Chapter 13

Free Particle and Tunneling

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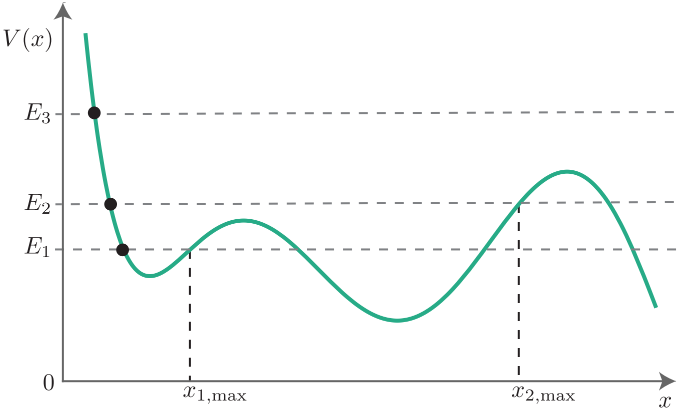
Chem. 4300

Bound or free particle in classical mechanics?

$$E_{\text{total}} = K(\dot{x}) + V[x]$$



Bound or free particle in quantum mechanics?

Back to Schrödinger equation:

$$E\,\Psi[x,t] = \underbrace{\left[\hat{K} + \hat{V}[x]\right]}_{\hat{\mathcal{H}}}\Psi[x,t] = i\hbar\frac{\partial\Psi[x,t]}{\partial t}$$

We divide the potentials, $V[x]$, into two groups

1. those that bind a particle to a particular region of space
2. those that do not bind a particle to a particular region of space

We saw example of 1st with particle in infinite well in last chapter.

As example of 2nd, imagine particle moving from left to right with constant momentum and no forces acting on it—a free particle.

A Quantum Free Particle

- Let's define a free particle as having $E > 0$ and $\hat{V}[x] = 0$,

$$\hat{\mathcal{H}}\,\psi[x] = (\cancelto{0}{\hat{V}[x]} + \hat{K})\,\psi[x] = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi[x]}{dx^2} = E\,\psi[x]$$

- $\psi[x]$ is eigenstate of $\hat{\mathcal{H}}$ with stationary state wave function

$$\Psi[x,t] = \psi[x]e^{-iEt/\hbar}$$

- Wave function for free particle traveling left to right with $p = \hbar k$ and $E = \hbar\omega$

$$\Psi[x,t] = Ae^{i(kx-\omega t)} = Ae^{ikx}e^{-iEt/\hbar}$$

where

$$k = \frac{p}{\hbar} = \frac{\sqrt{2mE}}{\hbar} \qquad \text{and} \qquad \psi[x] = Ae^{ikx} \quad \text{right traveling particle}$$

- For particle traveling right to left we use $p = -\hbar k$ and have

$$\psi[x] = Ae^{-ikx} \quad \text{left traveling particle}$$

Interesting thing about this free particle wave function: $\psi[x] = Ae^{ikx}$

There is no uncertainty in its momentum.

- Calculate expectation value: $\langle p \rangle = \int_{-\infty}^{\infty} \psi^*[x]\, \hat{p}\, \psi[x]\, dx = -i\hbar \int_{-\infty}^{\infty} \psi^*[x] \frac{d\psi[x]}{dx}\, dx$
- Substituting right traveling particle, $\psi[x] = Ae^{ikx}$, gives

$$\langle p \rangle = -i\hbar \int_{-\infty}^{\infty} |A|^2 e^{-ikx} \frac{d\left(e^{ikx}\right)}{dx} dx = \hbar k \int_{-\infty}^{\infty} |A|^2 e^{-ikx} e^{ikx} dx = \hbar k \int_{-\infty}^{\infty} \psi^*[x]\psi[x] dx = \hbar k$$

- Calculate expectation value for $\hat{p}^2$ from $\psi[x]$,

$$\langle p^2 \rangle = (-i\hbar)^2 \int_{-\infty}^{\infty} |A|^2 e^{-ikx} \frac{d^2(e^{ikx})}{dx^2}\, dx = (-i\hbar)^2 (ik)^2 \int_{-\infty}^{\infty} |A|^2 e^{-ikx} e^{ikx} dx = \hbar^2 k^2 \int_{-\infty}^{\infty} \psi^*[x]\psi[x] dx = \hbar^2 k^2$$

- Uncertainty in momentum is $\Delta p = \sqrt{\langle p^2 \rangle - (\langle p \rangle)^2} = \sqrt{\hbar^2 k^2 - (\hbar k)^2} = 0$
- Since $\Delta x \Delta p \geq \hbar/2$ then $\Delta x = \infty$, momentum precisely known, but no idea where particle is.

Another thing about this free particle wave function

Did you noticed a small problem with this free particle wave function?

It can't be normalized.

$$\int_{-\infty}^{\infty} \psi^*[x]\psi[x]dx = \infty.$$

We have an "end effect", or better stated a "no-end effect."

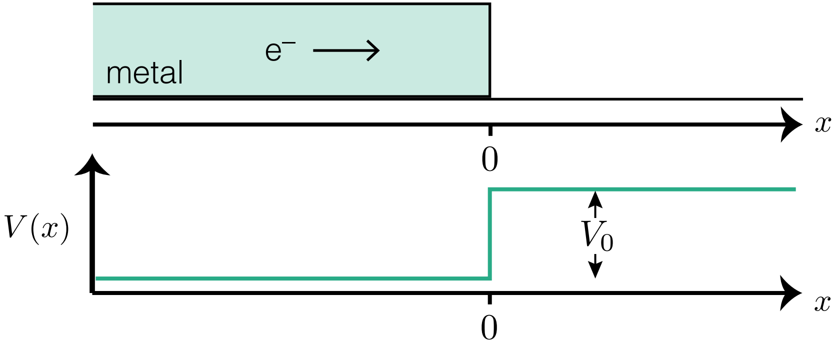
Could solve this problem with traveling wave packet, but then rest of math would get more difficult while we gain little new physical insight.

Keeping this caveat in mind we'll continue working with an un-normalizable free particle wave function and assume it does not seriously affect our conclusions.

Free particle approaches a step potential

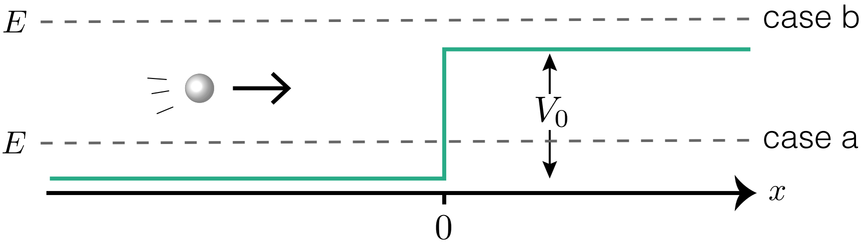
Free particle approaches a step potential

Imagine conduction electron in metal moving towards surface of metal.



- Inside metal electron feels attraction to positively charged metal nuclei.
- Classical particle must overcome attractive potential, V_0, to escape from surface
- Take approximate potential energy function of $V[x] = \begin{cases} 0 & \text{if } x < 0 \\ V_0 & \text{if } x > 0 \end{cases}$

Two cases when free particle approaches a step potential



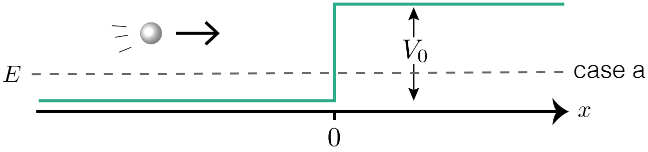
We consider 2 separate cases:

(a) $E < V_0$

(b) $E \geq V_0$

Let's examine wave function for quantum particle with total energy E in each case.

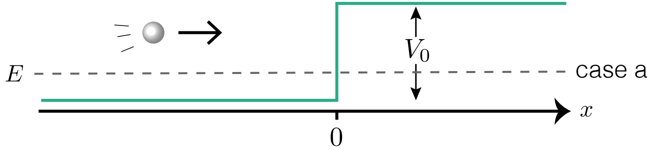
Free particle approaches a step potential



Case (a) $E < V_0$

Free particle approaches a step potential, Case: (a) $E < V_0$

Start by breaking total wave function into 2 parts:



Wave function in metal, ψ_{in}

Left of $x = 0$ where $\hat{V}[x] = 0$

$$\frac{d^2\psi_{\text{in}}[x]}{dx^2} + \underbrace{\frac{2mE}{\hbar^2}}_{k_1^2 > 0,\ \text{real}} \psi_{\text{in}}[x] = 0$$

Has general solution

$$\psi_{\text{in}}[x] = Ae^{ik_1 x} + Be^{-ik_1 x} \quad \text{for } x \leq 0$$

$$\text{where} \quad k_1 = \sqrt{2mE}/\hbar$$

Wave function outside metal, ψ_{out}

Right of $x = 0$, where $\hat{V}[x] = V_0$

$$\frac{d^2\psi_{\text{out}}[x]}{dx^2} - \underbrace{\frac{2m(V_0 - E)}{\hbar^2}}_{k_2^2 > 0,\ \text{real}} \psi_{\text{out}}[x] = 0$$

Has general solution

$$\psi_{\text{out}}[x] = Ce^{k_2 x} + De^{-k_2 x} \quad \text{for } x \geq 0$$

$$\text{where} \quad k_2 = \sqrt{2m(V_0 - E)}/\hbar$$

Free particle approaches a step potential, Case: (a) $E < V_0$

At $x = \infty$ the C term goes unphysically to ∞. Setting $C = 0$ leaves

$$\psi_{\text{out}}[x] = De^{-k_2 x}$$

Where ψ_{in} and ψ_{out} meet at $x = 0$ wave function must be finite, single valued, and continuous.

$$\psi_{\text{in}}[0] = \psi_{\text{out}}[0] \quad \text{and} \quad \frac{\mathrm{d}\psi_{\text{in}}[0]}{dx} = \frac{\mathrm{d}\psi_{\text{out}}[0]}{dx}$$

Gives 2 equations,

$$A + B = D \quad \text{and} \quad ik_1 A - ik_1 B = -k_2 D$$

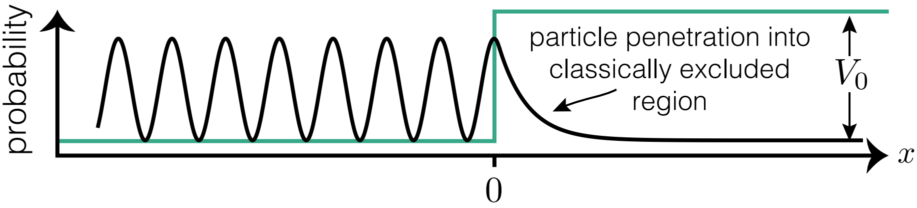
Taking sum and difference of 2 equations gives

$$A = \frac{D}{2}\left(1 + \frac{ik_2}{k_1}\right) \quad \text{and} \quad B = \frac{D}{2}\left(1 - \frac{ik_2}{k_1}\right)$$

Free particle approaches a step potential, Case: (a) $E < V_0$

Wave function when $E < V_0$ is given by

$$\psi[x] = \begin{cases} \underbrace{\frac{D}{2}\left(1 + \frac{ik_2}{k_1}\right)}_{A} \underbrace{e^{ik_1 x}}_{\longrightarrow} + \underbrace{\frac{D}{2}\left(1 - \frac{ik_2}{k_1}\right)}_{B} \underbrace{e^{-ik_1 x}}_{\longleftarrow} & x \leq 0 \quad \text{(in)} \\ De^{-k_2 x} & x \geq 0 \quad \text{(out)} \end{cases}$$

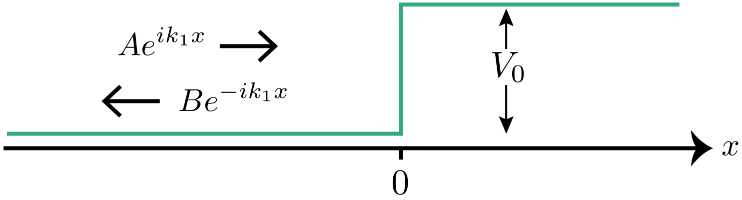


Free particle approaches a step potential, Case: (a) $E < V_0$

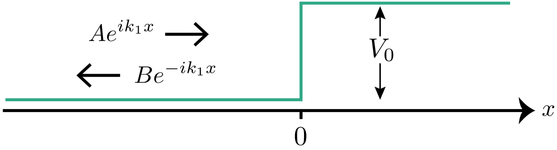
The total wave function can be written

$$\Psi[x,t] = \begin{cases} Ae^{i(k_1 x - Et/\hbar)} + Be^{i(-k_1 x - Et/\hbar)} & x \le 0 \quad \text{(in)} \\ De^{-k_2 x} e^{-iEt/\hbar} & x \ge 0 \quad \text{(out)} \end{cases}$$

We recognize two terms in ψ_{in} (when $x \le 0$) as corresponding to right and left traveling waves.



Free particle approaches a step potential, Case: (a) $E < V_0$



- Ae^{ik_1x} is incident wave coming from inside metal towards surface
- Be^{-ik_1x} is reflected wave traveling back into metal.
- We can define *reflection coefficient*, R, as

$$R = \frac{B^*B}{A^*A} = \frac{\left(1 - \frac{ik_2}{k_1}\right)^* \left(1 - \frac{ik_2}{k_1}\right)}{\left(1 + \frac{ik_2}{k_1}\right)^* \left(1 + \frac{ik_2}{k_1}\right)} = \frac{\left(1 + \frac{ik_2}{k_1}\right)\left(1 - \frac{ik_2}{k_1}\right)}{\left(1 - \frac{ik_2}{k_1}\right)\left(1 + \frac{ik_2}{k_1}\right)} = 1$$

- $R = 1$ means total reflection and electron doesn't escape metal just as we expected for classical free particle.

Free particle approaches a step potential, Case: (a) $E < V_0$

But, electron is wave, so how far away from metal surface does wave go?

Look at probability

$$\psi^*_{\text{out}}\psi_{\text{out}} = D^* D e^{-2k_2 x} = D^* D e^{-2x/\Delta x} = |D|^2 e^{-2x/\left(\hbar/\sqrt{2m(V_0-E)}\right)}$$

Normalization issues aside, if we take $\Delta x = 1/k_2$ as the barrier penetration distance, then

$$\Delta x = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

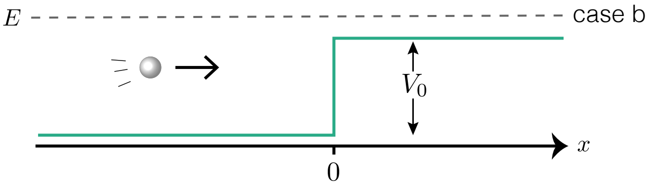
Example

Measurement of copper work function shows that $V_0 - E = 4$ eV. Estimate distance Δx that electron can penetrate into classically excluded region outside metal block.

$$\Delta x = \frac{\hbar}{\sqrt{2m(V_0 - E)}} = \frac{\hbar}{\sqrt{2m_e(4 \text{ eV})}} \approx 1 \text{ Å}$$

Extends out distance that is roughly diameter of an atom.

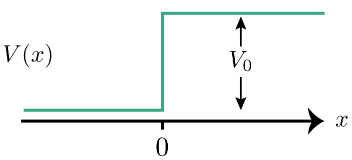
Free particle approaches a step potential

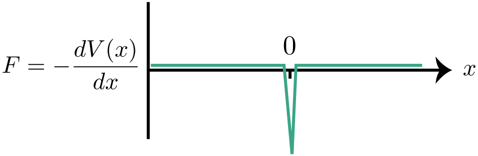


Case (b) $E \geq V_0$

Free particle approaches a step potential, Case: (b) $E \geq V_0$

- Consider situation when total energy of particle exceeds V_0.
- Recall $F = -dV/dx$.





- Effect of changing potential is to exert a force on particle.
- Step potential will exert an impulsive force on a particle.
- In this case impulsive force will slow down particle but won't stop it from continuing to travel into positive x region.

Free particle approaches a step potential, Case: (b) $E \geq V_0$

Particle kinetic energy is ...

$$E = \frac{p_{\text{in}}^2}{2m} \text{ for } x < 0$$

$$(E - V_0) = \frac{p_{\text{out}}^2}{2m} \text{ for } x > 0$$

Schrödinger equation for 2 regions would be

$$\frac{\mathrm{d}^2\psi_{\text{in}}[x]}{dx^2} + \frac{2mE}{\hbar^2}\psi_{\text{in}}[x] = 0$$

oscillatory solution for $\psi_{\text{in}}[x]$:

$$\psi_{\text{in}}[x] = Ae^{ik_1 x} + Be^{-ik_1 x} \quad \text{for } x \leq 0$$

where

$$k_1 = \sqrt{2mE}/\hbar = p_{\text{in}}/\hbar$$

$$\frac{\mathrm{d}^2\psi_{\text{out}}[x]}{dx^2} + \frac{2m(E - V_0)}{\hbar^2}\psi_{\text{out}}[x] = 0$$

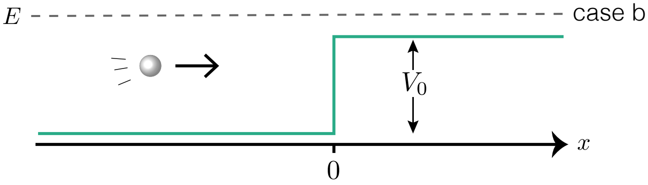
oscillatory solution for $\psi_{\text{out}}[x]$:

$$\psi_{\text{out}}[x] = Ce^{ik_2 x} + De^{-ik_2 x} \quad \text{for } x \geq 0$$

where

$$k_2 = \sqrt{2m(E - V_0)}/\hbar = p_{\text{out}}/\hbar$$

Free particle approaches a step potential, Case: (b) $E \geq V_0$



$$\psi_{\text{in}}[x] = Ae^{ik_1 x} + Be^{-ik_1 x} \quad \text{for } x \leq 0 \qquad\qquad \psi_{\text{out}}[x] = Ce^{ik_2 x} + De^{-ik_2 x} \quad \text{for } \geq 0$$

- Particle traveling from $x < 0$ is allowed to pass through $x = 0$ and head into $x > 0$. Nothing in our model causes it to return. To account for this we set $D = 0$.

- Can't assume particle traveling in $x < 0$ towards $x = 0$ will make it past $x = 0$. Particle might be reflected, like $E < V_0$ case, even though this is $E > V_0$ case, where classical free particle would never be reflected.

Free particle approaches a step potential, Case: (b) $E \geq V_0$

Require that ψ_{in} and ψ_{out} meet at $x = 0$ with

$$\psi_{\text{in}}[0] = \psi_{\text{out}}[0] \quad \text{and} \quad \frac{d\psi_{\text{in}}[0]}{dx} = \frac{d\psi_{\text{out}}[0]}{dx}$$

This gives 2 equations,

$$A + B = C \quad \text{and} \quad k_1(A - B) = k_2 C$$

Solving for B and C in terms of A gives

$$B = \frac{k_1 - k_2}{k_1 + k_2} A \quad \text{and} \quad C = \frac{2k_1}{k_1 + k_2} A$$

Free particle approaches a step potential, Case: (b) $E \geq V_0$

Wave function when $E \geq V_0$ is given by

$$\psi[x] = \begin{cases} Ae^{ik_1 x} + \underbrace{A\left(\frac{k_1 - k_2}{k_1 + k_2}\right)}_{B} e^{-ik_1 x} & x \leq 0 \quad \text{(in)} \\ \underbrace{A\left(\frac{2k_1}{k_1 + k_2}\right)}_{C} e^{ik_2 x} & x \geq 0 \quad \text{(out)} \end{cases}$$

Again $Ae^{ik_1 x}$ is forward wave and $Be^{-ik_1 x}$ as reflected wave.
Calculating reflection coefficient gives

$$R = \frac{B^* B}{A^* A} = \frac{(k_1 - k_2)^* (k_1 - k_2)}{(k_1 + k_2)^* (k_1 + k_2)} = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2}$$

Free particle approaches a step potential, Case: (b) $E \geq V_0$

Taking $Ce^{ik_2 x}$ as transmitted wave calculate a *transmission coefficient*.
Oops! Forgot to mention reflection and transmission coefficients represent probability flux—change in probability per unit time.

- Taking wave speed into account reflection coefficient derivation is

$$R = \frac{v_1 B^* B}{v_1 A^* A} = \frac{B^* B}{A^* A} \qquad \text{where } v_1 = \omega_1/k_1 \text{ and } E = \hbar\omega_1$$

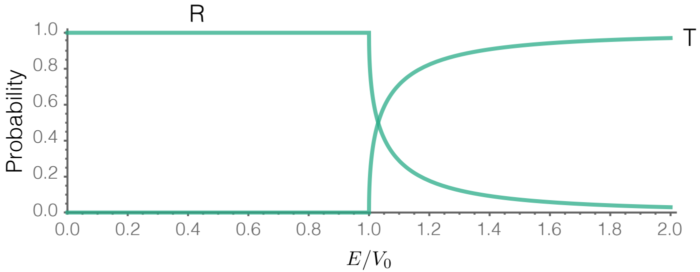
- For transmission coefficient: $T = \dfrac{v_2 C^* C}{v_1 A^* A}$, where $v_2 = \omega_2/k_2$ and $E - V_0 = \hbar\omega_2$
- Taking $v_1 = p_1/m = \hbar k_1/m$ and $v_2 = p_2/m = \hbar k_2/m$ we obtain: $T = \dfrac{4k_1 k_2}{(k_1 + k_2)^2}$ when $E/V_0 \geq 1$
- Since $T + R = 1$, we calculate R from T. After some algebra (see homework)

$$R = 1 - T = \left(\frac{1 - \sqrt{1 - V_0/E}}{1 + \sqrt{1 - V_0/E}}\right)^2 \quad \text{when } E/V_0 > 1$$

Free particle approaches a step potential, Cases (a) $E < V_0$ and (b) $E \geq V_0$

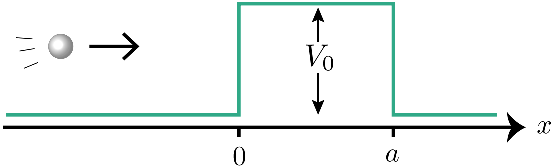
Bring reflection and transmission coefficients together for two cases

$$R = 1 - T = \begin{cases} 1 & \text{when } E < V_0 \\ \left(\dfrac{1 - \sqrt{1 - V_0/E}}{1 + \sqrt{1 - V_0/E}} \right)^2 & \text{when } E \geq V_0 \end{cases}$$



Particle with $E \geq V_0$ has enough energy to enter $x > 0$ but wave function have a significant probability to be reflected back to $x < 0$. This would not happen to classical particle.

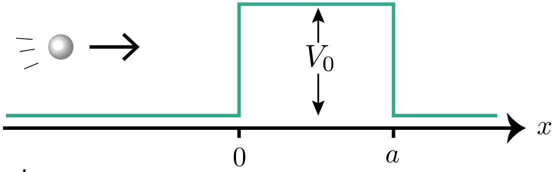
Free particle approaches a barrier potential



Free particle approaches a barrier potential

Free particle approaching square barrier potential

$$V[x] = \begin{cases} 0 & \text{if } x < 0 \\ V_0 & \text{if } 0 \le x \le a \\ 0 & \text{if } x > a \end{cases}$$

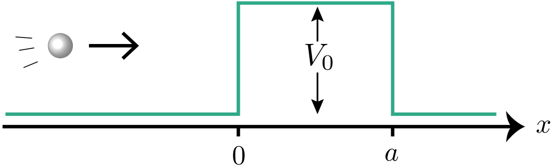


Can be model for number of interesting phenomena

- rates of electron or proton transfer reactions
- inversion of ammonia molecules,
- emission of α particles from radioactive nuclei
- tunnel diodes used in fast electronic switches
- atomic-scale imaging of surfaces with scanning tunneling microscopy

Free particle approaches a barrier potential

$$V[x] = \begin{cases} 0 & \text{if } x < 0 \\ V_0 & \text{if } 0 \le x \le a \\ 0 & \text{if } x > a \end{cases}$$



1st writing wave function outside barrier as

$$\begin{matrix} \text{outside} \\ \text{barrier} \end{matrix} \left\{ \begin{matrix} \psi_{\text{left}}[x] = Ae^{ik_I x} + Be^{-ik_I x} & \text{for } x < 0 \\ \psi_{\text{right}}[x] = Ce^{ik_I x} + De^{-ik_I x} & \text{for } x > a \end{matrix} \right\} \text{ with } k_I = \frac{2mE}{\hbar}$$

Inside barrier solution depends on whether (II) $E < V_0$ or (III) $E \ge V_0$

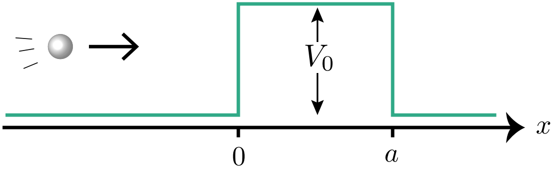
$$\psi_{\text{in}}^{(\text{II})}[x] = Fe^{-k_{\text{II}} x} + Ge^{k_{\text{II}} x} \quad \text{for} \quad 0 \le x \le a, \qquad k_{\text{II}} = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

or

$$\psi_{\text{in}}^{(\text{III})}[x] = Fe^{ik_{\text{III}} x} + Ge^{-ik_{\text{III}} x} \quad \text{for} \quad 0 \le x \le a, \qquad k_{\text{III}} = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

Free particle approaches a barrier potential

$$V[x] = \begin{cases} 0 & \text{if } x < 0 \\ V_0 & \text{if } 0 \le x \le a \\ 0 & \text{if } x > a \end{cases}$$



$$\left.\begin{array}{ll} \text{outside} \\ \text{barrier} \end{array} \begin{cases} \psi_{\text{left}}[x] = Ae^{ik_I x} + Be^{-ik_I x} & \text{for } x < 0 \\ \psi_{\text{right}}[x] = Ce^{ik_I x} + De^{-ik_I x} & \text{for } x > a \end{cases} \right\} \text{ with } k_I = \frac{2mE}{\hbar}$$

Take particle as coming from $-x$ towards $+x$—as shown in figure.

If it makes it to $+x$ then it won't be reflected back.

To account for this we set $D = 0$.

Free particle approaches a barrier potential

Requirement of finite, single valued and continuous function means

$$\psi_{\text{left}}[0] = \psi_{\text{in}}[0] \quad \text{and} \quad \frac{d\psi_{\text{left}}[0]}{dx} = \frac{d\psi_{\text{in}}[0]}{dx}$$

and

$$\psi_{\text{in}}(a) = \psi_{\text{right}}(a) \quad \text{and} \quad \frac{d\psi_{\text{in}}(a)}{dx} = \frac{d\psi_{\text{right}}(a)}{dx}$$

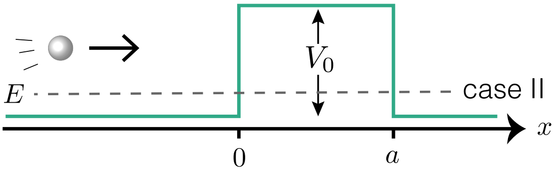
Homework: Consider 2 separate cases:

(II) $E < V_0$

(III) $E \geq V_0$

Insert trial wave functions into top expressions to express coefficients in terms of wave numbers in 3 different regions.

Free particle approaches a barrier potential

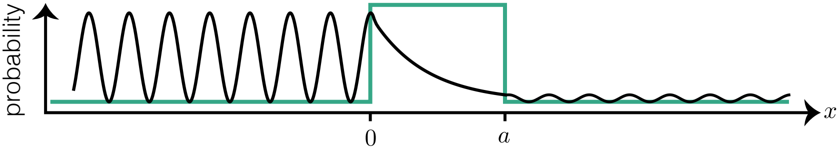


Case (II) $E < V_0$

Free particle approaches a barrier potential, Case: $E < V_0$

$$\psi_{\text{in}}^{(\text{II})}[x] = Fe^{-k_{\text{II}}x} + \cancelto{0}{G}\, e^{k_{\text{II}}x} \quad \text{for} \quad 0 \le x \le a, \qquad\qquad k_{\text{II}} = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

- In this case, wave function inside barrier, $\psi_{\text{in}}^{(\text{II})}[x]$, has form of exponential decay.
- If barrier is thin enough then wave function will not have decayed to zero when it reaches other side, and wave continues on for $x > a$.



Remarkable result!
Classical particle with $E < V_0$ would never penetrates barrier yet quantum particle does.
Quantum particle "tunnels" through barrier and appears on other side.

Free particle approaches a barrier potential, Case: $E < V_0$

Homework: Calculate the transmission coefficient through the barrier

$$T = \frac{v_1 C^* C}{v_1 A^* A} = \frac{1}{1 + \dfrac{\sinh^2 k_{\rm II} a}{4\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)}} \qquad \text{where} \qquad k_{\rm II} a = \sqrt{\frac{2mV_0 a^2}{\hbar^2}\left(1 - \frac{E}{V_0}\right)}$$

If $\sinh$ argument is large we can approximate

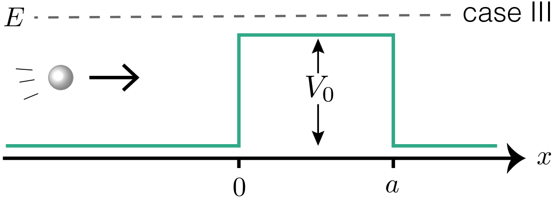
$$\sinh k_{\rm II} a = \frac{1}{2}\left(e^{k_{\rm II} a} - e^{-k_{\rm II} a}\right) \approx \frac{1}{2} e^{k_{\rm II} a}$$

Works in limit of increasing particle mass, m, increasing V_0, or increasing thickness, a, and gives

$$T \approx 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right) e^{-2k_{\rm II} a} \quad \text{Since } T + R = 1 \text{ we find } \; R \approx 1 - 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right) e^{-2k_{\rm II} a}$$

Has right limiting behavior. In limit that $a \to \infty$, $V_0 \to \infty$, or $m \to \infty$ then $R \to 1$ and $T \to 0$.

Free particle approaches a barrier potential



Case (III) $E \geq V_0$

Free particle approaches a barrier potential, Case: $E \geq V_0$

$$\psi_{\text{in}}^{(\text{III})}[x] = Fe^{ik_{\text{III}}x} + Ge^{-ik_{\text{III}}x} \quad \text{for} \quad 0 \leq x \leq a, \qquad k_{\text{III}} = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

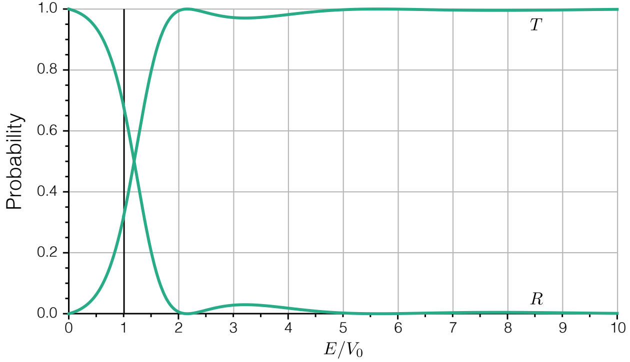
- Wave function inside barrier, $\psi_{\text{in}}^{(\text{III})}[x]$, has an oscillatory form.
- Classical particle will always penetrate barrier when $E > V_0$
- Have to include possibility that quantum particle will be reflected even though $E > V_0$.

Homework: Calculate transmission coefficient

$$T = \frac{v_1 C^* C}{v_1 A^* A} = \frac{1}{1 + \dfrac{\sin^2 k_{\text{III}} a}{4\frac{E}{V_0}\left(\frac{E}{V_0} - 1\right)}} \qquad \text{where} \qquad k_{\text{III}} a = \sqrt{\frac{2mV_0 a^2}{\hbar^2}\left(\frac{E}{V_0} - 1\right)}$$

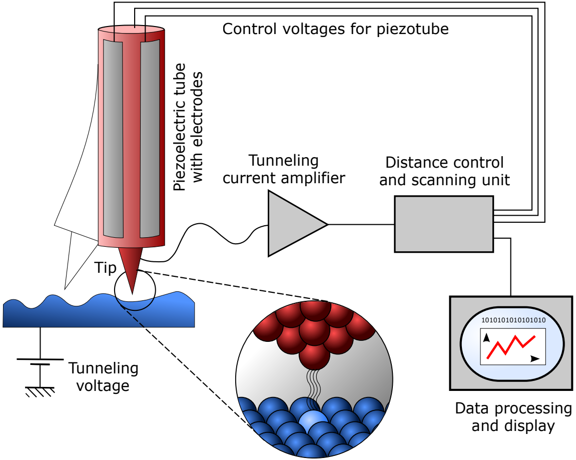
Free particle approaches a barrier potential

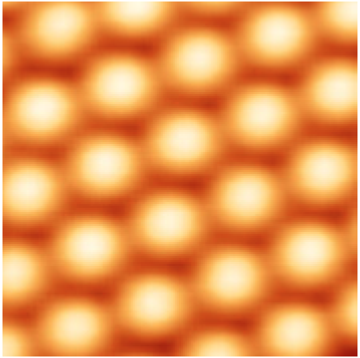
With $T + R = 1$ we can calculate R from T.
Reflection and transmission coefficients for $E < V_0$ and $E \geq V_0$ together.



In region just beyond $E/V_0 > 1$, particle has enough energy to go into x, but wave function has a significant probability to be reflected.
This would not happen to classical particle.

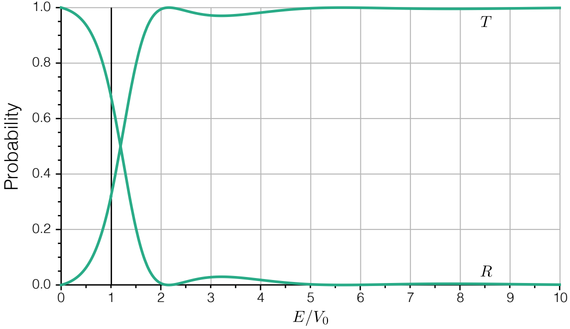
Scanning Tunneling Microscope

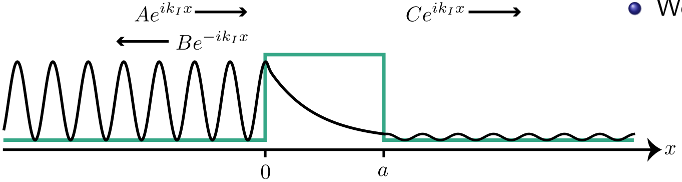




STM image of atoms on the surface of a crystal of silicon carbide (SiC).
Atoms are arranged in a hexagonal lattice and are 0.3 nm apart.

Free Particle and Tunneling in Quantum Mechanics





- Web Video:Minute Physics–Fusion and Quantum Tunneling
- Web Video:Minute Physics–Quantum Tunneling
- Web Video:Transistors