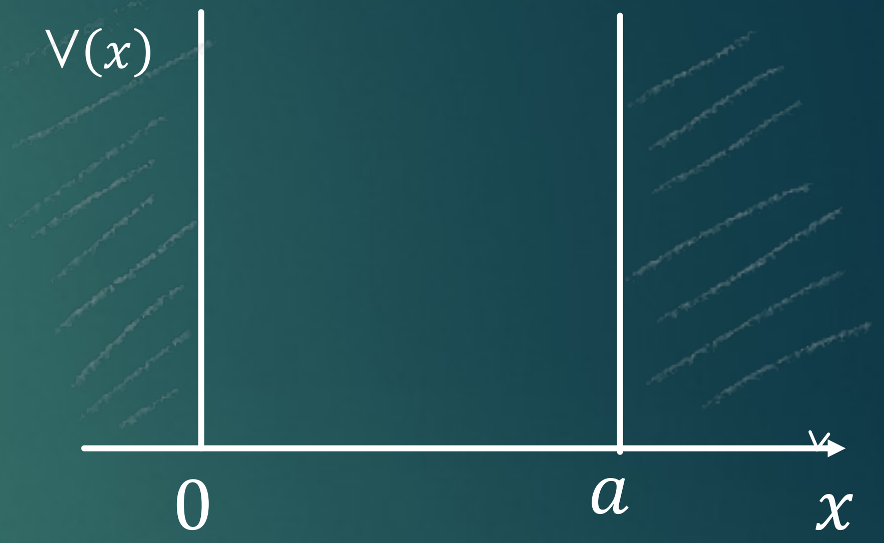
One-Dimensional Potentials

(with extension to the 3D case)

Infinite Square Well (or particle in 1D box)

Consider a particle of mass m and energy E moving in the following potential:

$$V(x) = \begin{cases} 0, & for\ 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$$



**Because these potentials are infinitely high,
but the particle's energy E is finite,
we presume there is no possibility of finding the particle in these regions outside the well (box)**

Infinite Square Well (or particle in 1D box)

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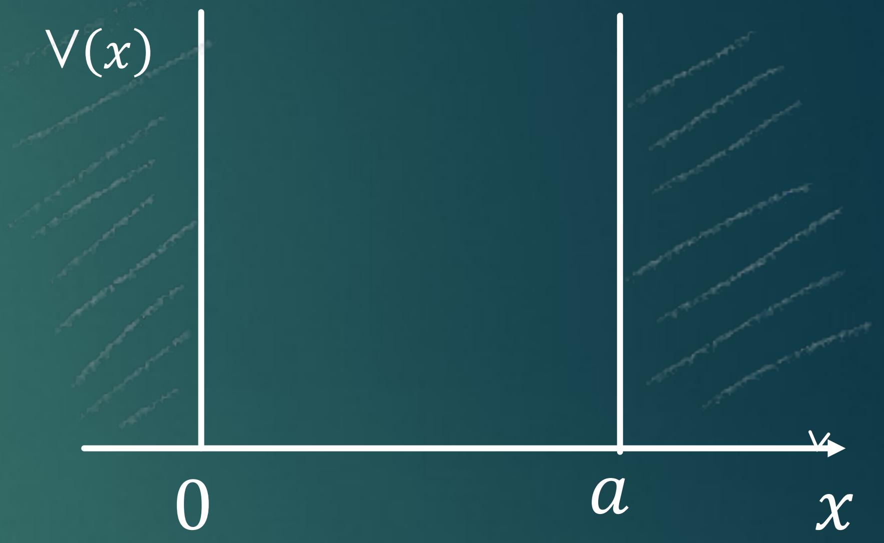


Since $\frac{d^2}{dx^2}\psi(x) = \frac{2m}{\hbar^2}[V(\mathrm{x}) - E]\,\psi(x)$

to have finite $\frac{d^2}{dx^2}\psi(x)$, boundary conditions are:

$$\psi(0) = \psi(a) = 0$$

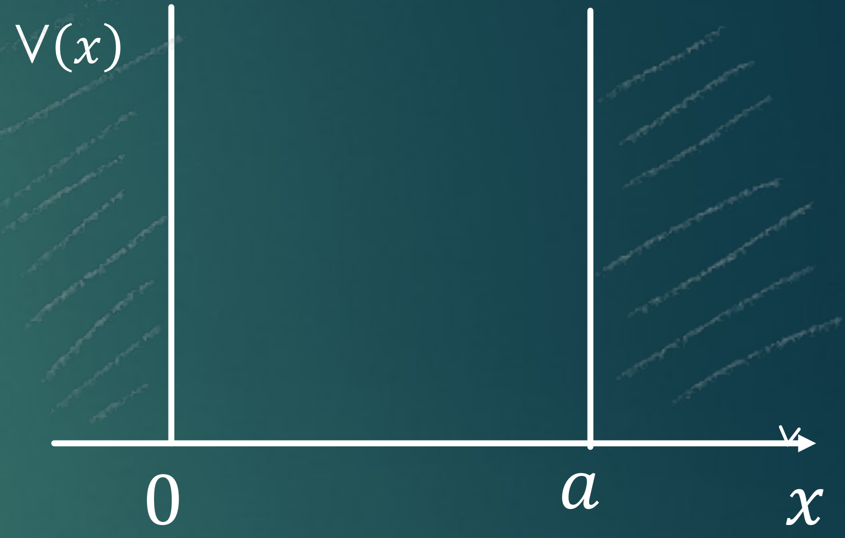
While inside the well, for 0<x<a the S.E. can be written (i.e. Helmholtz wave eq.):

$$\frac{\mathrm{d}^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) = -\frac{2m}{\hbar^2}\frac{\hbar^2k^2}{2m}\psi(x) \Rightarrow \frac{\mathrm{d}^2\psi(x)}{dx^2} = -k^2\psi(x)$$

Infinite Square Well (or particle in 1D box)

Consider a particle of mass m and energy E moving in the following potential:

$$V(x) = \begin{cases} 0, & \text{for } 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$$



$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

$$\boxed{E = \frac{p^2}{2m} = \frac{k^2\hbar^2}{2m} \;\Downarrow\; k^2 = \frac{2mE}{\hbar^2} \;\Downarrow\; k = \frac{\sqrt{2mE}}{\hbar} \Rightarrow E \ge 0}$$

$\rightarrow$ If I would consider negative Energy one can show that it is impossible to satisfy the boundary conditions

Possible solutions are:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Infinite Square Well (or particle in 1D box)

$$\frac{\mathrm{d}^2\psi(x)}{dx^2} = -k^2\psi(x)$$

Possible solutions are:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

A and B are arbitrary constant that must be fixed by imposing the boundary conditions:

$$\psi(0) = \psi(a) = 0$$

Considering @ boundary x=0:

$$\psi(0) = A\sin(0) + B\cos(0) = B = 0$$

Thus: $$\psi(x) = A\sin(kx)$$

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Thus: $$\psi(x) = A\sin(kx)$$

And @ a: $$\psi(a) = A\sin(ka) = 0$$

This is verified if:

1. $A = 0 \Rightarrow \psi(x) = 0$ Trivial solution

2. $sin(ka) = 0 \Rightarrow ka = \cancel{0}, \pm\pi, \pm 2\pi, \dots$

Infinite Square Well (or particle in 1D box)

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

Possible solutions are:

$$\psi(x) = A\sin(kx)$$

Because B=0

With boundary conditions:

$$\psi(a) = A\sin(ka) = 0$$

$\Rightarrow$ $if:\ sin(ka) = 0$ $\Rightarrow$ $ka = \pm\pi, \pm 2\pi, \pm 3\pi, \ldots$

Thus: $k_n = n\frac{\pi}{a}$ with $n = 1, 2, 3 \ldots$

Then:

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}}$$

Infinite Square Well (or particle in 1D box)

t.i.S.E.

$$\frac{\mathrm{d}^2\psi(x)}{dx^2} = -k^2\psi(x)$$

Solutions

$$\mathrm{E_n} = \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}$$

$$\psi_n(x) = A\sin\left(\frac{n\pi}{\mathrm{a}}x\right)$$

The energy values are discrete!

In contrast to the classical case, a quantum particle in the infinite square well cannot have just any energy.

Infinite Square Well (or particle in 1D box)

t.i.S.E.

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

Solutions

$$E_n = \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}$$ Eigenvalues

$$\psi_n(x) = A\sin\left(\frac{n\pi}{a}x\right)$$ Eigenfunctions

This was the (time independent) S.E. : $E\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right)\psi$

In general, solving the S.E. means finding eigenvalues and eigenfunctions of the eigenvalue equation for the matrix $\hat{H}$, which is the Hamiltonian (energy) operator:

$$\hat{H}\psi_i = E_i\ \psi_i$$ t.i.S.E.

Eigensolutions

Each eigenfunction ψ_i is associated with a particular eigenvalue E_i :

$$\hat{H}\psi_i = E_i\ \psi_i$$

It is possible to have more than one eigenfunction with a given eigenvalue, this is known as degeneracy.
The number of such states with the same eigenvalue is called the degeneracy.

Normalization of the wavefunctions

t.i.S.E.

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

Solutions

$$E_n = \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}$$

Eigenvalues

$$\psi_n(x) = A\sin\left(\frac{n\pi}{a}x\right)$$

Eigenfunctions

The eigenvalues of the energy operator are discrete!
In contrast to the classical case, a quantum particle in the infinite square well cannot have just any energy.

How can we find the constant A?
By exploiting the ortho-normalization condition

$$\int_0^a \psi_n(x)^*\,\psi_m(x)\,dx = \delta_{nm}$$

Infinite Square Well (or particle in 1D box)

How can we find the constant A?
By exploiting the normalization condition

$$\int_0^a |\psi_n(x)|^2 dx = 1 \qquad \text{with} \quad \psi_n(x) = A\sin\left(\frac{n\pi}{\mathrm{a}}x\right)$$

$$\int_0^a |A|^2 \sin^2(kx)\,\mathrm{d}x = 1$$

$$= |A|^2\left[-\frac{1}{2}\frac{a}{n\pi} sin\left(\frac{n\pi}{a}x\right)\cos\left(\frac{n\pi}{a}x\right) + \frac{1}{2}x\right]_0^a = |A|^2\frac{1}{2}a = 1$$

$$\Rightarrow \quad A = \sqrt{2/a} \qquad \text{and} \qquad \psi_n(x) = \sqrt{2/a}\,\sin\left(\frac{n\pi}{\mathrm{a}}x\right)$$

Infinite Square Well (or particle in 1D box)

What about the orthogonality of the w.f.?
One can check that

$$\int_0^a \psi_n(x)^* \, \psi_m(x) \, dx = 0$$

with $\psi_n(x) = A \sin\left(\frac{n\pi}{a} x\right)$

and $n \neq m$

Proof on Griffiths's chap 2.2.

$$\int \psi_m(x)^* \psi_n(x) \, dx = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx$$

$$= \frac{1}{a} \int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right)\right] dx$$

$$= \left\{\frac{1}{(m-n)\pi} \sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi} \sin\left(\frac{m+n}{a}\pi x\right)\right\}\Bigg|_0^a$$

$$= \frac{1}{\pi}\left\{\frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi}{(m+n)}\right\} = 0.$$

We can say that the ψ_n are always orthogonal, for any value of A.

Infinite Square Well (or particle in 1D box)

t.i.S.E.

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

Solutions

$$E_n = \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}$$

$$\psi_n(x) = \sqrt{2/a}\,\sin\left(\frac{n\pi}{a}x\right)$$

For n=1: $\psi_1(x) = \sqrt{2/a}\,\sin\left(\frac{\pi}{a}x\right)$ $E_1 = \frac{\pi^2}{a^2}\frac{\hbar^2}{2m}$

$\psi_1(x)$ is called the ground state, corresponding to the minimum eigenvalue, thus minimum energy of the particle, the so called "zero-point energy.

The other $\psi_n(x)$ are the excited states.

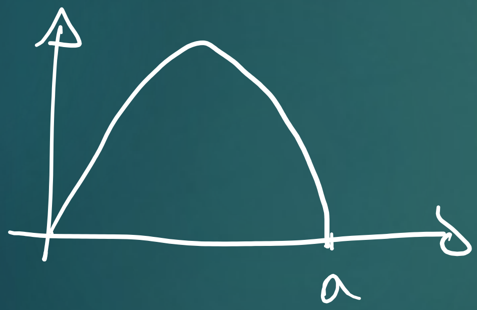
Infinite Square Well (or particle in 1D box)

Solutions

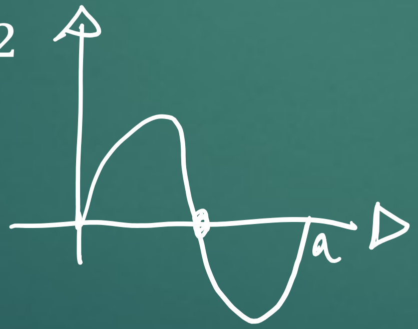
$$E_n = \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}$$

$$\psi_n(x) = \sqrt{2/a}\,\sin\left(\frac{n\pi}{a}x\right)$$

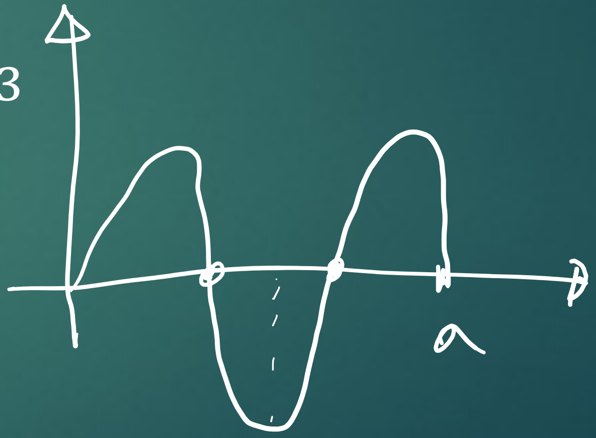
ψ_1



ψ_2



ψ_3



1 node

2 nodes

... n-1 nodes

$\psi_n(x)$ are like the standing waves on the string.

Infinite Square Well (or particle in 1D box)

Solutions

$$E_n = \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}$$

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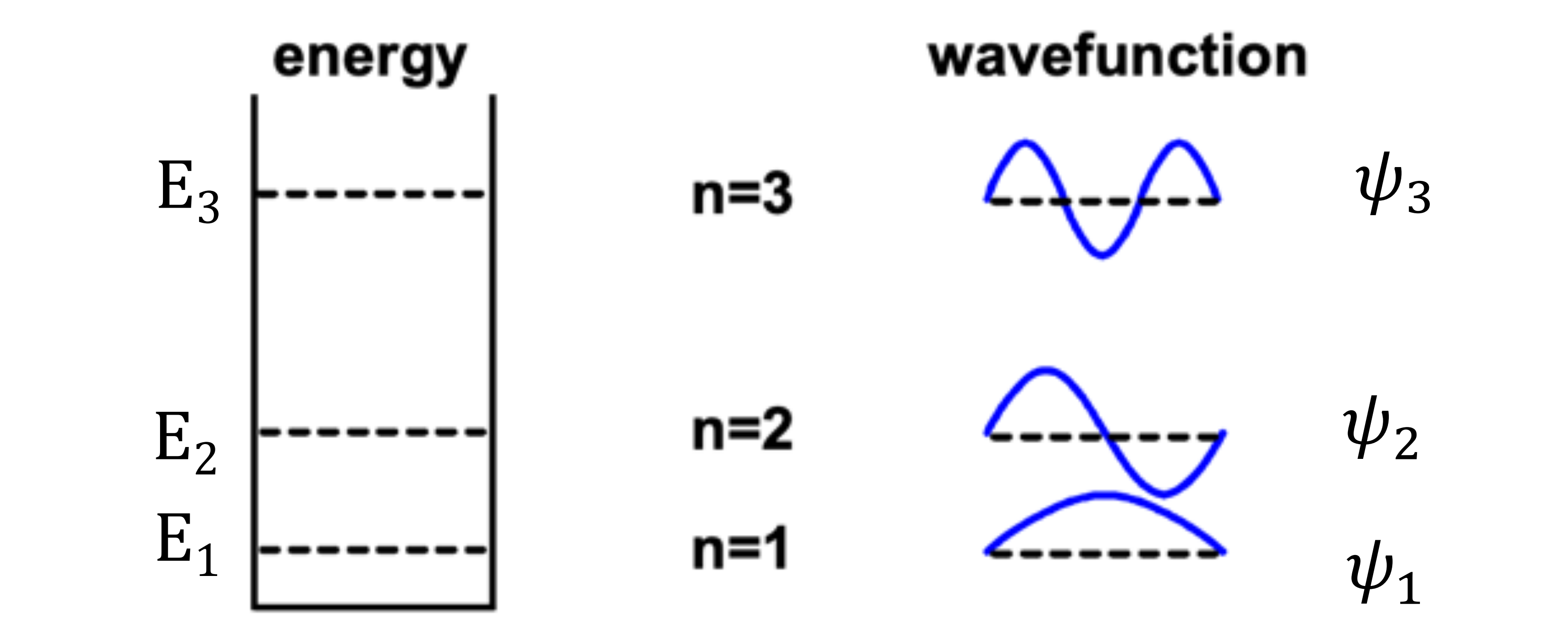


$\psi_n(x)$ are like the standing waves on the string.

$\psi_n(x)$ are orthonormal.

$\psi_n(x)$ form a complete basis set (it will be clearer in a few slides)

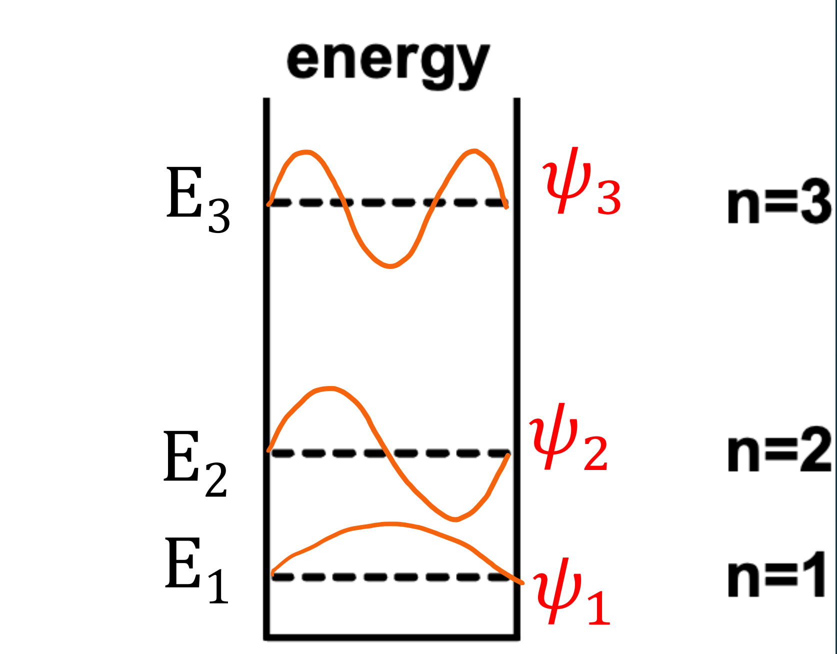
Infinite Square Well (or particle in 1D box)

- We started out using the de Broglie hypothesis: electrons behave like propagating waves
- We constructed a simple wave equation that could describe such effects for electrons.

Now we find that,
if we put that particle in a box, then we find that:

- there are only discrete values of that energy possible, with specific wave functions associated with each such value of energy.

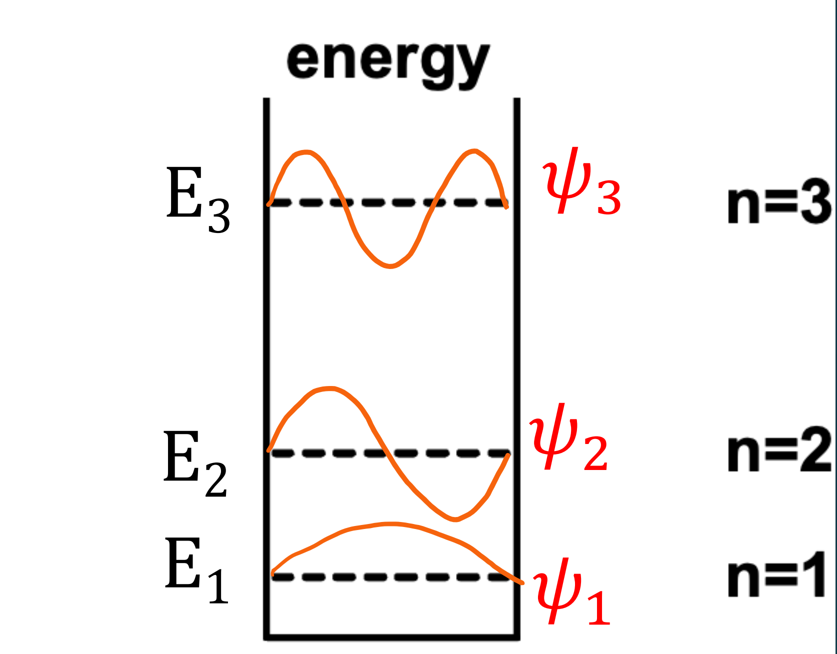
We have found the first truly "quantum" behaviour showing "quantum" steps in energy between the different allowed states.



Infinite Square Well (or particle in 1D box)

This "quantum" behaviour is very different from the classical case:

- there is only a discrete set of possible values for the energy
- there is a minimum possible energy for the particle, corresponding to $n = 1$, the "zero-point" energy.
- the particle is not uniformly distributed over the box, and its distribution is different for different energies.
- Each successively higher energy state has one more "node" in the eigenfunction.



Parity of wavefunctions

This "quantum" behaviour is very different from the classical case:

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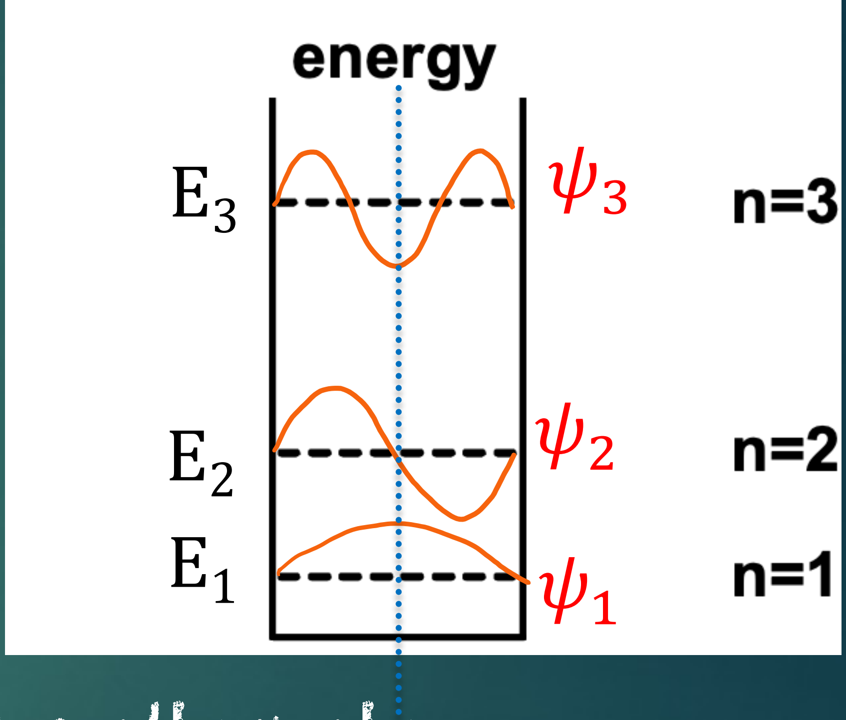


For this symmetric well problem the functions alternate between being even ($\psi_1, \psi_3,\ldots$) and odd ($\psi_2, \psi_4,\ldots$).

Thus, all the solutions have a definite parity.

Orders of magnitude for energy in QM

1 eV (electron-volt) $\cong 1.602 \times 10^{-19}$ J is the kinetic energy acquired by an electron as it passes through 1 V of electrical potential.

Let's assume the dimension a of the box is 0.5 nm (i.e. Bohr radius):

$$\mathrm{E}_1 = \frac{\pi^2}{a^2}\frac{\hbar^2}{2m} \approx 2.4 \times 10^{-19}\,\mathrm{J} \approx 1.5\ \mathrm{eV}$$

$$\mathrm{E}_2 = 4\ \mathrm{E}_1 = 6\ \mathrm{eV}$$

$$\mathrm{E}_2 - \mathrm{E}_1 = 4.5\ \mathrm{eV}$$

Complete basis set

$$\psi_n(x) = \sqrt{2/_a}\,\sin\left(\frac{n\pi}{\mathrm{a}}x\right)$$

$\psi_n(x)$ form a complete basis set.

Thus, any other function (between x=0 and x=a) can be written as a linear superposition of them:

$$f(x) = \sum_{n=1}^{\infty} c_n\,\psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=2}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)$$

Basis set

$$f(x) = \sum_{n=1}^{\infty} c_n \, \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=2}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right)$$

"basis set of functions" or "basis : set of functions such as the $\psi_n(x)$ that can be used to represent a function such as the $f(x)$

The set of coefficients (amplitudes) c_n is then the "representation" of $f(x)$ in the basis ψ_n.

The sets of eigenfunctions, solutions of our quantum mechanical problems are complete sets (mathematically very useful).

Basis set

$$f(x) = \sum_{n=1}^{\infty} c_n \, \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=2}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right)$$

This is nothing but the Fourier series for $f(x)$.

How do we find c_n?

...by the so-called Fourier trick:

Fourier series

This is something that can be applied in general, not just for the square well.

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

Let's multiply both sides by $\psi_m(x)^*$

$$\int \psi_m(x)^* f(x)\,dx = \sum_{n=1}^{\infty} c_n \int \underbrace{\psi_m(x)^* \psi_n(x)dx}_{\delta_{m,n}}$$

Fourier series

This is something that can be applied in general, not just for the square well.

$$f(x) = \sum_{n=1}^{\infty} c_n \, \psi_n(x)$$

Let's multiply both sides by $\psi_m(x)^*$

$$\int \psi_m(x)^* \, f(x) \, dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \, \psi_n(x) dx$$

$$= \sum_{n=1}^{\infty} c_n \delta_{mn}(x) dx \; = c_m$$

Fourier series

This is something that can be applied in general, not just for the square well.

$$f(x) = \sum_{n=1}^{\infty} c_n \, \psi_n(x)$$

$$c_n = \int \psi_n(x)^* \, f(x) dx$$

Orthogonality of eigenfunctions

In addition to being "complete", the set of functions $\psi_n(x)$ are "orthogonal".

$$\int \psi_n(x)^* \, \psi_m(x)\, dx = 0 \qquad \text{for} \qquad n \neq m$$

Thus, the different eigenfunctions are orthogonal to one another.

If the functions are also normalized:

$$\int \psi_n(x)^* \, \psi_m(x)\, dx = \delta_{nm}$$

Kronecker delta

$$\delta_{nm} = 0, \qquad n \neq m$$
$$\delta_{nn} = 1$$

Orthogonality of eigenfunctions is also quite general in QM and orthonormal sets are very convenient mathematically

Orthogonality of eigenfunctions

Orthogonality of eigenfunctions is also quite general in QM and orthonormal sets are very convenient mathematically

Two wavefunctions that are orthogonal, represent *mutually exclusive* quantum states

Or...they represent mutually exclusive possibilities: a particle cannot be in two different states at the same time

e.g. a particle cannot be in two different places at the same time, nor can it have two different values of momentum (or velocity) at the same time

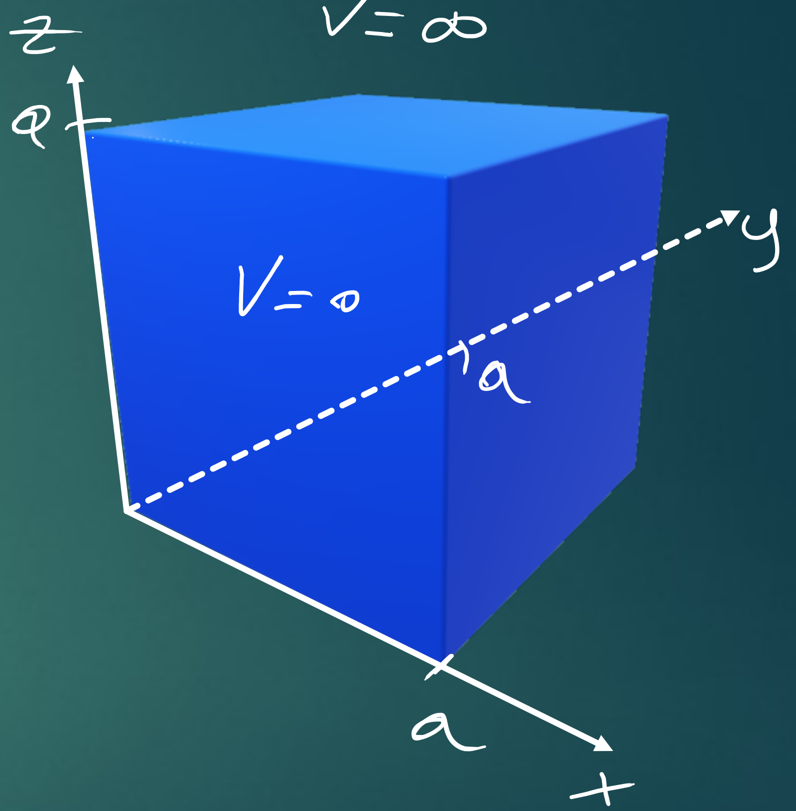
Particle in a 3D box

T.I.S.E. in 3D:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathrm{r})\right]\psi(r) = E\psi(r)$$

Thus if V=0:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = -\frac{2m}{\hbar^2}E\,\psi(r)$$



The boundary conditions are

$X(0)=X(a)=0$

$Y(0)=Y(a)=0$

$Z(0)=Z(a)=0$

Let's us separate the variables by writing the w.f. as:

$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

Particle in a 3D box

By inserting the W.F. in the T.I.S.E.:

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = -\frac{2m}{\hbar^2}E\,\psi(r)$$

$$E=\frac{\hbar^2 k^2}{2m}$$

We have:

$$\left(\frac{\partial^2 X}{\partial x^2}+\frac{\partial^2 Y}{\partial y^2}+\frac{\partial^2 Z}{\partial z^2}\right)\psi = -\frac{\cancel{2m}}{\cancel{\hbar^2}}\frac{\cancel{\hbar^2}\mathrm{k}^2}{\cancel{2m}}\psi(r)$$

$$=\left(-\mathrm{k}_x^2-\mathrm{k}_y^2-\mathrm{k}_z^2\right)\psi(r)$$

k_x^2, k_y^2 and k_z^2 are spatial coordinates.

This equation is satisfied if:

$$\frac{\partial^2 X}{\partial x^2}=-\mathrm{k}_x^2$$

$$\frac{\partial^2 X}{\partial y^2}=-\mathrm{k}_y^2$$

$$\frac{\partial^2 X}{\partial z^2}=-\mathrm{k}_z^2$$

Particle in a 3D box

One should find the solution of:

$$\frac{\partial^2 X}{\partial x^2} = -\mathrm{k}_\mathrm{x}^2$$

$$\frac{\partial^2 X}{\partial y^2} = -\mathrm{k}_\mathrm{y}^2$$

$$\frac{\partial^2 X}{\partial z^2} = -\mathrm{k}_\mathrm{z}^2$$

- The solution to these equations are identical to that found for the 1D case:

$$X(x) = \sqrt{\frac{2}{a}} \sin(k_x x)$$

$$Y(y) = \sqrt{\frac{2}{a}} \sin(k_y y)$$

$$Z(z) = \sqrt{\frac{2}{a}} \sin(k_z z)$$

Particle in a 3D box

The solution to these equations are identical to that found for the 1D case:

$$X(x) = \sqrt{\frac{2}{a}}\sin(k_x x) \qquad \text{with} \qquad k_x = \frac{l_x \pi}{a}$$

$$Y(y) = \sqrt{\frac{2}{a}}\sin(k_y y) \qquad \text{with} \qquad k_y = \frac{l_y \pi}{a}$$

$$Z(z) = \sqrt{\frac{2}{a}}\sin(k_z z) \qquad \text{with} \qquad k_z = \frac{l_z \pi}{a}$$

l_x, l_y, and l_z are positive integers and the energy of the system will be:

$$E = \frac{l^2 \pi^2 \hbar^2}{2 m a^2} \qquad \text{with} \qquad l^2 = l_x^2 + l_y^2 + l_z^2$$