Lecture 8

Approximations

(1) WKB

(2) Rayleigh Schrodinger Perturbation Theory

(3) Variational Methods

(4) Feynman Hellmann Theorem

(5) Virial Theorem

(7) Born Oppenheimer approximation

(8) Time dependent perturbation theory

WKB (Wentzel, Kramers, Brillouin)

Semiclassical – long wavelength approximation

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)}$$

To implement this approximation write

$$\psi(x) = A(x)\, e^{iS(x)/\hbar}$$

$$\frac{d\psi}{dx} = \frac{dA}{dx} e^{iS(x)/\hbar} + \frac{i}{\hbar} A(x) \frac{dS}{dx} e^{iS(x)/\hbar}$$

$$\frac{d^2\psi}{dx^2} = \frac{d^2A}{dx^2} e^{iS(x)/\hbar} + \frac{2i}{\hbar} \frac{dA}{dx}\frac{dS}{dx} e^{iS(x)/\hbar}$$
$$+ \frac{i}{\hbar} A(x) \frac{d^2S}{dx^2} e^{iS(x)/\hbar} - \frac{1}{\hbar^2} A(x) \left(\frac{dS}{dx}\right)^2 e^{iS(x)/\hbar}$$

we insert this in the schrodinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V(x)\psi(x) = E\psi(x)$$

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

$$\left(\frac{d^2A}{dx^2} + \frac{2i}{\hbar}\frac{dA}{dx}\frac{dS}{dx} + \frac{i}{\hbar}A(x)\frac{d^2S}{dx^2} - \frac{\ }{\hbar^2}\left(\frac{dS}{dx}\right)^2\right.$$
$$\left. - \frac{2m}{\hbar^2}(V(x)-E)\right) e^{iS(x)/\hbar} = 0$$

cancel off the $e^{iS(x)/\hbar}$ factor and equating the parts that are even or odd in $1/\hbar$ gives 2 coupled equations

$$\frac{d^2A}{dx^2} - \frac{1}{\hbar^2} A \left(\frac{dS}{dx}\right)^2 - \frac{2m}{\hbar^2}(V-E)A = 0$$

$$2 \frac{dA}{dx}\frac{dS}{dx} + A\frac{d^2S}{dx^2}$$

recall classically

$$\frac{P_{CL}^2}{2m} + V = E \Rightarrow$$

$$P_{CL}^2 = 2m\,(E - V(x))$$

P_{CL}^2 is a function of x that is not always positive

$$\frac{d^2A}{dx^2} - \frac{1}{\hbar^2} A\left(\frac{dS}{dx}\right)^2 + \frac{P_{CL}^2}{\hbar^2}A = 0$$

The other equation has the form

$$\frac{2}{A}\frac{dA}{dx} = -\frac{1}{\frac{ds}{dx}}\frac{d}{dx}\left(\frac{ds}{dx}\right)$$

Integrating both sides gives

$$2\ln A = -\ln\frac{ds}{dx} + c$$

where c is a constant.

Taking exponents using

$$2\ln A = \ln A^2$$

$$* \quad A^2\frac{ds}{dx} = \text{constant}$$

or

$$\frac{ds}{dx} = \frac{\text{constant}}{A^2}$$

The first equation can be written as

$$\frac{A''}{A} - \frac{1}{\hbar^2}\left(\frac{ds}{dx}\right)^2 + \frac{P_{cl}^2}{\hbar^2} = 0$$

$\frac{A''}{A}$ can be eliminated

using $*$

$$2\frac{\frac{dA}{dx}}{A} = -\frac{\frac{d}{dx}\left(\frac{dS}{dx}\right)}{\left(\frac{dS}{dx}\right)}$$

To simplify notation use

$$A' = \frac{dA}{dx} \qquad S' = \frac{dS}{dx} \qquad S'' = \frac{d^2S}{dx^2}$$

$$2\frac{A'}{A} = -\frac{S''}{S'}$$

$\frac{d}{dx}$ gives

$$2\frac{A''}{A} - 2\left(\frac{A'}{A}\right)^2 = -\left(\frac{S''}{S'}\right)'$$

$$2\frac{A''}{A} - 2\frac{1}{4}\left(\frac{S''}{S'}\right)^2 + \left(\frac{S''}{S'}\right)' = 0$$

$$\boxed{\frac{1}{\hbar^2}\left((S')^2 - P_{cl}^2\right) = \frac{1}{4}\left(\frac{S''}{S'}\right)^2 - \frac{1}{2}\left(\frac{S''}{S'}\right)'}$$

This is a complicated non-linear differential equation – it dose not look like an improvement over the schrodinger equation

The WKB approximation holds when the quantities on the right can be neglected. We will come back to the conditions for this to be valid — but if we set those terms to 0 we get

$$\boxed{\begin{aligned} \left(\frac{dS}{dx}\right)^2 &= P_{cl}^2(x) = 2m(E - V(x)) \\ \frac{dS}{dx} &= \pm\sqrt{2m(E - V(x))} \end{aligned}}$$

unlike the exact equation this is a first order differential equation with solution

$$S(x) = \pm\int^x \sqrt{2m(E - V(x'))}\, dx' + \text{constant}$$

$$A(x) = \frac{\text{const}}{\sqrt{\frac{dS}{dx}}} = \frac{\text{const}}{\sqrt[4]{2m(E-V(x))}}$$

$$= \frac{\text{const}}{\sqrt{P_{cl}(x)}}$$

This gives a solution to the problem as long as

$$\frac{P_{cl}^2(x)}{\hbar^2} \gg \left(\frac{S''}{S'}\right)^2 \text{ and } \left(\frac{S''}{S'}\right)^1$$

Note also that $P_{cl}^2(x) > 0$ only when $E > V(x)$ — which is called the classically allowed region, when $V(x) > E$ $P_{cl}^2(x)$ becomes negative and $P_{cl}(x)$ becomes imaginary

This results in 2 kinds of solutions

case 1 x such that $E > U(x)$

(classically allowed region)

$$\boxed{\psi(x) = \frac{C_\pm}{\sqrt{P_{cl}(x)}} e^{\pm \frac{i}{\hbar}\int^x P_{cl}(x')\,dx'}}$$

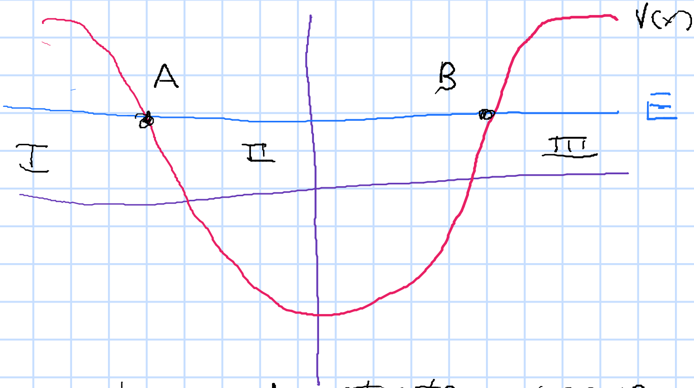
(there are 2 independent solution.

case 2 x such that $V(x) > E$

(classically forbidden region)

$$\boxed{\psi(x) = \frac{C_\pm}{\sqrt{|P_{cl}(x)|}} e^{\pm \frac{1}{\hbar}\int^x |P_{cl}(x')|\,dx'}}$$

as expected the approximat wave function oscillator in the classically allowed region and grows or falls off exponentially in the classically forbidden region



For a bound state wave function we want it to fall off for large |x|

This tells how to pick signs in regions I and III (classically forbidden)

Region I

$$\psi(x) = \frac{C_I}{\sqrt{|P_{cl}(x)|}} e^{\frac{1}{\hbar}\int^x |P_{cl}(x')|\,dx'}$$

Region III

$$\psi(x) = \frac{C_{III}}{\sqrt{|P_{cl}(x)|}} e^{-\frac{1}{\hbar}\int^x |P_{cl}(x')|\,dx'}$$

while in regim II

$$\Psi(x) = \frac{C_{II}^{+}}{\sqrt{P_{cl}(x)}} e^{\frac{i}{\hbar}\int^{x} P_{cl}(x')dx'} +$$

$$\frac{C_{II}^{-}}{\sqrt{P_{cl}(x)}} e^{-\frac{i}{\hbar}\int^{x} P_{cl}(x')dx'}$$

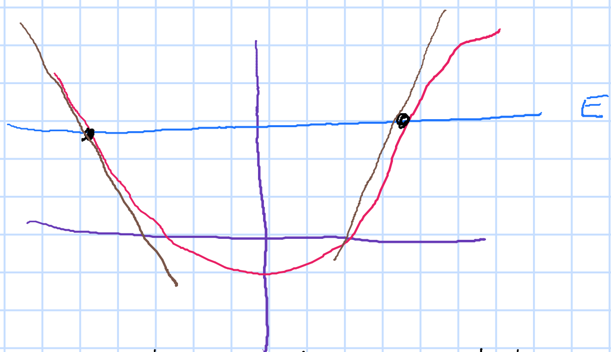
normally we would use matching conditions and normalization to determine C_{I} C_{II}^{+} C_{II}^{-} and C_{III}

The problem is that at the classical turning points A and B that are the boundaries of these regions

$$P_{cl}(x_A) = P_{cl}(x_B) = 0 \not> \hbar^2 \left(\frac{1}{2}\left(\frac{S''}{S'}\right), \frac{1}{4}\left(\frac{S''}{S'}\right)^2\right.$$

so the approximation breaks down at the precise point where we need to match the solutions in both regions

to treat this consider the figure below



The strategy to match solutions in both regions is to approximate the potential at each turning point by a linear potential tangent to the exact potential at the turning point

$$V(x) \simeq V(x_A) + \frac{dV}{dx}(x_A)(x-x_A)$$

$$V(x_A) - F\,(x-x_A)$$

where x_A is the turning point and $F = -\frac{dV}{dx}(x_A)$ is a constant "force"

The we solve the schrodinger equation for this potential near x_A and match for $x < x_A$, $x > x_A$

* It is possible to simply ignore this problem and match the WKB solutions in regions I, II, III. They give something close to what you get by doing

the boundary conditions correctly

Before we do this we come back to the question of the conditions for the approximation to be good. To do this we use a self consistency check –

(1) we start by assuming that the approximation is good

(2) we substitute the approximate solution in the correction term

(3) then we ask if the resulting correction terms are small

① $S'_{WKB}(x) \simeq \sqrt{2m(E-V)}$

we want to show

$$\frac{2m(E-V)}{\hbar^2} \gg \left(\frac{S''}{S'}\right)^2 ; \left(\frac{S''}{S'}\right)'$$

$$S''_{WKB}(x) = \frac{1}{2}\frac{1}{\sqrt{2m(E-V)}}\left(-2m\frac{dV}{dx}\right)$$

$$= -\frac{m}{\sqrt{2m(E-V)}}\frac{dV}{dx}$$

$$\left(\frac{S''}{S'}\right) = \frac{m}{2m(E-V)}\frac{dV}{dx}$$

$$\left(\frac{S''}{S'}\right)' = \frac{1}{2(E-V)}\frac{d^2V}{dx^2} + \frac{1}{2}\frac{1}{(E-V)^2}\left(\frac{dV}{dx}\right)^2$$

The condition for validity become

$$2m(E-V) \gg \hbar^2\left(\frac{1}{2(E-V)}\frac{dV}{dx}\right)^2$$

$$\hbar^2\left(\frac{1}{2(E-V)}\frac{d^2V}{dx^2} + \frac{1}{2}\frac{1}{(E-V)^2}\left(\frac{dV}{dx}\right)^2\right.$$

$$1 \gg \frac{\hbar^2}{8m}\frac{1}{(E-V)^3}\left(\frac{dV}{dx}\right)^2$$

$$\frac{\hbar^2}{4m}\left[\frac{1}{(E-V)^2}\frac{dV}{dx}{}^2 + \frac{1}{(E-V)^3}\left(\frac{dV}{dx}\right)^2\right.$$

This means that the force varies slowly with x.

To treat the boundary conditions consider

$$-\frac{1}{2m}\frac{d^2\psi}{dx^2} = (E - V(x))\psi$$
$$\simeq \left(E - V(x_A) - \frac{dV}{dx}(x_A)(x - x_A)\right)\psi$$
$$= \left((E - V(x_A) - F x_A) + F x\right)\psi$$

where F is the effective force, where E, $V(x_A)$ Fx_A are all constants

Let $E' = E - V(x_a)$

$$-\frac{\hbar}{2m}\frac{d^2\psi}{dx^2} = (E' + F(x - x_A))\,\psi(x)$$

we start by writing this as

$$\frac{d^2\psi}{dx^2} = -\frac{2mF}{\hbar^2}\left(x - x_A + \frac{E'}{F}\right)\psi$$

Next define

$$\sigma = -\left(\frac{2mF}{\hbar^2}\right)^{1/3}\left(x - x_A + \frac{E'}{F}\right)$$

$$\frac{d}{dx} = \frac{d\sigma}{dx}\frac{d}{d\sigma} = -\left(\frac{2mF}{\hbar^2}\right)^{1/3}\frac{d}{d\sigma}$$

$$-\frac{d^2}{dx^2} = -\left(\frac{2mF}{\hbar^2}\right)^{2/3}\frac{d^2}{d\sigma^2}$$

$$-\left(\frac{2mF}{\hbar^2}\right)^{2/3}\frac{d^2\psi}{d\sigma^2} = \frac{2mF}{\hbar^2}\left(x - x_A + \frac{E'}{F}\right)\psi$$

$$= -\left(\frac{2mF}{\hbar^2}\right)^{2/3}\sigma\psi$$

Canceling the $-\left(\frac{2mF}{\hbar^2}\right)^{2/3}$ gives

$$* \quad \boxed{\frac{d^2}{d\sigma^2}\psi(\sigma) = \sigma\psi(\sigma)}$$

This is called Airy's equation. The solutions are called Airy functions

$$Ai(\sigma),\quad Ai(e^{2\pi i/3}\sigma)$$

are independent solutions of *

The solutions have the following integral representations that can be checked by substitution

$$Ai(\sigma) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i(s\sigma + \frac{s^3}{3})}$$

$$= \frac{1}{\pi}\int_{0}^{\infty} \cos\left(s\sigma + \frac{s^3}{3}\right)$$

Airy functions have the following properties

(1) $\int_{-\infty}^{\infty} Ai(x)\,dx = 1$

(2) $\int_{-\infty}^{\infty} Ai(x-y)\,Ai(x-z)\,dx = \delta(y-z)$

(3) $Ai(\sigma) = \sqrt{\frac{6}{3\pi}}\,K_{1/3}\left(\frac{2}{3}x^{3/2}\right)$

where $K_{1/3}$ is an analytic continuation of $H_{1/3}$

$$K_{\frac{1}{3}} = \frac{i\pi}{2} e^{\frac{i\pi}{6}} H^{1}_{1/3}(iz)$$

The most important property for matching is

$$\boxed{\begin{aligned} &\lim_{\sigma\to\infty} Ai(\sigma) \to \frac{1}{\sqrt{\pi}}\sigma^{-1/4} e^{-\frac{2}{3}\sigma^{3/2}} \\ &\lim_{\sigma\to-\infty} Ai(\sigma) \to \frac{1}{2\sqrt{\pi}}|\sigma|^{-1/4}\cos\left(\frac{2}{3}|\sigma|^{3/2}-\frac{\pi}{4}\right) \end{aligned}}$$

we will see that these can be used to match with the WKB solution

In order to perform matching we express this in term of the classical momentum

$$\sigma = -\left(\frac{2mF}{\hbar^2}\right)^{1/3}\left(x - x_A + \frac{E'}{F}\right)$$

$$\frac{P_{cl}^2}{2m} = E - V(x) \simeq E - V(x_A) - \frac{dV}{dx}(x_A)(x - x_A)$$

$$= E' + F(x - x_A)$$

$$P_{cl}^2 = 2mF\left(x - x_A + \frac{E'}{F}\right)$$

$$\sigma = -\left(\frac{2mF}{\hbar^2}\right)^{1/3} \times \frac{P_{cl}^2}{2mF} = -\frac{1}{(2mF\hbar)^{2/3}} P_{cl}^2$$

next we express the asymptotic forms of the Airy function in terms of $p_{cl}(x)$ — we use a single normalization in both regions

$$\sigma \longrightarrow -\frac{p_{cl}^2}{(2mF\hbar)^{2/3}} \qquad \sigma^{3/2} = -\frac{p_{cl}^3}{2mF\hbar}$$

$$\boxed{\frac{2}{3}\sigma^{3/2} = \frac{p^3}{3mF\hbar} =}$$

remark

$$p_{cl} = \sqrt{2mF}\sqrt{x - x_A + E'/F}$$

$$\int^x p_{cl}\,dx = \int^x \sqrt{2mF}\sqrt{x' - x_A + E'/F}$$

$$u = x' - x_A + E'/F$$

$$\int u^{1/2}\,du = \frac{2}{3}u^{3/2} = \frac{2}{3}\frac{p_{cl}^3}{(2mF)^{3/2}}$$

$$\boxed{\frac{1}{\hbar}\int^x p_{cl}(x) = \frac{2}{3}\frac{p_{cl}^3}{2mF\hbar} = \frac{2}{3}\sigma^{3/2}}$$

Thus if we cancel common factors the asymptotic form of the exact wave function is

$$\frac{1}{\sqrt{P_{cl}(x)}} e^{\pm \frac{i}{\hbar}\int^x P_{cl}(x')\,dx'}$$

$$\frac{1}{\sqrt{2|P_{cl}(x)|}} \cos\left(\frac{1}{\hbar}\int^x |P_{cl}(x')|\,dx' - \frac{\pi}{4}\right)$$

These give the desired matching conditions – not the factors $\frac{1}{\sqrt{2}}$ and $-\frac{\pi}{4}$ in red

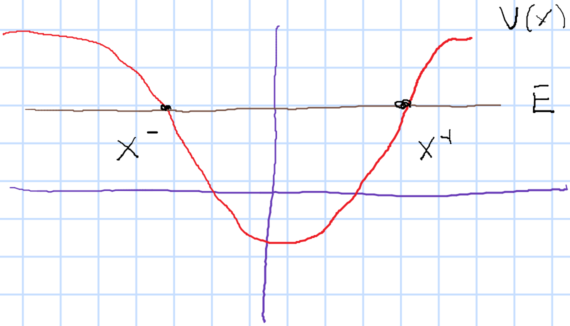
Here

$$P_{cl}(x) = \sqrt{2mF}\sqrt{x' - x_A + E'/F}$$

$$E' = E - V(x_A)$$

For an attractive potential there are 2 classical turning points – at those points $E - V(x_A) = 0$

$F = -\frac{dV}{dx}(x_A)$ depends on the turning point



The approximate wave function in the classically allowed region can be expressed in one of two ways

$$\frac{C}{\sqrt{2}} \cos\left(\frac{1}{\hbar}\int_{x^-}^{x} p_{cl}(x')\,dx' - \frac{\pi}{4}\right) =$$

$$\pm \frac{C}{\sqrt{2}} \cos\left(\frac{1}{\hbar}\int_{x}^{x_+} p_{cl}(x')\,dx' - \frac{\pi}{4}\right)$$

These are both the same function of x

The can differ by at most a sign

since $\cos(\theta)$ is even

we write the second term as

$$= \frac{C}{\sqrt{2}} \cos\left(-\int_x^{x^+} \frac{1}{\hbar} p_{cl}(x')\,dx' + \frac{\pi}{4}\right)$$

$$\frac{C}{\sqrt{2}} \cos\left(-\int_{x^-}^{x^+} \frac{1}{\hbar} p_{cl}(x')\,dx' + \int_{x^-}^{x} \frac{1}{\hbar} p_{cl}(x') + \frac{\pi}{4}\right)$$

$$\frac{C}{\sqrt{2}} \cos\left(-\int_{x^-}^{x^+} \frac{p_{cl}(x')}{\hbar}\,dx' + \int_{x^-}^{x} \frac{p_{cl}(x')}{dx'} + \frac{\pi}{4}\right) =$$

This must be equal to

$$\pm \frac{C}{\sqrt{2}} \cos\left(\int_{x^-}^{x} \frac{p_{cl}(x')}{\hbar}\,dx' - \frac{\pi}{4}\right)$$

the difference of the arguments must be $n\pi$

$$-\int_{x^-}^{x^+} \frac{p_{cl}(x)}{\hbar}\,dx' - \frac{\pi}{4} - \frac{\pi}{4} = n\pi$$

or

$$\boxed{\int_{x^-}^{x^+} p_{cl}(x')\,dx' = \hbar\left(n + \tfrac{1}{2}\right)\pi}$$

(the overall sign does not matter — this is the WKB quantization rule

It determines the energy E.