

Lecture 5

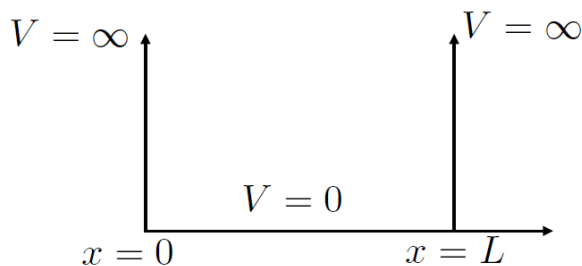
Particle in 2D & 3D Box

We are solving Schrödinger equation for various simple model systems (with increasing complexity).

The recipe that we are using for solving Schrödinger equation is as follows:

- Define the potential energy function (system dependent)
- Define the boundary conditions (system dependent)
- Write down the Hamiltonian operator for the system and solve the resulting SE to obtain a general solution for the differential equation.
- Find particular solution applying the boundary conditions

In the last class, we solved the quantum mechanical problem of a particle trapped in an infinite potential well (box). We considered a particle of mass m was confined in a one-dimensional box of length L (for e.g. a particle moving in a piece of a straight wire). The potential inside the box was zero. The ends of the box were at $x = 0$ and $x = L$ and the potential at these positions were infinite such that the particle cannot escape the box.



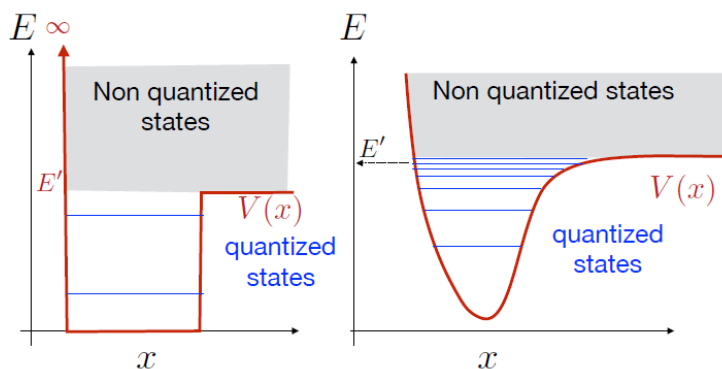
For the particle within the box, the Schrödinger equation for the particle inside the box is the same as in case of the free particle. We were not interested in Hamiltonian operator of the particle outside the box, as particle will have zero probability to be outside the box (and thus wavefunction = 0) which is forced by the infinite potential at $x = 0$ and $x = L$.

Origin of Quantization

We realized while solving particle in a box problem that we solve the wave functions only for some values of E . In general, it is impossible to find a quantum mechanically acceptable solution to the problem for an arbitrary value of E . Note that for any arbitrary value of E we can have a mathematically acceptable solution, but this might not give us a well behaving solution, which is required by quantum mechanics.

The quantized energy levels or quantum numbers is a consequence of the boundary conditions. Quantization will occur only when the particle is confined to a finite region of space by the potential.

In the Figure below, for energy $E > E_0$, particle is not confined, and behave like a free particle.



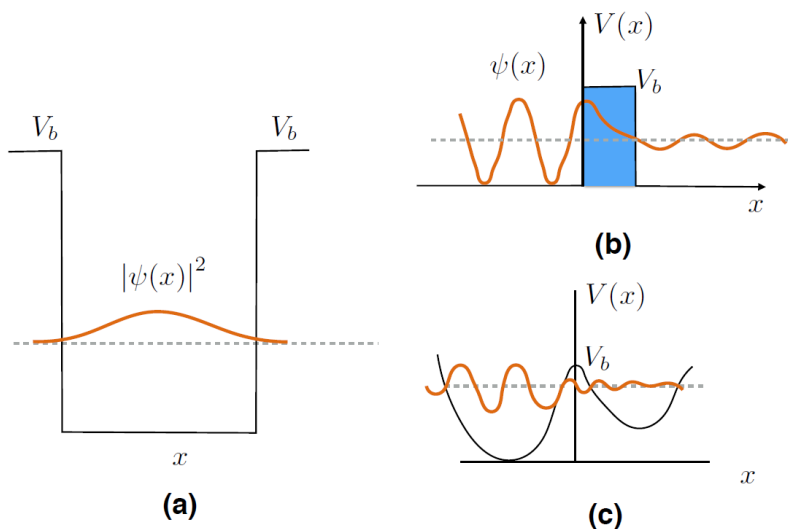
Quantized and non-quantized energies arising due to the boundary conditions

Quantum Mechanical Tunneling

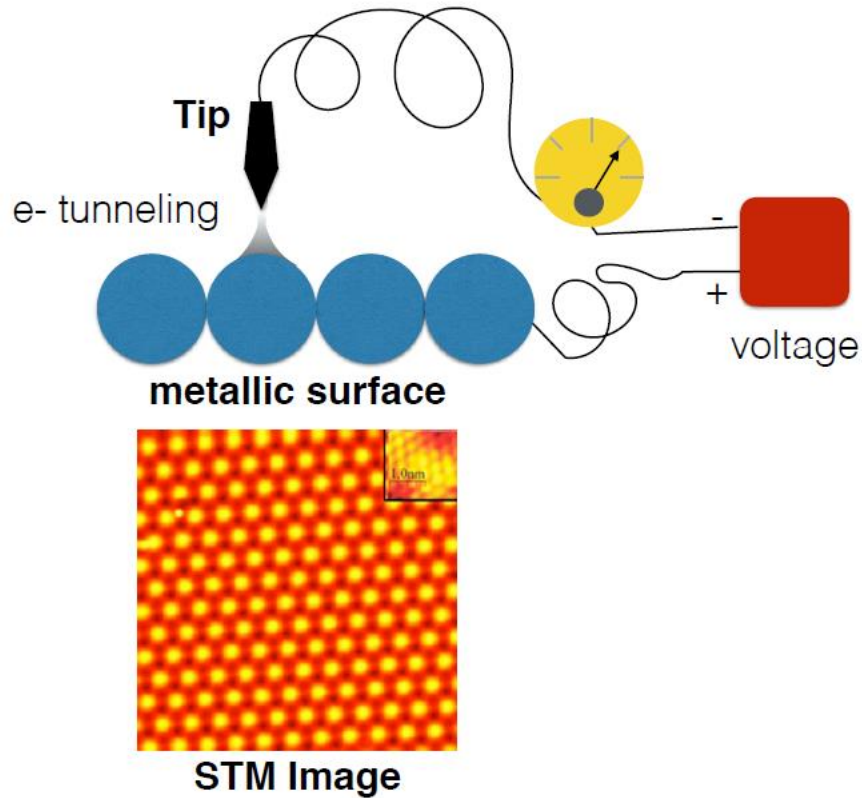
When the potential wall encompassing the particle is not infinitely high, then particle would escape, even when its kinetic energy is not as large as the potential barrier. There is a finite probability of finding the particle outside the box, even if the kinetic energy of the particle is smaller than the barrier, which is called a quantum-mechanical **tunneling**.

This phenomenon is having large importance in chemistry and biology. Reaction rate is controlled by the number of reactant molecules acquiring sufficient energy to overcome the activation energy barrier. But, if tunneling occurs, reaction can take place even when molecules don't have sufficient energy to cross the activation energy barrier.

The technique called the scanning tunneling microscope (STM), which is used for imaging surface at an atomic level resolution, is based on the principle of quantum tunneling. A voltage is applied between an electrode tip and a metallic surface. The electrons are allowed to tunnel from the tip to the surface. Tunneling current depends on the distance of the tip from the surface, and thus helps to image the surface structure of the metallic surface.



Schematic diagrams showing wave function is tunneling through a finite potential barrier for states whose energy is less than the potential barrier V_b .

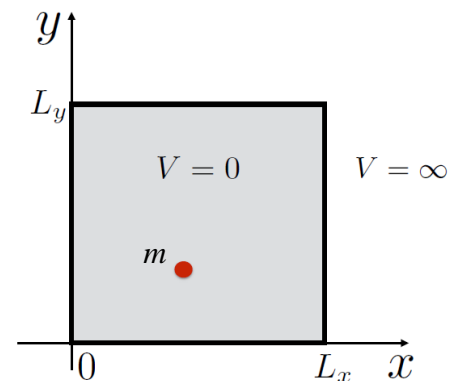


Schematic diagram of STM. A sample of STM image is also shown

Particle in a Two-Dimensional Box

Let us consider a particle (mass m) within a two-dimensional box, defined by the wall potentials:

$$V(x, y) = \begin{cases} 0 & \text{if } 0 < x < L_x \text{ \& } 0 < y < L_y \\ \infty & \text{otherwise} \end{cases}$$



One can visualize this problem as an electron in a very thin rectangular plate. Wave function of the system should explain the probability of finding the particle in the X-Y space, thus will be two dimensional; *i. e.*, $\psi \equiv \psi(x, y)$.

The Hamiltonian of this system can be written as:

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + V(x, y) \\ &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + 0\end{aligned}$$

Note the usage of partial derivatives ($\frac{\partial}{\partial x}$) instead of full derivatives. The Schrödinger equation for the problem is:

$$\begin{aligned}\hat{H}\psi(x, y) &= E\psi(x, y) \\ -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] \psi(x, y) &= E\psi(x, y).\end{aligned}$$

The above equation is a partial differential equation which can be solved by using the separation of variable technique. Boundary conditions for $\psi(x, y)$ are:

$$\begin{aligned}\psi(0, y) &= \psi(L_x, y) = 0 \text{ for all } y \\ \psi(x, 0) &= \psi(x, L_y) = 0 \text{ for all } x\end{aligned}$$

Let us assume that solutions exist that the form

$$\psi(x, y) = \psi_x(x) \psi_y(y)$$

where $\psi_x(x)$ is a function of only x , and $\psi_y(y)$ is a function of only y . Then the Schrödinger equation becomes:

$$\begin{aligned}-\frac{\hbar^2}{2m} \left[\psi_y(y) \frac{d^2 \psi_x(x)}{dx^2} + \psi_x(x) \frac{d^2 \psi_y(y)}{dy^2} \right] &= E \psi_x(x) \psi_y(y), \\ \text{or, } \frac{1}{\psi_x(x)} \frac{d^2 \psi_x(x)}{dx^2} + \frac{1}{\psi_y(y)} \frac{d^2 \psi_y(y)}{dy^2} &= -\frac{2mE}{\hbar^2}.\end{aligned}$$

The first term is a function of x only and the second term is a function of y only. The sum of the two terms is equal to the constant $-2mE/\hbar^2$ and this implies that each term in the left-hand side of the above equation is a constant. Say, the first term is $-2mE_x/\hbar^2$ and the second term is $-2mE_y/\hbar^2$. Then we have

$$\begin{aligned}-\frac{\hbar^2}{2m} \frac{d^2 \psi_x(x)}{dx^2} &= E_x \psi_x(x), \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi_y(y)}{dy^2} &= E_y \psi_y(y),\end{aligned}$$

and

$$E = E_x + E_y$$

Each of the above two ordinary differential equations are the same as the Schrödinger equation of a particle in 1-D box. We know the solutions for them. As the boundary conditions have to be followed independently by $\psi_x(x)$ and $\psi_y(y)$, they can have different quantum numbers. We will denote them by n_x and n_y . Thus, one finally gets the total energy as:

$$E_{n_x, n_y} = \frac{h^2}{8m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right], \quad n_x, n_y = 1, 2, 3, \dots$$

And the wavefunctions as: $\psi_{n_x, n_y}(x, y) = \left(\sqrt{\frac{2}{L_x}} \sin \frac{n_x \pi x}{L_x} \right) \left(\sqrt{\frac{2}{L_y}} \sin \frac{n_y \pi y}{L_y} \right), \quad n_x, n_y = 1, 2, 3, \dots$

Probability of finding a particle within the 2D box, say between a_1 and a_2 along x , and b_1 and b_2 along y can be computed as:

$$P(x \in (a_1, a_2), y \in (b_1, b_2)) = \frac{2}{L_x} \frac{2}{L_y} \int_{a_1}^{a_2} dx \sin^2 \frac{n_x \pi x}{L_x} \int_{b_1}^{b_2} dy \sin^2 \frac{n_y \pi y}{L_y}$$

The quantum numbers (n_x, n_y) defines the wavefunction, or the state of the system.

Consider the case of a square box, where $L_x = L_y = L$.

The energy levels for such a system are shown here. The

states $\psi_{1,2}$ and $\psi_{2,1}$ have the same energy

and are called degenerate state.

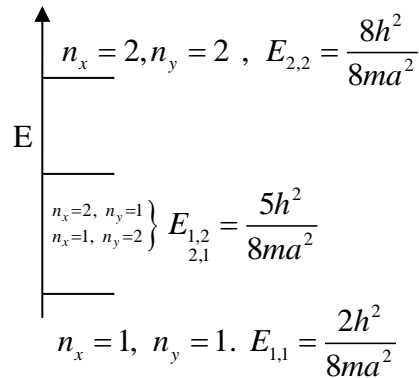
Similarly, $\psi_{1,3}$ and $\psi_{3,1}$ are degenerate.

The degeneracy is lifted when the box is

distorted by making $L_x \neq L_y$, i.e. rectangular

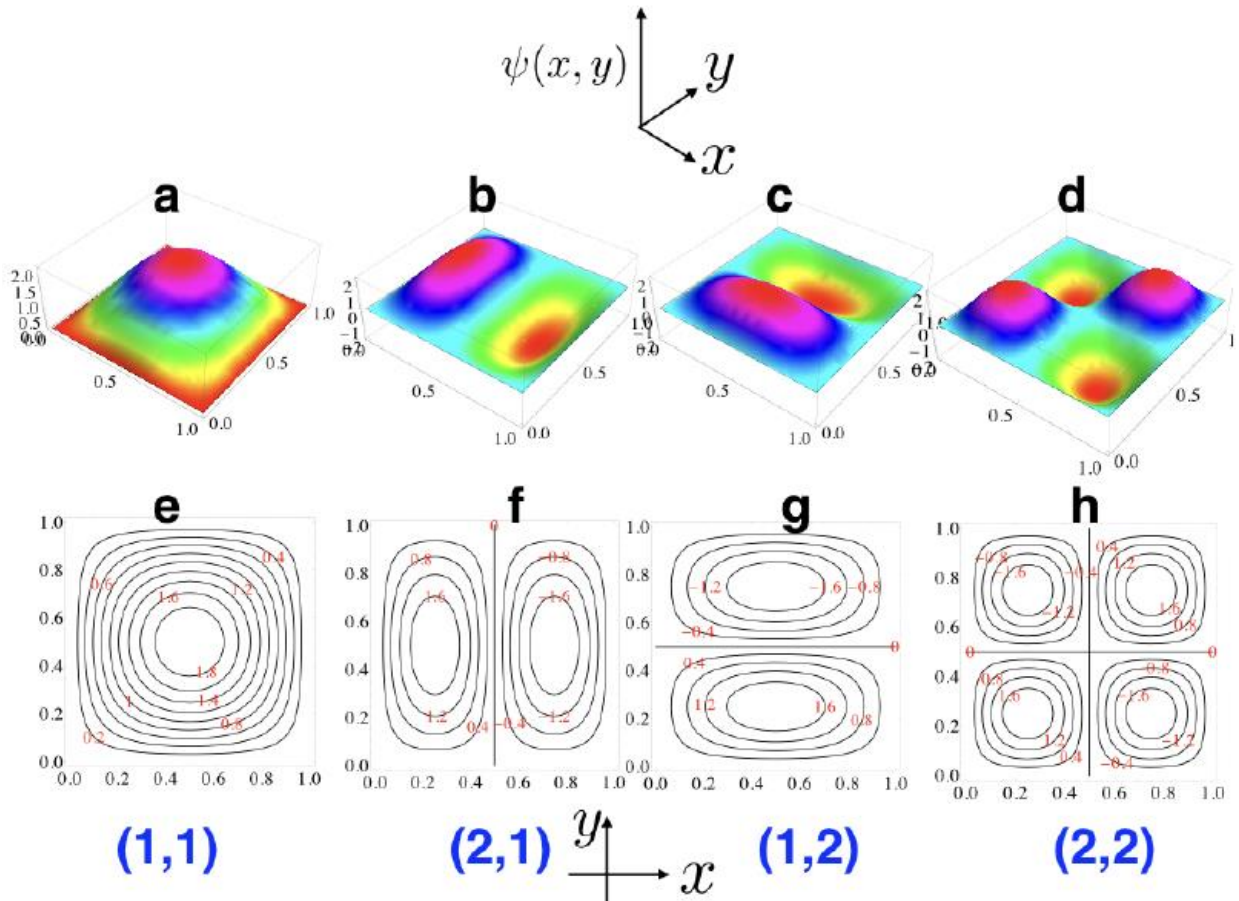
box. Thus, where the symmetry is broken,

degeneracy is lifted.



Degenerate states have same energy. Note that these two states have different wave function (with different quantum numbers). The **degeneracy** of the energy level is 2 (as there are two states of same energy that are degenerate). Note the difference between an **energy level** and a **state**. A state is **non-degenerate** when not more than one set of quantum numbers can result in the same energy.

Some pictures of the 2D wavefunctions are given in Figure below. There are nodal lines (like nodal points in 1D case), and they increase with the quantum numbers.



The above Figure depicts the wavefunctions for a particle in a 2-D box for various (n_x, n_y) quantum numbers for unitary square box such that $L_x=L_y=1$ has been presented. Top row figures (a-d) show the wavefunction as a three-dimensional graph; the axes are defined at the top of the figure. Bottom row figures (e-h) show the wavefunction as a two-dimensional contour graph corresponding to the wavefunction directly above it. The states of these wavefunctions are specified using quantum numbers (n_x, n_y) given below these figures (in blue color); the axes for the contour diagrams are defined at the bottom.

In Figures (e-h), wave functions are plotted in two dimensions (in x-y plane) as **contour diagrams**. Contour lines are made by drawing lines in the x-y plane joining points where the value of the wave function is some chosen value. Along the contour line, the value of the wave function is the same. Drawing such contour lines for various values of the wave function captures the features of a three-dimensional data.