

5. The Schrödinger equation

The previous the chapters were all about “kinematics” — how classical and relativistic particles, as well as waves, move in free space.

Now we add the influence of forces and enter the realm of “dynamics”.

Before we take the giant leap into wonders of Quantum Mechanics, we shall start with a brief review of classical dynamics.

Classical 1D motion under the influence of a potential

In 1 dimension (2, if you count time), the equation of motion of a mass with kinetic energy K , under the influence of a time-independent potential, $V(x)$, is, in classical physics, given by the energy balance equation:

$$E = K + V(x) \quad (5.1)$$

$$= \frac{1}{2}m\dot{x}^2 + V(x) \quad (5.2)$$

where E , the sum of the energy associated with the motion of the particle, and its potential energy at its location, is a “constant of the motion”.

Thus, when the particle is in motion, the energy is being transferred between K and V .

To see how the equation of motion is developed, $\frac{d}{dt}$ of (5.2):

$$0 = \frac{1}{2} \times 2m\ddot{x}\dot{x} + \frac{dV}{dx}\dot{x} = \left(m\ddot{x} + \frac{dV}{dx} \right) \dot{x} . \quad (5.3)$$

The zero results since E is a constant, and the V term arises since it is implicitly dependent on t , through the particle position, x .

5.1 Classical 1D motion under the influence of a potential

There are two solutions:

$$\dot{x} = 0 . \quad (5.4)$$

This is “statics”. This is for Civil Engineers. (Buildings are not supposed to move.)

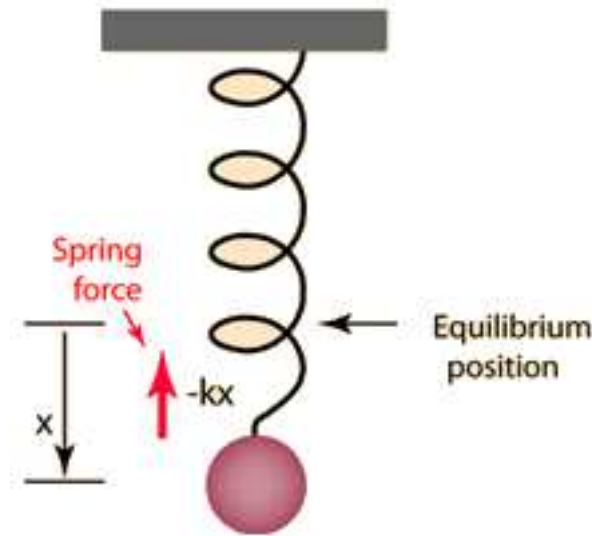
The other is dynamics:

$$m\ddot{x} + \frac{dV}{dx} = 0 , \quad (5.5)$$

which when you replace dV/dx by $-F(x)$, is recognized as Newton’s 2nd Law of Motion.

This is a 2nd-order, ordinary differential equation (ODE), that yields complete knowledge of $v(t) = \dot{x}(t)$ and $x(t)$ given knowledge of any two positions, or any two velocities, or any combination of two, at any time.

5.1.1 The harmonic oscillator ...



For this case, the ideal harmonic oscillator, which is conveniently represented by a spring¹, the potential and force are:

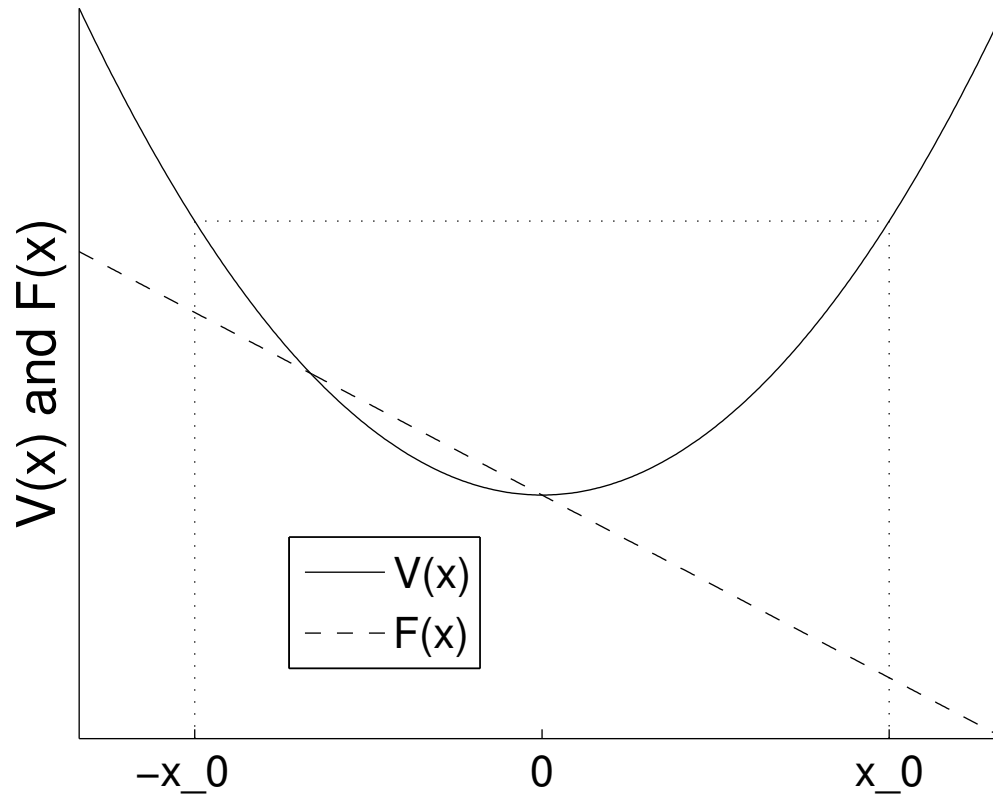
$$V(x) = \frac{1}{2}kx^2, \quad (5.6)$$

$$F(x) = \frac{dV}{dx} = -kx, \quad (5.7)$$

where k is the “spring constant”. The larger the k , the stronger the spring.

¹OK, it is a very idealized spring. The spring is massless, there are no dissipative forces in the spring, it's attached to something infinitely heavy just floating there, the whole assembly is in vacuum, it all happens in one dimension, and there's no gravity! Other than that, it's pretty realistic!

... The harmonic oscillator ...



$V(x)$ and $F(x)$ are plotted above. m moves along x between the “turning points”, $\pm x_0$. Note that the force always pulls the mass back toward the origin.

... The harmonic oscillator ...

Let's obtain the equations of motion:

From (5.5)

$$\begin{aligned} 0 &= m\ddot{x} + \frac{dV}{dx} \\ &= m\ddot{x} + kx \quad (\text{substituted for } V(x)) \\ &= \ddot{x} + \omega^2 x, \end{aligned} \tag{5.8}$$

where $\omega \equiv \sqrt{\frac{k}{m}}$, which has the dimension of frequency (T^{-1}).

(5.8) has the general solution:

$$x(t) = A \sin \omega t + B \cos \omega t, \tag{5.9}$$

where A and B are constants that are fixed by the initial conditions.

... The harmonic oscillator ...

There are many ways to do this, but let's choose that following:

At $t = 0$, set $x = 0$. That forces us to set $B = 0$.

Now we can write:

$$x(t) = x_0 \sin \omega t , \quad (5.10)$$

$$\dot{x}(t) = x_0 \omega \cos \omega t \quad \text{or,} \quad (5.11)$$

$$v(t) = v_0 \cos \omega t , \quad (5.12)$$

and the equations of motion are known.

x_0 is the “classical turning point”. We know that $|x(t)| \leq x_0$. where the mass stretches the spring to its limit, and it comes temporarily, to rest, that is, at $\omega t = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2} \dots, x(t) = \pm x_0$.

v_0 is the “maximum speed”. We know that $|v(t)| \leq v_0$, where the mass passes through the origin, and reaches its maximum speed, that is, at $\omega t = 0, \pi, 2\pi \dots, v(t) = \pm v_0$.

... The harmonic oscillator ...

This allows us to write the energy balance equation as:

$$\begin{aligned} E &= K + V(x) \\ &= \frac{1}{2}m[v(t)]^2 + \frac{1}{2}k[x(t)]^2 \\ &= \frac{1}{2}mv_0^2 \cos^2 \omega t + \frac{1}{2}kx_0^2 \sin^2 \omega t , \end{aligned} \tag{5.13}$$

$$= \frac{1}{2}mv_0^2 = \frac{1}{2}kx_0^2 . \tag{5.14}$$

Since $\langle \sin^2() \rangle = \langle \cos^2() \rangle = \frac{1}{2}$ we can also write:

$$\langle K \rangle = \langle V \rangle = \frac{E}{2} . \tag{5.15}$$

This means that the spring is a machine that equipartitions the kinetic energy and the potential energy, when averaged over time. We shall see this in Quantum Mechanics soon!

Forecasting Quantum Mechanics with the oscillator ...

Although, this is a completely classical system, let's see what happens when we ask it questions that resemble the kinds of questions we would ask of "matter waves".

What are $\langle x \rangle, \langle x^2 \rangle, \langle p \rangle = \langle mv \rangle, \langle p^2 \rangle$?

Since the average position is zero, and the system is, on average, stationary we know:

$$\langle x \rangle = \langle p \rangle = 0 . \quad (5.16)$$

And, since

$$\frac{E}{2} = \langle K \rangle = \frac{1}{2}m\langle v^2 \rangle ,$$

and

$$\frac{E}{2} = \langle V \rangle = \frac{1}{2}k\langle x^2 \rangle ,$$

$$\langle p^2 \rangle = mE \quad ; \quad \langle x^2 \rangle = \frac{E}{k} . \quad (5.17)$$

Therefore,

$$\Delta p \Delta x = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{mE} \sqrt{\frac{E}{k}} = \frac{E}{\sqrt{k/m}} = \frac{E}{\omega} \quad (5.18)$$

... Forecasting Quantum Mechanics with the oscillator

Later on, in Quantum Mechanics, we will find that the ground state (lowest energy solution) has energy $E = \frac{\hbar}{2}$, for which

$$\Delta p \Delta x = \frac{\hbar}{2}, \quad (5.19)$$

that has the lowest value allowed by Quantum Mechanics.

And, if I told you that the ground state wave function is a Gaussian, would you be surprised?

5.1. Justifying the Schrödinger Equation ...

Recall our representation of a “matter wave” from the previous chapter²:

$$A(x, t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} dk A(k) e^{i[kx - \omega(k)t]} . \quad (5.20)$$

Recall as well, that our x -space operator for the wavenumber was found to be:

$$\tilde{k} = -i \frac{\partial}{\partial z} . \quad (5.21)$$

(We'll use the $\sim$ symbol to denote that the object is an operator in either the x -space or the k -space, rather than a function. It should be clear, from the form of the operator, what space it is operating on.)

Since, for waves, $p = \hbar k$, it is reasonable to assume that the momentum operator is given by:

$$\tilde{p} = -i\hbar \frac{\partial}{\partial x} , \quad (5.22)$$

since

$$\tilde{p}A(x, t) = -i\hbar \frac{\partial}{\partial x} A(x, t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} dk (\hbar k) A(k) e^{i[kx - \omega(k)t]} . \quad (5.23)$$

²In this chapter the 1D space variable will be x , rather than z . At some point I will make them uniform.

... Justifying the Schrödinger Equation ...

Following the same logic:

$$\tilde{K} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} , \quad (5.24)$$

since

$$\tilde{K} A(x, t) = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} A(x, t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} dk \left(\frac{\hbar^2 k^2}{2m} \right) A(k) e^{i[kx - \omega(k)t]} , \quad (5.25)$$

for the kinetic energy, and

$$\tilde{E} = i\hbar \frac{\partial}{\partial t} , \quad (5.26)$$

since

$$\tilde{E} A(x, t) = i\hbar \frac{\partial}{\partial t} A(x, t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} dk [\hbar\omega(k)] A(k) e^{i[kx - \omega(k)t]} , \quad (5.27)$$

for the total energy.

... Justifying the Schrödinger Equation ...

In analogy with Classical Physics, where:

$$K + V = E , \quad (5.28)$$

Schrödinger hypothesized that the non-relativistic wave equation should be:

$$\tilde{K}\psi(x, t) + V(x, t)\psi(x, t) = \tilde{E}\psi(x, t) , \quad (5.29)$$

or

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t)\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} . \quad (5.30)$$

Voila! One Nobel Prize!

(5.30) is **the** equation that describes the motion of non-relativistic particles under the influence of external forces.

The “trajectory” in Classical Mechanics, *viz.* $x(t)$ and $v(t)$ are replaced by the wave amplitude, $\psi(x, t)$, and the attributes we associate with $\psi(x, t)$.

Take the Schrödinger equation, that is intrinsically complex, with complex 2-part solutions,

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

and its expectation value that yields the conservation of energy equation.

$$\langle \psi | \tilde{K} | \psi \rangle + \langle \psi | V | \psi \rangle = \langle \psi | \tilde{E} | \psi \rangle$$

The potential in the above equation is real, for now.

Henceforth functional dependencies will be repressed.

Now, split $\psi()$ into real and imaginary parts, viz. $\psi() = \psi_R() + i\psi_I()$ and see what results for these equations.

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

Now taking the expectation values of the above gives

$$\langle \psi | \tilde{K} | \psi \rangle + \langle \psi | V | \psi \rangle = \langle \psi | \tilde{E} | \psi \rangle$$

Substituting this into the above gives two coupled differential equations, and shows the connection between the real and complex parts of ψ and a “new looking” energy conservation equation.

For the differential equations:

$$\begin{aligned} \frac{-\hbar^2}{2m} \frac{\partial^2 \psi_R}{\partial x^2} + V\psi_R &= -\hbar \frac{\partial \psi_I}{\partial t} , \\ \frac{-\hbar^2}{2m} \frac{\partial^2 \psi_I}{\partial x^2} &= \hbar \frac{\partial \psi_R}{\partial t} \end{aligned}$$

Note that both equations contain ψ_R and ψ_I .

For the Conservation of Energy equation:

$$\langle \psi_R | \tilde{K} | \psi_R \rangle + \langle \psi_I | \tilde{K} | \psi_I \rangle + i[\langle \psi_R | \tilde{K} | \psi_I \rangle - \langle \psi_I | \tilde{K} | \psi_R \rangle]$$

Kinetic energy

+

$$\langle \psi_R | V | \psi_R \rangle + \langle \psi_I | V | \psi_I \rangle + i[\langle \psi_R | V | \psi_I \rangle - \langle \psi_I | V | \psi_R \rangle]$$

Potential energy

=

$$\langle \psi_R | \tilde{E} | \psi_R \rangle + \langle \psi_I | \tilde{E} | \psi_I \rangle + i[\langle \psi_R | \tilde{E} | \psi_I \rangle - \langle \psi_I | \tilde{E} | \psi_R \rangle]$$

Total energy

The Schrödinger equation: “norm”, “one particle”

Important concept: the norm associates $\psi(x, t)$ with “one particle”

The association of “one particle” is associated with the “norm” of $\psi(x, t)$.

We require that $\psi(x, t)$ be normalized so that:

$$1 = \int_{-\infty}^{+\infty} dx \psi^*(x, t) \psi(x, t) . \quad (5.31)$$

Interpretation: That one particle is, somehow, smeared over all of space. This is the giant leap that Quantum Mechanics takes. There is no concept of this in Classical Mechanics. A particle is described as a point in space $x(t)$, that moves in time.

Consequence: In order for (5.31) to be true, the integral over all space, implied by that equation, must exist. If the norm is undefined, 0 or ∞ , it cannot describe a particle.

The norm is time-independent. Despite the time independence on the right hand side (RHS) of (5.31) one can show (we will, later) that this is always true if the particle is moving in a real potential.

The Schrödinger equation: the “probability current density”

“Where is the particle?”

In Classical Mechanics, the answer is: $x(t)$.

In Quantum Mechanics, the closest answer is $|\psi(x, t)|^2$.

This quantity is called the “probability density”, $P(x, t)$:

$$P(x, t) = \psi^*(x, t)\psi(x, t) = |\psi(x, t)|^2 . \quad (5.32)$$

Interpretation: Although the particle is smeared over all space with amplitude $\psi(x, t)$, we can definitely say that the likelihood of finding the particle at x is given by $P(x, t)$. That is, if $P(x_1, t) > P(x_2, t)$, we are more likely to observe the particle interacting with something at x_1 rather than x_2 .

The Schrödinger equation: the probability current density

“Where is the particle going?”

In Classical Mechanics, the answer is: $v(t)$.

In Quantum Mechanics, we answer this by deriving the “continuity equation”:

$$\frac{\partial}{\partial t}P(x, t) + \frac{\partial}{\partial x}S(x, t) = 0 , \quad (5.33)$$

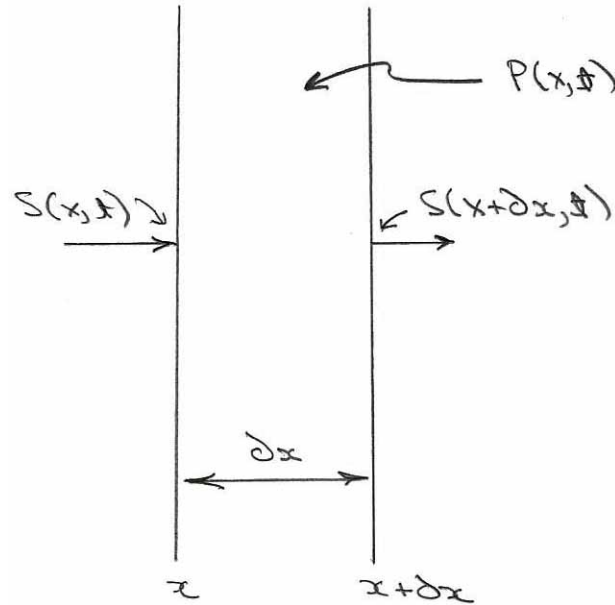
where the “probability current density” is given by:

$$S(x, t) = -\frac{\hbar}{m}\mathcal{I} \left(\psi(x, t) \frac{\partial}{\partial x} \psi^*(x, t) \right) . \quad (5.34)$$

*Optional material

Derivation of the continuity equation and the probability current density

Consider the following figure:



where a probability density, P , in a slab Δx , changes since a current density, S , has a different value on exit, than on entrance to the slab.

Balancing this is given by:

$$\frac{\partial P(x, t + \partial t) - \partial P(x, t)}{\partial t} + \frac{\partial S(x + \partial x, t) - \partial S(x, t)}{\partial x} = 0. \quad (5.35)$$

*Optional material...

Derivation of the continuity equation and the probability current density

In words, (5.34) is saying, “The change in probability with time plus the change in current with space must balance.”

In the limit that $\partial x \longrightarrow 0$ and $\partial t \longrightarrow 0$,

$$\frac{\partial}{\partial t}P(x, t) + \frac{\partial}{\partial x}S(x, t) = 0 ,$$

as given in (5.33).

Note that we have said nothing about Quantum Mechanics at this point in the derivation. (5.33) is completely general.

Now we invoke Quantum Mechanics to get through the rest of the derivation.

*Optional material...

Derivation of the continuity equation and the probability current density

From (5.32)

$$P(x, t) = \psi^* \psi .$$

$$\frac{\partial P}{\partial t} = \frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} . \quad (5.36)$$

From (5.30):

$$\frac{\partial \psi(x, t)}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} - \frac{i}{\hbar} V(x, t) \psi(x, t) . \quad (5.37)$$

(5.30)* $\Rightarrow$:

$$\frac{\partial \psi^*(x, t)}{\partial t} = \frac{-i\hbar}{2m} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} + \frac{i}{\hbar} V^*(x, t) \psi^*(x, t) . \quad (5.38)$$

... *Optional material

Derivation of the continuity equation and the probability current density

From (5.32) Combining (5.36), (5.37) and (5.38):

$$\begin{aligned}\frac{\partial P}{\partial t} &= \left(\frac{-i\hbar}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + \frac{i}{\hbar} V^* \psi^* \right) \psi - \psi^* \left(\frac{i\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} - \frac{i}{\hbar} V \psi \right) \\ &= \frac{i\hbar}{2m} \left(\psi^* \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial^2 \psi^*}{\partial x^2} \psi \right) - \frac{i}{\hbar} [\psi^* (V - V^*) \psi] \\ &= \frac{i\hbar}{2m} \left[-\frac{\partial}{\partial x} \left\{ \frac{\partial \psi^*}{\partial x} \psi - \psi^* \frac{\partial \psi}{\partial x} \right\} \right] + \frac{2}{\hbar} [\psi^* \mathcal{I}(V) \psi] \\ &= \frac{\partial}{\partial x} \left[\frac{\hbar}{m} \mathcal{I} \left(\psi \frac{\partial \psi^*}{\partial x} \right) \right] + \frac{2}{\hbar} [\psi^* \mathcal{I}(V) \psi] \\ &= -\frac{\partial S}{\partial x} + \frac{2}{\hbar} [\psi^* \mathcal{I}(V) \psi] ,\end{aligned}\tag{5.39}$$

or,

$$\frac{\partial P}{\partial t} + \frac{\partial S}{\partial x} = \frac{2}{\hbar} \psi^* \mathcal{I}(V) \psi .\tag{5.40}$$

When V is real we have the continuity equation given in (5.33). *Q.E.D.*

The Schrödinger equation: Properties of $\psi(x, t)$...

To be a proper wavefunction:

- $\psi(x, t)$ must be normalized.³ That is:

$$\int_{-\infty}^{+\infty} dx \psi^*(x, t) \psi(x, t) = 1 .$$

Note that this implies that $V(x, t)$ is real.

- A “candidate” wave function, $\phi(x, t)$, must be normalized, before it can be considered to be admissible as a wavefunction. (It also has to pass other criteria described below.)

To normalize it, see if:

$$\int_{-\infty}^{+\infty} dx |N|^2 \phi^*(x, t) \phi(x, t) = 1$$

can be calculated. If it can, you have a new candidate, $N\phi(x, t)$, that may or may not be a true wavefunction. Note that if it passes the other tests, then

$$\psi(x, t) = N\phi(x, t)$$

is a wavefunction, where N is, in general, complex constant.

³An important exception to this are asymptotically free waves, like plane waves that are used, for example, in scattering problems. There we can make sense of ratios of scattered to incident probability current densities. At the very worst, the probability density of this free wave may be a constant as $x \rightarrow \infty$.

... The Schrödinger equation: Properties of $\psi(x, t)$...

- $\psi(x, t)$ must be continuous everywhere.
- $\frac{\partial \psi(x, t)}{\partial x}$ must be continuous everywhere, except at the boundaries of infinite potentials. (We shall discuss this peculiar case later.) At those boundaries, ψ must go to zero.

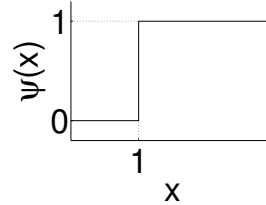
Examples ...

Can the following “candidates” be wavefunctions? (Examine at $t = 0$ only.)

- $\phi(x, 0) = \theta(x - 1)$

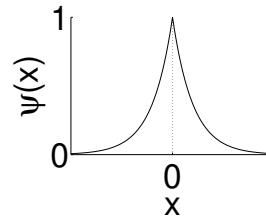
No, because not normalizable.

No, because of non-continuous slope.



- $\phi(x, 0) = \sqrt{\alpha} e^{-\alpha|x|}$

No, because of non-continuous slope.



- $\phi(x, 0) = 2\sqrt{\alpha^3} x e^{-\alpha x} \theta(x)$

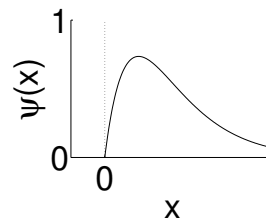
$V(x) = \infty$ for $x \leq 0$, else 0.

Yes! It is normalized

It is continuous everywhere.

Its slope is continuous, except at $x = 0$ where the potential goes to ∞ .

It is a wavefunction. $\psi(x, 0) = \phi(x, 0)$.



More examples ...

Can the following “candidate” be a wavefunction?

$$\phi(x, t) = \frac{N e^{-i \frac{E_0}{\hbar} t}}{(a^2 + x^2)^{\frac{1}{4}}}$$

- ✓ It is continuous everywhere.
- ✓ It's slope is continuous everywhere.
- ✗ It is not normalizable.

Note:

$$\lim_{x_0 \rightarrow \infty} \int_{-x_0}^{x_0} dx |\phi(x, t)|^2 = \lim_{x_0 \rightarrow \infty} 2|N|^2 \log [(x_0 + \sqrt{x_0^2 + a^2})/a] \longrightarrow \infty .$$

In general, if an integrand's asymptotic large- x limit is of the form x^{-1} , then its integral $\int^{\infty} dx$ will have a “logarithmic divergence”.

The case above is a specific example.

Let's look at something that converges better.

More examples ...

Can the following “candidate” be a wavefunction?

$$\phi(x, t) = \frac{\sqrt{\frac{|a|}{\pi}} e^{-i\frac{E_0}{\hbar}t}}{\sqrt{a^2 + x^2}}$$

- ✓ It is continuous everywhere.
- ✓ It's slope is continuous everywhere.
- ✓ It is normalized. (Show on your own.)

It is a wavefunction. $\phi(x, t) = \psi(x, t)$

Note that $\langle x \rangle = 0$ since $|\psi|^2$ is an even function of x .
However, $\langle x^2 \rangle$ diverges, and consequently, so does Δx .
Yet, it is a particle wavefunction.
It just is not localized very well.

Knowledge of the wavefunction gives the potential! ...

Recall the Schrödinger equation:

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t} ,$$

and rewrite it:

$$V = \left(i\hbar \frac{\partial \psi}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \right) / \psi . \quad (5.41)$$

This implies that if one knows, or guesses at the form of a wavefunction, that the potential that binds this particle can be obtained.

A bound particle means that it is localized in space, and that can be achieved by having a binding potential.

Knowledge of the wavefunction gives the potential! ...

Example:

Let's see how this works, with the wavefunction:

$$\psi = \left(\frac{\alpha}{\sqrt{\pi}} \right)^{1/2} \exp[-(\alpha x)^2/2] \exp(itE_0/\hbar) ; \quad \text{where } \int_{-\infty}^{+\infty} dx \psi^* \psi = 1 \quad (5.42)$$

(5.41) $\rightarrow$ (5.42) $\Rightarrow$

$$V(x) = \left(E_0 - \frac{\hbar^2 \alpha^2}{2m} \right) + \frac{1}{2} \left[\frac{\hbar^2 \alpha^4}{m} \right] x^2 . \quad (5.43)$$

One can identify the “spring constant” of the harmonic potential as the contents of the large $[\]$'s, giving:

$$V(x) = \left(E_0 - \frac{\hbar^2 \alpha^2}{2m} \right) + \frac{kx^2}{2} . \quad (5.44)$$

Then, recalling that the fundamental oscillation frequency is $\omega = \sqrt{k/m}$, we get:

$$V(x) = E_0 - \frac{\hbar\omega}{2} + \frac{kx^2}{2} . \quad (5.45)$$

... Knowledge of the wavefunction gives the potential!...

Finally, if we choose $V(0) = 0$, we have identified the “zero-point” energy of the ground state of the quantum oscillator to be:

$$E_0 = \frac{\hbar\omega}{2} , \quad (5.46)$$

and

$$V(x) = \frac{kx^2}{2} . \quad (5.47)$$

This technique can be generalized to find the higher-order wavefunctions, and this is something that we shall discuss later.

... Knowledge of the wavefunction gives the potential!...

Admittedly, that was an inspired guess for the wavefunction!

Let's choose something a little more random, if only to demonstrate that creating a localized wavefunction, produces a “binding” potential.

To that end, let us try:

$$\psi(x, t) = \frac{\sqrt{\frac{|a|}{\pi}} e^{-i\frac{E_0}{\hbar}t}}{\sqrt{a^2 + x^2}} \quad (5.48)$$

We have encountered this example before, and verified that it is normalized.

If we let

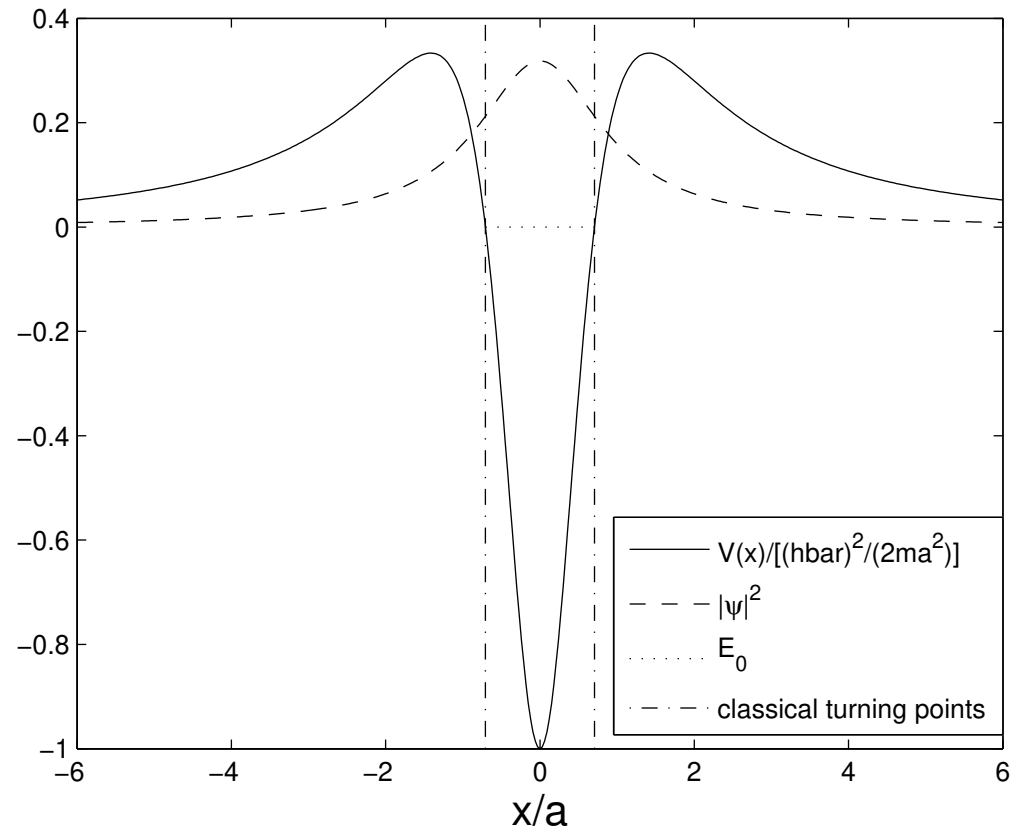
$$f(x) = \frac{1}{\sqrt{a^2 + x^2}},$$

using (5.41) gives us:

$$V(x) = E_0 + \frac{\hbar^2}{2m} \frac{f''}{f} = E_0 + \frac{\hbar^2}{2m} \left(\frac{2}{x^2 + a^2} - \frac{3a^2}{(x^2 + a^2)^2} \right) \quad (5.49)$$

Choosing $V(\pm\infty) = 0$ fixes $E_0 = 0$. The potential is sketched on the next page.

... Knowledge of the wavefunction gives the potential!...



General classes of Schrödinger equation problems

E is monoenergetic in all regions of space

If we are seeking monoenergetic problems, then we may write:

$$\psi(x, t) = u(x)e^{-i(E/\hbar)t} . \quad (5.50)$$

Using (5.50) in the Schrödinger equation, (5.30) gives:

$$\frac{-\hbar^2}{2m}u''(x)e^{-i(E/\hbar)t} + V(x, t)u(x)e^{-i(E/\hbar)t} = Eu(x)e^{-i(E/\hbar)t} . \quad (5.51)$$

Note that the $e^{-i(E/\hbar)t}$ factors all divide out, leaving us with:

$$\frac{-\hbar^2}{2m}u''(x) + V(x, t)u(x) = Eu(x) . \quad (5.52)$$

Solving for $V(x, t)$, we get:

$$V(x) = E + \frac{\hbar^2}{2m} \frac{u''(x)}{u(x)} . \quad (5.53)$$

Hence, by considering monoenergetic solutions only, we necessarily restrict ourselves to time-independent potentials.

Another way to reach the same conclusion is to start with the Schrödinger equation,

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

with the assumption that the potential is time-independent, as indicated above.

Assume that the wavefunction is separable in space and time, *viz.*

$$\psi(x, t) = u(x)T(t) .$$

Substituting for $\psi(x, t)$ in the Schrödinger equation above results in

$$\frac{-\hbar^2}{2m} u''(x)T(t) + V(x)u(x)T(t) = u(x) i\hbar \frac{dT(t)}{dt} .$$

Dividing the above by $u(x)T(t)$ gives the classic "Separation of Variables" result:

$$\frac{-\hbar^2}{2m} \frac{u''(x)}{u(x)} + V(x) = i\hbar \frac{dT(t)/dt}{T(t)} .$$

Identifying the separation constant as E , the total energy, gives the time-independent, monoenergetic Schrödinger equation,

$$\frac{-\hbar^2}{2m}u'' + V(x)u(x) = Eu(x) ,$$

the differential equation for the time component $T(t)$,

$$i\hbar \frac{dT(t)/dt}{T(t)} = E ,$$

and the full wavefunction, separated into space and time components,

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

Time-independent (steady-state) monoenergetic solutions

Therefore, the Schrödinger equation for this general class of problems becomes:

$$-\frac{\hbar^2}{2m}u''(x) + V(x)u(x) = Eu(x) . \quad (5.54)$$

(5.54) is further divided into two subclasses:

Unbound problems:



and bound problems:



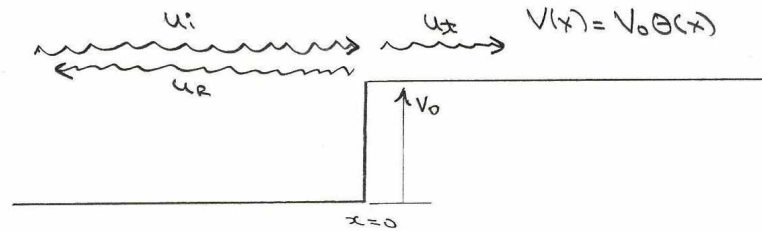
We shall be dealing with these two types of problems exclusively, for the entirety of NERS 311 and 312. They cover a very wide range of phenomena in nuclear and atomic physics.

Initially we shall focus on unbound problems.

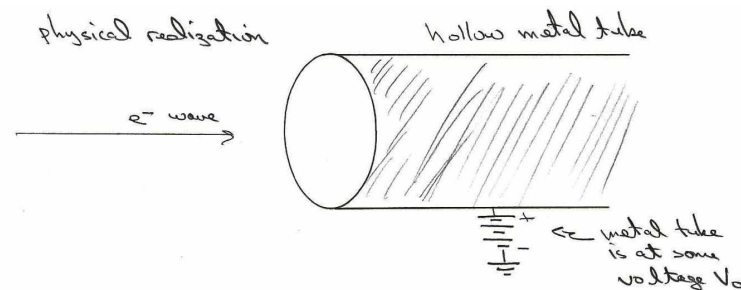
Unbound, steady-state, monoenergetic problem

Scattering of a wave from a potential barrier

Consider a potential of the form shown below, where, $V(x) = V_0\theta(x)$. V_0 is a constant.



This is sometimes called a “step” potential.⁴ A physical realization of this situation is seen below. An electron is directed toward a hollow tube (everything is in vacuum). The inside of the tube is at a constant potential V_0 , that can have either sign, depending on how the battery is connected. The electron wave arrives at $x = 0$. Then what happens?



⁴Please be aware that a discontinuous potential is a mathematical fiction, much like the concept of ∞ . This application is deceptively simple, and illustrates, with minimum effort, some of the subtleties and beauties of Quantum Mechanics. Interested students, who want to follow up on this, are encouraged to research this on their own. You can do no better than to start with:

Correspondence principle and scattering from potential steps, by David Branson, American Journal of Physics 47, 1101 (1979); doi: 10.1119/1.11582

Continuity conditions on Schrödinger equation wave functions at discontinuities of the potential by David Branson, Am. J. Phys. 47, 1000 (1979); doi: 10.1119/1.11688

Scattering of a wave from a potential barrier ...

Let region “1” be the domain $x < 0$. In this region, we have prepared an incident wave with known energy E .

That incident wave has the form:

$$u_i(x) = Ae^{ik_1x} , \quad (5.55)$$

where A is the amplitude of the wave we have prepared. That is also known.

Its wavenumber is determined by putting it into the Schrödinger equation for that region, namely:

$$\frac{-\hbar^2}{2m}u_i''(x) = Eu_i(x) , \quad (5.56)$$

that is obtained from (5.52) by setting $V = 0$.

... Scattering of a wave from a potential barrier ...

Doing the derivatives leads us to the expression:

$$\frac{\hbar^2}{2m}k_1^2 u_i(x) = E u_i(x) . \quad (5.57)$$

Dividing by $u_i(x)$ and solving for k_1 , gives:

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} . \quad (5.58)$$

However, when the incident wave encounters the barrier, it can cause there to be a reflected wave in region 1. (Think of a wave on a pond encountering a rock and reflecting back. It is exactly the same phenomenon.)

That reflected wave is given by:

$$u_r(x) = B e^{-ik_1 x} , \quad (5.59)$$

where B is the amplitude of the reflected wave we have prepared. That is unknown, but we shall determine it shortly.

... Scattering of a wave from a potential barrier ...

Note that the sign in the exponential has reversed, because the reflected wave is traveling in the direction of $-x$. Also, the wavenumber is the same, because we are considering monoenergetic waves only. The barrier causes a reflection and an amplitude change, but it does not change the wavenumber.

Therefore the total wavefunction in region 1 is given by the sum of the incident and reflected parts: The solution in this region is:

$$u_1(x) = u_i(x) + u_r(x) = Ae^{ik_1x} + Be^{-ik_1x} . \quad (5.60)$$

Now we consider the solution in region 2, $x > 0$.

What we do know, is that there is no wave incident from $+\infty$, that means there can be no wave of the form e^{-ik_2x} .

However, there can be a transmitted wave,

$$u_t(x) = u_2(x) = Ce^{ik_2x} , \quad (5.61)$$

where C is its amplitude.

... Scattering of a wave from a potential barrier ...

Note that the wavenumber is different because there is a potential in region 2. We solve for it the same way, by putting (5.61) into (5.52), but this time with $V = V_0$:

$$\frac{-\hbar^2}{2m}u_t''(x) + V_0u_t(x) = Eu_t(x) , \quad (5.62)$$

and after a little bit of arithmetic, obtain the wavenumber in region 2:

$$k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} . \quad (5.63)$$

... Scattering of a wave from a potential barrier ...

Let's gather up everything we know up to now:

$$u_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \quad \text{Region 1 solution, from (5.60)}$$

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{Region 1 wavenumber, from (5.58)}$$

$$u_2(x) = Ce^{ik_2x} \quad \text{Region 2 solution, from (5.60)}$$

$$k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \quad \text{Region 2 wavenumber, from (5.63)}$$

E is known. Only B and C need to be found.

We use the requirements that $u(x)$, and $u'(x)$ must be continuous everywhere.

They already are in region 1 ($x < 0$) and region 2 $x > 0$.

By insisting on slope and value continuity, we may obtain what B and C are.

... Scattering of a wave from a potential barrier ...

$$u_1(0) = u_2(0) \Rightarrow$$

$$A + B = C . \quad (5.64)$$

$$u'_1(0) = u'_2(0) \Rightarrow$$

$$k_1(A - B) = k_2C . \quad (5.65)$$

(5.64) and (5.65) may be used to solve for B and C in terms of the known quantities.

After a few steps:

$$B = \frac{k_1 - k_2}{k_1 + k_2} A \quad (5.66)$$

$$C = \frac{2k_1}{k_1 + k_2} A \quad (5.67)$$

... Scattering of a wave from a potential barrier ...

So, after all this work, we can state the solution for the wavefunction over all space:

Given that

1. we have prepared a wavefunction incident from the left of the form $u_i(x) = Ae^{ik_1x}$ with known energy, E , and wavenumber $k_1 = \sqrt{2mE/\hbar^2}$,
2. there is no wave incident from $+\infty$ traveling to the left,
3. the incident wave, moving to the right in a potential $V = 0$ encounters a potential of the form $V(x) = V_0$ for $x > 0$ producing a reflected wave of the form, $u_r(x) = Be^{-ik_1x}$ with the same energy, that moves to the left in region 1,
4. the incident wave also creates a transmitted wave, that moves to the right in region 2, with form $u_t(x) = Ce^{ik_2x}$, where $k_2 = \sqrt{2m(E - V_0)/\hbar^2}$,

we can determine the reflected and transmitted amplitudes:

$$B = \frac{k_1 - k_2}{k_1 + k_2}A$$

$$C = \frac{2k_1}{k_1 + k_2}A$$

Yay! OK, now what does all this mean?

... Scattering of a wave from a potential barrier ...

What it means

This is a scattering problem, involving an external beam of individual particles *e.g.* n , p , or $e^\pm$ impinging upon a potential and being redirected.

In 3 dimensions we already know something about “cross sections” the ability of something (a potential, or another particle) to deflect the projectile.

The results of this scattering are expressed in terms of a cross section, σ (the effective size of the scatterer) or its relative probability of scattering the projectile into some set of angles, $d\sigma/(d\theta d\phi)$, where θ and ϕ are the polar and azimuthal angles of the deflected particle.

However, we are in one dimension only. There are no angles. There is only forward and backward, the direction of the projectile (forward) and its reverse (backward).

Therefore, we have a simpler analysis to consider.

... Scattering of a wave from a potential barrier ...

It starts with the probability current density, that calculation that tells us where the operator is going, namely [from (5.34)]:

$$S(x, t) = -\frac{\hbar}{m} \mathcal{I} \left(\psi(x, t) \frac{\partial}{\partial x} \psi^*(x, t) \right) .$$

Recall that the $\mathcal{I}()$ operator extracts the imaginary part of its argument.⁵

Now, substitute for $\psi(x, t)$ in the above, with a generic monoenergetic plane wave,

$$\psi(x, t) = N e^{ikx} e^{-i(E/\hbar)t} .$$

$$\begin{aligned} S(x, t) &= -\frac{\hbar}{m} \mathcal{I} \left(N e^{ikx} e^{-i(E/\hbar)t} \frac{\partial}{\partial x} N^* e^{-ik^*x} e^{-i(E/\hbar)t} \right) \\ &= -\frac{\hbar}{m} \mathcal{I} \left(|N|^2 e^{ikx} (-ik^*) e^{-ik^*x} \right) \\ &= |N|^2 \frac{\hbar}{m} \mathcal{I} \left(ik^* e^{i(k-k^*)x} \right) \\ &= |N|^2 \frac{\hbar}{m} k_{\text{R}} e^{-2k_{\text{I}}x} , \end{aligned} \tag{5.68}$$

where we allow k to be complex, that is, $k = k_{\text{R}} + ik_{\text{I}}$.

⁵We have already argued that anything that is complex can be written as a sum of its real and imaginary parts. That is $f = f_{\text{R}} + if_{\text{I}}$. The $\mathcal{R}()$ and $\mathcal{I}()$ operators work as follows: $\mathcal{R}(f) = f_{\text{R}}$ and $\mathcal{I}(f) = f_{\text{I}}$.

... Scattering of a wave from a potential barrier ...

This is a beautiful, interesting, and complex (pun intended) result.
The math is saying many things.

Recall from the barrier scattering problem,

$$\text{for } x < 0 \quad k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{from (5.58) for region 1}$$

$$\text{for } x > 0 \quad k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \quad \text{from (5.63) for region 2}$$

k_1 is always real because kinetic energy is always positive.

If $V_0 \leq E$, k_2 is always real and $S = |N|^2 \hbar k_R / m$. S has no x dependence.

If $V_0 > E$, k_2 is always pure complex (no real part) and $S = 0$, because $\mathcal{R}(k) = 0$.

... Scattering of a wave from a potential barrier ...

In lieu of cross sections, we define the reflection, R , and transmission, T , coefficients as follows:

$$R = \left| \frac{S_r}{S_i} \right| \quad (5.69)$$

$$T = \left| \frac{S_t}{S_i} \right| \quad (5.70)$$

where S_i , S_r , and S_t are the probability current densities for the incident, reflected, and transmitted waves, respectively. Note that the probability current densities are real, and the $|\dots|$ takes the absolute value of real quantities that make be negative.

For this problem, the step potential:

$$S_i = |A|^2 \frac{\hbar k_1}{m} \quad (5.71)$$

$$S_r = |B|^2 \frac{\hbar k_1}{m} \quad (5.72)$$

$$S_t = |C|^2 \frac{\hbar k_{2,R}}{m} \exp(-2k_{2,I}x) \quad (5.73)$$

... Scattering of a wave from a potential barrier ...

The $|\dots|^2$ in (5.71)–(5.73) is the modulus squared, as A , B , and C are, in general, complex constants.

Also, k_1 is real, by design (see (5.58)), but k_2 is either pure real, or pure imaginary, depending on the value of V_0 (see (5.63)). This is seen in the form for S_t above. k_2 is pure real for $V_0 \leq E$, and pure imaginary⁶ if $V_0 > E$.

For this application:

$$R = \frac{|B|^2}{|A|^2} \quad (5.74)$$

$$T = \frac{|C|^2}{|A|^2} \frac{k_{2,R}}{k_1} \exp(-2k_{2,I}x) \quad (5.75)$$

Substituting from (5.66) and (5.67) in the above gives:

$$R = \frac{(k_1 - k_2^*)(k_1 - k_2)}{(k_1 + k_2^*)(k_1 + k_2)} \quad (5.76)$$

$$T = \frac{4k_1 k_{2,R}}{(k_1 + k_2^*)(k_1 + k_2)} \exp(-2k_{2,I}x) \quad (5.77)$$

⁶If we had allowed V_0 to be a complex constant, k_2 would have had both real and imaginary parts.

... Scattering of a wave from a potential barrier ...

For plotting (5.76) and (5.77), it is best left in that form for the complex-variable-savvy Matlab.

However, for human consumption, R and T may be written more suggestively as:

$$R = \frac{k_1^2 - 2k_1k_{2,R} + |k_2|^2}{k_1^2 + 2k_1k_{2,R} + |k_2|^2} \quad (5.78)$$

$$T = \frac{4k_1k_{2,R} \exp(-2k_{2,I}x)}{k_1^2 + 2k_1k_{2,R} + |k_2|^2} \quad (5.79)$$

$$R + T = 1 \quad (5.80)$$

(5.80) is universally true if k_2 is pure real ($V_0 \leq E$) and pure imaginary ($V_0 > E$), and this is seen easily by considering the two cases separately!

$$R = \theta(V_0 - E) + \theta(E - V_0) \frac{k_1^2 - 2k_1k_2 + k_2^2}{k_1^2 + 2k_1k_2 + k_2^2} \quad (5.81)$$

$$T = \theta(E - V_0) \frac{4k_1k_2}{k_1^2 + 2k_1k_2 + k_2^2} \quad (5.82)$$

... Scattering of a wave from a potential barrier ...

(5.82) shows that there is no transmission for $E < V_0$. This is to be expected from classical physics since a classical particle has to overcome the repulsive potential with its kinetic energy. So, we expect no transmission and complete reflection, as evident from (5.81).

However, as we shall see soon that waves do enter this “forbidden” region. This leads to “quantum tunneling” — the ability for matter waves to penetrate through potentials. There is no classical analog for tunneling. It is a completely quantum phenomenon.

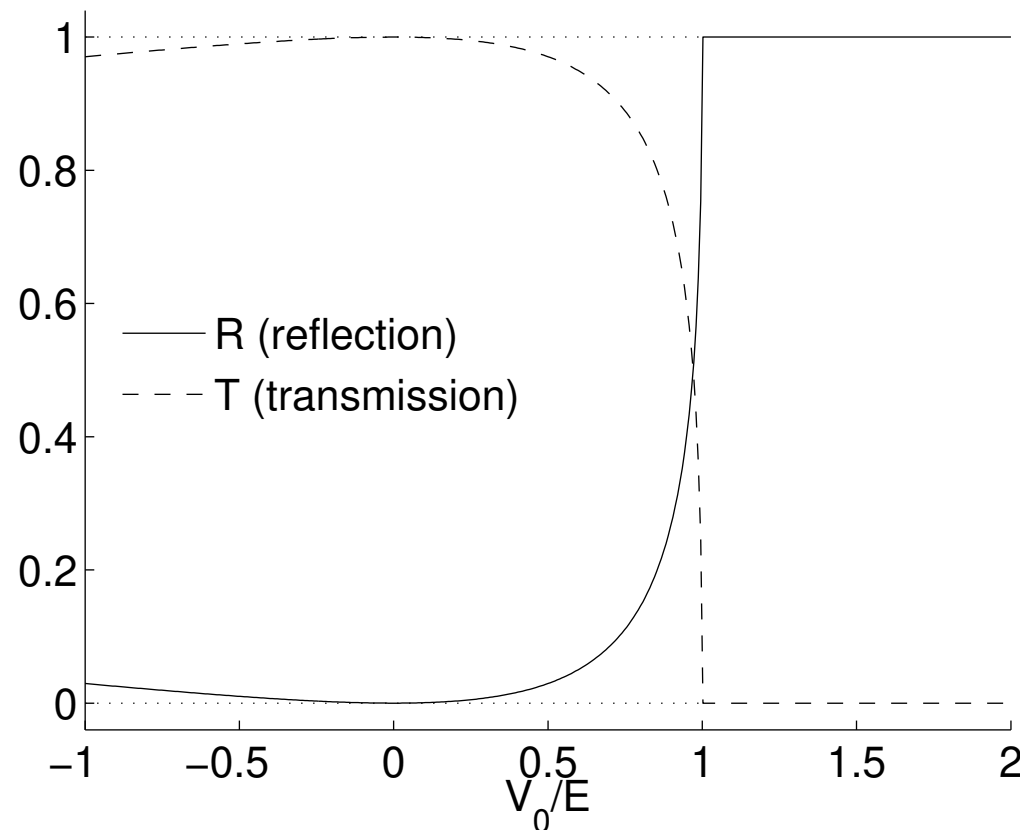
When a classical particle enters the potential region it would slow down when $0 < E < V_0$ according to the prescription $K = K_0 - V_0$, where K_0 is its kinetic energy in the “no potential region”. If V_0 was less than 0, it would speed up, with the same prescription.

Quantum particles, on the other hand, divide into reflected and transmitted amplitudes, according to the prescription in (5.81) and (5.82).

These behaviors are shown graphically on the next two pages.

... Scattering of a wave from a potential barrier ...

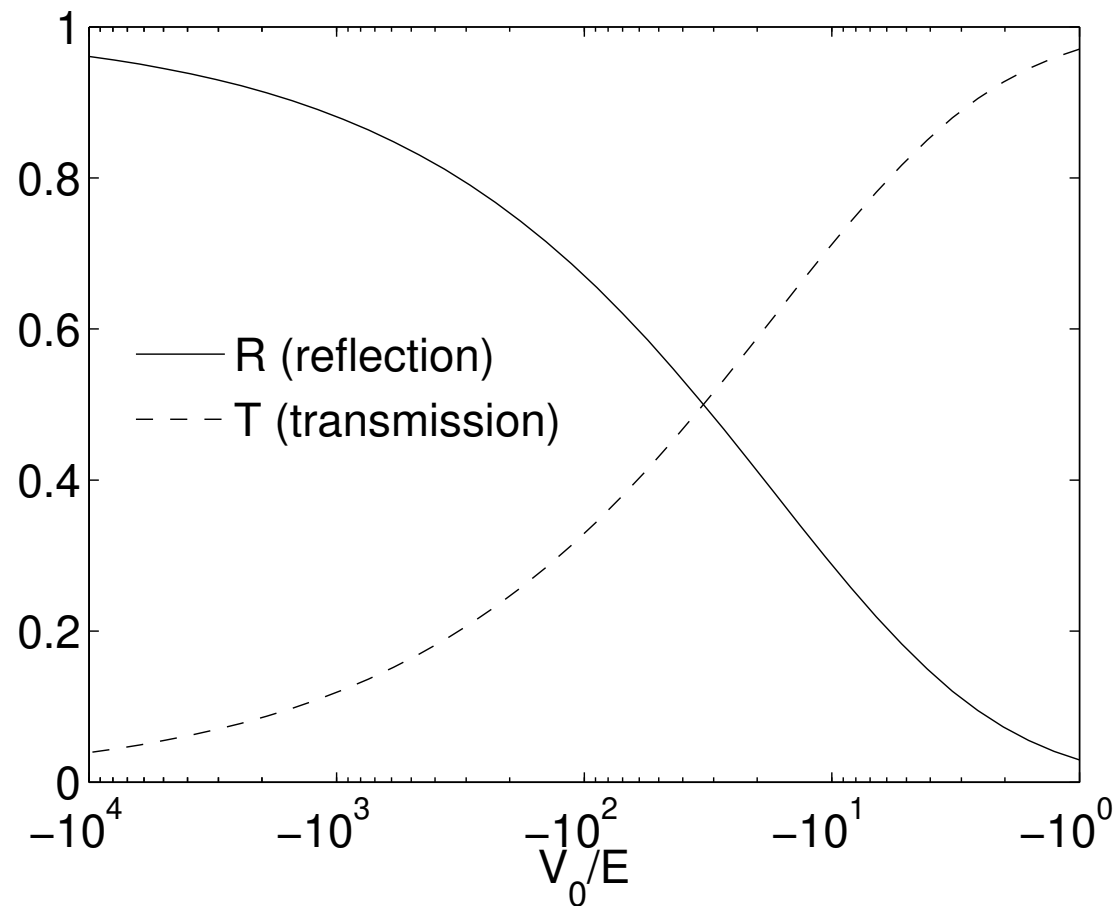
The figure below shows R and T for a range of potentials between $-E$ and $+2E$. Note that when $V_0 \geq E$, $R = 1$ and $T = 0$. Also, when $V_0 = 0$, $T = 1$ and $R = 0$. No potential implies no scattering.



... Scattering of a wave from a potential barrier ...

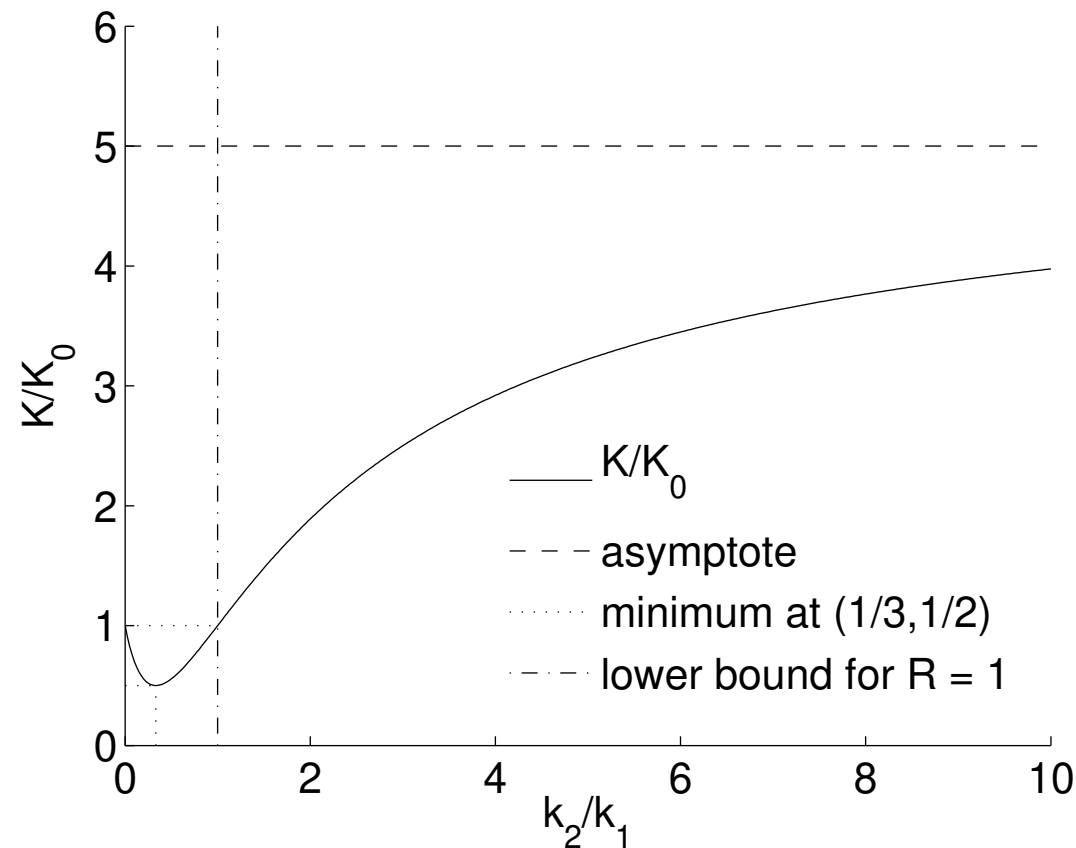
This graph shows R and T for potentials less than $V = -E$. You can show that $R = T$ when $V_0/E = 1 - (3 \pm \sqrt{8})^2[-32.9807, 0.9706]$.

When $V_0 \rightarrow -\infty$, we also see that $R \rightarrow 1$ and $T \rightarrow 0$. It is counter-intuitive, but true!



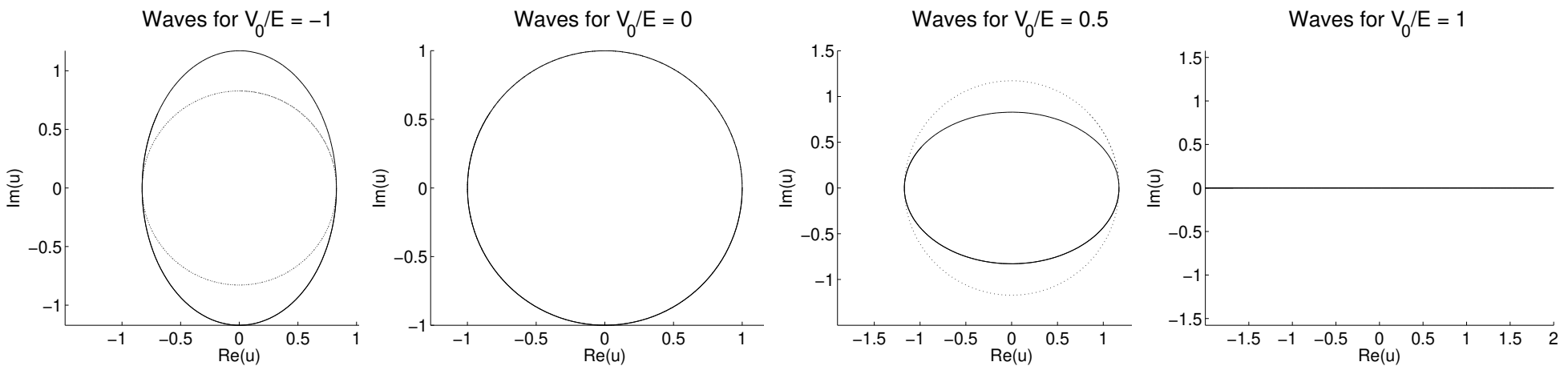
... Scattering of a wave from a potential barrier ...

If we consider this in before/after scattering terms, it is no surprise, from classical considerations, that total kinetic energy is not conserved. (Total energy is always conserved.) The relationship between the kinetic energy afterward, divided by the initial kinetic energy, K_0 is shown below. The ratio of kinetic energies is: $K/K_0 = (|B|^2 k_1^2 + |C|^2 k_2^2)/(|A|^2 k_1^2)$



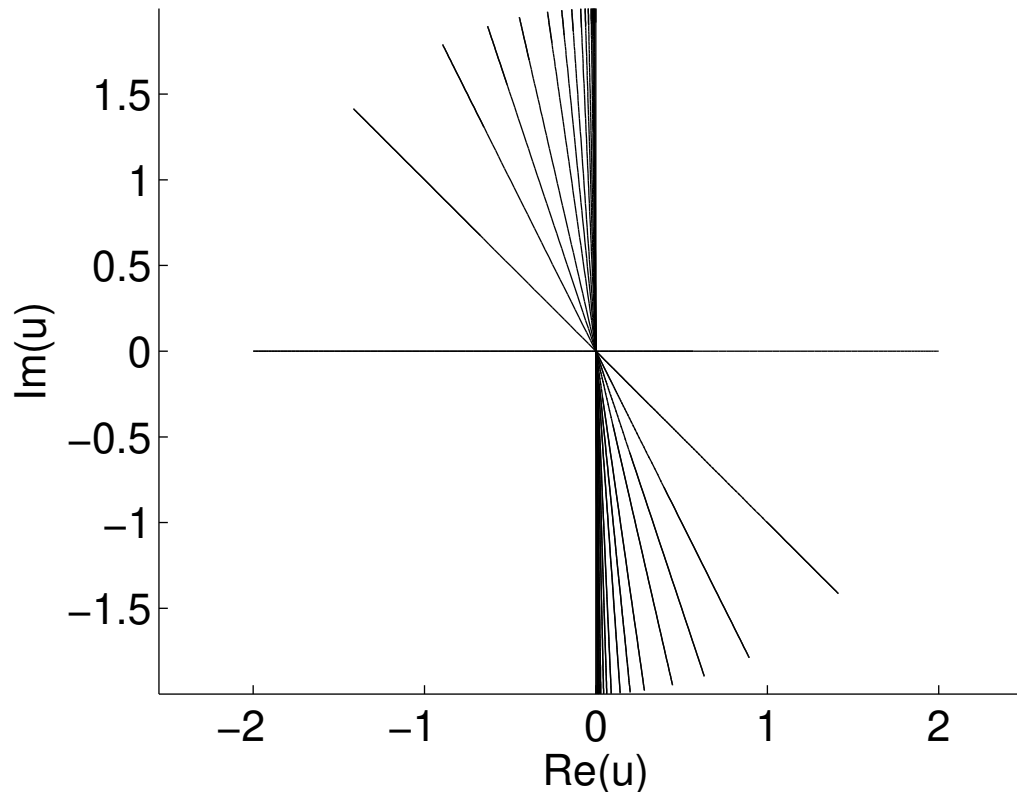
... Scattering of a wave from a potential barrier ...

Here are several plots of the reflected and transmitted waves for the case $0 \leq V_0 \leq E$. The waves are complex and sinusoidal. Imagine yourself sighting down the x -axis. The composite incident and reflected wave (solid line) in this projection is an ellipsoid in $[\mathcal{R}(u_1), \mathcal{I}(u_1)]$ with major/minor axes being $1 \pm B/A$. The transmitted wave has no constructive or destructive interference; it is a circle with radius C/A .



... Scattering of a wave from a potential barrier ...

Waves for $V_0/E = 1, 2, 5, 10, \dots$



At $V_0 = E$ the ellipsoid has collapsed to a horizontal line, with no imaginary part. This collapse of this projection persists for $V_0 > E$, except that the lines become more and more vertical, picking up an imaginary component that increases as V_0 is increased. In the limit that $V_0 \rightarrow \infty$ the line becomes vertical, pure imaginary. What is going on?

... Scattering of a wave from a potential barrier ...

After some inspiration ...

Note that, in this regime, $R = 1$, hence $|B| = |A|$. Thus we can rewrite (5.60) as:

$$\begin{aligned} u_1(x) &= u_i(x) + u_r(x) \\ &= A[e^{ikx} + e^{i\phi}e^{-ikx}] \quad [\text{only a phase difference}] \\ &= Ae^{i\phi/2}[e^{i(kx-\phi/2)} + e^{-i(kx-\phi/2)}] \quad [\text{pulled out } e^{i\phi/2}] \\ &= \tilde{A}[e^{i(kx-\phi/2)} + e^{-i(kx-\phi/2)}] \quad [\text{defined } \tilde{A} = Ae^{i\phi/2}] \\ &= 2\tilde{A}\cos(kx - \phi/2) , \end{aligned} \tag{5.83}$$

where $k \equiv \sqrt{2mE/\hbar^2}$. The phase idea rotated the solution onto the real axis!

Solving for region 2,

$$u_2(x) = u_t(x) = \tilde{C}e^{-\kappa x} , \tag{5.84}$$

where $\kappa \equiv \sqrt{2m(V_0 - E)/\hbar^2}$. Applying boundary conditions gives:

$$2\tilde{A}\cos(\phi/2) = \tilde{C} \quad \text{and} \quad 2\tilde{A}k\sin(\phi/2) = -\kappa\tilde{C} ,$$

that is easily solved to give:

$$\tan(\phi/2) = -\kappa/k \tag{5.85}$$

$$\tilde{C} = 2\tilde{A}\sqrt{\kappa^2 + k^2}/k , \tag{5.86}$$

... Scattering of a wave from a potential barrier ...

or

$$\tan(\phi/2) = -\sqrt{(V_0 - E)/E} \quad (5.87)$$

$$\tilde{C} = 2\tilde{A}\sqrt{V_0/E}, \quad (5.88)$$

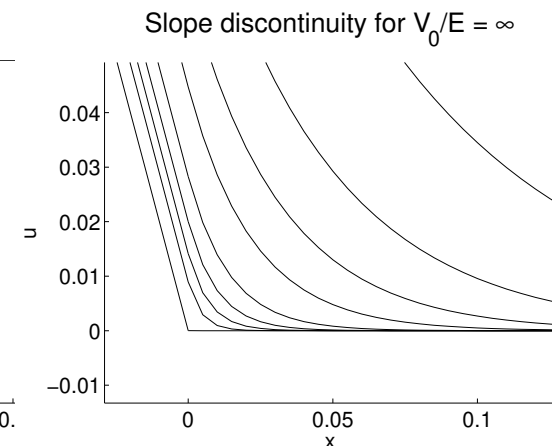
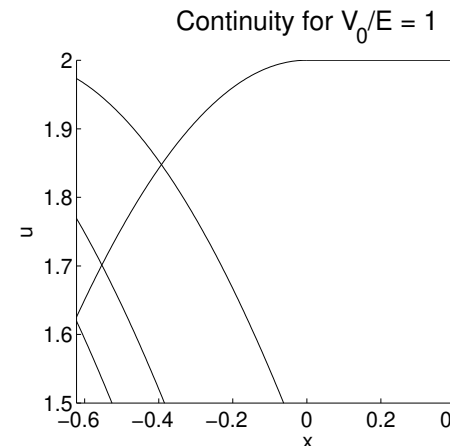
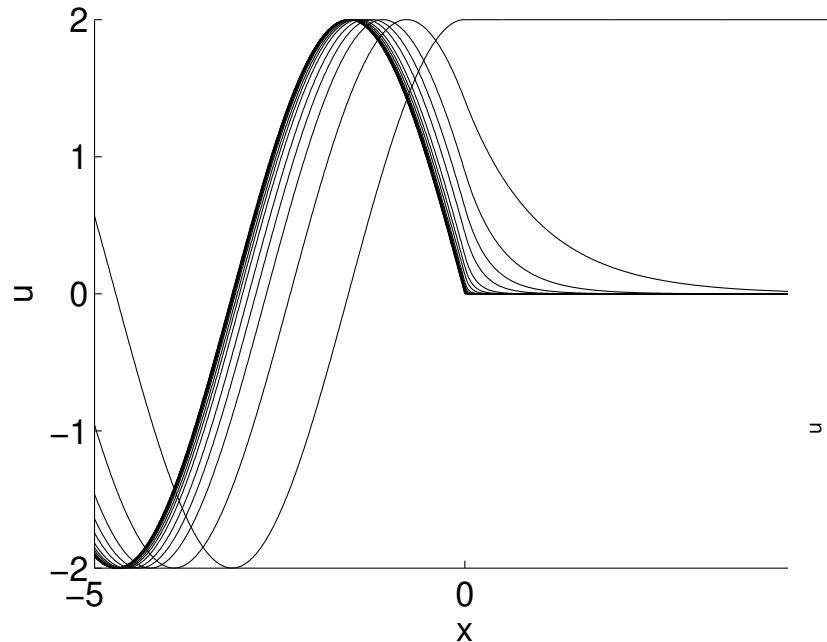
Note that the phase, $\phi/2$ goes from 0 for $V_0 = 0$ to $-\pi/2$, as $V_0 \rightarrow \infty$, rotating from the real axis to the imaginary axis, over the possible values of the potential, as observed in the previous figure.

(5.83)—(5.86) represent a real function in x . It is plotted on the next page for several values of V_0 , with zoom-ins at the boundary of the potential at $x = 0$.

... Scattering of a wave from a potential barrier ...

The potential range $V_0 \geq E$.

Waves for $V_0/E = 1, 2, 5, 10, \dots$



In the above plots, the curves are for the potentials:

$V_0/E = 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000, 10000, 20000, 50000, \infty$.

The first zoom-in shows the continuity of the $V_0 = E$ solution.

The second zoom in shows the apparent slope discontinuity for the $V_0 = \infty$ solution.

... Scattering of a wave from a potential barrier

That discontinuity only happens for infinite potentials. Finally, one sees that the second bullet item on Slide 22 is truly consistent. An infinite potential is a mathematical fiction.

One may say, "In reality, for real physical systems, the slope of the wavefunction must be continuous."

Even such a simple system exhibits interesting quantum behavior.

This is the simplest example of the scattering of a free wave from a potential. Your assignment 5 is devoted to a similar potential, though finite in extent.

Now, on to a new topic ... bound systems!

One-dimensional bound systems ...

This is a **HUGE** topic, and we shall spend many lectures on it.

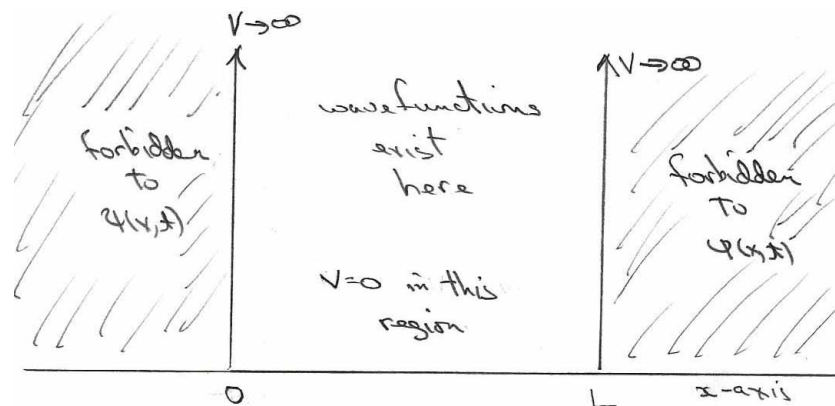
In a bound system, the particle is trapped in a potential, similar to the harmonic oscillator we talked about at the beginning of this chapter.

We shall start with a monochromatic solution starting with (5.54):

$$-\frac{\hbar^2}{2m}u''(x) + V(x)u(x) = Eu(x) .$$

The simplest (but still relevant for much we shall do later) potential is:

$$\begin{aligned} V(x) &= 0 \quad \text{for } 0 \leq x \leq L \\ &= \infty \quad \text{otherwise} \end{aligned} \tag{5.89}$$



... One-dimensional bound systems ...

For this potential, the Schrödinger equation is:

$$u''(x) + k^2 u(x) = 0, \quad (5.90)$$

where $k = \sqrt{2mE/\hbar^2}$, that we have found in the case of the scattered free wave of the last example.

However, there is one important difference ... we must force the wavefunctions to be 0 at the two boundaries, that delimit the infinite potential.

The only solutions that do this are:

$$u_n(x) = \sqrt{\frac{2}{L}} \sin k_n x, \quad \text{wavefunctions, where} \quad (5.91)$$

$$n = 0, 1, 2, \dots \infty, \quad \text{the "quantum number"} \quad (5.92)$$

$$k_n = \frac{(n+1)\pi}{L}, \quad \text{discrete } k\text{'s} \quad (5.93)$$

$$E_n = \frac{(n+1)^2 \hbar^2 \pi^2}{2mL^2}, \quad \text{energy "eigenvalues"} \quad (5.94)$$

We have adopted the convention that the lowest energy state, the "ground state" is given index (quantum number) $n = 0$.

... One-dimensional bound systems ...

Note the distinction between the free-wave scattering solutions and the bound-state solutions. The free-wave scattering solutions may have any k and E . The bound-state solutions have discrete energies.⁷

Bound states result in what are called “eigenvalue” problems, where the boundary conditions result in the discretization of the energies.

It is a regular feature of all bound-state problems in Quantum Mechanics.

Note that the wavefunctions given in (5.91) were normalized. Thus we may interpret that a particle may exist in a single quantum state, n . We may also discover that a single particle may co-exist in several, or even many quantum states, by the process of superposition. (More on this later.)

The normalization constant, $\sqrt{2/L}$, in this case, did not depend on the quantum number n . This is not a general feature of this class of solutions. In general, it may depend on the quantum number.

⁷In fact, they are not all that distinct. One notes that as $L \rightarrow \infty$, the discrete space becomes a continuous space. This fact is what may be used to circumvent the normalization problem of the free wave.

... One-dimensional bound systems ...

General properties of eigenfunctions ...

- The solution of the bound-state problem results in wavefunctions, $u_n(x)$, (n may be a finite or infinite series.) that are all different for different n . We will call these the eigenfunctions.⁸
- The eigenfunctions are all normalized. That is:

$$\int dx |u_n(x)|^2 = 1 \quad \forall n, \quad (5.95)$$

where the integral is over the domain “governed” by the binding potential.

- The eigenfunctions with different quantum numbers are all “orthogonal”.⁹ That is:

$$\int dx u_n^*(x)u_m(x) = 0 \quad \forall n, m \mid n \neq m. \quad (5.96)$$

- The set of eigenfunctions is “orthonormal” (both normalized for equal quantum numbers, and orthogonal for different ones), and is expressed by the equation:

$$\int dx u_n^*(x)u_m(x) = \delta_{nm} \quad \forall n, \quad (5.97)$$

⁸The root of the this word, “eigen” is shorted from the German composite word, “eigen” (own) and “wert” (worth) literally translating to “own worth”, or, more suggestively, “intrinsic value”.

⁹This language is borrowed from discrete vectors. The integral in (5.96) is often called an “inner product”, otherwise known as a “dot product” in discrete space. Hence, when the inner product evaluates to 0, the “vectors” are orthogonal.

... One-dimensional bound systems ...

... General properties of eigenfunctions

where the Kronecker delta, δ_{nm} is defined by:

$$\begin{aligned}\delta_{nm} &= 1 \text{ if } n = m , \\ &= 0 \text{ if } n \neq m .\end{aligned}\tag{5.98}$$

... One-dimensional bound systems ...

Proof of orthonormality for the ∞ -well potential

$$\begin{aligned}\delta_{nm} &\stackrel{?}{=} \int dx u_n^*(x) u_m(x) \quad [\text{general}] \\&= \frac{2}{L} \int_0^L dx \sin \frac{(n+1)\pi x}{L} \sin \frac{(m+1)\pi x}{L} \quad [\text{specific for this example}] \\&= \frac{2}{L} \frac{L}{\pi} \int_0^\pi d\theta \sin(n+1)\theta \sin(m+1)\theta \quad [\text{changed variable } x = L\theta/\pi] \\&= \frac{2}{\pi} \frac{1}{2} \int_{-\pi}^\pi d\theta \sin(n+1)\theta \sin(m+1)\theta \quad [\text{used anti-symmetry and changed the limits}] \\&= \frac{1}{\pi} \int_{-\pi}^\pi d\theta \left[\frac{e^{i(n+1)\theta} - e^{-i(n+1)\theta}}{2i} \right] \left[\frac{e^{i(m+1)\theta} - e^{-i(m+1)\theta}}{2i} \right] \quad [\text{used Euler's theorem}] \\&= \frac{-1}{4\pi} \int_{-\pi}^\pi d\theta \{ e^{i(n+m)\theta} + e^{-i(n+m)\theta} - [e^{i(n-m)\theta} + e^{-i(n-m)\theta}] \} \quad [\text{reorganizing}] \\&= \frac{1}{2\pi} \int_{-\pi}^\pi d\theta \{ \cos[(n-m)\theta] - \cos[(n+m)\theta] \} \quad [\text{used Euler's theorem again}] \\&= \frac{1}{2\pi} \int_{-\pi}^\pi d\theta \cos[(n-m)\theta] \quad [\text{second term above is always 0}] \\&= \delta_{nm} \quad [0, \text{ if } n \neq m, \text{ integrand is 1, when } n = m]\end{aligned}$$

Q.E.D.

... One-dimensional bound systems ...

Composite states

A composite state is made up 2 or more, (up to ∞ number) of eigenfunctions, in the following way:

$$\psi(x, t) = \sum_{n=0}^{N_S} a_n u_n(x) e^{-i(E_n/\hbar)t}, \quad (5.99)$$

where N_S is the number of states in the composite, and

$$\sum_{n=0}^{N_S} |a_n|^2 = 1, \text{ to preserve the norm, since} \quad (5.100)$$

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} dx \psi^*(x, t) \psi(x, t) \\ &= \int_{-\infty}^{\infty} dx \sum_{n=0}^{N_S} a_n^* u_n^*(x) e^{-i(E_n/\hbar)t} \sum_{m=0}^{N_S} a_m u_m(x) e^{i(E_m/\hbar)t} \\ &= \sum_{n=0}^{N_S} \sum_{m=0}^{N_S} a_n^* a_m e^{-i(E_n - E_m)t/\hbar} \int_{-\infty}^{\infty} dx u_n^*(x) u_m(x) \\ &= \sum_{n=0}^{N_S} \sum_{m=0}^{N_S} a_n^* a_m e^{-i(E_n - E_m)/\hbar t} \delta_{nm} \\ &= \sum_{n=0}^{N_S} |a_n|^2 \end{aligned}$$

Example of a composite state ...

To qualify as a state, a function must first have all the qualities of a wavefunction (normalized [or normalizable, slope and value continuous], and, if it is to exist as a bound state in a potentials that are infinite, it must be 0 when $V = \infty$, but its slope may be non-zero there.

So, let us pick an example out of the air, that lives in the infinite well potential described by (5.89).

$$u(x) = \psi(x, 0) = \sqrt{\frac{30}{L^5}} x(L - x) . \quad (5.101)$$

One can show that this wavefunction is normalized, and it is zero where the potential goes infinite. ✓

You can also show that it is not a single energy solution of this potential.¹⁰

We can determine some properties of this wavefunction:

¹⁰However, you can find that it is a solution for the potential. $V(x) = \frac{\hbar^2}{mL^2} \left[5 - \frac{L^2}{x(L-x)} \right] \quad \forall 0 \leq x \leq L$, a bizarre object, to be sure!

... Example of a composite state ...

$$\langle K \rangle = \int_0^L dx u^*(x) \left(\frac{-\hbar^2}{2m} \right) u(x)'' = \frac{5\hbar^2}{mL^2} \quad (5.102)$$

$$\langle x \rangle = \int_0^L dx u^*(x) x u(x) = \frac{L}{2} \quad (5.103)$$

$$\langle x^2 \rangle = \int_0^L dx u^*(x) x^2 u(x) = \frac{2L^2}{7} \quad (5.104)$$

$$\langle p \rangle = \int_0^L dx u^*(x) (-i\hbar) u'(x) = 0 \quad (5.105)$$

$$\langle p^2 \rangle = \int_0^L dx u^*(x) (-\hbar^2) u''(x) = \frac{10\hbar^2}{L^2} \quad (5.106)$$

$$\Delta p \Delta x = \sqrt{\frac{5}{14}} \hbar > \frac{\hbar}{2} \checkmark \sqrt{\frac{5}{14}} \approx 0.600 \quad (5.107)$$

... Example of a composite state ...

Let's work out the “power spectrum”, the a_n s for this wavefunction.

But, before we do that, it is time to workout a more compact notation ...

The Dirac bra-ket notation.

Dirac's bra-ket notation

- $|n\rangle$ or just $n\rangle$, stands for $u_n(x)$, the n 'th eigenfunction that relates to some binding potential under discussion. This object is called the “ket”.
- $\langle n|$ and $\langle n$ are each called a “bra”. A bra is the complex conjugate of a “ket”. That is, $\langle n|$ is identified as $u_n^*(x)$.
- $\langle n|\mathcal{O}|n\rangle$ is call the bra-ket of $\mathcal{O}$, or sometimes just “braket- $\mathcal{O}$ ”. Recall that $\mathcal{O}$ stands for some quantum mechanics operator (a function, a differential operator, or something even more exotic) that operates on the ket. What the braket stands for is why it was invented ... to save a lot of writing!

$$\langle n|\mathcal{O}|n\rangle = \int dx u^*(x)\mathcal{O}u(x) . \quad (5.108)$$

The integral extends over the range of the potential that binds the wavefunctions, and the operator is considered to operate to the right.

- When quantum numbers do not appear, the bra and ket simply stand for a wavefunction of any sort, whose meaning is clear from the discussion. For example, $\langle u|\mathcal{K}|u\rangle$ could mean the right hand side of (5.102).

There are other subtleties of this notation that will be revealed as needed. For now, we have enough to get through the near future.

Dirac's bra-ket notation examples

- $\langle n|1|m\rangle$, usually abbreviated $\langle n|m\rangle$ is the statement of orthonormality. That is:

$$\langle n|m\rangle = \int dx u_n^*(x)u_m(x) = \delta_{nm} . \quad (5.109)$$

- We could have save a lot of writing by rewriting (5.102) — (5.106) as:

$$\begin{aligned}\langle K\rangle &= \langle u|\mathcal{K}|u\rangle = \frac{5\hbar^2}{mL^2} \\ \langle x\rangle &= \langle u|x|u\rangle = \frac{L}{2} \\ \langle x^2\rangle &= \langle u|x^2|u\rangle = \frac{2L^2}{7} \\ \langle p\rangle &= \langle u|p|u\rangle = 0 \\ \langle p^2\rangle &= \langle u|p^2|u\rangle = \frac{10\hbar^2}{L^2}\end{aligned}$$

... Example of a composite state ...

Now let's do the power spectrum for the wavefunction $u(x)$ given in (5.101) for the infinite well potential (5.89).

$$\begin{aligned} u &= \sum_{n=0}^{\infty} a_n |n\rangle \\ \langle m|u\rangle &= \sum_{n=0}^{\infty} a_n \langle m|n\rangle \quad \text{combining (5.99) and (5.101)} \\ \langle m|u\rangle &= \sum_{n=0}^{\infty} a_n \delta_{mn} \quad \text{using (5.109)} \\ a_m &= \langle m|u\rangle \end{aligned} \tag{5.110}$$

It's not all magic! We actually have to do the integral implied by (5.110)!

... Example of a composite state ...

From (5.91) — (5.93) and (5.101)

$$\begin{aligned}a_n &= \int_0^L dx \left(\sqrt{\frac{2}{L}} \right) \sin \left[\left(\frac{(n+1)\pi}{L} \right) x \right] \left(\sqrt{\frac{30}{L^5}} \right) x(L-x) \\&= \frac{\sqrt{60}}{L^3} \int_0^L dx \sin \left[\left(\frac{(n+1)\pi}{L} \right) x \right] x(L-x) \quad [\text{gathering terms}] \\&= \sqrt{60} \int_0^1 dx \sin [(n+1)\pi z] z(1-z) \quad [z = x/L] \\&= \frac{2\sqrt{60}[1 - (-1)^{n+1}]}{(n+1)^3\pi^3} \quad \text{Mathematica!}\end{aligned} \tag{5.111}$$

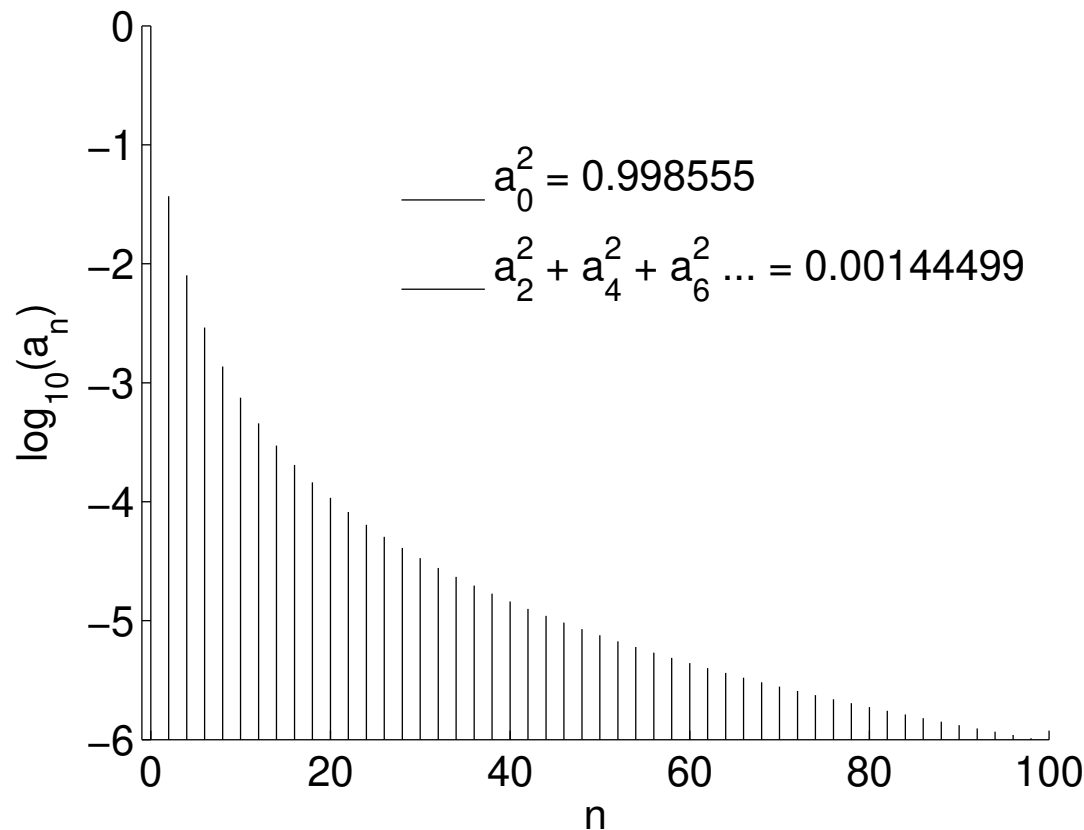
that may also be written:

$$\begin{aligned}a_n &= \frac{8\sqrt{15}}{(n+1)^3\pi^3} \quad \text{when } n \text{ is even} \\&= 0 \quad \text{when } n \text{ is odd}\end{aligned} \tag{5.112}$$

The power spectrum is plotted on the next page.

... Example of a composite state ...

The power spectrum is shown below, for even ns , starting with 0. Recall that the odd ns do not contribute.

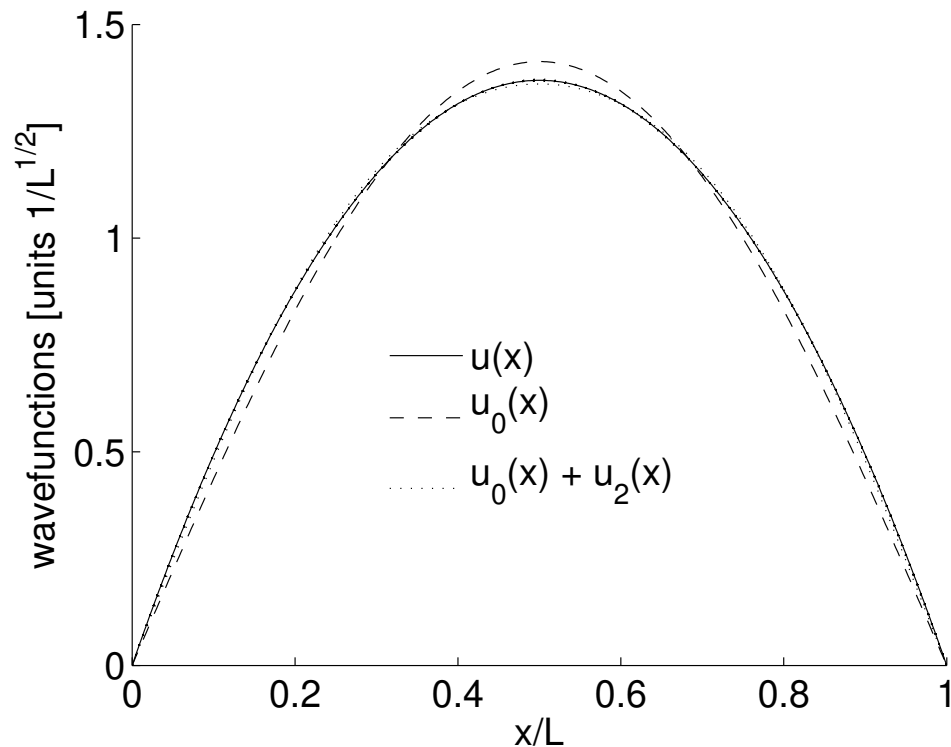


Note that most of the amplitude of the composite is in the ground state, in this example, all but about 0.15% of the probability density.

The reason why is given on the next page.

... Example of a composite state ...

The wavefunction $u(x)$ and its eigenvalue composition ... are shown below.



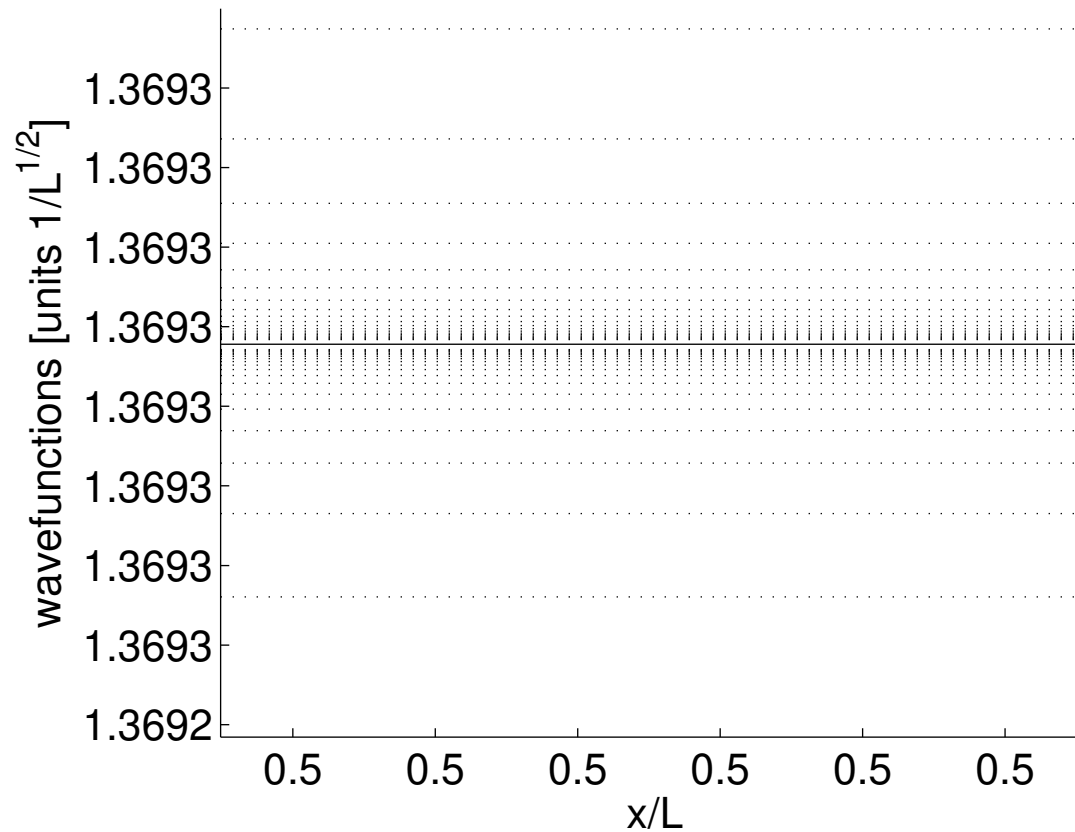
What is actually plotted here are 52 separate plots:

$u(x)$, $u_0(x)$, $u_0(x) + u_1(x)$, $\dots$, $\sum_{n=0}^{50} u_n(x)$. However, only the first 3 are visible; the rest are hidden by the $u(x)$ line. That's how quickly the convergence happens in this example.

The next page shows a zoom-in of the peak region.

... Example of a composite state ...

Zooming into the peak region to show how the composite converges.



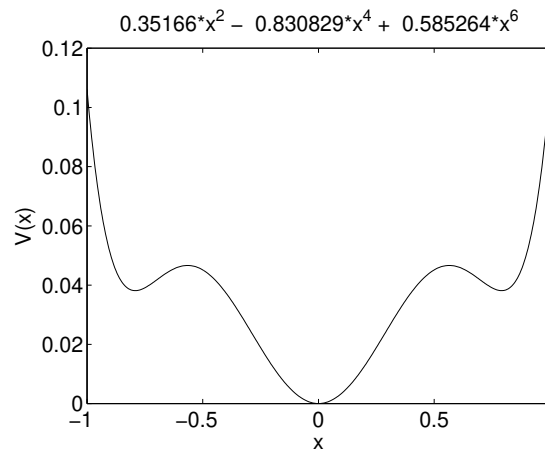
Parity ...

Fact Every symmetry in Nature results in a conserved quantity, expressed by a quantum number, and something that can be measured.

“Parity” results from the inversion of spatial coordinates, $x \rightleftharpoons -x$

How does this work?

Consider a potential that is arbitrary, except for the fact that it is symmetrical, that is, $V(-x) = V(x)$. For example, the randomly-generated potential:



that is explicitly symmetric since it is a function of x^2 only.

... Parity ...

The time-independent Schrödinger equation is:

$$\left(\frac{-\hbar^2}{2m}\right) \frac{d^2 u(x)}{dx^2} + V(x)u(x) = Eu(x) . \quad (5.113)$$

Let Π represent the parity operator, the operator that inverts space.

That is, if $f(x)$ is any function of x ,

$$\Pi[f(x)] = f(-x) . \quad (5.114)$$

Applying Π to the components of (5.113):

$$\begin{aligned} \Pi[u(x)] &= u(-x) \\ \Pi\left[\frac{d^2}{dx^2}\right] &= \frac{d^2}{dx^2} \end{aligned}$$

... Parity ...

Applying Π to (5.113) directly:

$$\begin{aligned}\Pi \left[\left(\frac{-\hbar^2}{2m} \right) \frac{d^2 u(x)}{dx^2} \right] + \Pi [V(x)u(x)] &= \Pi [Eu(x)] \\ \left(\frac{-\hbar^2}{2m} \right) \frac{d^2 u(-x)}{dx^2} + V(x)u(-x) &= Eu(-x) \\ \Pi^2 \left[\left(\frac{-\hbar^2}{2m} \right) \frac{d^2 u(x)}{dx^2} \right] + \Pi^2 [V(x)u(x)] &= \Pi^2 [Eu(x)] \\ \left(\frac{-\hbar^2}{2m} \right) \frac{d^2 u(x)}{dx^2} + V(x)u(x) &= \Pi^2 [Eu(x)] = Eu(x)\end{aligned}\tag{5.115}$$

(5.115) $\Rightarrow$

$$\Pi^2[u(x)] = u(x) = p^2 u(x) ,\tag{5.116}$$

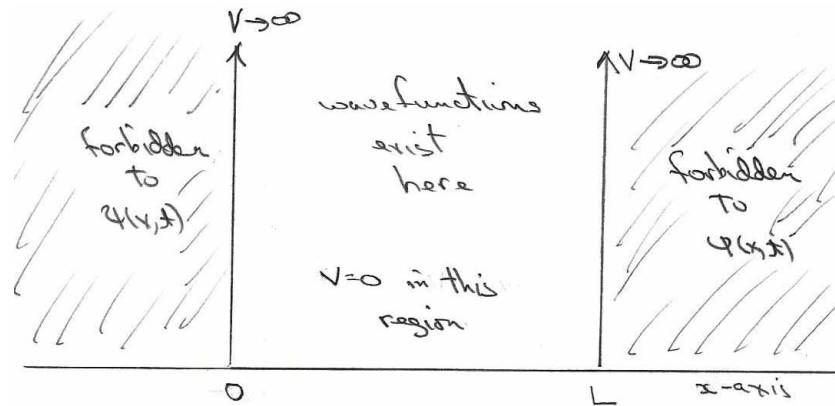
that is interpreted to mean that parity is a conserved quantity with quantum number p . (5.116) shows that the numerical values of this quantum number, p , can only have one of two possible values, $+1$ (positive parity), and -1 (negative parity).

... Parity ...

So, if $V(-x) = V(x)$, that is, the potential is a symmetric function of x , the solutions must divide themselves into positive parity eigenfunctions, for which $\Pi[u(x)] = u(x)$, and negative parity eigenstates, for which $\Pi[u(x)] = u(-x)$!

There were hints of this in the one example we worked out. Recall the infinite square well, where:

$$\begin{aligned} V(x) &= 0 \quad \text{for } 0 \leq x \leq L \\ &= \infty \quad \text{otherwise} \end{aligned}$$

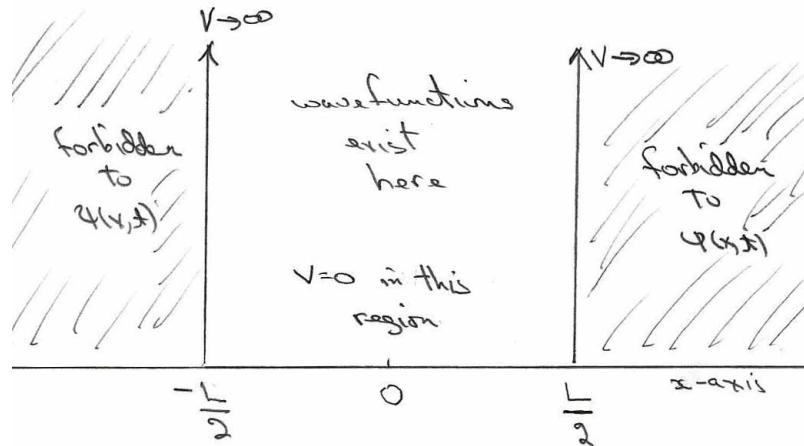


... Parity ...

We'll call this the “hidden parity” case, which we found the solution for given in (5.91)—(5.94):

$$\begin{aligned}u_n(x) &= \sqrt{\frac{2}{L}} \sin k_n x , \\n &= 0, 1, 2, \dots \infty , \\k_n &= \frac{(n+1)\pi}{L} , \\E_n &= \frac{(n+1)^2 \hbar^2 \pi^2}{2mL^2} .\end{aligned}$$

We will now make an “explicit-parity” solution by shifting the origin of our coordinate system. Nothing changes by the wavefunctions:



... Parity ...

$$u_n(x) = \sqrt{\frac{2}{L}} \sin [k_n(x + L/2)] , \quad [\text{potential is now symmetric}] \quad (5.117)$$

$$n = 0, 1, 2, \dots \infty , \quad [\text{same quantum numbers}] \quad (5.118)$$

$$k_n = \frac{(n + 1)\pi}{L} , \quad [\text{same discrete } k\text{'s}] \quad (5.119)$$

$$E_n = \frac{(n + 1)^2 \hbar^2 \pi^2}{2mL^2} . \quad [\text{same energy "eigenvalues"}] \quad (5.120)$$

The only change is in $u_n(x)$, shifted by $L/2$.

Using trigonometric identities, (5.117) can be cast into a form that explicitly expresses the parity:

$$u_n(x) = \sqrt{\frac{2}{L}} [\cos ([n + 1]\pi x/L) \sin ([n + 1]\pi/2) + \sin ([n + 1]\pi x/L) \cos ([n + 1]\pi/2)] .$$

Note that the symmetric term, $\cos ([n + 1]\pi x/L)$ is 0 when n is odd, because of the $\sin ([n + 1]\pi/2)$ term. These are the $p = +1$ or even-parity solutions, for $n = 0, 2, 4, \dots$ Similarly, the antisymmetric term, $\sin ([n + 1]\pi x/L)$ is 0 when n is even, because of the $\cos ([n + 1]\pi/2)$ term.

... Parity ...

Therefore, the explicit-parity solution is:

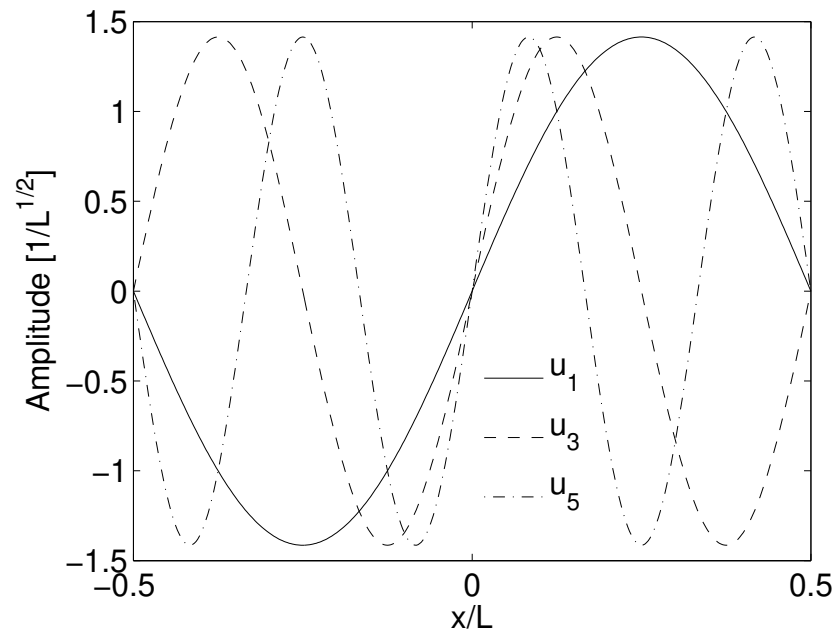
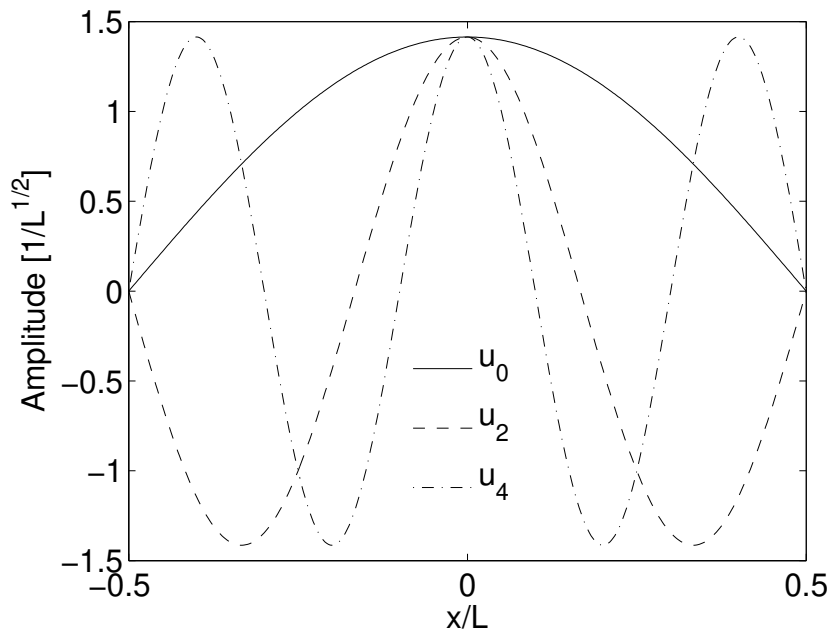
$$u_n(x) = (\sqrt{2/L}) \cos([n+1]\pi x/L), \quad [\text{even parity, even } n \text{ only}] \quad (5.121)$$

$$u_n(x) = (\sqrt{2/L}) \sin([n+1]\pi x/L), \quad [\text{odd parity, odd } n \text{ only}] \quad (5.122)$$

$$n = 0, 1, 2, \dots \infty, \quad [\text{same quantum numbers}] \quad (5.123)$$

$$k_n = \frac{(n+1)\pi}{L}, \quad [\text{same discrete } k\text{'s}] \quad (5.124)$$

$$E_n = \frac{(n+1)^2 \hbar^2 \pi^2}{2mL^2}. \quad [\text{same energy "eigenvalues"}] \quad (5.125)$$



Why is parity important? ...

- Parity is a conserved quantum number.
- It is something we can measure.
- Nature expresses its wavefunctions this way.
- Nuclei in their ground state will have even or odd parity.
- Making parity explicit can save you a lot of calculation. Example...

Recall our example of the composite wave in the asymmetric potential from (5.101):

$$u(x) = \psi(x, 0) = \sqrt{\frac{30}{L^5}} x(L - x)$$

In the symmetric potential, we shift by $-L/2$ to get:

$$u(x) = \sqrt{\frac{30}{L^5}} (x^2 - L^2/4) . \quad (5.126)$$

This wavefunction is symmetric. Therefore we may immediately write:

$$u(x) = \sum_{\substack{n=0 \\ \text{even } n}}^{\infty} a_n u_n(x) , \quad (5.127)$$

... Why is parity important?...

- Using parity, you can immediately tell, in many case, that the expectation value of an operator is zero. That is:

$\langle m|\mathcal{O}|n\rangle = 0$ if $\mathcal{O}$ has even parity, and $m\rangle$ and $n\rangle$ have different parities.

$\langle m|\mathcal{O}|n\rangle = 0$ if $\mathcal{O}$ has odd parity, and $m\rangle$ and $n\rangle$ have the same parities.

e.g. without calculation, you can say:

$$\langle 5|x^3|3\rangle = 0,$$

$$\langle 18|x^5|2\rangle = 0,$$

$$\langle 4|x^2|3\rangle = 0 \text{ and}$$

$$\langle 1027|x^4|1026\rangle = 0.$$

On to a new topic ... transition rates.

Transition rates ...

Up to this point in the course, we have eigenfunctions and composite states, and understand them to mean that a particle occupies this level, or simultaneously a set of levels (in the case of a composite wavefunction).

However, we know that Nature likes to reduce all systems, classical or otherwise, to a state of minimum energy. Now we discuss how transitions to lower (in some examples higher) levels occur.

The relative transition rate, in Quantum Mechanics, from an initial state “ i ” to a final state “ f ”, is given by:

$$\lambda_{i \rightarrow f} \propto |\langle f | \mathcal{O} | i \rangle|^2 . \quad (5.128)$$

This construct is sometimes called the “transition matrix element”. It has an interesting, physical interpretation.

The operator, $\mathcal{O}$ operates on $i\rangle$, modifying it so that parts of the modified $i\rangle$, that is $\mathcal{O}|i\rangle$, may or may not overlap with $\langle f$. If it does, the degree of overlap affects the transition rate. No overlap, no transition. Greater overlap, faster transition rate.

... Transition rates ...

Using (5.128), we can compare the transition rates between levels.

Example:

Assume that $\mathcal{O} = x$. (This is very close to the γ -transition “dipole” operator.)

For the infinite well potential, we started discussing with (5.101), what is:

$$r = \frac{\lambda_{2 \rightarrow 0}}{\lambda_{1 \rightarrow 0}} \quad ; \quad \frac{\lambda_{3 \rightarrow 0}}{\lambda_{1 \rightarrow 0}} \quad ; \quad \frac{\lambda_{4 \rightarrow 0}}{\lambda_{1 \rightarrow 0}} \quad ; \quad \frac{\lambda_{5 \rightarrow 0}}{\lambda_{1 \rightarrow 0}}$$

After some calculation, one can show:

i	1	2	3	4	5
$r_i = \frac{\lambda_{i \rightarrow 0}}{\lambda_{1 \rightarrow 0}}$	1	0	0.0064	0	0.00049

$$r_3/r_5 \approx 13.2.$$

The zeros in the table above arise from parity arguments.

... Transition rates

Details of the calculations

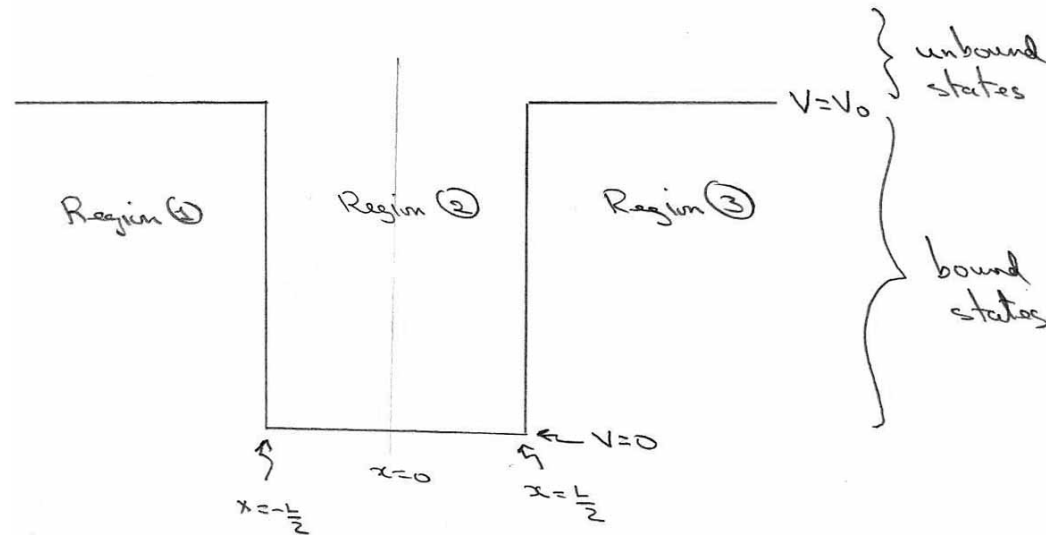
$$\begin{aligned} r_3 &= \frac{\lambda_{3 \rightarrow 0}}{\lambda_{1 \rightarrow 0}} \\ &= \frac{\left| \int_{-L/2}^{L/2} dx \left(\sqrt{2/L} \right) \cos(\pi x/L) x \left(\sqrt{2/L} \right) \sin(4\pi x/L) \right|^2}{\left| \int_{-L/2}^{L/2} dx \left(\sqrt{2/L} \right) \cos(\pi x/L) x \left(\sqrt{2/L} \right) \sin(2\pi x/L) \right|^2} \\ &= \frac{\left| \int_{-\pi/2}^{\pi/2} dz z \cos(z) \sin(4z) \right|^2}{\left| \int_{-\pi/2}^{\pi/2} dz z \cos(z) \sin(2z) \right|^2} \\ &= 4/625 \approx 0.0064 \quad [\text{Thanks to Mathematica!}] \end{aligned}$$

Replacing the “4” above by “6” gives:

$$r_5 = 729/1500625 \approx 0.00049$$

Bound states of the 1D finite well potential ...

So far, we have only considered the unbound states of the 1D finite well potential. Now we consider the bound states.¹¹



$$\begin{aligned} V(x) &= V_0 \quad \text{for } x < -L/2 \text{ [Region 1]} \\ &= 0 \quad \text{for } -L/2 < x < L/2 \text{ [Region 2]} \\ &= V_0 \quad \text{for } x > L/2 \text{ [Region 3]} \end{aligned} \tag{5.129}$$

The Schrödinger equation for this potential: is

$$\left(\frac{-\hbar^2}{2m} \right) \frac{d^2 u(x)}{dx^2} + V(x)u(x) = Eu(x) . \tag{5.130}$$

¹¹This derivation is the start of our understanding of the wave functions of the nucleus. It also begs the question: How do neutrons and protons form this potential? We will have to wait for NERS 312 to answer that question.

... Bound states of the 1D finite well potential ...

$$(5.130) \times \left(\frac{-2m}{\hbar^2} \right) \Rightarrow$$

$$u''(x) + k^2 u(x) = 0 \quad [\text{Region 2, inside the well}], \quad (5.131)$$

where

$$k^2 = \frac{2mE}{\hbar^2}, \quad (5.132)$$

and

$$u''(x) - K^2 u(x) = 0 \quad [\text{Regions 1 and 3, outside the well}], \quad (5.133)$$

where

$$K^2 = \frac{2m(V_0 - E)}{\hbar^2}, \quad (5.134)$$

... Bound states of the 1D finite well potential ...

Let's start with the outside solution first.

The solution for region 1 and 3 is of the form:

$$u(x) = Ae^{Kx} + Ce^{-Kx} . \quad (5.135)$$

However, if we are to have a normalizable solution for region 1, C must be 0 there. Similarly, $A = 0$ for region 3.

Inside the well, region 2, the solution is of the form:

$$u(x) = B \begin{pmatrix} \cos kx \\ \sin kx \end{pmatrix} , \quad (5.136)$$

where we consider two solutions simultaneously, the even and odd parity solutions, that we know, from our discussion on parity, is guaranteed, since we started with a symmetric potential.

... Bound states of the 1D finite well potential ...

Putting this all together:

$$u(x) = \begin{cases} u_1(x) = Ae^{Kx} & \text{for } x < -L/2 \\ u_2(x) = B \begin{pmatrix} \cos kx \\ \sin kx \end{pmatrix} & \text{for } -L/2 < x < L/2 \\ u_3(x) = Ce^{-Kx} & \text{for } x > L/2 \end{cases} \quad (5.137)$$

and

$$k^2 = \frac{2mE}{\hbar^2} \quad (5.138)$$

$$K^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad (5.139)$$

To complete the solution, we have to impose slope and value continuity at both boundaries, and then we have to normalize the solution.

Recall from our discussion of the infinite well, it was the boundary conditions that quantized the energies.

... Bound states of the 1D finite well potential ...

We shall start with the even parity states.

Consider the logarithmic derivative at the left boundary:

$$\begin{aligned}\frac{u_1'(-L/2)}{u_1(-L/2)} &= \frac{u_2'(-L/2)}{u_2(-L/2)} \Rightarrow \\ \frac{AKe^{-KL/2}}{Ae^{-KL/2}} &= \frac{Bk \sin kL/2}{B \cos kL/2} \Rightarrow \\ K &= k \tan kL/2\end{aligned}\tag{5.140}$$

Similarly for the odd parity states.

$$\begin{aligned}\frac{u_1'(-L/2)}{u_1(-L/2)} &= \frac{u_2'(-L/2)}{u_2(-L/2)} \Rightarrow \\ \frac{AKe^{-KL/2}}{Ae^{-KL/2}} &= \frac{-Bk \cos kL/2}{B \sin kL/2} \Rightarrow \\ K &= -k \cot kL/2\end{aligned}\tag{5.141}$$

... Bound states of the 1D finite well potential ...

The combination of $KL/2$ and $kL/2$ would appear so frequently, that we give them special names to save writing:

$$\alpha = kL/2 \quad (5.142)$$

$$\beta = KL/2 . \quad (5.143)$$

Recalling the definitions of k and K from (5.138) and (5.139), we see that:

$$\alpha^2 + \beta^2 = \frac{L^2}{4} \left(\frac{2mE}{\hbar^2} + \frac{2m(V_0 - E)}{\hbar^2} \right) = \frac{mV_0L^2}{2\hbar^2} , \quad (5.144)$$

which does not depend on energy, just the depth of the potential.

With this new compact notation, the quantization conditions are:

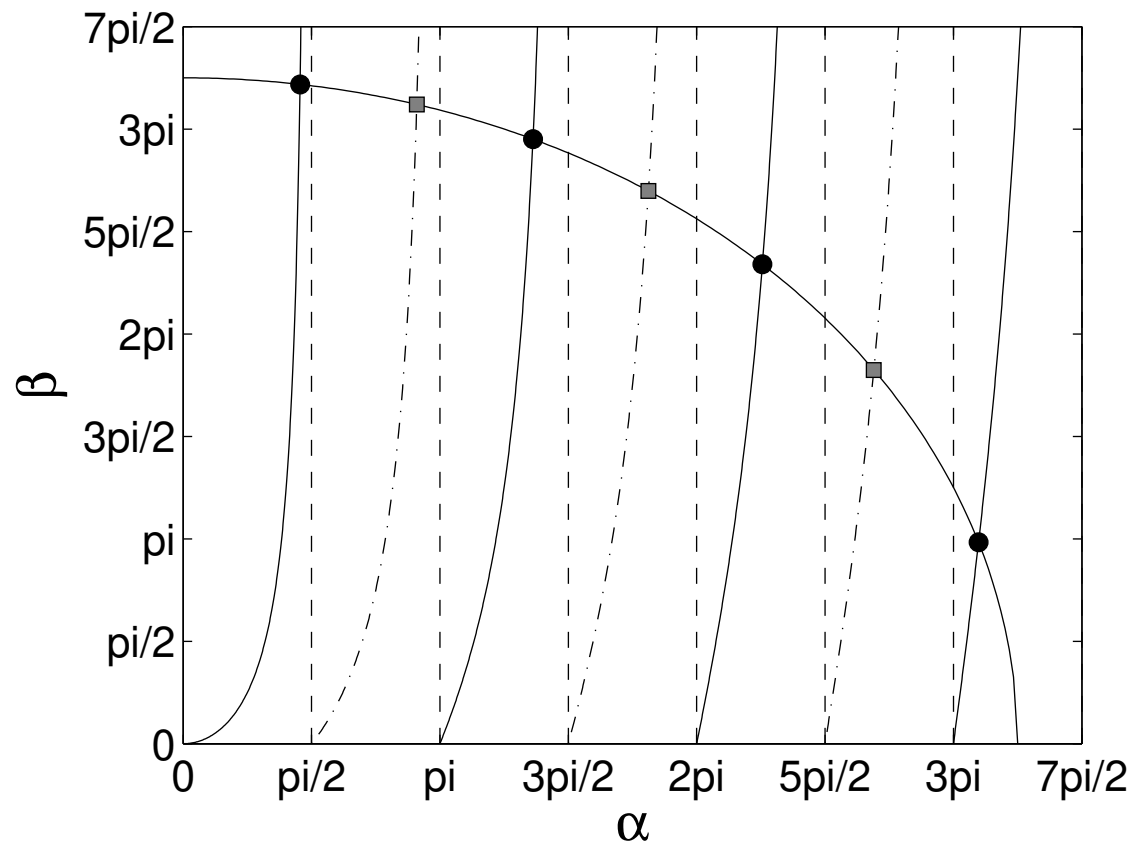
$$\beta = \alpha \tan \alpha \quad [\text{for the even-parity states}] \quad (5.145)$$

$$\beta = -\alpha \cot \alpha . \quad [\text{for the odd-parity states}] \quad (5.146)$$

... Bound states of the 1D finite well potential ...

Quantization conditions????? Really?????

Consider the following graph of the first few branches of $\beta = \alpha \tan \alpha$ and $\beta = -\alpha \cot \alpha$ as well as $\alpha^2 + \beta^2 = mV_0L^2/(2\hbar^2)$. (This example comes from Assignment 6.)



... Bound states of the 1D finite well potential ...

The intercepts of these graphs determine the quantized energies!

There are many things in play here:

- The curve from the upper left corner to the bottom right is the relationship:
 $\alpha^2 + \beta^2 = mV_0L^2/(2\hbar^2)$.
- The 4 near-vertical solid line curves are the first 4 branches of the relationship:
 $\beta = \alpha \tan \alpha$ (for even-parity states).
- The 3 near-vertical dot-dashed line curves are the first 3 branches of the relationship:
 $\beta = -\alpha \cot \alpha$ (for odd-parity states).
- The quantized energies for the even-parity states are obtained from the intercept of the $\beta = \alpha \tan \alpha$ curve with the $\alpha^2 + \beta^2 = mV_0L^2/(2\hbar^2)$ curve.
- The quantized energies for the odd-parity states are obtained from the intercept of the $\beta = -\alpha \cot \alpha$ curve with the $\alpha^2 + \beta^2 = mV_0L^2/(2\hbar^2)$ curve.
- In this graph, the quantized energies for a nucleon in a 40 MeV box potential are found for $L = 14.7$ fm.
- The quantized energies are: $E_0 = 0.785$, $E_1 = 3.13$, $E_2 = 7.03$, $E_3 = 12.4$, $E_4 = 19.3$, $E_5 = 27.4$, $E_6 = 36.3$ MeV.

... Bound states of the 1D finite well potential ...

These quantized energy states are found by a numerical procedure:

1. Find α_0 for $0 < \alpha_0 < \pi/2$.
 2. Do a numerical search for $0 = \sqrt{mV_0L^2/(2\hbar^2)} - \alpha_0^2 - \alpha_0 \tan \alpha_0$. once you have found α_0 , $E_0 = 2\alpha_0^2\hbar^2/(mL^2)$.
 3. Repeat for $\pi/2 < \alpha_1 < \pi$ using $0 = \sqrt{mV_0L^2/(2\hbar^2)} - \alpha_1^2 + \alpha_1 \cot \alpha_1$ and so on, for all the possible even and odd-parity states.
- Eventually, there are no more bound states, as the higher branches of the $\beta = \alpha \tan \alpha$ and $\beta = -\alpha \cot \alpha$ curves can no longer intercept the $\alpha^2 + \beta^2 = mV_0L^2/(2\hbar^2)$ circle.
 - A finite-depth potential can only bind a finite number of quantum states.
 - If $\frac{\hbar^2(N-1)^2\pi^2}{2mL^2} < V_0 < \frac{\hbar^2N^2\pi^2}{2mL^2}$, then exactly N states are bound. (5.147)
 - There is always at least one bound state, no matter how small V_0 is.
 - When $V_0 \longrightarrow \infty$, $E_n \longrightarrow \frac{\hbar^2(n+1)^2\pi^2}{2mL^2}$, the solutions for the infinite well (as expected).

... Bound states of the 1D finite well potential ...

Before we can declare this problem solved, we have to complete the calculation by finding the normalization constant for this potential.

From the boundary conditions, we may find:

$$u_1(-L/2) = u_2(-L/2) \Rightarrow$$

$$Ae^{-\beta} = B \begin{pmatrix} \cos \alpha \\ -\sin \alpha \end{pmatrix} \quad \text{and} \quad (5.148)$$

$$u_2(L/2) = u_3(L/2) \Rightarrow$$

$$Ce^{-\beta} = B \begin{pmatrix} \cos \alpha \\ \sin \alpha \end{pmatrix} \quad \therefore \quad (5.149)$$

$$A = Be^{\beta} \begin{pmatrix} \cos \alpha \\ -\sin \alpha \end{pmatrix} \quad \text{and} \quad (5.150)$$

$$C = Be^{\beta} \begin{pmatrix} \cos \alpha \\ \sin \alpha \end{pmatrix} \quad (5.151)$$

... Bound states of the 1D finite well potential ...

and the normalization integral is:

$$1 = |B|^2 \left\{ e^{2\beta} \left(\frac{\cos^2 \alpha}{\sin^2 \alpha} \right) \int_{-\infty}^{-L/2} dx e^{2Kx} + \int_{-L/2}^{L/2} dx \left(\frac{\cos^2 kx}{\sin^2 kx} \right) + e^{2\beta} \left(\frac{\cos^2 \alpha}{\sin^2 \alpha} \right) \int_{L/2}^{\infty} dx e^{-2Kx} \right\} \quad (5.152)$$

which, after a considerable amount of arithmetical calisthenics, turns out to be:

$$B = \sqrt{\frac{2}{L}} \sqrt{\frac{\beta}{1 + \beta}}. \quad (5.153)$$

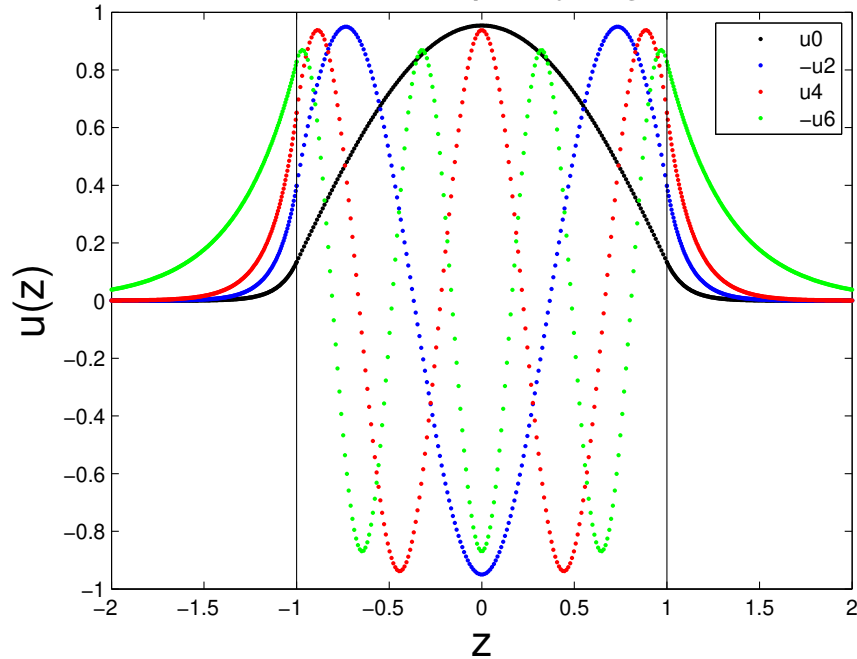
if we choose B to be a purely real number.

Note that the limit $V_0 \longrightarrow \infty$, $B \longrightarrow \sqrt{2/L}$, the normalization factor for the infinite well (as expected).

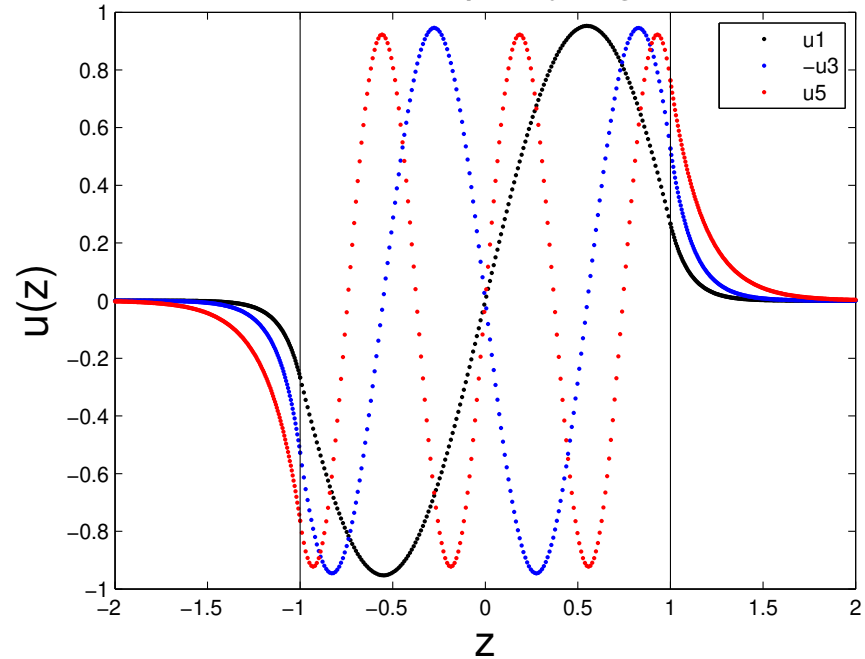
... Bound states of the 1D finite well potential ...

Here are some graphs of the numerical example for Assignment 6.

The 4 bound even-parity eigenfunctions



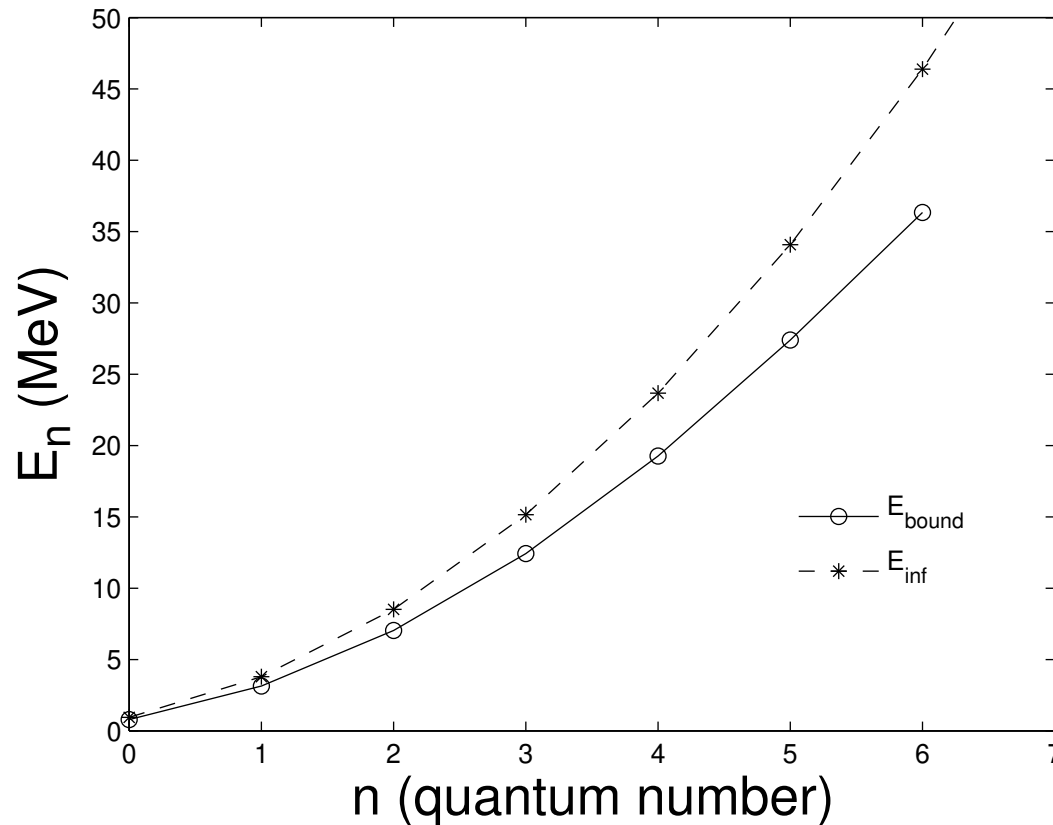
The 3 bound odd-parity eigenfunctions



... Bound states of the 1D finite well potential ...

This graph also uses the data of Assignment 6, but also shows the first 7 infinite well energies.

Comparison of finite vs. ∞ well discrete energies



The harmonic potential $V_h(x) = \frac{1}{2}kx^2$ in Quantum Mechanics ...

Why is the harmonic potential important in Quantum Mechanics?

- The general solution to the time-independent SE, namely:

$$\left(\frac{-\hbar^2}{2m}\right) \frac{d^2u(x)}{dx^2} + V(x)u(x) = Eu(x) , \quad (5.154)$$

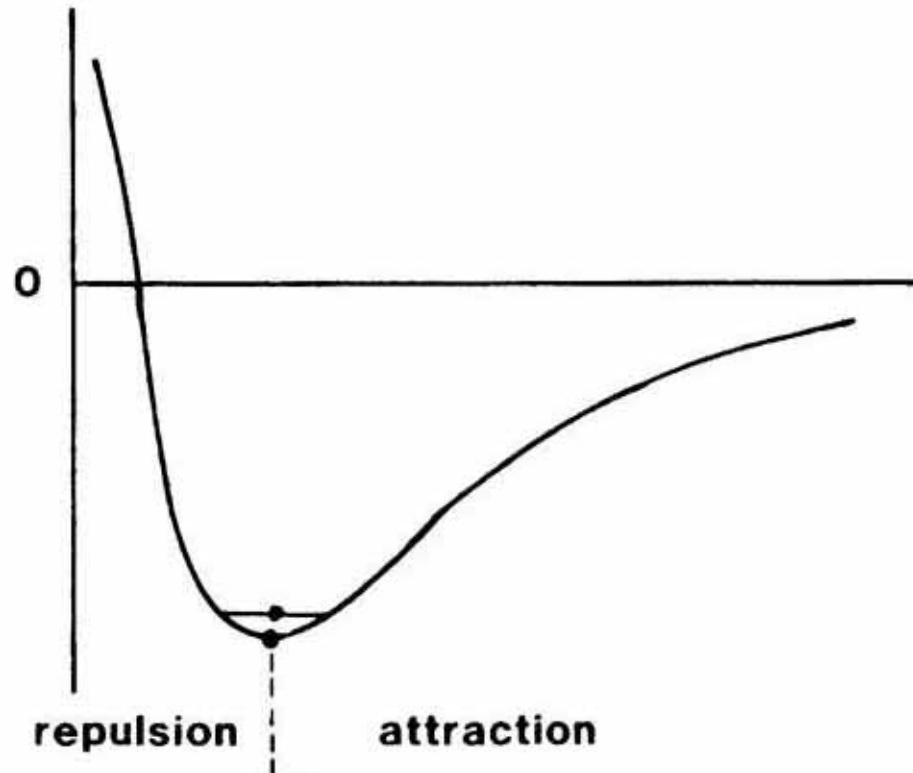
is known analytically, for only a few special cases.

- In general, the solutions must be worked out numerically.
- Sometimes, you are only interested in the first few states of a binding potential, E_0 , the ground state, E_1 , the first excited state, and so on.
- It can be shown that the first few low-lying states can be estimated by doing a fit of the harmonic potential, to an arbitrary, binding potential.

Here is the demonstration:

... The harmonic potential in Quantum Mechanics ...

Consider a binding potential, such as in this schematic representation¹² of the potential energy, $V(x)$, for two adjacent atoms as a function of internuclear separation, r .



In the vicinity of the minimum, x_0 , do a Taylor expansion of the form:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \mathcal{O}[(x - x_0)^3] . \quad (5.155)$$

... The harmonic potential in Quantum Mechanics ...

The $V'(x_0)$ denotes the derivative of $V(x)$ with respect to x , evaluated at x_0 and $V''(x_0)$ the double derivative of $V(x)$ with respect to x , evaluated at x_0 .

$$V_h = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 . \quad (5.156)$$

The first derivative, $V'(x_0) = 0$ at the minimum, and with the identification of $V''(x_0)$ as the spring constant, k , and $V(x_0) = V_0$ as the minimum we have identified the harmonic potential approximation to $V(x)$.

$$V_h = V_0 + \frac{1}{2}k(x - x_0)^2 . \quad (5.157)$$

The quantum mechanical solution of this is well known, and we shall describe it soon.

The major result of the quantum-mechanical analysis is a full description of the wavefunctions as well as the energy quantization:

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (5.158)$$

$$n = 0, 1, 2 \dots \quad (5.159)$$

$$\omega = \sqrt{\frac{k}{m}} . \quad (5.160)$$

... The harmonic potential in Quantum Mechanics ...

Only a few potentials in the Schrödinger equation have been completely characterized in terms of wavefunctions and energy levels.

Most $V(x)$'s have not. However, before resorting to some numerical work to characterize the solutions, performing the harmonic approximation gives one the chance of at least approximating the first few lowest bound states, as well as their wavefunctions.

An illustration is in order ... the Morse interatomic force.

The Morse potential is given by:

$$V(x) = V_0(1 - e^{-a(x-x_0)})^2 - V_0 , \quad (5.161)$$

where the parameter a controls the width of the potential.

It is easily determined that:

$$V(x_0) = -V_0 \quad (5.162)$$

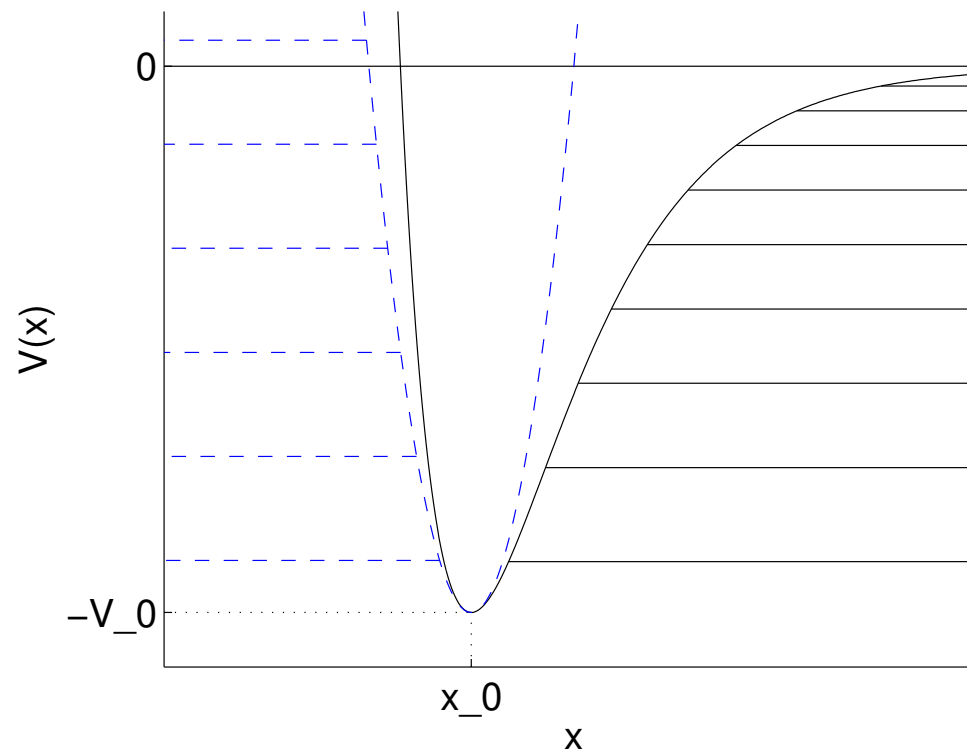
$$V'(x_0) = 0 \quad (5.163)$$

$$k = 2V_0a^2 . \quad (5.164)$$

... The harmonic potential in Quantum Mechanics ...

The Morse potential is shown in the solid black curve, similar in shape to the schematic on the near (5.155).

The horizontal solid lines are the ground state and the first 8 excited states of the Morse potential.

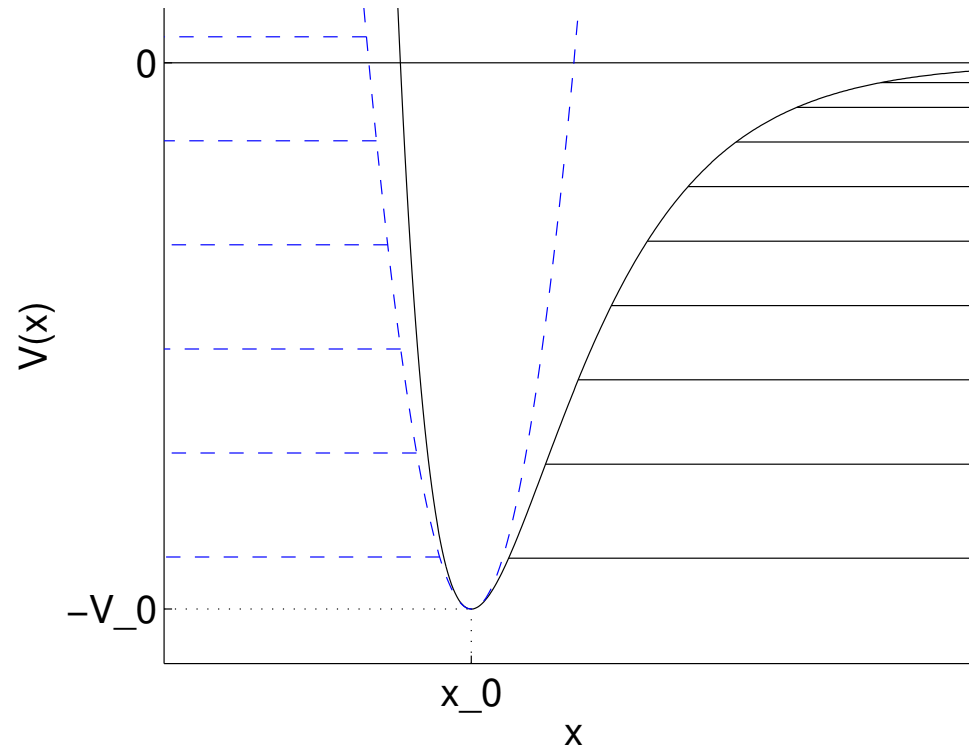


... The harmonic potential in Quantum Mechanics ...

The Morse potential has the following energy levels:

$$E_n = \hbar\omega (n + 1/2) - \frac{[\hbar\omega (n + 1/2)]^2}{4V_0} . \quad (5.165)$$

The dashed lines represent the harmonic approximation. The first few energy levels of the harmonic approximation are quite good, but then it deteriorates for higher excitation levels.

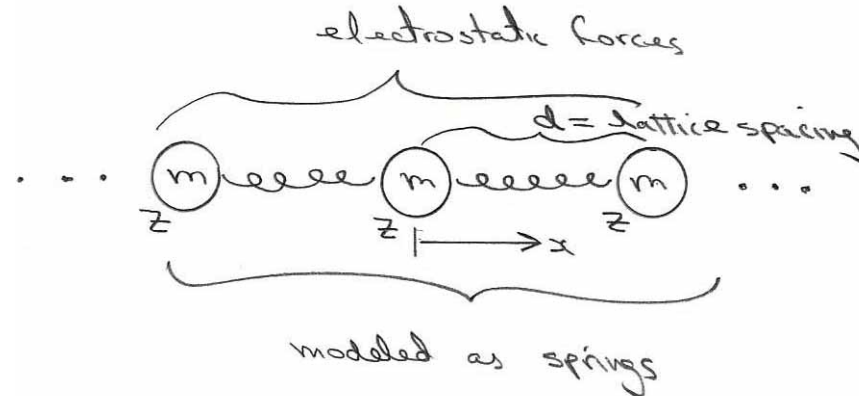


... The harmonic potential in Quantum Mechanics ...

Another example: Vibrations in a metal crystal

The atoms in crystals are held together by attractive electrostatic forces.

Consider the following model for a 1D crystal, where d is the lattice spacing. We are considering the atom near its equilibrium position, $x_0 = 0$.



... The harmonic potential in Quantum Mechanics ...

This potential, and its harmonic approximation are given by;

$$V(x) = \frac{Z^2}{4\pi\epsilon_0} \left[\frac{1}{d+x} + \frac{1}{d-x} \right] \quad (5.166)$$

$$V_0 = \frac{Z^2}{2\pi\epsilon_0 d} \quad (5.167)$$

$$V'(x) = \frac{Z^2}{4\pi\epsilon_0} \left[\frac{1}{(d+x)^2} - \frac{1}{(d-x)^2} \right] \quad (5.168)$$

$$V'(0) = 0 \quad (5.169)$$

$$V''(x) = \frac{Z^2}{4\pi\epsilon_0} \left[\frac{2}{(d+x)^3} + \frac{2}{(d-x)^3} \right] \quad (5.170)$$

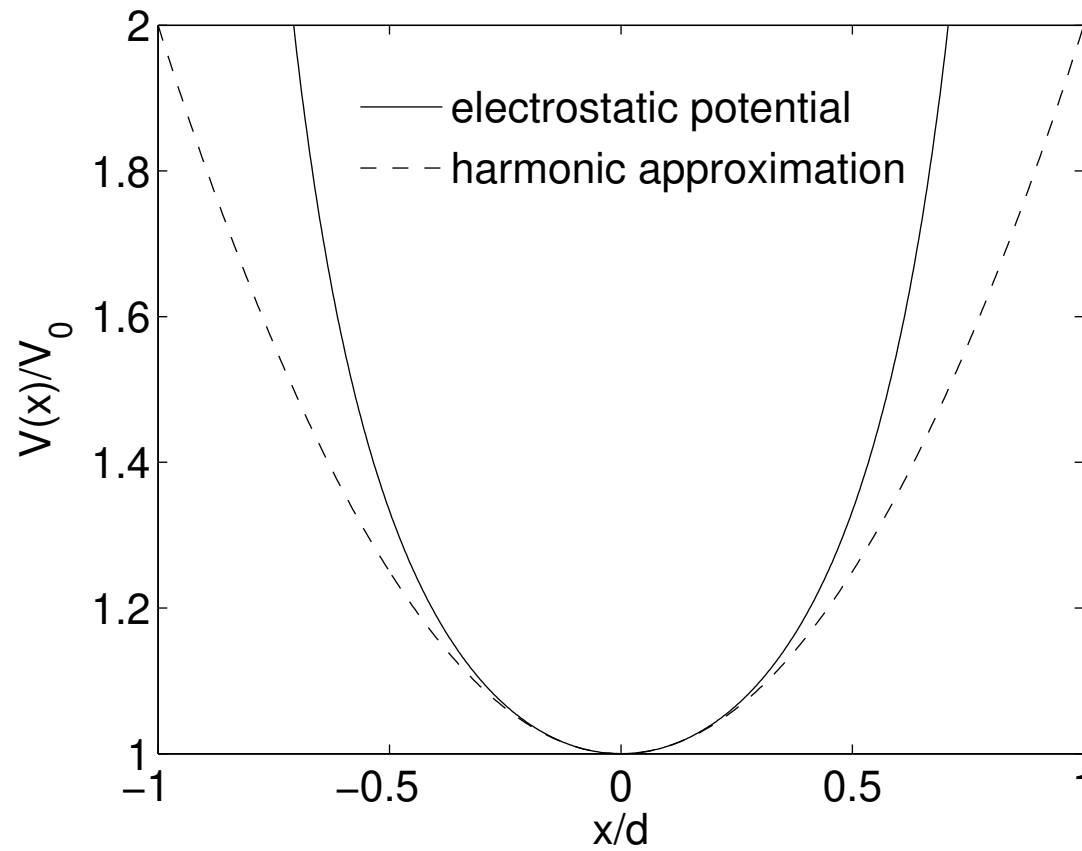
$$k = \frac{Z^2}{\pi\epsilon_0 d^3} \quad [\text{Since } k = V''(0)] \quad (5.171)$$

Therefore, the harmonic approximation is given by

$$V_h(x) = \frac{Z^2}{2\pi\epsilon_0 d} + \frac{1}{2} \frac{Z^2}{\pi\epsilon_0 d^3} x^2. \quad (5.172)$$

A graphical comparison is given on the next page.

... The harmonic potential in Quantum Mechanics ...



The QM solution of the harmonic oscillator ...

It starts with the time-independent SE with the harmonic potential, namely:

$$\frac{-\hbar^2}{2m}u''(x) + \frac{1}{2}kx^2u(x) = Eu(x) , \quad (5.173)$$

Which can be found by the Frobenius method.¹³ After considerable work ...

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (5.174)$$

$$n = 0[\text{the ground state}], 1, 2 \dots \quad (5.175)$$

$$\omega^2 = \frac{k}{m} \quad (5.176)$$

$$u_n(x) = \left(\frac{\alpha}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{(-[\alpha x]^2/2)} H_n(\alpha x) \quad (5.177)$$

[The H_n are the “Hermite polynomials”]

$$\alpha = \left(\frac{mk}{\hbar^2} \right)^{1/4} = \left(\frac{m\omega}{\hbar} \right)^{1/2} \quad (5.178)$$

$$\langle n|m \rangle = \delta_{mn} \quad (5.179)$$

¹³More information can be found at:

Wikipedia: http://en.wikipedia.org/wiki/Frobenius_method (general discussion)

Online supplemental notes: <http://www.umich.edu/~ners311/CourseLibrary/Harmonic%20Potential.pdf> (Frobenius applied to (5.173) — 27 pages!)

You can also google: “Hermite polynomials”, “Charles Hermite” (1822-1901), “Ferdinand Georg Frobenius” (1849-1917)

...The QM solution of the harmonic oscillator ...

Note that:

$$\begin{aligned}\langle n|m \rangle &= \int_{-\infty}^{\infty} dx \left(\frac{\alpha}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{(-[\alpha x]^2/2)} H_n(\alpha x) \left(\frac{\alpha}{2^m m! \sqrt{\pi}} \right)^{1/2} e^{(-[\alpha x]^2/2)} H_m(\alpha x) \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{1}{2^{(n+m)} n! m!} \right)^{1/2} \int_{-\infty}^{\infty} dz e^{-z^2} H_n(z) H_m(z) \\ &\quad [z = \alpha x, \text{ and some reorganization}] \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{1}{2^n n!} \right) \int_{-\infty}^{\infty} dz e^{-z^2} H_n^2(z) = 1 \quad [\text{for } n = m] \\ &= 0 \quad [\text{for } n \neq m]\end{aligned}\tag{5.180}$$

These integrals are easily checked using Mathematica with the code:

```
n = any integer >= 0
m = any integer >= 0
Sqrt[(1/2^n)*(1/n!)]*Sqrt[(1/2^m)*(1/m!)]*(1/Sqrt[Pi])*
Integrate[HermiteH[n,z]HermiteH[m,z] Exp[-z^2],{z,-Infinity,Infinity}]}}
```

... The QM solution of the harmonic oscillator ...

One can also calculate (see the supplemental notes) that for any n ,

$$\langle n|V|n\rangle = \langle n|K|n\rangle = E_n/2 = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right) , \quad (5.181)$$

where $\mathcal{V} \equiv kx^2/2$ is the potential energy “operator” and $\mathcal{K}$ is the kinetic energy operator. This result agrees with the classical result we found at the start of this chapter.

Properties of the H_n 's

The explicit forms of the of the Hermite polynomials are:

$$\begin{aligned} H_0(z) &= 1 \\ H_1(z) &= 2z \\ H_2(z) &= 4z^2 - 2 \\ H_3(z) &= 8z^3 - 12z \\ H_4(z) &= 16z^4 - 48z^2 + 12 \\ &\vdots \end{aligned} \quad (5.182)$$

Note that $H_n(z)$ always starts with a $(2z)^n$.

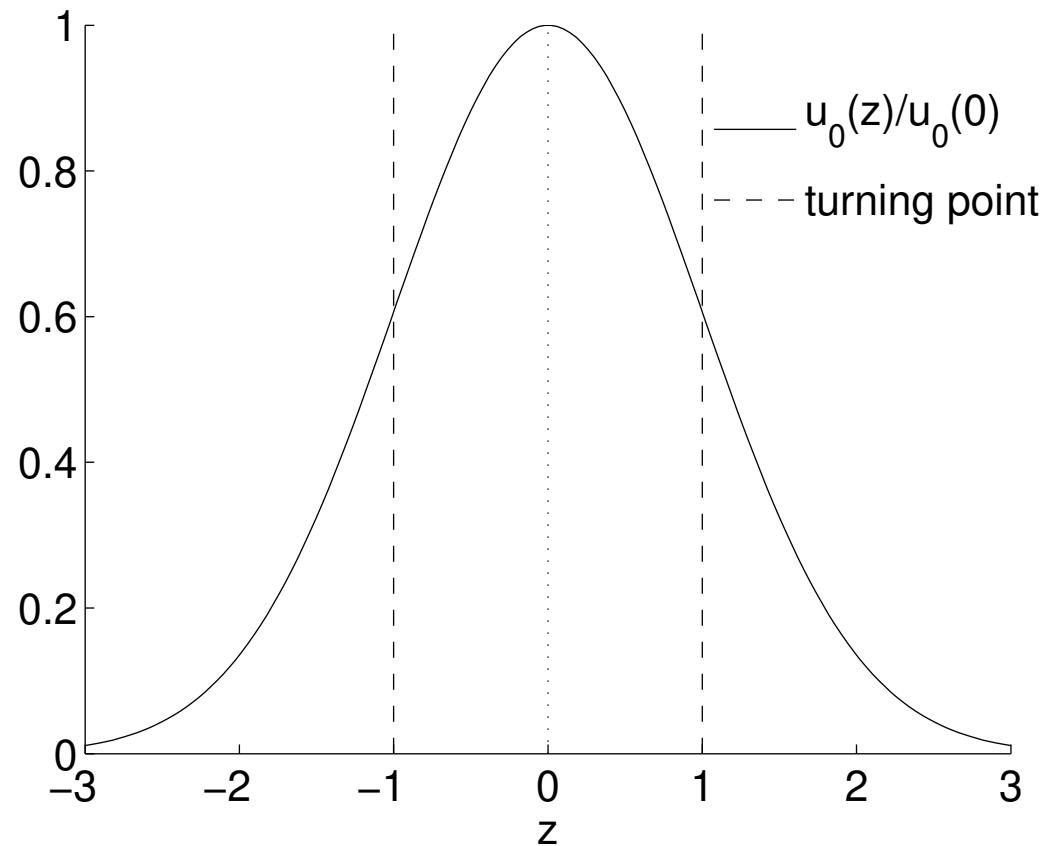
... The QM solution of the harmonic oscillator ...

Recursion relationship to obtain the H_n 's

$$H_{n+1}(z) = 2zH_n(z) - 2nH_{n-1}(z) \quad \text{for } n \geq 1 \quad (5.183)$$

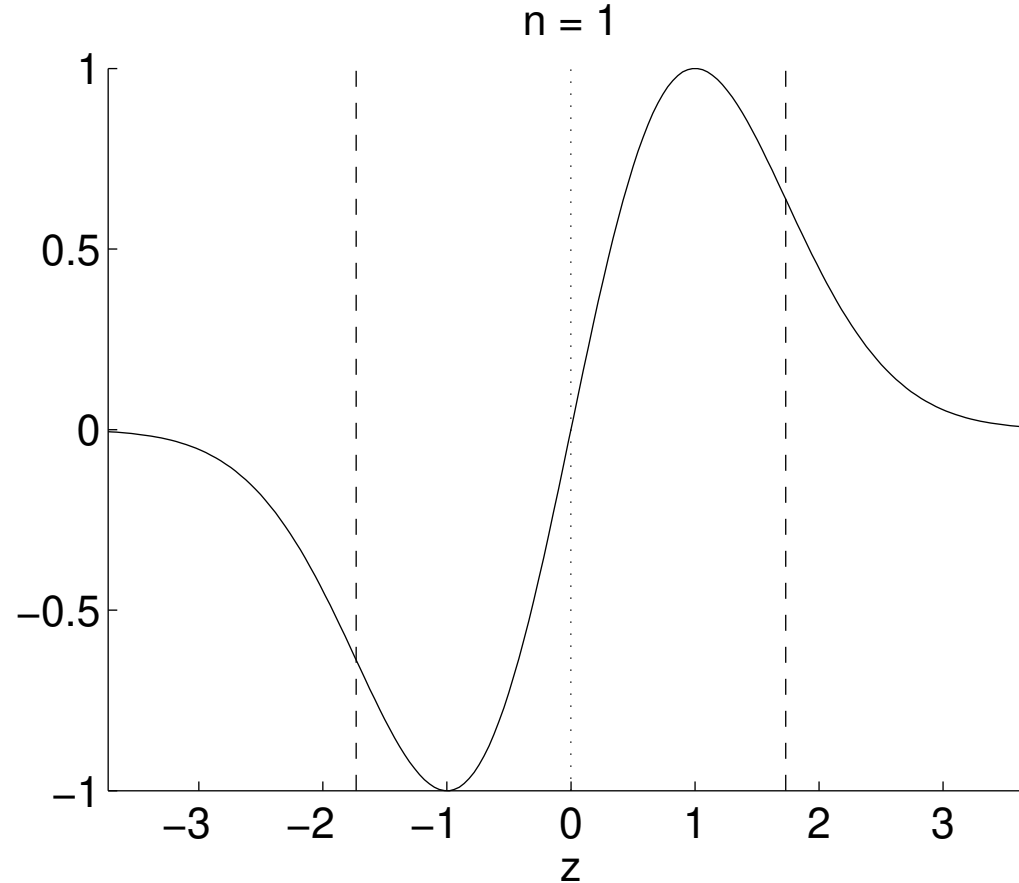
The wavefunctions are plotted on the next few pages.

... The QM solution of the harmonic oscillator ...



One can show that the “classical turning point”, the maximum extent of the classical trajectory of a particle in harmonic potential, at the energy of the quantum state, E_n , is given by $z_{\max} = \sqrt{2n + 1}$.

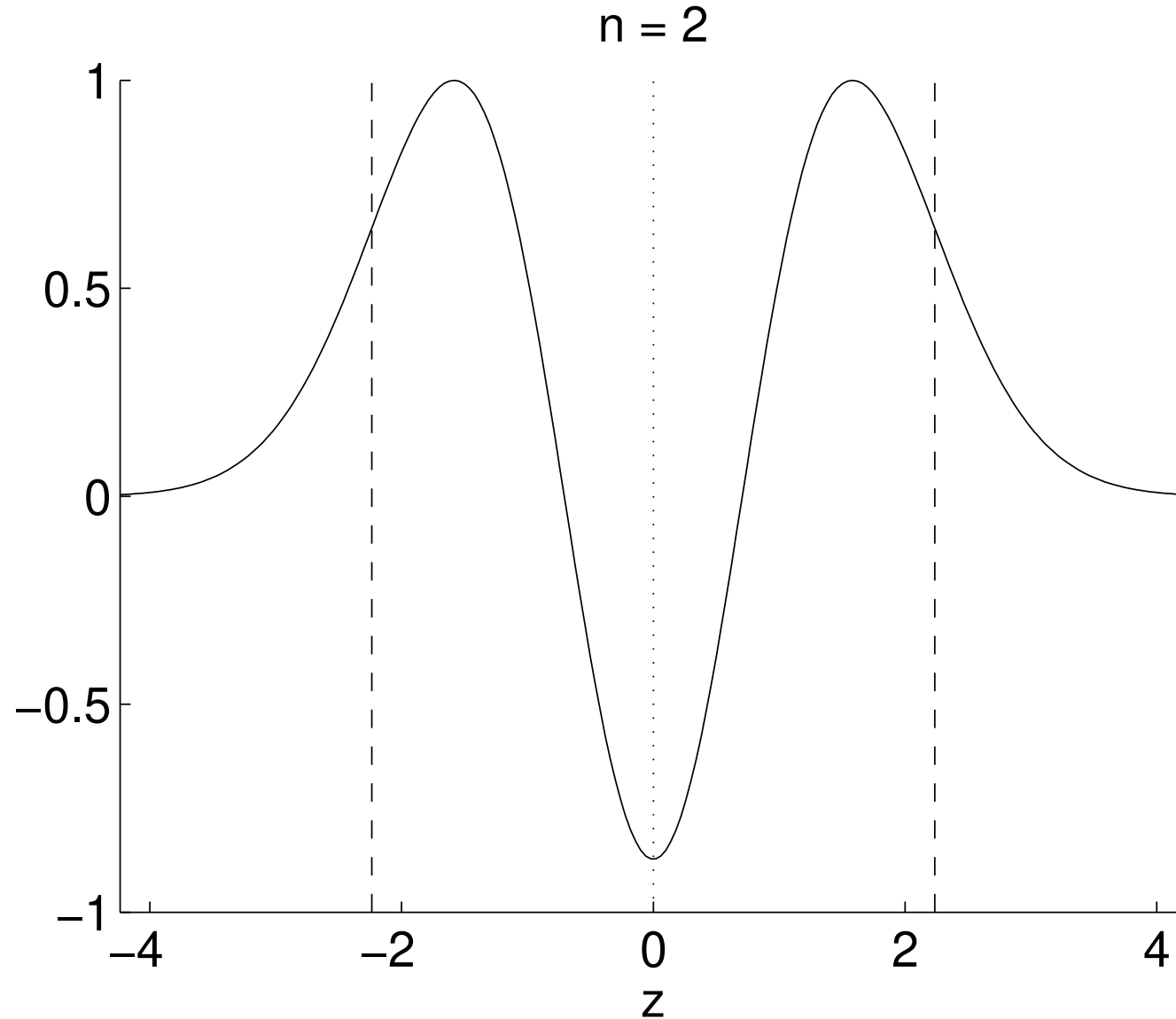
... The QM solution of the harmonic oscillator ...



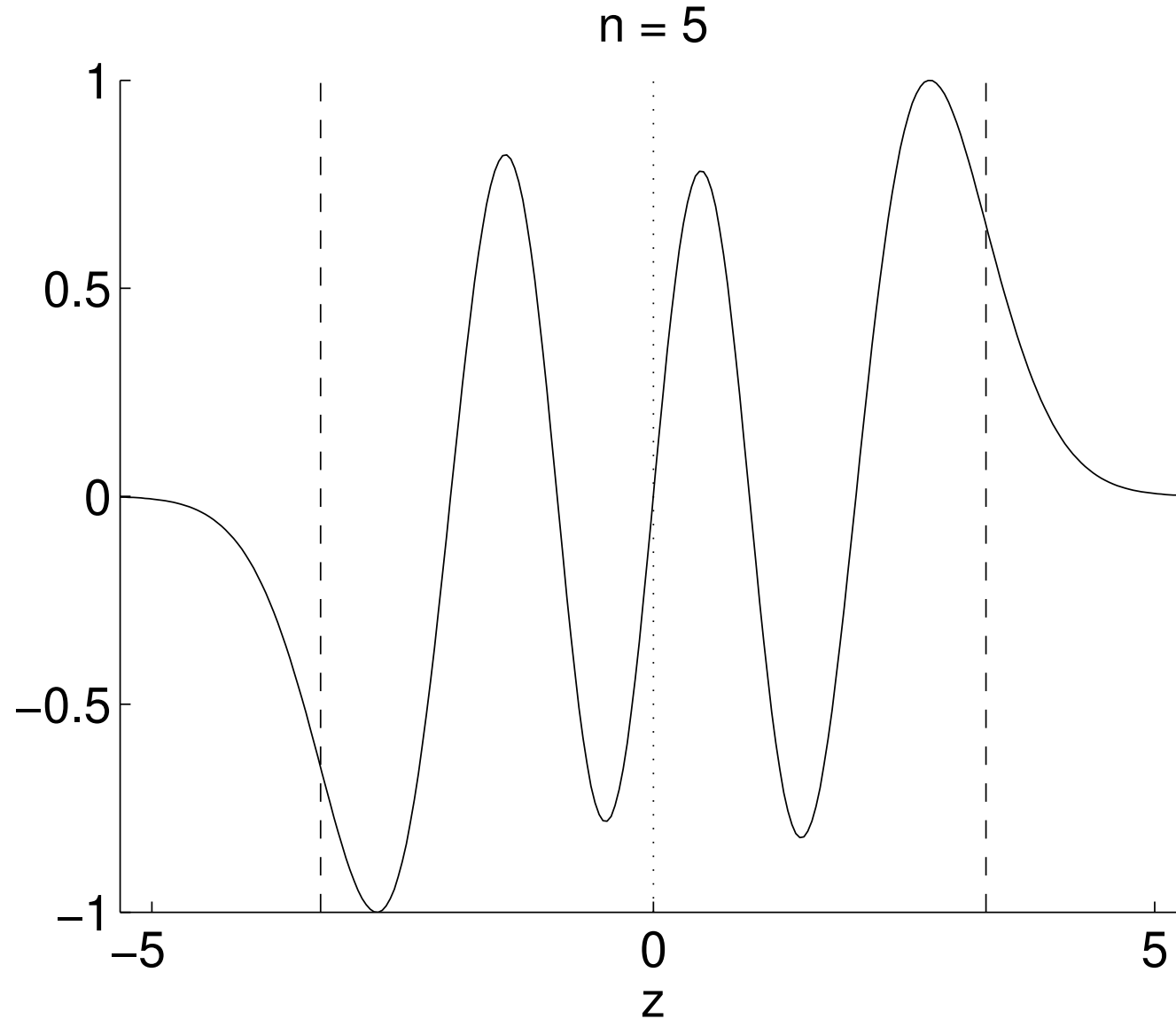
For presentation purposes, these wavefunctions are not normalized, and are scaled to between ± 1 on the vertical axis.

Note that the odd-numbered wavefunctions have odd parity.

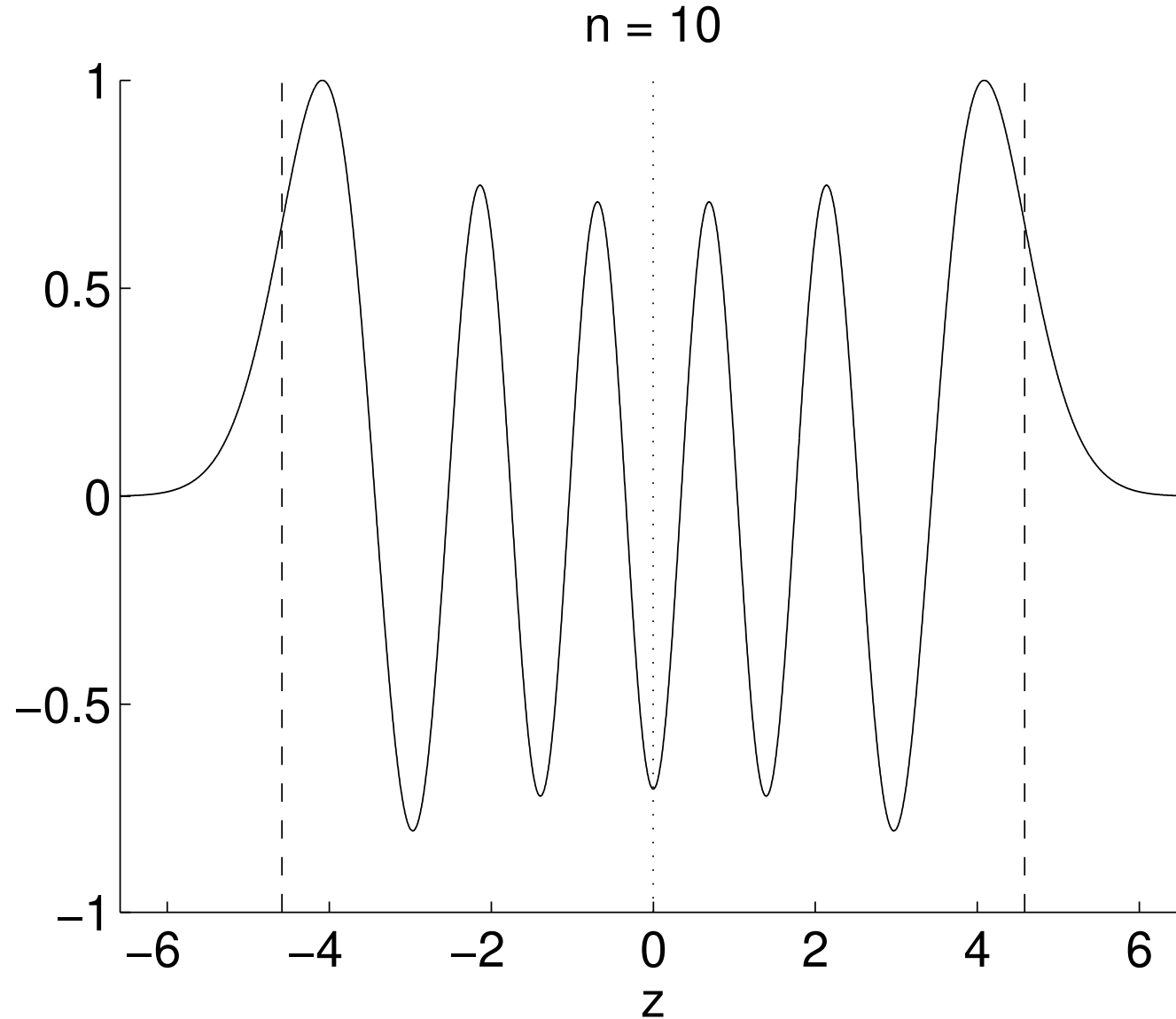
... The QM solution of the harmonic oscillator ...



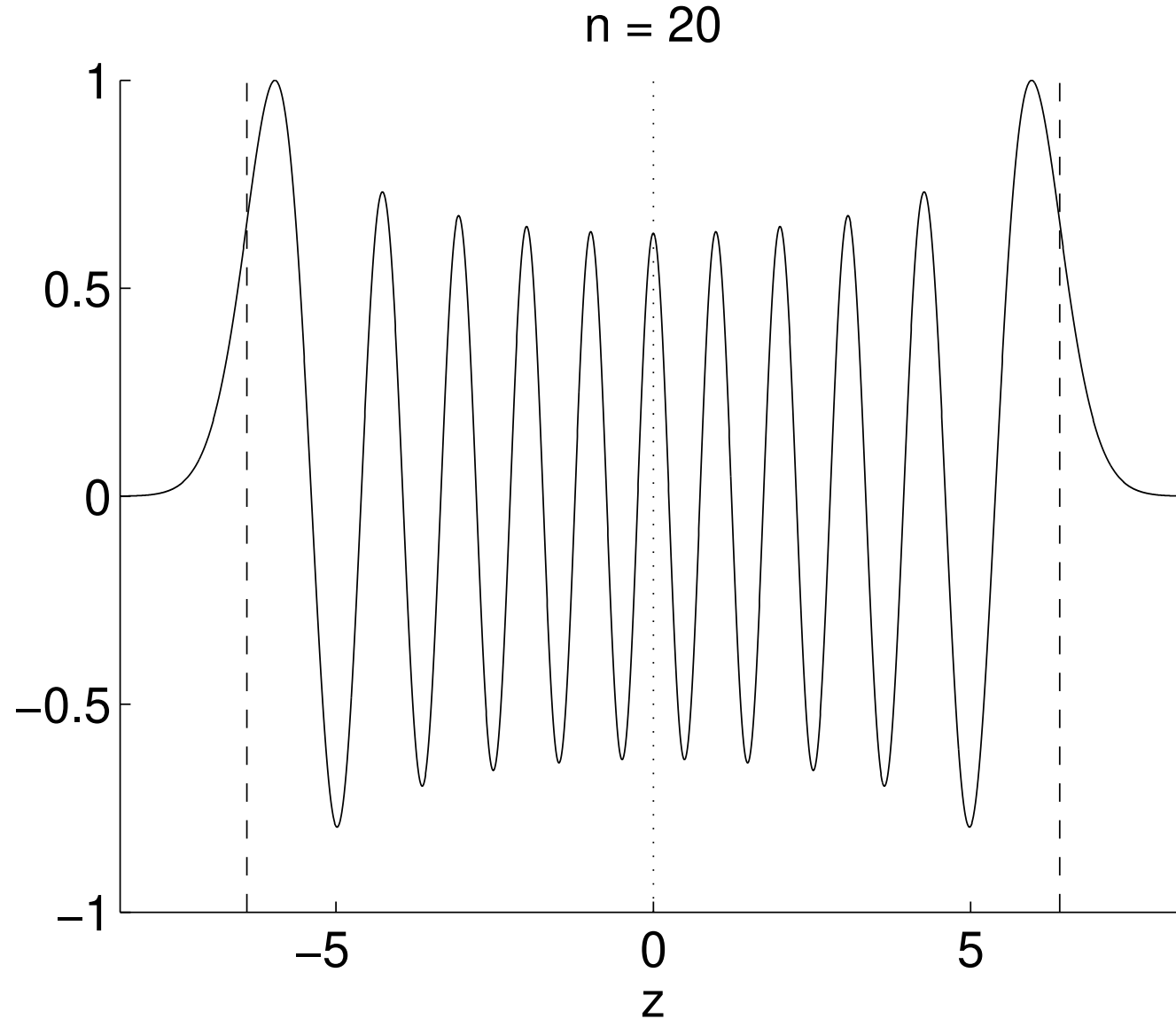
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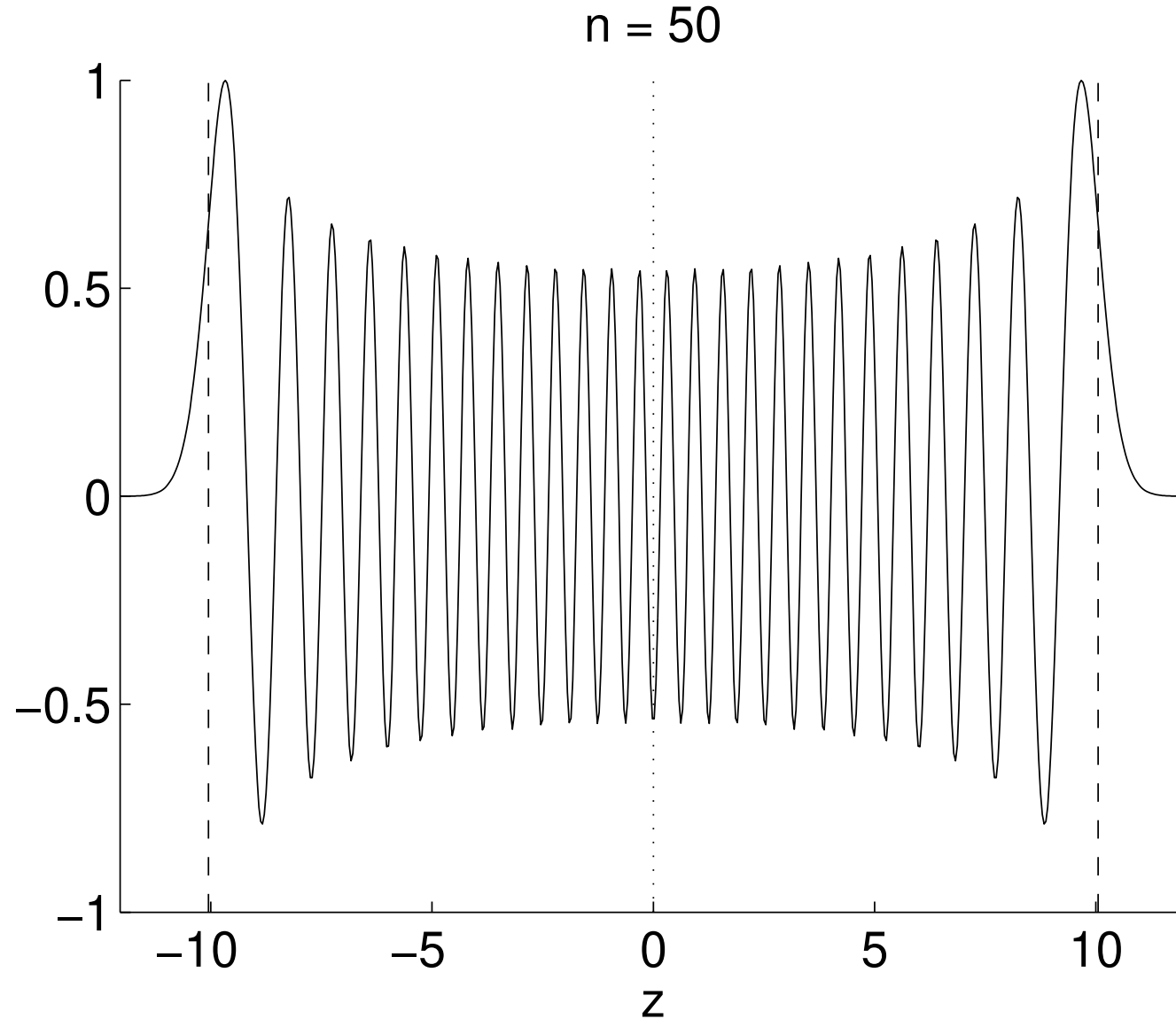
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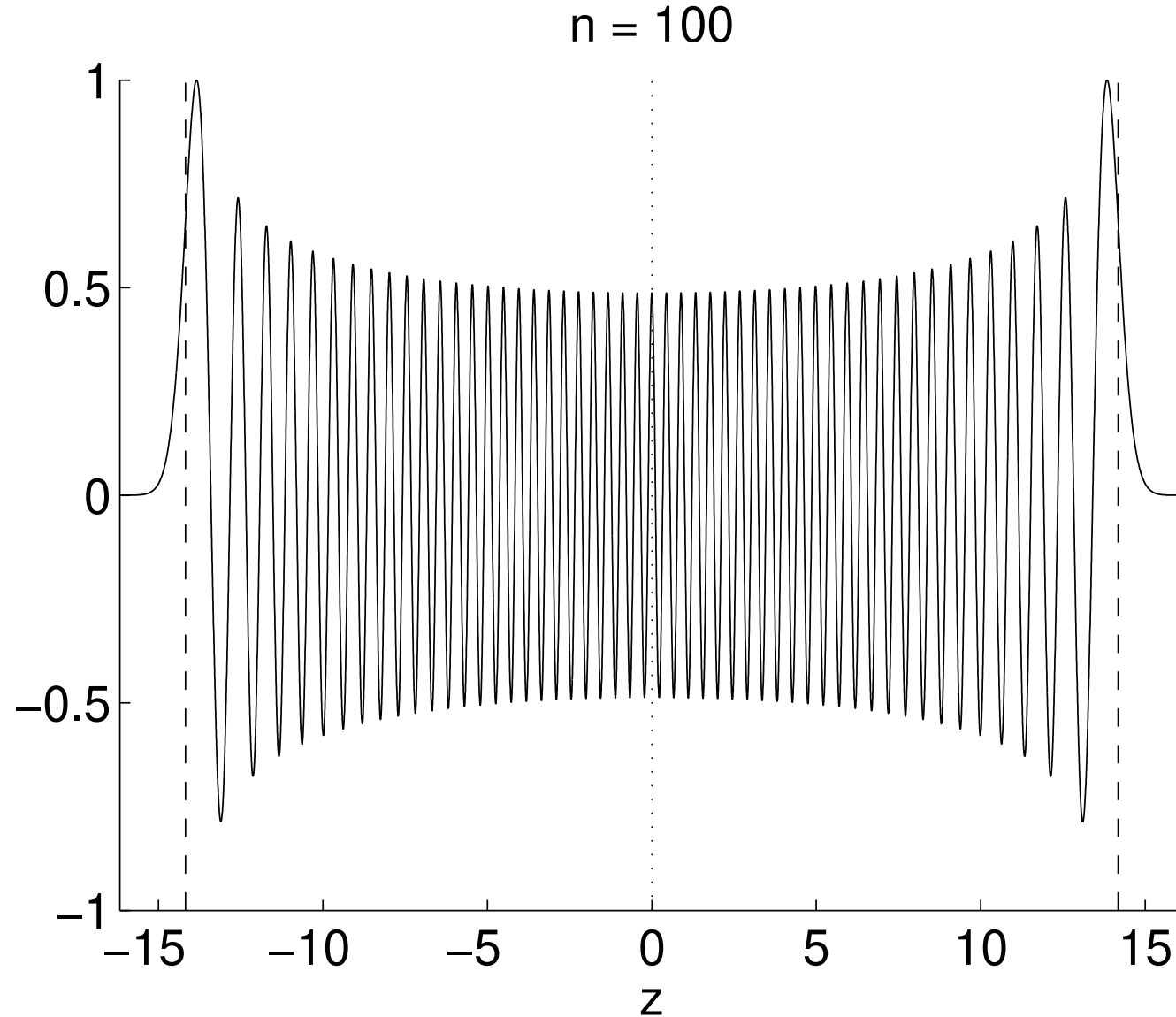
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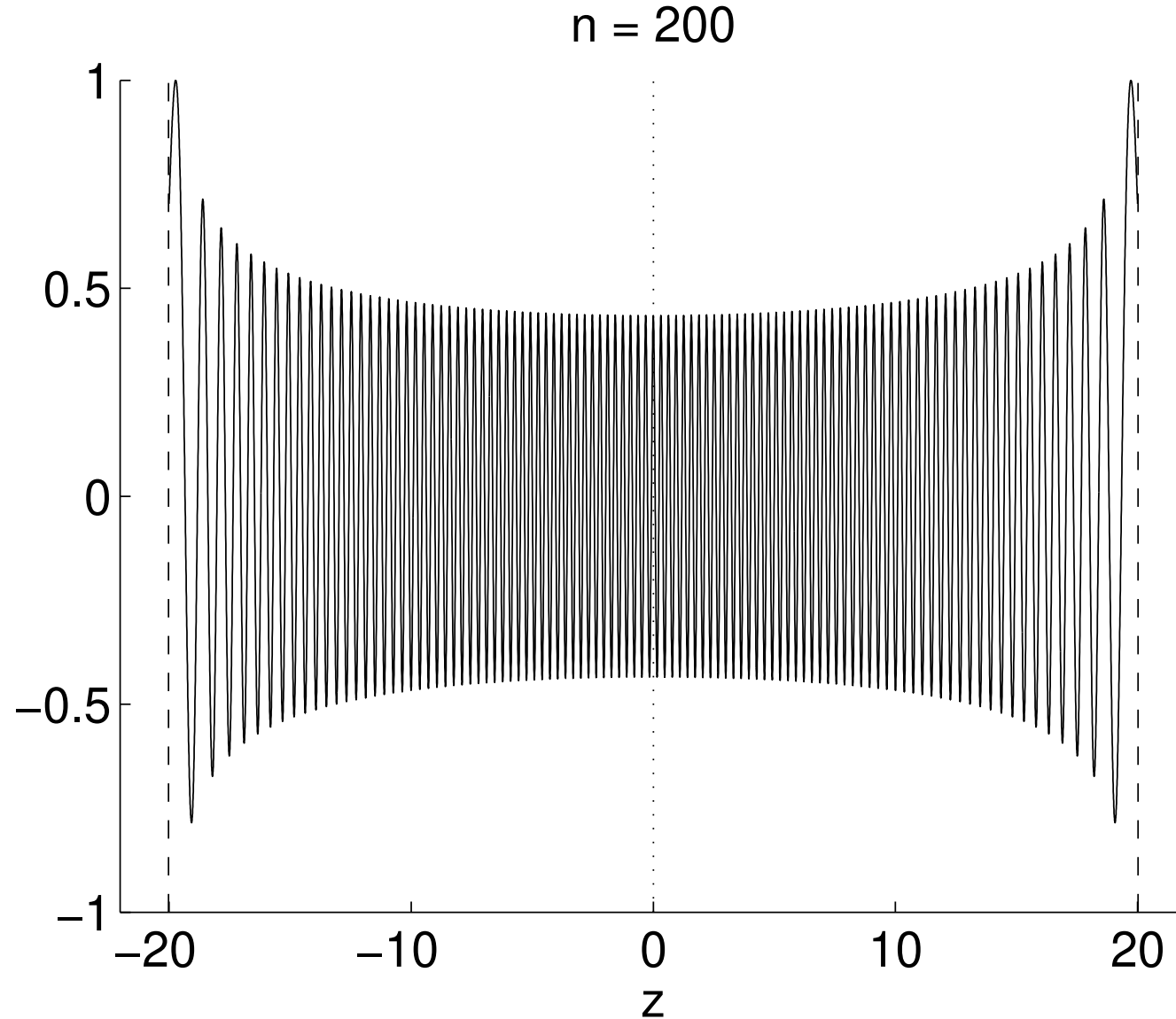
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... The QM solution of the harmonic oscillator ...

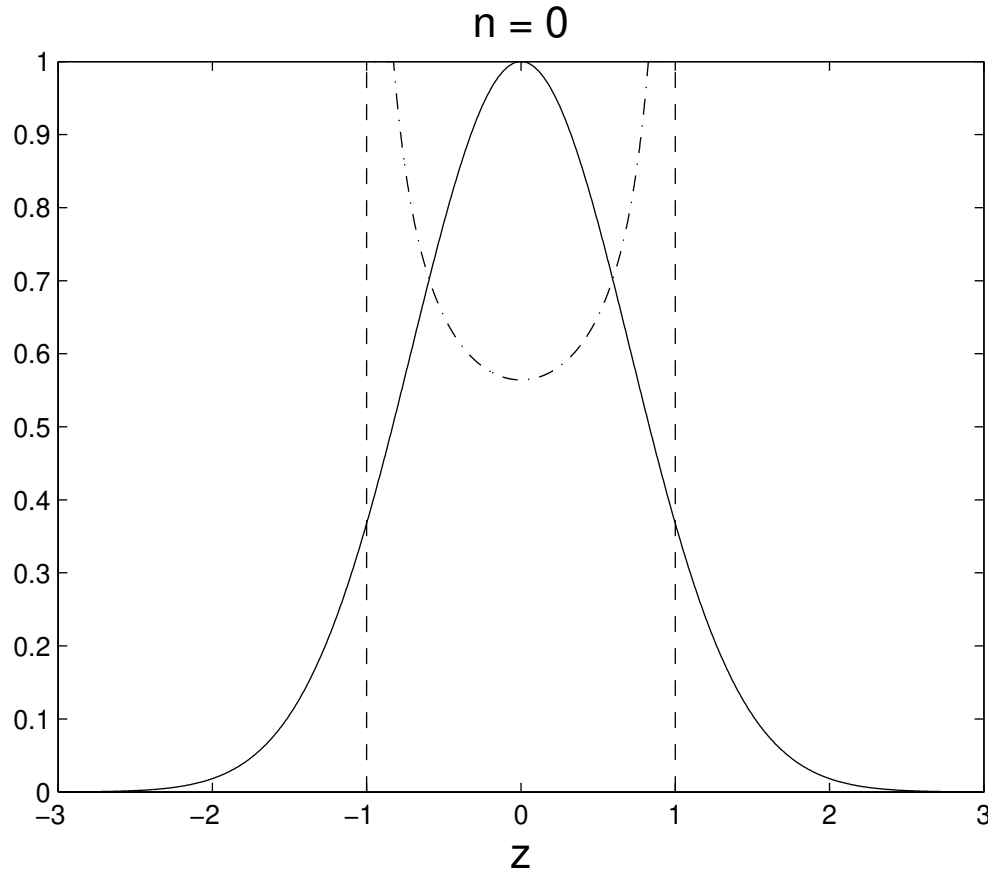


... The QM solution of the harmonic oscillator ...



... The QM solution of the harmonic oscillator ...

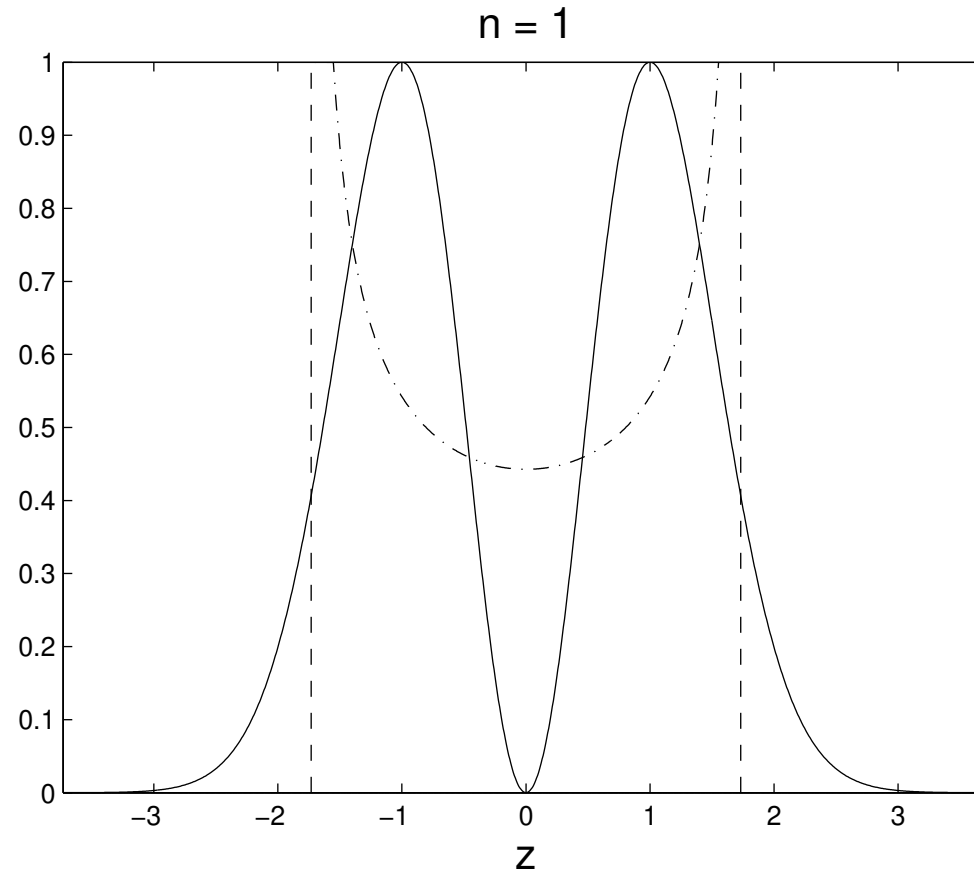
The probability densities:



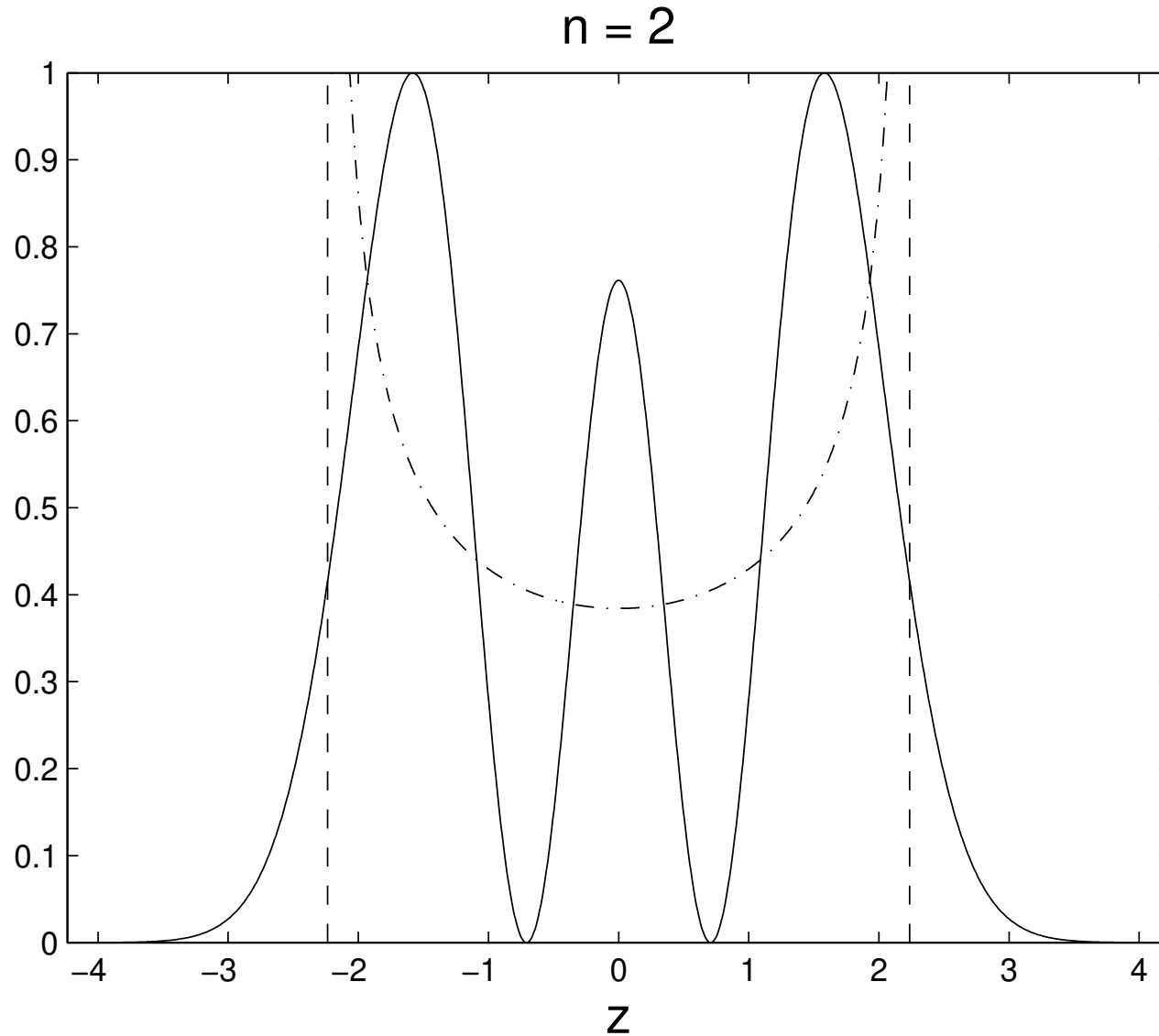
For presentation purposes, these probability densities are not normalized, and are scaled to have a maximum value of 1.

The dash-dot line represents the classical trajectory.

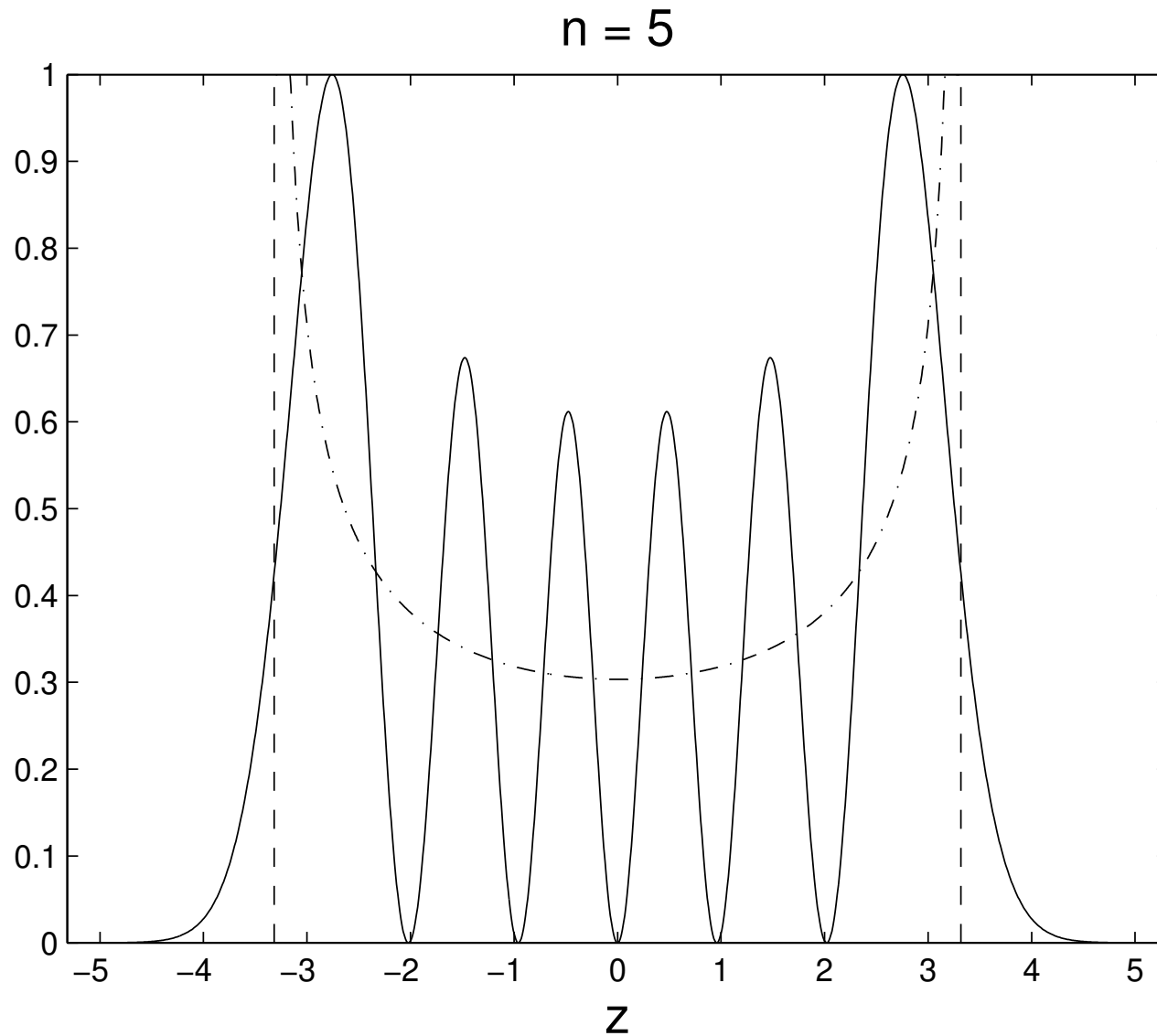
... The QM solution of the harmonic oscillator ...



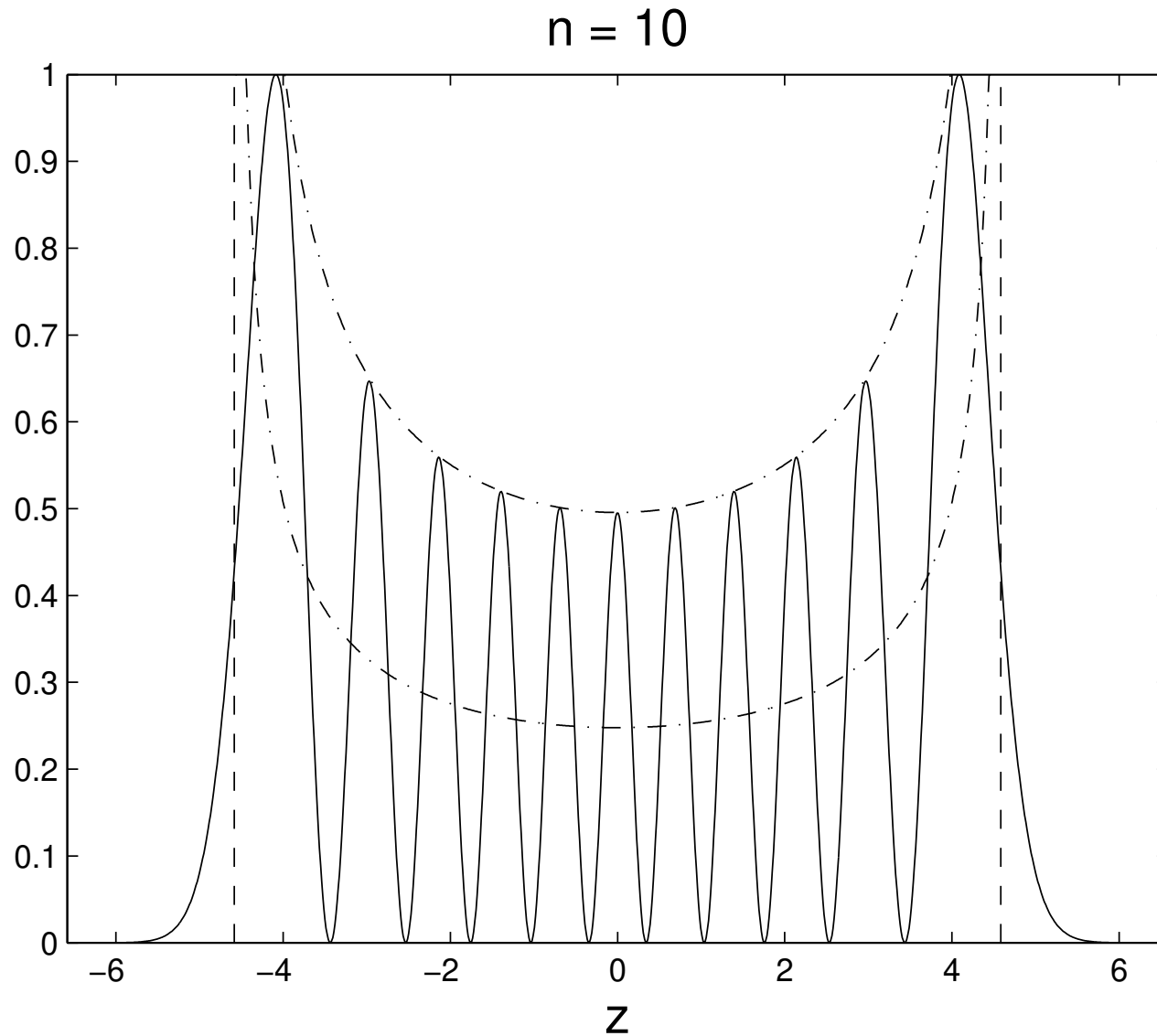
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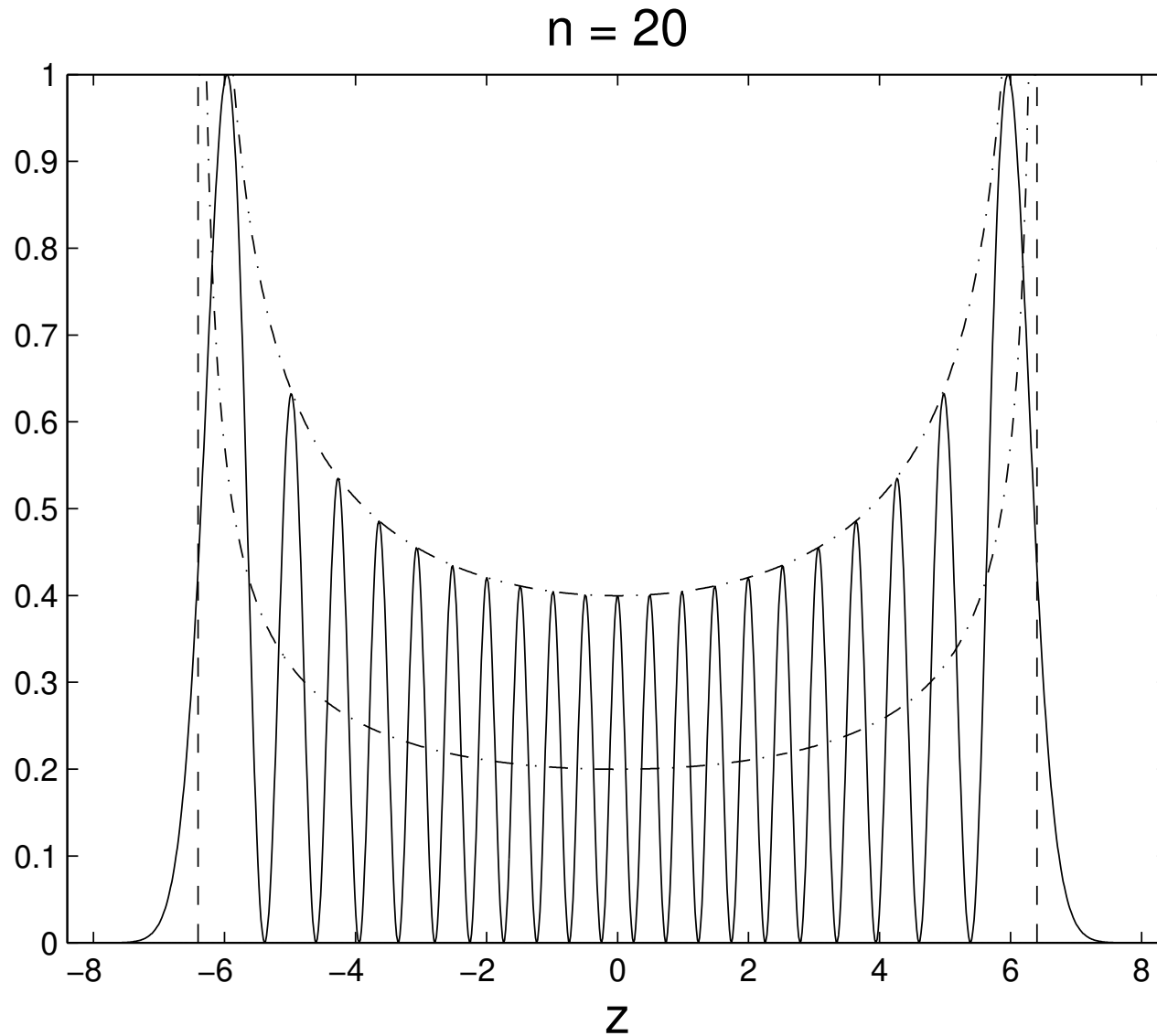
... The QM solution of the harmonic oscillator ...



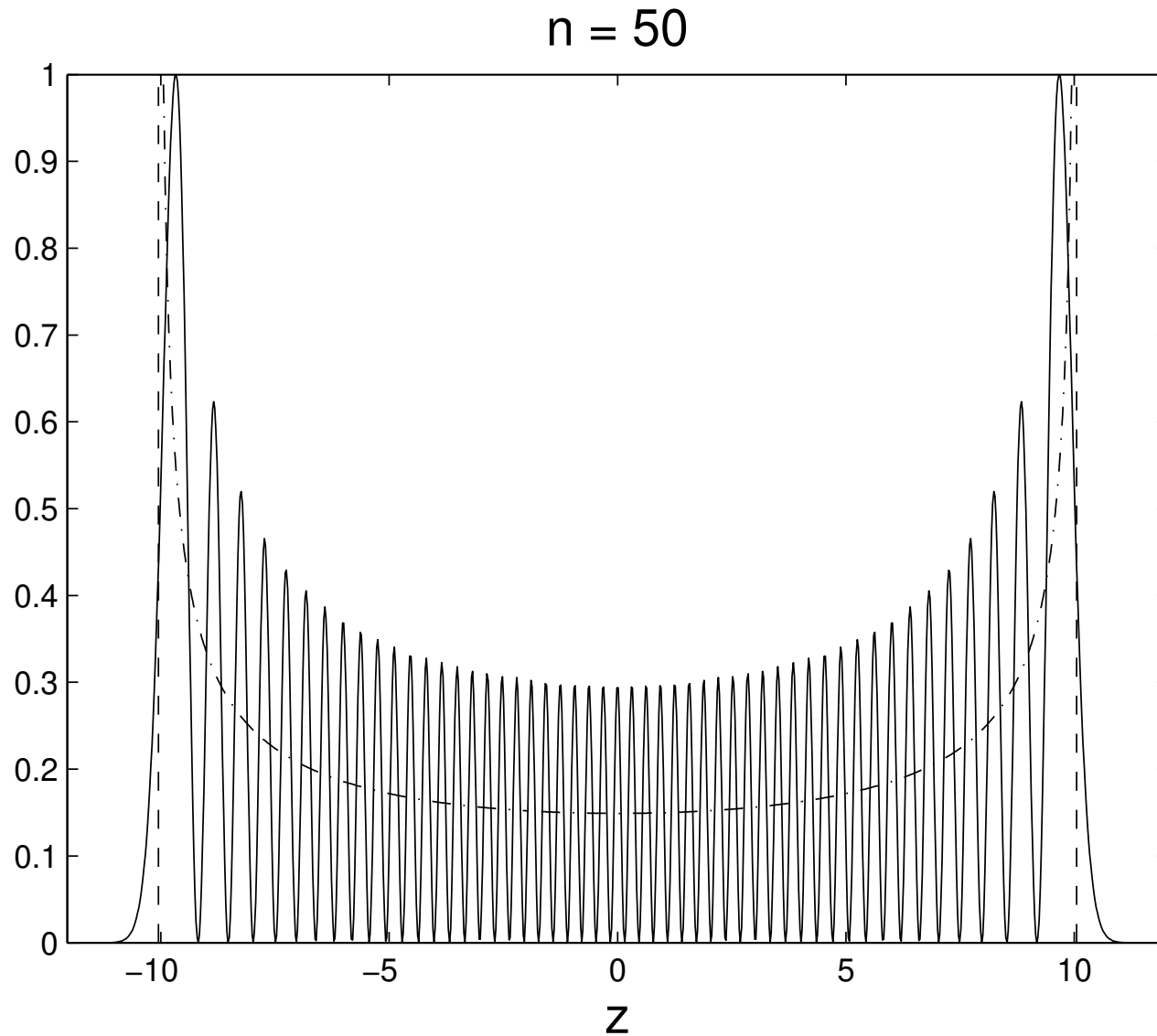
... The QM solution of the harmonic oscillator ...



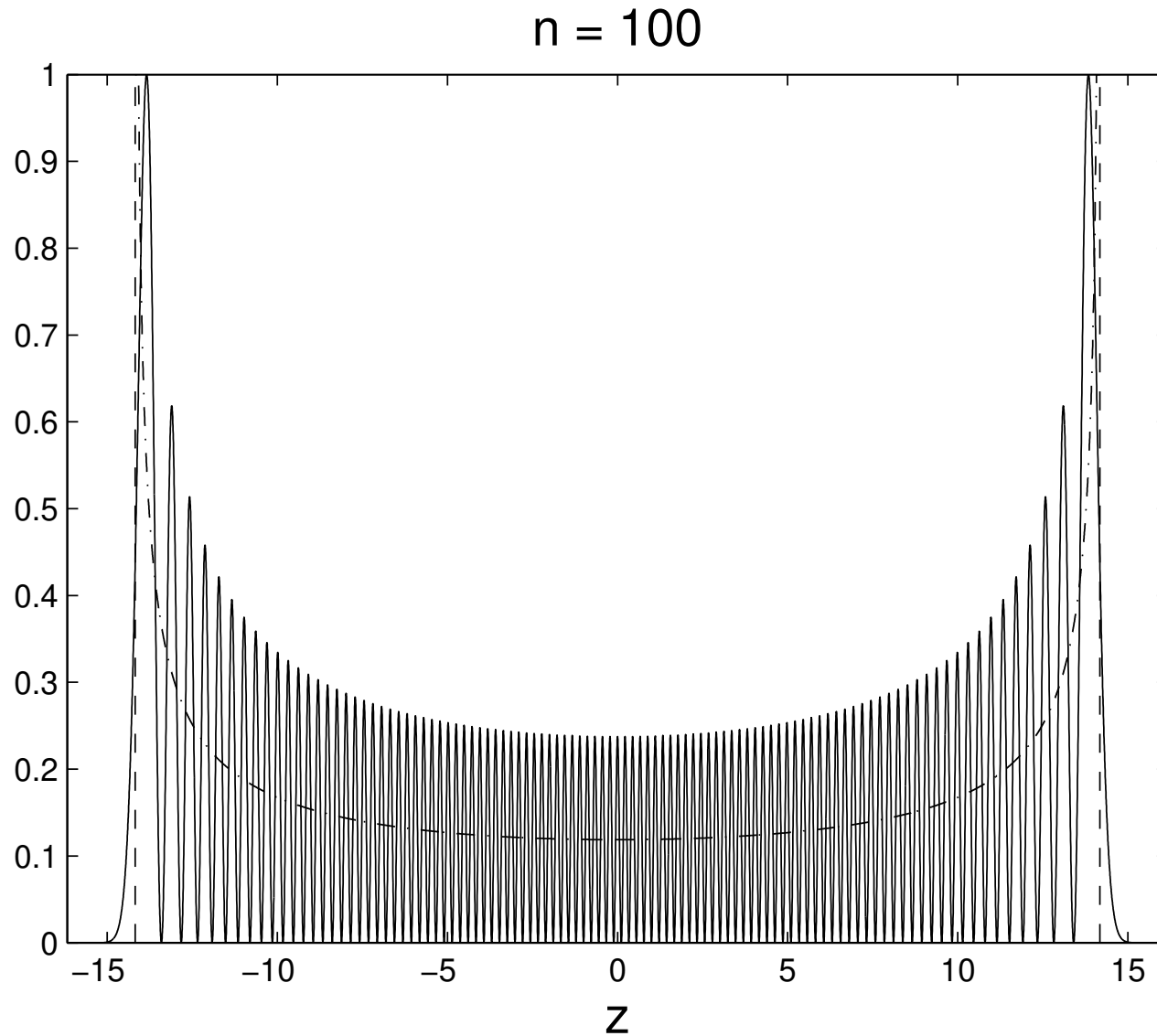
... The QM solution of the harmonic oscillator ...



... The QM solution of the harmonic oscillator ...

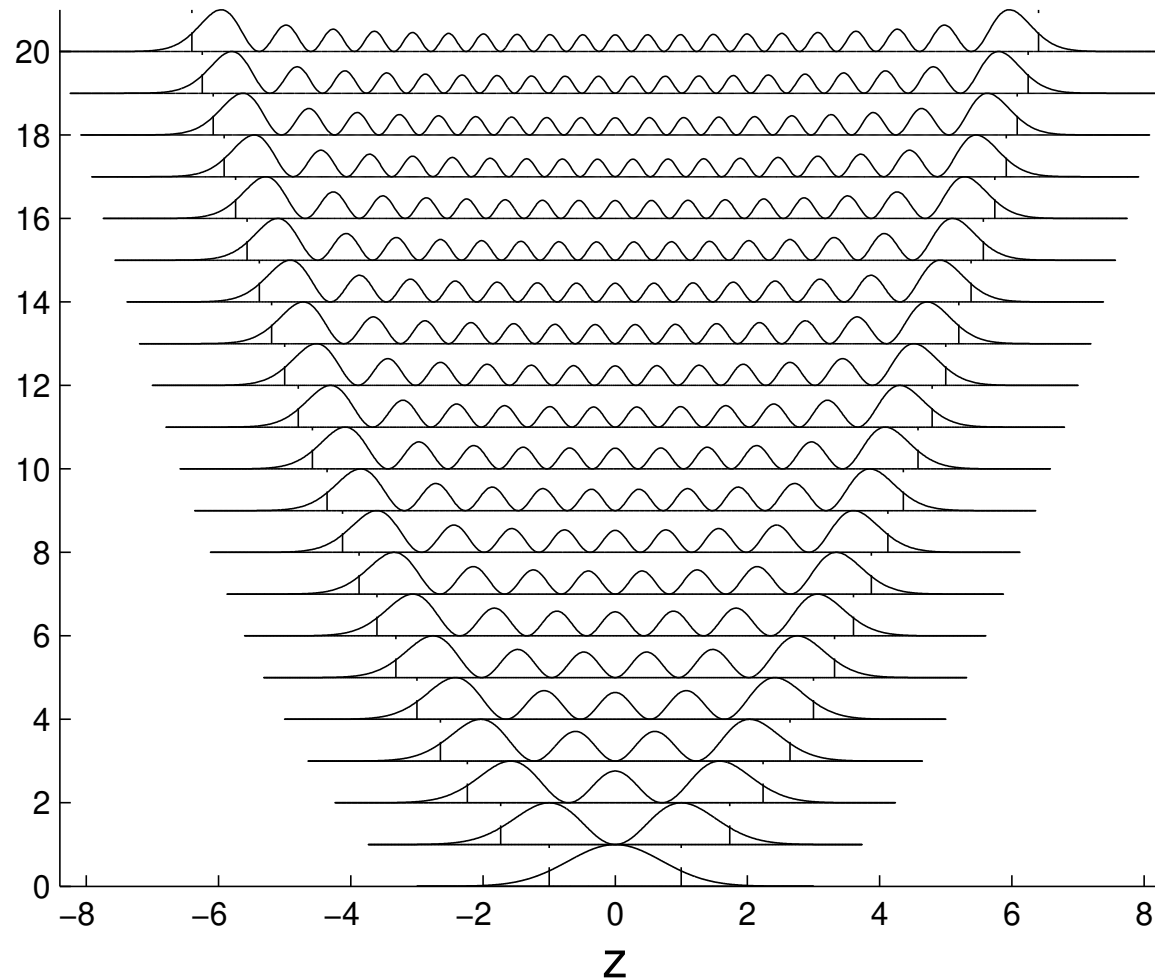


... The QM solution of the harmonic oscillator ...



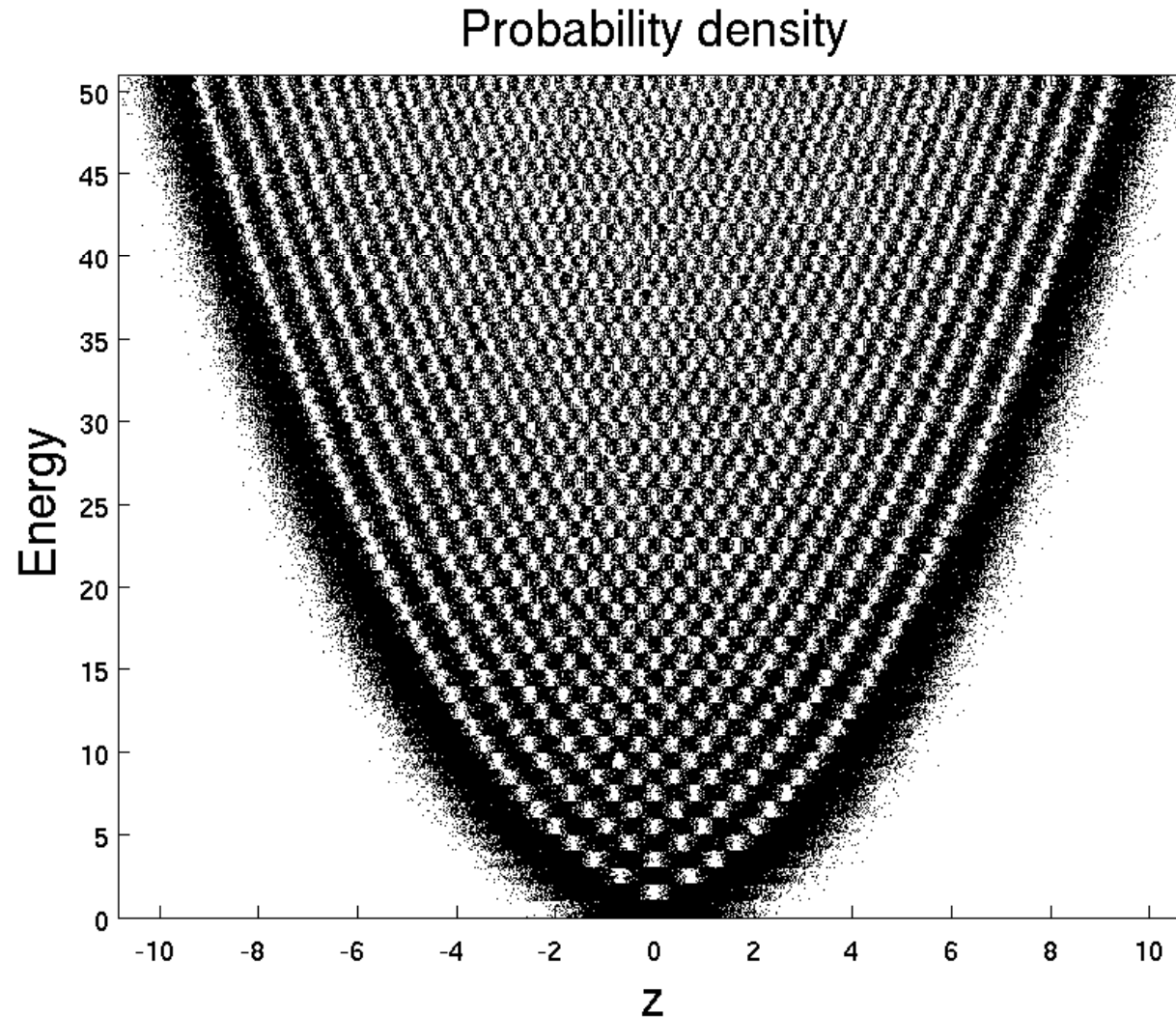
... The QM solution of the harmonic oscillator ...

An offset-overlay of $P(x)$ for $n = 0, 1, 2, \dots, 20$.



... The QM solution of the harmonic oscillator ...

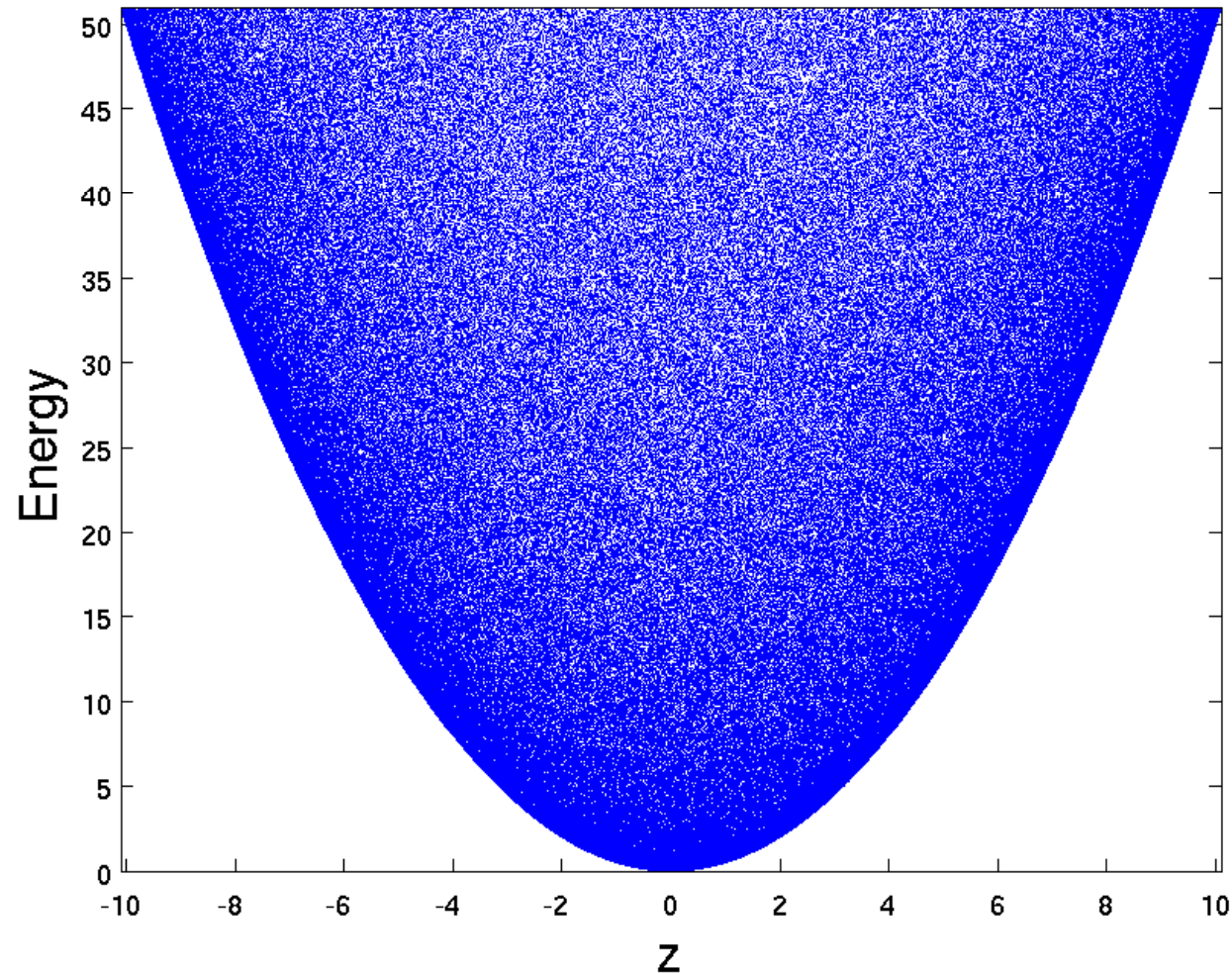
Random samples of $P(x)$ for $n = 0, 1, 2, \dots, 50$.



... The QM solution of the harmonic oscillator ...

Random samples of $P(x)$ for $n = 0, 1, 2, \dots, 50$ for a classical trajectory.

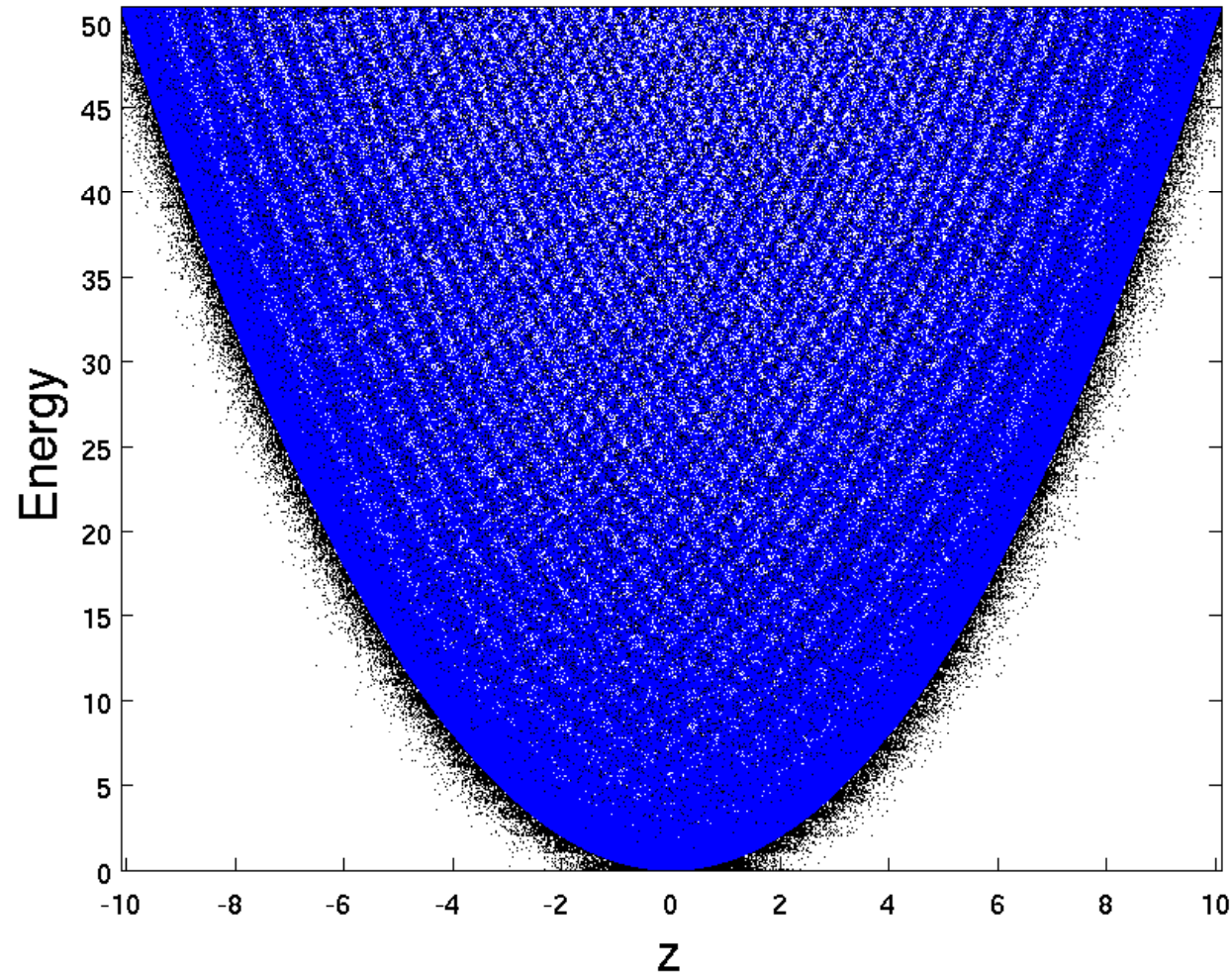
Classical particle snapshots



... The QM solution of the harmonic oscillator

Random samples of $P(x)$ for $n = 0, 1, 2, \dots, 50$ for both.

Classical and Quantum together



3D Solutions to the Schrödinger equation ...

Examples of time-independent solutions in the Cartesian coordinate system

In complete generality, the Schrödinger equation in 3D is:

$$\left(\frac{-\hbar^2}{2m}\right) \nabla^2 \psi(\vec{x}, t) + V(\vec{x}, t) \psi(\vec{x}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{x}, t) , \quad \text{where} \quad (5.184)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad [\text{Laplacian operator}] \quad (5.185)$$

$$\vec{p} = -i\hbar \vec{\nabla} \quad [\text{momentum operator}] \quad (5.186)$$

$$\vec{\nabla} = \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} \quad [\text{gradient operator}] \quad (5.187)$$

$\hat{x}, \hat{y}, \hat{z}$ are unit vectors in the x, y, z directions

$$\mathcal{K} = \frac{\vec{p} \cdot \vec{p}}{2m} = \frac{-\hbar^2}{2m} \nabla^2 \quad [\text{kinetic energy operator}] \quad (5.188)$$

$$P(\vec{x}, t) = \psi^*(\vec{x}, t) \psi(\vec{x}, t) \quad [\text{probability density}] \quad (5.189)$$

$$\vec{S}(\vec{x}, t) = -\frac{\hbar}{m} \mathcal{I}[\psi(\vec{x}, t) \vec{\nabla} \psi^*(\vec{x}, t)] \quad [\text{probability current density}] \quad (5.190)$$

$$\mathcal{E} = i\hbar \frac{\partial}{\partial t} \quad [\text{energy operator}] \quad (5.191)$$

... 3D Solutions to the Schrödinger equation

The 3D version of the continuity equation is:

$$\frac{\partial P(\vec{x}, t)}{\partial t} + \vec{\nabla} \cdot \vec{S}(\vec{x}, t) = \frac{2}{\hbar} \psi^*(\vec{x}, t) \mathcal{I}[V(\vec{x}, t)] \psi(\vec{x}, t) . \quad (5.192)$$

However, for the remainder of this course, we shall be treating only time-independent real potentials, with single-energy wavefunctions or eigenfunctions.

Therefore, we write:

$$\psi(\vec{x}, t) = u(\vec{x}) e^{i(E/\hbar)t} , \quad (5.193)$$

and (5.184) becomes

$$\left(\frac{-\hbar^2}{2m} \right) \nabla^2 u(\vec{x}) + V(\vec{x}) u(\vec{x}) = E u(\vec{x}) . \quad (5.194)$$

Also, (5.189) and (5.189) become independent of time, and the right-hand side of (5.192) is zero.

The 3D infinite box ...

In this case we consider an infinite 3D box potential, with $V(\vec{x}) = 0$, inside a rectilinear box with sides L_x, L_y, L_z . Outside of the box, the potential is infinite.

The Schrödinger equation in this case is

$$\left(\frac{-\hbar^2}{2m} \right) \nabla^2 u(\vec{x}) = E u(\vec{x}) , \quad (5.195)$$

or,

$$\nabla^2 u(\vec{x}) + k^2 u(\vec{x}) = 0 , \quad (5.196)$$

where

$$k^2 = \frac{2mE}{\hbar^2} . \quad (5.197)$$

Assume the solution is separable, that is, assume:

$$u(x, y, z) = X(x)Y(y)Z(z) . \quad (5.198)$$

The, substituting (5.198) into (5.196) gives:

$$X''(x)Y(y)Z(z) + X(x)Y''(y)Z(z) + X(x)Y(y)Z''(z) + k^2 X(x)Y(y)Z(z) = 0 \quad (5.199)$$

... The 3D infinite box ...

Dividing (5.199) by (5.198) gives

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} + k^2 = 0 . \quad (5.200)$$

This is really a sum of 3 independent differential equations in x, y, z that can differ at most by only a constant.

If we now call:

$$k^2 = k_x^2 + k_y^2 + k_z^2 , \quad (5.201)$$

we have identified the solution derived previously, but just in one dimension.

... The 3D infinite box ...

Therefore, the explicit parity solution is:

$$u(\vec{x}) = u_{(n_x, n_y, n_z)}(\vec{x}) = u_{n_x}(x)u_{n_y}(y)u_{n_z}(z) \quad (5.202)$$

$$u_{n_x}(x) = (\sqrt{2/L_x}) \cos([n_x + 1]\pi x/L_x) \quad [\text{even parity, even } n_x \text{ only}] \quad (5.203)$$

$$u_{n_x}(x) = (\sqrt{2/L_x}) \sin([n_x + 1]\pi x/L_x) \quad [\text{odd parity, odd } n_x \text{ only}] \quad (5.204)$$

$$u_{n_y}(y) = (\sqrt{2/L_y}) \cos([n_y + 1]\pi y/L_y) \quad [\text{even parity, even } n_y \text{ only}] \quad (5.205)$$

$$u_{n_y}(y) = (\sqrt{2/L_y}) \sin([n_y + 1]\pi y/L_y) \quad [\text{odd parity, odd } n_y \text{ only}] \quad (5.206)$$

$$u_{n_z}(z) = (\sqrt{2/L_z}) \cos([n_z + 1]\pi z/L_z) \quad [\text{even parity, even } n_z \text{ only}] \quad (5.207)$$

$$u_{n_z}(z) = (\sqrt{2/L_z}) \sin([n_z + 1]\pi z/L_z) \quad [\text{odd parity, odd } n_z \text{ only}] \quad (5.208)$$

$$(n_x, n_y, n_z) = 0, 1, 2, \dots \infty \quad [\text{independent quantum numbers}] \quad (5.209)$$

$$(k_x, k_y, k_z) = \left(\frac{(n_x + 1)\pi}{L_x}, \frac{(n_y + 1)\pi}{L_y}, \frac{(n_z + 1)\pi}{L_z} \right) \quad [\text{independent } k\text{'s}] \quad (5.210)$$

$$E_{(n_x, n_y, n_z)} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{(n_x + 1)^2}{L_x^2} + \frac{(n_y + 1)^2}{L_y^2} + \frac{(n_z + 1)^2}{L_z^2} \right) \quad [\text{energy}] \quad (5.211)$$

$$\Pi[u(\vec{x})] = (-1)^{n_x}(-1)^{n_y}(-1)^{n_z} = (-1)^{n_x + n_y + n_z} \quad (5.212)$$

Degeneracy

Consider the case where the rectilinear box has all equal sides.

In that case, the energy eigenvalues are:

$$E_{(n_x, n_y, n_z)} = \frac{\hbar^2 \pi^2}{2mL^2} [(n_x + 1)^2 + (n_y + 1)^2 + (n_z + 1)^2] \quad . \quad (5.213)$$

We see that some energies may have the same value, but with different sets of quantum numbers.

This is called the “degeneracy”, of the energy, or just D .

On the next page is a partial list of the energy levels, and the enumeration of the degenerate states.

The energy levels are given as R (for ratio) in dimensionless form.

The column labeled R is defined by:

$$R = \frac{E_{(n_x, n_y, n_z)}}{\hbar^2 \pi^2 / (2mL^2)} = [(n_x + 1)^2 + (n_y + 1)^2 + (n_z + 1)^2] \quad .$$

Degeneracy

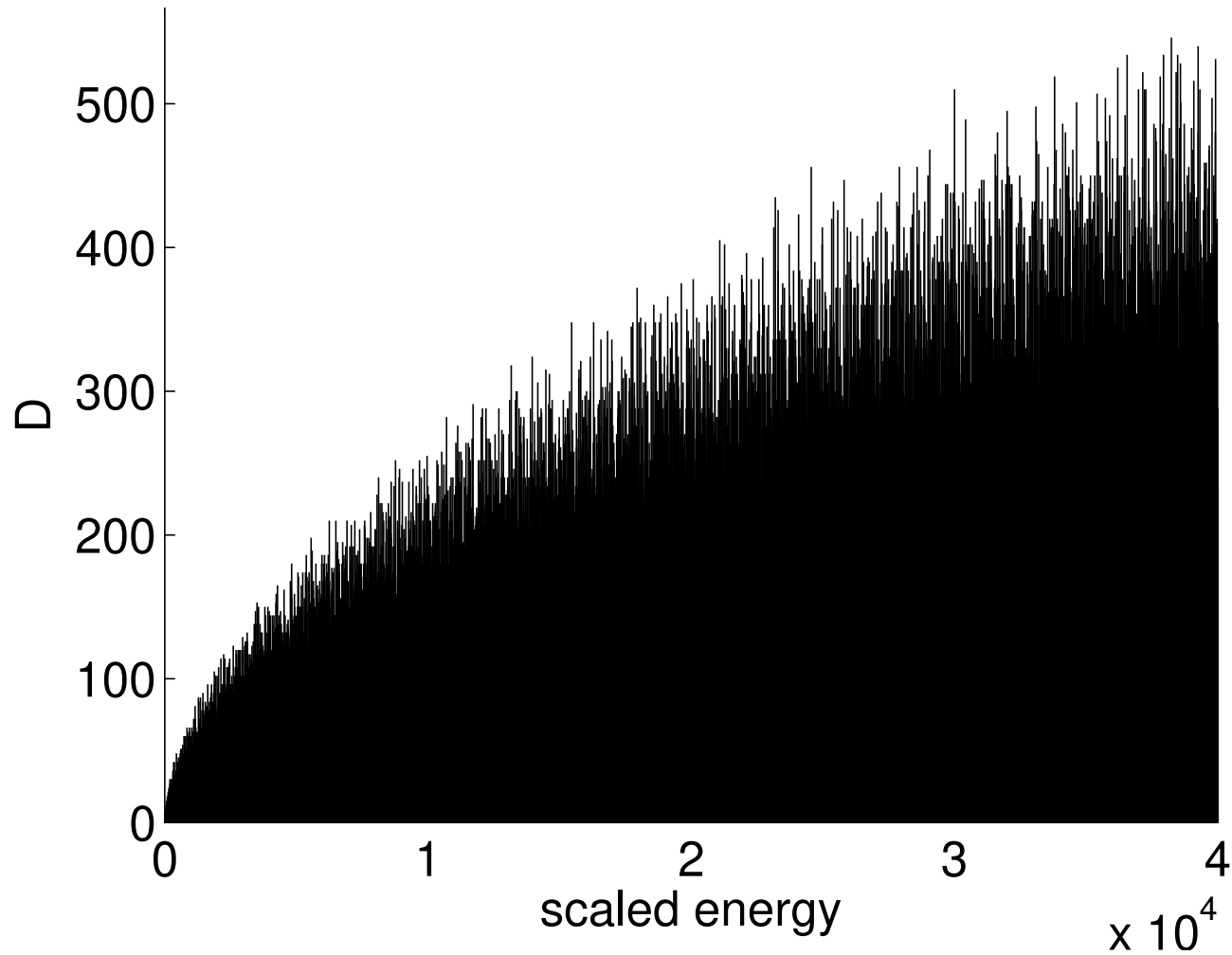
R	quantum states	D	Π
3	(0, 0, 0)	1	+1
6	(1, 0, 0), (0, 1, 0), (0, 0, 1)	3	-1
9	(1, 1, 0), (1, 0, 1), (0, 1, 1)	3	+1
11	(2, 0, 0), (0, 2, 0), (0, 0, 2)	3	+1
12	(1, 1, 1)	1	-1
14	(2, 1, 0), (1, 0, 2), (0, 2, 1), (1, 2, 0), (2, 0, 1), (0, 1, 2)	6	-1
17	(1, 1, 2), (1, 2, 1), (2, 1, 1)	3	+1
18	(3, 0, 0), (0, 0, 3), (0, 3, 0)	3	-1
19	(2, 2, 0), (2, 0, 2), (0, 2, 2)	3	+1
⋮			

This behavior seems “chaotic”, but only for low values of the quantum numbers.

In NERS 312, we shall see that this degeneracy calculation will play a critical role in determining the proportionality factor for transition rates.

On the next page is plotted a much wider range of quantum numbers.

Degeneracy



Some chaotic behavior is detected, but there is a general trend that will be explored in NERS 312.

The 3D quantum harmonic oscillator

The 3D quantum oscillator plays an important role in both nuclear materials and nuclear structure.

The potential in this case is:

$$V(\vec{x}) = \frac{1}{2} \sum_{i=1}^3 k_i x_i^2 , \quad (5.214)$$

where $i = 1, 2, 3$ now signifies the 3 directions x, y, z .

We allow the spring constants for each direction to be different.

Having expressed the potential in Cartesian coordinates allows us to look for a separated solution of the form:

$$u(\vec{x}) = \prod_{i=1}^3 X_i(x_i) .$$

The 3D quantum harmonic oscillator

Applying the technique of separation of variables to this potential results in:

$$\sum_{i=1}^3 \left[\frac{-\hbar^2 X_i''(x_i)}{2m X_i(x)_i} + \frac{1}{2} k_i x_i^2 - E_i \right] = 0 \quad (5.215)$$

effectively 3 independent quantum oscillators.

The solution, we can now write down by inspection.

$$u(\vec{x}, \vec{n}) = \prod_{i=1}^3 \left(\frac{\alpha_i}{2^{n_i} n_i! \sqrt{\pi}} \right)^{1/2} e^{-(\alpha_i x_i)^2/2} H_{n_i}(\alpha_i x_i) \quad (5.216)$$

$$E(\vec{n}) = \hbar \left(\omega_1 n_1 + \omega_2 n_2 + \omega_3 n_3 + \frac{3}{2} \right) \quad \text{Note the } 3/2 \text{ !!!} \quad (5.217)$$

$$n_i = 0, 1, 2, \dots \quad (5.218)$$

$$\omega_i^2 = \frac{k_i}{m} \quad (5.219)$$

$$\alpha_i = \left(\frac{m k_i}{\hbar^2} \right)^{1/4} = \left(\frac{m \omega_i}{\hbar} \right)^{1/2} \quad (5.220)$$

$$\pi[u(\vec{x}, \vec{n})] = (-1)^{n_1+n_2+n_3} \quad (5.221)$$

Degeneracy in the 3D harmonic potential

Assume a symmetric potential, where all the ω_i s are the same.

$$R = \frac{E_{(n_x, n_y, n_z)}}{\hbar\omega} - \frac{3}{2}$$

R	quantum states	D	Π
0	(0, 0, 0)	1	+1
1	(1, 0, 0), (0, 1, 0), (0, 0, 1)	3	-1
2	(1, 1, 0), (1, 0, 1), (0, 1, 1), (2, 0, 0), (0, 2, 0), (0, 0, 2)	6	+1
3	(3, 0, 0), (0, 3, 0), (0, 0, 3), (2, 1, 0), (1, 2, 0), (1, 0, 2)		
	(2, 0, 1), (0, 1, 2), (1, 2, 0), (1, 1, 1)	10	-1
4	Too many to show!	15	+1
5	⋮	21	-1
⋮			

This behavior has a regular pattern.