

Lecture 12

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1 General properties

You will be proving the following facts in your homework:

1. Given the Schrödinger equation with potential $V(x)$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + (V(x) - E)\psi = 0 \quad (1.1)$$

there are no energy eigenstates with $E < \min_x V(x)$. In other words, the situation indicated in Fig.1 cannot occur.

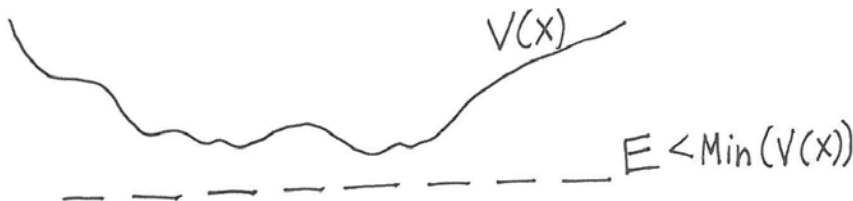


Figure 1: There are no solutions with energy E less than the minimum of the potential $V(x)$.

2. For a one-dimensional potential over $-\infty \leq x \leq \infty$, there are no degenerate bound states. Recall that a bound state is a normalizable energy eigenstate. Given that, $\lim_{x \rightarrow \infty} \psi = 0$.

We now show that the reality of $V(x)$ allows us to work with real wavefunctions $\psi(x)$. Even though there are complex solutions, we can choose real ones without loss of generality.

Theorem 1. The energy eigenstates $\psi(x)$ can be chosen to be real.

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

$$\psi'' + \frac{2m}{\hbar^2} (E - V(x))\psi = 0. \quad (1.2)$$

Since $(\psi'')^* = (\psi^*)''$ and $V(x)$ is real, the complex conjugation of the above equation gives

$$(\psi^*)'' + \frac{2m}{\hbar^2}(E - V(x))\psi^* = 0. \quad (1.3)$$

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 ψ^* and ψ represent two degenerate solutions and, by superposition, we can obtain two *real* degenerate solutions:

$$\psi_r \equiv \frac{1}{2}(\psi + \psi^*), \quad \psi_{im} \equiv \frac{1}{2i}(\psi - \psi^*). \quad (1.4)$$

These are, of course, the real and imaginary parts of ψ . 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 real, up to an overall constant phase.

Proof. Recall that in one dimensional potentials there are no degenerate bound states. This means that the two real solutions ψ_r and ψ_{im} considered above must be equal up to a constant that can only be real:

$$\psi_{im}(x) = c\psi_r(x), \quad \text{with } c \in \mathbb{R} \quad (1.5)$$

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 β , shows that ψ is, up to a constant phase β , 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 2. 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

$$\psi'' + \frac{2m}{\hbar^2}(E - V(x))\psi = 0. \quad (1.6)$$

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

$$\psi''(-x) + \frac{2m}{\hbar^2}(E - V(x))\psi(-x) = 0, \quad (1.7)$$

where we used that 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 a function $\varphi(x)$ and take two derivatives of it

$$\varphi(x) \equiv \psi(-x) \quad \rightarrow \quad \frac{d}{dx}\varphi(x) = \psi'(-x) \cdot (-1), \quad \frac{d^2}{dx^2}\varphi(x) = \psi''(-x). \quad (1.8)$$

Using the last equation (1.7) becomes

$$\frac{d^2}{dx^2}\varphi(x) + \frac{2m}{\hbar^2}(E - V(x))\varphi(x) = 0. \quad (1.9)$$

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

$$\psi_s(x) \equiv \frac{1}{2}(\psi(x) + \psi(-x)), \quad \psi_a(x) \equiv \frac{1}{2}(\psi(x) - \psi(-x)). \quad (1.10)$$

These are the solutions claimed to exist. □

Note that the above proof would not work for the case of odd potentials $V(-x) = -V(x)$. We can't say much in this case!

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

Corollary 2. Any bound state of a one-dimensional even potential is either even or odd.

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

$$\psi(-x) = c\psi(x), \quad \text{with } c \in \mathbb{R}. \quad (1.11)$$

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 $x \rightarrow -x$. □

We used the result of this theorem to find the bound states of the finite square well. Since that potential is even, we could restrict our work to search for even bound states and odd bound states. The potential cannot have bound states that are neither even nor odd!

2 Bound states in slowly varying potentials

We will now consider some insights that classical physics gives us about the behavior of energy eigenstates. This is sometimes called the **semi-classical approximation** because classical physics can sometime give an approximate description of the quantum physics.

We begin with an example we already understand. We consider the total energy E of a particle that is the sum of a potential energy V and a kinetic energy K . When V is a function of position, K must also be a function of position in order for the sum E to be conserved, as it must be. In our first example, shown in Figure 2, the potential V is constant and the energy E is greater than V . A particle in such a potential will have a constant potential energy K and thus a constant momentum $p = \sqrt{2mK}$. It is a fact that the wave representing the quantum particle has a de Broglie wavelength λ equal to Planck's constant h divided by the classical momentum.

Indeed from the Schrödinger equation

$$\psi'' = -\frac{2m}{\hbar^2}(E - V)\psi = -\frac{2mK}{\hbar^2}\psi = -\frac{p^2}{\hbar^2}\psi, \quad (2.1)$$

leading to real solutions of the form

$$\psi \sim \cos\left(\frac{p}{\hbar}x\right) = \cos\left[\frac{2\pi}{(h/p)}x\right], \quad (2.2)$$

where we see that the wavelength of ψ is the de Broglie wavelength of a particle with momentum p . This wavefunction is real and thus is not a momentum eigenstate. It represents a superposition of a

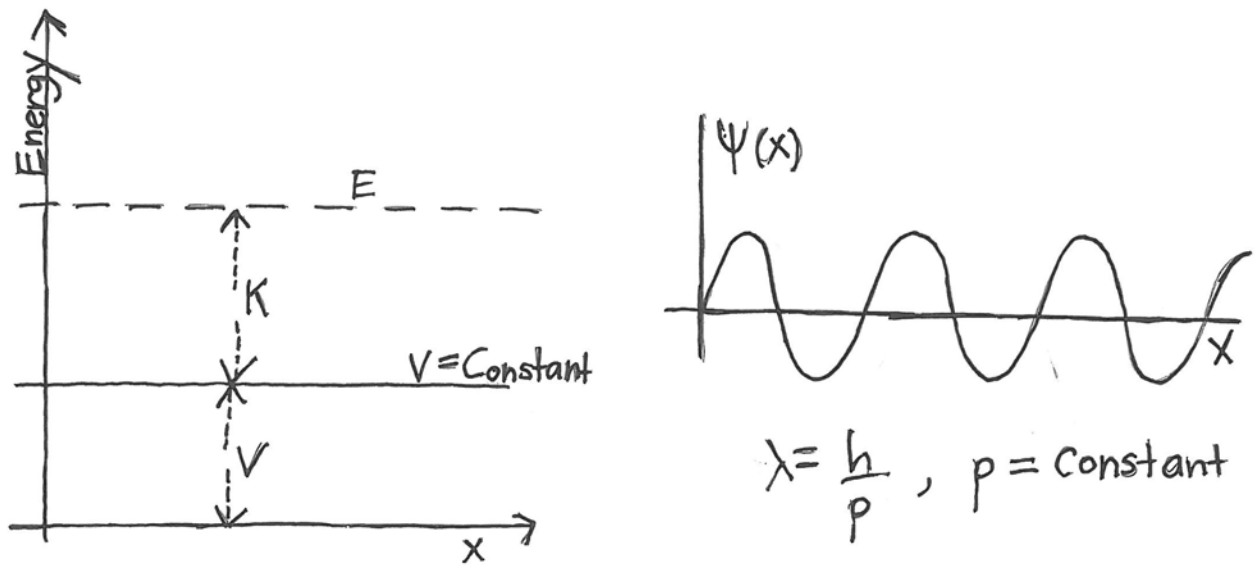


Figure 2: On the left is an example of a constant potential, $V = V_0 < E$ where K is kinetic energy, and $E = K + V_0$ is the total energy. On the right is a sketch of the wavefunction for a particle in this potential. Constant $V \implies$ constant K , thus momentum is also constant.

state with momentum p and a state of momentum $-p$. Even in the classical case, the kinetic energy K only determines p^2 and not the sign of p . Our interest here is in real wavefunctions $\psi(x)$ as appropriate for *energy eigenstates* and what we have seen is that, for a constant potential, the wavelength of $\psi(x)$ is the de Broglie wavelength associated to the classical momentum.

Consider now the situation depicted in figure 3, where we imagine a classical particle moving in a linearly increasing potential $V(x)$. This time the kinetic energy $K(x)$ is also position dependent. As a result, the momentum of the classical particle $p(x) = \sqrt{2mK(x)}$ is also position dependent. The insight now is that, if the potential is slowly varying, to a good approximation the wavefunction will have a position-dependent de Broglie wavelength $\lambda(x)$ given by

$$\lambda(x) = \frac{h}{p(x)}. \tag{2.3}$$

By this we mean that ψ is some combination of functions

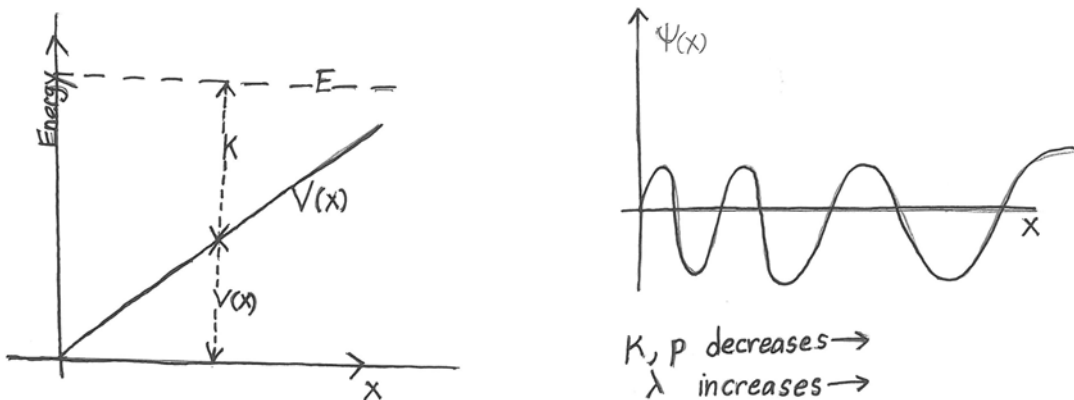


Figure 3: A linearly varying potential, $V(x) = \alpha x$. The energy $E = K + V(x)$ is fixed, and as x increases $K(x)$ decreases, $p(x)$ decreases, and $\lambda(x)$ increases, resulting in a wavefunction of increasing wavelength.

$$\cos\left(\frac{2\pi x}{\lambda(x)}\right), \sin\left(\frac{2\pi x}{\lambda(x)}\right). \tag{2.4}$$

As we see in Figure 3, because of the linearly growing $V(x)$ a particle with total energy E will have decreasing kinetic energy $K(x)$ as x increases. Thus the classical momentum will decrease, and we anticipate that the wavefunction will have an increasing local de Broglie wavelength $\lambda(x)$ as x increases. This is illustrated to the right of the figure. We will discuss below what we expect to happen to the amplitude of the wavefunction.

The semiclassical approximation – setting the $\psi(x)$ wavelength equal to the de Broglie wavelength of the classical particle – is accurate when the potential changes slowly. By slowly we mean that the change in the potential over a distance comparable to the local de-Broglie wavelength is very small compared to the potential:

$$\lambda(x) \left| \frac{dV}{dx} \right| \ll |V(x)|. \quad (2.5)$$

The left side of the inequality is an estimate for the change in V over a distance $\lambda(x)$, and therefore this quantity must be very small compared to the potential for the semiclassical approximation to be valid. This inequality above is the key condition for the semiclassical approximation. It is in fact the condition that allows one to set up the WKB analysis of the Schrödinger equation (8.06!).

In figure 4 we show an arbitrary potential $V(x)$ and consider the classical motion of a particle of total energy E . For any point x_0 , we have $V(x_0) + K(x_0) = E$. The maximum kinetic energy occurs for the minimum value of the potential. Classically a particle cannot have negative kinetic energy, thus the particle cannot be found at points where $V(x)$ is greater than the energy E . In the figure, this happens for $x > x_R$ and for $x < x_L$, and these regions are called classically forbidden regions. A particle of energy E will oscillate from x_L to x_R and back. As it moves its velocity changes, it is a function $v(x)$ of position. The points x_L and x_R are called **turning points**, because at these points the particle motion reverses direction.

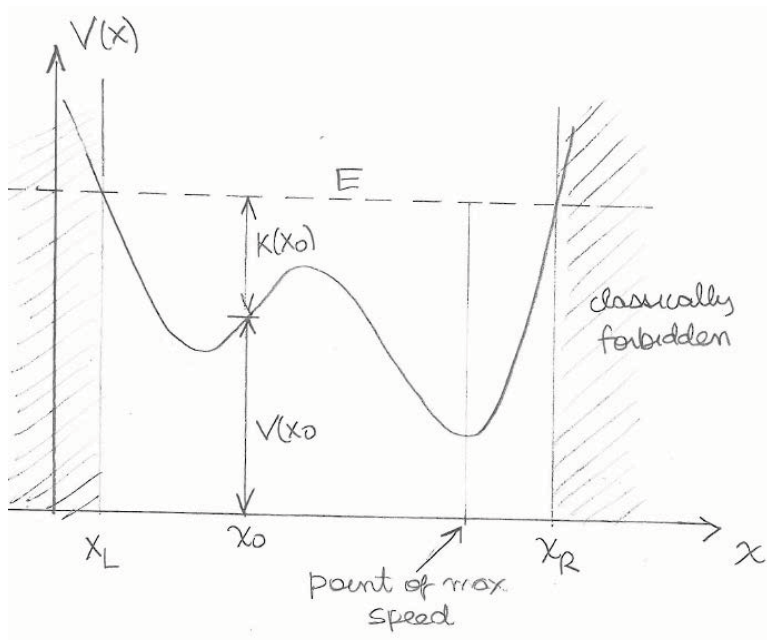


Figure 4: An arbitrary potential showing turning points x_L and x_R . The region to the right of x_R and the region to the left of x_L are classically forbidden regions. At any point $x \in [x_L, x_R]$ the sum of the potential energy $V(x)$ and the kinetic energy $K(x)$ is equal to the total energy E .

The oscillating classical particle spends more time in the regions where its velocity is small and less time in the regions where its velocity is large. This has quantum mechanical implications. Indeed, in the semiclassical approximation we find that the wavefunction amplitude is bigger at the places the particle spends more time and smaller at places it spends less time. This can be quantified. Consider the probability $|\psi(x)|^2 dx$ to find the particle within the infinitesimal region dx around x . This is set this proportional to the fraction of time the particle spends at dx :

$$|\psi(x)|^2 dx \simeq \frac{dt}{T} . \tag{2.6}$$

where dt the time require to traverse dx and T is the half-period of oscillation, the time to go from the left turning point to the right turning point. With $v(x)$ the local velocity of the particle, we have

$$|\psi(x)|^2 dx \simeq \frac{dx}{v(x)T} = \frac{m}{T} \frac{1}{p(x)} dx \rightarrow |\psi(x)|^2 \sim \frac{1}{p(x)} . \tag{2.7}$$

This relation has to be interpreted with some care. Recall that $\psi(x)$ has very small wavelength for large $p(x)$. So $|\psi(x)|^2$ oscillates between zero and some peak value over very short distances along x . On the other hand, the momentum $p(x)$ appearing on the right has no such oscillations. Therefore, by $|\psi(x)|^2$ in the above relation we really mean the average of $|\psi(x)|^2$ over a few oscillations near x , in other words the square of the **amplitude** of the wave $\psi(x)$. Writing the amplitude (a positive real number, of course) as $\text{Amp}(\psi(x))$, we have

$$\text{Amp}(\psi(x)) \sim \frac{1}{\sqrt{p(x)}} \sim \sqrt{\lambda(x)} . \tag{2.8}$$

The amplitude of the wave is proportional to the square root of the de Broglie wavelength. Thus in figure 5, the momentum of the particle decreases and $\lambda(x)$ increases as x increases. So we expect the amplitude of the wave to increase, as sketched to the right.

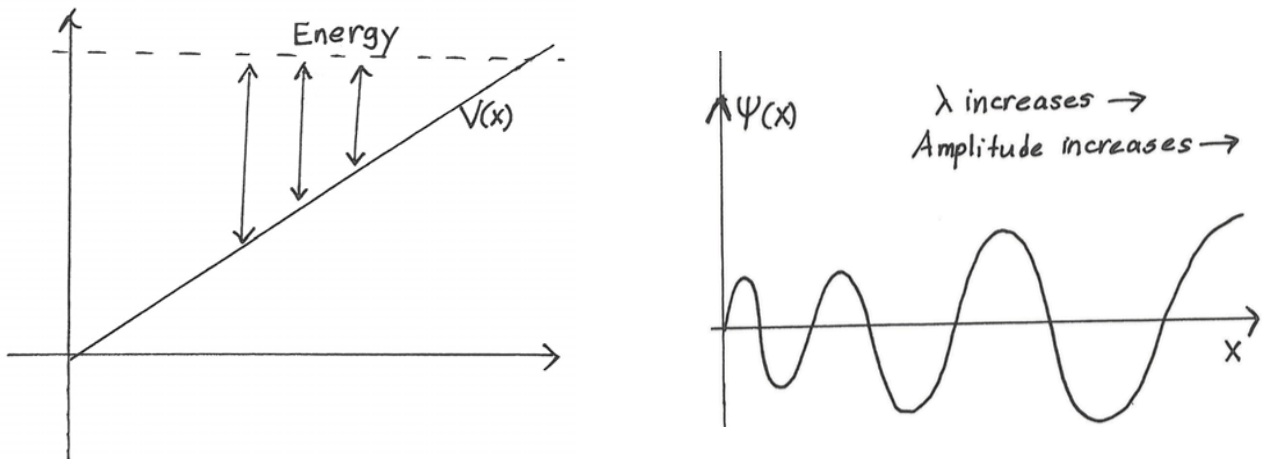


Figure 5: A potential $V(x)$ and a kinetic energy that decreases for increasing x . Then the de Broglie wavelength increases with x . Equation 2.8 then implies that the amplitude of $\psi(x)$ also increases with x .

As a simple illustration of the importance of averaging $|\psi|^2$ consider a state of large energy in the infinite well potential, as shown in Fig. 6. Within the box, the classical particle “bounces” between the walls with constant velocity. As a result the particle spends the same amount of time in every equal

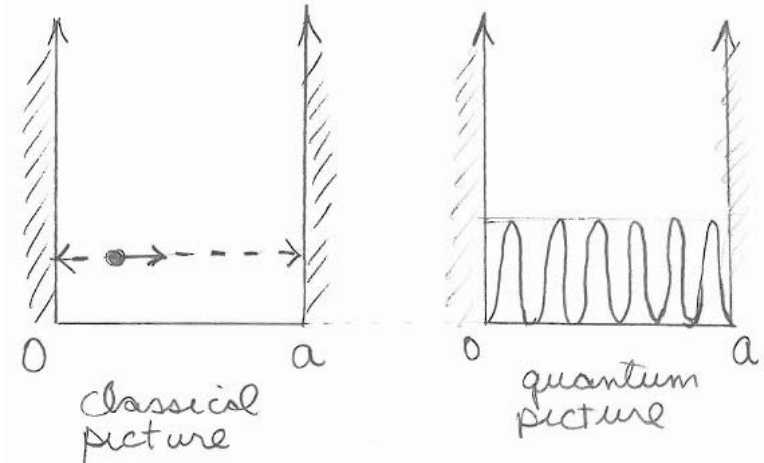


Figure 6: Particle in a one dimensional box. The particle bounces with constant velocity.

size interval dx within the box. The classical probability distribution \mathbb{P}_{cl} within the box is uniform:

$$\mathbb{P}_{\text{cl}}(x)dx = \frac{1}{a} dx \quad \rightarrow \quad \mathbb{P}_{\text{cl}}(x) = \frac{1}{a}, \quad (2.9)$$

since the integral over the box $x \in [0, a]$ of $\mathbb{P}_{\text{cl}}(x)dx$ gives one. Now consider an energy eigenstate $\psi_n(x)$ with large n

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad \rightarrow \quad |\psi_n(x)|^2 = \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right). \quad (2.10)$$

The associated quantum-mechanical probability density \mathbb{P}_{qm} is

$$\mathbb{P}_{\text{qm}}(x) = |\psi_n(x)|^2 = \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right), \quad (2.11)$$

and it is, for large n a rapidly oscillating function, seemingly quite different from the classical probability $\mathbb{P}_{\text{cl}} = 1/a$. While the classical probability never vanishes, the quantum probability has many zeroes! Still, over arbitrary distances larger than the a/n (presumed small since n is very large) the average of the quantum probability density approaches the classical probability density. Recall that the average of \sin^2 over any integer number of oscillations is $1/2$, so that its average over *any* interval that includes a large number of oscillations (not necessarily integer) is approximately equal to $1/2$. We then have

$$\text{Average}_x(\mathbb{P}_{\text{qm}}(x)) \simeq \frac{2}{a} \cdot \frac{1}{2} = \frac{1}{a} = \mathbb{P}_{\text{cl}}(x). \quad (2.12)$$

The semiclassical approximation is an explicit realization of what is loosely called the “Correspondence principle”, the idea that there are limits of quantum states in which their properties can be understood by a classical analysis of the system.

3 Sketching wavefunction behavior in different regions

Let's examine the behavior of an energy eigenstate for the case of a general potential $V(x)$. We rewrite the time-independent Schrödinger equation by dividing by ψ to get:

$$\frac{\psi''(x)}{\psi(x)} = -\frac{2m}{\hbar^2}(E - V(x)), \quad (3.1)$$

which is convenient because there is no wavefunction on the right-hand side. We will consider the equation in two regions and at some special points.

- $E - V(x) < 0$, classically forbidden region because the total energy is smaller than the potential. In this case the right hand side of eqn. (3.1) is positive. This means there are two possibilities: both ψ and ψ'' are positive or both ψ and ψ'' are negative. These possibilities are shown here

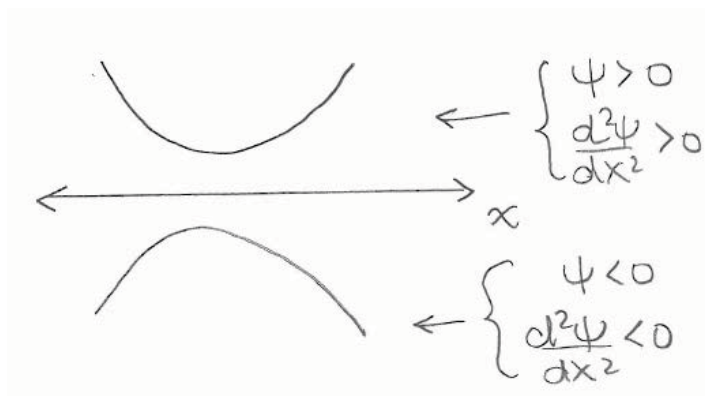


Figure 7: In the classically forbidden region either $\psi > 0, \psi'' > 0$ or $\psi < 0, \psi'' < 0$. In both cases the wavefunction is *convex towards* the x -axis.

Such possible behaviors are summarized by saying that **the wavefunction is convex towards the axis**. When classically forbidden regions reach to $x = -\infty$ or $x = \infty$ the behavior is of the type shown below:



Figure 8: Wavefunctions approaching $x = -\infty$ or $x = \infty$ within classically forbidden regions.

- $E - V > 0$, classically allowed region: the right hand side of eqn. 3.1 is negative. Thus either $\psi > 0, \psi'' < 0$ or one has $\psi < 0, \psi'' > 0$. Both options are shown below and are summarized by saying that **the wavefunction is concave towards the axis**:

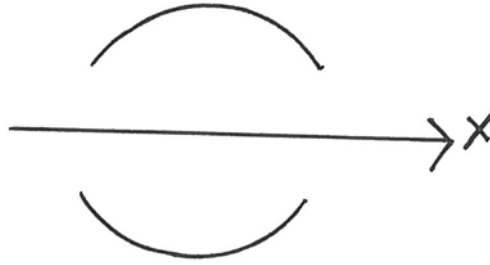


Figure 9: $\psi > 0, \psi'' < 0$ or $\psi < 0, \psi'' > 0$. The wavefunction is *concave towards* the x-axis.

A classically allowed region that is large would have the the top and bottom parts of the figure above alternating to form a function resembling a sin or cos.

- $V(x_0) = E$. Turning point: defined as a point x_0 at which the potential energy $V(x_0)$ is equal to the total energy E . Turning points separate classically allowed and classically forbidden regions. A turning point is an **inflection point** in the graph of $\psi(x)$, a point where the second derivative vanishes, since

$$\psi''|_{x_0} = -\frac{2m}{\hbar^2} \cdot 0 \cdot \psi(x_0) = 0, \quad (3.2)$$

Not all inflection points are turning points. In fact nodes of the wavefunction are inflection points. This is clear from $\psi'' = -\frac{2m}{\hbar^2}(E - V(x))\psi$, since vanishing ψ implies vanishing ψ'' .

Note, however, that having vanishing ψ and ψ' at any point in the domain of the wavefunction is not allowed. This is because the Schrödinger equation is a second order linear differential equation. One can quickly show that $\psi = \psi' = 0$ at some point x_0 implies that all higher derivatives of ψ vanish at that point. Assuming the wavefunction has a Taylor expansion we conclude that the wavefunction must vanish identically.

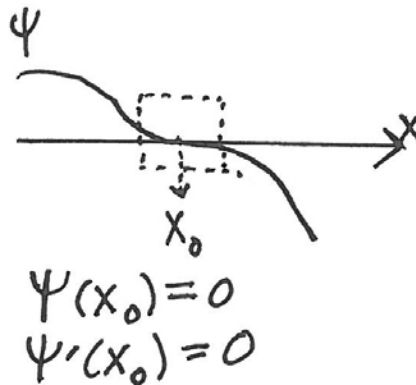


Figure 10: It is impossible to have both ψ and ψ' at any point x_0 : the Schrödinger equation would then force $\psi(x)$ to vanish identically.

We conclude this section by illustrating the quantization of the energy levels for bound states of an even potential. As shown in Figure 11, at the top, we have an even potential and we have marked four energies $E_1 < E_2 < E_3 < E_4$. Not all correspond to energy eigenstates. We imagine integrating the Schrödinger equation from $x = \infty$ down to $x = 0$. As shown in the small figure slightly to the right and below the potential, we assume $\psi > 0$ as $x \rightarrow \infty$. Since any bound state is automatically even or odd, the picture at $x \rightarrow -\infty$ must either be the one with $\psi > 0$ (the even extension) or the one

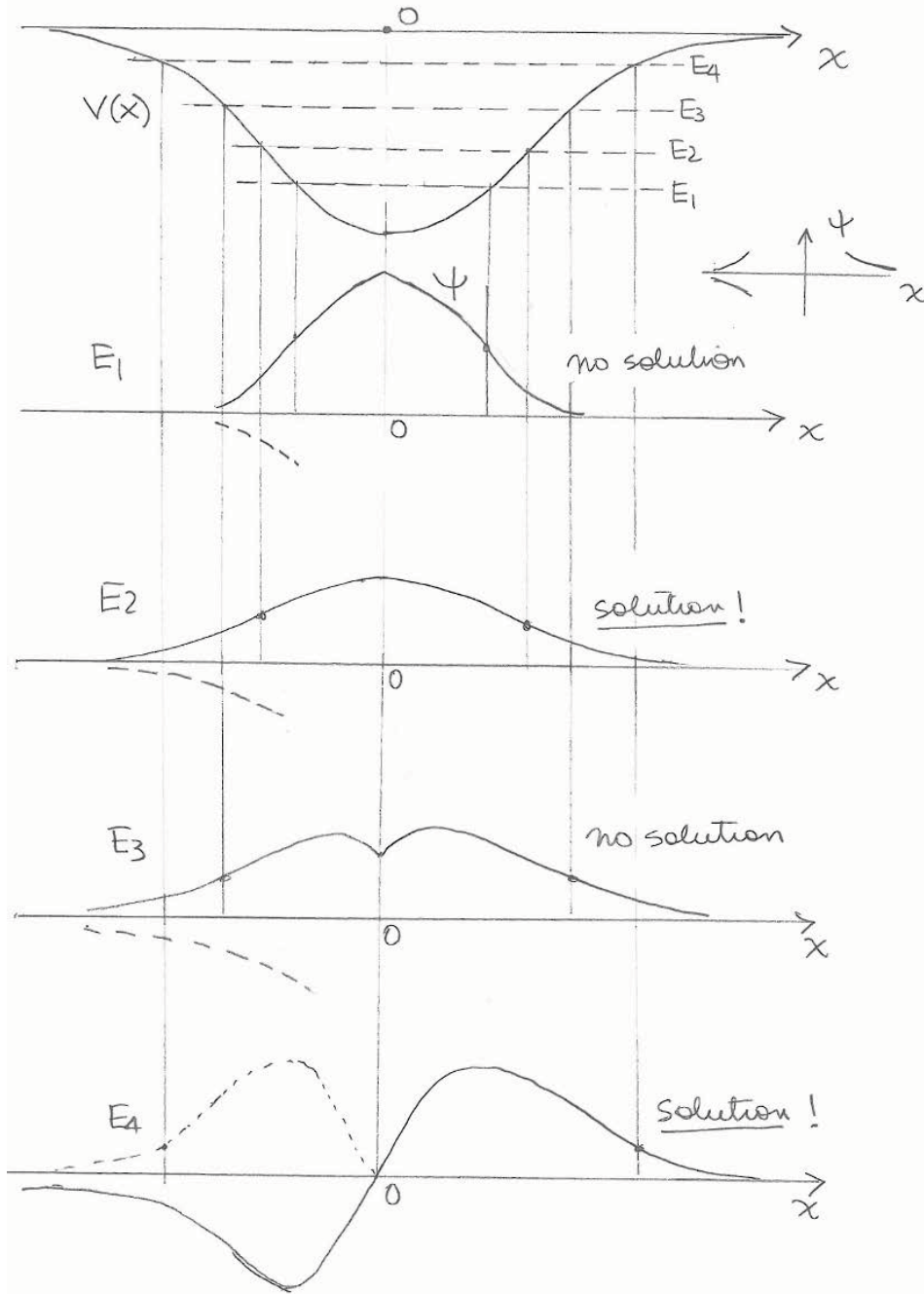


Figure 11: An even potential (top figure) and the result of integrating the equation from $x = \infty$ towards zero for various values of the energy. We get a solution when $\psi(x)$ for $x \geq 0$ can be matched with continuous ψ and ψ' to an even or odd extension valid for $x < 0$. There is no solution for E_1 and E_3 . The ground state arises for E_2 and the first excited state arises for E_4 .

with $\psi < 0$ (the odd extension). To have a solution, the picture from the right must match properly at $x = 0$ with one of the two possible extensions at $x < 0$.

Consider, for example, the integration of the equation for $E = E_1$. Coming in from $x = \infty$ the solution has an inflection point and becomes concave towards the axis. Beyond this point the first derivative ψ' decreases. Still, as shown in the picture ψ' does not vanish at $x = 0$, so that the even extension for $x < 0$ does not match properly with the $x > 0$ solution at $x = 0$, because ψ' fails to be continuous. Matching with the odd extension is not a possibility because then ψ would fail to be continuous at $x = 0$. Thus E_1 is not an allowed energy.

As we increase the energy to $E = E_2$, the turning point occurs for larger x and ψ' manages to get exactly to zero at $x = 0$, matching ψ and ψ' from the even extension. This time we have a solution. Of course this occurs for $E = E_2$ precisely; a bit more energy or a bit less energy and the derivative is not continuous at $x = 0$.

As we increase the energy to E_3 the turning point moves to even larger x and ψ' is negative by the time we get to $x = 0$, while ψ is still positive. The solution can't be matched with the even extension because of the discontinuous derivative.

If we now increase the energy further to some value E_4 , by the time we reach $x = 0$ the derivative ψ' will be negative and ψ will be exactly zero. As you can see in the figure, we can get a good match to the odd extension for $x < 0$. This is the first excited state. It is an odd wavefunction with a single node at $x = 0$.

4 Shooting Method

The **shooting method** is a numerical method to find the form of bound-state solution to the the Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi = 0. \quad (4.1)$$

The method is easily implemented for even potentials $V(x)$ in which case we can search for even and for odd bound states.

Consider first even bound states. We will attempt to integrate the differential equation from $x = 0$ to $x = \infty$. To start at $x = 0$ we need to fix ψ and ψ' at this point. Since the normalization of the bound state is not determined by the equation, we can choose

$$\psi(x = 0) = 1. \quad (4.2)$$

The derivative must also be zero at this point: if the derivative is not zero the even wavefunction will have a discontinuous derivative at $x = 0$ (can you see that?). Therefore we must set

$$\psi'(x = 0) = 0. \quad (4.3)$$

To integrate the differential equation we now need to choose some energy. Pick some arbitrary value E_0 . We know already that arbitrary values of the energy do not yield bound states. So what goes wrong if we now integrate the differential equation. What happens typically is that you get a solution that could not be normalized. As you work with your computer you notice that beyond certain point along x the solution diverges, perhaps by having $\psi \rightarrow \infty$, that is ψ going up.

You must then change the value of the energy until you find some value E_1 for which the solution also diverges, but this time with $\psi \rightarrow -\infty$, or ψ going down. This is a signal that there is some energy in the interval between E_0 and E_1 for which a normalizable solution exists. You then try to narrow the interval. If $E_0 < E_1$ you can do that by finding values larger than E_0 for which the divergence is still up and values lower than E_1 for which the divergence is still down. As you narrow the interval

you will still find these divergences, but they occur for larger and larger values of x . As you do so, you are getting a better and better approximation to the bound-state energy (see Fig.12).

For odd solutions, the procedure is the same, but the boundary conditions at $x = 0$ are:

$$\begin{aligned}\psi(x = 0) &= 0, \\ \psi'(x = 0) &= 1.\end{aligned}\tag{4.4}$$

The first is needed for a continuous odd function. The second is arbitrary, up to normalization.

If a potential is not even but has a hard wall, this provides a good starting point for integration of the Schrödinger equation. At this point the wavefunction is set to zero and the derivative set to one. If the potential has two hard walls, we can integrate starting from one wall and then demand that the solution reach exactly zero by the time we get to the second wall.

A practical note: When working with computers to carry out these numerical integrations, it is first necessary to “clean out” the units from the differential equation. The first step in this process is to replace x for a unit free variable u . The relation between them is of the form $x = bu$ where b is a quantity with units of length built from the parameters in the problem.



Figure 12: Numerical integration of the Schrödinger equation leads to solutions that diverge up ($\psi \rightarrow \infty$) or down ($\psi \rightarrow -\infty$) beyond some value of x . Bound states are found for values of energies at which the divergence changes from up to down, or from down to up.

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