SCHRODINGER'S WAVE EQUATION

Time-Dependent Wave Equation

We now turn to the Schrodinger picture and examine the time evolution of $|a, t_0 ;t>$ in the x-representation.

In other words, our task is to study the behavior of the wave function as a function of time

$$\psi(\mathbf{x}', t) = \langle \mathbf{x}' | \alpha, t_0; t \rangle$$

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

The potential V(x) is a Hermitian operator; it is also local in the sense that in the x-representation we have

$$\langle \mathbf{x}'' | V(\mathbf{x}) | \mathbf{x}' \rangle = V(\mathbf{x}') \delta^3(\mathbf{x}' - \mathbf{x}'')$$

We now derive Schrodinger's time-dependent wave equation.

$$i\hbar\frac{\partial}{\partial t}\langle \mathbf{x}'|\alpha, t_0; t\rangle = \langle \mathbf{x}'|H|\alpha, t_0; t\rangle$$

Why?

$$i\hbar\frac{\partial}{\partial t}\left|\alpha, t_0; t\right\rangle = i\hbar\frac{\partial}{\partial t}U(t)\left|\alpha, t_0\right\rangle$$

$$= i\hbar\frac{\partial}{\partial t}e^{\frac{-iHt}{\hbar}}\left|\alpha, t_0\right\rangle$$

$$= He^{\frac{-iHt}{\hbar}}\left|\alpha, t_0\right\rangle$$

$$= H\left|\alpha, t_0; t\right\rangle$$

$$i\hbar \frac{\partial}{\partial t} \langle \mathbf{x}' | \alpha, t_0; t \rangle = \langle \mathbf{x}' | H | \alpha, t_0; t \rangle$$

$$\left\langle \mathbf{x}' \left| \frac{\mathbf{p}^2}{2m} \right| \alpha, t_0; t \right\rangle = -\left(\frac{\hbar^2}{2m} \right) \nabla'^2 \langle \mathbf{x}' | \alpha, t_0; t \rangle$$

$$\langle \mathbf{x}' | V(\mathbf{x}) = \langle \mathbf{x}' | V(\mathbf{x}')$$

$$i\hbar \frac{\partial}{\partial t} \langle \mathbf{x}' | \alpha, t_0; t \rangle = -\left(\frac{\hbar^2}{2m} \right) \nabla'^2 \langle \mathbf{x}' | \alpha, t_0; t \rangle + V(\mathbf{x}') \langle \mathbf{x}' | \alpha, t_0; t \rangle$$

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}', t) = -\left(\frac{\hbar^2}{2m} \right) \nabla'^2 \psi(\mathbf{x}', t) + V(\mathbf{x}') \psi(\mathbf{x}', t)$$

This equation is, in fact, the starting point of many textbooks on quantum mechanics. In our formalism, however, this is just the Schrodinger equation for a state ket written explicitly in the x-basis.

The Time-Independent Wave Equation

We now derive the partial differential equation satisfied by energy eigenfunctions.

$$\langle \mathbf{x}'|a', t_0; t\rangle = \langle \mathbf{x}'|a'\rangle \exp\left(\frac{-iE_{a'}t}{\hbar}\right)$$

We had

$$i\hbar\frac{\partial}{\partial t}\langle \mathbf{x}'|\alpha, t_0; t\rangle = -\left(\frac{\hbar^2}{2m}\right)\nabla'^2\langle \mathbf{x}'|\alpha, t_0; t\rangle + V(\mathbf{x}')\langle \mathbf{x}'|\alpha, t_0; t\rangle$$

So by substituting the first equation into the second one we have

$$-\left(\frac{\hbar^2}{2m}\right)\nabla'^2\langle \mathbf{x}'|a'\rangle + V(\mathbf{x}')\langle \mathbf{x}'|a'\rangle = E_{a'}\langle \mathbf{x}'|a'\rangle$$

$$-\left(\frac{\hbar^2}{2m}\right)\nabla'^2 u_E(\mathbf{x}') + V(\mathbf{x}')u_E(\mathbf{x}') = Eu_E(\mathbf{x}')$$

This is the time-independent wave equation of E. Schrodinger.

Interpretations of the Wave Function

The quantity ρ(x', t) defined by

$$\rho(\mathbf{x}', t) = |\psi(\mathbf{x}', t)|^2 = |\langle \mathbf{x}'|\alpha, t_0; t\rangle|^2$$

is regarded as the probability density in wave mechanics.

In the remainder of this section we use x for x' because the position operator will not appear.

Using Schrodinger's time-dependent wave equation, it is straightforward to derive the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

$$\mathbf{j}(\mathbf{x}, t) = -\left(\frac{i\hbar}{2m}\right)[\psi^* \nabla \psi - (\nabla \psi^*)\psi]$$

$$= \left(\frac{\hbar}{m}\right) \mathrm{Im}(\psi^* \nabla \psi)$$

The reality of the potential V has played a crucial role in our obtaining this result.

To understand the physical significance of the wave function, let us write it as

$$\psi(\mathbf{x}, t) = \sqrt{\rho(\mathbf{x}, t)} \exp\left[\frac{iS(\mathbf{x}, t)}{\hbar} \right]$$

with S real and $\rho > 0$, which can always be done for any complex function of x and t.

The meaning of ρ has already been given.

What is the physical interpretation of S?

$$\psi(\mathbf{x}, t) = \sqrt{\rho(\mathbf{x}, t)} \exp\left[\frac{iS(\mathbf{x}, t)}{\hbar}\right]$$

$$\psi^* \nabla \psi = \sqrt{\rho}\, \nabla(\sqrt{\rho}) + \left(\frac{i}{\hbar}\right) \rho \nabla S$$

$$\mathbf{j} = \frac{\rho \nabla S}{m}$$

We now see that there is more to the wave function than the fact that |ψ|2 is the probability density; the gradient of the phase S contains a vital piece of information.

$$\mathbf{j} = \frac{\rho \nabla S}{m}$$

From this relation we see that the spatial variation of the phase of the wave function characterizes the probability flux:

The stronger the phase variation, the more intense the flux.

The direction of j at some point x is seen to be normal to the surface of a constant phase that goes through that point.

In the particularly simple example of a plane wave (a momentum eigenfunction)

$$\psi(\mathbf{x}, t) \propto \exp\left(\frac{i\mathbf{p}\cdot\mathbf{x}}{\hbar} - \frac{iEt}{\hbar}\right)$$

All this is evident because

$$\nabla S = \mathbf{p}$$

More generally, it is tempting to regard ∇S/m as some kind of " velocity,"

$$\text{“}\mathbf{v}\text{”} = \frac{\nabla S}{m}$$

and to write the continuity equation as

$$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\text{“}\mathbf{v}\text{”}) = 0$$

$$\Psi(x,t) = Ae^{(i\mathbf{p}.\mathbf{x}/\hbar - iEt/\hbar)}$$

$$\mathbf{j} = \frac{\rho \nabla S}{m}$$

$$j(x,t) = \frac{\hbar}{m}\operatorname{Im}\left(\Psi^{*}\nabla\Psi\right)$$

$$\nabla\Psi(x,t) = Ai\mathbf{p}/\hbar e^{(i\mathbf{p}.\mathbf{x}/\hbar - iEt/\hbar)} = i\mathbf{p}/\hbar\Psi(x,t)$$

$$j(x,t) = \frac{\hbar}{m}\operatorname{Im}\left(\Psi^{*}\nabla\Psi\right) = \mathbf{p}/m\left|\Psi(x,t)\right|^{2} = \frac{\mathbf{p}\rho}{m}$$

$$\nabla S = \mathbf{p}$$

The Classical Limit

We now discuss the classical limit of wave mechanics.

First, we substitute ψ written in the following form

$$\psi(\mathbf{x},t)=\sqrt{\rho(\mathbf{x},t)}\exp\left[\frac{iS(\mathbf{x},t)}{\hbar}\right]$$

into both sides of the time-dependent wave equation.

$$-\left(\frac{\hbar^2}{2m}\right)\left[\nabla^2\sqrt{\rho}+\left(\frac{2i}{\hbar}\right)(\nabla\sqrt{\rho})\cdot(\nabla S)-\left(\frac{1}{\hbar^2}\right)\sqrt{\rho}\,|\nabla S|^2+\left(\frac{i}{\hbar}\right)\sqrt{\rho}\,\nabla^2 S\right]+\sqrt{\rho}\,V$$

So far everything has been exact.

$$=i\hbar\left[\frac{\partial\sqrt{\rho}}{\partial t}+\left(\frac{i}{\hbar}\right)\sqrt{\rho}\,\frac{\partial S}{\partial t}\right]$$

Let us suppose now that ħ can, in some sense, be regarded as a small quantity.

The precise physical meaning of this approximation, to which we will come back later, is not evident now, but let

$$\hbar|\nabla^2 S| \ll |\nabla S|^2$$

Using the above approximation the following equation

$$-\left(\frac{\hbar^2}{2m}\right)\left[\nabla^2\sqrt{\rho}+\left(\frac{2i}{\hbar}\right)(\nabla\sqrt{\rho})\cdot(\nabla S)-\left(\frac{1}{\hbar^2}\right)\sqrt{\rho}|\nabla S|^2+\left(\frac{i}{\hbar}\right)\sqrt{\rho}\,\nabla^2 S\right]+\sqrt{\rho}\,V=i\hbar\left[\frac{\partial\sqrt{\rho}}{\partial t}+\left(\frac{i}{\hbar}\right)\sqrt{\rho}\,\frac{\partial S}{\partial t}\right]$$

reduces to the following equation, where its terms do not explicitly contain ħ to obtain a nonlinear partial differential equation for S:

$$\frac{1}{2m}|\nabla S(\mathbf{x},t)|^2+V(\mathbf{x})+\frac{\partial S(\mathbf{x},t)}{\partial t}=0$$

Hamilton-Jacobi equation in classical mechanics

where S(x,t) stands for Hamilton's principal function.

So, not surprisingly, in the ħ —» 0 limit, classical mechanics is contained in Schrodinger's wave mechanics.

We have a semiclassical interpretation of the phase of the wave function:

ħ times the phase is equal to Hamilton's principal function provided that ħ can be regarded as a small quantity.

Let us now look at a stationary state with time dependence exp(-iEt/h).

This time dependence is anticipated from the fact that for a classical system with a constant Hamiltonian, Hamilton's principal function S is separable:

$$S(x,t) = W(x) - Et$$

where W(x) is called Hamilton's characteristic function (Goldstein 1980, 445-46).

As time goes on, a surface of a constant S advances in much the same way as a surface of a constant phase in wave optics—a "wave front“ —advances.

The momentum in the classical Hamilton-Jacobi theory is given by

$$\mathbf{p}_{\text{class}} = \nabla S = \nabla W$$

which is consistent with our earlier identification of ∇S/m with some kind of velocity.

In classical mechanics the velocity vector is tangential to the particle trajectory, and as a result we can trace the trajectory by following continuously the direction of the velocity vector.

The particle trajectory is like a ray in geometric optics because the ∇S that traces the trajectory is normal to the wave front defined by a constant S.

In this sense geometrical optics is to wave optics what classical mechanics is to wave mechanics.

One might wonder, in hindsight, why this optical-mechanical analogy was not fully exploited in the nineteenth century.

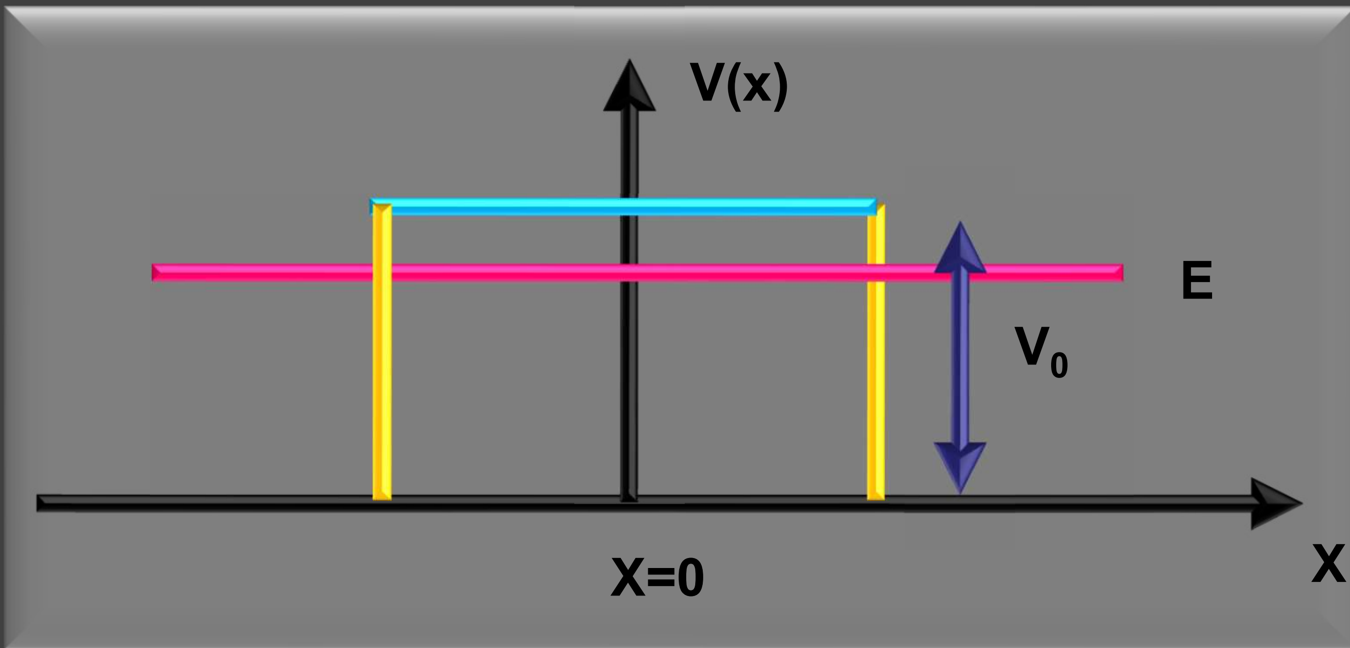
The reason is that there was no motivation for regarding Hamilton's principal function as the phase of some traveling wave; the wave nature of a material particle did not become apparent until the 1920s.

Besides, the basic unit of action ħ, which must enter into the phase of the wave function for dimensional reasons:

$$\psi(\mathbf{x}, t) = \sqrt{\rho(\mathbf{x}, t)} \exp\left[\frac{iS(\mathbf{x}, t)}{\hbar}\right]$$

was missing in the physics of the nineteenth century.

Semiclassical (WKB) Approximation



$$V(x)=\begin{cases}0 & |x|>a\\ V_0 & |x|\le a\end{cases}$$

$$\frac{2mE}{\hbar^2}=k^2$$

$$\frac{2m}{\hbar^2}(E-V_0)=-\kappa^2$$

$$T=e^{-2ika}\frac{2k\kappa}{2k\kappa\cosh 2\kappa a-i(\kappa^2-k^2)\sinh 2\kappa a}$$

$$u(x)=\begin{cases}e^{ikx}+Re^{-ikx} & x<-a\\ Ae^{\kappa x}+Be^{-\kappa x} & |x|\le a\\ T\,e^{ikx} & x>a\end{cases}$$

$$|T|^2=\frac{2k\kappa}{\left(k^2+\kappa^2\right)^2\sinh^2 2\kappa a+(2k\kappa)^2}$$

$$\kappa a >> 1 \Rightarrow \sinh \kappa a \approx e^{\kappa a}$$

$$|T|^2 = \frac{2k\kappa}{\left(k^2+\kappa^2\right)^2 \sinh^2 2\kappa a + (2k\kappa)^2} \qquad \boxed{0}$$

$$\approx \frac{2k\kappa}{\left(k^2+\kappa^2\right)^2 \sinh^2 2\kappa a} \approx \frac{2k\kappa}{\left(k^2+\kappa^2\right)^2} e^{-4\kappa a}$$

$$\ln|T|^2 \approx \ln \frac{2k\kappa}{\left(k^2+\kappa^2\right)^2} + \ln e^{-4\kappa a}$$

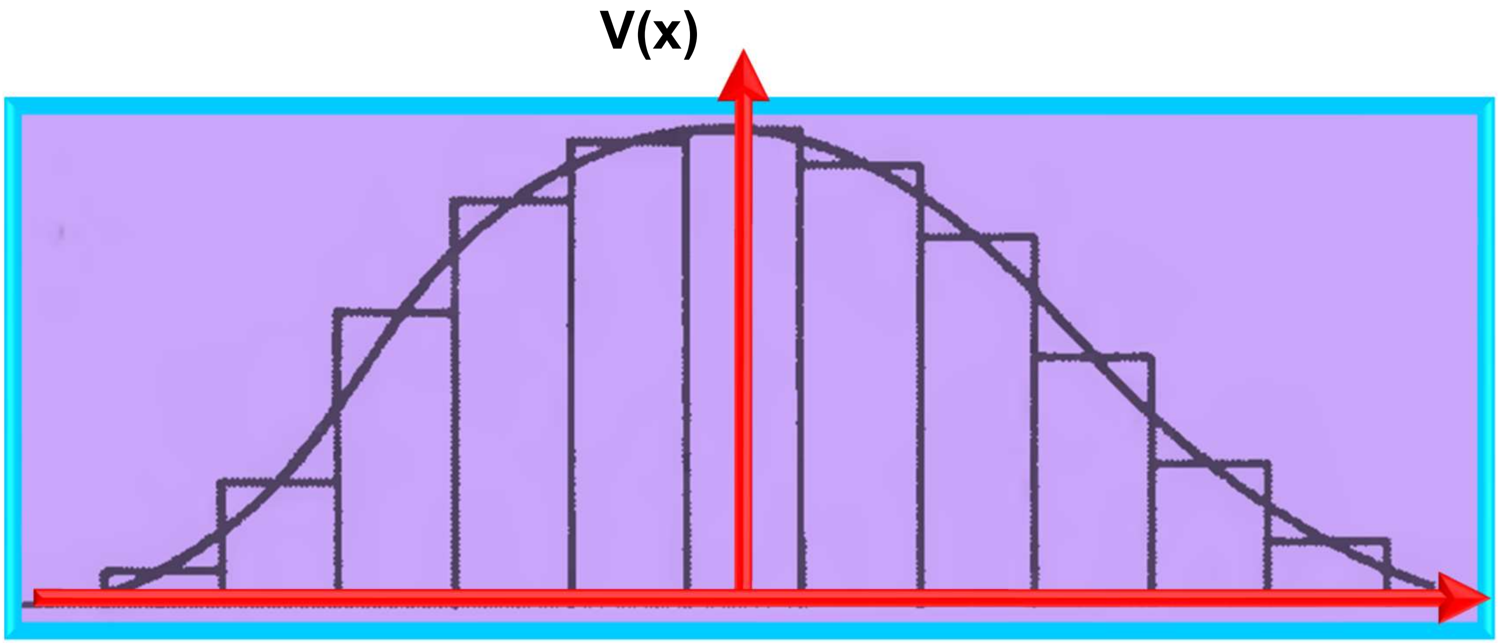
$$\ln|T|^2 \approx -2\kappa(2a)$$

$$\ln|T|^2 \approx \ln \frac{2k\kappa}{\left(k^2+\kappa^2\right)^2} - 4\kappa a \qquad \boxed{0}$$

$$\ln|T|^2 \approx -2[\kappa \Delta x]$$

$$\kappa a >> 1$$

$$\ln|T|^2 \approx -4\kappa a$$



$$\ln\left|T\right|^2 = \sum_{\substack{\text{Partial}\\ \text{Barrier}}} \ln\left|T\right|^2_{\substack{\text{Partial}\\ \text{Barrier}}} \approx -2\sum \Delta x[\kappa]$$

$$= -2\int_{\text{barrier}} dx\sqrt{\frac{2m}{\hbar^2}\left[V(x)-E\right]}$$

$$\left|T\right|^2 = \exp\left\{-2\int dx\sqrt{\frac{2m}{\hbar^2}\left[V(x)-E\right]}\right\}$$

Let us now restrict ourselves to one dimension and obtain an approximate stationary-state solution to Schrodinger's wave equation.

This can easily be accomplished by noting that the corresponding solution of the classical Hamilton-Jacobi equation is

$$\frac{1}{2m}|\nabla S(\mathbf{x},t)|^2 + V(\mathbf{x}) + \frac{\partial S(\mathbf{x},t)}{\partial t} = 0$$

$$S(x,t) = W(x) - Et$$

$$= \pm \int^x dx' \sqrt{2m[E - V(x')]} - Et$$

$$\frac{\partial \rho}{\partial t} + \frac{1}{m}\frac{\partial}{\partial x}\left(\rho \frac{\partial S}{\partial x}\right) = 0$$

$$\rho \frac{dW}{dx} = \pm \rho \sqrt{2m[E - V(x)]} = \text{constant}$$

$$\frac{\partial \rho}{\partial t} = 0, \quad (\text{all } x)$$

$$\sqrt{\rho} = \frac{\text{constant}}{[E - V(x)]^{1/4}} \propto \frac{1}{\sqrt{v_{\text{classical}}}}$$

$$\sqrt{\rho} = \frac{\text{constant}}{[E - V(x)]^{1/4}} \propto \frac{1}{\sqrt{v_{\text{classical}}}}$$

This makes good sense because classically the probability for finding the particle at a given point should be inversely proportional to the velocity.

Combining everything, we obtain an approximate solution:

$$\psi(x,t) \simeq \left\{ \frac{\text{constant}}{[E - V(x)]^{1/4}} \right\} \times \exp\left[\pm \left(\frac{i}{\hbar} \right) \int^{x} dx' \sqrt{2m[E - V(x')]} - \frac{iEt}{\hbar} \right]$$

This is the WKB solution, G. Wentzel, A. Kramers, and L. Brillouin.

$$|T| = \exp\left\{ -\int dx \sqrt{\frac{2m}{\hbar^2}[V(x) - E]} \right\}$$

Having obtained the above wave function, let us return to the question of what we mean when we say that ħ is small.

Our derivation of the Hamilton-Jacobi equation from the Schrodinger equation rested on $\hbar|\nabla^2 S| << |\nabla S|^2$ equation, which, in one-dimensional problems, is equivalent to

$$\hbar\left|\frac{d^2W}{dx^2}\right| \ll \left|\frac{dW}{dx}\right|^2$$

$$\rho\frac{dW}{dx} = \pm\rho\sqrt{2m[E-V(x)]} = \text{constant}$$

In terms of the de Broglie wavelength divided by 2π, this condition amounts to

$$\lambda\!\!\!^{-} = \frac{\hbar}{\sqrt{2m[E-V(x)]}} \ll \frac{2[E-V(x)]}{|dV/dx|}$$

In other words, λ must be small compared with the characteristic distance over which the potential varies appreciably.

Roughly speaking, the potential must be essentially constant over many wavelengths. Thus we see that the semiclassical picture is reliable in the short-wavelength limit.

Our last solution has been derived for the classically allowed region where E-V(x) is positive.

We now consider the classically forbidden region where E-V(x) is negative.

The classical Hamilton-Jacobi theory does not make sense in this case, so our last approximate solution, which is valid for E>V, must therefore be modified.

Fortunately an analogous solution exists in the $E < V$ region; by direct substitution we can check that

$$\psi(\mathbf{x}, t) \simeq \left\{ \frac{\text{constant}}{[V(x) - E]^{1/4}} \right\} \exp\left[\pm \left(\frac{1}{\hbar} \right) \int^{x} dx' \sqrt{2m[V(x') - E]} - \frac{iEt}{\hbar} \right]$$

satisfies the wave equation provided that $\hbar/[2m(V - E)]^{1/2}$ is small compared with the characteristic distance over which the potential varies.

Neither

$$\psi(x,t) \simeq \left\{\frac{\text{constant}}{[E-V(x)]^{1/4}}\right\} \times \exp\left[\pm\left(\frac{i}{\hbar}\right)\int^x dx'\sqrt{2m[E-V(x')]} - \frac{iEt}{\hbar}\right]$$

nor

$$\psi(\mathbf{x},t) \simeq \left\{\frac{\text{constant}}{[V(x)-E]^{1/4}}\right\}\exp\left[\pm\left(\frac{1}{\hbar}\right)\int^x dx'\sqrt{2m[V(x')-E]} - \frac{iEt}{\hbar}\right]$$

makes sense near the classical turning point defined by the value of x for which

$$V(x) = E$$

because λ (or its purely imaginary analogue) becomes infinite at that point, leading to a violent violation of:

$$\lambda\!\!\!^{-} = \frac{\hbar}{\sqrt{2m[E-V(x)]}} \ll \frac{2[E-V(x)]}{|dV/dx|}$$

In fact, it is a nontrivial task to match the two solutions across the classical turning point.

The standard procedure is based on the following steps:

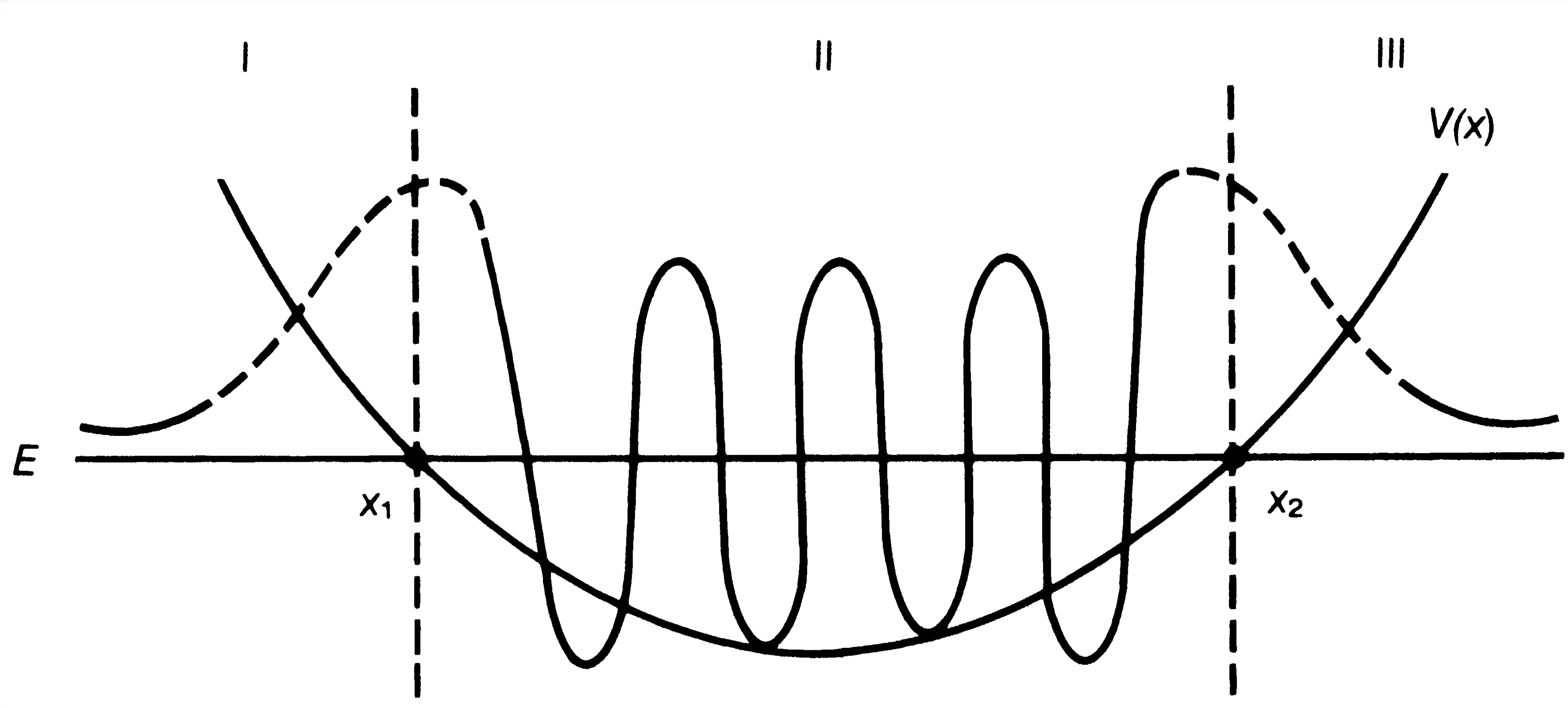
1. Make a linear approximation to the potential $V(x)$ near the turning point x_0, defined by the root of (2.4.39).
2. Solve the differential equation

$$\frac{d^2 u_E}{dx^2} - \left(\frac{2m}{\hbar^2}\right)\left(\frac{dV}{dx}\right)_{x=x_0}(x-x_0)u_E = 0 \tag{2.4.40}$$

   exactly to obtain a third solution involving the Bessel function of order $\pm\frac{1}{3}$, valid near x_0.
3. Match this solution to the other two solutions by choosing appropriately various constants of integration.

We do not discuss these steps in detail, as they are discussed in many places (Schiff 1968, 268-76, for example).

Instead, we content ourselves to present the results of such an analysis for a potential well, schematically shown in the following Figure, with two turning points, x_1 and x_2.



The wave function must behave in region II like

$$\psi(x,t) \simeq \left\{ \frac{\text{constant}}{[E - V(x)]^{1/4}} \right\} \times \exp\left[\pm\left(\frac{i}{\hbar}\right) \int^x dx' \sqrt{2m[E - V(x')]} - \frac{iEt}{\hbar} \right]$$

The wave function must behave in region I and III like

$$\psi(\mathbf{x},t) \simeq \left\{ \frac{\text{constant}}{[V(x) - E]^{1/4}} \right\} \exp\left[\pm\left(\frac{1}{\hbar}\right) \int^x dx' \sqrt{2m[V(x') - E]} - \frac{iEt}{\hbar} \right]$$

The correct matching from region I into region II and from region III into region II results in:

$$\int_{x_1}^{x_2} dx \sqrt{2m[E - V(x)]} = \left(n + \tfrac{1}{2}\right)\pi\hbar \quad (n = 0, 1, 2, 3, \ldots)$$

Apart from the difference between n+1/2 and n, this equation is simply the quantization condition of the old quantum theory due to A. Sommerfeld and W. Wilson, originally written in 1915 as

$$\oint p\,dq = nh$$

where h is Planck's h, not Dirac's ħ, and the integral is evaluated over one whole period of classical motion, from x_1 to x_2 and back.

The following equation

$$\int_{x_1}^{x_2} dx\sqrt{2m[E - V(x)]} = (n + \tfrac{1}{2})\pi\hbar \quad (n = 0, 1, 2, 3, \ldots)$$

can be used to obtain approximate expressions for the energy levels of a particle confined in a potential well.

As an example, we consider the energy spectrum of a ball bouncing up and down over a hard surface:

$$V = \begin{cases} mgx, & \text{for } x > 0 \\ \infty, & \text{for } x < 0 \end{cases}$$

where x stands for the height of the ball measured from the hard surface.

One might be tempted to use the equation directly with

$$x_1 = 0, \qquad x_2 = \frac{E}{mg}$$

which are the classical turning points of this problem.

A much more satisfactory approach to this problem is to consider the odd-parity solutions—guaranteed to vanish at x = 0 — of a modified problem defined by

$$V(x) = mg|x| \quad (-\infty < x < \infty)$$

whose turning points are

$$x_1 = -\frac{E}{mg}, \qquad x_2 = \frac{E}{mg}$$

The energy spectrum of the odd-parity states for this modified problem must clearly be the same as that of the original problem. The quantization condition then becomes

$$\int_{-E/mg}^{E/mg} dx\,\sqrt{2m(E - mg|x|)} = \left(n_{\text{odd}} + \tfrac{1}{2}\right)\pi\hbar, \quad (n_{\text{odd}} = 1, 3, 5, \ldots)$$

or, equivalently,

$$\int_0^{E/mg} dx\,\sqrt{2m(E-mgx)} = (n-\tfrac{1}{4})\pi\hbar, \quad (n=1,2,3,4,\dots)$$

This integral is elementary, and we obtain

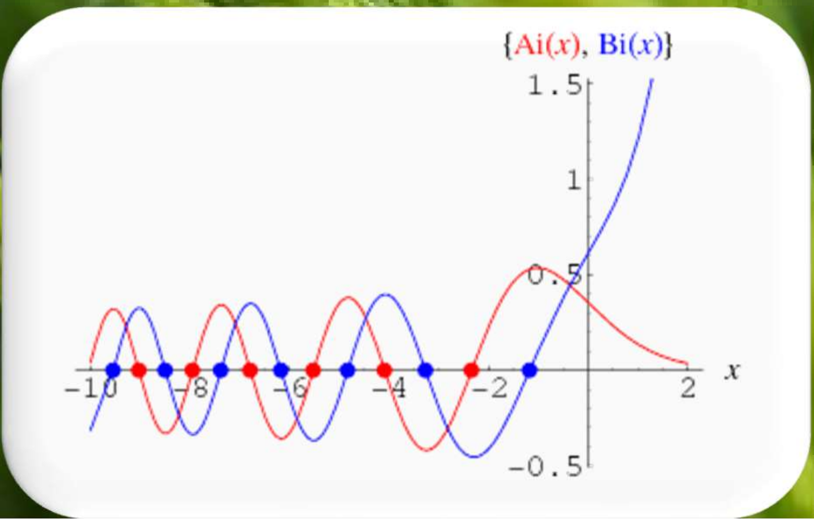
$$E_n = \left\{ \frac{[3(n-\frac{1}{4})\pi]^{2/3}}{2} \right\} (mg^2\hbar^2)^{1/3}$$

for the quantized energy levels of the bouncing ball.

It is known that this problem is soluble analytically without any approximation.

The energy eigenvalues turn out to be expressible in terms of the zeros of the Airy function

$$Ai(-\lambda_n) = 0$$



$$E_n = \left(\frac{\lambda_n}{2^{1/3}} \right) (mg^2\hbar^2)^{1/3}$$

n	WKB	Exact
1	2.320	2.338
2	4.082	4.088
3	5.517	5.521
4	6.784	6.787
5	7.942	7.944
6	9.021	9.023
7	10.039	10.040
8	11.008	11.009
9	11.935	11.936
10	12.828	12.829

The quantum-theoretical treatment of a bouncing ball may appear to have little to do with the real world. It turns out, however, that a potential of type (2.4.45) is actually of practical interest in studying the energy spectrum of a quark-antiquark bound system, called quarkonium. To go from a bouncing ball to a quarkonium, the x in (2.4.45) is replaced by the quark-antiquark separation distance r. The analogue of the downward gravitational force mg is a constant (that is, r-independent) force believed to be operative between a quark and an antiquark. This force is empirically estimated to be in the neighborhood of

$$1\ \mathrm{GeV/fm} \simeq 1.6 \times 10^{5}\ \mathrm{N}$$

which corresponds to about 16 tons. This contrasts with the gravitational force of 0.98 N on a ball of 0.1 kg.