

Bound States in One Dimension

In this chapter we will concern ourselves with obtaining stationary state solution of the time independent Schrödinger Equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x)\psi(x) = E\psi(x) \quad (1)$$

for particles (such as electrons) bound in one dimensional potential wells. In general these solutions can be chosen to be real rather than complex functions which can often be considerable simplification. To see this lets take the complex conjugate of the time independent SE given in Eq. (1):

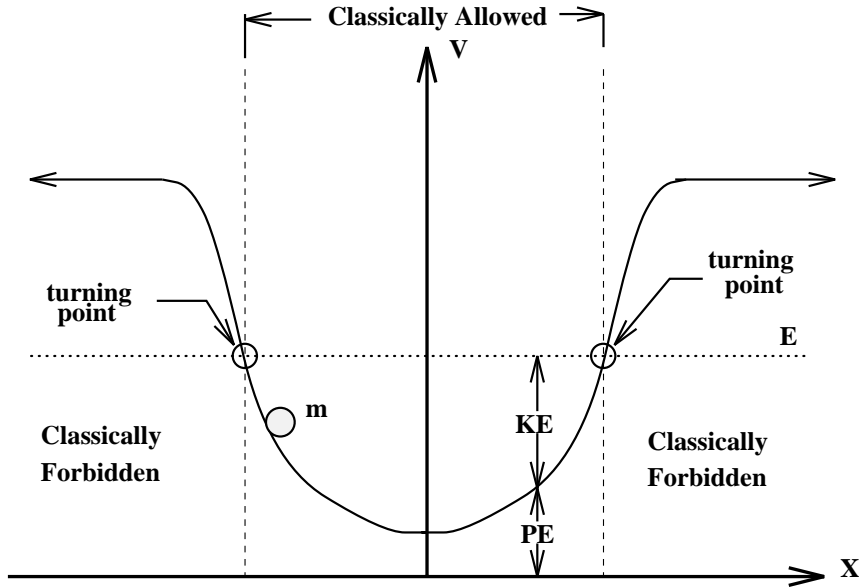
$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi^*(x) + V(x)\psi^*(x) = E\psi^*(x) \quad (2)$$

Because all the factors which operate on $\psi(x)$ are real, they don't change under complex conjugation and hence $\psi(x)$ and $\psi^*(x)$ are equally valid solutions of the same potential $V(x)$ with the same energy E . Since the SE is a homogenous linear differential equation, we can always form new valid solutions by taking linear combinations of valid solutions. In particular, the solution $\psi_r(x)$ which is constructed out of a general solutions $\psi(x)$ and $\psi^*(x)$ according to

$$\psi_r(x) \propto \psi(x) + \psi^*(x) \quad (3)$$

is an intrinsically real. Of course $\exp(i\phi) \times \psi_r(x)$ is an equally valid solution with any complex phase ϕ that one cares to choose. We will generally choose real bound state solutions to the problems posed in this chapter.

Some of the problems which we will address are a bit artificial but they are easily solvable and give considerable insight into perhaps more realistic but less tractable problems. I begin by describing the general “potential well” illustrated below in hopefully familiar classical terms.



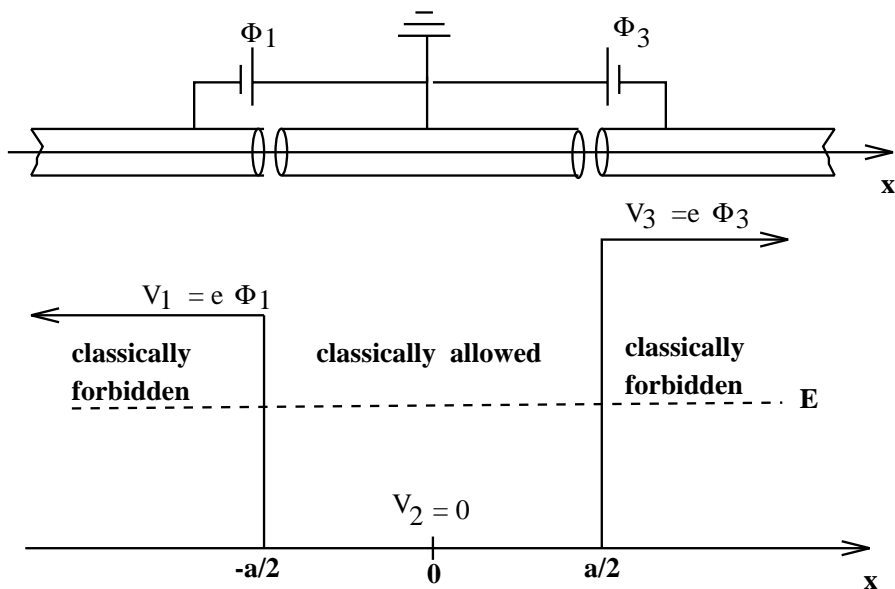
By a potential well, we mean a graph of potential energy as a function of coordinate x . In this well picture, we indicate a constant energy level (total potential plus kinetic energy) for the particle of mass m by the horizontal “dotted line”. The picture is meant to evoke conservation of energy *ie* the particle has the same total energy $E = KE + PE$ independent of x . As a particle of mass m slides back and forth in x along the well much like a mass sliding down a frictionless valley, it constantly exchanges potential energy for kinetic energy while keeping a constant E .

The (energy) distance between the energy level and the potential curve represents the kinetic energy since $KE = E - V(x)$. Classically the kinetic energy is an intrinsically positive quantity because $KE = mv^2/2$. The classical turning points are the two intersections of the energy level and the potential well where the particle has zero kinetic energy. In the region between the turning points $E > V(x)$ and $KE = E - V > 0$. Since the kinetic energy is positive this is a perfectly reasonable or “allowed” region for the particle to exist. In the region outside of the turning points, $E < V(x)$ and $KE = E - V < 0$ which is a classically “forbidden” condition. Classically the particle can never be found outside of the interval between the classical turning points.

Think of the particle as released from rest down at the left turning point on the frictionless gravitational valley represented by the potential, the particle picks up maximum speed at the bottom of the well, slows down as it approaches the right turning point. It stops at the right turning point, turns around and heads back down the well valley. Turning points where the particle turns around and reverses are aptly named.

Stepwise constant potentials

Perhaps the simplest solvable systems are constructed out of constant mechanical potentials. To make life interesting we can use different potentials steps in different x regions. A physical system that approaches the ideal of a stepwise potential is provided by the ion trap depicted below:

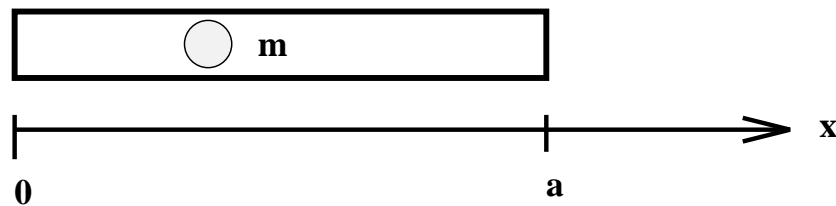


We think of the motion of the charged electron (serving as the ion) as constrained to small diameter metal tubes which serve as “Faraday cages”. When the electron is within the electrostatic environment of one of the tubes comprising the trap, it has the constant electrical potential of the tube. In the asymmetric trap depicted above, the center tube is grounded and the outside tubes ride at a negative voltage with respect to the central tube. To the negatively charged

electron, the outside tubes are at a higher mechanical potential than the zero potential central tube. We've given the electron a total energy of E which traps in the center tube by making it impossible for the electron to classically travel to the outside tube. In this idealized system the only electrical forces act at the tube gaps where the potential is changing since since the electrical field is the negative of the potential gradient. If the mechanical potential actually makes discrete jumps as depicted above, the forces and electrical fields at the tube gaps become infinite. The potential is maintained by the batteries and we've drawn it for the general case of unequal voltages.

Particle in the box

A particularly simple case to consider involves taking the limit where the potential on the outer tubes in the ion trap depicted above approaches infinity. This is a way of insuring that the electron is constrained in the region of the central tube which serves as a confining "box". We will consider the case where the electron has zero potential ($V = 0$) inside the box and is always found within the walls of the impenetrable box. We can place the origin of our x coordinate system anywhere we choose for convenience. One convenient choice for the particle in the box problem is to put the origin on the left side of the box (which has a width a) as shown below:



Within the walls of the box, we have a free particle and we know from the previous chapter that valid solutions of the free particle problem are complex travelling waves of the form $\psi(x) = \exp(ikx)$ where we have suppressed the time dependence given by $\exp(-i\omega t)$. Without regard to the the boundary condition (the box walls) any combination of k 's is possible. We get some guidance by

restricting ourselves to real $\psi(x)$ which can be obtained by $\exp(ikx) \pm \exp(-ikx)$. The real combinations of these complex traveling waves are just sines and cosines:

$$\cos(kx) = \frac{\exp(ikx) + \exp(-ikx)}{2} \quad , \quad \sin(kx) = \frac{\exp(ikx) - \exp(-ikx)}{2i}$$

$$\psi(x) = b \cos(kx) + c \sin(kx) \tag{4}$$

and the real wave function for the free particle can be constructed as a linear combination of sines and cosines with unknown coefficients b and c .

Like any problem involving differential equations, once the general solution is written down, we need to match the boundary conditions to obtain a fully explicit solution. What are the boundary conditions for the particle in the box? To answer this question we need to return to our interpretation of the wave function as a PDF amplitude $\text{PDF}(x) = \psi^*(x)\psi(x) = \psi^2(x)$. Because (for real wave functions) the square of the wave function gives the probability density for finding the electron from $x \rightarrow x + dx$, we must insist that $\psi(x)$ is well defined at every point x , *eg* $\psi(x)$ must be continuous in the sense

Continuity of the Wave Function

$$\psi(x + \Delta) = \psi(x - \Delta) \quad \text{as } \Delta \rightarrow 0$$

In particular this means that the wave function cannot make discrete jumps at boundaries. In the particle in the box problem, we assume that the electron has **no probability** of being found outside the box. Hence $\psi(x) = 0$ for $x < 0$ and $x > a$. By continuity requirement since the wave function vanishes outside the box it must vanish on the walls of the box as well and thus:

$$\psi(0) = \psi(a) = 0 \tag{5}$$

The condition that $\psi(0) = 0$, tells us that our wave function of the general form $\psi(x) = b \cos(kx) + c \sin(kx)$ cannot include a $\cos(kx)$ piece since:

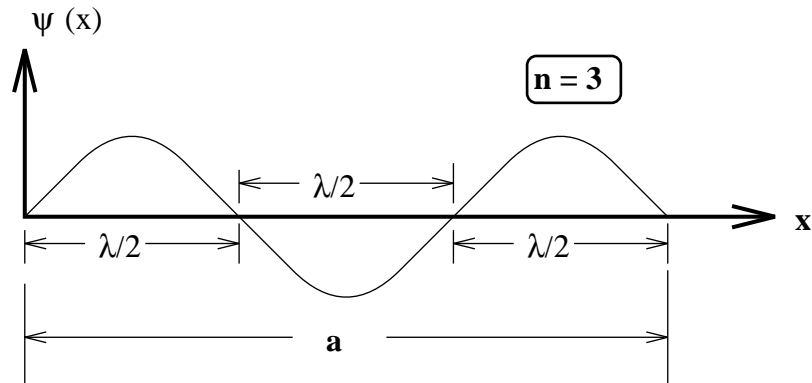
$0 = \psi(0) = b \cos(k0) + c \sin(k0) = b$. This limits us to the form $\psi(x) = c \sin(kx)$. We can limit this further by invoking the $\psi(a) = 0$ condition:

$$0 = \psi(a) = c \sin(ka) \rightarrow ka = n\pi \rightarrow k = \frac{n\pi}{a} \text{ where } n = 1, 2, 3... \quad (6)$$

The condition $\sin(ka) = 0$ occurs when the argument of the $\sin()$ vanishes which occurs at an integral multiple of π radians. We thus have decided that the particle in the box wave function is of the form:

$$\psi(x) = c \sin\left(\frac{n\pi x}{a}\right) \quad (7)$$

There is also a far simpler and less formal way of obtaining Eq. (7). Since the wave function vanishes outside the box, it must vanish on the walls of the box at $x = 0$ and $x = a$. Since we know that the wave function is comprised of sinusoidal functions we are searching for a wave function with a nodes at $x = 0$ and $x = a$. Only a pure sine function has a node at the origin. The distance between nodes of a sinusoidal function is $\lambda/2$. We need to cram an integral number of $1/2$ wavelengths in the box width a .



Therefore we require

$$n \frac{\lambda}{2} = a \rightarrow \lambda = \frac{2a}{n}$$

$$\psi(x) = c \sin\left(\frac{2\pi x}{\lambda}\right) \rightarrow c \sin\left(\frac{n\pi x}{a}\right) \quad (8)$$

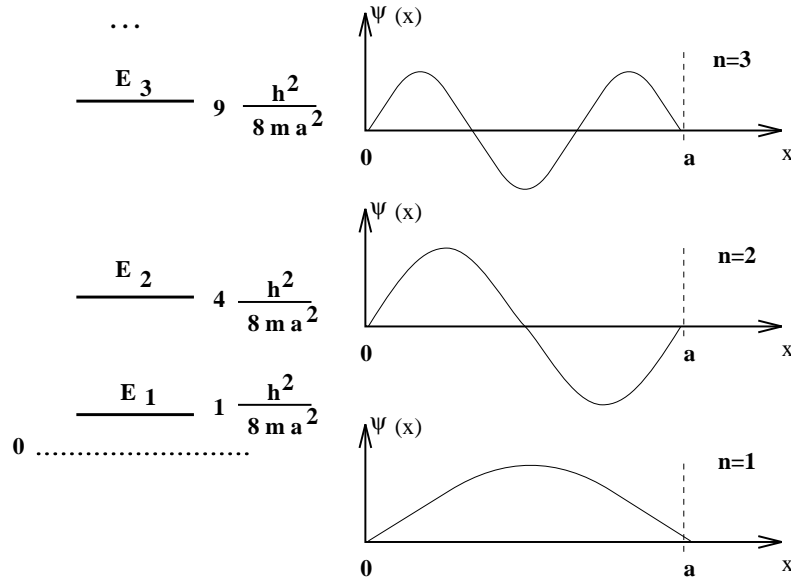
It is of interest to find the energy levels. We can formally do this by inserting our solution in the time independent SE:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E \psi(x)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} c \sin\left(\frac{n\pi x}{a}\right) = \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2 c \sin\left(\frac{n\pi x}{a}\right) = E c \sin\left(\frac{n\pi x}{a}\right)$$

$$\text{Thus } E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2} = \frac{n^2 h^2}{8ma^2} \quad (9)$$

Here is a sketch of the energy levels and wave functions for the ground state ($n = 1$) and first two excited states ($n=2, 3$) for the particle in a box of width a .



There is also a very quick informal way of obtaining the energy spectrum:

$$E = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{h}{\lambda}\right)^2, \quad \lambda = \frac{2a}{n} \rightarrow E_n = \frac{n^2 h^2}{8ma^2} \quad (10)$$

This leaves just one final unknown constant – the amplitude c – which can

be set by the normalization condition:¹

$$\int_0^a dx \psi^*(x)\psi(x) = 1 \rightarrow c = \frac{1}{\sqrt{\int_0^a dx \sin^2\left(\frac{n\pi x}{a}\right)}} = \sqrt{\frac{2}{a}} \quad (11)$$

where we use the following trick to rapidly do the integrals.

Useful trick

If x_1 and x_2 are both on nodes of a sine or cosine function then:

$$\int_{x_1}^{x_2} dx \begin{pmatrix} \sin^2(kx) \\ \text{or} \\ \cos^2(kx) \end{pmatrix} = \frac{x_2 - x_1}{2} \quad (12)$$

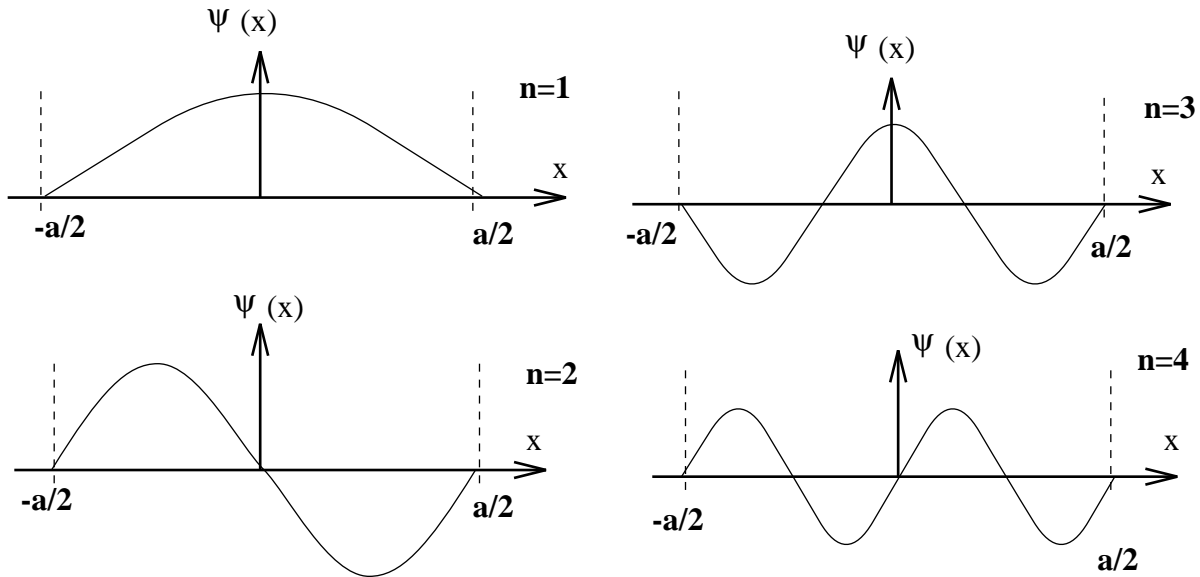
Hence our fully explicit, normalized expression becomes:

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad (13)$$

Wave function symmetry

By placing the $x = 0$ at the left wall of the box at a node of the wave function we simplified the problem since the wave function was always of the form $\psi_n(x) = c \sin k_n x$ rather than a mixture of sines and cosines. However choosing the origin at one end rather than at the center obscures the basic symmetry of the wave functions which we illustrate below:

¹ We've evaluated the normalization constant just to be fully explicit. Unless we need to have a fully explicit PDF we can often just leave the amplitude as a constant.



As you can see, with a centered origin, the ground state ($n=1$) wave function is a symmetric ($f(x) = f(-x)$) wave function built out of a cosine, the first excited state ($n=2$) is an antisymmetric wave function ($f(x) = -f(-x)$) built out of a sine etc. The alternating symmetric versus antisymmetric pattern is a general feature of all symmetric wells ($V(x) = V(-x)$). Since the potential is left-right symmetric it stands to reason that the electron $PDF(x)$ must be left-right symmetric as well ($PDF(x) = PDF(-x)$) since the electron shouldn't have a preference for being in the left or right half of a perfectly symmetric well. Since one can always choose a purely real wave function where $PDF(x) = \psi^2(x)$ this means:

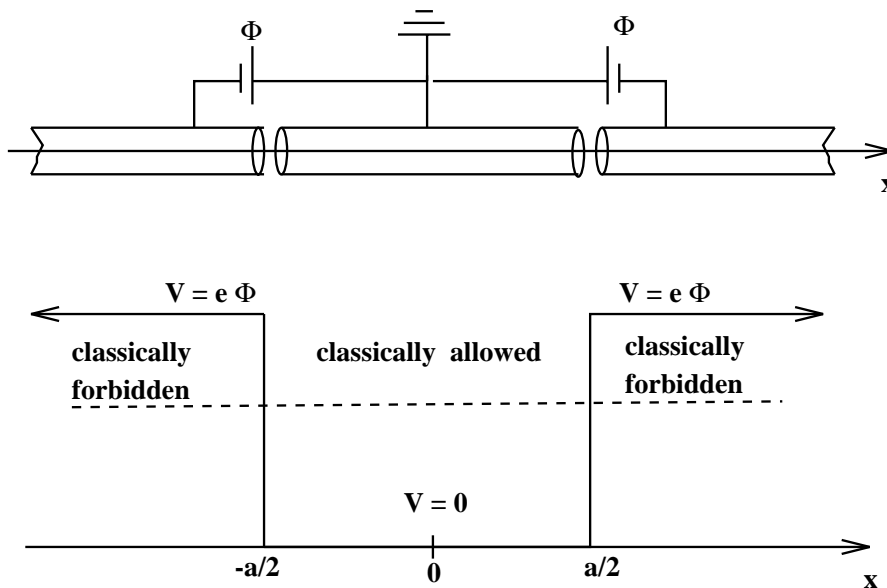
$$\psi^2(x) = \psi^2(-x) \quad \text{or} \quad \psi(x) = \pm\psi(-x) \quad (14)$$

Hence the stationary state wave functions for a symmetric well are either symmetric or antisymmetric. This symmetry is often referred to as “parity”. Symmetric wave functions have even parity; antisymmetric wave functions have odd parity. Here is a one line summary of a particle in a symmetric square well.

$$-\frac{a}{2} < x < \frac{a}{2} \quad E_n = \frac{n^2}{2m} \left(\frac{\hbar\pi}{a} \right)^2 \quad \psi_{n=1,3,5\dots} = \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) \quad \psi_{n=2,4,6\dots} = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

Particle in a finite, symmetric square well

We turn next to the problem of an electron bound in the finite, symmetric square well depicted below:



As we shall show shortly, we will obtain a different type of solution in the classically allowed region ($-a/2 < x < +a/2$) compared to the solution in the two classically forbidden regions $x > a/2$ and $x < -a/2$. Since we centered the origin and have a symmetric well we need only work the problem in the positive half of the x axis since we know $\psi(-x) = \psi(x)$ for the even parity states such as (ground, second excited, and fourth excited state) and $\psi(-x) = -\psi(x)$ for odd parity states (such as for the first excited, third excited, and fifth excited state).

We will have to smoothly join the two solutions using the continuity of the wave function along with a new condition on the continuity of the wave function derivative:

Continuity of the Wave Function Derivative

$$\boxed{\frac{\partial\psi}{\partial x}(x + \Delta) = \frac{\partial\psi}{\partial x}(x - \Delta) \text{ as } \Delta \rightarrow 0}$$

We require that $\partial\psi/\partial x$ be continuous across a boundary so that the momentum operator $\hat{p} = -i\partial/\partial x$ is well defined for the wave function. Later we will also introduce a way of computing a probability “current” which is a physical observable based on the existence of derivatives. It is already very non-intuitive that the electron can even have a non-zero wave function in the classically forbidden region of the well. This means the electron has a finite chance of being found outside of the classical turning points!

Solutions in classically allowed and forbidden step regions

We begin by re-writing the time independent SE in a region of constant potential:

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{2m(E - V)}{\hbar^2} \psi = -\frac{2m \text{ KE}}{\hbar^2} \psi \quad (15)$$

where we note that $E - V = \text{KE}$ is the kinetic energy of the electron.

Classically allowed regions are defined as those regions with $\text{KE} > 0$ and the factor $-2m \text{ KE}/\hbar^2 < 0$. We will therefore replace the factor by a negative constant which we write $-2m \text{ KE}/\hbar^2 = -k^2$ to obtain:

$$\frac{\partial^2\psi}{\partial x^2} = -k^2 \psi \quad (16)$$

You might recognize this as analogous to the equation for a harmonic oscillator $\partial^2 x/\partial t^2 = -\omega^2 x$ which has the general solution $x = a \sin(\omega t) + b \cos(\omega t)$. The general solution to Eq. (16) is:

$$x = a \sin(kx) + b \cos(kx) \text{ where } k = \sqrt{\frac{2m(E - V)}{\hbar^2}} = \sqrt{\frac{2m(E)}{\hbar^2}} \quad (17)$$

It is very easy to show that Eq. (17) is a valid solution in a region where $E > V$ by direct substitution into the Schrödinger Equation.

In classically forbidden regions $KE < 0$ and we write SE in the form

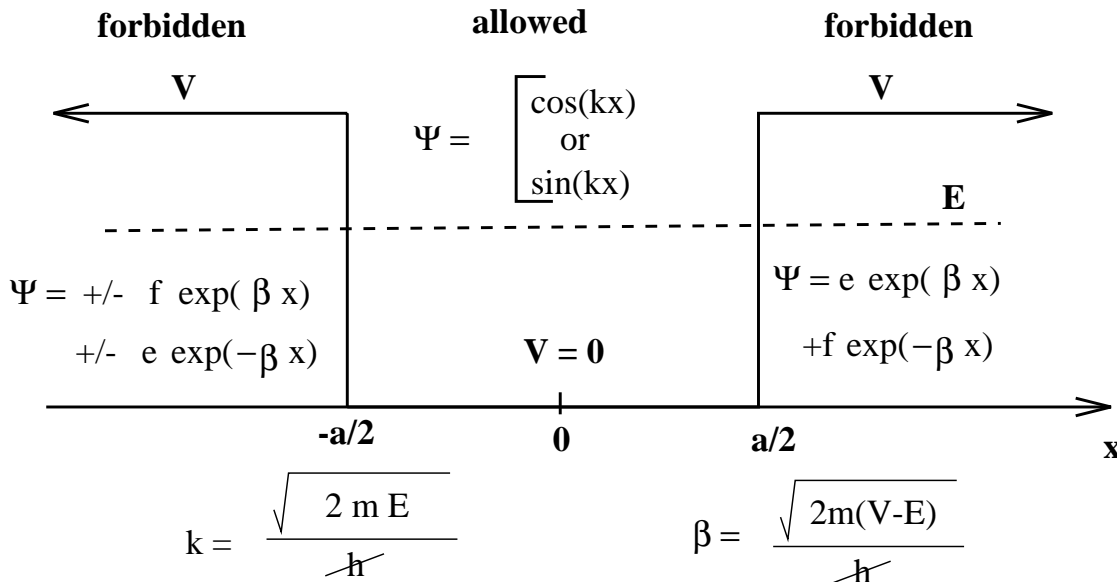
$$\frac{\partial^2 \psi}{\partial x^2} = \beta^2 \psi \quad \text{where} \quad \beta = \sqrt{\frac{2m(V - E)}{\hbar^2}} \quad (18)$$

The two solutions to Eq. (18) which the reader can verify by direct substitution are:

$$\psi(x) = e \exp(\beta x) + f \exp(-\beta x) \quad (19)$$

Selecting solutions and boundary condition matching

It appears that we have a long way to go in uniquely determining the wave function. We don't know the values of the total energy E or any of the six amplitude coefficients (two for each region of the well). We do know from the symmetry of the well that we need either an even function or odd wave function which means we must either choose a pure cosine or sine solution in the central region depending on which n state we want. Furthermore we can arbitrarily set the amplitude the central wave function equal to one since the overall scale of the wave function can later be determined through normalization. Finally the parity condition $\psi(x) = \pm\psi(-x)$ allows us to relate the coefficients in the region $x < -a/2$ to the coefficients in the region $x > a/2$. Here is a graphic summary of which solutions apply in which regions:



This leaves us with essentially three unknowns: (E, e, f) and right now we have only two boundary conditions to apply: continuity of the wave function and continuity of its derivative. We are short by one boundary condition! The final boundary condition (I swear) is that the wave function must have reasonable behavior at infinity.

$\psi(x)$ is finite at infinity

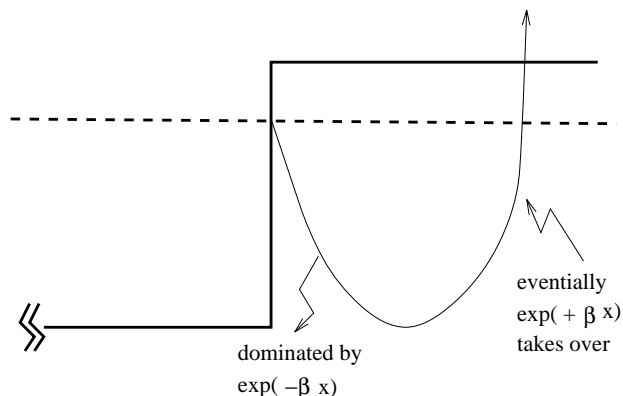
We require $\psi(x)$ to be finite as $x \rightarrow \pm\infty$

The fact that the wave function cannot be allowed to run away at infinity insures us that it is usually possible to normalize the wavefunction.[†] It also makes no physical sense that the electron would have an infinite PDF infinitely away and still be bound in the well.

For the case of stepwise constant potential, the finite behavior at infinity is a very powerful constraint since it tells us that $e = 0$ and we must have $\psi(x) = f \exp(-\beta x)$ in the region $x > +a/2$. Even the smallest amount of

[†] One exception is the traveling wave solution $\psi = \exp(ikx - \omega t)$ which is an unbound solution. The traveling wave has a constant PDF and must be normalized using special tricks.

$\exp(+\beta x)$ will eventually blow the wave function up as $x \rightarrow +\infty$ and produce an unnormalizable wave function as illustrated below:



We now have two continuity conditions and two unknowns E and f . Let's write these equations for the even parity states where we choose a cosine function for the well center. We begin with the wave function continuity condition which requires $\psi(a/2)_{\text{left}} = \psi(a/2)_{\text{right}}$ or

$$\cos\left(\frac{ka}{2}\right) = f \exp\left(\frac{-\beta a}{2}\right) \quad (20)$$

To apply the continuity of the derivative condition, we begin by taking the derivative of the wave functions:

$$\frac{\partial \cos(kx)}{\partial x} \Big|_{x=a/2} = -k \sin(kx) \Big|_{x=a/2} = -k \sin\left(\frac{ka}{2}\right)$$

$$\frac{\partial f \exp(-\beta x)}{\partial x} \Big|_{x=a/2} = -\beta f \exp(-\beta x) \Big|_{x=a/2} = -\beta f \exp\left(\frac{-\beta a}{2}\right)$$

Hence the condition $\partial\psi/\partial x(a/2)_{\text{left}} = \partial\psi/\partial x(a/2)_{\text{right}}$ gives:

$$-k \sin\left(\frac{ka}{2}\right) = -\beta f \exp\left(\frac{-\beta a}{2}\right) \quad (21)$$

Taking the ratio of Eq. (21) to Eq. (20) we have:

$$k \tan\left(\frac{ka}{2}\right) = \beta$$

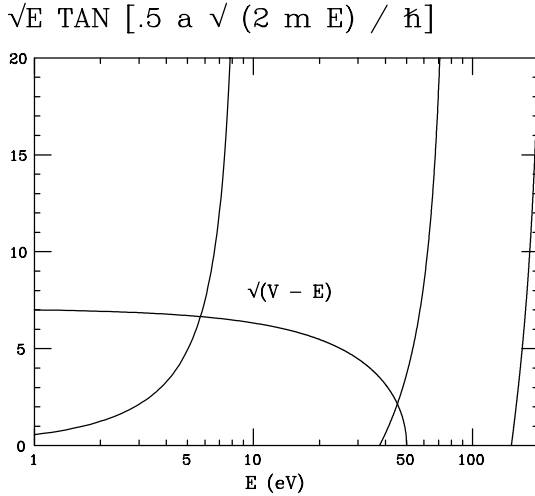
Inserting expressions for k and β as a function of E we have:

$$\sqrt{\frac{2mE}{\hbar^2}} \tan\left(\frac{a}{2} \sqrt{\frac{2mE}{\hbar^2}}\right) = \sqrt{\frac{2m(V-E)}{\hbar^2}}$$

Taking out the common factor of $\sqrt{2m/\hbar^2}$ leaves us with the transcendental equation:

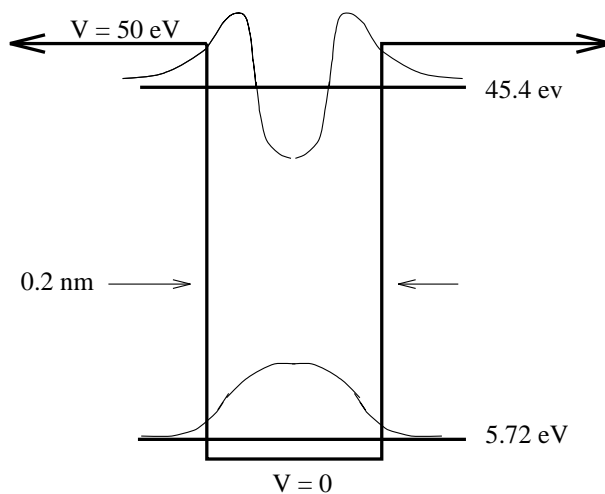
$$\sqrt{E} \tan\left(\frac{a}{2} \sqrt{\frac{2mE}{\hbar^2}}\right) = \sqrt{V-E} \quad (22)$$

A transcendental equation is an equation which “transcends” solution by conventional analytical methods. We solve Eq. (22) by graphing the left and right sides of the equation on a semilog plot. The periodicity of the tangent function implies that there will be multiple branches of the left side of Eq. (22). Valid solutions occur at the intersection of the two plots.



From the nature of the functions it is easy to see that there will always be at least one bound state since the 1st tangent branch must pass through the origin. As you can see, the function $\sqrt{V-E}$ intersects the first two branches of the tangent function but goes to zero at $E = V$ before intersecting the third branch. There are thus exactly two intersections and thus exactly two even bound states in the well $n = 1$ and $n = 3$. One of the even bound states occurs at $E = 5.72 \text{ eV}$,

the other occurs near the top of the well at an energy of $E = 45.4 \text{ eV}$. A crude sketch of the two even bound states is shown below:



We note that as the state gets closer to the top of the well, the wave function penetrates much further into the classically forbidden region. For the wave function $\psi \propto \exp(-\beta x)$, β^{-1} is a measure of the extent of the wave function into the classically forbidden region. Essentially what happens is that as the state energy approaches the well depth ($E \rightarrow V$), $\beta = \sqrt{2m(V - E)/\hbar^2} \rightarrow 0$ and $\beta^{-1} \rightarrow \infty$. The limiting case is $\beta = 0$ where the electron is just barely bound and the wave function outside the well becomes a constant. There is an odd bound state corresponding to $n = 2$ at roughly 20 eV that you will explore in the exercises.

The Atomic Clock

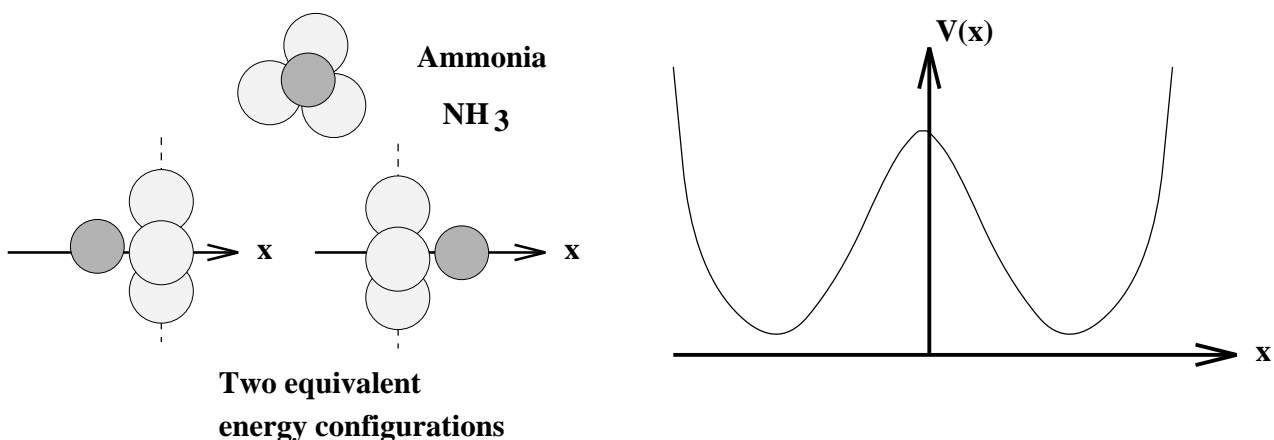
As a practical example of stepwise constant bound states, we consider the historical development of the “atomic clock”. The “atomic” clock was first developed in 1949 by the National Bureau of Standards as a means of establishing a highly reproducible, highly accurate time standard based on a resonant frequency of ammonia molecule. An accurate time standard is presently crucial in satellite based communications. The first atomic clock exploited the amazingly small energy difference of 98.32 microelectron volts between the ground and first

excited state of the ammonia molecule. Recall that typical atomic energy levels are several electron volts which are larger by factors of ten thousand. The photons capable of exciting ammonia from the ground to its first excited state have a wavelength of

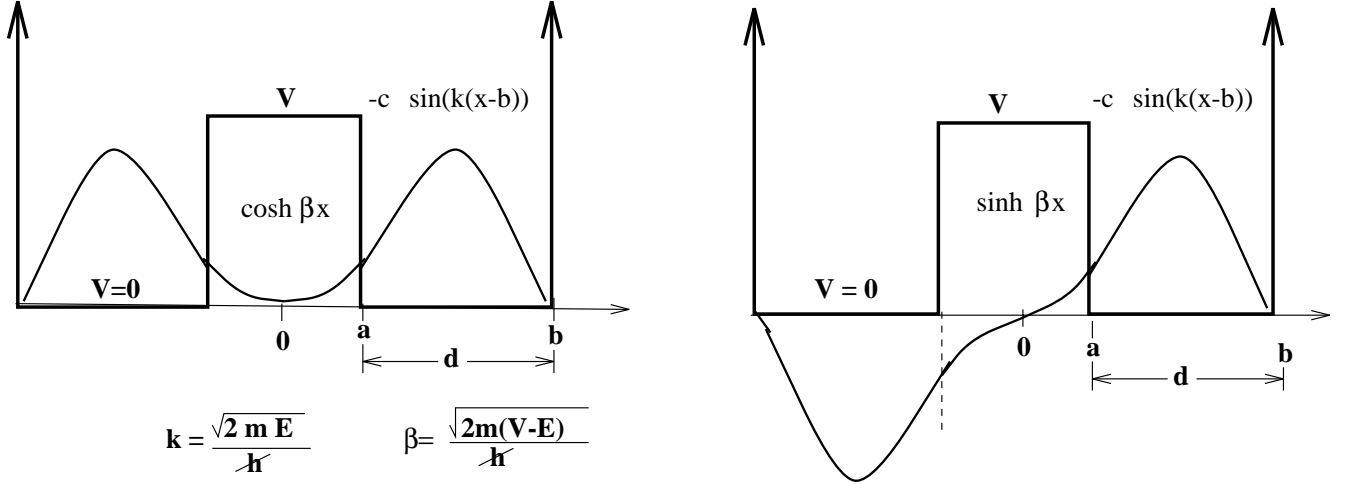
$$\lambda = \frac{2\pi\hbar c}{\Delta E} = \frac{1240 \text{ eV nm}}{98.32 \times 10^{-6} \text{ eV}} = 1.26 \times 10^7 \text{ nm} = 1.26 \text{ cm}$$

These photons are microwaves with a frequency of only 23.8 GHz. which could be generated in 1949 using commercial microwave oscillators developed as part of the World War II radar program. One could build circuits which “lock” in to the 23.8 GHz frequency which maximizes the absorption in ammonia.

Ammonia is a very simple tetrahedral molecule consisting of a heavy nitrogen atom sitting on a base of three hydrogen atoms. By symmetry, the most energetically favorable configuration of the molecule is to have the nitrogen atom on one side or the other of the triatomic hydrogen plane as illustrated below:



A graph of the potential energy as a function of nitrogen out of plane distance $V(x)$ would have two symmetric minima with an unstable maximum at $x = 0$. We can idealize this potential in terms of the symmetric, stepwise constant potential well illustrated below:



We use classically allowed sinusoidal wave functions with nodes at $x = \pm b$ of the form $-c \sin(k(x-b))$. We will typically operate in a limit where V in the barrier region $-a < x < a$ is large so we require classically forbidden, exponential wave functions. As the central, “barrier” region becomes very wide or very high, we will show that $E_2 - E_1 \rightarrow 0$ which can account for the very small energy difference present in ammonia.

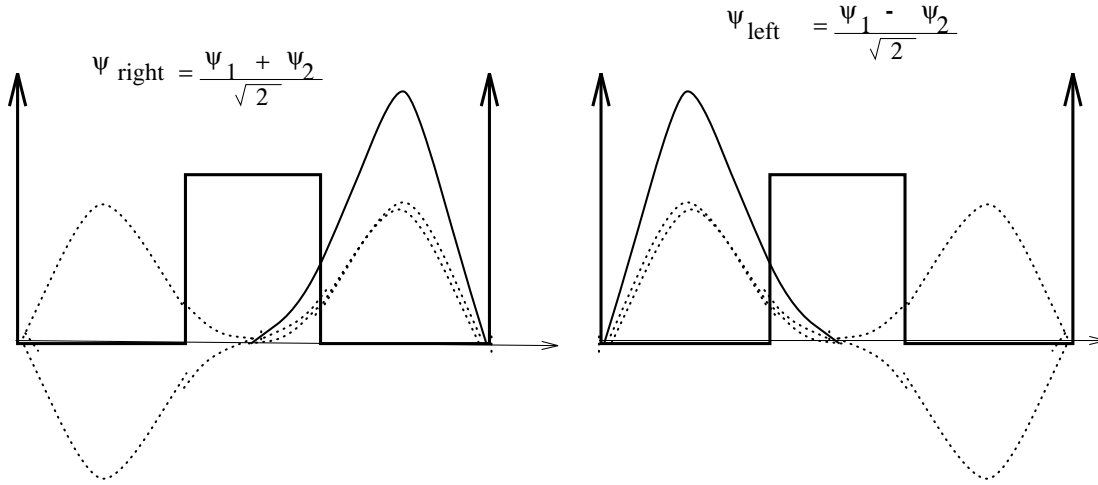
The ground state is constructed from the symmetric exponential combination $\cosh(\beta x) = (\exp(\beta x) + \exp(-\beta x))/2$; while the first excited state is constructed from the antisymmetric combination $\sinh(\beta x) = (\exp(\beta x) - \exp(-\beta x))/2$. In the limit $\beta \times a \gg 1$ the symmetric and antisymmetric wavefunctions in the barrier region approach each other at $x = a$ since $\cosh(\beta x), \sinh(\beta x) \rightarrow \exp(\beta a)/2$. Since the ground and 1st excited state sinusoidal solutions in the region $a < x < b$ must match up with nearly identical forbidden solutions at point x , it follows that they have nearly identical wavelengths and therefore nearly identical energies. Because $\cosh(\beta a) > \sinh(\beta a)$, the sinusoidal ground state wave function joins the barrier wavefunction at a slightly higher point which implies a slightly larger wavelength and slightly lower energy.

In the more restrictive limit of $V \rightarrow \infty$ or $\beta \rightarrow \infty$, the wave function has negligible penetration into the forbidden region and approaches a node at $x = a$ as well as $x = b$ or an internodal distance of $d \equiv b - a$. Hence the wavelength for

both the ground and first excited state is $\lambda = 2d$ and the energy of either state approaches $E_{1,2} \rightarrow h^2/(8md^2) \rightarrow (\pi\hbar)^2/(2md^2)$.

Exciting the molecule

If one bombards the ammonia molecule with microwaves of an energy equal to ΔE , the nitrogen wave function can be in a linear combination of ψ_1 and ψ_2 . For example the combination $\psi_r = (\psi_1(x) + \psi_2(x))/\sqrt{2}$ has a PDF which places the nitrogen primarily on the right whereas $\psi_\ell = (\psi_1(x) - \psi_2(x))/\sqrt{2}$ has the nitrogen atom on the left.



Starting with ψ_ℓ and restoring the time dependence we have:

$$\Psi(x, t) = \frac{1}{\sqrt{2}} (\psi_1(x) e^{-i\omega_1 t} - \psi_2(x) e^{-i\omega_2 t}) = \frac{e^{-i\omega_1 t}}{\sqrt{2}} (\psi_1(x) - \psi_2(x) e^{-i\Delta\omega t}) \quad (23)$$

If we wait a time of $\tilde{t} = \pi/\Delta\omega$, the wave function and PDF becomes:

$$\Psi(x, \tilde{t}) = \frac{e^{-i\omega_1 \tilde{t}}}{\sqrt{2}} (\psi_1(x) + \psi_2(x)) \quad , \quad \text{PDF}(x, \tilde{t}) = \frac{1}{2} (\psi_1(x) + \psi_2(x))^2 = \psi_r(x)^* \psi_r(x) \quad (24)$$

At time \tilde{t} the nitrogen PDF has moved from the left well to the right well. The oscillation frequency is then $\tau = 2\tilde{t} = 2\pi/\Delta\omega$. Classically the ammonia molecule acts as an oscillating dipole antenna which will absorb energy at its natural frequency.

The discrete spectrum and continuum

In the Bohr atom an electron bound in a hydrogen atom was required to lie on a set of discrete energy levels given by $E_n = -13.6/n^2$. However it is certainly possible to have a electrons with positive energies as well. Classically this would correspond to having the electron traveling with some velocity , once it is an infinite distance from the proton. We could call this the case of an “unbound” electron which has “escaped” from its potential well. If the electron is infinitely far away with a finite velocity, the total energy of the electron will be positive since:

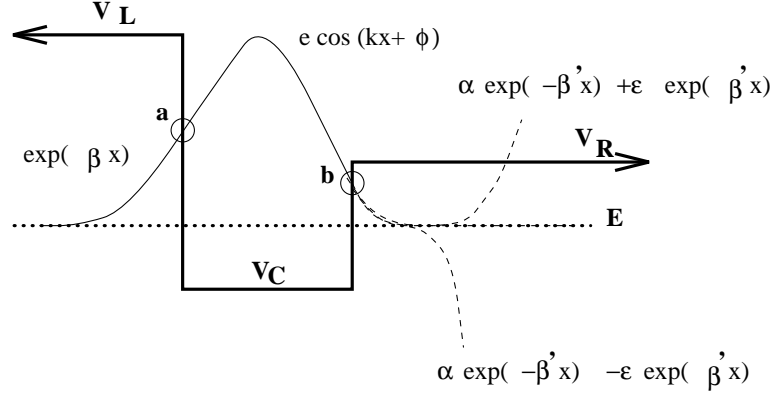
$$E = -\frac{\kappa}{r} + \frac{1}{2}m v^2 \text{ as } r \rightarrow \infty , E = \frac{1}{2}mv^2 > 0 \quad (25)$$

Are only certain, discrete energy levels possible for the case where $E > 0$? If the electron is unbound and is infinitely far from the proton, the proton exerts no force on the electron and the electron will follow a straight line classical trajectory. This suggests that the electron can have any velocity at infinity, and thus any $E > 0$ is possible. The spectrum becomes continuous rather than discrete and we say the electron is in the *continuum*.

Of course, it might be dangerous to argue a quantum mechanical point with a semi-classical argument. The stepwise constant potential well provides a good insight into the nature of the discrete versus continuum spectrum.

Numerical Method

We begin by discussing a numerical approach used for iteratively finding solutions for the general stepwise potential which we illustrate for the well below.



Lets begin by guessing an energy for a bound electron state in the region from $V_C < E < V_R$. We will then let the computer try to draw a wave function for this state. If the wave function is acceptable (continuous , continuous derivative, and well behaved at infinity), our initial energy guess for E was acceptable. If not, we must guess again. The computer program begins by drawing the wave function in the classically forbidden region at the extreme left of the well. We know the wave function must be exponential in this region and in order that it be well behaved at $-\infty$ it must be of the pure $\exp(\beta x)$ where β is determined from the energy as $\beta = \sqrt{2m (V_L - E)}/\hbar$. Hence we set $\psi_L(x) = \exp(\beta x)$ since we can arbitrarily set the overall multiplicative factor equal to one and find its true value later by normalization.

Since we have an explicit form for $\psi_L(x)$ in the V_L region, we can evaluate both the wave function and slope of $\psi_L(x = a)$. The electron is classically allowed in the region V_C and we therefore know that it must be of the sinusoidal form: $\psi(x) = e \cos(kx + \phi)$ where neither the amplitude e nor the phase ϕ are known but the wave number is known ($k = \sqrt{2m (E - V_C)}/\hbar$). We can evaluate both $\psi_C(x = a)$ and $\frac{\partial \psi_C}{\partial x}(x = a)$ in terms of the unknown e and ϕ and equate them with the values $\psi_L(x = a)$ and $\frac{\partial \psi_L}{\partial x}(x = a)$. This gives us two equations and two unknowns and allows us to evaluate e and ϕ .

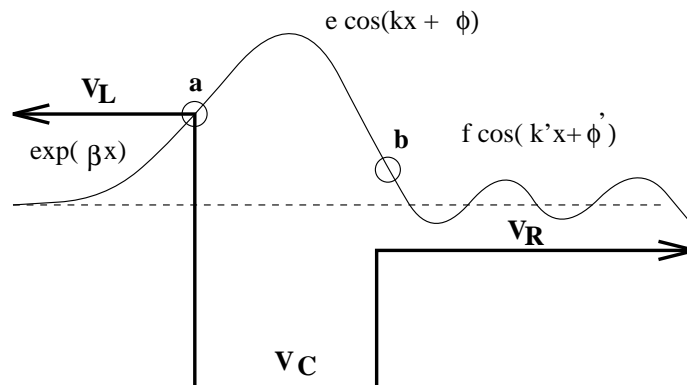
We now can repeat this exercise for point b . The electron is classically forbidden in the region V_R which means that it must have a wave function of the

form $\psi_R = \alpha \exp(\beta'x) + \epsilon \exp(-\beta'x)$. The value of β' follows from the guessed energy E according to $\beta' = \sqrt{2m(V_R - E)}/\hbar$. The unknown coefficients α and ϵ can be solved by matching ψ and $\partial\psi/\partial x$ at boundary b since we already have a fully explicit form for $\psi_C(x)$.

Unless one guesses E **exactly correctly** one will have either a positive or negative value for ϵ . A positive value for ϵ which multiplies $\exp(\beta x)$ will cause $\psi(x) \rightarrow +\infty$ as $x \rightarrow +\infty$. Similarly a negative value for ϵ will cause $\psi(x) \rightarrow -\infty$ as $x \rightarrow +\infty$. Neither of these options is acceptable. The only acceptable solution is to have selected E **just perfectly** such that $\epsilon = 0$. Clearly values in the neighborhood of an acceptable solution will result in $\epsilon \neq 0$ and will be unacceptable. Hence we conclude that the energy spectrum for the case of $V_C < E < V_R$ is discrete.

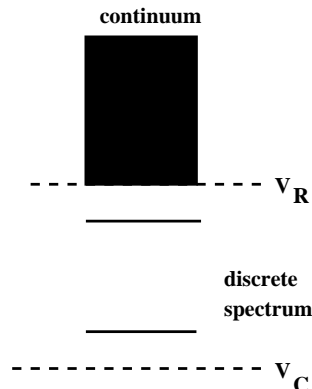
The Continuum

Lets contrast this for the situation where $V_R < E < V_L$ as illustrated below.



Again the wave function in the region V_L is classical forbidden and entirely determined. The wave function in the region V_C is sinusoidal with amplitude e and phase ϕ which can be solved for by matching the wave function and derivative at point a . Since $E > V_R$, the wave function in the region V_R is classically allowed and sinusoidal. The wave number $k' = \sqrt{2m(E - V_R)}/\hbar$ and amplitude f and phase ϕ' can be determined by matching wavefunction and slope at point b . Now the essential thing to realize is that **any** value of f and ϕ' will provide an

acceptable wave function. Since the solution in the region V_R is sinusoidal, it can never blow up to infinity. This means that any choice of $E > V_R$ will result in a valid wave function and the spectrum is therefore continuous.



We say the electron resides in the continuum. The criteria for being in the continuum is that the electron is unbounded in the sense that there is classically allowed region which extends to either $+\infty$ and/or $-\infty$.

The Harmonic Oscillator

Recall that the potential energy for the harmonic oscillator is given by $V(x) = Kx^2/2$. It is useful to express this in terms of the mass and angular frequency ($\omega = \sqrt{K/m}$)

$$V = \frac{1}{2}K x^2 = \frac{1}{2}m \omega^2 x^2$$

The time independent Schrödinger Equation for the harmonic oscillator is then:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + \frac{1}{2}m \omega^2 x^2 \psi(x) = E \psi(x) \tag{26}$$

The solution for Eq. (26) is far from obvious! As a guess², we will try a ground state wavefunction of the symmetric form: $\psi = \exp(-\beta x^2/2)$ and see if we can

² It really helps when you know the answer in advance!

find a value of β which solves Eq. (26). We begin with the double derivative.

$$\frac{\partial \exp(-\beta x^2/2)}{\partial x} = -\beta x \exp(-\beta x^2/2)$$

$$\frac{\partial^2 \exp(-\beta x^2/2)}{\partial x^2} = \frac{\partial(-\beta x \exp(-\beta x^2/2))}{\partial x} = (-\beta + \beta^2 x^2) \exp(-\beta x^2/2)$$

We next insert the double derivative into the SE.

$$E \exp(-\beta x^2/2) = -\frac{\hbar^2}{2m} \frac{\partial^2 \exp(-\beta x^2/2)}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \exp(-\beta x^2/2)$$

$$-\frac{\hbar^2}{2m} (-\beta + \beta^2 x^2) \exp(-\beta x^2/2) + \frac{1}{2} m \omega^2 x^2 \exp(-\beta x^2/2) = E \exp(-\beta x^2/2)$$

Dividing both sides by $\exp(-\beta x^2/2)$ and re-arranging a bit we have:

$$\frac{\hbar^2}{2m} \beta + \left(\frac{1}{2} m \omega^2 - \frac{\hbar^2}{2m} \beta^2 \right) x^2 = E \quad (27)$$

In order to eliminate the x^2 term, we set its coefficient to zero which gives us a condition on β .

$$\left(\frac{1}{2} m \omega^2 - \frac{\hbar^2}{2m} \beta^2 \right) = 0 \rightarrow \beta = \frac{m\omega}{\hbar} \quad (28)$$

we can then insert this value of β back into Eq. (27) to obtain the ground state energy, E_o ³

$$E_o = \frac{\hbar^2}{2m} \beta = \frac{\hbar^2}{2m} \frac{m\omega}{\hbar} = \frac{1}{2} \hbar \omega \quad (29)$$

The wave function for the ground state is then:

$$\psi(x) = \varphi_0(x) = \mathcal{N} \exp\left(-\frac{1}{2} \frac{m\omega}{\hbar} x^2\right) = \mathcal{N} \exp\left(-\frac{1}{2} \left(\sqrt{\frac{m\omega}{\hbar}} x\right)^2\right) \quad (30)$$

We will often write the harmonic oscillator stationary states as $\varphi_n(x)$ where $n = 0, 1, 2, \dots$ since they serve as such good examples of one dimensional bound

³ Unfortunately it is conventional to label the principle quantum numbers for the harmonic oscillator by $n = 0, 1, 2, 3, \dots$ whereas the principle quantum numbers for the finite and infinite square well along with the Bohr atom are generally labeled by $n = 1, 2, 3, \dots$

state solutions over the full x axis $-\infty < x < +\infty$. The combination $\xi = \sqrt{\beta}x = \sqrt{m\omega/\hbar} x$ serves as a convenient dimensionless coordinate for the φ_n wave functions.

In general, one can show (but I will not) that stationary states of the harmonic oscillator are given by:

$$\varphi_n(x) = \mathcal{N}_n H_n(\xi) \exp(-\xi^2/2) \quad \text{where} \quad \xi = \sqrt{\beta} x \equiv \sqrt{\frac{m\omega}{\hbar}} x \quad (31)$$

The functions $H_n(\xi)$ are called the Hermite polynomials and were first encountered as solutions to a classical differential equation. Here is a table of a few of them:

$H_0 = 1$	$H_3 = 8 \xi^3 - 12 \xi$
$H_1 = 2 \xi$	$H_4 = 16 \xi^4 - 48 \xi^2 + 12$
$H_2 = 4 \xi^2 - 2$	$H_5 = 32 \xi^5 - 160 \xi^3 + 120 \xi$

One can generate additional H_n polynomials through the simple recurrence formula:

$$H_{n+1}(\xi) = 2 \xi H_n(\xi) - 2n H_{n-1}(\xi) \quad (32)$$

The energy levels are very simple:

$$E = \left(n + \frac{1}{2} \right) \hbar\omega \quad \text{where} \quad n = 0, 1, 2, \dots \quad (33)$$

Dealing with harmonic oscillator wave functions

We will frequently want to use harmonic oscillator solutions as examples in this class. It is frequently more convenient to use regular coordinates x rather than dimensionless coordinates ξ . The manipulations will frequently involve integrals over Gaussian forms such as $I_n = \int_{-\infty}^{+\infty} dy y^n e^{-\beta y^2}$. Here is a trick that

can be used to compute such integrals: If we differentiate I_n with respect to β we get:

$$\frac{\partial I_n}{\partial \beta} = \int_{-\infty}^{+\infty} dy y^n \frac{\partial}{\partial \beta} (e^{-\beta y^2}) = - \int_{-\infty}^{+\infty} dy y^{n+2} e^{-\beta y^2} = -I_{n+2} \rightarrow I_{n+2} = -\frac{\partial I_n}{\partial \beta}$$

One can differentiate repeatedly from $I_0 = \sqrt{\pi}\beta^{-1/2}$ to rapidly get a full integral table:

$$I_0 = \sqrt{\pi}\beta^{-1/2}; \quad I_2 = \sqrt{\pi} \left(\frac{1}{2}\right) \beta^{-3/2}; \quad I_4 = \sqrt{\pi} \left(\frac{1}{2}\right) \left(\frac{3}{2}\right) \beta^{-5/2}$$

$$I_6 = \sqrt{\pi} \left(\frac{1}{2}\right) \left(\frac{3}{2}\right) \left(\frac{5}{2}\right) \beta^{-7/2}$$

One immediate use of the integral table is to compute the normalization of the simple harmonic oscillator ground state:

$$\varphi_0 = N_0 \exp\left(-\frac{\beta x^2}{2}\right) \quad \text{where } \beta = \frac{m\omega}{\hbar}; \quad N_0^2 \int_{-\infty}^{\infty} dx e^{-\beta x^2} = N_0^2 I_0 = N_0^2 \sqrt{\frac{\pi}{\beta}} = 1$$

$$\text{Thus } N_0^2 = \left(\sqrt{\frac{\beta}{\pi}}\right) \quad \text{and} \quad \varphi_0 = \left(\sqrt{\frac{\beta}{\pi}}\right)^{1/2} \exp\left(-\frac{\beta x^2}{2}\right)$$

The other normalization constants are obtained in the same way.

Normalized Harmonic Oscillator Wave Functions

$$\varphi_0 = \left(\sqrt{\frac{\beta}{\pi}}\right)^{1/2} \exp\left(-\frac{\beta x^2}{2}\right); \quad \varphi_1 = \left(2\beta\sqrt{\frac{\beta}{\pi}}\right)^{1/2} x \exp\left(-\frac{\beta x^2}{2}\right)$$

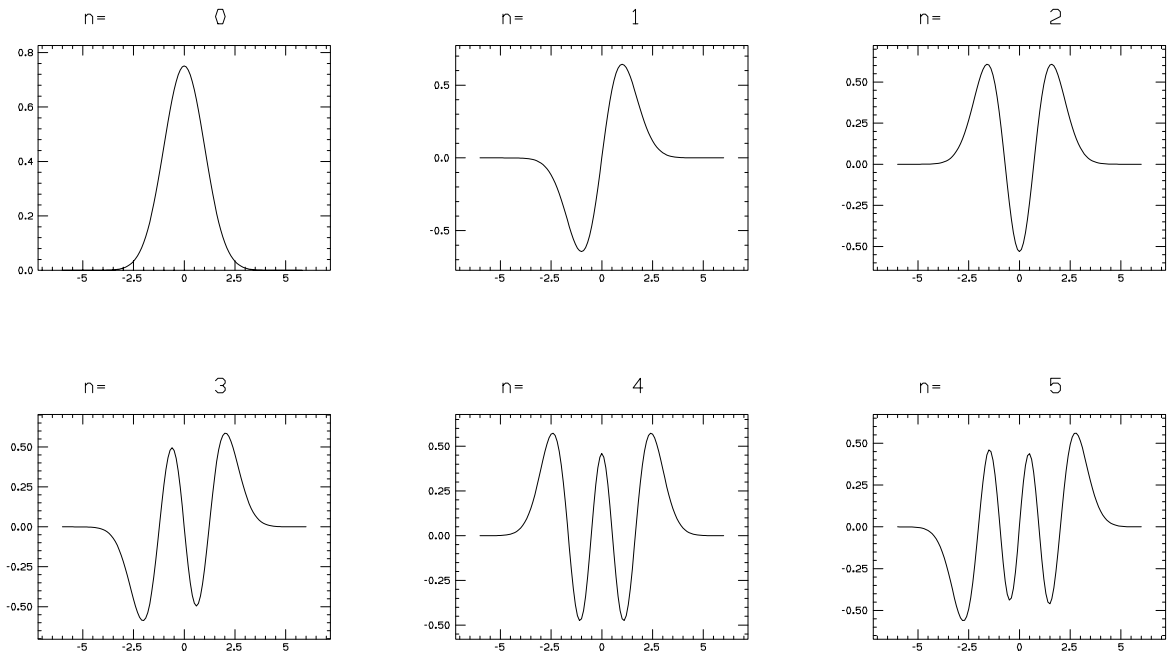
$$\varphi_2 = \left(\frac{1}{2}\sqrt{\frac{\beta}{\pi}}\right)^{1/2} [2\beta x^2 - 1] \exp\left(-\frac{\beta x^2}{2}\right)$$

where $\beta = m\omega/\hbar$

In the above table, the polynomials are not exactly the same as the Hermite polynomials but are proportional to them. The overall scale of the “official”

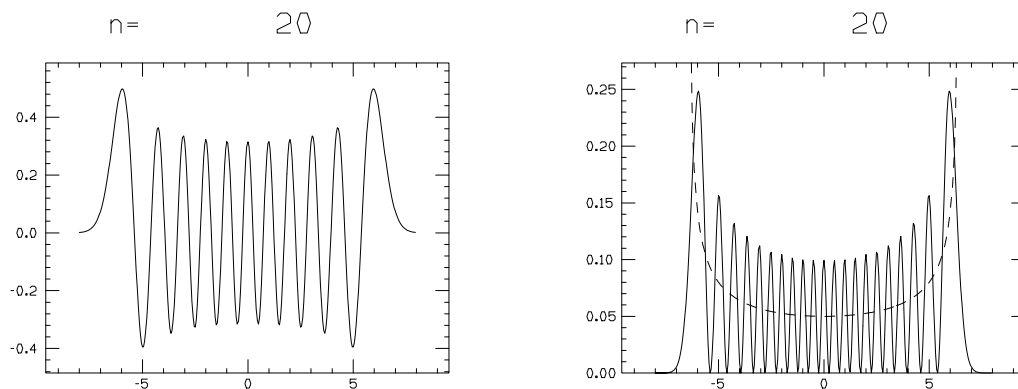
H_n was chosen to simplify the recurrence formula (Eq. (32)) but is fairly arbitrary for our purposes since one must normalize the wave function anyway. Note that we need to add factors of β in the polynomials in order to get dimensional consistency. β has dimensions of $1/\text{length}^2$ and hence in φ_2 the βx^2 piece is dimensionless and can therefore be combined with -1 in a dimensionally consistent fashion.

Here is a plot of the first 6 stationary state wave functions:



We note the striking similarity between the wave functions for the harmonic oscillator and the wave functions for the square wells. In both cases the ground state is even, and each subsequent state alternates between being odd, then even, then odd, etc. Each subsequent energy state has an additional node in the wave function.

The harmonic oscillator wave functions also exhibit significant differences from the wave functions for stepwise constant potentials. These differences are fairly striking for the highly excited harmonic oscillator states. We illustrate both $\varphi_{20}(x)$ and $\text{PDF}(x) = |\varphi_{20}|^2(x)$ for the $n = 20$ state.



We note that the apparent wavelength of the wave function is shortest near $\xi = 0$ and longest at large $|\xi|$. This makes a great deal of sense since the center of the well is where the kinetic energy is largest. The momentum is therefore the largest at the well center and since $\lambda = h/p$, the wavelength is the smallest.

A connection with classical physics

We further note that the magnitude of the harmonic oscillator wave function increases as one gets further from the center of well. This is a beautiful illustration of the connection between classical and quantum physics. The dashed curve superimposed on the figure to the right represents a “classical” $\text{PDF}(x)$ describing the probability for finding the particle from x to $x + dx$. It may seem odd to

discuss a probability density for a classical particle given the fact that a classical particle executes a deterministic orbit. Imagine setting the mass in motion in a dark room and then at random intervals making thousand of flash photographs of the mass's position. We can then assign a probability density PDF(x) by counting the fraction of photographs where the mass is observed between x and $x + \Delta$ and dividing this fraction by Δ . A little reflection will show that this classical PDF(x) is related to the time interval that the mass spends between x and $x + \Delta$. This time interval is the distance interval divided by the particle velocity at x :

$$\text{probability} = \text{PDF}(x) \Delta \propto \Delta t = \frac{\Delta}{v(x)} \rightarrow \text{PDF}(x) \propto \frac{1}{v} \quad (34)$$

The velocity at any position can easily be obtained through the conservation of energy equation.

$$\frac{1}{2}m v^2 + \frac{1}{2}m \omega^2 x^2 = E = (n + \frac{1}{2})\hbar\omega \quad (35)$$

Note that we set the energy of state n to the quantum mechanical energy.

$$v^2 = \frac{\hbar\omega}{m}(2n + 1) - \omega^2 x^2 \quad \text{Let } x^2 = \frac{\hbar}{m\omega}\xi^2 \quad (36)$$

$$\text{PDF}(\xi) \propto \frac{1}{v} = \frac{\sqrt{m/(\hbar\omega)}}{\sqrt{(2n + 1) - \xi^2}} \quad (37)$$

Eq. (37) is the dashed curve plotted on $\varphi^2(\xi)$ for $n = 20$. As you can see this classical PDF does an excellent job of “averaging” the quantum PDF. The average φ^2 tends to be largest where the particle is traveling the slowest.

Important Points

1. One can always find a real wave function for the stationary states of particle bound in a potential well.

2. We introduced the concepts of classical turning points, classically allowed, and classically forbidden regions in a potential well.
3. When an electron is constrained within a one dimensional box of width a , it has a sinusoidal wave function with nodes on the walls of the box. For the case of a symmetric box we have.

$$-\frac{a}{2} < x < \frac{a}{2} \quad E_n = \frac{n^2}{2m} \left(\frac{\hbar\pi}{a} \right)^2 \quad \psi_{n=1,3,5\dots} = \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) \quad \psi_{n=2,4,6\dots} = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

4. In a symmetric well with an origin at the well center, the wave function is either even ($\psi(x) = \psi(-x)$) or odd ($\psi(x) = -\psi(-x)$). The ground state is even, first excited is odd, second excited is even and so it goes.
5. In classically allowed regions of a constant potential, the solutions are of the form

$$\psi(x) = \begin{array}{c} \sin(kx) \\ \text{or} \\ \cos(kx) \end{array} \quad \text{where } k = \frac{\sqrt{2m(E - V)}}{\hbar}$$

6. In classically forbidden regions of a constant potential, the solutions are of the form

$$\psi(x) = \begin{array}{c} \exp(\beta x) \\ \text{or} \\ \exp(-\beta x) \end{array} \quad \text{where } \beta = \frac{\sqrt{2m(V - E)}}{\hbar}$$

7. The solutions to the stepwise constant potential problem involves satisfying three boundary conditions:
 - (a) $\psi(x)$ is continuous across a boundary
 - (b) $\partial\psi/\partial x$ is continuous across a boundary
 - (c) $\psi(x)$ must remain finite even as $x \rightarrow \pm\infty$

8. We discussed the ammonia clock as an example of a molecular double well which we modeled as an infinite square well with a finite barrier in the center. In the limit of large barrier height or width we saw that the ground and first excited states have a separation of only 98 microvolts since the left side of the well nearly decouples from the right side. Microwaves have sufficient frequency necessary to excite the ammonia molecule between the ground and 1st excited state and cause the nitrogen atom to slosh back and forth relative to the triatomic hydrogen plane.
9. If the electron has a classically allowed region which extends to either $\pm\infty$, it is unbounded and has a continuous energy spectrum. The continuum begins once an electron can classically escape from the well. If the electron is bound in the well, one has a discrete energy spectrum.
10. The solutions electrons in a harmonic oscillator $V = \frac{1}{2} K x^2 = \frac{1}{2} m \omega^2 x^2$ have an energy spectrum given by

$$E = \left(n + \frac{1}{2} \right) \hbar\omega \quad \text{where } n = 0, 1, 2, \dots$$

The wave functions are of the form

$$\varphi_n(x) = \mathcal{N}_n H_n(\sqrt{\beta}x) \exp\left(-\frac{\beta x^2}{2}\right) \quad \text{where } \beta = \frac{m\omega}{\hbar}$$

The $H_n(\xi)$ are simple polynomials which include powers of ξ up to and including ξ^n .

11. Both the wavelength and $\psi^*(x)\psi(x)$ increases as the electron's $|x|$ increases. The increase in the wavelength is because the electron momentum becomes smaller as $|x|$ increases. The increase in $\psi^*(x)\psi(x)$ reflects the fact that a classical electron is most likely to be found where it is traveling the slowest.