Chapter 2. The Particle in a Box

In this chapter, we solve the time-independent Schrodinger equation for a very simple system, a particle in a 1D box. First, we review diff. equations.

Differential Equations:

Ordinary

(only one variable)

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

time-independent S.E (x only variable).

Partial

(more than one variable)

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

time-dependent S.E (x and t are variables)

Ordinary differential equations:

Order of a differential equation is the order of the highest derivative in the equation. For example, a third order differential equation is:

$$y^{'''}+2x(y^{'})^2+\sin x\cos y=3e^x$$

What is the order of time-independent S.E.?

Differential Equations:

Linear differential equation has the form:

$$A_n(x)y^{(n)} + A_{n-1}(x)y^{(n-1)} + \ldots + A_1(x)y' + A_0(x)y = g(x)$$

If g(x)=0: homogeneous linear equation.

What kind of diff. equation is 1D time-independent S.E.?

- It is a linear homogeneous differential equation of second order.

Second order linear homogeneous equation can be written as:

$$\boxed{y'' + P(x)y' + Q(x)y = 0}$$

The solution can be written as a linear combination of two independent solutions y_1 and y_2:

$$y=c_1y_1 + c_2y_2$$

To determine constants, we need boundary conditions.

Differential Equations:

Let’s assume the solution has the form:

$$y = e^{sx}$$

Then, equation becomes:

$$y'' + py' + qy = 0$$

$$s^2 e^{sx} + pse^{sx} + qe^{sx} = 0$$

$\boxed{s^2 + ps + q = 0} \longrightarrow$ *auxiliary equation* We get s_1 and s_2 from here.

The solution is: $\boxed{y = c_1 e^{s_1 x} + c_2 e^{s_2 x}}$

Example: Solve the following differential equation:

$$3y\frac{d^2y}{dx^2} + 3y\frac{dy}{dx} - 18y^2 = 0$$

With boundary conditions:

$y = 0$ at $x = 0$

$\frac{dy}{dx} = 1$ at $x = 0$

Differential Equations:

First, we need to write it in the form:

$$y'' + py' + qy = 0 \longrightarrow y'' + 1y' - 6y = 0$$

Then, auxiliary equation becomes:

$$s^2 + ps + q = 0 \longrightarrow s^2 + s - 6 = 0$$

The solutions of the auxiliary equation are:

$$\boxed{x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}$$

$$s_{1,2} = \frac{-1 \pm \sqrt{1+24}}{2} = 2 \ \ and -3$$

So, the solution of differential equation is: $y = c_1 e^{2x} + c_2 e^{-3x}$

To get c_1 and c_2, we use boundary conditions:

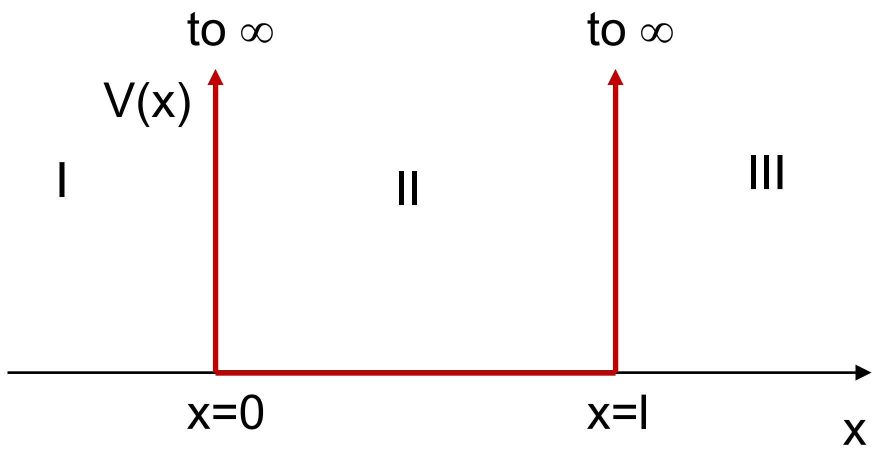
$$c_1 + c_2 = 0$$

$$2c_1 - 3c_2 = 1$$

The solution of differential equation is: $y = 0.2e^{2x} - 0.2e^{-3x}$

Particle in 1D Box:

A particle subjected to a potential energy function that is infinite everywhere except on a line segment of length l:



Regions I and III:
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E-\infty)\psi$$

Neglecting E in comparison with ∞, we have:

$$\psi = \frac{1}{\infty}\frac{d^2\psi}{dx^2} \xrightarrow{\text{So:}} \boxed{\begin{array}{l}\psi_I = 0 \\ \psi_{III} = 0\end{array}}$$

Particle in 1D Box:

Region II:

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2}E\psi_{II} = 0$$

What are we solving for? E and Ψ

This is a linear homogeneous second-order differential equation. The auxiliary equation is:

$$s^2 + \frac{2m}{\hbar^2}E = 0$$

$$s = \pm\frac{i\sqrt{2mE}}{\hbar}$$

So, the wavefunction is:

$$\psi_{II} = c_1e^{i\theta} + c_2e^{-i\theta}$$

$$\theta = \frac{x\sqrt{2mE}}{\hbar}$$

Now, we need to determine the coefficients. But, first we need to convert the wavefunction into a more convenient form. From Chapter 1, we know that:

$$\boxed{e^{i\theta}=\cos\theta+i\sin\theta}$$

$$e^{-i\theta} = \cos(-\theta) + i\sin(-\theta) = \cos\theta - i\sin\theta$$

Particle in 1D Box:

Our wave function then becomes:

$$\psi_{II} = c_1\cos\theta + ic_1\sin\theta + c_2\cos\theta - ic_2\sin\theta$$

$$= (c_1 + c_2)\cos\theta + (ic_1 - ic_2)\sin\theta$$

$$= A\cos\theta + B\sin\theta$$

Now, we determine A and B by applying boundary conditions. If ψ is to be continuous at x=0, then ψ_I and ψ_{II} must approach the same value at x=0:

$$\lim_{x\to 0}\psi_I = \lim_{x\to 0}\psi_{II}$$

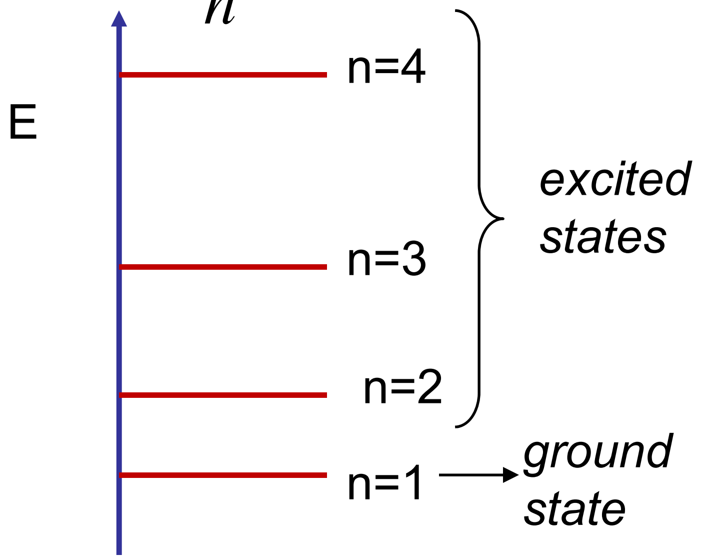
$$0 = \lim_{x\to 0}\left(A\cos\left(\frac{x\sqrt{2mE}}{\hbar}\right) + B\sin\left(\frac{x\sqrt{2mE}}{\hbar}\right)\right)$$

$$0 = A$$

Applying the continuity condition at x=l: $$B\sin\left(\frac{l\sqrt{2mE}}{\hbar}\right) = 0$$

Particle in 1D Box:

B cannot be zero, so: $\sin\left(\frac{l\sqrt{2mE}}{\hbar}\right)=0 \longrightarrow \frac{l\sqrt{2mE}}{\hbar}=\pm n\pi$



n=0 is not allowed, because it gives Ψ=0. Thus:

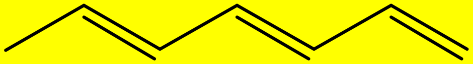
$$\boxed{E=\frac{n^2h^2}{8ml^2}}$$

n=1,2,3….

What does this equation tell us:

1. Energy is quantized.
2. For n=0, zero-point energy exists (the particle would move even at T=0 K). This is in contrast with classical physics which predicts a particle to be perfectly still at T=0 K. The zero-point energy is in agreement with Heisenberg uncertainty principle: if E=0, then $p_x=0$, and uncertainty in momentum would be $\Delta p_x=0$, which violates the uncertainty principle.
3. The spacing between energy levels increases as n increases.
4. Energy increases as the box length decreases (this explains why electron does not fall into nucleus: potential energy decreases due to electrostatic interactions, but the kinetic energy increases due to confinement effect).

Particle in a box is a very simple model, but can be used to predict the behavior of conjugated molecules:



Example:

Using particle in 1D box model, estimate the absorption wavelength of butadiene. Experimental value is 217 nm.

HOMO: n=2; LUMO: n=3

$$E_3 - E_2 = \frac{h^2}{8ml^2}(3^2 - 2^2) = \frac{5h^2}{8ml^2}$$

$$\frac{hc}{\lambda} = \frac{5h^2}{8ml^2}$$

$$\lambda = \frac{8cml^2}{5h} = \frac{8\cdot(3\cdot10^8\frac{m}{s})\cdot(9.1\cdot10^{-31}kg)\cdot(7\cdot10^{-10}m)^2}{5(6.63\cdot10^{-34}Js)} = 3.2\cdot10^{-7}m = 320\,nm$$

Particle in 1D Box:

The wave function now becomes: $\psi_{II} = B\sin\left(\frac{n\pi x}{l}\right)$

But, we still do not know the value B. To get it, we use the normalization requirement:

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

$$\int_{-\infty}^{0} |\psi_I|^2 dx + \int_{0}^{l} |\psi_{II}|^2 dx + \int_{l}^{+\infty} |\psi_{III}|^2 dx = 1$$

$$B^2 \int_0^l \sin^2(\frac{n\pi x}{l}) dx = 1$$

To solve the integral, we use the trigonometric transformation: $2\sin^2 x = 1 - \cos 2x$

$$B^2 \int_0^l \sin^2(\frac{n\pi x}{l}) dx = B^2 \int_0^l \left(\frac{1}{2} - \frac{1}{2}\cos\left(\frac{n\pi x}{l}\right)\right) dx$$

$$\int \frac{1}{2} dx = \frac{x}{2}$$

Particle in 1D Box:

To solve the second integral, we use substitution method:

$$\int_0^l \frac{1}{2}\cos\left(\frac{2n\pi x}{l}\right)dx$$

$$t = \frac{2n\pi x}{l}$$

$$\frac{dt}{dx} = \frac{2n\pi}{l}$$

$$\int_0^l \frac{1}{2}\cos\left(\frac{2n\pi x}{l}\right)dx = \frac{1}{2}\int \frac{l}{2n\pi}\cos t\,dt = \frac{l}{4n\pi}\sin\frac{2n\pi x}{l}$$

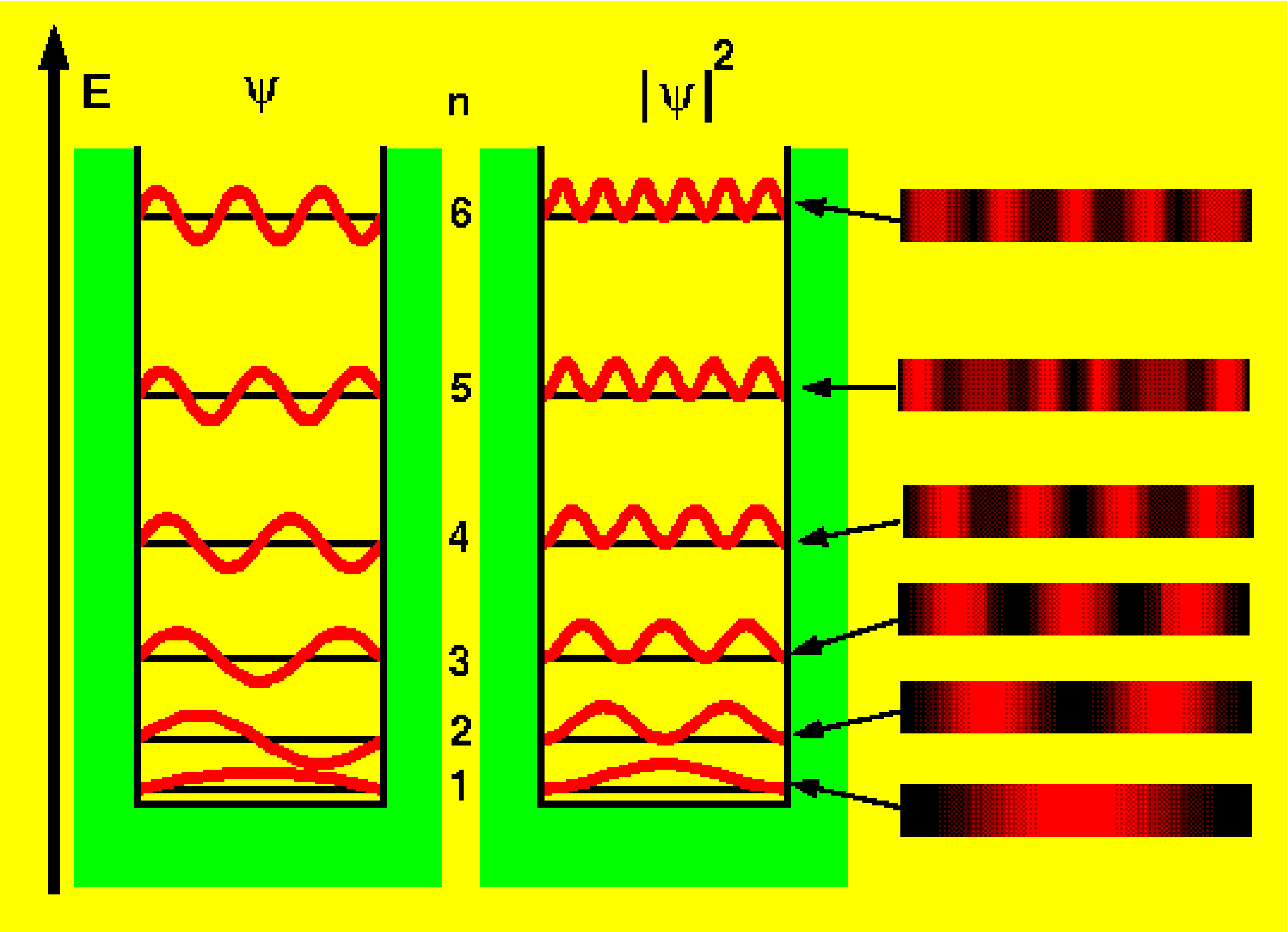
So, the final solution is:

$$B^2\int_0^l \left(\frac{1}{2} - \frac{1}{2}\cos\left(\frac{n\pi x}{l}\right)\right)dx = B^2\left(\frac{1}{2}x - \frac{l}{4n\pi}\sin\left(\frac{2n\pi x}{l}\right)\right)\Bigg|_0^l = \frac{lB^2}{2} \quad \Rightarrow \quad \boxed{B = \sqrt{\frac{2}{l}}}$$

Particle in 1D Box:

Finally, the wave function is:

$$\boxed{\psi_{II} = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right)}$$



Particle in 1D Box:

What can we learn from the wavefuction:

-Nodes exist at which the probability of finding a particle is zero. This is in contrast with classical mechanics, which predicts the same probability of finding a particle anywhere in the box.

-One might ask: how does the particle go from one part of the box to another without ever crossing the nodes? This is simply the weirdness of quantum particles in action.

-For higher n, the number of nodes increases. This means that the underlying wavefunction has shorter and shorter wavelength. According to De Broglie’s relationship, the shorter wavelength means higher linear momentum, that is higher kinetic energy.

-As n becomes large, the system starts behaving according to classical physics: Bohr’s *correspondence principle*. According to classical mechanics: even probability of finding the particle enywhere in the box. In quantum mechanics, for n=1, the probability is highest at the center of the box (very different from classical prediction). But, as n increases, number of nodes will be big and so close to each other that we cannot distinguish between them experimentally. Thus, the probability distribution will be even, which corresponds to the classical description.

Example: Determine the probability of finding a particle in the left quarter of the box.

$$\int_0^{\frac{l}{4}} \psi^2 dx = \frac{2}{l}\int_0^{\frac{l}{4}} \sin^2\left(\frac{n\pi x}{l}\right) dx = \frac{2}{l}\left[\frac{x}{2} - \frac{l}{4n\pi}\sin\left(\frac{2n\pi x}{l}\right)\right]\Bigg|_0^{\frac{l}{4}}$$

$$= \frac{1}{4} - \frac{1}{2n\pi}\sin\left(\frac{n\pi}{2}\right) \longrightarrow$$

For large n, the probability will be 0.25 (as predicted by classical mechanics).

Orthonormality

-Since the wave function is normalized, we have: $\int_{-\infty}^{\infty} \psi\psi^* dx = 1$

-If we use two wave functions corresponding to different energy levels, then:

$$\int_{-\infty}^{\infty} \psi_i \psi_j{}^* dx = 0$$

Two wave functions are orthogonal to each other

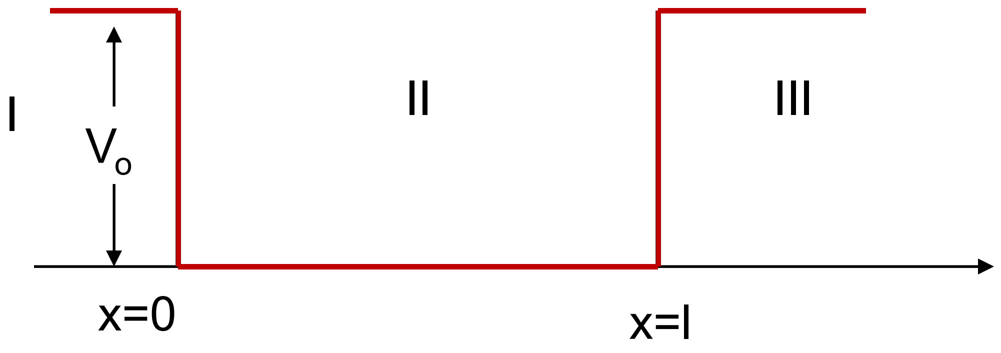
In general form, these two expressions can be written as:

$$\boxed{\begin{gathered}\int_{-\infty}^{\infty} \psi_i \psi_j{}^* dx = \delta_{ij} \\ \delta_{ij} = \begin{cases} 0 & for i \neq j \\ 1 & for i = j \end{cases}\end{gathered}}$$

δ is called the Kronecker delta.

Particle in a Rectangular Well

What happens if the wall has a finite height?



There are two cases: when $E<V_o$ and $E>V_o$. We first consider $E<V_o$. The Schrodinger equation in regions I and III is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V_0\cdot\psi=E\cdot\psi$$

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-V_0)=0$$

$$\Rightarrow$$

The auxiliary equation is:

$$s^2+\frac{2m}{\hbar^2}(E-V_0)=0$$

$$s=\pm\frac{\sqrt{2m(V_0-E)}}{\hbar}$$

So, the solutions are:

$$\psi_I=C\cdot e^{\frac{x\sqrt{2m(V_0-E)}}{\hbar}}+D\cdot e^{-\frac{x\sqrt{2m(V_0-E)}}{\hbar}}$$

$$\psi_{III}=F\cdot e^{\frac{x\sqrt{2m(V_0-E)}}{\hbar}}+G\cdot e^{-\frac{x\sqrt{2m(V_0-E)}}{\hbar}}$$

Wavefunction Ψ_I must be finite as $x \rightarrow -\infty$. Since $E<V_0$, the expression $(V_0-E)^{1/2}$ is a real positive number. So, it must be that D=0.

In the same way, F=0.

So, the wavefunctions become:

$$\psi_I = C\cdot e^{\frac{x\sqrt{2m(V_0-E)}}{\hbar}}$$

$$\psi_{III} = G\cdot e^{-\frac{x\sqrt{2m(V_0-E)}}{\hbar}}$$

In region II, the solution is the same as what we had with the particle in a box:

$$\psi_{II} = A\cdot\cos\frac{x\sqrt{2mE}}{\hbar} + B\cdot\sin\frac{x\sqrt{2mE}}{\hbar}$$

To obtain the constants, we need to apply boundary conditions:

1. $\psi_I(0) = \psi_{II}(0)$
2. $\psi_{II}(l) = \psi_{III}(l)$
3. $\dfrac{d\psi_I}{dx} = \dfrac{d\psi_{II}}{dx} \quad at \quad x = 0$
4. $\dfrac{d\psi_{II}}{dx} = \dfrac{d\psi_{III}}{dx} \quad at \quad x = l$

Since we have four constants, we need more boundary conditions. We already applied a condition that wavefunction needs to be continuous. Now, we will apply that the first derivative needs to be continuous (justification: if the first derivative is discontinuous, the second derivative will be infinite at that point. But the Schrodinger equation does not contain anything infinite in it).

We will not derive the equations further. The final equation for energy is:

$$(2\varepsilon-1)\sin\left(b\sqrt{\varepsilon}\right)-2\sqrt{\varepsilon-\varepsilon^2}\cos\left(b\sqrt{\varepsilon}\right)=0$$

$$\varepsilon=\frac{E}{V_0}$$

$$b=\frac{l\sqrt{2mV_0}}{\hbar}$$

Only the particular values of E that satisfy this equation give a wavefunction that is continuous and has a continuous derivative, so the energy levels are quantized for $E<V_0$. To obtain possible energy values, we can plot the left side of the equation versus ε for $0<\varepsilon<1$

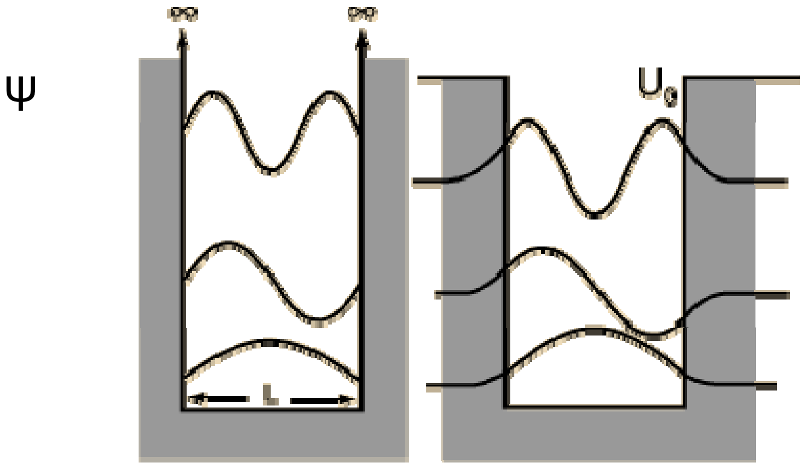
The number of allowed energy levels with $E<V_0$ is N, where N satisfies:

$$\boxed{N-1<\frac{l\sqrt{2mV_0}}{\pi\cdot\hbar}\leq N}$$

For example, if $V_0=h^2/ml^2$, then $b/\pi=2(2^{1/2})=2.83$, and N=3.

For $E>V_0$: the quantity $(V_0-E)^{1/2}$ is imaginary. So, the wavefunctions Ψ_I and Ψ_{III} oscillate as x goes to ±∞ (similar to the free particle wavefunction). All energies are allowed: *unbound state*.

Particle in a Rectangular Well

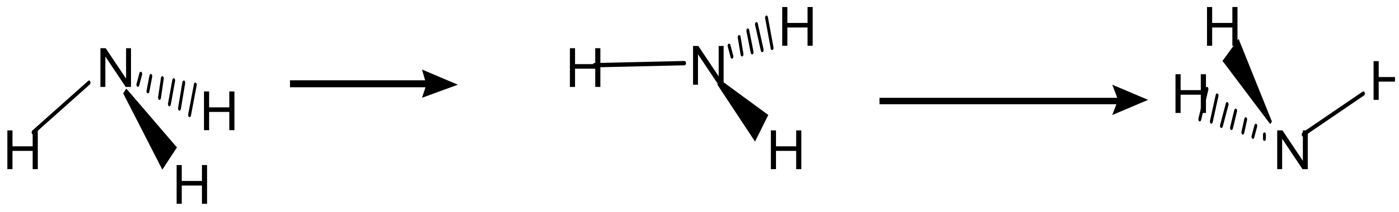


A particle can penetrate into a classically-forbidden region (tunneling). Common for reactions involving electron and proton transfers.

Does this mean that the kinetic energy of the particle is negative? No.

The **kinetic energy** of an object is the extra energy which it possesses due to its motion. If we could consider the particle as an object that could be located at a point: In medium 1 the kinetic energy would be positive, in medium 2 the kinetic energy would be negative. There is no inconsistency in this, because physics knows that the nature of the physical world is such that particles are not objects that can *physically* be located at a point: they are always spread out ("delocalized") to some extent, and the kinetic energy of the *delocalized* object is *always* positive.

Example 1:



Planar intermediate has high energy, but the N-inversion still occurs because of the tunneling of hydrogen atom.

Example 2:

The energy of most stars is a result of a fusion of H-nuclei to form He- nuclei. The T of the interior of the sun is 15x10^6 K. At this T, nuclei do not have enough energy to overcome the electrostatic repulsion. Still, the process occurs due to tunneling.