space, the left-hand adds 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:

$$\int_{-\infty}^{\infty} dx\, |\Psi(x, t_0)|^2 = 1, \quad \forall\, t. \tag{1.7}$$

As mentioned above, knowledge of the wavefunction at one time implies, via the Schrödinger equation, knowledge 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:

$$\frac{d}{dt} \int_{-\infty}^{\infty} dx\, |\Psi(x,t)|^2 \; = \; 0\,. \tag{1.8}$$

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

- - - - - - - - - - - - - -

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

$$J(x,t) \;=\; \frac{\hbar}{m}\mathrm{Im}\left(\Psi^*\frac{\partial\Psi}{\partial x}\right)\,. \tag{1.9}$$

The analogy in electromagnetism is useful. There we have the current density vector $\vec{J}$ and the charge density ρ. The statement of charge conservation is the differential relation

$$\nabla\cdot\vec{J} + \frac{\partial\rho}{\partial t} \;=\; 0\,. \tag{1.10}$$

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 $\vec{J}$ across the surface S that bounds the volume:

$$\frac{dQ_V}{dt}(t) \;=\; -\oint_S \vec{J}\cdot d\vec{a}\,. \tag{1.11}$$

Make sure you know how to get this equation from (1.10)! While the probability current in more than one spatial dimension is also a vector, in our present one-dimensional case, it has just one component. The conservation equation is the analog of (1.10):

$$\frac{\partial J}{\partial x} + \frac{\partial\rho}{\partial t} \;=\; 0\,. \tag{1.12}$$

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 $x \in [a,b]$

$$P_{ab}(t) \;\equiv\; \int_a^b dx\,|\Psi(x,t)|^2 \;=\; \int_a^b dx\,\rho(x,t)\,. \tag{1.13}$$

You can then quickly show that

$$\frac{dP_{ab}}{dt}(t) \;=\; J(a,t) - J(b,t)\,. \tag{1.14}$$

3

Here $J(a,t)$ denotes the rate at which probability flows in (in units of one over time) at the left boundary of the interval, while $J(b,t)$ denotes the rate at which probability flows out at the right boundary of the interval.

It is sometimes easier to work with wavefunctions that are not normalized. The normalization can be perfomed if needed. We will thus refer to wavefunctions in general without assuming normalization, otherwise we will call them *normalized* wavefunction. In this spirit, two wavefunctions Ψ_1 and Ψ_2 solving 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

$$\Psi_1 \sim \Psi_2 \quad \longleftrightarrow \quad \Psi_1(x,t) = \alpha \, \Psi_2(x,t), \quad \alpha \in \mathbb{C}. \tag{1.15}$$

If the wavefunctions Ψ_1 and Ψ_2 are normalized they are equivalent if they differ by an overall constant phase:

$$\text{Normalized wavefunctions:} \quad \Psi_1 \sim \Psi_2 \quad \longleftrightarrow \quad \Psi_1(x,t) = e^{i\theta} \, \Psi_2(x,t), \quad \theta \in \mathbb{R}. \tag{1.16}$$

2 Stationary Solutions

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 (1.2) can be written more briefly as

$$i\hbar \frac{\partial \Psi}{\partial t}(x,t) \;=\; \hat{H} \, \Psi(x,t), \tag{2.1}$$

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

$$\hat{H} \;\equiv\; -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x). \tag{2.2}$$

$\hat{H}$ is an operator in the sense that 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 $V(x)$ acts just by multiplication. Note that the operator $\hat{H}$ is time independent – it does not involve time at all.

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

$$\Psi(x,t) \;=\; e^{-iEt/\hbar} \, \psi(x), \tag{2.3}$$

where $\psi(x) \in \mathbb{C}$ is a function of x only 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

$$P(x,t) \;=\; \Psi^*(x,t)\,\Psi(x,t) \;=\; e^{+iEt/\hbar}\,\psi^*(x)\,e^{-iEt/\hbar}\,\psi(x) \;=\; \psi^*(x)\psi(x) \;=\; |\psi(x)|^2. \tag{2.4}$$

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

$$\begin{aligned} P(x,t) &= \Psi^*(x,t)\,\Psi(x,t) = e^{+iE^*t/\hbar}\,\psi^*(x)\,e^{-iEt/\hbar}\,\psi(x) \\ &= e^{i(E^*-E)t/\hbar}\psi^*(x)\psi(x) = e^{-2\Gamma t/\hbar}\,|\psi(x)|^2\,. \end{aligned} \tag{2.5}$$

This kind of state is not acceptable: the normalization cannot be preserved in time.

Let us consider the equation that $\psi(x)$ must satisfy. Plugging (2.3) into (2.1) we find

$$i\hbar\frac{\partial}{\partial t}e^{-iEt/\hbar}\,\psi(x) = \hat{H}e^{-iEt/\hbar}\,\psi(x)\,, \tag{2.6}$$

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

$$i\hbar\left(\frac{\partial}{\partial t}e^{-iEt/\hbar}\right)\psi(x) = e^{-iEt/\hbar}\,\hat{H}\psi(x)\,. \tag{2.7}$$

Taking the derivative and canceling the exponentials we get

$$i\hbar\left(-i\frac{E}{\hbar}\right)\psi(x) = \hat{H}\,\psi(x)\,, \tag{2.8}$$

which we write as

$$\boxed{\hat{H}\,\psi(x) = E\,\psi(x)\,.} \tag{2.9}$$

Recalling the expression for the Hamiltonian we have

$$\boxed{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\,\psi(x)\,.} \tag{2.10}$$

Note that the derivatives along x need not be denoted as partial derivatives since the functions they act on have no other argument except x. Using primes to denote derivatives with respect to the argument, the above equation is

$$\boxed{-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\,\psi(x)\,.} \tag{2.11}$$

This is the equation for ψ 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.

Since the time-independent Schrödinger equation is a second-order differential equation in x, a solution is completely determined by the value of ψ and ψ' at some point x_0 ($\neq \infty$). If $V(x)$

is nowhere infinite, $\psi = \psi' = 0$ at some point implies $\psi = 0$ everywhere. Alternatively, if we know the solution for *any* size x-interval, the full solution is fully determined. A full solution means finding all the values E for which acceptable solutions $\psi(x)$ exist and, of course, finding those solutions for each E.

A solution $\psi(x)$ associated with an energy E 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 depend on the properties of the potential $V(x)$. We will consider potentials $V(x)$ that can fail to be continuous (but are piece-wise continuous, like the finite square well) and can fail to be bounded (like the potential for the harmonic oscillator). We allow delta function contributions in the potential but do not allow worse singularities, such as squares or derivatives of delta functions. We allow hard walls, as in the infinite square-well.

On the wavefunction we impose the following regularity condition:

$$\boxed{\psi(x) \text{ is continuous and bounded and its derivative } \psi'(x) \text{ is bounded.}} \qquad (2.12)$$

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 ψ 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:

$$\boxed{\text{An energy eigenstate } \psi(x) \text{ is a } \textbf{bound} \text{ state if } \psi(x) \to 0 \text{ when } |x| \to \infty \,.} \qquad (2.13)$$

Since a normalizable eigenstate must have a wavefunction that vanishes as $|x| \to \infty$, a bound state is just a normalizable eigenstate.

The eigenstates of $\hat{H}$ provide a useful set of functions. Let us denote the possible energies by E_n with $n = 1, 2, \ldots$, ordered as follows

$$E_1 \leq E_2 \leq E_3 \leq \ldots \qquad (2.14)$$

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

$$\hat{H}\psi_n(x) \;=\; E_n\,\psi_n(x)\,, \quad n \geq 1\,. \qquad (2.15)$$

For simplicity we discuss the case when the spectrum is denumerable so that, as above, we can label the states and energies with the integer label n. 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 of the continuum spectrum are not normalizable.

It is a known result about differential equations that for rather general potentials the $\hat{H}$ eigenstates $\psi_n(x)$ can be chosen to be orthonormal. What does it mean for two functions to be orthogonal? Orthogonal vectors have a vanishing dot product, where the dot product is a (clever) rule 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 $\int f_1^* f_2$. 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 (this requires the complex conjugation in the definition, can you see that?). As a result, orthonormality means that

$$\boxed{\text{Orthonormality:} \quad \int_{-\infty}^{\infty} dx \; \psi_m^*(x)\, \psi_n(x) \;=\; \delta_{m,n} \, .} \tag{2.16}$$

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

The energy eigenstates are also *complete* in the sense that any reasonable (see (2.12) wavefunction $\psi(x)$ can be expanded as a superposition of energy eigenstates. Namely, there exist complex numbers b_n such that

$$\psi(x) \;=\; \sum_{n=1}^{\infty} b_n\, \psi_n(x)\,, \quad b_n \in \mathbb{C}\,. \tag{2.17}$$

This is a very powerful statement: it means that if the energy eigenstates are known, the general solution of the Schrödinger equation is known. Indeed assume that the wavefuntion at time equal zero is the $\psi(x)$ above. Then we have

$$\boxed{\Psi(x, t = 0) \;=\; \psi(x) \;=\; \sum_{n=1}^{\infty} b_n\, \psi_n(x)\,.} \tag{2.18}$$

If this wavefunction is normalized then we have

$$\int_{-\infty}^{\infty} dx \; \psi^*(x)\psi(x) \;=\; 1 \quad \rightarrow \quad \sum_{n=1}^{\infty} |b_n|^2 \;=\; 1\,. \tag{2.19}$$

We now claim that the wavefunction at all times can be written down immediately

$$\boxed{\Psi(x, t) \;=\; \sum_{n=1}^{\infty} b_n\, e^{-iE_n t/\hbar} \psi_n(x)\,.} \tag{2.20}$$

7

To prove that this is the solution we first note that we have produced a solution to the Schrödinger equation: this follows by linearity because each term in the above sum is a solution (a stationary state). Second, the solution reduces for $t = 0$ to the correct value $\Psi(x, t = 0)$ in (2.18). By the first remark below (1.2) this is all that is needed.

It should be emphasized that the superposition of stationary states is generally *not* a stationary state. The expansion coefficients b_n used above can be calculated explicitly if we know the energy eigenstates. Indeed using (2.16) and (2.17) a one-line computation (do it!) gives

$$b_n \ = \ \int_{-\infty}^{\infty} dx \, \psi_n^*(x)\psi(x) \,. \tag{2.21}$$

A curious identity can be derived by substituting this result back into (2.17):

$$\psi(x) \ = \ \sum_{n=1}^{\infty} \Big(\int_{-\infty}^{\infty} dx' \, \psi_n^*(x')\psi(x') \Big) \, \psi_n(x) = \ \int_{-\infty}^{\infty} dx' \Big(\sum_{n=1}^{\infty} \psi_n^*(x')\psi_n(x) \Big) \, \psi(x') \,, \tag{2.22}$$

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

$$f(x) \ = \ \int_{-\infty}^{\infty} dx' K(x', x) f(x') \tag{2.23}$$

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

$$\delta(x - x_0) \ = \ \int dx' K(x', x) \delta(x' - x_0) \ = \ K(x_0, x) \,. \tag{2.24}$$

We therefore conclude that $K(x', x) = \delta(x - x')$ (recall that $\delta(x) = \delta(-x)$). Back in (2.22) we thus find

$$\boxed{ \text{Completeness:} \ \ \sum_{n=1}^{\infty} \psi_n^*(x')\psi_n(x) \ = \ \delta(x - x') \,. } \tag{2.25}$$

Let us compare the completeness relation above with the orthonormality relation (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 (2.20). For arbitrary time-independent operators $\hat{A}$ one defines the (generally) time-dependent expectation value on a *normalized* state Ψ by

$$\langle\,\hat{A}\,\rangle_\Psi(t) \;\equiv\; \int_{-\infty}^{\infty} dx\, \Psi^*(x,t)(\hat{A}\Psi(x,t))\,. \tag{2.26}$$

What happens when we take the operator to be $\hat{H}$? Using (2.20) twice, we get

$$\begin{aligned}
\langle\,\hat{H}\,\rangle_\Psi(t) \;&=\; \int_{-\infty}^{\infty} dx\, \Psi^*(x,t)(\hat{H}\Psi(x,t)) \\
&=\; \sum_{n,n'} \int_{-\infty}^{\infty} dx\, b_n^*\, e^{iE_n t/\hbar}\psi_n^*(x)\ b_{n'}\, e^{-iE_n' t/\hbar}\hat{H}\psi_{n'}(x) \\
&=\; \sum_{n,n'} b_n^* b_{n'} E_{n'}\, e^{i(E_n - E_{n'})t/\hbar} \int_{-\infty}^{\infty} dx\, \psi_n^*(x)\,\psi_{n'}(x) \\
&=\; \sum_{n,n'} b_n^* b_{n'} E_{n'}\, e^{i(E_n - E_{n'})t/\hbar}\delta_{n,n'}\,,
\end{aligned} \tag{2.27}$$

so that we get

$$\langle\,\hat{H}\,\rangle_\Psi(t) \;=\; \sum_{n=1}^{\infty} |b_n|^2 E_n\,. \tag{2.28}$$

The expectation value of the Hamiltonian is 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.

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

$$\frac{\Psi(x,t)}{\sqrt{\int dx\,\Psi^*\Psi}} \tag{2.29}$$

is normalized. We can thus use this normalized wavefunction in the definition on $\langle\hat{A}\rangle$ to find the expectation value is given by

$$\langle\,\hat{A}\,\rangle_\Psi(t) \;\equiv\; \frac{\int_{-\infty}^{\infty} dx\, \Psi^*(x,t)(\hat{A}\Psi(x,t))}{\int dx\,\Psi^*(x,t)\Psi(x,t)}\,. \tag{2.30}$$

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

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

$$\hat{p} \;\equiv\; \frac{\hbar}{i}\,\frac{\partial}{\partial x}\,. \tag{2.31}$$

9

3   Properties of energy eigenstates in one dimension

In order to simplify our notation we rewrite the time-independent Schrödinger equation (2.10) as follows

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi = 0. \tag{3.1}$$

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

$$\mathcal{E} \equiv \frac{2m}{\hbar^2}E, \quad \mathcal{V}(x) \equiv \frac{2m}{\hbar^2}V(x). \tag{3.2}$$

With this the Schrödinger equation (3.1) becomes

$$\boxed{\psi'' + (\mathcal{E} - \mathcal{V}(x))\psi = 0.} \tag{3.3}$$

We are now ready to consider a basic result: in a one-dimensional potential there cannot be two or more bound states for any given energy.

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

$$\begin{aligned}
\psi_1'' + (\mathcal{E} - \mathcal{V}(x))\psi_1 &= 0, \\
\psi_2'' + (\mathcal{E} - \mathcal{V}(x))\psi_2 &= 0.
\end{aligned} \tag{3.4}$$

Multiplying the top equation by ψ_2 and the bottom one by ψ_1 and subtracting them we find

$$\psi_2\psi_1'' - \psi_1\psi_2'' = 0. \tag{3.5}$$

The left-hand side is actually a derivative

$$(\psi_2\psi_1' - \psi_1\psi_2')' = 0. \tag{3.6}$$

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

$$\psi_2\psi_1' - \psi_1\psi_2' = c. \tag{3.7}$$

The constant can be evaluated by examining the left-hand side for $|x| \to \infty$. We then have that $\psi_1 \to 0$ and $\psi_2 \to 0$, since they are bound states, while the derivatives are bounded, as assumed in (2.12). It follows that the left-hand side vanishes as $|x| \to \infty$ and therefore $c = 0$. We thus have

$$\psi_2\psi_1' = \psi_1\psi_2' \quad \to \quad \frac{\psi_1'}{\psi_1} = \frac{\psi_2'}{\psi_2} \quad \to \quad \frac{d}{dx}(\ln\psi_1 - \ln\psi_2) = 0. \tag{3.8}$$

This implies that we have for some constant c'

$$\ln \psi_1 = \ln \psi_2 + \ln c' \quad \rightarrow \quad \psi_1(x) = c' \psi_2(x) \,. \tag{3.9}$$

We have thus shown that the wavefunctions ψ_1 and ψ_2 are equivalent. In contradiction with the initial assumption, they are the same energy eigenstate. This concludes the proof.

For our second theorem we show that the reality of $\mathcal{V}$ allows us to work with real wavefunctions.

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

Proof. Consider our main equation and a possibly complex wavefunction that correspond

$$\psi'' + (\mathcal{E} - \mathcal{V}(x))\psi \; = \; 0 \,, \tag{3.10}$$

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

$$(\psi^*)'' + (\mathcal{E} - \mathcal{V}(x))\psi^* \; = \; 0 \,. \tag{3.11}$$

So ψ^* if different from ψ defines a degenerate solution. By superposition we can then get two real (degenerate) solutions

$$\psi_r \equiv \frac{1}{2}(\psi + \psi^*) \,, \quad \psi_{im} \equiv \frac{1}{2i}(\psi - \psi^*) \,. \tag{3.12}$$

These are, of course, the real and imaginary parts of ψ.

If we are dealing with bound states of one-dimensional potentials more can be said: any such solution is, up to a phase, *equal* to a real solution. Indeed, the absence of degenerate bound states means that the two real solutions ψ_r and ψ_{im} must be equal up to a constant that can only be real:

$$\psi_{im} = c\,\psi_r \,, \quad \text{with} \;\; c \in \mathbb{R} \tag{3.13}$$

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 ψ is, up to a phase β, equal to a real solution.

Theorem 3. If the potential is an even function of x: $V(-x) = V(x)$ the eigenstates can be chosen to be even or odd under $x \to -x$.

Proof. Again, we begin with our main equation

$$\psi''(x) + (\mathcal{E} - \mathcal{V}(x))\psi(x) \; = \; 0 \,. \tag{3.14}$$

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

$$\psi''(-x) + (\mathcal{E} - \mathcal{V}(x))\psi(-x) \; = \; 0 \,, \tag{3.15}$$

11

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

$$\varphi(x) \equiv \psi(-x) \quad \rightarrow \quad \frac{d}{dx}\varphi(x) = \psi'(-x) \cdot (-1). \tag{3.16}$$

Taking a second derivative and using (3.15)

$$\frac{d^2}{dx^2}\varphi(x) = \psi''(-x) = -(\mathcal{E} - \mathcal{V}(x))\varphi(x), \tag{3.17}$$

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

$$\frac{d^2}{dx^2}\varphi(x) + (\mathcal{E} - \mathcal{V}(x))\varphi(x) = 0. \tag{3.18}$$

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 $x \to -x$:

$$\psi_s(x) \equiv \frac{1}{2}(\psi(x) + \psi(-x)), \quad \psi_a(x) \equiv \frac{1}{2}(\psi(x) - \psi(-x)). \tag{3.19}$$

These are the solutions claimed to exist in Theorem 3.

Again, if we focus on bound states of one-dimensional potentials the absence of degeneracy implies that $\psi(x)$ and $\psi(-x)$ must be the same solution. Because of Theorem 2 we can choose $\psi(x)$ to be real and thus we must have

$$\psi(-x) = c\,\psi(x), \quad \text{with } c \in \mathbb{R}. \tag{3.20}$$

Letting $x \to -x$ 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 $x \to -x$. Any one-dimensional bound state solution with an even potential *must be* either even or odd under $x \to -x$.

4 The nature of the spectrum

Consider the time-independent Schrödinger equation written as

$$\psi'' = -\frac{2m}{\hbar^2}(E - V(x))\,\psi. \tag{4.1}$$

We always have that $\psi(x)$ is continuous, otherwise ψ'' has singularities worse than delta functions and we would require potentials $V(x)$ that are worse than delta functions – something we will not consider. Consider now three possibilities concerning the potential:

1. $V(x)$ is continuous. In this case the continuity of $\psi(x)$ and (4.1) imply ψ'' is also continuous. This requires ψ' continuous.

2. $V(x)$ has finite jumps. In this case ψ'' has finite jumps (it is the multiplication of ψ with no jumps times V with jumps). But then ψ' can have no jumps (it is continuous, with non-continuous derivative).

3. $V(x)$ contains delta functions. In this case ψ'' also contains delta functions (it is the multiplication of the continuous ψ times a delta function in V). Thus ψ' has finite jumps.

4. $V(x)$ contains a hard wall. A potential that is finite immediately to the left of $x = a$ and becomes infinite for $x > a$ is said to have a hard wall at $x = a$. In such a case, the wavefunction will vanish for $x \geq a$. The slope ψ' will be finite as $x \to a$ from the left, and will vanish for $x > a$. Thus ψ' is discontinuous at the wall.

In conclusion

> Both ψ and ψ' are continuous unless the potential has delta functions or hard walls in which cases ψ' may have finite jumps.

$$(4.2)$$

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 as (a), (b), and (c). We will consider the number of parameters needed to write a solution 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 α_1 is a constant to be determined and κ is known if the energy E is known. So thus far we got one unknown constant α_1. In the middle region where $E > V$ the solution is oscillatory $\alpha_2 \cos kx + \alpha_3 \sin kx$, with two unknown constants α_2 and α_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 $x \to \infty$. So we got four (real) unknown constants α_i, $i = 1, 2, 3, 4$. Since ψ and $c\psi$ are the same solution we can scale the solution and thus we only have three unknown constants to determine. There are, however, four constraints from boundary conditions: the continuity of ψ and ψ' at each of the two interfaces. With three coefficients and four conditions we cannot expect a solution to exist. 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.

(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
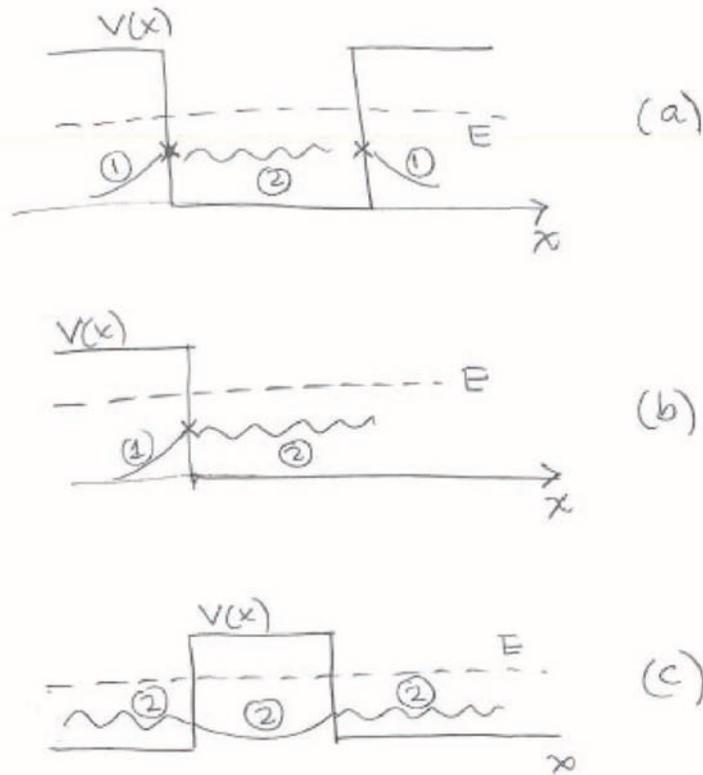
Figure 1: Discussing the number of constants needed to specify a solution. (a) Energy is smaller than the potential for $x \to \pm\infty$. (b) Energy is smaller than the potential for $x \to -\infty$ and larger than the potential for $x \to \infty$. (c) Energy is larger than the potential for $x \to \pm\infty$.

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.

14

Figure 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 the various intervals defined: $E > V_+$, then $V_- < E < V_+$, then $V_0 < E < V_-$ and finally $E < V_0$.
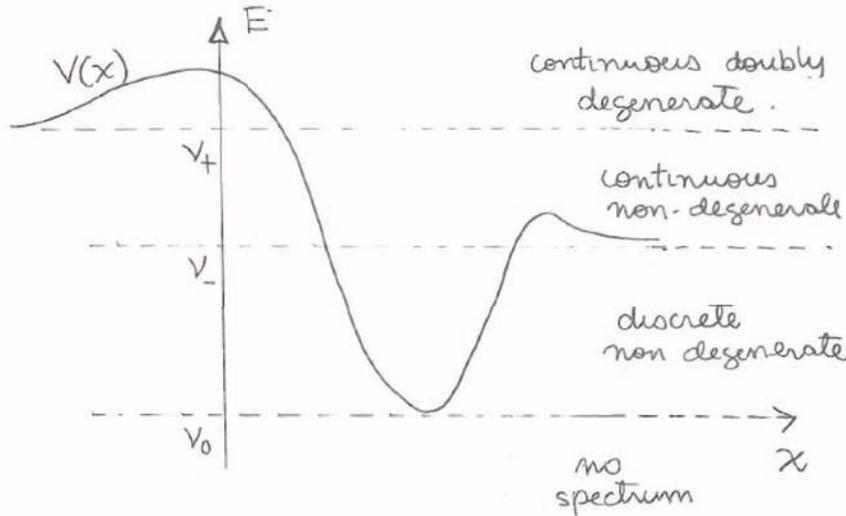
Figure 2: A generic potential and the type of spectrum for various energy ranges.

A **node** in a wavefunction is a point x_0 where $\psi(x_0) = 0$ (a zero of ψ) and $\psi'(x_0) \neq 0$. For a bound state the zeroes are nodes or the points at infinity (where typically $\psi' \to 0$).

Theorem 4 For the discrete bound-state spectrum of a one-dimensional potential let the allowed energies be $E_1 < E_2 < E_3 < \ldots$ with E_1 the ground state energy. Let the associated energy eigenstates be $\psi_1, \psi_2, \psi_3, \ldots$. The wavefunction ψ_1 has no nodes, ψ_2 has one node, and each consecutive wavefunction has one additional node. In conclusion ψ_n has $n-1$ nodes.

We will not prove this theorem here. In fact you will show in the homework that ψ_{k+1} has at least one node between two consecutive zeroes of ψ_k. This implies that ψ_{k+1} has at least one more node than ψ_k. This can be illustrated in Figure 3 that shows a bound state $\psi_4(x)$ with three nodes at x_1, x_2, and x_3 and zeroes at $x = -\infty$ and $x = \infty$. For ψ_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 $w_4 \in (x_3, \infty)$.

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

$$V(x) \;=\; -V_0 a \sum_{n=-2}^{2} \delta(x - na)\,. \tag{4.3}$$

15
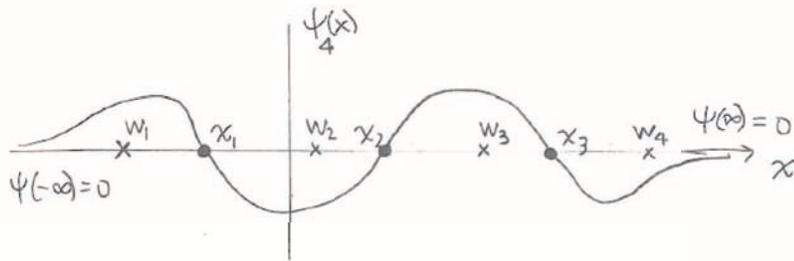
Figure 3: A wavefunction ψ_4 with three nodes (x_1, x_2, x_3) and zeroes at $x\pm\infty$. The next wavefunction ψ_5 must have four nodes, with positions indicated by w_1, w_2, w_3 and w_4.
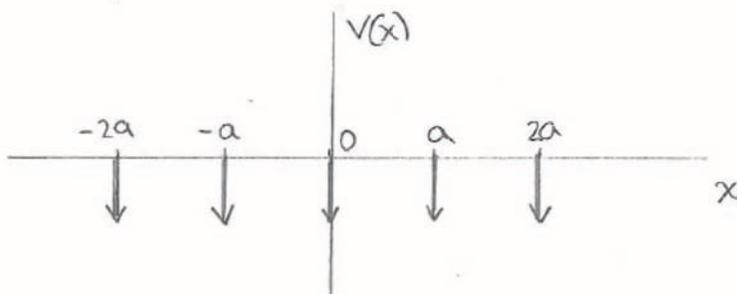
Figure 4: A potential $V(x)$ with five downwards pointing delta-functions.

This potential has delta functions at x equal to $-2a, -a, 0, a$, and $2a$, as shown in Figure 4.

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

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x), \tag{4.4}$$

and integrate this equation from $a - \epsilon$ to $a + \epsilon$, where ϵ 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

$$-\frac{\hbar^2}{2m}\int_{a-\epsilon}^{a+\epsilon} dx \frac{d^2\psi}{dx^2} + \int_{a-\epsilon}^{a+\epsilon} dx V(x)\psi(x) = E\int_{a-\epsilon}^{a+\epsilon} dx\,\psi(x). \tag{4.5}$$

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 ψ is continuous its value at $x = a$ gives the leading contribution:

$$-\frac{\hbar^2}{2m}\frac{d\psi}{dx}\Big|_{a-\epsilon}^{a+\epsilon} - V_0 a \int_{a-\epsilon}^{a+\epsilon} dx\delta(x-a)\psi(x) = E(2\epsilon)\psi(a) + \mathcal{O}(\epsilon^2). \tag{4.6}$$

16

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

$$-\frac{\hbar^2}{2m} \left(\psi'(a^+) - \psi'(a^-) \right) \; - \; V_0 \, a \psi(a) \; = \; 0 \,. \tag{4.7}$$

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

$$\boxed{\Delta \psi'(a) \;\equiv\; \psi'(a^+) - \psi'(a^-) \;=\; \frac{2m}{\hbar^2} \left(-V_0 a \right) \psi(a) \,.} \tag{4.8}$$

The discontinuity of ψ' at the position of the delta function is proportional to the value of ψ 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 ψ vanishes then both ψ and ψ' 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

$$\psi'' \;=\; -\frac{2mE}{\hbar^2} \, \psi \;=\; \kappa^2 \, \psi, \;\; \text{with} \; \kappa^2 \equiv -\frac{2mE}{\hbar^2} > 0 \,, \; \kappa > 0 \,. \tag{4.9}$$

The solutions are therefore the linear combinations

$$\psi(x) \;=\; ae^{-\kappa x} + be^{\kappa x} \,, \tag{4.10}$$

with a and b real constants to be determined (recall the wavefunction can be taken to be real). In Figure 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.
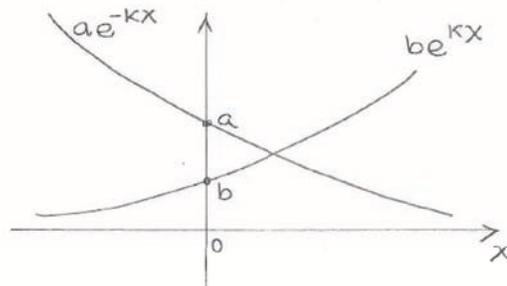
Figure 5: Plots of $ae^{-\kappa x}$ and $be^{\kappa x}$ with $a, b > 0$. This can be used to show that any linear superposition of these two functions can at most have one zero.

Let us then make the following remarks:

1. *There cannot be zeroes of the wavefunction 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 have a zero if $c = 0$. In this case the wavefunction would vanish identically for $x \geq 2a$. This does not look good. Since $\psi(2a) = 0$ then ψ' is not discontinuous and, by continuity, a bit to the left of $2a$ both ψ and ψ' 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 ψ would have to be zero everywhere. This is not acceptable.

2. *There is at most one zero in between each pair of contiguous δ-functions.* This follows because the solution must take the form (4.10) and we argued that such function can at most have one zero.

3. Zeroes appear at $x = 0$ for all the antisymmetric bound states. In those cases, there cannot be another zero in the interval $[-a, a]$. Zeroes may appear at $x = \pm a$, but this is presumably not generic. 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 6.
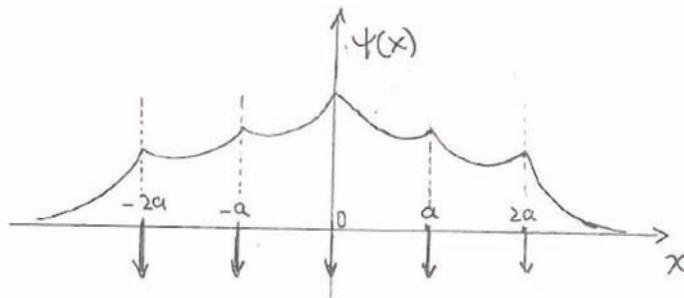
Figure 6: A sketch of the ground state wavefunction.

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

5   Variational Principle

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

$$\hat{H}\psi(\vec{x}) \;=\; E\psi(\vec{x})\,. \tag{5.11}$$

Let us assume that the system is such that it has a collection of energy eigenstates that are normalizable. This collection includes 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 $\psi(\vec{x})$:

$$\int d\vec{x}\, \psi^*(\vec{x})\psi(\vec{x}) \;=\; 1\,. \tag{5.12}$$

By arbitrary we mean a wavefunction that need not satisfy the time-independent Schrödinger equation, a wavefunction that need not be an energy eigenstate. 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 ψ, namely,

$$\boxed{\; E_{gs} \;\leq\; \langle \hat{H}\rangle_\psi \;=\; \int d\vec{x}\, \psi^*(\vec{x})\, \hat{H}\psi(\vec{x})\,, \quad \text{Normalized } \psi \;}\,. \tag{5.13}$$

The wavefunction $\psi(\vec{x})$ here is sometimes called a *trial* wavefunction. 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 was 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 (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

$$E_{gs} = E_1 \leq E_2 \leq E_3 \leq \dots \,. \tag{5.14}$$

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 (2.18)):

$$\psi(\vec{x}) \;=\; \sum_{n=1}^{\infty} b_n\, \psi_n(\vec{x})\,. \tag{5.15}$$

Such a ψ is not an energy eigenstate in general. The normalization condition (5.12) gives us,

$$\sum_{n=1}^{\infty} |b_n|^2 = 1\,. \tag{5.16}$$

The evaluation of the right-hand side in (5.13) was done before in (2.28) so we have

$$\int d\vec{x}\, \psi^*(\vec{x})\, \hat{H}\psi(\vec{x}) \;=\; \sum_{n=1}^{\infty} |b_n|^2 E_n\,. \tag{5.17}$$

19

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:

$$\int d\vec{x}\, \psi^*(\vec{x})\, \hat{H}\psi(\vec{x}) \;\geq\; \sum_{n=1}^{\infty} |b_n|^2 E_1 \;=\; E_1 \sum_{n=1}^{\infty} |b_n|^2 \;=\; E_1 = E_{gs}\,, \tag{5.18}$$

where we used (5.16). This is in fact the claim in (5.13).

Is is sometimes more convenient not to worry about the normalization of the trial wavefunctions. Given a trial wavefunction ψ that is not normalized, the wavefunction

$$\frac{\psi(x)}{\sqrt{N}} \quad \text{with} \quad N = \int d\vec{x}\psi^*(\vec{x})\psi(\vec{x})\,, \tag{5.19}$$

is normalized and can be used in (5.13). We therefore find that

$$\boxed{\; E_{gs} \;\leq\; \frac{\int d\vec{x}\, \psi^*(\vec{x})\, \hat{H}\psi(\vec{x})}{\int d\vec{x}\, \psi^*(\vec{x})\psi(\vec{x})} \;\equiv\; \mathcal{F}[\psi]\,. \;} \tag{5.20}$$

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 gives us a number. Our result states that the ground state energy arises as the minimum value that the functional can take.

One application of this variational principle is 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 $\psi(\vec{x}; \beta_1, \beta_2, \cdots \beta_m)$ that depend on a set of parameters β. 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. (Griffiths). Consider a one-dimensional problem with the delta function potential

$$V(x) \;=\; -\alpha\, \delta(x)\,, \quad \alpha > 0\,. \tag{5.21}$$

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

$$E_{gs} \;=\; -\frac{m\alpha^2}{2\hbar^2}\,. \tag{5.22}$$

So this problem is just for illustration. Consider an unnormalized gaussian trial wavefunction, with a real parameter β:

$$\psi(x) \;=\; e^{-\frac{1}{2}\beta^2 x^2}\,, \quad \int_{-\infty}^{\infty} dx\, \psi^2 \;=\; \frac{\sqrt{\pi}}{\beta}\,. \tag{5.23}$$

The functional $\mathcal{F}$ in (5.20) is then[1]

$$
\begin{aligned}
\frac{\int dx\, \psi^*(x)\, \hat{H}\psi(x)}{\int dx\, \psi^*(x)\psi(x)} &= \frac{\beta}{\sqrt{\pi}} \int dx\, e^{-\frac{1}{2}\beta^2 x^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x) \right) e^{-\frac{1}{2}\beta^2 x^2} \\
&= \frac{\beta}{\sqrt{\pi}} \frac{\hbar^2}{2m} \int dx \left[\frac{d}{dx} e^{-\frac{1}{2}\beta^2 x^2} \right]^2 - \frac{\beta}{\sqrt{\pi}}\alpha \\
&= \frac{\beta}{\sqrt{\pi}} \frac{\hbar^2}{2m} \frac{\beta\sqrt{\pi}}{2} - \frac{\beta}{\sqrt{\pi}}\alpha \\
&= \frac{\beta^2\hbar^2}{4m} - \frac{\beta}{\sqrt{\pi}}\alpha \,.
\end{aligned}
\tag{5.24}
$$

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 β 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

$$
E_{gs} \leq \mathrm{Min}_\beta \left(\frac{\beta^2\hbar^2}{4m} - \frac{\beta}{\sqrt{\pi}}\alpha \right).
\tag{5.25}
$$

The minimum is easily found

$$
\beta = \frac{2m\alpha}{\hbar^2\sqrt{\pi}} \qquad \rightarrow \qquad E_{gs} \leq -\frac{m\alpha^2}{\pi\hbar^2} = \frac{2}{\pi}\left(-\frac{m\alpha^2}{2\hbar^2} \right).
\tag{5.26}
$$

Comparing with (5.22) we see that the bound we found is in fact $\frac{2}{\pi}E_{gs} \simeq 0.64 E_{gs}$. The trial wavefuntion brought us to about 64% of the correct value.

In the exercises you will develop the following results:

1. With trial wavefunctions orthogonal to the ground state, the functional $\mathcal{F}$ gives upper bounds for the energy of the first excited state.

2. For any attractive one-dimensional potential (a nowhere positive potential that approaches zero at infinity) there 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 for ψ equal to the ground state wavefunction. Interestingly, this functional is stationary at each and every energy eigenstate. For eigenstates of energies higher than the ground state $\mathcal{F}$ has a saddle point.

---

[1] We use the integrals $\int du\, e^{-u^2} = \sqrt{\pi}$ and $\int du\, u^2 e^{-u^2} = \frac{1}{2}\sqrt{\pi}$.

6 Position and momentum

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

$$[\hat{x}, \hat{p}] = i\hbar. \tag{6.27}$$

When we deal with wavefuntions $\psi(x)$ the position operator acts on them in a simple way.[2] We define

$$\hat{x}\,\psi(x) \equiv x\psi(x). \tag{6.28}$$

In words the position operator acting on an x-dependent wavefuntion simply multiplies the wavefunction by x. In quantum mechanics it is useful think of states as vectors and operators as matrices. A wavefuntion 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 ϵ such that $N\epsilon = a$. In that case we can represent the information in $\psi(x)$ in a large column vector

$$\psi(x) \quad \longleftrightarrow \quad \begin{pmatrix} \psi(0) \\ \psi(\epsilon) \\ \psi(2\epsilon) \\ \vdots \\ \psi(N\epsilon) \end{pmatrix}. \tag{6.29}$$

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 $N \to \infty$ or $\epsilon \to 0$. Associated with the description (6.29) the operator $\hat{x}$ can be viewed as the $(N + 1) \times (N + 1)$ diagonal matrix

$$\hat{x} \quad \longleftrightarrow \quad \begin{pmatrix} 0 & 0 & 0 & \dots & 0 \\ 0 & \epsilon & 0 & \dots & 0 \\ 0 & 0 & 2\epsilon & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & N\epsilon \end{pmatrix}. \tag{6.30}$$

You can see that the action of the matrix $\hat{x}$ on the vector (6.29) gives the vector

$$\begin{pmatrix} 0 \cdot \psi(0) \\ \epsilon \cdot \psi(\epsilon) \\ 2\epsilon \cdot \psi(2\epsilon) \\ \vdots \\ N\epsilon \cdot \psi(N\epsilon) \end{pmatrix}, \tag{6.31}$$

---

[2]The time dependence is irrelevant to the present discussion, which applies without changes to time-dependent wavefunctions $\Psi(x, t)$.

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

$$\langle \hat{x} \rangle \equiv \int dx' \, \psi^*(x') \, (x'\psi(x')) \, . \tag{6.32}$$

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

$$\psi_{x_0}(x) \equiv \delta(x - x_0) \, , \tag{6.33}$$

we verify that

$$\hat{x}\psi_{x_0}(x) = x \, \psi_{x_0}(x) = x\delta(x - x_0) = x_0\delta(x - x_0) = x_0\psi_{x_0}(x) \, , \tag{6.34}$$

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.

When we speak about the state of a particle and describe it with the wavefunction $\psi(x)$ we are using the "position" representation of the state. The momentum operator in the position representation is given by

$$\hat{p} \equiv \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{6.35}$$

This is to say that acting on a wavefunction we have

$$\hat{p} \, \psi(x) = \frac{\hbar}{i} \frac{d\psi}{dx} \, . \tag{6.36}$$

Note that the commutation relation (6.27) is satisfied by the above definitions, as we can check acting on any wavefuntion:

$$\begin{aligned}
[\hat{x}, \hat{p}]\psi(x) &= (\hat{x}\hat{p} - \hat{p}\hat{x})\psi(x) \\
&= \hat{x}\hat{p} \, \psi(x) - \hat{p}\hat{x} \, \psi(x) \\
&= \hat{x} \, \frac{\hbar}{i} \frac{d\psi}{dx} - \hat{p} \, x\psi(x) \\
&= \frac{\hbar}{i} x \frac{d\psi}{dx} - \frac{\hbar}{i} \frac{d}{dx}(x\psi) \\
&= \frac{\hbar}{i} x \frac{d\psi}{dx} - \frac{\hbar}{i}\psi - \frac{\hbar}{i}x\frac{d\psi}{dx} \\
&= i\hbar \, \psi(x) \, .
\end{aligned} \tag{6.37}$$

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 $[\hat{x}, \hat{p}] = i\hbar$.

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

$$\psi_p(x) \equiv \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}, \tag{6.38}$$

we readily confirm that

$$\hat{p}\psi_p(x) = \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} = p\frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} = p\,\psi_p(x). \tag{6.39}$$

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

$$\tilde{\psi}(p) \equiv \int_{-\infty}^{\infty} dx\,\frac{e^{-ipx/\hbar}}{\sqrt{2\pi\hbar}}\,\psi(x). \tag{6.40}$$

The function $\tilde{\psi}(p)$ encodes the same amount 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

$$\psi(x) = \int_{-\infty}^{\infty} dp\,\frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}\,\tilde{\psi}(p). \tag{6.41}$$

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:

$$\psi(x) \longleftrightarrow \tilde{\psi}(p). \tag{6.42}$$

The arrow above is implemented by Fourier Transformation. Calculate now the action of $\frac{\hbar}{i}\frac{d}{dx}$ on (6.41)

$$\frac{\hbar}{i}\frac{d}{dx}\psi(x) = \frac{\hbar}{i}\frac{d}{dx}\int_{-\infty}^{\infty} dp\,\frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}\,\tilde{\psi}(p) = \int_{-\infty}^{\infty} dp\,\frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}\,p\,\tilde{\psi}(p). \tag{6.43}$$

In the language of (6.42) we write this as

$$\frac{\hbar}{i}\frac{d}{dx}\psi(x) \longleftrightarrow p\,\tilde{\psi}(p). \tag{6.44}$$

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

$$\hat{p}\,\tilde{\psi}(p) = p\,\tilde{\psi}(p). \tag{6.45}$$

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

$$\hat{x} \equiv i\hbar \frac{d}{dp}, \quad \text{(momentum representation)} \tag{6.46}$$

You can do this in two ways. Working with Fourier transforms, or by verifying (as in (6.37)) that it is consistent with $[\hat{x}, \hat{p}] = i\hbar$ acting on momentum space wavefunctions.

8.05 Quantum Physics II

Fall 2013