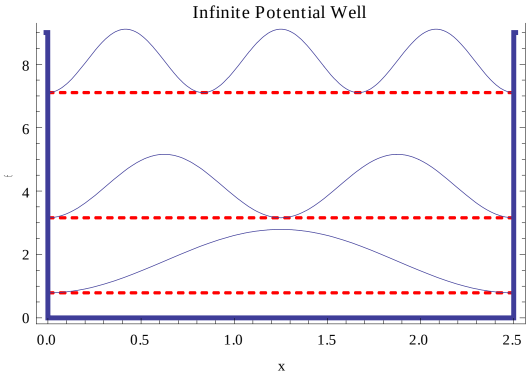
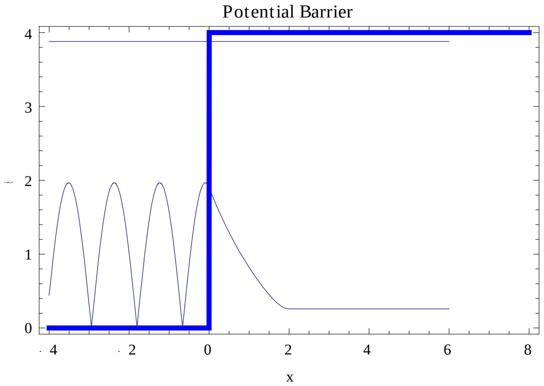
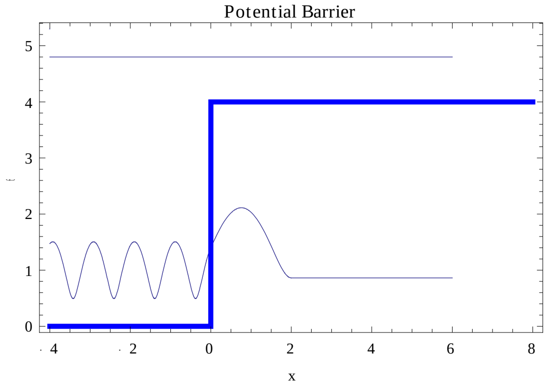
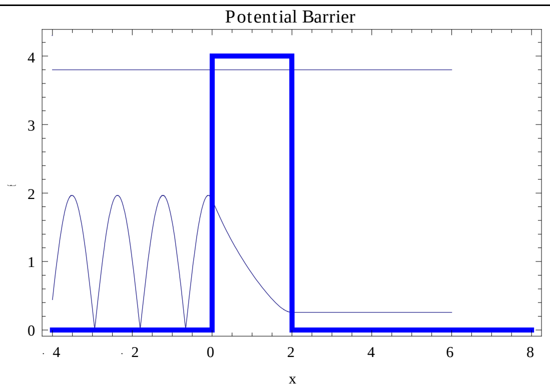
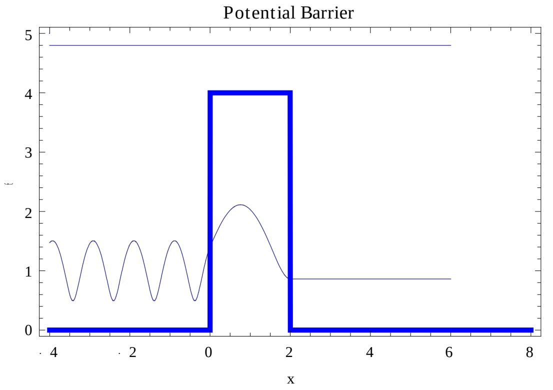
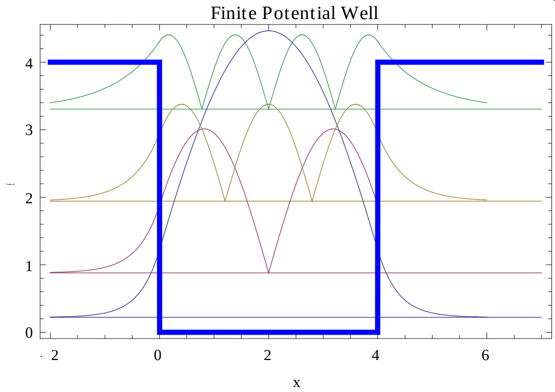
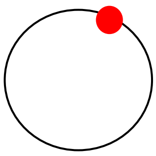
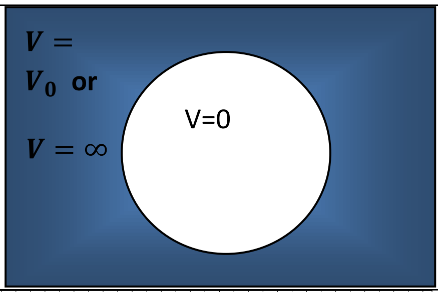
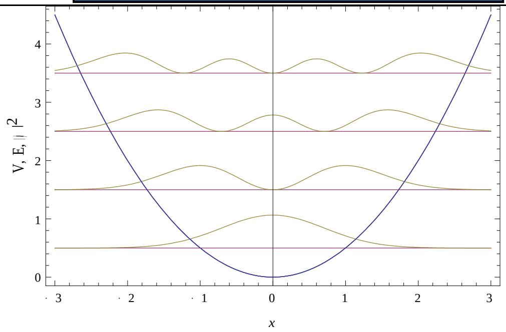
Chapter 2 (Lecture 4-6)

Schrodinger equation for some simple systems

Table: Various one dimensional potentials

System	**Physical correspondence**	**Potential Total Energies and Probability density $\psi^*\psi$**	**Significant feature**
Zero Potential	Free particle i.e. Proton beam	E $\psi^*\psi$ $V(x)$	Wave properties of particle
Infinite square well potential	Molecule confined to box		Approximation of finite well
Step Potential (E<V)	Conduction electron near surface of metal		Penetration of excluded region
Step potential (E>V)	Neutron trying to escape nucleus		Partial reflection at potential discontinuity
Barrier potential (E<V)	A particle trying to escape Coulomb barrier		Tunneling

Barrier potential (E>V)	Electron scattering from negatively ionized atom		No reflection at certain energies
Finite square well potential	Neutron bound in the nucleus		Energy quantization
Particle in a ring	Aromatic compounds contains atomic rings.		Degenerate quantum states
Particle in a spherical well	Model the nucleus with a potential which is zero inside the nuclear radius and infinite outside that radius.		Quantization of energy and degeneracy of states
Simple harmonic oscillator potential	Atom of vibrating diatomic molecule		Zero point energy Uncertainty

Example: Particle in a box (Infinite well potential)

As an example consider infinite well potential describes a particle free to move in a small space surrounded by impenetrable barriers.

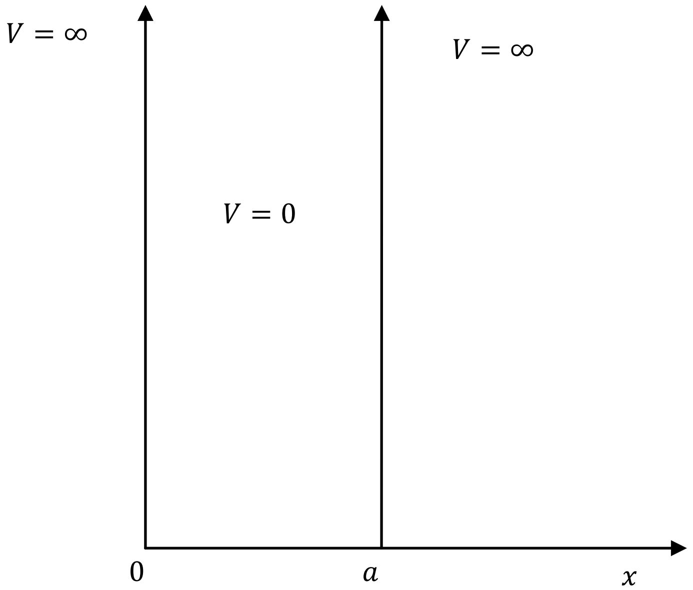
The model is mainly used as a hypothetical example to illustrate the differences between classical and quantum systems. In classical systems, for example a ball trapped inside a heavy box, the particle can move at any speed within the box and it is no more likely to be found at one position than another. However, when the well becomes very narrow (on the scale of a few nanometers), quantum effects become important. The particle may only occupy certain positive energy levels.

Likewise, it can never have zero energy, meaning that the particle can never "sit still". Additionally, it is more likely to be found at certain positions than at others, depending on its energy level. The particle may never be detected at certain positions, known as spatial nodes.

The particle in a box model provides one of the very few problems in quantum mechanics which can be solved analytically, without approximations. This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions. Due to its simplicity, the model allows insight into quantum effects without the need for complicated mathematics. It is one of the first quantum mechanics problems taught in undergraduate physics courses, and it is commonly used as an approximation for more complicated quantum systems.

Mathematically we can write:

$$V(x) = \begin{cases} \infty & x \leq 0 \\ 0 & 0 < x < a \\ \infty & x \geq a \end{cases}$$



We have three distinct regions, because the potential energy function (potential for short) changes discontinuously. So, we have to solve the Schrödinger Equation three times.

Fortunately, for $x \leq 0$ and $x \geq 0$, the solutions are trivial: $\psi(x) = 0$, since $V(x) = \infty$.

Within the well, $V(x) = 0$, so the particle is "free."

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

The general solution is $\psi = Asinkx + bcoskx$. The parameters *A*, *B*, and $k = \frac{\sqrt{2mE}}{\hbar}$ are determined by the *boundary conditions* on the ψ and by the normalization requirement.

That is, we expect that $\psi(a) = \psi(0) = 0$.

At $x = 0; Asin0 + Bcos0 = 0 => B = 0$

Then

At $x = a; Asinka = 0 => ka = n\pi; where\ n = 1,2,3, \ldots$

The choices of A=0 also solution but in that case $\psi = 0$ is not a valid solution.

From this we obtain the discrete allowed energy levels for the particle confined in the well.

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

The *n* is known as the *principle quantum number*. It labels the energy levels, or *energy states* of the particle. In other from classical physics we have obtained discrete energy values instead of continuous energy.

Stationary states are evidently

$$\Psi(x,t) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)e^{-\frac{in^2\pi^2\hbar}{2ma^2}t}$$

The most general solution is linear combination of stationary states

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-\frac{in^2\pi^2\hbar}{2ma^2}t}$$

Then the initial wave function can be written as

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

The coefficient c_n can be calculates using the relation

$$c_n = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0) dx$$

Discussion

1. Wave function is even or odd wrt center of the well
2. The wave functions are orthogonal
3. Each ψ_n has n-1 nodes

CW(Class work). Particle in the infinite well is in its groud state. Find probability of finding of particle between (0,a/4), (0,a/2), (a/4,a/2).

Example:

A particle in the infinite square well has the initial wave function

$$\Psi(x,0) = ASin[\frac{3\pi}{a}x]; \;\; 0 \le x \le a$$

For some constant A. Outside the well wave function is zero. Find $\Psi(x,t)$.

Solution:

Normalize the wave function: $A = \sqrt{\frac{2}{a}}$.

Calculate c_n;

$$c_n = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}x\right) dx = \begin{cases} 0 & if\ n \neq 3 \\ 1 & if\ n = 3 \end{cases}$$

Thus the wave function is

$$\Psi(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}x\right) e^{-\frac{i3^2\pi^2\hbar}{2ma^2}t}$$

CW. Show that sum of the probabilities

$$\sum_{n=1}^{\infty} |c_n|^2 = 1.$$

CW: Show that expectation values of energy must be

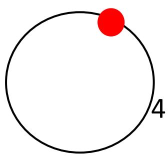
$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n.$$

CW. Calculate expectation values of $\langle x \rangle, \langle x^2 \rangle, \ \langle p \rangle, \langle p^2 \rangle, \langle H \rangle$ for the nth stationary state of the infinite well.

CW. Check the uncertainty principle is satisfied. Which state come closest to uncertainty principle.

Example: Particle in a Ring

Consider a variant of the one-dimensional particle in a box problem in which the x-axis is bent into a ring of radius. We can write the same Schrödinger equation



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

There are no boundary conditions in this case since the x-axis closes upon itself. A more appropriate independent variable for this problem is the angular position on the ring given by, $\phi = x/R$. The Schrödinger equation would then read:

$$-\frac{\hbar^2}{2mR^2}\frac{\partial^2\psi}{\partial\phi^2} = E\psi$$

The SE can be written more compactly:

$$\frac{\partial^2\psi}{\partial\phi^2} + m^2\psi = 0$$

where $m^2 = 2IE/\hbar^2$. Then wave function

$$\psi = cons\, e^{\mp im\phi}$$

with boundary condition

$$\psi(\phi + 2\pi) = \psi(\phi)$$

CW: we can easily show

$$m = \mp 1, \mp 2, \mp 3 \ldots$$

then

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

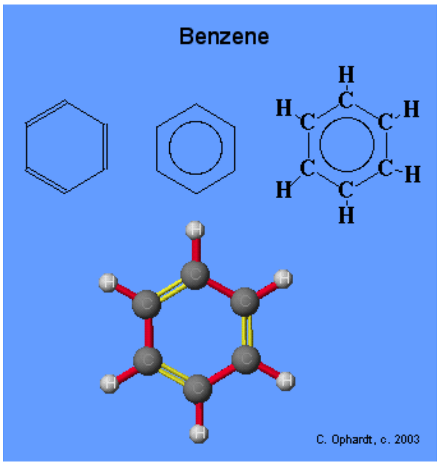
Normalized wavefunction is given by

$\psi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$

It satisfy both othogonality and orthonormality.

Uncertainty relation between z-componet of angular momentum $L_z = -i\hbar\frac{\partial}{\partial\phi}$

and ϕ also satisfied!

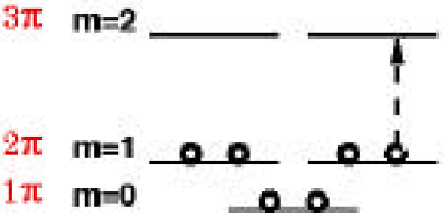


Example: Free Electron Model for Aromatic Molecules
The benzene molecule consists of a ring of six carbon atoms around which six delocalized π -electrons can circulate. A variant of the FEM for rings predicts the ground-state electron configuration which we can write as $1\pi^2, 2\pi^4$,as shown here:

Figure 1. Free electron model for benzene. Dotted arrow shows the lowest-energy excitation.
The longest wavelength absorption in the benzene spectrum can be estimated according to this model as

$$h\nu = \frac{hc}{\lambda} = E_2 - E_1 = \frac{\hbar^2}{2I}(2^2 - 1^2)$$

The ring radius R can be approximated by the C-C distance in benzene, 1.39Å. We predict $\lambda \approx 210\ nm$, whereas the experimental absorption has $\lambda_{max} = 268\ nm$.



The following sections to be lectured in details in the class

CW: Particle in the 2D-3D box problem.

CW: The lowest energy

CW: Degeneracy.

Example: Free particles in a box--separable in Cartesin coordinates

If the particle is confined in a box L^3, clearly the wavefunction is given by

$$\psi_{n_1,n_2,n_3} = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\frac{n_1\pi x}{L} \sin\frac{n_2\pi y}{L} \sin\frac{n_3\pi z}{L}$$

and the energies are given by

$$E = \frac{\hbar^2\pi^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$$

Thus there are three quantum numbers, n_1, n_2, n_3 to denote a give state and since the energy depends is given by , there are **degeneracy** in that different eigenstates can have the same energy. (learn the degenerate states)

Ground state energy of a particle in the 3D cubic box is

$$E_{111} = \frac{\hbar^2\pi^2}{2mL^2}(3)$$

A term "degenerate" referring to the fact that two or **more stationary states** of the same quantum-mechanical system may have **the same** energy even though their wave functions are not the same. In this case the common energy level of the stationary states is degenerate. The statistical weight of the level is proportional to the order of degeneracy, that is, to the number of states with the same energy; this number is predicted from Schrödinger's equation. The energy levels of isolated systems (that is, systems with no external fields present) comprising an odd number of fermions (for example, electrons, protons, and neutrons) always are at least twofold degenerate.

Example. The 6th energy level of a particle in a 3D Cube box is 6-fold degenerate.

a. What is the energy of the 7th energy level? (ans. $\frac{\hbar^2\pi^2}{2mL^2}(17)$
b. What is the degeneracy of the 7th energy level? (ans. 3-fold)

Filling the box with fermions (OPTIONAL)

If we fill a cold box with N fermions, they will all go into different low-energy states. In fact, if the temperature is low enough, they will go into the lowest energy N states.

If we fill up all the states up to some energy, that energy is called the **Fermi energy**. All the states with energies lower than E_F are filled, and all the states with energies larger than E_F are empty. Non zero temperature will put some particles in excited states, but, the idea of the Fermi energy is still valid.

$$\frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{\pi^2\hbar^2}{2mL^2} r_n^2 \leq E_F$$

Number of states within the radius

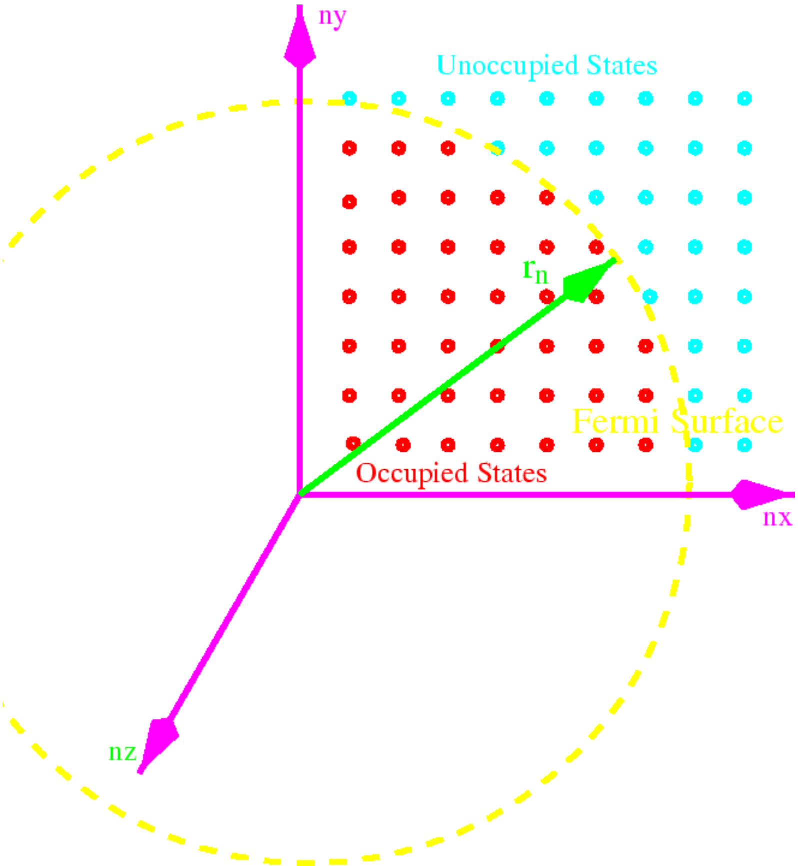
$$N = 2\frac{1}{8}\frac{4}{3}\pi r_n^3$$

the factor 2 is for spin of fermions, The factor of 1/8 indicates that we are just using one eighth of the sphere in n-space because all the quantum numbers must be positive.. The the fermi energy is:

$$E_F = \frac{\pi^2\hbar^2}{2m}\left(\frac{2N}{\pi L^3}\right)^{\frac{3}{2}} = \frac{\pi^2\hbar^2}{2m}\left(\frac{3n}{\pi}\right)^{\frac{3}{2}}$$

The total energy is

$$E_T = 2\frac{1}{8}\int_0^{r_n} 4\pi r^2 \frac{\pi^2\hbar^2}{2mL^2} r^2 dr = \frac{\pi^3\hbar^2}{10mL^2}\left(\frac{3N}{\pi}\right)^{\frac{5}{3}}$$



Degeneracy Pressure in Stars (OPTIONAL)

The pressure exerted by fermions squeezed into a small box is what keeps cold stars from collapsing. White Dwarfs are held up by electrons and Neutron Stars are held up by neutrons in a much smaller box. We can **compute the pressure** from the dependence of the energy on the volume for a fixed number of fermions.

$$dE = -\vec{F}.\overrightarrow{dl} = PAdl = -PdV$$

$$P = -\frac{\partial E}{\partial V} = \frac{\pi^3 \hbar^2}{15m}\left(\frac{3N}{\pi}\right)^{\frac{5}{3}} L^{-5}$$

This is greater than pressure of the gravity. Thereforewe understand why stars does not collapse. This pressure also explain:

- Why is the speed of sound much higher in metals than in ideal gasses?
- Why do atoms not collapse and become 100,000 times smaller than they are?

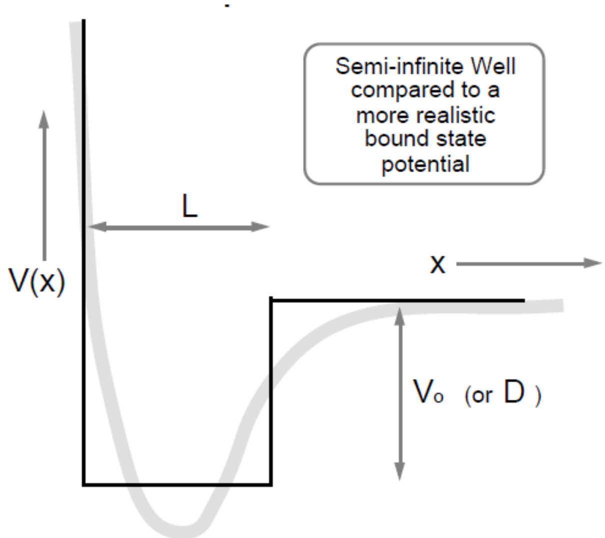
Application: 1D potentials and physical systems

In this chapter we will extend our study to the realistic physical systems modelled by approximate potentials. In the previous sections we have talked about infinite square well potentials, Coulomb and Harmonic oscillator potentials.

We now consider the situations that may arise when potential is low enough so that penetration of particles into classically forbidden regions is significant.

Semi infinite square well (asymmetric square well)

Rectangular potential with one side infinitely high, the other of depth V_0. Comparison is to the typical potential that **binds and electron to a nucleus**, or that binds a diatomic molecule (in which case the depth D is called the *dissociation energy* D).



The semi square well also resembles, in important ways, the potential that results when one combines the Coulomb potential with the "centrifugal potential" for discussion of the radial motion of an electron in a field of a point charge:

$$V \sim -\frac{a}{r} + \frac{b}{r^2}$$

Within the well solution of the Schrödinger equation gives us:

$$\psi_1(x) = A\sin(kx); where\ k = \sqrt{\frac{2mE}{\hbar^2}}$$

The solution outside the well, in the region $V_0 > E$, is of the form (at infinity the wave function will diverge then the solution $De^{\alpha x}$ should be zero, D=0):

$$\psi_2 = Be^{-\alpha x};\ where\ \alpha = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

We demand continuity in both the value and the slope of the state function at the boundary:

$$A\sin(kL) = Be^{-\alpha L}\ \ (Boundary)$$

$$kA\cos(kL) = -\alpha Be^{-\alpha L}\ \ (slope)$$

From these boundary conditions it follows that

$$\tan(kL) = -\frac{k}{\alpha}; \tan\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = -\sqrt{\frac{E}{V_0 - E}}$$

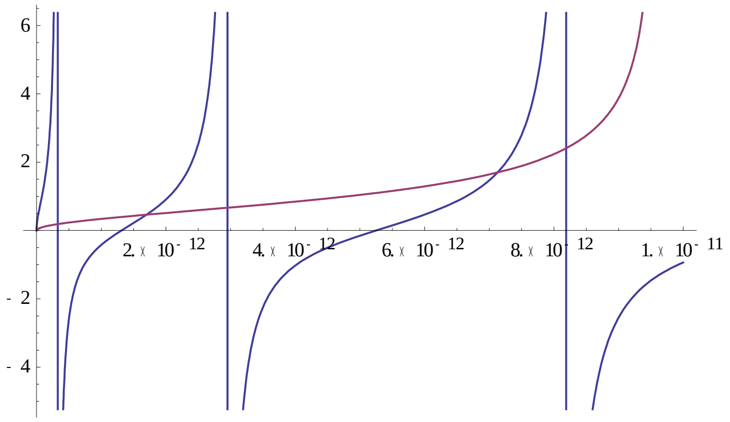
Solution of this equation for given V_0 gives the energy values. This shows that particle;

has discrete energy(energy quantized)

tunneling (penetration of partcile)

Example: Determine the allowed energy levels for a proton trapped in a semi-infinite square well of width 5.0 fm and depth 60 MeV. (1fm=10^{-15} m, 1MeV=10^6 eV, 1eV=$1.6\text{x}10^{-19}$ J, m_p=$1.67\text{x}10^{-27}$ kg)

Solution: We use a computer program to sketc graph of $\tan\left(\sqrt{\frac{2mE}{\hbar^2}}L\right)$ and $= -\sqrt{\frac{E}{V_0 - E}}$ on the same plane. The intersect of lines gives energy values. Or we can obtain numerical solution. The result gives 3 energy values: $\{6.5\ eV, 25.7\ eV, 55.1\ eV\}$.

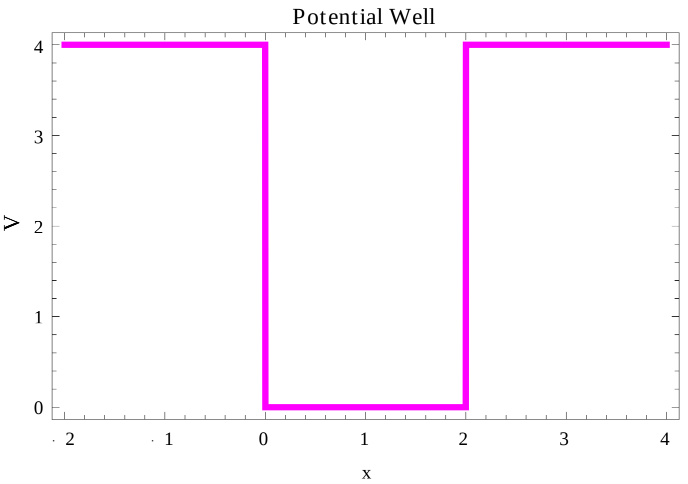


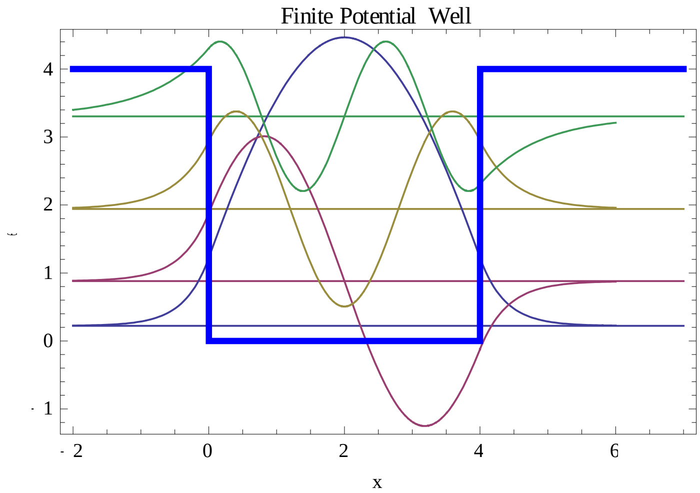
Finite Potential well

The **finite potential well** (also known as the **finite square well**) is an extension of the infinite potential well. We consider a particle is confined to a box, but one which has finite potential walls. Unlike the infinite potential well, there is a probability associated with the particle being found outside the box. The quantum mechanical interpretation is unlike the classical interpretation, where if the total energy of the particle is less than potential energy barrier of the walls it cannot be found outside the box. In the quantum interpretation, there is a non-zero probability of the particle being outside the box even when the energy of the particle is less than the potential energy barrier of the walls.

Consider a standard one-dimensional square potential well,

$$V(x) = \begin{cases} 0 \ \ if \ \ 0 < x < L \\ V_0 \quad otherwise \end{cases}$$





Determine eigenfunctions and eigenvalues of the particle and analyze the given graphs.

Wave function of the particle is given by

$$\psi_1 = Be^{-ik'x}$$

$$\psi_2 = Ce^{ikx} + De^{-ikx}$$

$$\psi_3 = Fe^{ik'x}$$

Using continuity equations at x=0 and x=L

$$B = C + D \ and \ k'(-B) = k(C - D)$$

$$Ce^{ikL} + De^{-ikL} = Fe^{ik'L} \ and \ k(Ce^{ikL} - De^{-ikL}) = k'Fe^{ik'L}$$

In order to obtain energy relation from first equation you eliminate B and C

$$B = \frac{2k}{k + k'}D; C = \frac{k - k'}{k + k'}D$$

Then second equation takes the form

$$\frac{k-k'}{k+k'}De^{ikL}+De^{-ikL}=Fe^{ik'L}\ and\ k\left(\frac{k-k'}{k+k'}De^{ikL}-De^{-ikL}\right)=k'Fe^{ik'L}$$

From first part of the equations

$$Fe^{ik'L}=D\left(\frac{k-k'}{k+k'}e^{ikL}+e^{-ikL}\right)$$

Substitute into second part

$$k\left(\frac{k-k'}{k+k'}De^{ikL}-De^{-ikL}\right)=k'D\left(\frac{k-k'}{k+k'}e^{ikL}+e^{-ikL}\right)$$

You can obtain

$$\frac{2ikk'}{k^2+k'^2}=tan[kL]\ or\ \frac{i(k^2+k'^2)}{2kk'}=cot[kL]$$

Remember

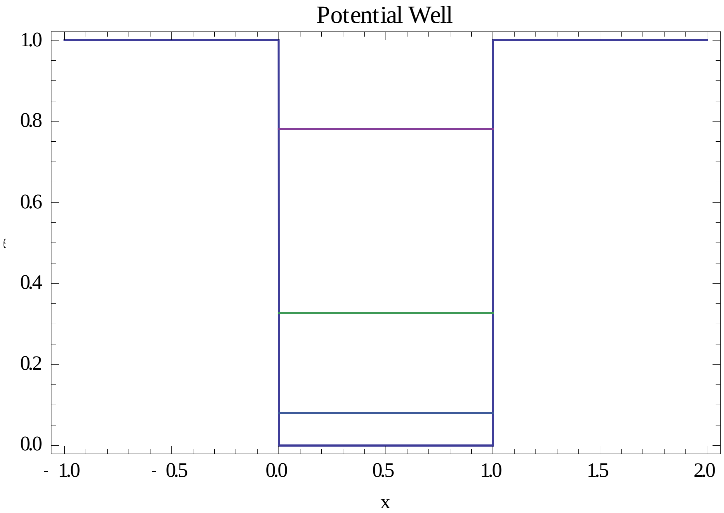
$$k=\sqrt{\frac{2mE}{\hbar}};\quad k'=\sqrt{\frac{2m}{\hbar}(E-V_0)}$$

When $E<V_0$ then k' is imaginary then we obtain physical solution. We conclude that energy should be smaller than potential.

Energy levels can be obtained by using Mathematica. (Use FindRoot[]) Before soving equation convert height of well V_0 and energy E, to unit of eV by substituting $E\rightarrow\frac{E}{e}\ and\ V_0\rightarrow\frac{V_0}{e}$.

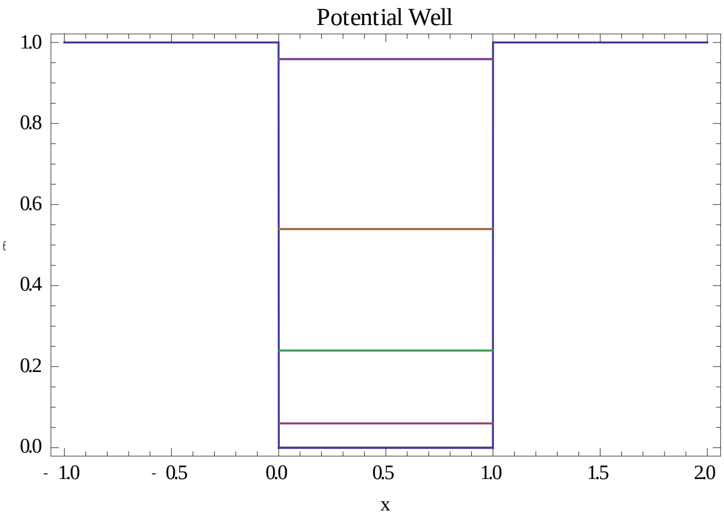
Below the graphs are given for eigenvalues for different values of potentials and width of the well. Analyze them carefully. $\{\hbar->6.62*10^\wedge-34, m->9.11*10^\wedge-31, L\rightarrow 10^\wedge-10, \mathrm{e1}\rightarrow 1.6*10^\wedge-19, \mathrm{V0}\rightarrow 1\}$

Energy levels are given by: $\{0.0802, 0.327,\ 0.781\}$



In the large limit of V_0 the well tends to the infinite well. Then the result is ($\mathrm{V0}\rightarrow 50\ eV$). Energy levels are:

$$\{0.0599,\qquad 0.2397,\qquad 0.5394,\qquad 0.959\}$$



Scattering of Particles in One Dimension

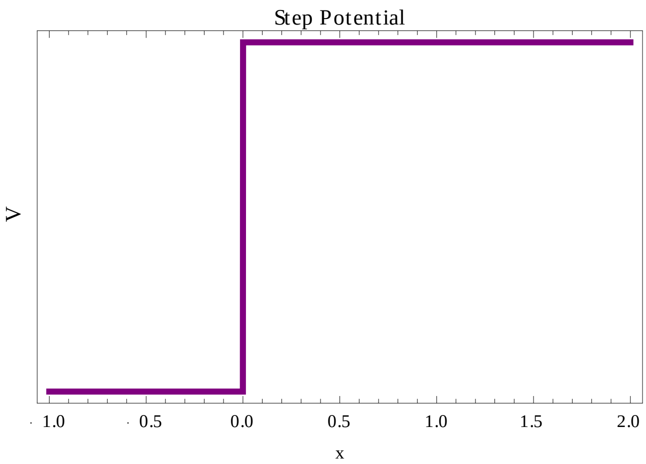
So far we have discovered that particles behave like waves, they obey the Schrödinger equation. This suggests that if we have an unknown potential it might be possible to determine its form if we can measure the probability of finding particles as a function of x. This obviously means we have to observe many particles in the potential.

Much of our knowledge of atomic, nuclear and particle physics has been determined from experiments that exploit the ideas discussed in this section.

Step Potential

The one dimensional **step potential** is an idealized system used to model incident, reflected and transmitted matter waves.

(Dashed lines are reflected wave and full lines are transmitted wave)



Consider a particle of mass m and energy $E > 0$ interacting with the simple square barrier:

$$V(x) = \begin{cases} 0 & if\ x < 0 \\ V_0 & if\ x > 0 \end{cases}$$

$$\psi = \begin{cases} e^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik'x} & x > 0 \end{cases}$$

Where

$$k = \sqrt{\frac{2mE}{\hbar}}; \quad k' = \sqrt{\frac{2m}{\hbar}(E - V_0)}$$

Continuity of the wave function at $x = 0$ give:

$$1 + B = C\,; k(1 - B) = k'C$$

Solution of the equations for B and C:

$$B = \frac{k - k'}{k + k'};\ C = \frac{2k}{k + k'}$$

Reflection and transmission coefficients can be calculated as follows: J is the probability current density.

$$J = \frac{\hbar}{i2m}\left(\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx}\right)$$

Then

$$J_i = \frac{\hbar}{i2m}(2ik);\ J_r = \frac{\hbar}{i2m}|B|^2(-2ik),\ J_t = \frac{\hbar}{i2m}|C|^2(2ik')$$

Reflection and transmission coefficients

$$R = \frac{|\psi_r|^2}{|\psi_i|^2} = \frac{J_r}{J_i} = |B|^2 = \left(\frac{k-k'}{k+k'}\right)^2$$

$$T = \frac{|\psi_t|^2}{|\psi_i|^2} = \frac{J_t}{J_i} = \frac{k'}{k}\ |C|^2 = \frac{k'}{k}\left(\frac{2k}{k+k'}\right)^2$$

Where subscripts t, r and i stand for transmission, reflection and incident respectively.

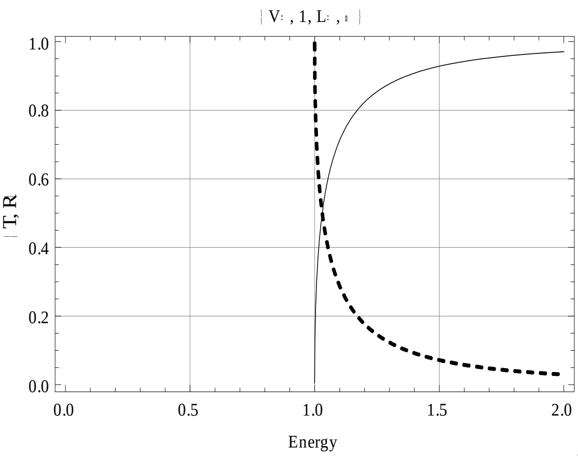
Since the current is a conserved quantity then

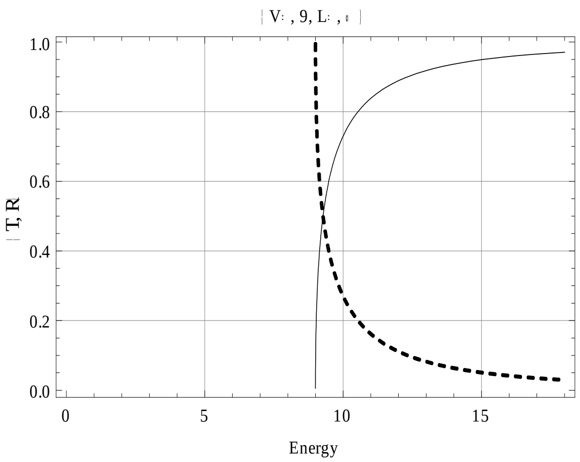
$$J_i + J_r = J_t$$

We check that

$$T + R = \left(\frac{k-k'}{k+k'}\right)^2 + \frac{k'}{k}\left(\frac{2k}{k+k'}\right)^2 = 1$$

For the step potential given in the figure, for the potentials 1, 5 and 9, Hartree, graph of the transmission and reflection coefficients are plotted. Analyze the graphs.(Maximum reflection points, maximum transmission points, critical points etc) (Dashed lines are reflected wave and full lines are transmitted wave)





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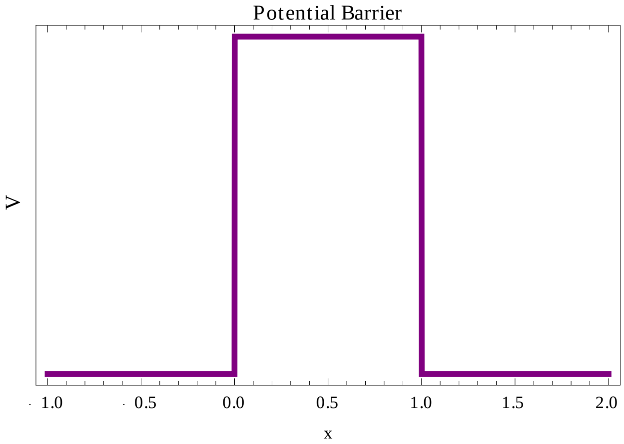
Potential Barrier(Dashed Lines are transmitted)

Consider a particle of mass m and energy E>0 interacting with the simple potential barrier. Write down equations and analyze the given results.



Wave function of the particle is given by

$$\psi_1 = e^{ikx} + Be^{-ikx}$$
$$\psi_2 = Ce^{ik'x} + De^{-ik'x}$$
$$\psi_3 = Fe^{ikx}$$

Using continuity equations at x=0 and x=L

$$1 + B = C + D \; and \; k(1 - B) = k'(C - D)$$
$$Ce^{ik'L} + De^{-ik'L} = Fe^{ikL} \; and \; k'(Ce^{ik'L} - De^{-ik'L}) = kFe^{ikL}$$

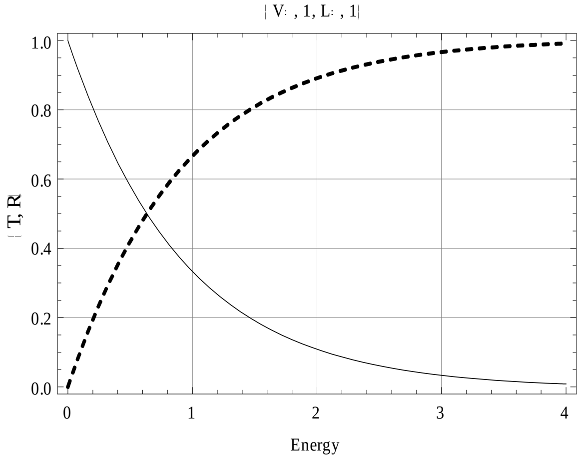
In order to obtain transmission and reflection coefficients you must eliminate C and D and you must calculate B and F. This calculation carried out by hand. From first equation we calculate C and D interms of B then substitute them into second equation. Please do this calculation. Your result will be:

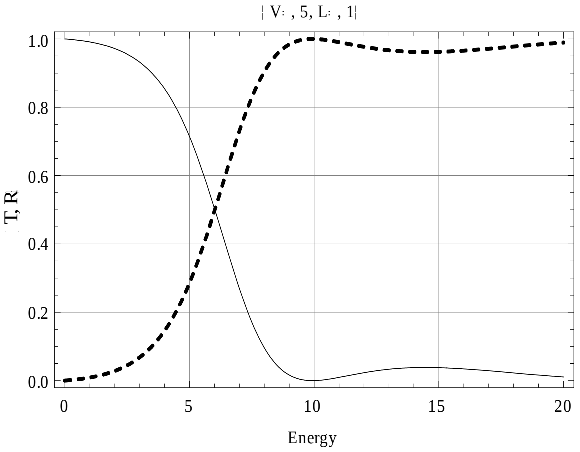
$$F = -\frac{4e^{-i(k-k')L}kk'}{e^{2ik'L}(k-k')^2 - (k+k')^2}, B = \frac{(k-k')(k+k')\mathrm{Sin}[k'L]}{2ikk'\mathrm{Cos}[k'L] + (k^2 + k'^2)\mathrm{Sin}[k'L]}$$

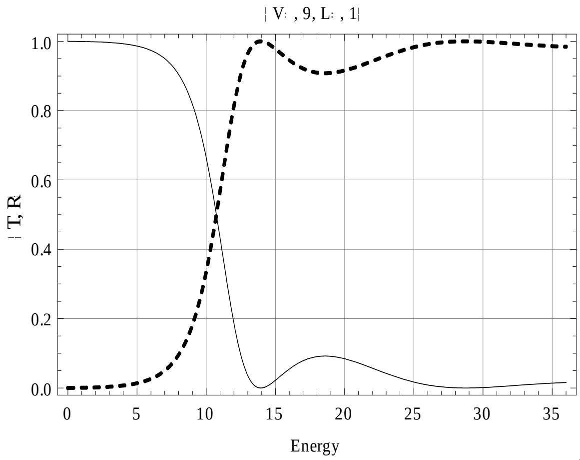
Reflection and transmission coefficients

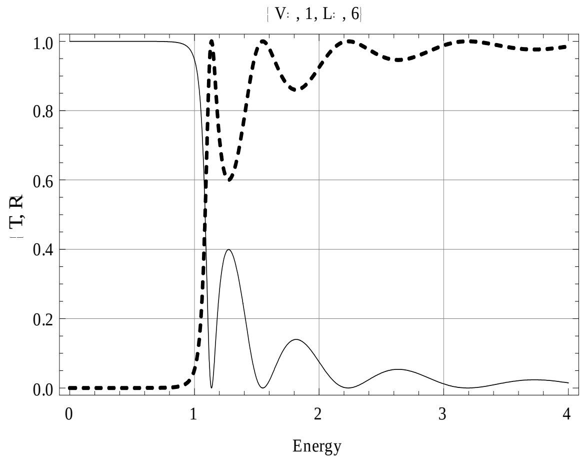
$$R = \frac{|\psi_r|^2}{|\psi_i|^2} = \frac{J_r}{J_i} = |B|^2$$
$$T = \frac{|\psi_t|^2}{|\psi_i|^2} = \frac{J_t}{J_i} = |C|^2$$

The barrier potential shown in the figure. For the potentials 1, 5 and 9 Hartree, and barrier width L=1 and 6 bohr graph of the transmission and reflection coefficients are plotted. Analyze the graphs.(Maximum reflection points, maximum transmission points, critical points, why are they oscillationg… etc)









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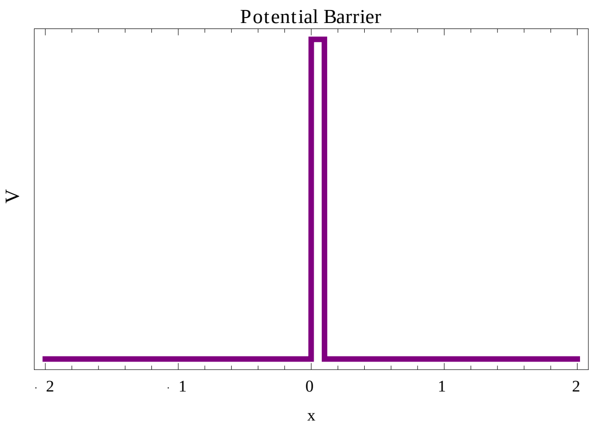
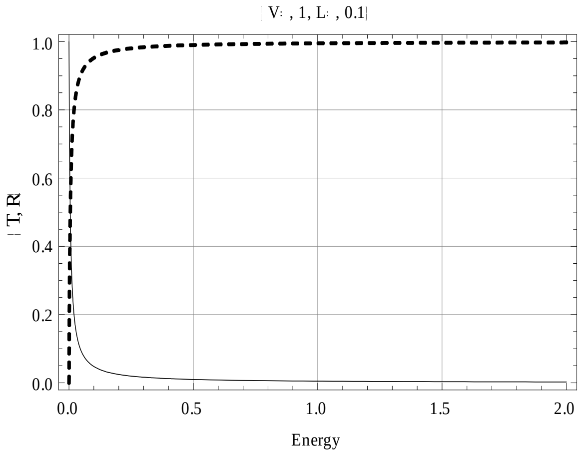
Consider a narrow barrier of width 0.1,0.6 and 1.1 Bohr. For 1, 5 and 9 hartree potentials, graph of the transmission and reflection coefficients are plotted. Analyze the graphs. Maximum reflection points, maximum transmission points, critical points, why are they oscillationg… etc)





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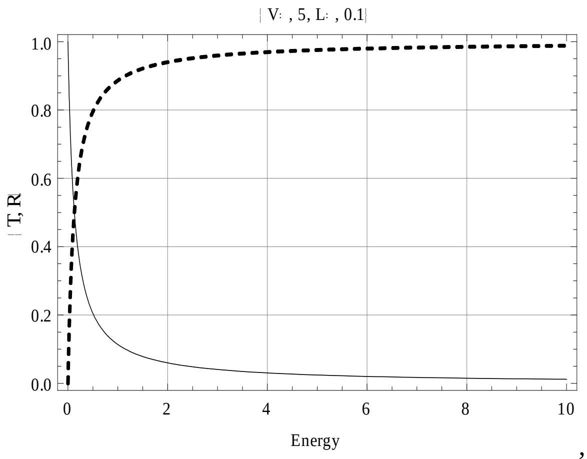
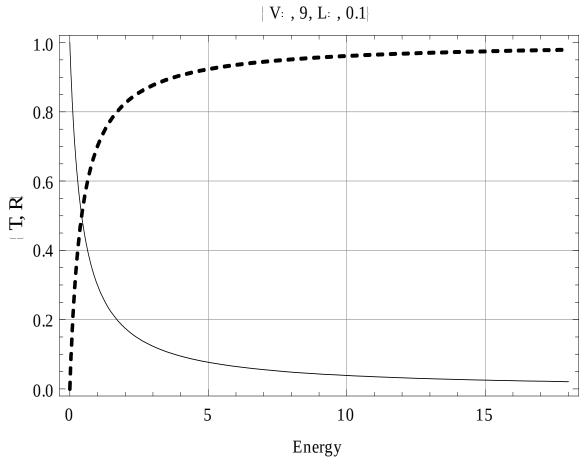
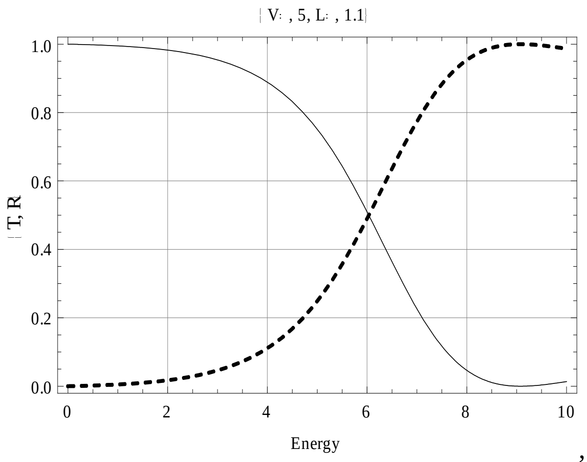
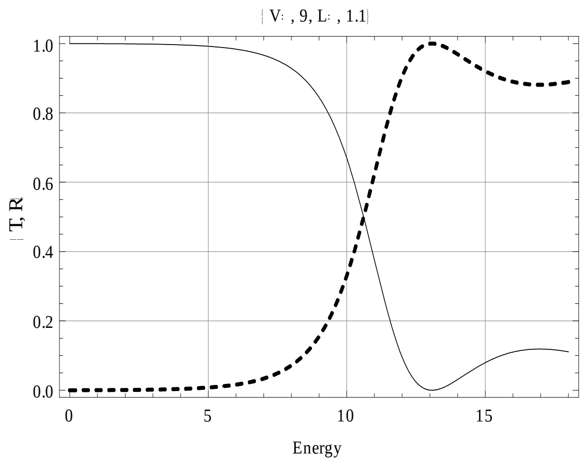


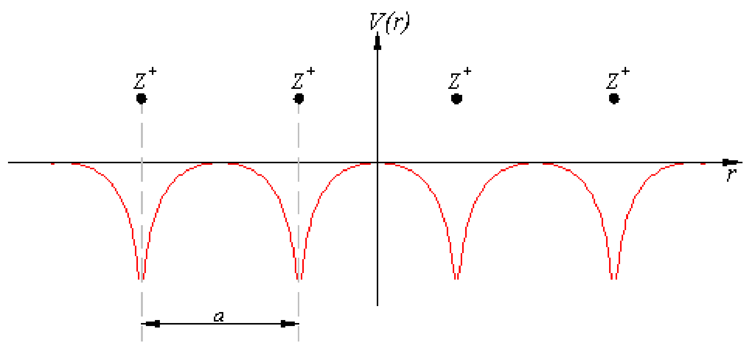




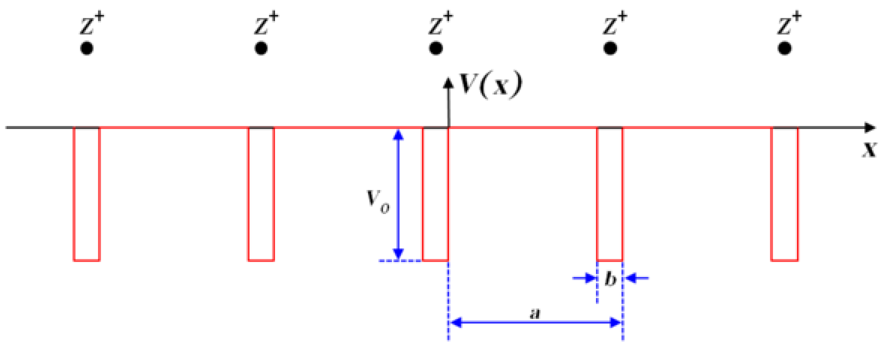


Periodic potential-- the existence of energy gap

Potential of a nucleus in the crystal is similar to the potential in the figure.



It can be approximated to (Kronig-Penney model)



Mathematical expression for the potential satisfies

$$V(x+a) = V(x); \;\; H(x+a) = H(x)$$

We will show that the solution $H\Psi(x) = E\Psi(x)$ can be written in the general form

$$\psi(x) = e^{ikx}u(x); where\ u(x+a) = u(x)$$

This is called the Bloch's theorem, or more generally, the Floquet theory.

Now if L is length of the Lattice ($say\ L = Na, L >> a$), we get a circular boundary condition

$$\psi(0) = \psi(L) => kL = 2\pi n => k = \frac{2\pi n}{L};\ \left(n = 0, \mp 1, \mp 2, \dots, \mp \frac{N}{2}\right)$$

Consider the approximated simple periodic potential:

$$V = \begin{cases} 0, & 0 < x < (a-b) \\ V_0, & -b < x < 0 \end{cases}$$

Solution of the Schrödinger equation for region $0 < x < (a-b)$

$$\psi(x) = Ae^{i\alpha x} + A'e^{-i\alpha x}; \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

For region $-b < x < 0$:

$$\psi(x) = Be^{i\beta\ x} + B'^{e^{-i\beta x}}; \beta = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$

Using boundary conditions:

$$u(-b) = u(a-b) and\ u'(-b) = u'(a-b)$$

After a tedious calculation we obtain:

$$\cos(ka) = \cos(\beta b)\cos\big(\alpha(a-b)\big) - \frac{\alpha^2+\beta^2}{2\alpha\beta}\sin(\beta b)\sin\big(\alpha(a-b)\big)$$

Further simplification

$$b \to 0; V_0 \to \infty;\ \sin(\beta b) \to \beta b;\ \ \cos(\beta b) \to 1$$

We obtain

$$\cos(ka) = \cos(\alpha a) - \frac{mV_0 b}{\hbar^2 \alpha}\sin(\alpha a)$$

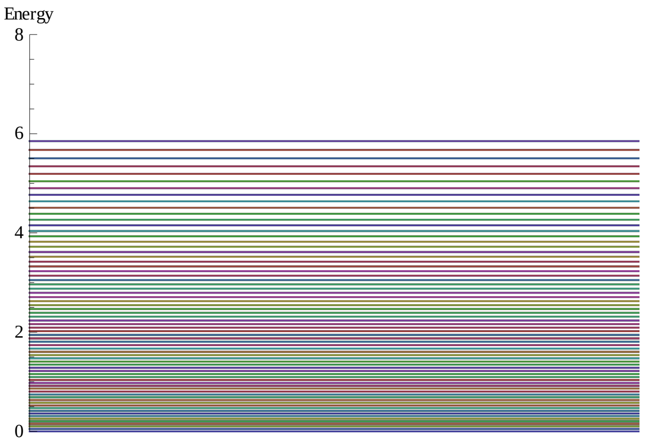
Since the left hand side is bound between -1 and +1, the allowed values of k are restricted. For values of k that this equation can be satisfied, $E = \hbar^2 k^2 / 2m$ gives the allowed energies. The forbidden region gives the energy gap. This leads to the band structure in periodic potentials. Here is a plot of the right-hand side of the above eq vs ka.

Let us discuss 4 cases: (first substitute $\alpha \to \frac{x}{a}$ $then\ E \to \frac{\hbar^2 x^2}{2ma^2}$, $a = 1.5\ nm; b = 0.5\ nm, P = -\frac{mV_0 ba}{\hbar^2}$) .

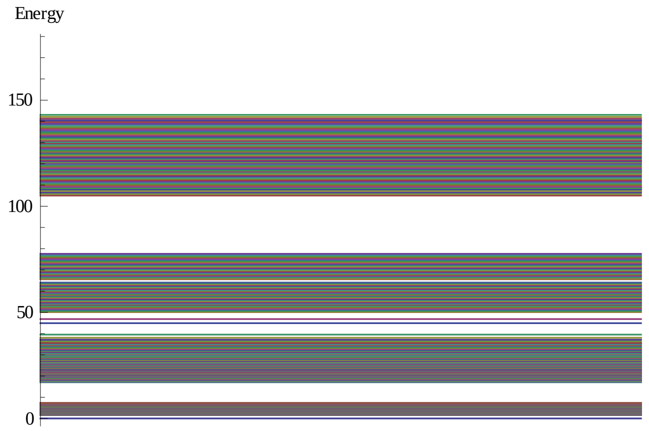
The energy equation takes the form

$$\cos(ka) = \cos(x) + \frac{P}{a\alpha}\sin(x)$$

Free electron $P = 0$ Energy



Nearly free electron model $P = 1$



Tight binding model $P = 20$

Free atom model $P = \infty\ (100)$