PAGE NO.:
DATE / /

Variational methods :-

$$\langle E \rangle = \langle \psi | H | \psi \rangle \geq E_0$$

We take parameters $\alpha, \beta, \gamma, \ldots$ and minimise the $E(\alpha, \beta, \gamma, \ldots)$ to get a upper bound on E_0.

* Consider an-Harmonic oscillator with $V(x) = \lambda x^4$.

the ground state will have no nodes, dissappear at ∞ and be even.

$\psi(x, \alpha) = e^{-\alpha x^2/2}$, be our trial wavefunction.

$$E(\alpha) = \frac{\int e^{-\alpha x^2/2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \lambda x^4\right) e^{-\alpha x^2/2}\, dx}{\int e^{-\alpha x^2}\, dx}$$

$$= \frac{\hbar^2 \alpha}{4m} + \frac{3\lambda}{4\alpha^2}$$

Minima at $\alpha_0 = \left(\frac{6m\lambda}{\hbar^2}\right)^{1/3}$

$$E(\alpha_0) = \frac{3}{8}\left(\frac{6\hbar^4 \lambda}{m^2}\right)^{1/3}$$

$$\Rightarrow E_0 \leq E(\alpha_0)$$

* Consider Helium atom.

$$H = \frac{p_1^2}{2m} - \frac{\tilde{Z} e^2}{|r_1|} + \frac{p_2^2}{2m} - \frac{\tilde{Z} e^2}{|r_2|} + \frac{(\tilde{Z} - Z) e^2}{|r_1|} + \frac{(\tilde{Z} - Z) e^2}{|r_2|} + \frac{e^2}{|r_2 - r_1|}$$

$$\Rightarrow \langle E \rangle = E_0 \left(4Z - Z^2 - \frac{5}{8} Z\right) \Rightarrow \tilde{Z} = 2 - \frac{5}{16}$$

Scanned with CamScanner

PAGE NO.:
DATE / /

$\Rightarrow E_0 \leq -77.4$ eV.

What if you want an approximation for higher states, just choose trial state $|\psi\rangle$ such that
$\langle E_0|\psi\rangle = 0$
giving you E_1 . . and so on.

for $V = \lambda x^4$, if one node $|\psi\rangle$ is chosen, then we get $\langle E\rangle \geq E_1$.

* 16.1.2.

$\psi(x) = (x-a)(x+a)$

$$E(\psi) = \frac{\int dx \cdot \psi^* \left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right)\psi}{\int dx\ \psi^* \psi}$$

$$E(\alpha) = \frac{5\hbar^2}{4ma^2}$$

$$E_0 = \frac{\hbar^2\pi^2}{8ma^2}$$

* 16.1.3.

for $V = -aV\delta(x)$.

take $\psi = e^{-\alpha x^2}$.

and $|\psi|^2 = \sqrt{\frac{\pi}{2\alpha}}$.

$$E(\psi) = \sqrt{\frac{2\alpha}{\pi}}\left(\int dx\ \psi^*\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx} - aV_0\delta(x)\right)\psi\right)$$

$$= -\frac{\hbar^2}{2m}\sqrt{\frac{2\alpha}{\pi}} \cdot \int dx\ \psi^*\psi'' - aV_0|\psi(0)|^2.$$

$$= -\frac{\hbar^2}{2m}\left(-\sqrt{\frac{\pi\alpha}{2}}\right)\left(\sqrt{\frac{2\alpha}{\pi}}\right) - aV_0\sqrt{\frac{2\alpha}{\pi}}$$

$$= \frac{\hbar^2}{2m}\left(\alpha - \frac{2maV_0}{\hbar^2}\sqrt{\frac{2\alpha}{\pi}}\right).$$

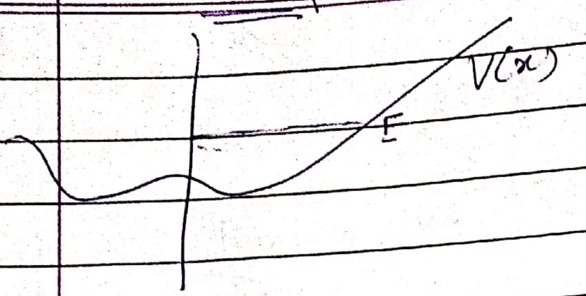
minima at $\alpha_0 = \left(\frac{a V_0}{2\pi}\right)^2\left(\frac{2m}{\hbar^2}\right)^2$

$$\Rightarrow E(\alpha_0) = \frac{\hbar^2}{2m}\left[\left(\frac{2m}{\hbar^2}\right)^2\frac{(aV_0)^2}{2\pi} - \frac{2maV_0}{\hbar^2}\left(\sqrt{\frac{2}{\pi}}\right)\frac{aV_0}{\sqrt{2\pi}}\cdot\frac{2m}{\hbar^2}\right]$$

$$= -\frac{ma^2V_0^2}{\pi\hbar^2} \quad \text{close to} \quad \frac{-ma^2V_0^2}{2\hbar^2}.$$

Scanned with CamScanner

WKB \ Semi-classical approximation :-



$$\frac{p^2}{2m} + V(x) = E$$

$$p = \sqrt{2m(E - V(x))}$$

$$\lambda = \frac{2\pi\hbar}{p(x)}$$

TISE :-

$$-\frac{\hbar^2}{2m}\nabla^2\psi = (E - V(x))\,\psi(x)$$

$$-\hbar^2\nabla^2\psi(x) = p^2(x)\,\psi(x)$$

$$\Rightarrow \hat{p}^2\psi(x) = p^2(x)\,\psi(x)$$

$$p^2 = 2m(E - V(x)) = \hbar^2 k^2(x) \qquad E > V.$$

$$-p^2 = \hbar^2 k^2(x) \qquad E < V.$$

$$\psi(x,t) = \sqrt{\rho(x,t)}\; e^{\frac{i}{\hbar}S(x,t)}.$$

Now $\rho = |\psi|^2$ is the probability density.

$$\nabla\psi = \frac{1}{2}\frac{\nabla\rho}{\sqrt{\rho}}\, e^{i\frac{S}{\hbar}} + \frac{i}{\hbar}\nabla S\,\psi.$$

$$J = \frac{\hbar}{m}\,\mathrm{Im}(\psi^*\nabla\psi) = \rho\,\frac{\nabla S}{m}$$

$$\therefore\; p(x) \approx \nabla S$$

Example :- Free particle. $\psi(x,t) = e^{\frac{i p\cdot x}{\hbar} - \frac{iEt}{\hbar}}$

$$\rho = 1, \quad S = p\cdot x - Et$$

$$\nabla S = p$$

$$\frac{\partial S}{\partial t} = -E$$

DATE / /

Approximation scheme :-

$\psi(x) = e^{\frac{i}{\hbar} S(x)}$ $S(x) \in \mathbb{C}$, (this provides the norm).

$-\hbar^2 \frac{d^2}{dx^2}\psi = p^2(x) \cdot e^{i/\hbar S}$

$-\hbar^2\left(\frac{i}{\hbar}S'' + \left(\frac{i}{\hbar}S'\right)^2\right) = p^2(x)$

$(S'(x))^2 - i\hbar S'' = p^2(x)$ ...... non-linear ODE.

Claim : $i\hbar S'' << 1$ if $V'(x) << 1$

* let $V(x) = V_0$, $p(x) = p_0 = \sqrt{2m(E - V_0)}$.

$\Rightarrow \psi(x) = e^{\left(\frac{i p_0 x}{\hbar}\right)}$

for this $S(x) = p_0 x$.

$S'(x) = p_0$, $S'' = 0$

let $S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \cdots$

$\Rightarrow \left(S_0' + \hbar S_1' + O(\hbar^2)\right)^2 - i\hbar\left(S_0'' + O(\hbar)\right) = p^2(x)$.

$\left(S_0'^2 - p^2(x)\right) + \hbar\left(2S_0'S_1' - iS_0''\right) + O(\hbar^2) = 0$

$\Rightarrow (S_0')^2 = p^2(x)$; $S_1' = \frac{i}{2}\frac{S_0''}{S_0'}$

$\Rightarrow S_0' = \pm p(x)$, $S_0 = \pm\int_{x_0}^{x} p(x')\,dx'$

$S_1' = \frac{i}{2}\frac{\pm p'(x)}{\pm p(x)} = \frac{i}{2}\frac{p'}{p} = \frac{i}{2}(\ln p)'$

$S_1 = \frac{i}{\hbar}\ln(p(x)) + c'$ (for slowly varying potential)

$$\psi(x) \approx e^{\frac{i}{\hbar}(S_0 + \hbar S_1)}$$
$$= e^{\frac{i}{\hbar} S_0(x)} \, e^{\frac{i}{\hbar}\left(\frac{i}{2} \ln(p(x))\right)}$$

$$\boxed{\psi(x) = \frac{A}{\sqrt{p(x)}} \, e^{\left(\pm \frac{i}{\hbar} \int_{x_0}^{x} p(x')dx'\right)}}$$

for $E > V$, $\quad p(x) = k(x)\,\hbar$

$$\psi(x) = \frac{A}{\sqrt{k(x)}} \, e^{i\int_{x_0}^{x} k(x')dx'} + \frac{B}{\sqrt{k(x)}} \, e^{-i\int_{x_0}^{x} k(x')dx'}$$

for $E < V$, $\quad p(x) = i\hbar\, k(x)$.

$$\psi(x) = \frac{C}{\sqrt{k(x)}} \exp\left(\int_{x_0}^{x} k(x')dx'\right) + \frac{D}{\sqrt{k(x)}} \exp\left(-\int_{x_0}^{x} k(x')dx'\right)$$

Probability density :- $\rho = \psi^* \psi = \frac{|A|^2}{p(x)}$

Probability current :-

$$J = \frac{\rho}{m} \frac{\partial S}{\partial x} = \frac{|A|^2}{p(x)} \cdot \frac{p(x)}{m} = \frac{|A|^2}{m}.$$

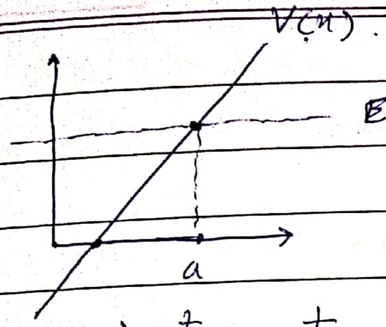
$$\lambda(x) \left| \frac{dV}{dx} \right| \ll \frac{p^2}{2m}$$

$$\left| \lambda \frac{d\lambda}{dx} \right| \ll \lambda$$

$\therefore$ The approximation is semi-classical for $\hbar \to 0$.

PAGE NO.:
DATE / /

linear potential



$$V(x) - E = g(x-a) \qquad g > 0$$

for $x < a$, ... allowed region.

$$E - V(x) = g(a-x)$$

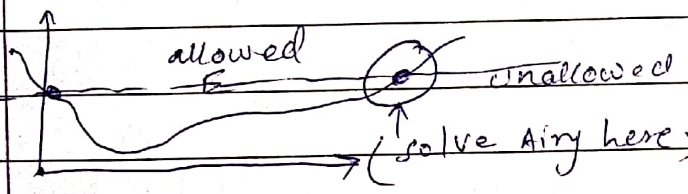
$$p(x) = \sqrt{2mg(a-x)}$$

$$\lambda = \frac{\hbar}{p} = \frac{\hbar}{\sqrt{2mg}} \frac{1}{\sqrt{a-x}}$$

$$\left|\frac{d\lambda}{dx}\right| = \frac{\hbar}{\sqrt{2mg}} \frac{1}{2} \cdot \frac{1}{(a-x)^{3/2}}$$

so as $a \to x$, the approximation crashes.

For finding bound states, we need to approximate at the allowed - unallowed crossing.



close to the crossing approximation fails.

* But near the crossing, the potential can be approximated to be linear, So we can just use the Airy function solution to connect the allowed & unallowed regions

$$x << a, \Rightarrow \frac{2A}{\sqrt{p(x)}} \cos\left(\int_x^a k(x)\,dx' - \frac{\pi}{4} \right)$$

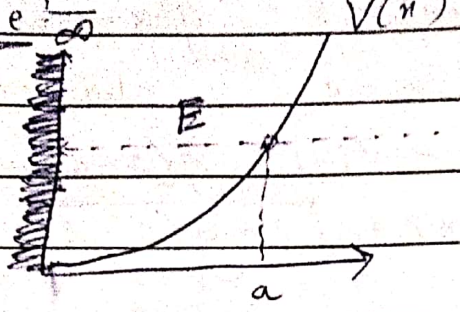
$$- \frac{B}{\sqrt{p(x)}} \sin\left(\int_x^a k(x)\,dx' - \frac{\pi}{4} \right)$$

$$x >> a \Rightarrow \frac{A}{\sqrt{k'(x)}} \exp\left(- \int_a^x k'(x)\,dx' \right)$$

$$+ \frac{B}{\sqrt{k'(x)}} \exp\left(\int_a^x k'(x)\,dx' \right)$$

Scanned with CamScanner

Example:



if the potential never turns

$X >> a$

$$\psi = \frac{A}{\sqrt{k'(x)}} \exp\left(-\int_a^x k'(x')\,dx'\right)$$

$X << a$ $\quad \psi(x) = \frac{1}{\sqrt{k(x)}} \cos\left(\int_x^a k(x')\,dx - \frac{\pi}{4}\right)$

$$\Rightarrow \psi(x) = \frac{1}{\sqrt{k(x)}} \cos\left(-\int_0^x k(x')\,dx' + \underbrace{\int_0^a k(x')\,dx' - \frac{\pi}{4}}_{\Delta}\right)$$

$$= \frac{1}{\sqrt{k(x)}} \left[\cos\left(\int_0^x k(x)\,dx\right)\cos(\Delta) + \sin\left(\int_0^x k(x)\,dx\right)\sin\Delta\right)$$

$\psi(0) = 0$ only if $\cos(\Delta) = 0$

$$\Rightarrow \psi(x) = \frac{1}{\sqrt{k(x)}} \sin\left(\int_0^x k(x)\,dx\right)\sin(\Delta)$$

$$\Rightarrow \int_0^a k(x')\,dx' = \frac{\pi}{4} + \frac{(2n+1)\pi}{2}$$

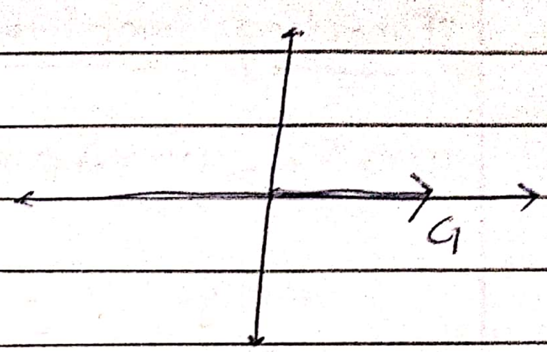
$$= \left(n + \frac{3}{4}\right)\pi$$

$$k(x) = \frac{1}{\hbar}\sqrt{2m(E - V(x))}$$

$$\Rightarrow \int_0^a \sqrt{\frac{2m}{\hbar^2}(E - V(x'))}\,dx' = \left(n + \frac{3}{4}\right)\pi$$

$E = V(a)$

Airy functions



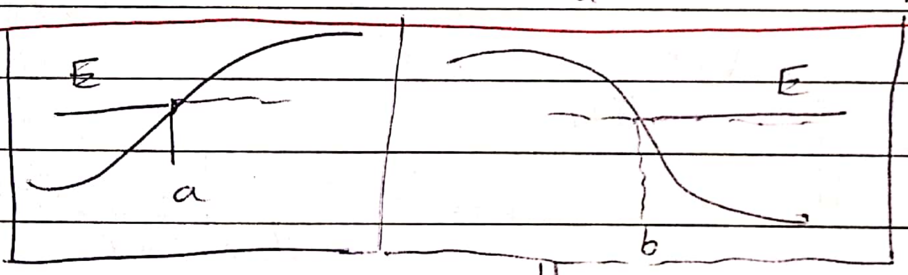
$$\frac{d^2\psi}{du^2} = u\psi$$

$$\psi(u) = c\int \frac{dk}{2\pi}\, e^{i\frac{k^3}{3}}\, e^{iku}$$

ψ decays if $\mathrm{im}(k^3) > 0$.

We can derive the results for wave function from these

$$\boxed{\begin{aligned}\psi(x)_{\text{allowed}} &= \frac{2A}{\sqrt{k(x)}}\cos\left(\int_x^a k(x)\,dx' - \frac{\pi}{4}\right) - \frac{B}{\sqrt{k(x)}}\sin\left(\int_x^a k(x)\,dx - \frac{\pi}{4}\right)\\ \psi(x)_{\text{unallowed}} &= \frac{A}{\sqrt{k'(x)}}\exp\left(-\int_a^x k'(x)\,dx'\right) + \frac{B}{\sqrt{k'(x)}}\exp\left(\int_a^x k'(x)\,dx'\right)\end{aligned}}$$

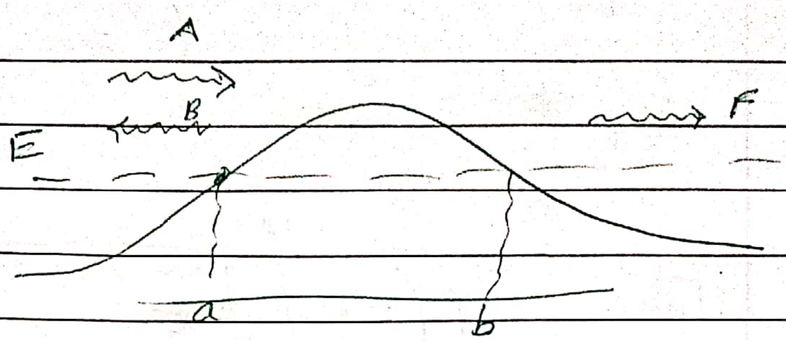


$$\Downarrow$$

$$\frac{1}{\sqrt{k(x)}}\exp\left(-\int_x^b k(x')\,dx'\right) \Rightarrow \frac{2}{k(x)}\cos\left(\int_b^x k(x')\,dx - \frac{\pi}{4}\right)$$

$$\frac{1}{\sqrt{k'(x)}}\sin\left(\int_b^x k'(x')\,dx' - \frac{\pi}{4}\right) \Rightarrow \frac{-1}{\sqrt{k'(x)}}\exp\left(\int_x^b k'(x')\,dx'\right)$$

Barrier tunneling



if the barrier is slowly varying.
and T needs to be small.

$$\psi_{Trans}(x) = \frac{F}{\sqrt{K(x)}} \exp\left(i\left[\int_b^x K(x')\,dx' - \frac{\pi}{4}\right]\right)$$

$x >> b$

$$= \frac{F}{\sqrt{K(x)}} \cos\left(\int_b^x K(x)\,dx - \frac{\pi}{4}\right) + \frac{iF}{\sqrt{K(x)}} \sin\left(\int_b^x K(x)\,dx - \frac{\pi}{4}\right)$$

This would cause the ψ_{barr} to decay left of $x = b$.

This is attributed to $\psi_{barr} \propto \exp\left(+\int K\,dx\right)$

$$\Rightarrow \psi(x)_{barr} \propto \frac{1}{\sqrt{K(x)}} \exp\left(\int_a^b K(x)\,dx - \int_a^x K(x)\,dx\right)$$

$$\Rightarrow \theta = \int_a^b K(x)\,dx \Rightarrow \psi(x)_{barr} = \frac{-2iFe^{\theta}}{\sqrt{K'(x)}} \cos\left(\int_a^x K'(x) - \frac{\pi}{4}\right)$$

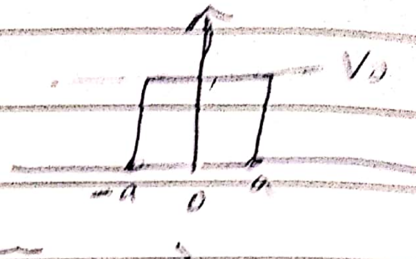
equate to ~~incoming~~ $\psi(x) = \frac{-2iFe^{\theta}}{\sqrt{K(x)}} \cos\left(\int_x^a K'(x)\,dx - \frac{\pi}{4}\right)$

$$\psi_{inc} = \frac{-iFe^{\theta}}{\sqrt{K(x)}} \exp\left(i\int_x^a K(x')\,dx + i\frac{\pi}{4}\right)$$

$$T = \frac{|F|^2}{|iFe^{\theta}|^2} = e^{-2\theta}$$

$$\boxed{T_{WKB} = \exp\left(-2\int_a^b K'(x)\,dx\right)}$$

Example : $V(x) = \begin{cases} V_0 & |x| < a \\ 0 & \end{cases}$



$$T_{WKB} = \exp\left(-2\int_{-a}^{a}\sqrt{\frac{2m}{\hbar^2}(V_0-E)}\,dx\right)$$

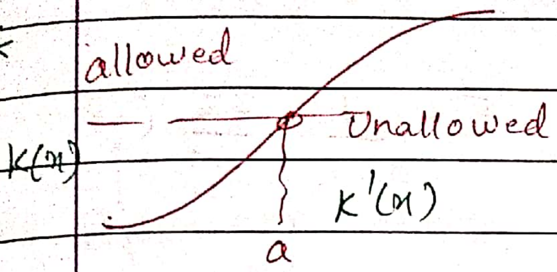
$$= \exp\left(-\frac{4a}{\hbar}\sqrt{2m(V_0-E)}\right)$$

The exact formula calculated before,

$$T_{ex} = \frac{1}{1 + \frac{V_0^2}{4E(V_0-E)}\sinh^2\left(\frac{2a}{\hbar}\sqrt{2m(V_0-E)}\right)}$$

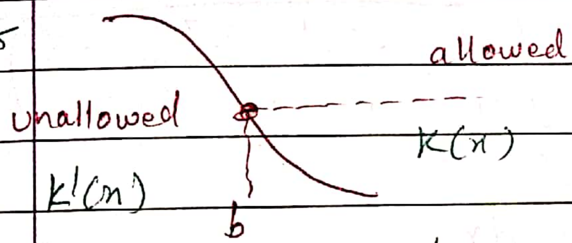
So for small energies 'E', $T_{WKB} \rightarrow T_{exact}$

The Final Airy connections one has to remember:—

* 

$$\frac{2}{\sqrt{k(x)}}\cos\left(\int_x^a k(x)\,dx-\frac{\pi}{4}\right) \Longleftrightarrow \frac{1}{\sqrt{k'(x)}}\exp\left(-\int_a^x k'(x)\,dx\right)$$

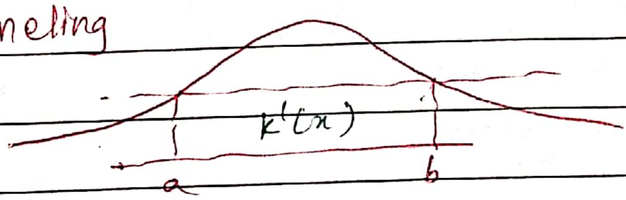
and $$-\frac{1}{\sqrt{k(x)}}\sin\left(\int_x^a k(x)\,dx-\frac{\pi}{4}\right) \Longleftrightarrow \frac{1}{\sqrt{k'(x)}}\exp\left(\int_a^x k'(x)\,dx\right)$$

* 

$$\frac{1}{\sqrt{k'(x)}}\exp\left(-\int_x^b k'(x)\,dx\right) \Longleftrightarrow \frac{2}{\sqrt{k(x)}}\cos\left(\int_b^x k(x)\,dx-\frac{\pi}{4}\right)$$

$$\frac{-1}{\sqrt{k'(x)}}\exp\left(\int_x^b k'(x)\,dx\right) \Longleftrightarrow \frac{1}{\sqrt{k(x)}}\sin\left(\int_b^x k(x)\,dx-\frac{\pi}{4}\right)$$

Tunnelling

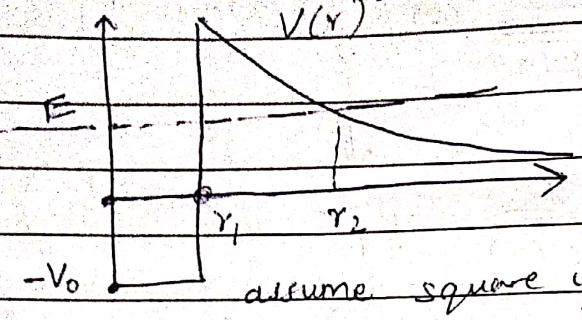
* 

$$T_{WKB} = \exp\left(-2\int_a^b k'(x)\,dx\right)$$

$$\tau = \left(2m\int_a^b \frac{dx}{p(x)}\right)\exp\left(2\int_a^b k(x)\,dx\right)$$

WKB example :-

Gamov's theory of alpha decay.



$$E = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{r_2^2}(2e)$$

alpha-particle

assume square well.

$$T = \exp\left(-2\int_{r_1}^{r_2} k'(x)\,dx\right)$$

$$\gamma = \int_{r_1}^{r_2} k(x)\,dx = \frac{1}{\hbar}\int_{r_1}^{r_2}\sqrt{2m\left(\frac{1}{4\pi\varepsilon_0}\frac{2Ze^2}{r} - E\right)}\,dr$$

$$= \frac{\sqrt{2m}}{\hbar}\int_{r_1}^{r_2}\sqrt{E\frac{r_2}{r} - E}\;dr$$

$$= \frac{\sqrt{2mE}}{\hbar^2}\left[r_2\left(\frac{\pi}{2} - \frac{1}{\sin\left(\sqrt{\frac{r_1}{r_2}}\right)}\right) - \sqrt{r_1(r_2 - r_1)}\right)$$

Assume like $r_2 \gg r_1$.

$$\gamma \simeq \frac{2}{\sqrt{E}}\underbrace{\left(\frac{\sqrt{2m}}{\hbar}\pi\frac{e^2}{4\pi\varepsilon_0}\right)}_{k_1} - \sqrt{2r_1}\underbrace{\left(\sqrt{\frac{e^2}{4\pi\varepsilon_0}}\cdot\frac{4\sqrt{m}}{\hbar}\right)}_{k_2}$$

$$\gamma = k_1\frac{Z}{\sqrt{E}} - k_2\sqrt{Zr_1}$$

$$T = e^{-2\gamma}$$

classical time for collision $= \frac{2r_1}{v}$.

$$\omega = \frac{v}{2r_1}$$

$$\therefore \tau = \frac{2r_1}{v}\cdot e^{2\gamma}.$$

~~Usually~~

$$\cancel{T = 2m\int_a^b \frac{dx}{p(x)}}$$