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Semiclassical approximations in wave mechanics

M V BERRY AND K E MOUNT

H H Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL

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Abstract. We review various methods of deriving expressions for quantum-mechanical quantities in the limit when $\hbar$ is small (in comparison with the relevant classical action functions). To start with we treat one-dimensional problems and discuss the derivation of WKB connection formulae (and their reversibility), reflection coefficients, phase shifts, bound state criteria and resonance formulae, employing first the complex method in which the classical turning points are avoided, and secondly the method of comparison equations with the aid of which uniform approximations are derived, which are valid right through the turning-point regions. The special problems associated with radial equations are also considered. Next we examine semiclassical potential scattering, both for its own sake and also as an example of the three-stage approximation method which must generally be employed when dealing with eigenfunction expansions under semi-classical conditions, when they converge very slowly. Finally, we discuss the derivation of semiclassical expressions for Green functions and energy level densities in very general cases, employing Feynman's path-integral technique and

emphasizing the limitations of the results obtained. Throughout the article we stress the fact that all the expressions obtained involve quantities characterizing the families of orbits in the corresponding purely classical problems, while the analytic forms of the quantal expressions depend on the topological properties of these families.

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1. Introduction

Three classes of approximation method are commonly employed in quantum mechanics. *Perturbation techniques* produce series expansions for quantities of interest in powers of a variable which specifies the departure of the given problem from an exactly soluble case (as in the Born approximation where scattering amplitudes, etc are expanded in powers of the strength of the potential). *Variational methods* produce the best estimate out of a given class of trial solutions. This article will deal with *semiclassical approximations* where expressions for wave functions, energy levels, phase shifts, scattering cross sections, etc are derived whose analytic forms are correct in the limiting case where Planck's (reduced) constant $\hbar$ is small in comparison with the action functions occurring in the corresponding classical problem. (We shall frequently abbreviate this description of the limit by using such phrases as '$\hbar$ is small' or 'correction terms are $O(\hbar)$' or 'as $\hbar \to 0$', bearing in mind that $\hbar$ is a dimensional quantity which can really have only one value, namely that found in nature.)

We emphasize that it is not generally possible to express quantum-mechanical quantities as power series in $\hbar$ whose first terms are the values of the quantities according to classical mechanics. This is because wave-mechanical functions are almost always highly nonanalytic in $\hbar$ as $\hbar \to 0$, so that ordinary perturbation theory cannot legitimately be applied. In fact the quantum–classical transition is a singular perturbation problem analogous to, but simpler than, the transition from viscous to frictionless flow. This arises because the Schrödinger equation which, for a particle of mass m and energy E moving in a potential field $V(\boldsymbol{r})$ is given by

$$\hbar^2 \nabla^2 \psi(\boldsymbol{r}) + 2m(E - V(\boldsymbol{r}))\psi(\boldsymbol{r}) = 0, \tag{1.1}$$

suffers a reduction of order on setting $\hbar$ equal to zero. The resulting formula, which is not a differential equation at all and does not give the classical limit correctly, implies that $\psi(\boldsymbol{r})$ is zero except at the *classical turning points*, where $E - V(\boldsymbol{r})$ is zero, and this is an even more drastic approximation than simply taking the classical limit would be, because it is at the turning points that classical quantities themselves frequently become infinite. However, the procedure does at least serve to direct attention to the turning points, which play a crucial role as we shall see.

It is however often possible to obtain perturbation series in ascending (not always integral) powers of $\hbar$, by starting not from the classical limit but from what we propose to call the *semiclassical limit*, which takes full account of the various types of singularity at $\hbar = 0$ (a simple example is discussed in § 2.1). In order to keep this article down to a reasonable length we have virtually ignored the problems of finding the correction terms and of analysing the nature of the resulting series; strictly these are matters of asymptotic theory, and the simpler cases can be studied in appropriate texts (eg Copson 1965, Dingle to be published). Instead, we have concentrated on finding the limiting semiclassical forms—the first terms—for a variety of problems. The resulting formulae are often analytically quite complicated, but they have the great merit of describing almost all the physics (see

eg the resonance formulae in § 3.3). As numerical approximations they are often astonishingly accurate (see § 6.3, particularly figure 20); this is important, because it is precisely in the semiclassical limit that many of the standard calculational methods of wave mechanics—for instance, eigenfunction expansions—converge very slowly.

The difficulty of solving a given problem in 'semiclassical mechanics' is, fairly obviously, directly related to the complexity of the pattern of classical paths. In particular, we shall find time and again that it is the *topology* of the orbits that affects the form of the semiclassical expressions. Furthermore, in all cases that have been fully worked out, it is found that the formulae involve only $\hbar$ in combination with purely classical quantities, suitably analytically continued (see §§ 6.3, 7.3).

Semiclassical methods are as old as quantum theory itself, and the literature is correspondingly enormous. Nevertheless, we have frequently found that these techniques are not as widely applied as they might be, and it is the purpose of this article to present them as simply as possible, without losing sight of the complications which are likely to occur in practice. Almost all the results derived here have appeared before, and are 'well known' to workers in various different fields. What we have tried to do is to gather together in one place a *variety* of methods which share the property of being applicable in the semiclassical limit; thus our treatment does not seriously overlap with that given in the books by Heading (1962) and Fröman and Fröman (1965), which concentrate on the complex method for one-dimensional problems (see our § 3). Nevertheless, we have left out a number of topics, the most important being the motion of wave packets (Furry 1963), the semiclassical approximation of relativistic wave equations (eg Rubinow and Keller 1963, Rosen and Yennie 1964), motion in magnetic fields (Furry 1963, Pippard 1969, Lifshitz and Kaganov 1960, 1962), and inelastic collision theory (Percival 1971, Crothers 1971, Child 1971).

We have designed the work to be read as a whole, although it is possible to read each section (but not subsection, except §§ 7.1, 7.4) separately without a great deal of reference to the others. The plan is inductive, starting in § 2 with the simplest one-dimensional problems not involving real classical turning points, and dealing with progressively more complicated cases until in § 7 we consider the semiclassical limit of very general situations. We conclude in § 8 by suggesting some areas where further research is particularly needed.

2. Problems with no classical turning points

2.1. *A simple illustrative example*

To clarify what we mean by the classical limit, it is sensible to begin by choosing a problem whose exact solution is known; if we were to use an approximate method at this stage, we would be tempted to doubt the validity of our results until we had considered the convergence or asymptotic nature of the series of which our approximation constituted the first term. We consider a particle incident from the left with an energy E which would be sufficient, in the classical case, for it to surmount a smooth potential step of height V_0 whose analytical form is taken to be

$$V(x) = \frac{V_0}{1+\mathrm{e}^{-x/L}}. \tag{2.1}$$

The distance L is a measure of the smoothness of the step (figure 1).

In addition to the incident wave, there will be a reflected wave for large negative x and a transmitted wave for large positive x, so that the wave function $\psi(x)$ for large $|x|$ takes the form

$$\left.\begin{aligned}\psi(x) &= \exp\left(\frac{ip_1 x}{\hbar}\right) + R\exp\left(\frac{-ip_1 x}{\hbar}\right) \qquad (x \ll 0)\\ &= T\exp\left(\frac{ip_2 x}{\hbar}\right) \qquad (x \gg 0)\end{aligned}\right\} \tag{2.2}$$

where R and T are the (amplitude) reflection and transmission coefficients, and p_1 and p_2 are the classical momenta in the two regions of constant potential, given by

$$\left.\begin{aligned}p_1 &\equiv (2mE)^{1/2}\\ p_2 &\equiv \{2m(E-V_0)\}^{1/2}\end{aligned}\right\}. \tag{2.3}$$

For the moment we are interested only in the power reflection coefficient $|R|^2$,

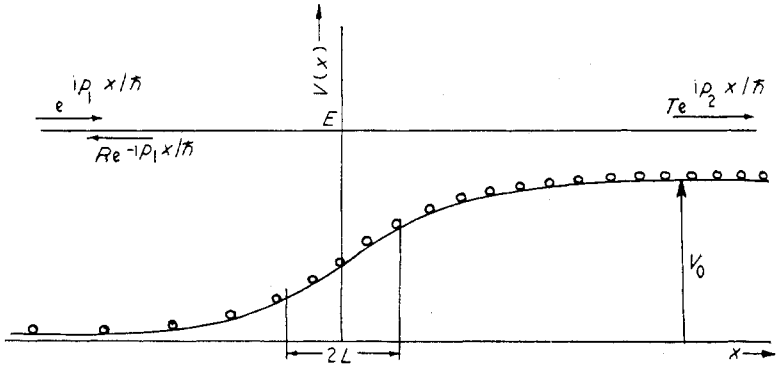

Figure 1. Smooth potential step (the circles indicate the classical particle density of § 2.2).

and it is shown by Landau and Lifshitz (1965 p78) by means of an exact solution for $\psi(x)$ in terms of hypergeometric functions that

$$R|^2 = \left(\frac{\sinh\{\pi(p_1-p_2)L/\hbar\}}{\sinh\{\pi(p_1+p_2)L/\hbar\}}\right)^2. \tag{2.4}$$

The semiclassical case arises when $\hbar$ is small compared with both products pL, a condition equivalent to requiring the de Broglie wavelength $\lambda = h/p$ to be small in comparison with the thickness L of the transition zone. The reflection coefficient (2.4) then takes the simple form

$$|R|^2 = \exp(-4\pi p_2 L/\hbar) \tag{2.5}$$

for $p_2 L \gg \hbar$. In the classical limit, when $\hbar$ is strictly zero, this expression becomes zero whatever the value of L, corresponding to the expected lack of reflection for classical particles sliding up a smooth incline whose profile is represented by figure 1. Even when L is zero, the classical reflection coefficient is zero. (It would not be correct to set $L = 0$ in the semiclassical formula (2.5), thus obtaining a reflection coefficient of unity, even though this result has a certain plausibility, because our intuition, which might predict complete classical elastic reflection at a sharp step, is based on the behaviour of deformable bodies of finite size.) Considered as a function of $\hbar$, the semiclassical reflection coefficient does not vanish

as some simple power in the classical limit, but has an essential singularity; there are many wave-mechanical quantities like this, which cannot be expanded in powers of $\hbar$, and in this simple fact (emphasized in a different context by Schipper 1969) lies much of the complexity (as well as the fascination) of semiclassical mechanics. We shall occasionally use the term 'semiclassical limit' to denote the *functional form* as $\hbar \to 0$, reserving the name classical limit for the actual limiting value.

There are at least three other limiting forms of the exact reflection coefficient (2.4), which we wish to distinguish from the semiclassical case. The 'weak scattering limit', or Born approximation, arises when $p_1 \simeq p_2$, so that

$$|R|^2 = \left(\frac{\pi(p_1-p_2)L}{\hbar \sinh\{\pi L(p_1+p_2)/\hbar\}}\right)^2. \tag{2.6}$$

(We cannot generally expand the square root in p_2 (2.3) to first order in V_0, because E may be small as well.) Secondly, there is the 'high energy limit' $E \gg V_0$, for which

$$|R|^2 = \frac{m}{2E}\left(\frac{\pi L V_0}{\hbar}\right)^2 \exp\left(-\frac{4\pi L}{\hbar}(2mE)^{1/2}\right). \tag{2.7}$$

(This is really a special case of (2.6) but it is very important in its own right.) Finally, there is the limit of a 'sharp step', $L \ll \hbar/p_1$ where

$$|R|^2 = \left(\frac{p_1-p_2}{p_1+p_2}\right)^2. \tag{2.8}$$

The weak-scattering and high energy formulae both reach the correct value of zero in the classical limit $\hbar \to 0$, but their analytic forms are wrong; the sharp-step result is independent of $\hbar$ and can never give the correct classical limit. The order in which $\hbar$ and L are set equal to zero is therefore important, which is not surprising since what is important is the ratio of the de Broglie wavelength to the size of the region of variation of the potential, and this is different in the two limiting cases.

In this article we shall be exclusively concerned with limits of the first type, where $\hbar$ is the small quantity (rather than L or V_0/E or $(p_2-p_1)/p_1$), so that we shall become familiar with formulae similar to (2.5) (that particular expression being derived from a more general approximate theory in §3.2). The sharp-step type of formula, similar to (2.8), is more familiar in optics, since cases where the refractive index changes suddenly on a wavelength scale (light entering a lens, for instance) are far commoner than problems in mechanics involving sudden finite changes in potential energy. The emphasis of our work will therefore differ from that of conventional shortwave diffraction theory (see eg Bouwkamp 1954, Keller 1958b, Born and Wolf 1970), whose problems typically involve large objects with sharply defined boundaries (diffracting spheres, apertures, etc).

2.2. *The basic WKB solutions*

There is a variety of methods available for finding the semiclassical approximate wave functions for the general one-dimensional case where there are no classical reflections; for our purposes it will be instructive to derive the basic results in two essentially different ways. In the first method, due to Bremmer (1951) (see also Heading 1962 p131, Bellman and Kalaba 1959) the potential $V(x)$ is approximated by a series of steps at the points x_i, between which the potential is constant, that is

$$V(x) \simeq V_i \equiv V(x_i) \qquad (x_{i-1} \leqslant x < x_i) \tag{2.9}$$

(see figure 2). At each step there will be reflection and transmission of waves which may themselves have previously undergone reflection and transmission; in the Bremmer theory, the effect of these contributions to the total wave function is calculated, and the process of taking the limit $x_{i+1}-x_i \to 0$, corresponding to a continuous potential, is examined.

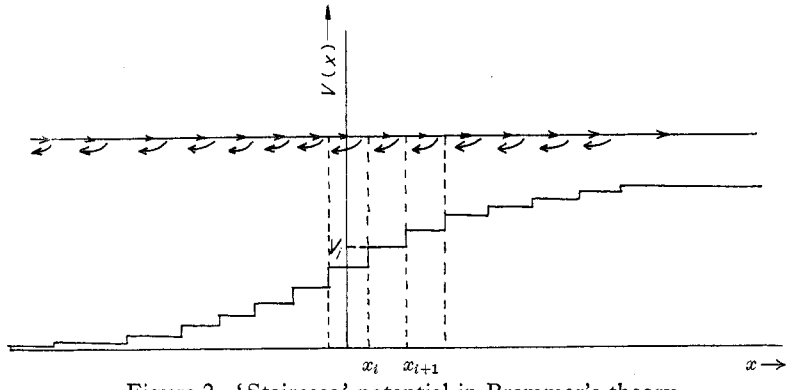

Figure 2. 'Staircase' potential in Bremmer's theory.

Since we are dealing with the semiclassical limit, let us first evaluate the wave function according to Bremmer's theory by ignoring all the reflections. Since the steps are sharp, the transmission coefficient T_i at x_i is given by the analogue of (2.6), which is easily shown to be

$$T_i = 2p_i/(p_i+p_{i+1}). \tag{2.10}$$

Between x_{i-1} and x_i, the wave function will gain a phase equal to

$$p_i(x_i-x_{i-1})/\hbar = \{2m(E-V_i)\}^{1/2}(x_i-x_{i-1})/\hbar$$

so that the total wave function that has accumulated at the point just prior to the step at x_n is

$$\begin{aligned}\psi(x_n) &= \exp\left(\frac{\mathrm{i}p_1 x_1}{\hbar}\right) T_1 \exp\left(\frac{\mathrm{i}p_2(x_2-x_1)}{\hbar}\right) T_2 \ldots T_{n-1} \exp\left(\frac{\mathrm{i}p_n(x_n-x_{n-1})}{\hbar}\right) \\ &= \prod_{i=1}^{n-1}\left(\frac{2p_i}{p_i+p_{i+1}}\right) \exp\left[\frac{\mathrm{i}}{\hbar}\left\{\sum_{i=2}^{n} p_i(x_i-x_{i-1})+p_1 x_1\right\}\right]. \end{aligned} \tag{2.11}$$

When the potential becomes continuous, the limit of the phase is obviously

$$\begin{aligned}\sum_{i=2}^{n} p_i(x_i-x_{i-1})+p_1 x_1 &\to p_1 x_1 + \int_{x_1}^{x_n} p(x)\,\mathrm{d}x \\ &= \int_{-\infty}^{0} (p(x')-p_1)\,\mathrm{d}x' + \int_0^x p(x')\,\mathrm{d}x' \end{aligned} \tag{2.12}$$

where we have introduced the momentum as a function of position (cf 2.3). The amplitude factor can be evaluated as follows:

$$\begin{aligned}\prod_{i=1}^{n-1}\frac{2p_i}{p_i+p_{i+1}} &= \prod_{i=1}^{n-1}\left(1-\frac{p_{i+1}-p_i}{p_{i+1}+p_i}\right) = \exp\left\{\sum_{i=1}^{n-1}\ln\left(1-\frac{p_{i+1}-p_i}{p_{i+1}+p_i}\right)\right\} \\ &\simeq \exp\left(-\sum_{i=1}^{n-1}\frac{p_{i+1}-p_i}{p_{i+1}+p_i}\right) \simeq \exp\left(-\int_{x_1}^{x_{n-1}}\mathrm{d}x\,\frac{\mathrm{d}p(x)/\mathrm{d}x}{2p(x)}\right) = \left(\frac{p_1}{p(x_{n-1})}\right)^{1/2}. \end{aligned} \tag{2.13}$$

Ignoring the irrelevant constant phase corresponding to the first term in (2.12), we obtain for the wave function the approximation

$$\psi(x) \simeq \left(\frac{p_1}{p(x)}\right)^{1/2} \exp\left(\frac{\mathrm{i}}{\hbar}\int_0^x p(x')\,\mathrm{d}x'\right). \tag{2.14}$$

The probability density of particles corresponding to this wave function is

$$|\psi(x)|^2 \simeq p_1/p(x). \tag{2.15}$$

In order to see that this is the correct classical limit, we must realize that the constant energy wave function we have been considering represents not a single particle (for that we would need a wave packet, involving a spectrum of energies), but a statistical ensemble of (independent) particles, all of energy E, incident from the left, distributed with unit density along the x axis prior to hitting the step. After sliding up the step to the region of potential V_0, the particles if considered classically must, for reasons of continuity, lie closer together (figure 1), with a density inversely proportional to their decreased velocity, so that (2.15) does indeed provide a correct description of the classical limit. Quantum mechanically, the approximate wave function (2.14) satisfies exactly the theorem of current conservation, namely

$$\mathrm{Im}(\psi^*(x)\,\mathrm{d}\psi(x)/\mathrm{d}x) = \text{constant}. \tag{2.16}$$

Our wave (2.14) travelling to the right is an approximate solution of Schrödinger's equation

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{p^2(x)}{\hbar^2}\psi(x) = 0. \tag{2.17}$$

A second independent approximate solution is clearly given by the analogous expression corresponding to a wave going to the left. For historical reasons (see Heading 1962 p3) that we shall not consider further, these two solutions are often known as the WKB approximation to Schrödinger's equation. In a symmetrical notation, they may be written in the form

$$\psi^{\pm}_{\mathrm{WKB}} \equiv \frac{1}{(p(x))^{1/2}} \exp\left(\pm\frac{\mathrm{i}}{\hbar}\int_0^x p(x')\,\mathrm{d}x'\right). \tag{2.18}$$

Exactly the same results can be derived by a second method (see eg Wentzel 1926), less physically appealing but mathematically simpler than Bremmer's, if we substitute

$$\psi(x) = \exp(\mathrm{i}g(x)) \tag{2.19}$$

into Schrödinger's equation, and expand g in ascending powers of $\hbar$. The equation for g, if we denote differentiations with respect to x by primes, is easily found to be

$$g'(x) = \pm\frac{p(x)}{\hbar}\left(1 + \frac{\mathrm{i}\hbar^2 g''(x)}{p^2(x)}\right)^{1/2}. \tag{2.20}$$

The first two terms are of order $\hbar^{-1}$ and $\hbar^0$, and are found by iteration of (2.15) to be

$$\begin{aligned} g(x) &= \pm\frac{1}{\hbar}\int^x p(x')\,\mathrm{d}x' + \frac{\mathrm{i}}{2}\int^x \frac{p'(x')}{p(x')}\,\mathrm{d}x' \\ &= \pm\frac{1}{\hbar}\int^x p(x')\,\mathrm{d}x' + \frac{\mathrm{i}}{2}\ln p(x) \end{aligned} \tag{2.21}$$

which, on substitution into (2.19), reproduce the two WKB solutions (2.18). The later contributions to $g(x)$ are of order $\hbar$, and so represent corrections which vanish in the semiclassical limit with which we are concerned.

The phase occurring in the WKB solutions (2.18) is the classical action S, measured in units of $\hbar$. We shall denote the phase itself by the symbol w, and when we wish to indicate both limits of integration we shall write

$$\int_{x_1}^{x_2} \frac{p(x)\,\mathrm{d}x}{\hbar} \equiv w(x_1, x_2) \equiv \frac{S(x_1, x_2)}{\hbar}. \tag{2.22}$$

Sometimes we shall use the symbols $w(x)$ or $S(x)$ with a single argument; in these cases the argument refers to the upper limit of integration, the lower limit being either understood or irrelevant. Where it is important, the lower limit will sometimes be called the 'phase reference level', following Heading (1962 p81).

2.3. *The semiclassical reflected wave*

Of the two methods that were employed in the last section to derive the basic WKB approximations (2.18), only Bremmer's is capable of being extended in an obvious way to provide information about the wave reflected by the potential step in all cases except the extreme classical limit. The second method is quite incapable of predicting even the existence of a reflected wave, since the contributions to $g(x)$ of odd and even powers in $\hbar$ merely provide correction terms to the phase and amplitude, respectively, occurring in (2.18) (Fröman 1966a, 1970, Garola 1969). This remains true even if the iteration and expansion of (2.20) are carried out to all orders in $\hbar$ (when the resulting series for $g(x)$ is asymptotic and not convergent) because the reflected wave (given by (2.5) in our example) has an essential singularity at $\hbar = 0$, as do the basic WKB waves (2.18), and this behaviour can never emerge from the higher terms of a Taylor expansion about $\hbar = 0$.

Let us see, then, how the Bremmer method, which can be extended to take systematic account of multiply reflected waves of all orders, copes with the semiclassical case, where the reflections are known (equation (2.5)) to be exponentially small. We shall not sum up all the individual reflections and transmissions (this calculation is carried out by Bremmer (1949, 1951)); instead we shall divide the total exact wave function ψ into two parts, ψ_+ and ψ_-, representing the waves travelling to the right and left respectively. We write

$$\psi(x) = \psi_+ + \psi_- \equiv \frac{b_+(x)}{(p(x))^{1/2}} \exp\left(\frac{\mathrm{i}}{\hbar}\int_0^x p(x')\,\mathrm{d}x'\right) + \frac{b_-(x)}{(p(x))^{1/2}} \exp\left(-\frac{\mathrm{i}}{\hbar}\int_0^x p(x')\,\mathrm{d}x'\right) \tag{2.23}$$

in which the slowly changing functions $b_+(x)$ and $b_-(x)$ describe the modifying effect of the reflections on the basic WKB functions (2.18).

To derive the equations satisfied by $b_+(x)$ and $b_-(x)$ we consider how ψ_+ and ψ_- change across the ith step of the potential staircase (figure 2) between the point $x_i^<$, just prior to x_i, and the point $x_{i+1}^<$, just prior to x_{i+1}. The partial wave ψ_+ will be altered by its transmission through the discontinuity at x_i, and it will gain a contribution from the reflection of ψ_- at the same step; there will also be small changes in phase, so that, taking care to use the correct transmission and reflection coefficients,

we have

$$\psi_+(x_{i+1}^<) = \left(\frac{2p_{i-1}}{p_i+p_{i-1}}\right)\psi_+(x_i^<)\exp\left\{\frac{\mathrm{i}}{\hbar}(x_{i+1}-x_i)p_i\right\} + \left(\frac{p_i-p_{i-1}}{p_i+p_{i-1}}\right)\psi_-(x_{i+1}^<)\exp\left\{\frac{2\mathrm{i}}{\hbar}(x_{i+1}-x_i)p_i\right\}. \tag{2.24}$$

In the limit of a continuous potential, this becomes:

$$\psi'_+(x) = -\frac{p'}{2p}\psi_+(x) + \frac{\mathrm{i}p}{\hbar}\psi_+ + \frac{p'}{2p}\psi_-. \tag{2.25}$$

A similar equation, for $\psi'_-(x)$ can be derived by considering the reflection and transmission affecting $\psi_-(x)$; substitution of (2.23) into these two equations yields

$$b'_\pm(x) = \frac{p'(x)}{2p(x)}b_\mp(x)\exp\left(\mp\frac{2\mathrm{i}}{\hbar}\int_0^x p(x')\,\mathrm{d}x'\right). \tag{2.26}$$

These coupled first-order equations are formally equivalent to Schrödinger's equation (2.17). The literature contains a variety of derivations of (2.26) and similar equations (see eg Kemble 1935, Bremmer 1951, Fröman and Fröman 1965, Rydbeck 1964, Bahar 1967, Baird 1970).

The different solutions of Schrödinger's equation are obtained by applying different boundary conditions to $b_\pm(x)$. In particular the 'scattering' solution (2.2) corresponds after a trivial change of normalization to the choice

$$\left.\begin{aligned} b_+(-\infty) &= 1 \\ b_-(+\infty) &= 0 \end{aligned}\right\} \tag{2.27}$$

indicating that the incident wave has unit intensity, and there is no reflected wave at large distances beyond the step. In terms of these boundary conditions, (2.26) can be written as a pair of integral equations:

$$\left.\begin{aligned} b_+(x) &= 1 + \int_{-\infty}^{x}\mathrm{d}x'\,\frac{p'(x')}{2p(x')}b_-(x')\exp\left(-\frac{2\mathrm{i}}{\hbar}\int_0^{x'}p(x'')\,\mathrm{d}x''\right) \\ b_-(x) &= -\int_{x}^{\infty}\mathrm{d}x'\,\frac{p'(x')}{2p(x')}b_+(x')\exp\left(+\frac{2\mathrm{i}}{\hbar}\int_0^{x'}p(x'')\,\mathrm{d}x''\right). \end{aligned}\right\} \tag{2.28}$$

Whenever the 'differential reflection coefficient' $p'/2p$ may be set equal to zero the constant values (2.27) for $b_\pm(x)$ are obtained; this corresponds simply to taking the WKB solution ψ^+_{WKB} (see 2.18) as our wave. Successive approximations to the effects of reflection are obtained by iterating (2.28) from the starting values (2.27); the resulting series is often convergent (see Atkinson 1960). The once-reflected waves only affect $\psi_-(x)$ and yield, as a first approximation to the reflection coefficient, the value

$$R \simeq -\int_{-\infty}^{\infty}\mathrm{d}x\,\frac{p'(x)}{2p(x)}\exp\left(\frac{2\mathrm{i}}{\hbar}\int_0^x \mathrm{d}x'p(x')\right). \tag{2.29}$$

Under semiclassical conditions $\hbar$ is small, and the large exponent causes the integrand to oscillate rapidly with changing x. In these circumstances the main contributions to the integral come from the neighbourhood of points where the potential is discontinuous in any of its derivatives, the precise value of R being found by successive integration by parts to be proportional to some positive power

of $\hbar$. Our primary interest, however, is in potentials which have no such discontinuities, so that the integrand in (2.29) oscillates all along the real x axis, and R is of exponentially small order in $\hbar^{-1}$, the precise value depending on the analytic properties of the function $p(x)$ for complex x. The subtle problems involved in the evaluation of (2.29) have been examined by Pokrovskii *et al* (1958a,b); following their treatment, we change the variable of integration to the phase

$$w \equiv \int_0^x \mathrm{d}x' p(x')/\hbar \tag{2.30}$$

obtaining

$$R \simeq -\int_{-\infty}^{\infty} \mathrm{d}w \frac{(\mathrm{d}p/\mathrm{d}w)\exp(2\mathrm{i}w)}{2p(w)} \tag{2.31}$$

the merit of the transformation being to eliminate the branch points of the exponent which occur at the poles of $p'/2p$ in (2.29). If such a pole occurs at $w = w_j$, then the contribution to R is

$$R_j = -\exp(2\mathrm{i}w_j)\oint \mathrm{d}w \frac{\mathrm{d}p/\mathrm{d}w}{2p(w)} \tag{2.32}$$

where the contour encloses w_j.

The commonest type of pole in $p'/2p$ arises from 'complex classical turning points', points x_j in the complex x plane where

$$E - V(x_j) \equiv \frac{p^2(x_j)}{2m} = 0. \tag{2.33}$$

If these points represent simple zeros of $p^2(x)$, then (2.32) is easily evaluated exactly, giving

$$R_j = -\tfrac{1}{8}\pi\mathrm{i}\exp(2\mathrm{i}w_j). \tag{2.34}$$

The next most common type of singularity of $p'/2p$ is a simple pole of the potential $V(x)$ for some complex argument x_j. This time (2.32) comes out to be

$$R_j = +\pi\mathrm{i}\exp(2\mathrm{i}w_j). \tag{2.35}$$

If we were evaluating the integral (2.31) exactly we would need to take account of all the singularities of $p'/2p$ in the upper half-plane of the complex variable w. In the semiclassical approximation, however, only the singularities w_j which lie nearest to the real axis need to be included, because the others are of a higher degree of exponential smallness (cf (2.32) and (2.30)).

Applying these considerations to the example of § 2.1, we find that the potential $V(x)$ given by (2.1) has poles at

$$x_j = (2j+1)\mathrm{i}\pi L \tag{2.36}$$

while $p(x)$ has zeros (classical turning points) at

$$x_j = L\ln\frac{E}{E-V_0} + (2j+1)\mathrm{i}\pi L \tag{2.37}$$

where j is any integer. A rather tricky contour integration shows that it is the turning point where $j = 0$ whose singularity in the w plane lies nearest to the real axis, with

$$\operatorname{Im} w_0 = \pi L\{2m(E-V_0)\}^{1/2} \equiv \pi L p_2/\hbar. \tag{2.38}$$

The resulting value for the power reflection coefficient is obtained from (2.34) as

$$|R|^2 \simeq (\pi^2/9) \exp(-4\pi L p_2/\hbar). \tag{2.39}$$

This differs from the correct semiclassical expression, which we know to be (2.5), by the factor $\pi^2/9 = 1{\cdot}097$.

The blame for this discrepancy does not lie in our method of evaluating the integral (2.31); even if we had included all the poles and zeros of $p^2(x)$, the results (2.34) and (2.35) show that we would never obtain the correct prefactor of unity that occurs in (2.5). In fact it is the approximation (2.29) that is at fault, for it is shown by Pokrovskii *et al* (1958a,b) that the multiple integrals resulting from the further iteration of (2.28), corresponding to the effect of multiple reflections, are all of the same order in $\hbar$ as our result (2.38). Pokrovskii *et al* do not explicitly evaluate the numerical factors appearing in these iterations; nor has anybody else, so far as we are able to ascertain. Presumably these factors form a series whose first term is $\pi^2/9$ and whose sum is unity.

The Bremmer series therefore, despite its convergence and the simple physical interpretation of its terms, does not tell us the origin of the reflection in the semiclassical case with which we are concerned. But our method for evaluating the total once-reflected wave does at least indicate the direction in which the true explanation lies: we must consider from a more fundamental viewpoint the effects on the wave function of the singularities of $p(x)$, in particular the *turning points*. It should be clear that these effects will be most profound when the turning points lie on the real axis, and it is such cases that we now consider.

3. The complex method for treating classical turning points

3.1. *The origin of the connection problem*

At a real turning point x_t, where $p^2(x_t) = 0$, classical particles incident from an accessible region, where $p^2 > 0$, reverse their velocity and return whence they came; the adjacent region, where $p^2 < 0$, is forbidden to particles according to classical mechanics. Quantum mechanically, of course, exponentially growing or damped waves can exist in forbidden regions, as predicted even by the basic WKB solutions (2.14), since $p(x)$ is imaginary there. Now, in quantum mechanics it is almost invariably the case that one is not interested in the possible solutions that may exist in one region of the x axis; rather, one deals with a *particular* solution, defined by boundary conditions at one or two points, and enquires about the properties of that solution in various regions of the x axis, which may be separated by one or more classical turning points. It is not permissible to use the WKB solutions at these points, since the differential reflection coefficient $p'/2p$ diverges there (cf 2.26), and there is no guarantee that the same combination of the WKB functions (2.14) will fit the particular solution on both sides of the turning point. We may express this more precisely as a 'connection problem' by using the exact expression (2.23): if the values of the WKB multipliers $b_\pm$ are known on a given region of the x axis, thus defining a solution to Schrödinger's equation (equation (2.27) is an example of such a choice of boundary conditions), what will be the values of $b_\pm$ in a different region of the x axis separated from the first by one or more turning points?

Over the last fifty years these connection problems and in particular the question of the *reversibility* of the formulae obtained have occasioned a great deal of controversy and even acrimony which has still not died down; we shall deal with this

matter in § 3.2. Two main methods have been employed in the past; the first is the 'complex method', where the two regions between which the solution is to be traced are joined by a path in the complex x plane (a 'good path') which is sufficiently far from the turning point(s) for the WKB solutions to be valid along it. The method was invented by Zwaan in 1929 (summarized and discussed in an elegant paper by Langer 1934) and applied to a number of problems by Kemble (1935, 1937). Furry (1947) provided a simplified derivation, the ideas of which were taken up by Heading (1962) and incorporated into a general theory capable of dealing with any number of turning points of any order, for a variety of equations more general than Schrödinger's. In the voluminous writings of Fröman and Fröman (1965, 1970) and Fröman (1966b, 1970), the validity conditions of the complex method are very carefully analysed with the aid of convergent series similar to those obtained in Bremmer's theory. As we shall see, the complex method, while furnishing much useful information about the connection between two parts of a solution, is frequently incapable of giving all the details that are required in practical applications.

The second method, which will be described in § 4, employs the technique of 'uniform approximation', where the required solution is mapped on the solution of a simpler equation which, however, has the same disposition of turning points as the original. As well as enabling the connection problem to be solved, this method also provides the wave function in the neighbourhood of the turning point, which was bypassed in the complex method. It is only in a few cases that sufficient is known about the solutions of the comparison equations for the method to be useful but in these cases it is possible to obtain the information about the connections which was not provided by the complex method. The method of uniform approximation for ordinary differential equations was pioneered by Langer (1937) and has been generalized by Dingle (1956) and by Miller and Good (1953); a simpler version of the method was provided earlier by Jeffreys (1923) and Kramers (1926) (see also Bertocchi *et al* 1965).

In addition to these two principal methods, a variety of special techniques have been employed, which are capable of solving particular aspects of the connection problem. General reviews are given by McHugh (1971) and Wasow (1965) (see also Turrittin 1964), and we shall refer to these special techniques at appropriate places in our argument.

In the complex method, no attempt is made to follow the detailed variation of the multipliers $b_{\pm}(x)$ (by for example, integrating equations (2.26)) as the good path is traced around the turning point(s) to connect the regions between which the solution is to be joined. Instead, appeal is made to two principles concerning the behaviour of the wave function; these principles restrict the ways in which $b_{\pm}$ can change, and in some cases enable the connection problem to be solved completely. Firstly, there is the *reality principle:* if the potential $V(x)$ is real then it is possible to choose two independent solutions which are both real all along the x axis. This principle can also be generalized to deal with the case of complex potentials, or paths off the real axis. In applying the reality principle, the changes of phase of the factor $p^{-1/2}$ in the WKB functions (2.14) must not be forgotten, as has been particularly emphasized by Keller (1958a).

The second principle involves the mechanism by which the $b_{\pm}$ multipliers change as we traverse the path. According to the basic equations (2.26), it is possible for b_+ or b_- to change on a good path only if the phase integral $w(x)$ (cf (2.22)) is complex, so that the exponentials in (2.26) can have a large modulus, outweighing

the smallness of $p'/2p$. In the extreme case where w is purely imaginary, say

$$w(x) = +\mathrm{i}|w(x)| \tag{3.1}$$

the wave function (2.23) is

$$\psi(x) = \frac{b_+(x)}{p^{1/2}(x)} \exp(-|w|) + \frac{b_-(x)}{p^{1/2}(x)} \exp(+|w|) \tag{3.2}$$

in which the second term ψ_- is vastly greater than the first unless b_- is exceedingly small. The equation describing the change of the coefficient b_- of this *dominant* exponential is (cf equation (2.26))

$$b'_- = \frac{p'}{2p} b_+ \exp(-2|w|) \tag{3.3}$$

from which it is clear that b_- does not change significantly in this region of the complex plane. The situation is very different for the coefficient b_+ of the *subdominant* exponential, which changes according to

$$b'_+ = \frac{p'}{2p} b_- \exp(+2|w|) \tag{3.4}$$

an equation whose right-hand side is very large unless b_- is very small (in which case the solution ψ_+ is no longer subdominant). The loci of points where w is imaginary are thus extremely important, since it is there that the multipliers of the WKB solutions can change their form; these loci take the form of lines in the complex x plane emanating from the turning points, referred to as 'Stokes lines' after their discoverer, who investigated the connection problem in very great detail for Bessel functions, where a single turning point is involved (see Stokes 1904, 1905). Classically forbidden regions are particular cases of Stokes lines which lie on the real axis. Between the Stokes lines lie lines on which $w(x)$ is purely real, where $b_\pm$ are constant far from turning points; these are 'anti-Stokes lines', of which classically allowed regions are particular cases. We can now state the second principle of the complex method, *the principle of exponential dominance*, as follows: a multiplier b_+ or b_- can only change on a good path when crossing a Stokes line on which its exponential is subdominant; the change is proportional to the magnitude of the multiplier of the dominant exponential (cf equation (3.4)). A very careful analysis of this principle is the theme of the book by Fröman and Fröman (1965).

We can write the solution of the coupled equations (2.26) in a formal way, as

$$\begin{pmatrix} b_+(x) \\ b_-(x) \end{pmatrix} = (F(x, x_0)) \quad \begin{pmatrix} b_+(x_0) \\ b_-(x_0) \end{pmatrix} \tag{3.5}$$

where F is a 2×2 matrix describing the changes in $b_\pm$ on moving from x_0 to x. The F matrix was introduced by Fröman and Fröman (1965 chap3), and forms the basis of their treatment. The principle of exponential dominance now tells us that $F(x, x_0)$ is the unit matrix if x and x_0 lie on the same anti-Stokes line, while if x and x_0 lie on opposite sides of a Stokes line at which, say, ψ_- is dominant, then

$$F = \begin{pmatrix} 1 & \alpha \\ 0 & 1 \end{pmatrix} \tag{3.6}$$

where the α is referred to as the Stokes constant for crossing the particular line considered; F would take a similar form if one of the points lay actually on a Stokes

line. The important point is that our principle implies that

$$\det\|F\| = 1 \tag{3.7}$$

in all cases. But this condition is easily shown to be equivalent to the constancy of the wronskian $W(x)$ for any pair of independent solutions $\psi_1(x)$ and $\psi_2(x)$, defined by

$$W(x) \equiv \psi_1(x)\,\psi_2'(x) - \psi_1'(x)\,\psi_2(x) \tag{3.8}$$

so that this constancy cannot provide any new information about the connection problem, once the principle of exponential dominance has been used. Nor can the principle of constancy of current (equation (2.16)) provide any extra information, since this is a special case of the wronskian principle, in which x is restricted to the real axis, and $\psi_2 = \psi_1^*$.

The wave function $\psi(x)$ must be single-valued if the potential $V(x)$ is, but the momentum function $p(x)$ and the phase $w(x)$ are multivalued, with branch points at the classical turning points, so that a system of branch cuts is necessary in order to make a consistent analysis possible. Heading (1962 p53) carefully specifies the rules which must be followed when tracing the WKB solutions across such cuts. However, the cuts can always be positioned so that the 'good path', between parts of the x axis, does not cross any of them. If we wish to make use of the condition of single-valuedness we must take a circular good path, which does cross the cut(s), but this procedure inevitably introduces additional Stokes constants, and it can be shown that no information can be obtained in this way concerning the connection problem along the real axis that cannot be found from the two basic principles we have discussed already. Of course it is possible to use the single-valuedness condition *instead* of the reality condition (Furry 1947), but this results in a more cumbersome formalism.

We now proceed to discuss some applications of the complex method, using the two principles adumbrated above. Of course we shall not deal with all the permutations of number and type of turning point that have been considered in the literature, but we do hope to clarify the applications and shortcomings of the method.

3.2. *The connection formulae for the case of one turning point: their reversibility*

This case is exemplified by the potential treated in § 2.1 (figure 1), if the energy E lies between 0 and V_0. We shall consider the turning point to lie at $x = 0$, with $x > 0$ classically forbidden and $x < 0$ accessible; near such a turning point of first order, $p^2(x)$ takes the form

$$p^2(x) \equiv 2m(E - V(x))_{x\sim 0} \simeq -ax. \tag{3.9}$$

In order to apply the complex method we specify that the function be positive real on the negative real axis, just below which we take a branch cut stretching from 0 to $-\infty$ (figure 3).

If we specify positions in the upper half-plane by

$$x = r\,\mathrm{e}^{\mathrm{i}\theta} \tag{3.10}$$

where θ goes from 0 to 2π, then we are stipulating that

$$p(x)_{x\sim 0} \simeq (ar)^{1/2} \exp\{\mathrm{i}(\theta - \pi)/2\} \tag{3.11}$$

which leads, on the real axis, to the values shown in figure 3. For the phase-integral, we have

$$w(x)_{x\sim 0} \simeq \tfrac{2}{3}(ar^3)^{1/2} \exp\{\mathrm{i}(3\theta - \pi)/2\} \tag{3.12}$$

from which it follows that there are three Stokes lines, one along the positive real axis, where ψ_+ is dominant, and two emanating from 0 along the lines $\theta = \pm 2\pi/3$, where ψ_- is dominant. We shall trace the solution from the negative real axis (line 1 in figure 3) where it is specified by $b_\pm(1)$, across the Stokes line 2 at $\theta = 2\pi/3$ to the anti-Stokes line 3 at $\theta = \pi/3$, and finally to the positive real axis (line 4), where we require $b_\pm(4)$ in terms of $b_\pm(1)$ to establish the required connection.

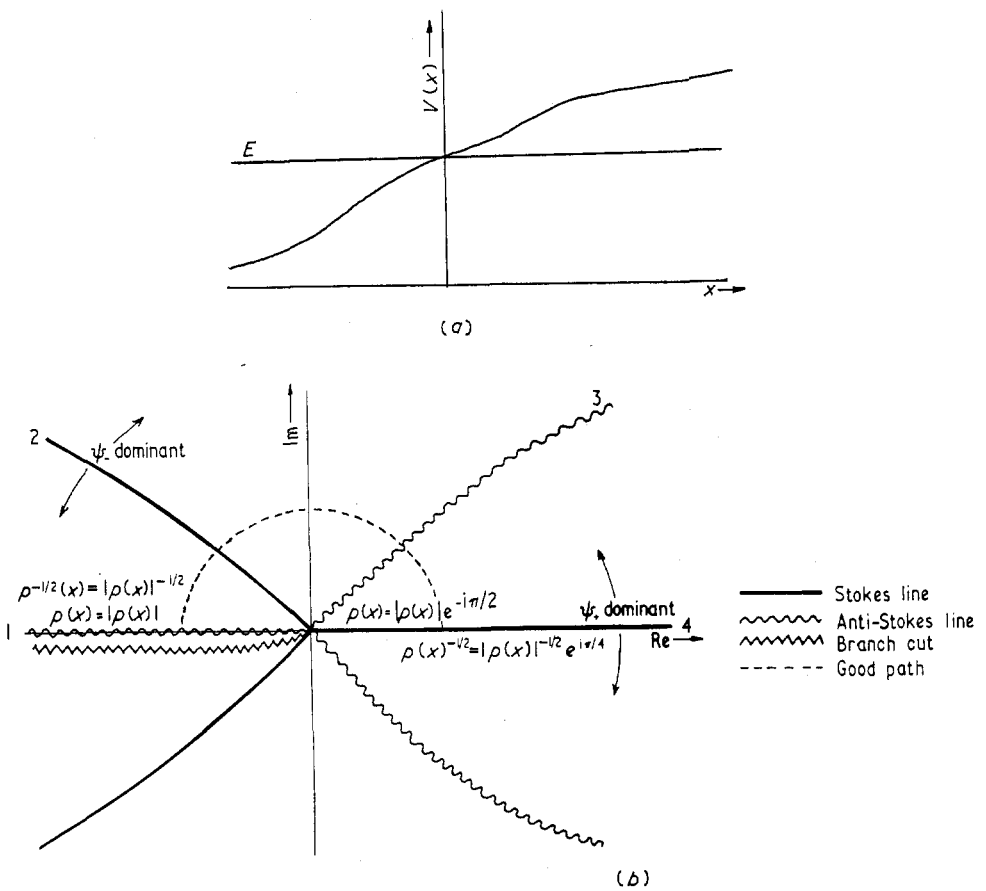

Figure 3. (*a*) Potential $V(x)$ near an isolated turning point. (*b*) Complex x plane near an isolated turning point.

On crossing the Stokes line 2 from anti-Stokes line 1 to the anti-Stokes line 3, ψ_- is dominant, so that only b_+ can change and according to (3.6) we must have, by the principle of exponential dominance,

$$F(3,1) = \begin{pmatrix} 1 & \alpha \\ 0 & 1 \end{pmatrix}. \tag{3.13}$$

When we trace the solution from line 3 to the Stokes line 4, ψ_+ is dominant, so that only b_- can change, and

$$F(4,3) = \begin{pmatrix} 1 & 0 \\ \beta & 1 \end{pmatrix} \tag{3.14}$$

where β is another Stokes constant. Thus the matrix relating the $b_\pm$ on opposite sides of the real axis is simply

$$F(4,1) = F(4,3)\,F(3,1) = \begin{pmatrix} 1 & \alpha \\ \beta & 1+\alpha\beta \end{pmatrix} \tag{3.15}$$

which of course satisfies (3.7). The connection formula for the two approximations to $\psi(x)$ must thus take the form

$$|p(x)|^{-1/2}(b_+(1)\,e^{iw(x)} + b_-(1)\,e^{-iw(x)}) \xleftarrow[x\ll 0]{} \psi(x) \xrightarrow[x\gg 0]{} \frac{e^{i\pi/4}}{|p(x)|^{1/2}}[(b_+(1)+\alpha b_-(1))\,e^{+|w(x)|} + \{\beta b_+(1) + (1+\alpha\beta)\,b_-(1)\}\,e^{-|w(x)|}]. \tag{3.16}$$

In order to make use of the reality principle to obtain information about the unknown Stokes constants α and β, we write

$$b_\pm(1) = \exp\{\pm i(\tfrac{1}{4}\pi - \mu)\} \tag{3.17}$$

which ensures that the solution in the classical region is always real, μ being a phase whose choice selects the different possible independent wave functions (the $\pi/4$ is inserted to simplify the subsequent formulae). Using these values for $b_\pm(1)$, the connection formula becomes

$$\frac{2\cos(w(x)-\mu+\frac{1}{4}\pi)}{|p(x)|^{1/2}} \xleftarrow[x\ll 0]{} \psi(x) \xrightarrow[x\gg 0]{} \frac{1}{|p(x)|^{1/2}}[(i\,e^{-i\mu} + \alpha\,e^{i\mu})\,e^{+|w(x)|} + \{i\beta\,e^{-i\mu} + (1+\alpha\beta)\,e^{i\mu}\}\,e^{-|w(x)|}].$$

The reality principle asserts that the right-hand side must be real for all x and for all solutions μ; this means that the two factors multiplying the exponentials $e^{\pm|w(x)|}$ must separately be real. The reality of the first factor gives, simply,

$$\alpha = -i \tag{3.18}$$

so that the reality of the second factor implies

$$i\beta = (i + i\beta^*) \tag{3.19}$$

which, if we write

$$\beta = |\beta|\,e^{i\gamma} \tag{3.20}$$

in turn implies that

$$|\beta| = -1/2\sin\gamma. \tag{3.21}$$

The final real connection formula resulting from these restrictions on the Stokes constants α and β can be obtained in a form that is valid in the general case where the turning point is not necessarily at $x = 0$ and the allowed region is not necessarily to the left of the forbidden region, by realizing that in our case, from formula (3.12)

$$w(x) = -|w(x)| \qquad (x<0). \tag{3.22}$$

This general connection formula is

$$\underset{\text{(allowed region)}}{\frac{\cos(|w| - \frac{1}{4}\pi + \mu)}{|p|^{1/2}}} \leftarrow \psi(x) \rightarrow \underset{\text{(forbidden region)}}{\frac{\sin\mu}{|p|^{1/2}}\,e^{|w|} - \frac{\sin(\mu-\gamma)}{2\sin\gamma\,|p|^{1/2}}\,e^{-|w|}}. \tag{3.23}$$

Thus our two principles are insufficient to provide a complete connection formula; we have failed to determine the phase angle γ of the Stokes constant β which describes the changes in $b_\pm$ as we move from an anti-Stokes line to a Stokes

line. There is, however, one very important case in which this underdetermination does not matter: if we seek the solution $\psi(x)$ for which the wave function is purely exponentially damped in the forbidden region, then (3.23) shows that we have to take μ equal to zero; the dependence on γ then drops out and we are left with the well known connection formula

$$\frac{\cos(|w|-\frac{1}{4}\pi)}{|p|^{1/2}} \leftarrow \psi(x) \rightarrow \frac{e^{-|w|}}{2|p|^{1/2}}. \tag{3.24}$$

Fröman and Fröman (1965 pp86ff), supported by numerical calculations (Fröman 1966b), argue forcefully that it is wrong to use this relation as a connection formula in the direction allowed→forbidden in the sense explained at the beginning of § 3.1. Their argument is that if a point x_1 is chosen in the allowed region, at which the left-hand side of (3.24) represents the wave function exactly, that is where (cf equation (3.17))

$$b_{\pm}(x_1) = \exp(\pm i\pi/4) \tag{3.25}$$

and the equations (2.26) integrated exactly to find $b_{\pm}(x)$ at points x_2 in the forbidden region, then in general we shall not find the values

$$\left.\begin{aligned} b_+(x_2) &= 0 \\ b_-(x_2) &= \exp(-i\pi/4) \end{aligned}\right\} \tag{3.26}$$

predicted by the connection formula. In particular, $b_+(x_2)$ will not be zero, so that the dominant exponential wave ψ_+ will appear and swamp the other term ψ_-. These conclusions are perfectly correct; the two sides of (3.24) refer to the *asymptotic forms* of the solution $\psi(x)$, and not to its *numerical values*. The phase of the solution $\psi(x)$ which decays into the forbidden region will not be *exactly* $|w|-\pi/4$, but will have some closely related value, $\phi(x)$, say, such that

$$\phi(x) = |w(x)| - \pi/4 + O(\hbar). \tag{3.27}$$

Conversely, the solution whose phase *is* exactly $|w|-\pi/4$ at some point will not be the solution which decays exponentially into the forbidden region.

Turning now to the general case where μ is not equal to zero, we see that the undetermined quantity γ only introduces uncertainty into our knowledge of the exponentially small term, the numerically dominant wave ψ_+ being uniquely known once the phase μ of the asymptotic wave function in the classical region is known. Conversely, if we know only that the wave function is growing exponentially into the forbidden region, but are ignorant of the magnitude b_- of any admixed decaying wave ψ_-, then we can deduce nothing whatever about the asymptotic phase μ, save that it is not close to zero. Thus it is not possible to use (3.23) as a connection formula in the direction forbidden→allowed in those cases where there is a growing exponential wave in the forbidden region, as explained by Fröman and Fröman (1965 p 87).

Fröman (1966b) goes further than asserting the one-directional nature of the connection formulae, and claims to have proved that an exponentially small wave function has no meaning in the presence of a growing exponential, because its coefficient (b_- in the notation of this section) varies rapidly, even along the x axis in the same forbidden region. To examine this point, we observe that there is a high degree of arbitrariness about the coefficient of the exponentially small term. According to equation (3.3), which is valid in a forbidden region, the coefficient of a

dominant exponential, while substantially constant, nevertheless does change by amounts of order $\exp(-2|w|)$; thus we may write for the growing wave

$$\psi_+(x) \equiv \frac{e^{i\pi/4} b_+(x)}{|p(x)|^{1/2}} e^{|w(x)|} = \frac{e^{i\pi/4}}{|p(x)|^{1/2}} (c(x) + d(x) e^{-2|w|}) e^{|w|} \tag{3.28}$$

where $c(x)$ is almost constant and nearly equal to $b_+(x)$, and $d(x)$ is to a large extent arbitrary. For the *total wave* we therefore have

$$\psi(x) = \psi_+ + \psi_- = \frac{e^{i\pi/4}}{|p|^{1/2}} \{c(x) e^{|w(x)|} + (b_-(x) + d(x)) e^{-|w(x)|}\}. \tag{3.29}$$

It is always possible to choose $d(x)$ in such a way that

$$b_-(x) + d(x) = \text{constant} + O(\hbar) \tag{3.30}$$

and this simple rearrangement will result in an exponentially decaying term which, although numerically insignificant, does have a constant coefficient (to order $\hbar$) and is therefore analytically meaningful. We are here taking the point of view expressed in a pungent review by Dingle (1965), from which we quote: 'such difficult questions as those of reversibility of connection formulae must always be discussed specifically in the framework of the theory actually under scrutiny, with careful reference to the precise manner in which orders of approximation are defined in that theory'. Fröman's proof that b_- may change rapidly is perfectly rigorous within the framework provided by (2.26) or similar equations, but it need not hold in the framework of (3.28)–(3.30) which define a quite different kind of coupling between ψ_+ and ψ_-. Within the framework of the theory of 'complete asymptotic expansions' (Olver 1964) where exponentially small quantities are carefully retained even when numerically swamped by other terms, it is actually possible explicitly to calculate the quantity γ which the methods used here were not sophisticated enough to determine; the result is

$$\gamma = -\pi/2 \tag{3.31}$$

so that the second Stokes constant β becomes, from (3.20) and (3.21), simply

$$\beta = -i/2 = \alpha/2 \tag{3.32}$$

(cf equation (3.18)), from which it follows that the change in the subdominant coefficient on crossing a Stokes line is simply twice the change accumulated by moving from an anti-Stokes line onto a Stokes line (see also Dingle 1958). While writing this section we have become indebted to Professor Dingle for letting us see some chapters from his forthcoming book.†

The notation $\leftarrow\psi(x)\rightarrow$ that we have used in our connection formulae was suggested by Heading (1962 p11); the need for such a notation was first recognized explicitly by Jeffreys (1956). We have not attempted to follow in detail the tortuous history of the reversibility problem; readers interested in doing that will find sufficient information in the references cited.

Now let us return to the solution (3.24) which is purely decaying into the forbidden region, corresponding physically to the complete reflection of the incident wave

$$\psi_+ \simeq \frac{\exp(iw(x))}{(p(x))^{1/2}} \tag{3.33}$$

† *Asymptotics as a Discipline of Precision* to be published by Academic Press.

travelling towards the right, in the form of the wave

$$\psi_- \simeq -\frac{\mathrm{i}\exp(-\mathrm{i}w(x))}{(p(x))^{1/2}} \tag{3.34}$$

travelling towards the left, corresponding to a reflection coefficient

$$R = -\mathrm{i} \tag{3.35}$$

(taking the WKB waves as basic, rather than $\exp(\pm \mathrm{i}px/\hbar)$ as in (2.2)). Since no part of our argument has depended essentially on the turning point lying on the real axis, we are at last able to solve the problem of semiclassical reflection above the step posed in § 2.1. The turning point is at x_0, given by (2.37); the Stokes lines and anti-Stokes lines in its neighbourhood, and the good path, are indicated in figure 4. If the incident and reflected waves are given by (3.33) and (3.34), then the phase reference level for the function $w(x)$ must be taken as the turning point x_0.

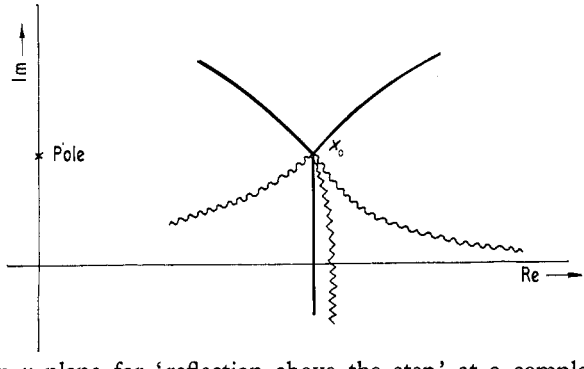

Figure 4. Complex x plane for 'reflection above the step' at a complex turning point x_0 (notation as in figure 3).

This phase is of course real for points x on the anti-Stokes line emanating from x_0, but becomes complex for points x on the negative real axis. It is then convenient to deform the contour, and write

$$w(x_0, x) = w(0, x) - w(0, x_0). \tag{3.36}$$

The complex quantity $w(0, x_0)$ has the same meaning as w_1 in § 2.3. We have now changed our phase reference level to 0, so that we can compare our results with those of § 2.3. The incident wave is now

$$\psi_+ \simeq \frac{\exp(\mathrm{i}w(0, x))}{(p(x))^{1/2}} \exp(-\mathrm{i}w(0, x_0)) \tag{3.37}$$

so that the reflection coefficient referred to 0 is

$$R = -\mathrm{i}\exp(2\mathrm{i}w(0, x_0)) \tag{3.38}$$

which is to be compared with the value (2.34) given by the Bremmer theory. The power reflected is

$$|R|^2 = \exp(-4|\operatorname{Im} w(0, x_0)|) \tag{3.39}$$

which on making use of (2.38) gives precisely the value (2.5), which we know to be correct since it comes directly from the exact solution (2.4).

Such simple results as (3.35) would not seem to require for their derivation the substantial formalism that we have built up, involving Stokes lines, etc; indeed,

some authors (eg Eckersley 1950, Landau and Lifshitz 1965), simply take a branch cut from $x = -\infty$ to the turning point x_0 (real or complex) and assert that if the incident wave is represented by

$$\frac{\exp(\mathrm{i}w(x_0, x))}{(p(x))^{1/2}}$$

on one side of the cut, then the reflected wave is given by the analytic continuation of this function, evaluated on the other side of the cut. This method certainly gives the correct results in simple cases, but there appears to be no valid derivation of it which does not rest ultimately on arguments similar to ours (see eg Heading 1962 p85).

Perhaps the most important application of the connection formula (3.24) is its use in determining the approximate phase shifts for scattering from a spherically symmetric potential (Mott and Massey 1965 § V5). The reduced one-dimensional Schrödinger equation involves the radial coordinate r, and an effective potential $V_{\mathrm{eff}}(r)$ and momentum function $p_{\mathrm{eff}}(r)$ whose peculiarities will be discussed in §5. Since the wave function must vanish at the origin $r = 0$, our formula (3.24) is directly applicable if there is only one turning point, at $r = r_0$, say (see figure 5).

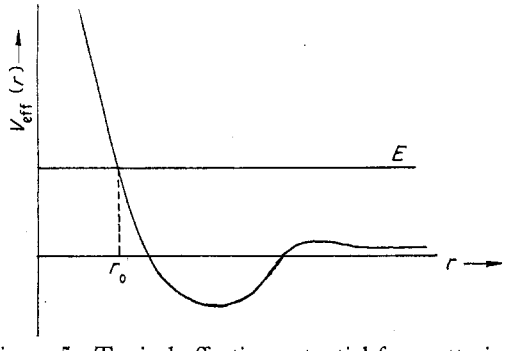

Figure 5. Typical effective potential for scattering.

The phase-integral w is thus

$$w(r) = \int_{r_0}^{r} \frac{p_{\mathrm{eff}}(r')\,\mathrm{d}r'}{\hbar}. \tag{3.40}$$

The phase shift $\eta_l(E)$, for angular momentum l and energy E, is defined by stipulating that the wave function for very large r (where $V_{\mathrm{eff}}(r) \to 0$) must have the form

$$\psi(r) \to \sin\left(\frac{p(\infty)\,r}{\hbar} - \frac{l\pi}{2} + \eta_l(E)\right) \tag{3.41}$$

which, on comparison with (3.24) gives immediately the result

$$\eta_l(E) \simeq \int_{r_0}^{\infty} \mathrm{d}r \frac{(p_{\mathrm{eff}}(r) - p(\infty))}{\hbar} + (l + \tfrac{1}{2})\frac{\pi}{2} - \frac{p(\infty)\,r_0}{\hbar}. \tag{3.42}$$

Finally, let us examine the classical limit of this 'reflection' wave function when the turning point is real. From (3.24), the probability density is

$$\frac{\cos^2(|w| - \frac{1}{4}\pi)}{|p(x)|} \leftarrow \psi^2(x) \to \frac{\mathrm{e}^{-2|w|}}{4|p(x)|}. \tag{3.43}$$

As $\hbar \to 0$, $|w|$ becomes very large (see equation (2.22)) everywhere except in a neighbourhood Δx of the turning point which shrinks to a point in the classical limit. The oscillations on the classically allowed side then become infinitely rapid, so that we can replace $\cos^2(|w| - \frac{1}{4}\pi)$ by its average value of $1/2$ for the purposes of using $\psi^2(x)$ to calculate the probability of finding particles in any finite range of x; on the forbidden side, the exponential vanishes and we have

$$\underset{\text{(allowed region)}}{1/p(x)} \quad \leftarrow 2\psi^2(x) \rightarrow \quad \underset{\text{(forbidden region)}}{0.} \tag{3.44}$$

This is exactly the expected result for the density of classical particles sliding smoothly part-way up a hill which they have insufficient energy to surmount. The singularity at the turning point is of the form

$$1/p(x) \propto 1/(x - x_0)^{1/2} \tag{3.45}$$

which is integrable, so that we are not predicting that an infinite total number of particles congregate in that neighbourhood.

Essentially the same methods that we have outlined here can be used to derive connection formulae, analogous to (3.23) for single turning points of higher order, in the neighbourhood of which we have, instead of (3.9)

$$p^2(x) \simeq x^n \tag{3.46}$$

(see eg Heading 1962 p89).

3.3. *More turning points*

In the case of a real potential barrier of height V_0 (figure 6(*a*)), there are two real classical turning points x_- and x_+ if $E < V_0$ (in the literature this is referred to as the 'overdense' barrier), and two complex turning points if $E > V_0$ (the 'underdense' case). We shall work out the overdense case, since it is easy to understand, but our results, if correctly interpreted, hold for the underdense case as well. The Stokes lines, choice of phase for $p(x)$, etc are shown in figure 6(*b*). If we introduce the Stokes constants α and β when crossing the lines 2 and 4 we can trace the solution round both turning points between the negative real axis (line 1) and the positive real axis (line 5); using the principle of exponential dominance outlined in § 3.1 and applied in § 3.2, we obtain successively

$$\left.\begin{aligned} F(3,1) &= \begin{pmatrix} 1 & 0 \\ \alpha & 1 \end{pmatrix} \\ F(5,3) &= \begin{pmatrix} 1 & \beta \\ 0 & 1 \end{pmatrix} \\ F(5,1) &= \begin{pmatrix} 1+\alpha\beta & \beta \\ \alpha & 1 \end{pmatrix}. \end{aligned}\right\} \tag{3.47}$$

Our connection formula between the two classical regions $x < x_-$, $x > x_+$ must therefore take the form

$$\frac{-\mathrm{i}}{|p(x)|^{1/2}}\left[b_+(1)\,\mathrm{e}^{\mathrm{i}w(x)} + b_-(1)\,\mathrm{e}^{-\mathrm{i}w(x)}\right] \leftarrow \psi(x) \rightarrow$$

$$\frac{1}{|p(x)|^{1/2}}\left[\{(1+\alpha\beta)\,b_+(1) + \beta b_-(1)\}\,\mathrm{e}^{\mathrm{i}w(x)} + (\alpha b_+(1) + b_-(1))\,\mathrm{e}^{-\mathrm{i}w(x)}\right].$$

The value of the Stokes constants α and β will depend on the choice of phase reference level, and we stipulate this to be the point x_+. For points in the classical region $x < x_-$, however, the phase will be complex, and it is more natural to rewrite

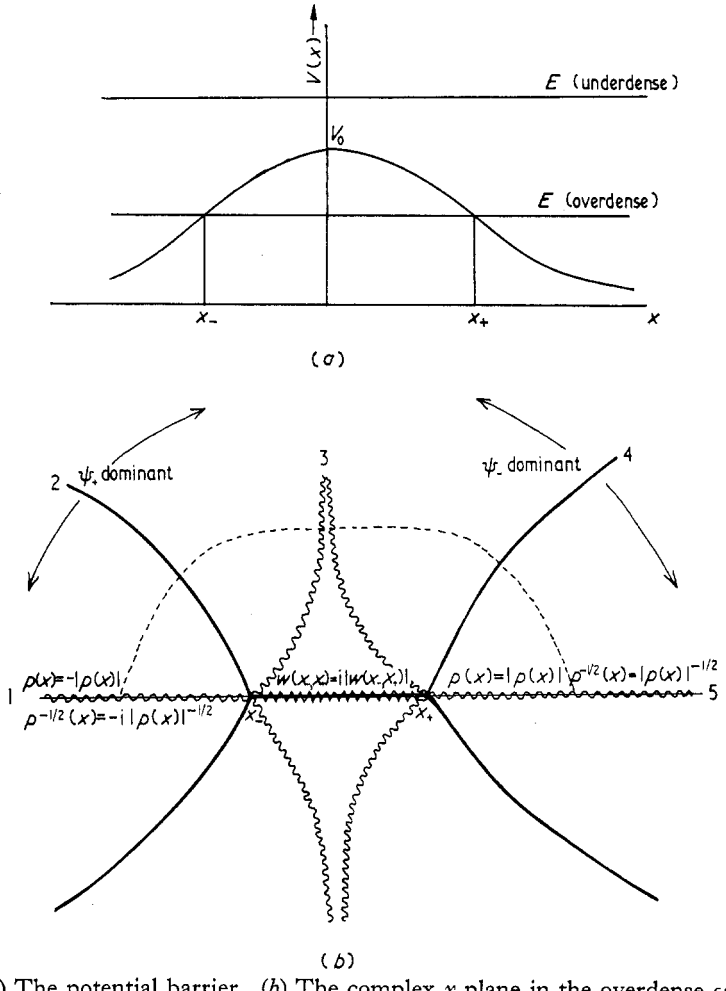

Figure 6. (*a*) The potential barrier. (*b*) The complex x plane in the overdense case (notation as in figure 3).

the phase on that side in terms of $w(x_-, x)$ using

$$\begin{aligned} w(x_+, x) &= w(x_-, x) - \mathrm{i}\,|w(x_-, x_+)| \\ &\equiv w(x_-, x) - \mathrm{i}W \\ &\equiv w(x_-, x) - \mathrm{i}\frac{K(E)}{\hbar} \end{aligned} \tag{3.48}$$

where $K(E)$ is defined as

$$K(E) = -\mathrm{i}\int_{x-}^{x+} \{2m(E - V(x))\}^{1/2}\,\mathrm{d}x \tag{3.49}$$

a positive quantity, evaluated in terms of *classical* quantities in the *forbidden* region.

The connection formula now becomes

$$\frac{-\mathrm{i}}{|p(x)|^{1/2}}(b_+(1)\,\mathrm{e}^{W}\,\mathrm{e}^{\mathrm{i}w(x_-,x)}+b_-(1)\,\mathrm{e}^{-W}\,\mathrm{e}^{-\mathrm{i}w(x_-,x)})\leftarrow\psi(x)\rightarrow$$

$$\frac{1}{|p(x)|^{1/2}}[\{(1+\alpha\beta)\,b_+(1)+\beta b_-(1)\}\,\mathrm{e}^{\mathrm{i}w(x_+,x)}+(\alpha b_+(1)+b_-(1))\,\mathrm{e}^{-\mathrm{i}w(x_+,x)}]. \quad (3.50)$$

The reflection of waves incident from the left corresponds to the solution

$$\frac{\mathrm{e}^{-\mathrm{i}w(x_-,x)}}{|p|^{1/2}}+\frac{R\,\mathrm{e}^{+\mathrm{i}w(x_-,x)}}{|p|^{1/2}}\leftarrow\psi(x)\rightarrow\frac{T\,\mathrm{e}^{\mathrm{i}w(x_+,x)}}{|p|^{1/2}} \quad (3.51)$$

(the term whose exponent is $-\mathrm{i}w$ represents the incident wave because $p(x)$ is negative for $x<x_-$ with our choice of phase (see figure 6(*b*))). Comparison of this function with the general case (3.50) gives expressions for T and R in terms of the Stokes constants:

$$\left.\begin{aligned} T&=-\frac{\mathrm{i}\,\mathrm{e}^{W}}{\alpha}\\ R&=-\frac{\mathrm{e}^{2W}}{\alpha}. \end{aligned}\right\} \quad (3.52)$$

To apply the reality condition the left-hand side of (3.50) must be real; this is ensured by choosing (cf equation (3.17))

$$b_\pm(1)=\mathrm{i}\exp(\pm\mathrm{i}\mu\mp W) \quad (3.53)$$

which, because of the consequent necessity of the reality of the right-hand side of (3.50) implies

$$(1+\alpha\beta)\,\mathrm{i}\,\mathrm{e}^{\mathrm{i}\mu}\,\mathrm{e}^{-W}+\beta\mathrm{i}\,\mathrm{e}^{-\mathrm{i}\mu}\,\mathrm{e}^{W}=-\alpha^*\,\mathrm{i}\,\mathrm{e}^{-\mathrm{i}\mu}\,\mathrm{e}^{-W}+\mathrm{i}\,\mathrm{e}^{\mathrm{i}\mu}\,\mathrm{e}^{W} \quad (3.54)$$

for all μ. In terms of α and β, this requires

$$\left.\begin{aligned} |\alpha|&=\mathrm{e}^{2W}(1+\mathrm{e}^{-2W})^{1/2}\\ \beta&=-\alpha^*\,\mathrm{e}^{-2W} \end{aligned}\right\} \quad (3.55)$$

so that once again we are able to determine the Stokes constants completely save for a single phase angle; if we denote this by δ, defined by

$$\alpha=-\mathrm{i}|\alpha|\,\mathrm{e}^{\mathrm{i}\delta} \quad (3.56)$$

then the general connection formula (3.50) takes its final form for real wave functions, namely

$$\frac{\cos(|w(x_-,x)|+\mu)}{|p(x)|^{1/2}}\leftarrow\psi(x)\rightarrow\frac{\mathrm{e}^{W}}{|p(x)|^{1/2}}\{2+\mathrm{e}^{-2W}+2(1+\mathrm{e}^{-2W})^{1/2}\sin(2\mu+\delta)\}^{1/2}$$

$$\times\sin\left[|w(x_+,x)|+\frac{\pi}{4}-\frac{\delta}{2}+\tan^{-1}\left\{\tan\left(\frac{\pi}{4}-\mu-\frac{\delta}{2}\right)\left(\frac{(1+\mathrm{e}^{-2W})^{1/2}-1}{(1+\mathrm{e}^{-2W})^{1/2}+1}\right)\right\}\right]. \quad (3.57)$$

Formulae equivalent to this have been derived by Fröman and Fröman (1970); this result is the analogue of our single turning-point formula (3.23).

We shall shortly describe an application of our formula (3.57); meanwhile let us examine the more familiar transmission and reflection coefficients. From (3.52),

(3.55) and (3.56) we have, making use of (3.48) and (3.49)

$$\left.\begin{aligned} T(E) &= \frac{\mathrm{e}^{-K(E)/\hbar}\,\mathrm{e}^{-\mathrm{i}\delta(E)}}{(1+\mathrm{e}^{-2K(E)/\hbar})^{1/2}} \\ R(E) &= \frac{-\mathrm{i}\,\mathrm{e}^{-\mathrm{i}\delta(E)}}{(1+\mathrm{e}^{-2K(E)/\hbar})^{1/2}} \end{aligned}\right\} \tag{3.58}$$

a result first derived by Kemble (1935), who showed by a process of analytical continuation that it is also valid in the underdense case, where $E > V_0$, when the limits of the integral $K(E)$ in (3.49) must be taken as the two complex turning

Figure 7. 'Good path' in the overdense case when $E \ll V_0$.

points, so that $K(E)$ is real and *negative*; the quantities R and T in (3.58) then refer to WKB waves whose phase reference level is the point

$$x_0 = \frac{x_+ + x_-}{2} \tag{3.59}$$

which lies on the real axis.

We thus know T and R over the entire range of energies to within the phase $\delta(E)$, which our methods are not powerful enough to determine. However, we can get rather a lot of information about δ by considering various limiting cases. In the extreme overdense case $E \ll V_0$ we can then choose a good path as in figure 7, and treat x_- and x_+ independently. T and R can then be derived by a double application of the single turning-point formula (3.23), taking due care to change the phase reference level. The undetermined quantity γ which that formula involved does not appear in the result if we only retain the limiting asymptotic forms as $K(E)/\hbar \to \infty$; problems of reversibility do not therefore arise, and this method gives

$$\left.\begin{aligned} T(E) &\xrightarrow[E \ll V_0]{} \mathrm{e}^{-K(E)/\hbar} \\ R(E) &\xrightarrow[E \ll V_0]{} -\mathrm{i}. \end{aligned}\right\} \tag{3.60}$$

The small value of T describes the particles which penetrate the barrier by tunnelling, while the reflection coefficient, being the same as (3.35), indicates that only the turning point x_- is effective for reflection in this limit. Direct comparison of these values R and T with the limits of general expressions (3.58) shows that, far below the barrier top, $\delta(E)$ is zero. Similar considerations for the extreme underdense case show that $\delta(E)$ is zero in this case also, and if one treats the intermediate case $E = V_0$ where the two turning points coalesce into a single turning point of second order by the methods of § 3.2, it is found that $\delta(E)$ is zero in this case as well. Thus the complex method shows that

$$\delta(E) = 0 \qquad \left.\begin{aligned} E &\gg V_0 \\ E &= V_0 \\ E &\ll V_0 \end{aligned}\right\}. \tag{3.61}$$

It is tempting to set δ equal to zero for all E, but this would be a mistake, as the following argument indicates. If we choose $\mu(E)$ in such a way that the left side of (3.57) is analytic in E (for a given x) near the region $E = V_0$ then $\delta(E)$ must be such that the right side is analytic also; a simple calculation of the form of $w(x_-,x)$ near the barrier top then leads to the result

$$\delta(E)_{E\simeq V_0} = \frac{K(E)}{\pi\hbar}\ln\left|\frac{K(E)}{\pi\hbar}\right| \tag{3.62}$$

so that δ cannot be zero everywhere. This indeterminacy of the phase has been discussed by Fröman and Fröman (1965 p50) and δ has been evaluated by more

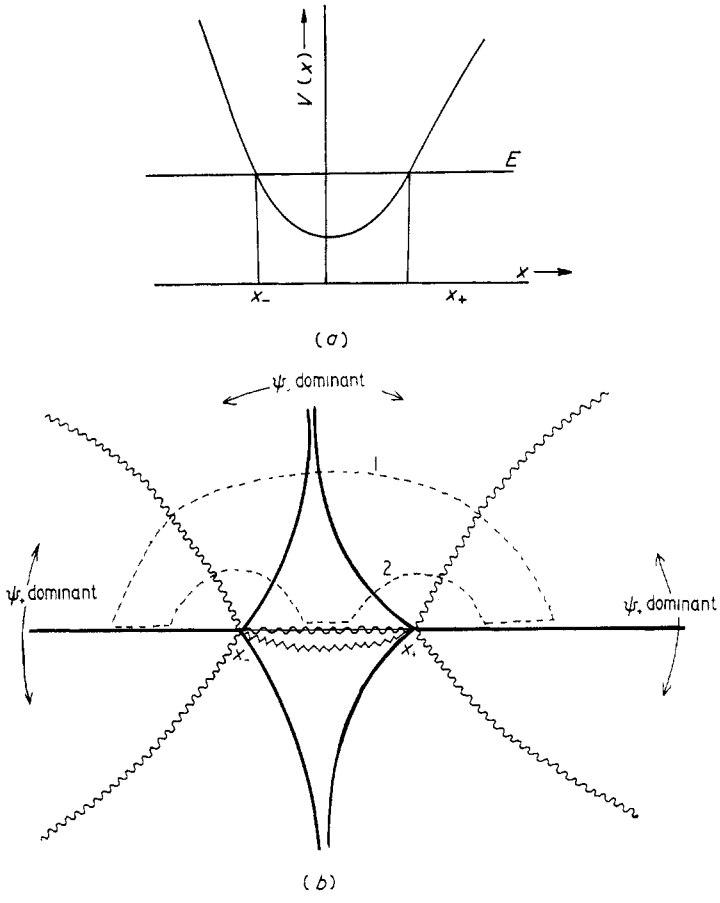

Figure 8. (*a*) The potential well. (*b*) Complex x plane for potential well (notation as in figure 3).

powerful methods, to which we shall refer in §4.2, by Ford *et al* (1959) and by Soop (1965), who show that $|\delta|$ never exceeds about 10°, this value occurring when $K(E)/\hbar \simeq \pm\pi/3$.

We must now discuss the case where two real turning points bound a classically allowed region; this is the case of the *potential well*, which is shown in figure 8(*a*), while its Stokes lines, etc appear in figure 8(*b*).

The 'good path' labelled 1 can validly be used however close the points x_- and x_+ are. But there are now three Stokes lines, so that we need three complex

Stokes constants, instead of two as in our previous examples; this seriously increases the underdetermination in the resulting connection formulae, even when account is taken of the slight amount of extra information provided by the reality condition for this case. The general connection formula involves three real unknown quantities; we shall write down only the connection formula for the case where the wave function is known to decay exponentially into the left-hand forbidden region:

$$\frac{\mathrm{e}^{-|w(x_-,x)|}}{|p|^{1/2}} \leftarrow \psi(x) \rightarrow \frac{A\cos\left(S(x_-,x_+)/\hbar\right)}{|p|^{1/2}}\,\mathrm{e}^{|w(x_+,x)|} - \frac{\cos\left(S(x_-,x_+)/\hbar+\gamma\right)}{\sin\gamma\,|p|^{1/2}}\,\mathrm{e}^{-|w(x_+,x)|}. \quad (3.63)$$

A and γ are the two unknown quantities introduced by the complex method while $S(x_-, x_+)$ is the classical action function across the well, defined by (2.22).

The limitations of the complex method are very clearly shown up by this example; not even the coefficient of the dominant wave can be determined. However, there are two special cases where more information can be obtained about the wave; the first involves energies for which

$$S(x_+, x_-) = (n+\tfrac{1}{2})\pi\hbar. \quad (3.64)$$

At these energies the coefficient of the dominant exponential vanishes and γ drops out of the coefficient of the other term; the wave, which we can denote by $\psi_n(x)$, becomes

$$\frac{\mathrm{e}^{-|w(x_-,x)|}}{|p(x)|^{1/2}} \leftarrow \psi_n(x) \rightarrow (-1)^n \frac{\mathrm{e}^{-|w(x_+,x)|}}{|p(x)|^{1/2}}. \quad (3.65)$$

This clearly represents a square-integrable wave function, admissible as an eigenfunction in quantum mechanics, and (3.64) is of course the well known quantization condition for a bound state whose derivation (see eg Dunham 1932) was one of the earliest successes of the semiclassical method. The $(-1)^n$ factor in (3.65) shows that the eigenfunctions are alternatively of even and odd parity, the ground state being even. There are several other ways of deriving (3.64) which will be discussed when we treat quantization in a more general way in § 7.4.

The coefficient A of the dominant wave in (3.63) can be found in the second special case we shall consider, where the energy is sufficiently far above the bottom of the well for the turning points to be well separated, so that the 'good path' labelled 2 in figure 8 can be used, enabling the simpler connection formula (3.23) to be used twice. When this is done the resulting connection formula is identical with (3.63), except that

$$A = 2 \quad (3.66)$$

so that for energies lying between the higher eigenvalues we do know the coefficient of the exponentially growing wave, although we still do not know the coefficient of the accompanying decaying wave (except where this wave exists alone at the eigenvalues themselves). Our eigenvalue condition (3.64) is of course not restricted to large values of n, as was realized by Kemble (1935).

As a final illustration, demonstrating the full power of the complex method, let us discuss the problem of calculating the scattering phase shifts $\eta_l(E)$ defined by (3.41) when there are *three turning points*, so that the effective potential, and the complex r plane, take the forms shown in figure 9(*a*,*b*), which are drawn for the case where E lies between the well bottom V_W and the barrier top V_B, so that the turning points are real although the theory works for $E > V_B$ as well. If E is not too near to V_W, r_3 and r_2 are sufficiently far apart for the good path to be taken as

indicated, so that the phase shift can be derived by starting with a real wave function decaying exponentially to the left away from r_3 (to satisfy the boundary condition at $r = 0$ (see § 5)) applying successively the single turning-point connection formula (3.24) and the 'barrier' connection formula (3.57), and finally comparing the wave

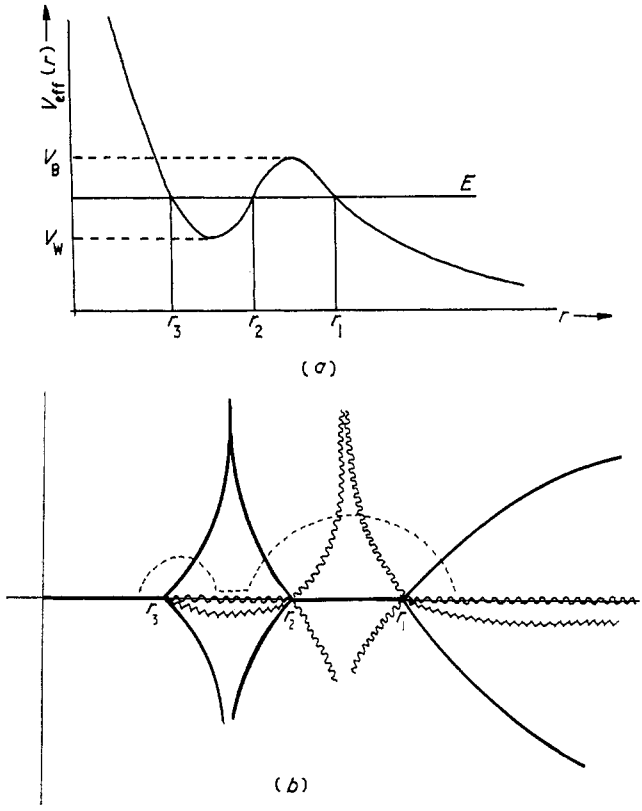

Figure 9. (*a*) Effective scattering potential when there are three turning points. (*b*) Complex r plane (notation as in figure 3).

function for $r \to \infty$ with the definition (3.41). The result is

$$\eta_l(E) = \eta_l^{(0)}(E) - \frac{\delta}{2} + \tan^{-1}\left\{\tan\left(\frac{S}{\hbar} - \frac{\delta}{2}\right)\left(\frac{(1+e^{-2K/\hbar})^{1/2}-1}{(1+e^{-2K/\hbar})^{1/2}+1}\right)\right\} \tag{3.67}$$

where $\eta_l^{(0)}(E)$ is the WKB phase shift (3.42), evaluated with respect to the outer turning point r_1, and (cf equation (3.49))

$$S \equiv S(r_3, r_2) \qquad K \equiv K(r_2, r_1). \tag{3.68}$$

The classical situation corresponding to figure 9(*a*) is that there are two mutually inaccessible regions where particles can exist, in the well ($r_3 < r < r_2$) and in the free space outside ($r > r_1$). The appearance of S, which refers to the well, in our semiclassical formula (3.67) would seem to imply (Barker and Johnson 1965) that in the classical limit the scattering depends on the behaviour of $V(r)$ in inaccessible regions. This 'paradox' was cleared up by Berry (1966a), who rederived the limit of (3.67) which is valid when E is not near the barrier top (ie $K/\hbar \ll 1$), namely

$$\eta_l(E) = \eta_l^{(0)}(E) + \tan^{-1}\left\{\tan\left(\frac{S}{\hbar}\right)\frac{e^{-2K/\hbar}}{4}\right\} \tag{3.69}$$

(a formula originally due to Buckingham and Dalgarno (1952)), and showed that the phase shift is insensitive to the potential for $r < r_1$ except very near to *resonance energies* where quasibound states (given by (3.64)) exist in the potential well, but that these resonances do not contribute to the classical limit of observable scattering phenomena (nor do they contribute to the *semi*classical limit, as we shall see in § 6).

The general formula (3.67) was originally derived by Dubrovskii (1964), and Miller (1968b), who gives a very clear discussion of the resonance behaviour (including the region $E \simeq V_B$); readers are cautioned that Miller uses the terms Stokes and anti-Stokes line in the opposite sense to that generally adopted. Using a 'good path' surrounding all three turning points, Miller shows also that (3.67) applies for energies near the bottom of the well, where S is small, provided that $K(E)$ is replaced by $K(E)+f(E)$, $f(E)$ being a function which the complex method is unable to determine completely, analogous to $\delta(E)$; in the general case, nothing is known about δ and f for $V_B > E > V_W$, so that we are totally ignorant of the phase shift, but in the more common cases, where $V_B - V_W$ is fairly large, use can be made of the limiting expression (3.69) to gain information about f and δ (see also § 4.2). Ford *et al* (1959) give a very thorough discussion of phenomena at energies in the immediate neighbourhood of a barrier maximum, and Herm (1967) finds that their results are in excellent numerical agreement with the exact phase shift calculations of Bernstein *et al* (1966); the notation used by Ford *et al* is not directly related to the corresponding classical problem, which makes their paper hard to follow (see also § 4.2). Finally, Livingston (1966) approached the same problem by using the WKB expressions for the transmission and reflection coefficients of a potential barrier, and summing up the effect of the waves multiply reflected by the potential well (see also § 7.4). The expression for the phase shift obtained by this method can be written as

$$\eta_l = \eta_l^{(0)}(E) + \tfrac{1}{2}\tan^{-1}\left(\frac{e^{-2W}\sin(2S/\hbar)}{2(1+e^{-2W})^{1/2}+(2+e^{-W})\cos(2S/\hbar)}\right). \qquad (3.70)$$

This result is equivalent to, but not so convenient as (3.67), with δ set equal to zero. In a discussion of this formula, Livingston by an incorrect choice of quadrant for the arctangent predicts a spurious pairing of the resonances (see Connor 1969).

Other problems can be treated by the complex method; they include the 'double-well' potential (Fröman 1966c, Dennison and Uhlenbeck 1932, Pshenichnov and Sokolov 1961) and the one-dimensional periodic lattice (Heading 1962 p118, Landauer 1951, Dykhne 1961, Balazs 1969). The main strength of the complex method lies in its simplicity—all turning-point problems can be treated using the two principles outlined in § 3.1. The method has two main drawbacks: certain quantities (eg γ in (3.23) and δ in (3.57)) cannot be determined, and we are left in complete ignorance of the behaviour of wave functions in the neighbourhood of turning points. It was to remedy these defects that the method of 'uniform approximation' was developed, and it is to this that we now turn.

4. Uniform approximations for one-dimensional problems

4.1. *The method of comparison equations*

This method for obtaining the approximate solutions of linear second-order differential equations, such as the Schrödinger equation, was first set out by Miller and Good (1953) and by Dingle (1956). It is a generalization of the basic WKB

method, the idea being to obtain an approximate solution of the differential equation

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+\chi(x)\,\psi(x)=0 \tag{4.1}$$

in terms of the known solutions $\phi(\sigma)$ of the equation

$$\frac{\mathrm{d}^2\phi(\sigma)}{\mathrm{d}\sigma^2}+\Gamma(\sigma)\,\phi(\sigma)=0. \tag{4.2}$$

$\Gamma(\sigma)$ is chosen to be similar in some way to $\chi(x)$, but simpler, so that the solutions of (4.2) are known. Because $\Gamma(\sigma)$ is similar to $\chi(x)$, the wave function $\phi(\sigma)$ should also be similar to $\psi(x)$ and can be changed into it by stretching or contracting it a little and changing the amplitude a little. $\psi(x)$ is expressed in terms of $\phi(\sigma)$ by

$$\psi(x)=f(x)\,\phi(\sigma(x)). \tag{4.3}$$

Substituting this definition into (4.1) and using (4.2) gives

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\phi+\chi f\phi-f\left(\frac{\mathrm{d}\sigma}{\mathrm{d}x}\right)^2\Gamma\phi+\frac{\mathrm{d}\phi}{\mathrm{d}\sigma}\left(\frac{2\mathrm{d}f}{\mathrm{d}x}\frac{\mathrm{d}\sigma}{\mathrm{d}x}+f\frac{\mathrm{d}^2\sigma}{\mathrm{d}x^2}\right)=0. \tag{4.4}$$

On making the identification

$$f=\left(\frac{\mathrm{d}\sigma}{\mathrm{d}x}\right)^{-1/2}$$

(4.4) simplifies to finding the 'mapping function' $\sigma(x)$ as the solution of

$$\chi=\left(\frac{\mathrm{d}\sigma}{\mathrm{d}x}\right)^2\Gamma-\left(\frac{\mathrm{d}\sigma}{\mathrm{d}x}\right)^{1/2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}x}\right)^{-1/2}. \tag{4.5}$$

If we have chosen the comparison function $\Gamma(\sigma)$ to be sufficiently similar to $\chi(x)$, $\sigma(x)$ will be a slowly varying function and the second term on the right-hand side of (4.5) will be negligible compared with the first so that

$$\frac{\mathrm{d}\sigma}{\mathrm{d}x}\simeq\left(\frac{\chi(x)}{\Gamma(\sigma)}\right)^{1/2}. \tag{4.6}$$

By selecting a pair of points σ_0 and x_0 which are 'equivalent', $\sigma(x)$ can be written implicitly as

$$\int_{\sigma_0}^{\sigma}(\Gamma(\sigma))^{1/2}\,\mathrm{d}\sigma=\int_{x_0}^{x}(\chi(x))^{1/2}\,\mathrm{d}x \tag{4.7a}$$

or

$$\int_{\sigma_0}^{\sigma}(-\Gamma(\sigma))^{1/2}\,\mathrm{d}\sigma=\int_{x_0}^{x}(-\chi(x))^{1/2}\,\mathrm{d}x \tag{4.7b}$$

whichever is more convenient. The approximate solution of (4.1) is then given by

$$\psi(x)\simeq\left[\frac{\Gamma(\sigma(x))}{\chi(x)}\right]^{1/4}\phi(\sigma(x)) \tag{4.8}$$

$\sigma(x)$ being given by (4.7 (a,b)). The condition for $\Gamma(\sigma)$ and $\chi(x)$ to be sufficiently similar for (4.8) to be a good solution is easily calculated from (4.5) to be

$$\epsilon(x)\equiv\left|\frac{1}{\chi(x)}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}x}\right)^{1/2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}x}\right)^{-1/2}\right|\ll 1. \tag{4.9}$$

Hecht and Mayer (1957), Moriguchi (1959) and Pechukas (1971) have studied the transformation between $\psi(x)$ and $\phi(\sigma)$ in great detail, developing a formalism enabling the higher terms to be studied.

The result (4.8) gives a uniform approximation for $\psi(x)$, valid for the whole range of x, including turning points. In order for the method to work, the mapping (change of variables) from x to σ must be one to one; this means that $\mathrm{d}\sigma/\mathrm{d}x$ must never be zero or infinite, so that (cf equation (4.6)) the zeros of $\chi(x)$ and $\Gamma(\sigma)$ must be made to correspond. We thus have what is potentially a very powerful principle: in the semiclassical limit all problems are equivalent which have the same *classical turning-point structure*. The problems discussed in § 3 have not been avoided, however, because it is still necessary to solve the connection problem for the comparison equation; happily, there are a few cases where the connection problem has been solved completely so that a uniform approximation can be found. We shall now look at two quite different applications of this method.

4.2. *Simple turning-point problems*

It is interesting to see first of all how the simple WKB results can be obtained from the method of § 4.1. In a classically allowed region, we choose $\Gamma(\sigma) = 1$, and the solutions of the Schrödinger equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{p^2(x)}{\hbar^2}\psi = 0 \tag{4.10}$$

are obtained in terms of the standard solutions

$$\phi = \mathrm{e}^{\pm \mathrm{i}\sigma} \tag{4.11}$$

of the comparison equation

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}\sigma^2} + \phi = 0.$$

The mapping relation equivalent to (4.6) is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}x} = \frac{p(x)}{\hbar} \tag{4.12}$$

and we regain the familiar solution

$$\psi(x) \simeq \frac{b_+}{(p(x))^{1/2}} \exp\left(\frac{\mathrm{i}}{\hbar}\int_{x_0}^{x} p(x')\,\mathrm{d}x'\right) + \frac{b_-}{(p(x))^{1/2}} \exp\left(-\frac{\mathrm{i}}{\hbar}\int_{x_0}^{x} p(x')\,\mathrm{d}x'\right). \tag{4.13}$$

This solution is not valid near a classical turning point where $p^2(x)$ has a zero, because the mapping in (4.12) is no longer one to one. (The second term in (4.5), which we dropped as negligible, will now be dominant and (4.9) is violated.) The WKB solution on the other side of the turning point, in the classically forbidden region, corresponds to the choice $\Gamma(\sigma) = -1$ and gives

$$\psi(x) \simeq \frac{C_+}{|p(x)|^{1/2}} \exp\left(\frac{1}{\hbar}\int_{x_0}^{x} |p(x)|\,\mathrm{d}x\right) + \frac{C_-}{|p(x)|^{1/2}} \exp\left(-\frac{1}{\hbar}\int_{x_0}^{x} |p(x)|\,\mathrm{d}x\right). \tag{4.14}$$

These are quite distinct solutions, obtained from different comparison functions, and so give us no information about the problem of connection across a turning point. The reason is that $\Gamma(\sigma)$ is not sufficiently like $p^2(x)/\hbar$.

Langer (1937) was the first to use a nonconstant comparison potential $\Gamma(\sigma)$ to deal with the case of a potential with one turning point. He considered a turning point of order ν—one in which $p^2(x)$ had a zero of order ν. For simplicity, and to fit in with the earlier treatment of one turning point by the complex method, we shall consider here just a first-order turning point.

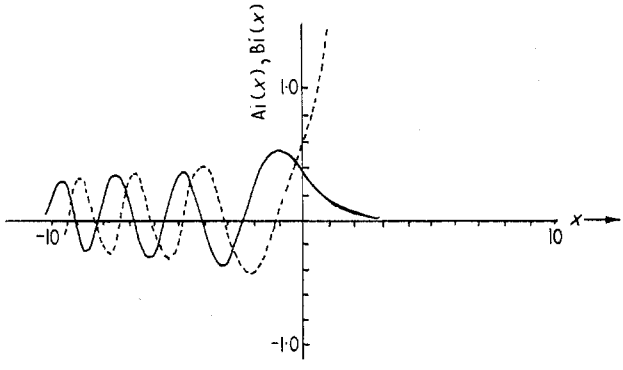

Figure 10. Solutions of the Airy equation. Full curve, Ai(x); broken curve, Bi(x).

We want to get an approximate solution to equation (4.10) in a region where $p^2(x)$ has a simple zero, say at $x = 0$ (see figure 3(a)). For such a potential, a suitable comparison function is $\Gamma(\sigma) = -\sigma$, and the comparison equation is then

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}\sigma^2} - \sigma\phi = 0. \tag{4.15}$$

This is the Airy equation (see Abramowitz and Stegun 1964 p446) with the two independent solutions Ai(σ) and Bi(σ) (figure 10). The mapping function $\sigma(x)$ is given by

$$\tfrac{2}{3}\sigma^{3/2} = \int_0^x \left(-\frac{p^2(x)}{\hbar^2}\right)^{1/2} \equiv w$$

and the approximate solution of the Schrödinger equation is

$$\psi(x) \simeq \left[\frac{\sigma(x)}{p^2(x)}\right]^{1/4} (\alpha \mathrm{Ai}(\sigma(x)) + \beta \mathrm{Bi}(\sigma(x))) \tag{4.16}$$

where α and β are constants determined by the boundary conditions. (For instance, if there is no other turning point for $x > 0$, $\psi(x)$ must decay exponentially to zero as $x \to \infty$ so that β, the coefficient of the 'increasing' solution Bi(σ), must be zero.)

The functions Ai(σ) and Bi(σ) are very well understood; in particular, *exact* connection formulae can be established by direct analysis of convergent series expansions, without the need to rely on the complex method. (The original analysis was carried out by Stokes (1904, 1905); a more accessible treatment is given by Heading (1962 p143).) Using these known asymptotic forms for Ai(σ) and Bi(σ), the general connection formula across a linear turning point is easily worked out to be

$$\frac{\cos(|w| - \frac{1}{4}\pi + \mu)}{|p(x)|^{1/2}} \leftarrow \cos\mu \mathrm{Ai}(\sigma) + \sin\mu \mathrm{Bi}(\sigma) \rightarrow \frac{\cos\mu\, \mathrm{e}^{-|w|}}{2|p(x)|^{1/2}} + \frac{\sin\mu\, \mathrm{e}^{+|w|}}{|p(x)|^{1/2}}. \tag{4.17}$$

Comparing this with (3.23), obtained by the complex method, we see that the previously undetermined phase γ can be taken as $(n + \frac{1}{2})\pi$. By using the present

method it has been possible to obtain more information; not only does the theory contain no undetermined factors, but equation (4.16) gives the form of the wave function *uniformly* throughout the whole range of x. As has been stressed by Murphy and Good (1964) this approach does not suggest that the connection formulae are in any sense unidirectional. The fact that $\mathrm{Ai}(\sigma)$ and $\mathrm{Bi}(\sigma)$ can be approximated by WKB-like expressions for large $|\sigma|$ was the basis of early determinations of the connection formulae by Jeffreys (1923) and Kramers (1926); they expanded the potential to first order in x, thus deriving the 'transitional approximations' valid very close to the turning point $x = 0$, but (unlike the uniform approximations) failing to match on correctly to the WKB forms for $x \ll 0$ and $x \gg 0$ (see also Kudriavtsev 1957). Imai (1948, 1950), Bailey (1954) and Tietz (1967), using special methods, have found different formulae giving approximations to the exponentially decreasing solution $\mathrm{Ai}(x)$ which are meant to be valid across a turning point, but numerical evaluation reveals that the results of Bailey and Tietz are seriously in error near $x = 0$, while the formalism of Imai is very complicated and not immediately amenable to generalization (see, however, an interesting application by Kuhn 1950).

These solutions, although they contain more information than is given by the WKB method, can only cope with a single isolated turning point and fail at a second turning point (eg for a potential well or barrier). If the two turning points are not too close together one can match two Langer-type solutions, one for each turning point (see Miller (1968a); this is equivalent to using $|x|$ as a comparison potential), but although this may be an improvement on using basic WKB solutions matched across the two turning points as in § 3.3, it is more satisfactory and elegant to use a better form for the comparison function $\Gamma(\sigma)$ to get a *uniform* approximation valid for all x, without resorting to a patching-up procedure.

The simplest comparison potential with two turning points is parabolic, and this was the example originally worked out by Miller and Good (1953). In the case of the *potential well*, the comparison equation is

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}\sigma^2} + (t - \sigma^2)\phi = 0 \tag{4.18}$$

which, in contrast to the one turning-point equation (4.15), involves a parameter t depending on the energy. To find t we use the principle of the correspondence of classical turning points which together with (4.7) gives

$$\int_{x-}^{x+} \frac{p(x)\,\mathrm{d}x}{\hbar} \equiv \frac{S(x_-, x_+)}{\hbar} = \int_{-\sqrt{t}}^{+\sqrt{t}} (t - \sigma^2)^{1/2}\,\mathrm{d}\sigma = \frac{t\pi}{2} \tag{4.19}$$

where x_- and x_+ are the two turning points (cf figure 8(a)); thus t is proportional to the classical action in the well at the energy considered. The real mapping function $\sigma(x)$ is given implicitly by

$$S(x_+, x)/\hbar = \int_{+\sqrt{t}}^{\sigma(x)} (t - \sigma^2)^{1/2}\,\mathrm{d}\sigma. \tag{4.20}$$

The independent solutions of equation (4.18) are the parabolic cylinder functions $D_{(t-1)/2}(\sigma\sqrt{2})$ and $D_{(t-1)/2}(-\sigma\sqrt{2})$ (Whittaker and Watson 1946 p347), whose exact asymptotic behaviour is known (see Heading 1962 p147, for an analysis based on convergent series expansions). In terms of these functions and the forms (4.20) and (4.19) of t and $\sigma(x)$, uniform approximations may be written for any wave function

$\psi(x)$; in particular, the connection formula (3.63), which involves the undetermined quantities A and γ, can be replaced by

$$\frac{\exp(-|w(x_-,x)|)}{|p(x)|^{1/2}} \xleftarrow[x\to-\infty]{} 2^{1/4}\left(\frac{2e}{t(E)}\right)^{t(E)/4}\left(\frac{d\sigma(x)}{dx}\right)^{-1/2} D_{(t(E)-1)/2}(-\sigma(x)\sqrt{2}) \xrightarrow[x\to+\infty]{}$$
$$\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{\pi\hbar e}{S(x_-,x_+)}\right)^{S(x_-,x_+)/\pi\hbar}\Gamma\left(\frac{S(x_-,x_+)}{\pi\hbar}+\frac{1}{2}\right)\frac{\cos S(x_-,x_+)/\hbar)\exp|w(x_+,x)|)}{|p(x)|^{1/2}}$$
$$+\frac{\sin(S(x_-,x_+)/\hbar)\exp(-|w(x_+,x)|)}{|p(x)|^{1/2}} \tag{4.21}$$

an expression which of course includes the limiting cases discussed following (3.63), in addition to being valid near the turning points. (At the energy corresponding to the nth bound state, given by (3.64), the comparison functions take the simple form

$$D_n(\sigma\sqrt{2}) = 2^{-n/2}H_n(\sigma)\,e^{-\sigma^2/2} \tag{4.22}$$

where H_n are the hermite polynomials (see eg Abramowitz and Stegun 1964 p691).)

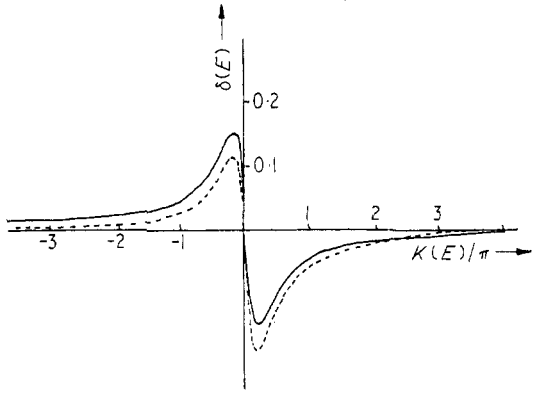

Figure 11. The phase $\delta(E)$ of the reflection coefficient from two barriers. Full curve, parabolic; broken curve, sech^2.

In the case of the *potential barrier* (figure 6(a)) the analysis is similar. A parabolic comparison potential leads to the comparison functions $D_{(it-1)/2}(\sqrt{2}\sigma\,e^{-i\pi/4})$ and $D_{(-it-1)/2}(\sqrt{2}\sigma\,e^{+i\pi/4})$, whose known asymptotic forms lead exactly to the connection formula (3.57), with the quantity δ given by

$$\delta(E) = \frac{K(E)}{\pi\hbar}\ln\left|\frac{K(E)}{\pi\hbar e}\right| + \arg\Gamma\left(\frac{1}{2}-\frac{iK(E)}{\pi\hbar}\right) \tag{4.23}$$

involving the barrier integral $K(E)$ defined by (3.49). It is easy to verify that this form for $\delta(E)$ satisfies the requirements (3.61) and (3.62). Ford *et al* (1959) realized the importance of $\delta(E)$ for a parabolic barrier, and gave a detailed analysis of its properties without however dealing with our problem of uniformly approximating the solutions for general potential barriers. Miller (1968b) has examined various analytic approximations to (4.23). Soop (1965) has calculated $\delta(E)$ exactly for a potential barrier of the form sech^2x and found (as sketched in figure 11) that provided the barrier is high enough the result hardly differs from (4.23) in the region of values of $K(E)$ where that expression is appreciably different from zero. A similar

conclusion was reached by Dickinson (1970), who calculated $\delta(E)$ for an inverted Morse potential, so that the results are not very sensitive to the details of the comparison potential. (For energies E very far below the barrier top, $\delta(E)$ for these other potentials will again differ from zero, a result which is obviously due to the different turning-point structures which then arise (figure 12).)

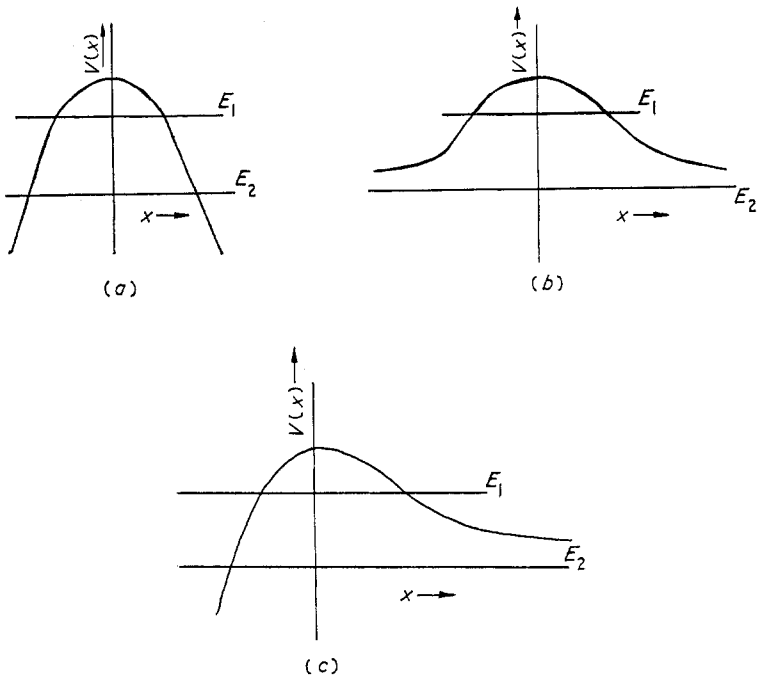

Figure 12. Different turning-point structures for three exactly soluble potential barriers. (*a*) Parabolic barrier, (*b*) sech^2 barrier, (*c*) inverted Morse potential.

The method we have been discussing is not generally very useful for situations involving more than two turning points, because the solutions of the comparison equation are not sufficiently well understood. Thus the three turning-point problem (figure 9(*a*)) cannot be solved in the general case when the turning points r_1, r_2 and r_3 may all lie close together. When the barrier height $V_B - V_W$ is large, however, it is always possible to consider r_3 or r_1 as being sufficiently distant from r_1 and r_2 or r_2 and r_3 to be treated separately. In the first case (Connor 1968, Dubrovskii 1964), which applies to energies above the region of the well bottom V_W, the barrier $r_1 r_2$ is treated as a unit, leading to the phase shift (3.67) with δ given by (4.23). The second case (Connor 1968), which applies to energies below the region of the barrier top V_B, involves considering the well $r_3 r_2$ as a unit, and leads to the phase shift (3.69) with K replaced by $K+f$, where

$$f(E) = \frac{\ln[\Gamma\{\frac{1}{2} + (S(r_3 r_2)/2\pi\hbar)\}]}{2} - \frac{\ln 2\pi}{4} - \frac{S(r_3 r_2)}{2\pi\hbar} \ln\left(\frac{S(r_3 r_2)}{\pi\hbar \mathrm{e}}\right). \qquad (4.24)$$

The results of these two patching procedures overlap in the range $V_B \gg E \gg V_W$, where neither K nor S is smaller than a few units of $\hbar$, to yield the same phase shift (3.69).

4.3. *Scattering lengths*

At extremely low energies, the scattering of a parallel beam of particles from a potential $V(r)$ is isotropic, the total cross section being

$$Q = 4\pi a^2 \tag{4.25}$$

where a is the *scattering length*, defined (Mott and Massey 1965 p45) by writing the large-r limit of the zero energy, zero angular momentum radial Schrödinger equation

$$\frac{\mathrm{d}^2\psi(r)}{\mathrm{d}r^2} - \frac{2mV(r)}{\hbar^2}\psi(r) = 0 \tag{4.26}$$

as

$$\psi(r) \xrightarrow[r\to\infty]{} A\left(1 - \frac{r}{a}\right). \tag{4.27}$$

At the origin $r = 0$, $\psi(r)$ must be zero. The limiting form (4.27) arises because $V(r)$ vanishes at infinity.

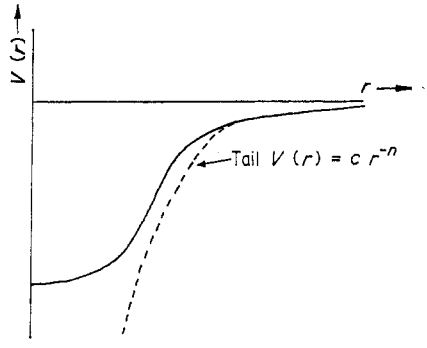

Figure 13. Potential with inverse power tail and no turning points for finite r.

The method of comparison equations is tailormade for the approximate calculation of scattering lengths, because the potentials occurring in physical problems have large-r tails of only a few standard types, despite their great variety nearer the origin. Furthermore, these 'tails' can often be used as comparison potentials, since (4.26) is simple enough to be solvable in very many cases. In order to illustrate the method we shall take a potential $V(r)$ which is attractive, falls off as cr^{-n} at infinity, and possesses no turning points at zero energy apart from that at $r = \infty$ (figure 13). It is not hard to modify the procedure to treat repulsive potentials, or potentials with turning points at finite values of r, or different types of tail (for instance, exponentially falling-off potentials, or 'muffin-tin' potentials vanishing suddenly at a finite value of r (Berry 1969b)).

For a potential such as that in figure 13, a suitable comparison equation (cf 4.2) is

$$\frac{\mathrm{d}^2\phi(\sigma)}{\mathrm{d}\sigma^2} + \frac{1}{\sigma^n}\phi(\sigma) = 0. \tag{4.28}$$

The variable $\sigma(r)$ is given by (4.7) as

$$\int_r^\infty \left(\frac{-2mV(r)}{\hbar^2}\right)^{1/2} \mathrm{d}r \equiv \frac{S(r,\infty)}{\hbar} = \int_{\sigma(r)}^\infty \sigma^{-n/2}\,\mathrm{d}\sigma = \frac{[\sigma(r)]^{1-n/2}}{n/2-1} \tag{4.29}$$

where we have used the equivalence of the turning points $r=\infty, \sigma=\infty$. The quantity $S(r,\infty)$ is the classical action acquired by a zero energy particle moving radially out from r to infinity. The solutions of (4.28) are Bessel functions of order $\pm(n-2)^{-1}$ (Abramowitz and Stegun 1964 p362) so that the uniform approximation to the solution of (4.26) which vanishes at the origin is, from (4.8)

$$\psi(r)=\left[\frac{\sigma(r)}{-V(r)}\right]^{1/4}[S(r,\infty)]^{1/2}\left\{J_{1/(n-2)}\left(\frac{S(r,\infty)}{\hbar}\right)J_{-1/(n-2)}\left(\frac{S(0,\infty)}{\hbar}\right)\right.$$
$$\left.-J_{-1/(n-2)}\left(\frac{S(r,\infty)}{\hbar}\right)J_{+1/(n-2)}\left(\frac{S(0,\infty)}{\hbar}\right)\right\}. \quad (4.30)$$

To find the scattering length, this wave function must be expanded for large r; $S(r,\infty)$ is then small, and comparison with (4.29) yields, after a short calculation, a scattering length given by

$$a=\frac{\Gamma\left(1-\frac{1}{n-2}\right)\left(\frac{c\hbar}{2m}\right)^{1/(n-2)}J_{-1/(n-2)}\left(\frac{S(0,\infty)}{\hbar}\right)}{\Gamma\left(1+\frac{1}{n-2}\right)(n-2)^{2/(n-2)}J_{+1/(n-2)}\left(\frac{S(0,\infty)}{\hbar}\right)}. \quad (4.31)$$

As the strength of the potential increases, $S(0,\infty)$ increases and the zeros of the denominator of this expression give a series of poles in a; at these poles, the scattering cross section is infinite, corresponding to a bound state at zero energy which has just been sucked into the potential well from the continuum. The location of these poles when $S(0,\infty)$ is not small can be found from the asymptotic form of the Bessel functions, giving the *quantization condition*

$$S(0,\infty)=\left(m+\frac{1}{2}+\frac{n}{4(n-2)}\right)\pi\hbar \quad (4.32)$$

for the action S corresponding to the appearance of the mth bound state. From the point of view of scattering, therefore, the strength of a potential is characterized by the form of the tail, and by the classical action $S(0,\infty)$. Using ideas similar to these, Dickinson and Bernstein (1970) have estimated the number of bound states in various types of interatomic potential.

5. The WKB method and the radial equation

5.1. *Origin of the Langer modification*

The scattering of particles of (reduced) mass m and energy E by a spherically symmetric potential $V(r)$ is described by the radial Schrödinger equation for the partial waves of angular momentum quantum number l:

$$\frac{d^2\psi_l(r)}{dx^2}+\left(\frac{2m(E-V(r))}{\hbar^2}-\frac{l(l+1)}{r^2}\right)\psi_l(r)=0 \quad \text{with } \psi_l(0)=0. \quad (5.1)$$

This differs from the one-dimensional equations (cf equation (2.17)) that we have so far considered because the radial coordinate r runs from 0 to ∞ (instead of $-\infty$ to ∞), and the 'centrifugal potential' $l(l+1)\hbar^2/2mr^2$ is singular at the origin (the true potential $V(r)$ is often singular too). In view of this, it is hardly surprising that a naive application of the WKB method as outlined in §3 yields manifestly unsatisfactory results.

Consider, for instance, bound states in the Coulomb potential

$$V(r) = -ze^2/r \tag{5.2}$$

(hydrogenic atom of charge z); application of the quantization condition (3.64) (see Young and Uhlenbeck 1930) yields, for the pth level with quantum number l:

$$E_{pl}^{\mathrm{WKB}} = \frac{-mz^2e^4}{2\hbar^2[p-\frac{1}{2}+\{l(l+1)\}^{1/2}]^2} \qquad p = 1, 2, 3, \ldots . \tag{5.3}$$

This formula predicts a splitting of levels which are in fact degenerate, as shown by the well known exact formula (Schrödinger 1926)

$$E_{pl}^{\mathrm{exact}} = -\frac{mz^2e^4}{2\hbar^2(p+l)^2} \tag{5.4}$$

(in more conventional notation, the 'principal quantum number' n, which labels the complete set of levels for all l, is equal to $p+l$).

Secondly, the phase shifts for positive energy which are predicted by the WKB formula (3.42) for the case where there is one turning point, namely

$$\eta_l^{\mathrm{WKB}} = \int_{r_0}^{\infty} \frac{\mathrm{d}r}{\hbar}\left[\left\{2m(E-V)-\frac{l(l+1)\hbar^2}{r^2}\right\}^{1/2}-(2mE)^{1/2}\right]-\frac{(2mE)^{1/2}r_0}{\hbar}+(l+\tfrac{1}{2})\frac{\pi}{2} \tag{5.5}$$

do not reduce to the correct value of zero when the potential $V(r)$ is set equal to zero. For the $l = 0$ (s wave) case when the potential is attractive, there are no classical turning points and the 'naive WKB' expression corresponding to (5.5) is easily calculated from the definition (3.41) to be

$$\eta_0^{\mathrm{WKB}} = \int_0^{\infty} \frac{\mathrm{d}r}{\hbar}\left[\{2m(E-V(r))\}^{1/2}-(2mE)^{1/2}\right]. \tag{5.6}$$

This does vanish as $V(r)$ does, but we shall see that it is nevertheless still not the correct expression in general cases.

Finally, the WKB method fails to give the correct form of the wave function near the origin in the case of regular potentials, which are dominated by the centrifugal potential as $r \to 0$ (singular potentials will be considered in § 5.2). The predicted limiting behaviour is

$$\psi_l^{\mathrm{WKB}} = \frac{\exp\{\pm(\mathrm{i}/\hbar)\int^r p(r)\,\mathrm{d}r\}}{\{p(r)\}^{1/2}} \to \text{constant} \times r^{1/2\pm\{l(l+1)\}^{1/2}} \tag{5.7}$$

whereas the exact behaviour is known (Newton 1966 p371) to be

$$\psi_l \to \text{constant} \times r^{l+1} \quad \text{or} \quad \text{constant} \times r^{-l}. \tag{5.8}$$

It was soon observed that all three of these defects are eliminated if the WKB method is applied, not to the momentum

$$p(r) = \{2m(E-V(r))-l(l+1)\hbar^2/r^2\}^{1/2} \tag{5.9}$$

that occurs in the radial equation (5.1), but to the 'effective momentum'

$$p^{\mathrm{eff}}(r) \equiv \{2m(E-V(r))-(l+\tfrac{1}{2})^2\hbar^2/r^2\}^{1/2} \tag{5.10}$$

where $\{l(l+1)\}^{1/2}$ has been replaced by $l+\frac{1}{2}$. Kramers (1926) had earlier shown that the same substitution was necessary in order to get the correct large-r behaviour of the wave functions for the case of a Coulomb potential. Kemble (1935) pointed out that the simple WKB method fails because it is not possible to find a 'good path'

(cf § 3.1) near the origin, but that the addition of an extra potential $\hbar^2/8mr^2$—which is equivalent to replacing p by p^{eff}—ensures that a good path can be found. The first full analysis of the situation was by Langer (1937) and led to the $\{l(l+1)\}^{1/2} \to l+\frac{1}{2}$ substitution being called the *Langer modification.*

Langer examined the condition for the validity of the WKB method near the origin; this condition is the special case resulting from (4.9) when the comparison potential is taken as constant, namely

$$\epsilon(r) \equiv \left| \frac{\hbar^2}{(p(r))^{3/2}} \frac{\mathrm{d}^2}{\mathrm{d}r^2} (p(r)^{-1/2}) \right| \ll 1. \tag{5.11}$$

The use of (5.9) for $p(r)$ in the case of regular potentials leads immediately to

$$\epsilon(r) \xrightarrow[r\to 0]{} \frac{1}{4l(l+1)} \tag{5.12}$$

so that it is only for very large l that the WKB method can be used at all in its naive form. l is in fact large in the semiclassical case which is our main concern, being related to the classical angular momentum L by

$$L = \{l(l+1)\}^{1/2}\hbar \to (l+\tfrac{1}{2})\hbar \tag{5.13}$$

and it is easily seen, for instance, that the Langer modification only alters the WKB phase shift (5.5) by an amount of order $\hbar$ which is negligible in the semiclassical limit. For smaller l the naive WKB method cannot be applied; it fails completely for s waves if $V(r)$ is coulombic (5.2) near the origin for in this case

$$\epsilon(r) \to \frac{3\hbar^2}{32me^2 zr}. \tag{5.14}$$

To remove the singularity at $r = 0$ which is the cause of the failure of the naive WKB method when l is not large, Langer made the substitutions

$$\left.\begin{array}{c} r = \mathrm{e}^x \\ \Psi_l(x) = \mathrm{e}^{x/2}\psi_l(r) \\ -\infty \leqslant x \leqslant \infty \end{array}\right\} \tag{5.15}$$

which convert (5.1) into

$$\frac{\mathrm{d}^2\Psi_l(x)}{\mathrm{d}x^2} + \frac{\Pi^2(x)}{\hbar^2}\Psi_l(x) = 0 \qquad \Psi_l(-\infty) = 0 \tag{5.16}$$

where

$$\Pi^2(x) = 2m[\mathrm{e}^{2x}E - V(\mathrm{e}^x)\,\mathrm{e}^{2x}] - \hbar^2(l+\tfrac{1}{2})^2. \tag{5.17}$$

This is an equation to which the WKB method can legitimately be applied, because $\Pi(x)$ tends to a constant value as $x \to -\infty$, and the validity condition analogous to (5.11), namely

$$\epsilon(x) \equiv \left| \frac{\hbar^2}{(\Pi(x))^{3/2}} \frac{\mathrm{d}^2}{\mathrm{d}x^2} (\Pi(x))^{-1/2} \right| \ll 1 \tag{5.18}$$

is satisfied as $r \to 0$. The phase in the WKB solutions of (5.16) is

$$\int^x \frac{\Pi(x)\,\mathrm{d}x}{\hbar} = \int^x \frac{\Pi(\ln r)}{\hbar}\frac{\mathrm{d}x}{\mathrm{d}r}\mathrm{d}r = \int^r \frac{p^{\text{eff}}(r)\,\mathrm{d}r}{\hbar} \tag{5.19}$$

where we have used the definition (5.10). The substitution $\{l(l+1)\}^{1/2} \to l+\frac{1}{2}$ has thus been justified for regular potentials, even for the case $l = 0$. A different

treatment of the radial equation, based on the complex method, is given by Fröman and Fröman (1965 p110), while the applicability of the Langer modification to the higher terms of asymptotic series for phase shifts etc, has been discussed by Beckel and Nakhleh (1963), Choi and Ross (1962) and Krieger and Rosenzweig (1967).

The possibility of more general changes of variable, leading to the substitution

$$l(l+1) \to l(l+1)+\alpha \tag{5.20}$$

($\alpha = 1/4$ for the Langer transformation) has been mentioned by Biedenharn *et al* (1955) in a long paper dealing in detail with the special case of a Coulomb potential (transformations more general than (5.20) have been considered by Engelke and Beckel (1970)). In fact the Langer choice of $1/4$ for α is the most natural for problems involving the semiclassical limit, for if we relate l to the *classical* angular momentum by a general linear relation

$$L = (l+\beta)\hbar \tag{5.21}$$

then (5.20) gives, for the transformation of the centrifugal potential,

$$\frac{l(l+1)\hbar^2}{2mr^2} \to \frac{L^2}{2mr^2}+\frac{L\hbar}{2mr^2}(1-2\beta)+\frac{\hbar^2}{2mr^2}(\beta^2-\beta+\alpha). \tag{5.22}$$

The choice of $1/2$ for β (cf equation (5.13)) and $1/4$ for α eliminates the correction terms for all l, so that the effective momentum (5.10) takes the *classical* form

$$p^{\text{eff}}(r) = \{2m(E-V(r))-L^2/r^2\}^{1/2} \tag{5.23}$$

which can be used to provide *uniform* approximations valid for any L. The phase shift now becomes

$$\eta_l^{\text{Langer}} = \int_{r_0}^{\infty} \frac{\mathrm{d}r}{\hbar}[\{2m(E-V)-L^2/r^2\}^{1/2}-(2mE)^{1/2}]-\frac{(2mE)^{1/2}r_0}{\hbar}+\frac{L\pi}{2\hbar} \tag{5.24}$$

which does go to zero as $V \to 0$, unlike (5.5). It is important to realize that this phase shift can be written as

$$\eta_l^{\text{Langer}} = \tilde{\eta}(L)/\hbar \tag{5.25}$$

where $\tilde{\eta}(L)$ involves only classical quantities.

5.2. *Semiclassical approximations for singular potentials*

Singular potentials, in the way the term is commonly employed in scattering theory, are those which are not merely nonanalytic at the origin, but which diverge more strongly than the centrifugal potential, so that

$$\lim_{r\to 0}\frac{r^2\,V(r)}{l(l+1)} = \pm\infty. \tag{5.26}$$

Their special properties are reviewed in detail by Frank *et al* (1971), and we shall confine ourselves to a brief analysis of the situation. To test the applicability of the ordinary WKB method, consider the singular potential

$$V(r) \xrightarrow[r\to 0]{} \frac{\lambda}{r^n} \quad (n>2). \tag{5.27}$$

The 'test quantity' $\epsilon(r)$ defined in (5.11) can be easily evaluated to give

$$\epsilon(r) \xrightarrow[r\to 0]{} \frac{\hbar^2 n(n-4)r^{n-2}}{32m\lambda}. \tag{5.28}$$

This vanishes at the origin, so that, in contrast to the situation with regular potentials, it is perfectly satisfactory to use the WKB method in an unmodified form, and the behaviour of the wave functions is correctly given for small r. Similar conclusions hold for other types of singular potential, such as $V(r) \propto e^{\alpha/r}$.

It is still valid, however, to introduce the Langer transformation for singular potentials, at least as far as the behaviour near the origin is concerned, since a modification of the coefficient of the angular momentum term leaves unaltered the dominant behaviour, which is due to the potential. (This conclusion may be checked easily by evaluating $\epsilon(x)$ from (5.18) and (5.17).) There is, moreover, a good reason for preferring the Langer modification even for singular potentials. To see this consider what happens in a very weak singular potential—for instance (5.27) as $\lambda \to 0$; there will be a value of λ for which the centrifugal potential begins to dominate, so that the Langer modification *must* be used. It therefore seems sensible to use the modification throughout, thus obtaining approximations which are *uniformly valid* in the strength λ of the potential.

To sum up, the substitution $\{l(l+1)\}^{1/2} \to l+\frac{1}{2}$ has the remarkable property of ensuring the applicability of the WKB method for large and small angular momenta and potentials which are attractive or repulsive, regular or singular. This does not mean, however, that the Langer modification is guaranteed always to give numerically superior results when the ordinary WKB method is also valid. One such case (where the unmodified WKB method gives *exact* results) is the r^{-4} potential for s waves and zero energy; another example is given by Beckel *et al* (1964).

5.3. *Uniformly approximate solutions of the radial equation*

An alternative approach to the difficulties associated with the origin for regular potentials, suggested by Good (1953), is to use the method of comparison equations outlined in § 4.1 to express the radial wave function $\psi_l(r)$ in terms of the spherical Bessel function free-particle solutions of the comparison equation

$$\frac{d^2\phi(\sigma)}{d\sigma^2} + \left(\frac{2mE - l(l+1)\hbar^2/\sigma^2}{\hbar^2}\right)\phi(\sigma) = 0. \tag{5.29}$$

It is very easy to apply the method whenever the presence of the potential does not alter the turning-point structure, to give

$$\psi_l(r) \simeq \left[\frac{d\sigma}{dr}\right]^{-1/2} j_l\left(\frac{(2mE)^{1/2}}{\hbar}\sigma(r)\right) \tag{5.30}$$

where the variable $\sigma(r)$ is given by

$$\int_{\{l(l+1)\hbar^2/2mE\}^{1/2}}^{\sigma(r)} \frac{\{2mE - l(l+1)\hbar^2/\sigma^2\}^{1/2}\, d\sigma}{\hbar} = \int_{r_0}^{r} \frac{p(r)\, dr}{\hbar} \tag{5.31}$$

$p(r)$ being defined by (5.9). Comparison of the asymptotic phase of (5.30) with the definition (3.41) yields yet another expression for the phase shifts, namely

$$\eta_l^{\text{uniform}} = \int_{r_0}^{\infty} \frac{dr}{\hbar}\left\{\left(2m(E-V) - \frac{l(l+1)\hbar^2}{r^2}\right)^{1/2} - (2mE)^{1/2}\right\} - \frac{(2mE)^{1/2} r_0}{\hbar} + \{l(l+1)\}^{1/2}\frac{\pi}{2} \tag{5.32}$$

which differs from η_l^{WKB} (equation (5.5)) in the replacement of the $(l+\frac{1}{2})\pi/2$ term by $\{l(l+1)\}^{1/2}\pi/2$ (except for the case $l = 0$ when the potential is attractive, for which

η_0^{uniform} is identical with η_0^{WKB} in (5.6)), and which differs also from η_l^{Langer} (equation (5.24)) in replacing L by $\{l(l+1)\}^{1/2}\hbar$ throughout, instead of $(l+\frac{1}{2})\hbar$.

This new phase shift vanishes when the potential does, as it should, and it would therefore seem to compete with η_l^{Langer}, given by (5.24), which also has this property. But an analysis of the applicability of the method of comparison equations, based on the criterion (4.9), reveals that although the approximation (5.30) represents the exact wave function near the origin for $l \neq 0$ when the potential is regular, it fails for singular potentials and for a Coulomb-type potential when $l = 0$. Furthermore, numerical calculations of Rosen and Yennie (1964), show that η_l^{Langer} is closer to the exact phase shift than is η_l^{uniform}, in the case of a Coulomb potential (for which the phase shift is, of course, defined in a different way because of the behaviour at *large r*).

Excellent numerical agreement with exact phase shifts is obtained by Rosen and Yennie (1964) by a modification of the uniform approximation (5.30), which consists in setting

$$\psi_l(r) = a(r)\,\mathrm{j}_l\left(\frac{(2mE)^{1/2}}{r}\sigma(r)\right) + b(r)\,\mathrm{j}_l'\left(\frac{(2mE)^{1/2}}{r}\sigma(r)\right) \tag{5.33}$$

and solving the equations satisfied by $a(r)$ and $b(r)$ to lowest order in $\hbar$ ($\sigma(r)$ is still given by (5.31) and the prime denotes differentiation with respect to the argument of j_l). This leads to the phase shift

$$\eta_l^{\text{Rosen-Yennie}} = \eta_l^{\text{uniform}} + \frac{\pi}{16\{l(l+1)\}^{1/2}} - \frac{\hbar}{24}\int_{r_0}^{\infty} \frac{\mathrm{d}r}{p(r)}\frac{\mathrm{d}^2}{\mathrm{d}r^2}\left(\ln\frac{\mathrm{d}}{\mathrm{d}r}p^2(r)\right). \tag{5.34}$$

This result contains explicit correction terms which vanish as $\hbar \to 0$ in the semiclassical limit, unlike the three phase shifts so far discussed, and should therefore properly be compared with the results of extensions of the earlier treatment to obtain the first-order corrections to η_l^{WKB}, η_l^{Langer} and η_l^{uniform}.

Uniform approximations based on the free-particle solutions can also be used for bound state wave functions at negative energies, but the inevitable appearance of a second turning point in such cases, which must be treated independently (by, for example, the methods of § 4.2) reduces the elegance of the method, although in numerical terms the results are excellent (see Bartlett *et al* 1957).

6. Short-wavelength potential scattering

6.1. *Transformation of the eigenfunction expansion*

The exact quantum-mechanical expressions for a great variety of observable quantities take the form of convergent series expansions over a discrete set of eigenvalues. Under semiclassical conditions these series converge very slowly, and bear no obvious relationship to the purely classical expressions, which involve summations over the classical paths contributing to the observable quantities under consideration. Of all the problems of this type, the one whose semiclassical limit has been examined most deeply is the elastic scattering of a beam of particles; because of this, and also because potential scattering is likely to be familiar to the greatest number of readers, we shall deal only with this case. But the concepts we shall introduce can be applied to the approximation of *any* eigenfunction series, including two particular problems which have been very extensively studied; these are the effect of the magnetic field on the motion of an electron, either free or in a metal

(see Lifshitz and Kaganov 1960, 1962, Pippard 1969, Chambers 1969), and the diffraction of particles in crystals, which forms the basis of high energy electron microscopy and heavy-ion channelling (see Berry 1971, Howie 1966, Chadderton 1970). The related problem of the density of states involves both the discrete and the continuous energy spectrum, and will be discussed in § 7.4.

Semiclassical scattering theory finds its most natural application in the interpretation of atomic and molecular beam experiments, and the calculation of the transport properties of gases; these subjects are well reviewed by Massey (1956), Pauly and Toennies (1965) and Bernstein (1966), so that we shall be able to concentrate on analysing the concepts which are involved. A semiclassical analysis is necessary because hundreds (and often thousands) of eigenfunctions contribute to the series, yet oscillatory effects are frequently observed, indicating that the classical limit has not yet been reached. For a lucid outline of the present status of semiclassical concepts in molecular dynamics see Miller (1971).

The quantity usually measured when a beam of particles of mass m and energy E is used to bombard a target with which the elastic interaction potential energy is $V(r)$ is the *differential scattering cross section* $\sigma(\theta)$; this is defined as the average number of particles emerging in unit time from unit solid angle in a direction making an angle of θ with the forward direction, if the incident beam intensity is such that one particle crosses unit area in unit time, on average. It is shown in any text on scattering theory (eg Mott and Massey 1965 § 2.1) that the exact quantum-mechanical formula for $\sigma(\theta)$ is

$$\sigma(\theta) = |f(\theta)|^2 \tag{6.1}$$

where $f(\theta)$, the *scattering amplitude*, is given by the series of angular eigenfunctions

$$f(\theta) = \frac{-i\hbar}{(2mE)^{1/2}} \sum_{l=0}^{\infty} (l+\tfrac{1}{2})\{\exp(2i\eta_l) - 1\} P_l(\cos\theta). \tag{6.2}$$

The *phase shifts* η_l are defined by the asymptotic form (3.41) of the solution of the radial Schrödinger equation (5.1), while $P_l(\cos\theta)$ denotes the Legendre polynomial of order l. A very rough estimate of the number of terms contributing significantly to $f(\theta)$ is $l_{\max}$, the number of de Broglie wavelengths fitting into the scattering region, given by

$$l_{\max} = \frac{R_0(2mE)^{1/2}}{h} \tag{6.3}$$

where R_0 is a measure of the range of the potential $V(r)$. In semiclassical cases, this number is large, so that the series (6.2) converges very slowly. It is only feasible to calculate $f(\theta)$ exactly when $l_{\max}$ does not exceed about fifty, and such calculations have been performed by various authors (eg Bernstein 1960, 1961); for larger values of $l_{\max}$ it is necessary to introduce approximations into the summand in (6.2) or to use an altogether different approach, based on classical mechanics. A simple analysis, based on the uncertainty principle, of the criteria that must be satisfied for a completely classical analysis to be valid was given by Williams (1945).

In the purely classical case, the only particles emerging at the angle of observation θ will be those with certain classical angular momenta $L_i(\theta)$, corresponding to *impact parameters* $b_i(\theta)$ (figure 14) given by

$$b = L/(2mE)^{1/2}. \tag{6.4}$$

The multivaluedness of $L(\theta)$ and $b(\theta)$ which is indicated by the suffix i, is eliminated if we consider instead the *classical deflection function* $\Theta(L)$, which is reckoned positive for net repulsion, negative for attraction. Owing to the possibility of classical paths which encircle the origin before emerging, $|\Theta|$ may exceed π, unlike

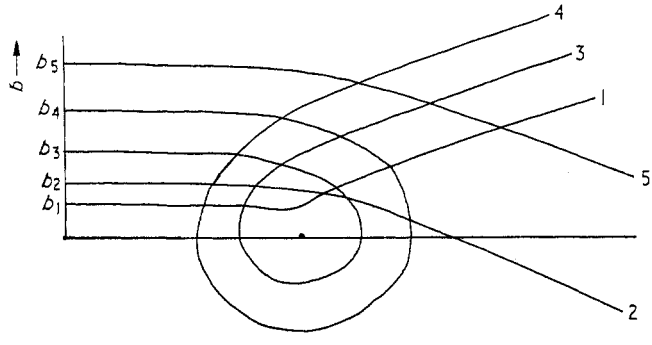

Figure 14. Paths contributing to scattering at an angle of observation θ.

the observation angle θ, which lies between 0 and π. Taking the cylindrical symmetry into account, the contributing angular momenta are found to satisfy

$$\Theta(L_i(\theta)) = \mp\theta - 2M\pi \qquad M = 0, 1, 2, \ldots \tag{6.5}$$

(negative values of M are excluded because values of Θ exceeding π are dynamically impossible); in the particular case represented by figure 14

$$\left.\begin{aligned} \Theta(L_1) &= +\theta \\ \Theta(L_2) &= -\theta \\ \Theta(L_3) &= -2\pi + \theta \\ \Theta(L_4) &= -2\pi + \theta \\ \Theta(L_5) &= -\theta. \end{aligned}\right\} \tag{6.6}$$

This behaviour might be produced by the deflection function Θ shown in figure 15; this corresponds to a type of potential commonly encountered in atomic physics, which is attractive at large distances and repulsive at short distances.

The particles which are observed to emerge in a solid angle $\mathrm{d}\Omega = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ (where ϕ is an azimuth angle) have originated from areas $\mathrm{d}A_i(\theta) = b_i(\theta)\,\mathrm{d}b\,\mathrm{d}\phi$ in the incident beam, and the definition of scattering cross section gives

$$\sigma(\theta)\,\mathrm{d}\Omega = \sum_i \mathrm{d}A_i \tag{6.7}$$

so that

$$\begin{aligned} \sigma(\theta) &= \sum_i \left(\frac{\mathrm{d}\Omega}{\mathrm{d}A_i}\right)^{-1} = \sum_i \frac{b_i(\theta)}{\sin\theta}\left(\left|\frac{\partial(\theta,\phi)}{\partial(b,\phi)}\right|\right)^{-1} \\ &= \sum_i \frac{L_i(\theta)}{2mE\sin\theta}\left(\left|\frac{\mathrm{d}\Theta(L_i(\theta))}{\mathrm{d}L}\right|\right)^{-1}. \end{aligned} \tag{6.8}$$

The appearance of the Jacobian $\partial(b,\phi)/\partial(\theta,\phi)$ is characteristic of the classical limits of quantum problems (cf §7.2). The equation (6.8) is analogous to the quantal formula (6.2); it involves not the phase shift η_l, which is determined by the quantum

mechanics of the problem, but the deflection function $\Theta(L)$ which is determined by simple classical mechanics (Mott and Massey 1965 p97) to be

$$\Theta(L) = \pi - 2L \int_{r_0}^{\infty} \frac{\mathrm{d}r}{r^2\{2m(E-V(r)) - L^2/r^2\}^{1/2}} \tag{6.9}$$

where r_0 denotes the outermost zero of the square root, this being the radius of

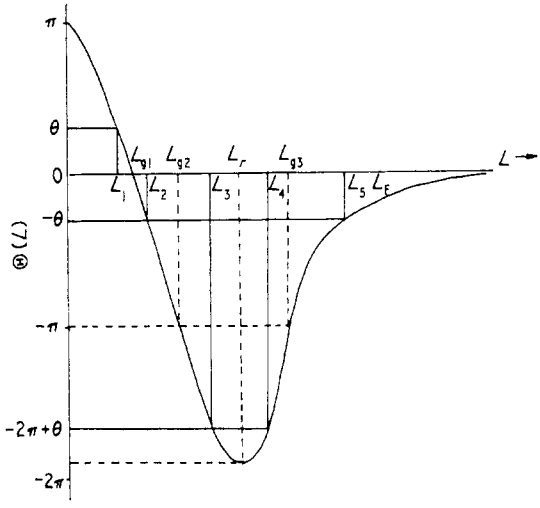

Figure 15. Deflection function $\Theta(L)$, giving rise to the classical paths observed at angle θ shown in figure 14.

closest approach to the scatterer. For the semiclassical case we shall later need to relate $\Theta(L)$ to the action $S(L)$ along the orbit of angular momentum L:

$$\text{if} \quad \left.\begin{aligned} \frac{\partial S}{\partial L}(L, \Theta) &= 0 \\ \Theta &= \Theta(L) \end{aligned}\right\} \tag{6.10}$$

where

$$S(L, \Theta) = 2\int_{r_0}^{\infty} [\{2m(E-V(r)) - L^2/r^2\}^{1/2} - (2mE)^{1/2}]\,\mathrm{d}r + L(\pi - \Theta) - 2(2mE)^{1/2} r_0(L). \tag{6.11}$$

There is no single approximation which makes the quantum sum over l (6.2) go over into the classical sum over paths (6.8); taking the semiclassical limit of such an eigenfunction expansion is a process involving three distinct stages, as was realized by Ford and Wheeler (1959a,b), in two pioneering papers which may be said to mark the 'coming-of-age' of the subject.

In the *first stage of approximation*, the summation over the discrete index l must be replaced by integration over the continuous classical angular momentum variable L, given by (cf § 5.1)

$$L = (l + \tfrac{1}{2})\hbar. \tag{6.12}$$

This procedure was first suggested by Massey and Mohr (1933). It is not sufficient, however, simply to write

$$\sum_{l=0}^{\infty} g(l) \to \frac{1}{\hbar}\int_0^{\infty} g\left(\frac{L}{\hbar} - \frac{1}{2}\right)\mathrm{d}L \tag{6.13}$$

thus replacing the sum (6.2) by a single integral in which the variable l in the summand is treated as a continuous variable; this was the original procedure of Massey and Mohr and the same replacement was made by many authors, including Ford and Wheeler (1959a,b). Nor is it sufficient to follow the suggestion of Mason *et al* (1964), and use the Euler–Maclaurin summation formula, which corrects (6.13) by means of the asymptotic expansion

$$\sum_{l=0}^{\infty} g(l) \to \frac{1}{\hbar}\int_0^{\infty} g\left(\frac{L}{\hbar}-\frac{1}{2}\right) - \frac{\hbar}{2}\left\{\frac{\mathrm{d}}{\mathrm{d}L}g\left(\frac{L}{\hbar}-\frac{1}{2}\right)\right\}_{L=0} + \frac{\hbar^3}{720}\left\{\frac{\mathrm{d}^3}{\mathrm{d}L^3}g\left(\frac{L}{\hbar}-\frac{1}{2}\right)\right\}_{L=0} + \ldots . \quad (6.14)$$

Such methods fail because $g(l)$ is an oscillatory function whose value alters substantially as l changes by unity, even in the semiclassical limit, as may be seen from the phase shift factor $\exp(2\mathrm{i}\eta_l)$ in (6.2), by using (5.25):

$$\exp(2\mathrm{i}\eta_{l+1}) = \exp\{2\mathrm{i}\tilde{\eta}(L+\hbar)/\hbar\} \simeq \exp(2\mathrm{i}\eta_l)\exp(2\mathrm{i}\mathrm{d}\tilde{\eta}/\mathrm{d}L). \quad (6.15)$$

An alternative procedure is to use the Watson–Regge transformation, in which the sum is replaced by a contour integral over l, whose evaluation involves the poles of $\exp(2\mathrm{i}\eta_l)$ in the complex l plane—the *Regge poles* (see eg Newton 1966 chap 13). Although the WKB method is a useful device for analysing the properties of these poles (see Bottoni *et al* 1962, Patashinskii *et al* 1963, 1964a,b) the scattering amplitude resulting from the transformation is useful not in the semiclassical limit but in the high energy limit, which is different as discussed in § 2.1 (see Schiff 1956, Saxon and Schiff 1957, Glauber 1958, Firsov 1969, Patashinskii *et al* 1964b, for various treatments of the high energy aspects of potential scattering). In the case of potentials which change discontinuously across a surface, as in the classical problems of diffraction theory, the Regge poles are also important, because in short-wavelength cases they describe waves which creep along the surface (see Nussenzveig 1969a,b). It might be supposed that a semiclassical analysis must involve the Regge poles whenever these lie close to the real positive l axis, indicating strong partial-wave resonances (see Remler 1971) such as occur when there are three turning points in the radial equation (§ 3.3); but this is not the case, as we shall see in § 6.3.

The proper transformation to use in semiclassical cases is the exact series given by the *Poisson summation formula* (see eg Morse and Feshbach 1953 p467), namely

$$\sum_{l=0}^{\infty} g(l) = \frac{1}{\hbar}\sum_{M=-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}M\pi}\int_0^{\infty} \mathrm{d}L\, g\{(L/\hbar)-\tfrac{1}{2}\}\,\mathrm{e}^{2\pi\mathrm{i}ML/\hbar} \quad (6.16)$$

whose general usefulness in dealing with eigenfunction expansions was suggested by Pekeris (1950) (see also Born and Ludwig 1958), and which was applied to the partial-wave series for scattering by Rubinow (1961) Nussenzveig (1969a) and Berry (1966b, 1969a). As we shall see in § 6.2 the merit of the transformation is that the index M characterizes the classical paths that have encircled the origin M times; with the simple replacement (6.13), which corresponds to setting $M = 0$, the contributions of many classical paths would be missed. For another application of the Poisson formula, see § 7.4. In a recent paper, Boas and Stutz (1971) give a general exposition and comparison of the three summation methods just outlined.

The *second stage of approximation* is to replace the quantities appearing in the summand $g(l)$ of (6.2) by their asymptotic forms for large L. The phase shift η_l

may be approximated by the Langer expression

$$\eta_{\{(L/\hbar)-\frac{1}{2}\}} \simeq \frac{\tilde{\eta}(L)}{\hbar} \tag{6.17}$$

where $\tilde{\eta}(L)$ is defined by (5.24) and (5.25). This formula may be used even when there is more than one turning point, provided that r_0 represents the outermost of these; we shall see in § 6.3 that it is not necessary to employ formulae such as (3.67) which describe the details of resonance behaviour. The Legendre polynomial may be approximated by the appropriate one of the following expressions, depending on whether or not θ lies within a distance of $O(\hbar/L)$ from the forward or backward directions:

$$P_{\{(L/\hbar)-\frac{1}{2}\}}(\cos\theta) \simeq \left(\frac{2\hbar}{\pi L \sin\theta}\right)^{1/2} \cos\left(\frac{L\theta}{\hbar} - \frac{\pi}{4}\right) \tag{6.18}$$

$$\simeq \left(\frac{\theta}{\sin\theta}\right)^{1/2} J_0\left(\frac{L\theta}{\hbar}\right) \tag{6.19}$$

$$\simeq \left(\frac{\pi-\theta}{\sin\theta}\right)^{1/2} J_0\left(\frac{L(\pi-\theta)}{\hbar}\right) \exp\left(-\frac{iL\pi}{\hbar} + \frac{i\pi}{2}\right). \tag{6.20}$$

for $O(\hbar/L) < \theta < \pi - O(\hbar/L)$, $0 \leqslant \theta < \pi - O(\hbar/L)$, and $O(\hbar/L) < \theta \leqslant \pi$ respectively. These approximations were derived by Szegö (1934). It is to be noted how the 'Langer' form (6.12) for the classical angular momentum occurs naturally in these approximations for η_l and P_l.

If, for the sake of clarity of exposition, we temporarily restrict ourselves to cases where θ is not near 0 or π, so that (6.18) can be used, the result of the first two stages of approximation is to transform the scattering amplitude (6.2) into

$$f(\theta) \simeq \frac{-i}{2(\pi\hbar m E \sin\theta)^{1/2}} \sum_{M=-\infty}^{\infty} e^{-iM\pi}(e^{-i\pi/4} I_M^+ + e^{+i\pi/4} I_M^-) \tag{6.21}$$

where

$$I_M^{\mp} \equiv \int_0^{\infty} dL\, L^{1/2} \exp\left[\frac{i}{\hbar}\{2\tilde{\eta}(L) + L(\pm\theta + 2M\pi)\}\right]. \tag{6.22}$$

(We have ignored the minus one in the curly brackets in (6.2) because this only affects the forward scattering.) It is the task of the *third stage of approximation* to evaluate the series of integrals $I_M^{\mp}$.

6.2. *Introduction of the classical paths*

It is necessary to evaluate the integrals $I_M^{\mp}$ in (6.22) only to order $\hbar^{1/2}$, since contributions of higher order will give rise to terms of order higher than $\hbar^0$ in $f(\theta)$ (equation 6.21) which vanish in the semiclassical limit. Such contributions can arise only from the *stationary points* of the exponent in (6.22), which occur at those values $L_i(\theta)$ of the classical angular momentum which satisfy

$$2\frac{d\tilde{\eta}}{dL}(L_i(\theta)) = \mp\theta - 2M\pi \tag{6.23}$$

by direct comparison of (5.24) with (6.9) it is easily seen that

$$2\frac{d\tilde{\eta}(L)}{dL} = \Theta(L) \tag{6.24}$$

so that the stationary points $L_i(\theta)$ satisfy precisely the condition (6.5), thus showing that only the *classical paths* corresponding to an observation angle of θ contribute to $f(\theta)$ in the semiclassical limit. The separation (6.21) of the scattering amplitude into the series of integrals thus effects a separation of the classical paths according to their *topology*: a classical path which suffers a net repulsion (or attraction) after circling the origin M times contributes to the integral I_M^- (or I_M^+).

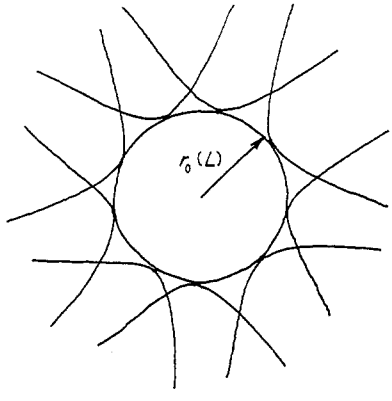

Figure 16. Family of classical paths with angular momentum L.

In the situation represented by figures 14 and 15, for example, we would expect L_2 and L_5 to contribute to I_0^+, L_1 to I_0^- and L_3 and L_4 to I_1^-, all of the other integrals being negligible. It is easily seen from (6.11) that at the angular momentum $L_i(\theta)$ corresponding to the ith classical path, the exponent in (6.22) is just the classical action $S_i(\theta)$ along the path, defined by

$$S_i(\theta) \equiv S(L_i(\theta), \Theta_i(\theta)). \tag{6.25}$$

Before proceeding to examine the precise manner in which the classical paths contribute to $f(\theta)$, we examine an interesting interpretation of the set of integrals (6.21). Comparing the exponents of the integrands with (6.11), it is clear that (6.21) is the sum of contributions from *all* L to particles suffering all the deflections Θ which correspond to the observation angle θ. What meaning can be given to the action $S(L, \Theta)$ corresponding to a particle, deflected by Θ, which does not have one of the classical angular momenta $L_i(\theta)$? To answer this, we consider the sphere of radius $r_0(L)$, where r_0 is the turning point. This sphere is the *envelope* of the family of classical paths with angular momentum L (figure 16), so that a line lying on the surface of the sphere, while not a true classical path, is nevertheless a *singular solution* of the equations of motion. A particle with any L can therefore be deflected by *any* angle Θ if it follows what we shall call a 'pseudoclassical path', which is composed of ordinary classical paths in and out between r_0 and infinity, but includes an intermediate section on the sphere r_0 (figure 17). A short calculation shows that the action along such a pseudoclassical path is precisely $S(L, \Theta)$ given by (6.11), so that the interpretation of (6.21) is that it represents the scattering amplitude as a sum over all the pseudoclassical paths emerging at an observation angle θ. Such a representation stands, in a sense, midway between classical and quantum mechanics, for we may either form the 'topological sum' of all the paths with different indices M, $+$, $-$, but the same values of L, thus reversing the application of the Poisson summation formula and regaining the 'quantized angular

momentum' expression (6.2), or we may sum all the paths with different L, but with the same indices M, $+$, $-$, thus deriving a representation where only the true classical angular momenta $L_i(\theta)$ contribute (this latter being, of course, the semiclassical limit). Maslov (summarized in English by Kravtsov 1968, see also §7.3) has shown how to form similar 'semiclassical integral representations' for very general problems; they are analogous to Kirchhoff's integral in physical optics.

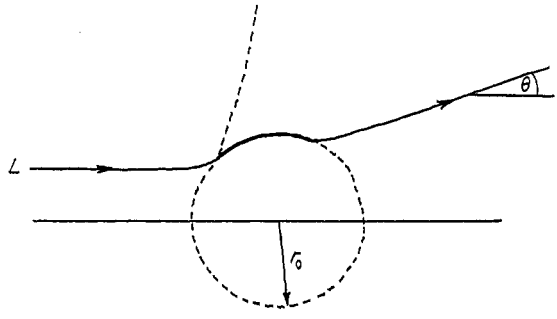

Figure 17. Pseudoclassical path enabling particle of angular momentum L to suffer a deflection Θ.

It was the important contribution of Ford and Wheeler (1959a) to realize that although it is the classical paths which determine the behaviour of the cross section, the simple method of stationary phase can be applied to the integrals $I^{\pm}_M$ only if the stationary points $L_i(\theta)$ are of first order and well separated from each other. This condition is violated for some angles θ for all scattering potentials of practical interest except the Coulomb potential. For angles near to $\theta = 0$ or $\theta = \pi$, the representation in terms of $I^{\pm}_M$ is not valid, because the formulae (6.19) or (6.20) must be used for the Legendre polynomials instead of (6.18); in these cases $f(\theta)$ still depends on the classical paths, as we shall see, but again it is necessary to use methods more complicated than stationary phase to evaluate the appropriate integrals. This dependence of the scattering integrals on the proximity and nature of the stationary points is closely analogous to the dependence of the solutions of differential equations on their turning-point structure, discussed in §§2–4. The contribution of a single stationary point of first-order corresponds to the basic WKB solution of a differential equation in a region with no turning points.

Nevertheless, the simple method of stationary phase is important in deriving the classical, rather than the semiclassical, limit. An isolated stationary point gives a contribution of order $\hbar^{1/2}$ to $I^{\pm}_M$, which arises from the evaluation of the gaussian integral resulting from expanding the exponent in the integrands to second order in $L - L_i(\theta)$. The resulting scattering amplitude is, from (6.21) and (6.24)

$$f(\theta) \simeq \sum_i \delta_i \left\{ \frac{L_i(\theta)}{2mE \sin\theta \left| \Theta'(L_i(\theta)) \right|} \right\}^{1/2} \exp\{iS_i(\theta)/\hbar\} \tag{6.26}$$

where $S_i(\theta)$ is defined by (6.25) and (6.11). The phase factor is determined by the topology of the ith classical path in a manner explained by Berry (1969a p384) (the prescription given by Ford and Wheeler 1959a p264 is incomplete because of their failure to include the higher-order integrals for which $M \neq 0$). The scattering cross

section is (cf equation (6.1))

$$\sigma(\theta) \simeq \sum_{ij} \frac{\delta_i \delta_j^*}{2mE \sin\theta} \left\{ \frac{L_i(\theta) L_j(\theta)}{|\Theta'(L_i(\theta))\, \Theta'(L_j(\theta))|} \right\}^{1/2} \exp\left\{ \frac{\mathrm{i}}{\hbar} (S_i(\theta) - S_j(\theta)) \right\} \qquad (6.27)$$

in which the terms $i \neq j$ show the interference oscillations between the different contributing classical paths. In the classical limit these angular oscillations (whose period is $O(\hbar)$) will be so rapid that no experiment will be able to resolve them, and it is necessary to introduce a *fourth stage of approximation*, consisting of *averaging* $\sigma(\theta)$ over a small angular range; only the terms $i = j$ survive in (6.27), leaving the

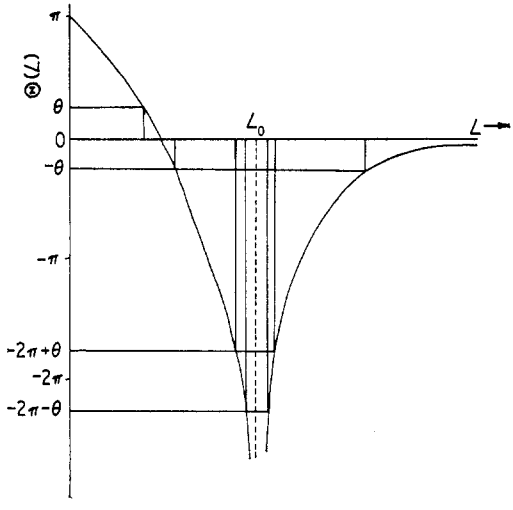

Figure 18. Deflection function showing orbiting and angular momenta giving scattering at θ.

known classical limit given by (6.8). In atomic scattering experiments, the periods of the angular oscillations due to different pairs of interfering classical paths are often sufficiently different for some but not all of the oscillations to be washed out by averaging; a beautiful experimental example of this partial execution of the fourth stage of approximation can be found in the paper by Hundhausen and Pauly (1965).

Returning now to the semiclassical case, there are four commonly occurring situations where the behaviour of the stationary points $L_i(\theta)$ necessitates a more careful evaluation of the integrals $I_M^{\pm}$ for certain angular ranges. We shall show how to deal with these situations in § 6.3; here we shall merely indicate how they arise. In the first case, the deflection function $\Theta(L)$ has an extremum for some value L_r (cf figure 15 between L_3 and L_4); the coalescence of two stationary points which the existence of this extremum implies gives rise to the 'rainbow effect', named after the corresponding optical effect of light in raindrops. In the second case, the potential and the energy E are such that the effective potential presents three turning points for a range of L; at the lower limit L_0 of this range, E takes a value equal to the height of the effective potential barrier, giving rise to 'orbiting', or 'spiral scattering', for which the $\Theta(L)$ exhibits a negative logarithmic singularity (figure 18); the true phase shift in this case displays resonance behaviour, whose effect on $f(\theta)$ must be ascertained. In the third case, a classical path which emerges in the forward or backward direction, indicated by the passing of $\Theta(L)$ through a

multiple of π (see $L_{q_1}, L_{q_2}, L_{q_3}$ in figure 15), requires the use of the Bessel function approximations (6.19 and 6.20) in order to estimate its contribution; this gives rise to 'glory scattering', named again by analogy with an optical effect. In the fourth case, the classical path with very large L contributing to the near-forward scattering (L_F in figure 15) must be treated in a special way, because as $L \to \infty$ the phase shift is so small that the integrand in $I_0^{\mp}$ no longer oscillates, causing the stationary phase method to break down; this behaviour gives rise to the 'diffraction peak' in the forward direction.

With the exception of orbiting, all these phenomena take place within angular ranges which get narrower as the classical limit is approached, so that the simple stationary phase approximation (6.26) suffices for most cases. But it is precisely near the 'special' angular regions that the cross section $\sigma(\theta)$ varies by many orders of magnitude, and a precise analytical description of this variation is vital for the correct interpretation of experiments (the crude classical approximation simply becomes infinite in these cases, as can be seen by setting θ equal to 0 or π, and/or $d\Theta/dL$ equal to zero in (6.8)).

6.3. *The phenomena of semiclassical scattering*

The failure of the method of stationary phase when the stationary points $L_i(\theta)$ of the integrands of $I_M^{\mp}$ (6.22) are close together, or when θ lies near 0 or π, cannot be dealt with by calculating correction terms (of higher order in $\hbar$) to the stationary phase method or to the phase shifts or by using the Euler–Maclaurin summation formula since $f(\theta)$ is a highly nonanalytic function of $\hbar$. Each nonsimple configuration of stationary points must be treated in its own way, since it corresponds to a phenomenon with a characteristic angular dependence whose onset is heralded by some feature in the classical deflection function, as outlined in four cases at the end of §6.2. Apart from the rather special case of orbiting, the correct mathematical method to use in these problems is the *method of uniform approximation for* integrals, which is the precise analogue of the comparison method for differential equations discussed in §4. The integrand in $I_M^{\mp}$ is mapped on to a simpler integrand with the same stationary-point structure, and the mapping is rendered one-to-one by adjusting parameters in the comparison integrand to bring the two sets of stationary points into correspondence; hopefully, the comparison integral is well understood in terms of standard functions.

In the papers of Ford and Wheeler (1959a,b) where the basic scattering phenomena were first identified, uniform approximations were not derived; instead, *transitional approximations*, valid over small ranges near the critical angles but not merging smoothly into the simple exponential forms (6.26), were found. Uniform approximations to an integral were first derived by Chester *et al* (1957) for a special case, which was applied directly to rainbow scattering by Berry (1966b), and in a modified form by Miller (1968a) (see also Nussenzveig 1969b, for an application to the case of a discontinuous potential and Khudyakov 1970 for a derivation of the rainbow cross section directly from the classical paths). Glory scattering was treated by Miller (1968a) and Berry (1969a,b) (who also dealt with the case of the forward diffraction peak). For extensive applications of these methods to problems in diffraction theory, see Ludwig (1966, 1967), Lewis *et al* (1967) and Kravtsov (1968), as well as §7.3.

We begin with *rainbow scattering*, which originates in the coalescence of two stationary points, $L_1(\theta)$ and $L_2(\theta)$ say, at the 'rainbow angle' θ_r, beyond which $L_1(\theta)$ and $L_2(\theta)$ are complex. It is shown by Berry (1966b) that the uniform approximation for the cross section in this case (if we ignore the interference effects represented by other classical paths whose contributions take the form (6.26)) is

$$\sigma_r^{\text{uniform}}(\theta) = \frac{\pi}{2mE\sin\theta}\left[\left\{\left(\frac{L_1}{|\Theta'(L_1)|}\right)^{1/2}+\left(\frac{L_2}{|\Theta'(L_2)|}\right)^{1/2}\right\}^2\frac{(-\zeta)^{1/2}}{\hbar^{1/3}}\,\mathrm{Ai}^2\left(\frac{\zeta}{\hbar^{2/3}}\right)\right.$$
$$\left.+\left\{\left(\frac{L_1}{|\Theta'(L_1)|}\right)^{1/2}-\left(\frac{L_2}{|\Theta'(L_2)|}\right)^{1/2}\right\}^2\frac{\hbar^{1/3}}{(-\zeta)^{1/2}}\,\mathrm{Ai}'^2\left(\frac{\zeta}{\hbar^{2/3}}\right)\right] \tag{6.28}$$

where

$$\zeta \equiv \left\{-\frac{3\mathrm{i}}{4}(S_2(\theta)-S_1(\theta))\right\}^{2/3} \tag{6.29}$$

Ai being the Airy function (cf § 4.2 and figure 10), and primes denoting differentiation with respect to the argument of a function. In (6.29) the branch is chosen that makes ζ negative in the classically illuminated angular region, and positive in the shadow where $L_1(\theta)$ and $L_2(\theta)$ are complex. For angles well within the illuminated region, ζ is large and negative, and (6.28) reduces to

$$\sigma_r(\theta) \xrightarrow[\theta \ll \theta_r]{} \frac{1}{2mE\sin\theta}\left\{\frac{L_1}{|\Theta'(L_1)|}+\frac{L_2}{|\Theta'(L_2)|}+2\left(\frac{L_1L_2}{|\Theta'(L_1)\,\Theta'(L_2)|}\right)^{1/2}\sin\left(\frac{S_2-S_1}{\hbar}\right)\right\} \tag{6.30}$$

consisting of the classical contributions from the two paths, plus an interference term. Very close to the rainbow angle, (6.28) reduces to the 'transitional approximation' derived by Ford and Wheeler (1959a) (see also Pechukas 1969) who expanded the exponent in the integral I_0^+ to third order in $L-L_r$ (where L_r is $L_{1,2}(\theta_r)$); the formula is

$$\sigma_r(\theta) \xrightarrow[\theta \simeq \theta_r]{} \frac{\pi L_r}{\hbar^{1/3}mE\sin\theta\{\tilde{\eta}'''(L_r)\}^{2/3}}\,\mathrm{Ai}^2\left(\frac{\theta-\theta_r}{\{\hbar^2\tilde{\eta}'''(L_r)\}^{1/3}}\right) \tag{6.31}$$

a result which shows that the cross section is large, of order $\hbar^{-1/3}$, at the rainbow angle, as compared with $\hbar^0$ in simple classical regions. The rainbow angle represents a caustic of the classical paths (see Khudyakov 1970, Ludwig 1966), across which the transition from illumination to shadow, described by (6.28), is different from the transition into the shadow cast by an edge (Keller 1958b) or by a smooth convex body (Ludwig 1967, Nussenzveig 1969a). The great advantage of the uniform approximation, apart from its applicability over all angular ranges, lies in its dependence only on quantities characterizing the two contributing classical paths. We shall presently examine a formula different from (6.28) but equivalent to it, derived by Miller (1968a), which applies also to glory scattering. Connor and Child (1970) have found a transitional approximation for the case where $\Theta(L)$ has two minima, leading to so-called 'cubic rainbows'; it is hoped that this may provide a model for the scattering of chemically reactive atoms.

Numerical calculations of the transitional approximation (6.31) were performed by Mason and Monchick (1964), who found the results to compare poorly with a partial-wave calculation. Hundhausen and Pauly (1965), obtained a much better fit, but Munn and Smith (1966) confirm the conclusion of Mason and Monchick, as do extensive calculations by one of us (K E Mount to be published). Results of

some of these computations are shown in figure 20 for the Lennard-Jones potential

$$V(r) = \epsilon\left(\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right) \tag{6.32}$$

which is sketched in figure 19(*a*) together with the resulting deflection function (figure 19(*b*)). The dimensionless parameters describing the scattering are

$$E_R = E/\epsilon \qquad K_R = (2mE)^{1/2} r_m/\hbar. \tag{6.33}$$

Figure 20(*a*) shows the simple classical formula (6.8), the 'interfering classical paths' formula (6.30), the transitional approximation (6.31) and the uniform approximation (6.28), ignoring in all cases the simple semiclassical contribution from the 'repulsive' branch $L_3(\theta)$ (cf figure 19(*b*)). The most striking result of these

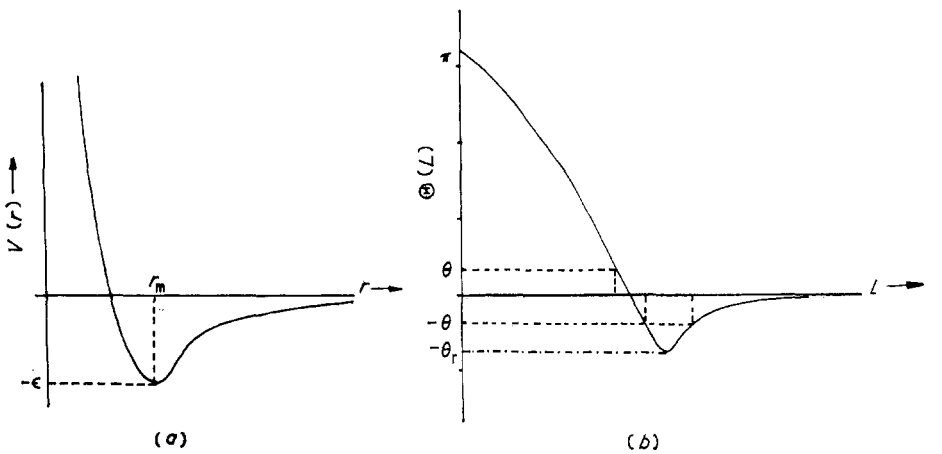

Figure 19. (*a*) Lennard-Jones potential. (*b*) Resulting classical deflection function.

calculations is the fact that the ranges of validity of the 'interfering classical paths' and the transitional formulae do not overlap at all. Figure 20(*b*) shows a comparison between the uniform approximation (6.28) (including now the contribution $L_3(\theta)$), and a partial-wave summation; the complete agreement between the curves, within the accuracy of the computations, leaves little doubt that (6.28) is indeed the correct semiclassical limiting form for this case.

We turn now to the case of *orbiting*, where the deflection function possesses, not a minimum, but a negative logarithmic singularity as in figure 18. For angular momenta L exceeding the value L_0 for which orbiting occurs, the effective potential shows three turning points, while if L is less than L_0 there is only one turning point; the phase shift then shows resonance behaviour, as discussed in §3.3. We wish to show that these resonances do not contribute to the semiclassical limit (qualitative arguments to this effect have already been given by Connor (1968) and Berry (1966a))—in effect, we are dealing with what Ford and Wheeler (1959a) call the 'thick-barrier' case. Only an outline of the argument will be given here, because we intend to publish the details separately, together with numerical calculations.

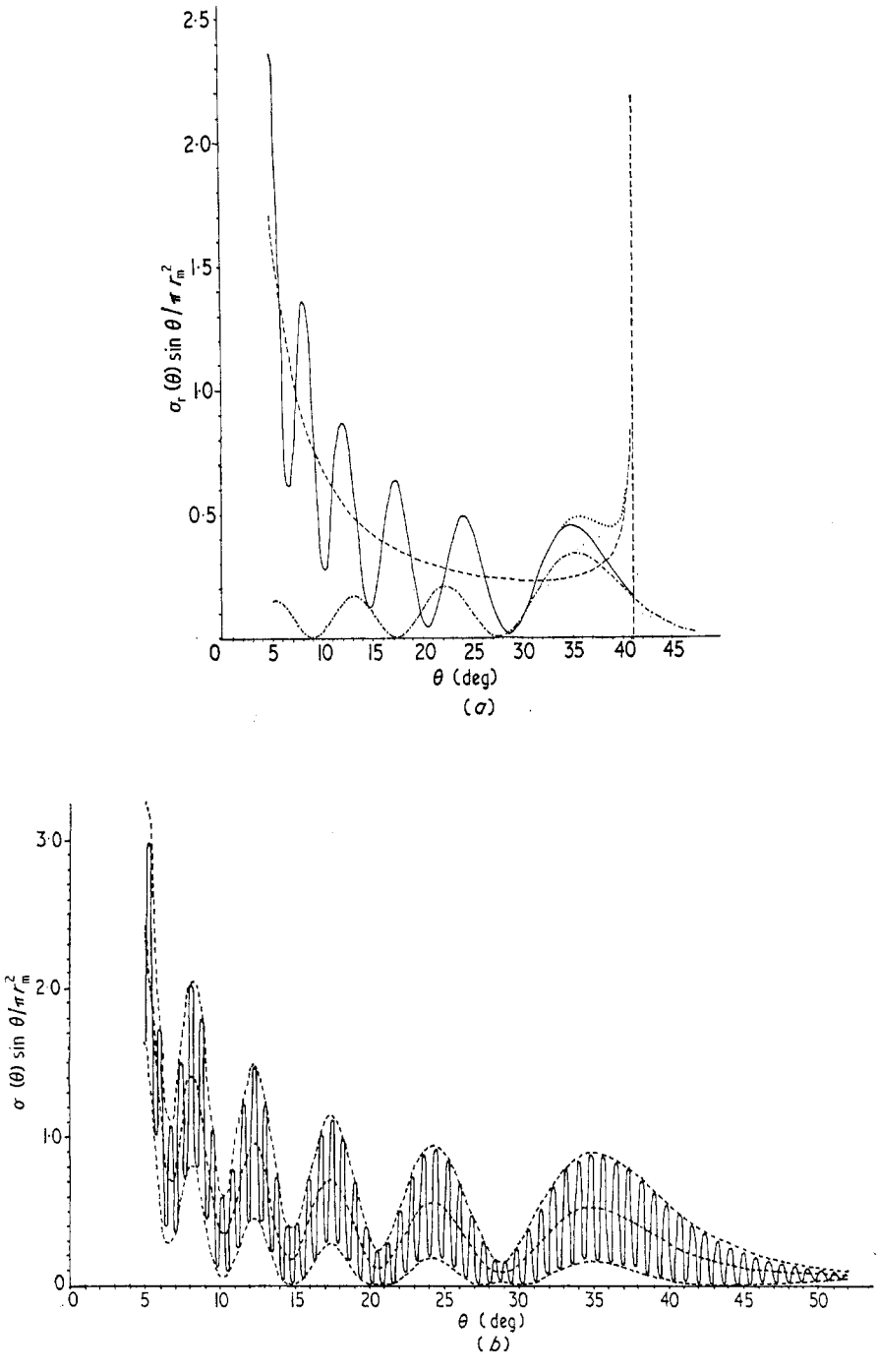

Figure 20. (*a*) Comparison of semiclassical formulae for rainbow scattering ($E_R = 3{\cdot}0$; $K_R = 200$). - - - - - Classical formula; . . . . . classical plus interference; –·–·–·– transitional formula; ——— uniform approximation. (*b*) Comparison of uniform approximation and partial wave calculation ($E_R = 3{\cdot}0$; $K_R = 200$). ——— Partial wave; - - - - - mean and envelope of interference oscillations from uniform approximation.

In terms of the notation of equation (3.67), the phase-shift factor in $I_M^{\pm}$ (equation 6.22) is the *S matrix*

$$\exp(2i\eta_{\{(L/\hbar)-\frac{1}{2}\}}) = \exp\left(\frac{2i\tilde{\eta}_0(L)}{\hbar} - i\delta\right)\exp\left[i\tan^{-1}\left\{\tan\left(\frac{S}{\hbar}-\frac{\delta}{2}\right)\left(\frac{1-|R|}{1+|R|}\right)\right\}\right]$$

$$= \exp\left(\frac{2i\tilde{\eta}_0(L)}{\hbar} - i\delta\right)\left[\frac{\exp\left\{i\left(\frac{S}{\hbar}-\frac{\delta}{2}\right)\right\}+|R|\exp\left\{-i\left(\frac{S}{\hbar}-\frac{\delta}{2}\right)\right\}}{\exp\left\{-i\left(\frac{S}{\hbar}-\frac{\delta}{2}\right)\right\}+|R|\exp\left\{i\left(\frac{S}{\hbar}-\frac{\delta}{2}\right)\right\}}\right] \quad (6.34)$$

where $|R|$ is the barrier reflection coefficient given by (3.58). Imitating the procedure of Nussenzveig (1969a) who treated the case of a square-well potential, we eliminate the resonances by expanding the denominator, to obtain a 'multiple-scattering series' (see also Livingston 1966), namely

$$\exp(2i\eta_{\{(L/\hbar)-\frac{1}{2}\}}) = \exp\left(\frac{2i\tilde{\eta}_0(L)}{\hbar} - i\delta\right)\left[|R| - |T|^2\sum_{n=1}^{\infty}|R|^{n-1}(-1)^n\exp\left\{2in\left(\frac{S}{\hbar}-\frac{\delta}{2}\right)\right\}\right] \quad (6.35)$$

where $|T|^2$ is the transmission factor $(1-|R|^2)$. The behaviour of the 'barrier integral' can be shown to imply that the product $|R||T|$ is exponentially small if L lies outside a region centred on L_0, whose width is of order $\hbar$; thus the terms for which $n>0$ can be neglected, and if the S matrix is replaced by

$$\left.\begin{aligned}\exp(2i\eta_{\{(L/\hbar)-\frac{1}{2}\}}) \simeq \exp(2i\tilde{\eta}_0(L)/\hbar) \qquad & L>L_0\\ \exp\{2i(\tilde{\eta}_0(L)+S)/\hbar\} \qquad & L<L_0\end{aligned}\right\} \quad (6.36)$$

the result will only be seriously in error in this small region near L_0. Since the S matrix is bounded by unity, this small region can affect $I_M^{\pm}$ by at most an amount of order $\hbar$, which vanishes in the semiclassical limit (cf the remarks at the beginning of § 6.2). Bearing in mind the meaning of $\tilde{\eta}_0$ and S (§ 3.3), we find that (6.36) is precisely equivalent to (6.17) which always involves the outermost turning point.

For any observation angle θ there will be an infinite number of classical paths from the deflection function in figure 18, falling into four groups according to whether L_i exceeds L_0 or not, and whether the path emerges after a 'repulsive' or 'attractive' deviation (distinguished by the $\pm$ sign in (6.5)); each of the integrals $I_M^{\pm}$ will contain contributions from just two of these paths, which may be treated separately so long as the appropriate L_i do not lie within a distance of order $\hbar^{1/2}$ of L_0. In the semiclassical limit this distance diminishes while the L_i remain unaltered, so that the scattering amplitude consists of four infinite series of the form (6.26), which are convergent because the 'amplitudes' $(d\Theta/dL)^{-1}$ diminish exponentially as M increases and L_i approaches the singularity at L_0. The phenomenon of orbiting does not therefore require a uniform approximation for its semiclassical description and all the interesting effects associated with it arise solely from the fact that an infinite number of classical paths contribute. In particular, while the effect on $\sigma(\theta)$ of a narrow spike may not be noticed, the effect of a broad spike, for which $(d\Theta/dL)^{-1}$ hardly changes on successive circuits, is to produce a set of angular resonances. The sharpness-to-width ratio of these resonances is independent of $\hbar$, which makes them quite different from the 'Regge-pole' resonances in the phase shifts (6.34), whose sharpness-to-width ratio is of order $\hbar^{-1}e^{-O(\hbar^{-1})}$; the

angular resonances are in fact of the type identified by Gutzwiller (1971, see §7.4) as being due to the presence of an unstable periodic classical orbit (in this case it is a circle at $L = L_0$). Orbiting may be described by three different methods, all involving infinite series: summation of partial waves, Regge poles or classical paths. Of these, only the classical-path series converges in a manner independent of $\hbar$, so that it alone is the correct approach in the semiclassical limit. (The spacing of the Regge poles introduced by Remler (1971) to deal with this problem is of order $\hbar$, so that the method is no better than the original partial-wave summation; the situation is quite different, however, when the potential is discontinuous because then an additional set of Regge poles appears, corresponding to surface waves—see Nussenzveig 1969a.)

Now we consider the semiclassical phenomena associated with the near-forward and near-backward directions, starting with *glory scattering*. The effect arises from the three-dimensional geometry of scattering from a sphere, which is responsible for the equivalence of deflection angles $M\pi \pm \theta$. If there exists a classical path emerging with a deflection angle $M\pi$ and angular momentum L_g, then for angles near $M\pi$ there will exist two contributing stationary points $L_1(\theta)$ and $L_2(\theta)$, which coalesce at L_g when $\theta = 0$ (forward glory) or $\theta = \pi$ (backward glory). In figure 15, there is a forward glory at L_{g_1} and backward glories at L_{g_2} and L_{g_3}. Forward glories are never observed on their own, because they are dominated by the forward diffraction peak, to which they add oscillations in angle or energy, as we shall see; backward glories may be observed, however, for instance in α particle scattering from nuclei (Eisberg and Porter 1961).

Near the forward and backward directions the series of integrals (6.21) is not a valid representation of $f(\theta)$, but a similar series can be derived using the approximations (6.19) and (6.20) for $P_l(\cos\theta)$ (which remain valid when $\theta \to 0$ or π). The uniform approximation for this case involves the ordinary Bessel functions J_0 and J_1 instead of the Airy functions Ai and Ai'; otherwise it is rather similar to the rainbow result (6.28). Berry (1969a) shows that the glory cross section, ignoring interference effects due to classical paths other than $L_1(\theta)$ and $L_2(\theta)$, is

$$\sigma_g^{\text{uniform}}(\theta) = \frac{\pi |S_2 - S_1|}{8mE\hbar \sin\theta}\left[\left\{\left(\frac{L_1}{|\Theta'(L_1)|}\right)^{1/2} + \left(\frac{L_2}{|\Theta'(L_2)|}\right)^{1/2}\right\}^2 J_0^2\left(\frac{|S_2 - S_1|}{2\hbar}\right) + \left\{\left(\frac{L_1}{|\Theta'(L_1)|}\right)^{1/2} - \left(\frac{L_2}{|\Theta'(L_2)|}\right)^{1/2}\right\}^2 J_1^2\left(\frac{|S_2 - S_1|}{2\hbar}\right)\right]. \tag{6.37}$$

Far from the forward (or backward) direction this reduces to the expected 'interfering-path' formula (6.30), while if θ is very close to 0 (or π) it reduces to the transitional approximation derived by Ford and Wheeler (1959a) (see also Pechukas 1969) who first identified the glory effect as a semiclassical scattering phenomenon:

$$\sigma_g(\theta) \xrightarrow[\theta \to 0]{} \frac{L_g^2 \pi\theta}{mE\hbar \sin\theta |\Theta'(L_g)|} J_0^2\left(\frac{L_g \theta}{\hbar}\right) \tag{6.38}$$

(for a backward glory θ must here be replaced by $\pi - \theta$). This last result shows that the cross section rises to a large value, of order $\hbar^{-1}$, as $\theta \to 0$ or π in the presence of a glory.

Miller (1968a) in an ingenious application of a modification, due to Carrier (1966), of the original method of Chester *et al* (1957), has derived a uniform approximation which deals with the rainbow and glory effects in a single formula.

It can be shown to be identical with our results (6.28) and (6.37) over the whole angular range, to within terms which vanish in the semiclassical limit. The advantage of Miller's formalism is that each classical path contributes to a separate term, so that the formula is a modification of (6.26). Each path contribution, however, involves the functions $H_{\frac{1}{3}}^{(1),(2)}, H_0^{(1),(2)}$, which are singular at the rainbow and glory angles, so that the formalism is awkward for computational purposes. Miller's results break down, as do ours, when the rainbow angle is close to 0 or π (Pechukas 1969 gives a transitional approximation for this case), and when one of the contributing angular momenta becomes infinite as $\theta \to 0$, giving rise to the forward diffraction peak.

The *forward diffraction peak* is in fact the last effect we shall deal with; it arises from those trajectories with very large impact parameters, which are very slightly deflected by the long range tail of the potential $V(r)$. Only one classical path contributes to $\sigma(\theta)$, with angular momentum $L_F(\theta)$ (cf figure 15 and L_2 in figure 19(*b*)), so that we do not expect interference oscillations (unless we take possible glory effects into account). The large-L tail $N(L)$ of the phase shift $\tilde{\eta}(L)$ is simply related to the large-r tail of the potential, and it can easily be found from (5.24) that

$$\tilde{\eta}(L) \xrightarrow[L\to\infty]{} N(L) = -\left(\frac{m}{2E}\right)^{1/2} \int_{L/(2mE)^{1/2}}^{\infty} \frac{rV(r)\,\mathrm{d}r}{(r^2-(L^2/2mE))^{1/2}} \tag{6.39}$$

(see also Massey and Mohr 1934, Massey and Smith 1933). The 'comparison integral' which correctly takes account of the effects on $f(\theta)$ arising from this tail is (Berry 1969a)

$$K(\alpha) \equiv 2\int_0^{\infty} \mathrm{d}z\, zN'(z)\, \mathrm{J}_1\left(\frac{z\alpha}{\hbar}\right) \mathrm{e}^{2\mathrm{i}N(z)/\hbar}. \tag{6.40}$$

To derive a uniform approximation, the variable L occurring in the semiclassical integral (analogous to $I_{\frac{1}{M}}^{\pm}$)—which of course involves the true WKB phase $\tilde{\eta}(L)$ and not merely its limiting form $N(L)$—must be mapped on to the variable z occurring in $K(\alpha)$. The result is

$$\sigma_{\substack{\text{uniform}\\ \text{forward}\\ \text{peak}}}(\theta) = \frac{\theta}{2mE\hbar^2 \sin\theta} \left\{ \left| \frac{2N''(z_F(\theta))}{\Theta'(L_F(\theta))} \frac{\alpha(\theta)}{\theta} \frac{L_F(\theta)}{z_F(\theta)} \right| \right\} \frac{K^2(\alpha(\theta))}{\alpha^2(\theta)} \tag{6.41}$$

where $z_F(\theta)$ and $\alpha(\theta)$ are functions chosen to ensure the one-to-oneness of the mapping, whose limiting forms are

$$\left.\begin{aligned} \alpha(\theta) &\xrightarrow[\theta\to 0]{} \theta \\ z_F(\theta) &\longrightarrow L_F(\theta). \end{aligned}\right\} \tag{6.42}$$

This uniform approximation is analogous to the results of § 4.3 for scattering lengths in its dependence on the form of the tail of $V(r)$.

The limiting cases of (6.41) are the simple 'classical-path' result

$$\sigma_{\substack{\text{forward}\\ \text{peak}}}(\theta) \xrightarrow[\theta \gg 0]{} \frac{L_F(\theta)}{2mE \sin\theta \left| \Theta''(L_F(\theta)) \right|} \tag{6.43}$$

and the transitional approximation

$$\sigma_{\substack{\text{forward}\\ \text{peak}}}(\theta) \xrightarrow[\theta \simeq 0]{} \frac{1}{2mE\hbar^2} \frac{K^2(\theta)}{\theta^2}. \tag{6.44}$$

Some workers (eg Helbing and Pauly 1964, Mason *et al* 1964, Pauly and Toennies 1965, Pope and Tassie 1970) have employed various approximation schemes to work out what are essentially 'approximations to the transitional approximation'. The first two papers cited use the relation

$$\sigma_{\substack{\text{forward}\\\text{peak}}}(\theta) \simeq \sigma(0)\, \mathrm{e}^{-\theta^2/\tau^2} \tag{6.45}$$

which is found experimentally (see eg Pauly 1959) to hold very near the forward direction. We wish to emphasize that such methods, which do not involve the evaluation of the fundamental integral $K(\alpha)$, will never yield approximations valid over the entire near-forward region. One of us (K E Mount to be published) has made an extensive numerical comparison of (6.41) with a partial-wave calculation; excellent agreement is found over the whole angular range (where $\sigma(\theta)$ may vary by many orders of magnitude—see Berry 1969a) provided the weak oscillations due to the glory effect are taken into account when necessary.

The *total* scattering cross section, defined by

$$Q(E) \equiv 2\pi \int_0^\pi \sigma(\theta) \sin\theta \, \mathrm{d}\theta \tag{6.46}$$

diverges if evaluated purely classically, because all particles, no matter how large their impact parameter, suffer some deflection from the long range tail of $V(r)$. Quantum mechanically, $Q(E)$ is finite for potentials which fall off faster than r^{-2}, being given by

$$Q(E) = \frac{4\pi\hbar}{(2mE)^{1/2}} \operatorname{Im} f(0) = \frac{4\pi\hbar^2}{2mE} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l. \tag{6.47}$$

The dominant contribution to $f(0)$ comes from the forward diffraction peak at large L. This contribution was calculated by Massey and Mohr (1934) for inverse-power law potential tails; they simply replaced $\sin^2\eta_l$ by its average value of $1/2$ for all l below a cutoff value l_m, and summed the series for higher l using the approximation (6.39) for the phase shifts. Landau and Lifshitz (1965) and Keller and Levy (1963), do not make the random phase approximation, but use (6.39) for all L; this procedure yields more accurate results, as was shown by comparison with exact partial wave calculations of Bernstein (1961) and Bernstein and Kramer (1963). The exactly calculated cross sections also show weak oscillations in energy, which arise (Duren and Pauly 1963, 1964) from the contribution of finite values of L in the glory effect.

7. General semiclassical theory

7.1. *Feynman's formulation of quantum mechanics*

Instead of beginning this article with an account of the general connections between classical and quantum mechanics, we stood logic on its head, and dealt in some detail with relatively simple problems, because our main aim was to focus attention on the mathematical methods involved. But very profound general connections do exist, and they are the subject of continuing research. We shall approach this field via the path-integral formulation of quantum mechanics devised by Feynman (1948) as a result of some remarks by Dirac (1947 p128) (see also Whittaker 1941). Although Feynman's theory can be regarded as an independent

postulational statement of quantum mechanics, we shall in this section derive it from the more familiar operator formalism because the basic feature of the derivation gives a clue which will prove useful in §7.2 in providing a step which has hitherto always been missing in the deduction of the semiclassical formulae.

We consider a general system, described by N generalized coordinates q^α ($\alpha = 1, \ldots, N$) and the corresponding momenta p^α. The motion of the system is controlled by the classical hamiltonian function, which depends on these variables and, in general, on the time t; we write it as $H(\boldsymbol{q}, \boldsymbol{p}, t)$, where $\boldsymbol{q}$ and $\boldsymbol{p}$ represent N-dimensional column vectors. In classical mechanics the system evolves from the configuration $\boldsymbol{q}_\mathrm{A}$ at time t_A to $\boldsymbol{q}_\mathrm{B}$ at a later time t_B by passing through a sequence of well defined intermediate configurations $\boldsymbol{q}(t)$, which constitute the classical path(s) from A to B, obtained by solving the equations of motion.

According to Feynman's theory, the corresponding quantum-mechanical evolution involves the set of all conceivable paths between A and B, not just the classical path(s). To see this, we start from the hamiltonian operator

$$\hat{H} \equiv H(\hat{\boldsymbol{q}}, \hat{\boldsymbol{p}}, t) \tag{7.1}$$

(the $\hat{}$ denotes an operator, and we take the operators $\hat{q}^\alpha$ and $\hat{p}^\alpha$ as being time-independent), in terms of which the 'time evolution operator' $\hat{U}(t_\mathrm{B}, t_\mathrm{A})$ is defined by

$$\left.\begin{aligned} H(\hat{\boldsymbol{q}}, \hat{\boldsymbol{p}}, t_\mathrm{B})\,\hat{U}(t_\mathrm{B}, t_\mathrm{A}) &= \mathrm{i}\hbar(\partial \hat{U}(t_\mathrm{B}, t_\mathrm{A})/\partial t_\mathrm{B}) \\ \hat{U}(t_\mathrm{A}, t_\mathrm{A}) &= \hat{1}. \end{aligned}\right\} \tag{7.2}$$

It is easy to show that $\hat{U}$ is unitary if $\hat{H}$ is hermitian. The operator $\hat{U}$ transforms states at time t_A into states at time t_B. In particular, if the system is known to have the configuration $\boldsymbol{q}_\mathrm{A}$ at time t_A, represented in Dirac notation by the state vector $|\boldsymbol{q}_\mathrm{A}\rangle$, then at time t_B the probability that it has a configuration in the range $|\boldsymbol{q}_\mathrm{B}\rangle$ to $\boldsymbol{q}_\mathrm{B} + \mathrm{d}\boldsymbol{q}_\mathrm{B}\rangle$ is

$$\left.\begin{aligned} P(\boldsymbol{q}_\mathrm{B}, t_\mathrm{B};\, \boldsymbol{q}_\mathrm{A}, t_\mathrm{A})\,\mathrm{d}\boldsymbol{q}_\mathrm{B} &= |\langle \boldsymbol{q}_\mathrm{B}|\,\hat{U}(t_\mathrm{B}, t_\mathrm{A})\,|\boldsymbol{q}_\mathrm{A}\rangle|^2\,\mathrm{d}\boldsymbol{q}_\mathrm{B} \\ &\equiv |K(\mathrm{B}, \mathrm{A})|^2\,\mathrm{d}\boldsymbol{q}_\mathrm{B} \end{aligned}\right\} \tag{7.3}$$

where in the second equation we have introduced the notation $K(\mathrm{B}, \mathrm{A})$—the time-dependent Green function, or 'propagator'—for the matrix element

$$\langle \boldsymbol{q}_\mathrm{B}|\,\hat{U}(t_\mathrm{B}, t_\mathrm{A})\,|\boldsymbol{q}_\mathrm{A}\rangle.$$

It is $K(\mathrm{B}, \mathrm{A})$ that we are interested in evaluating.

The path-integral formulation depends on the 'composition property' of $\hat{U}$, namely

$$\hat{U}(t_\mathrm{B}, t_\mathrm{A}) = \hat{U}(t_\mathrm{B}, t)\,\hat{U}(t, t_\mathrm{A}) \tag{7.4}$$

which follows in a straightforward manner from (7.2), and holds for arbitrary t, although we shall only consider values lying between t_A and t_B. By using this relation repeatedly, for a series of intermediate times t_i ($i = 1, \ldots, n-1$) (thus dividing the time interval t_A ($\equiv t_0$) to t_B ($\equiv t_n$) into n intervals) we can express the evolution operator from t_A to t_B as a succession of unitary transformations involving much shorter times:

$$\hat{U}(t_\mathrm{B}, t_\mathrm{A}) = \prod_{i=0}^{n-1} \hat{U}(t_{i+1}, t_i). \tag{7.5}$$

To derive a path representation we express this equation in a position representation, making use of the identity (see Dirac 1947 p63)

$$\int \mathrm{d}\boldsymbol{q}_i\,|\,\boldsymbol{q}_i\rangle\langle\boldsymbol{q}_i\,| \equiv \hat{1} \tag{7.6}$$

where $\mathrm{d}\boldsymbol{q}_i$ denotes the N-dimensional coordinate volume element at each of the intermediate times t_1 to t_{n-1}. If we take the limit as $n\to\infty$, thus achieving a continuous transition between t_A and t_B, the resulting equation is:

$$K(\mathrm{B},\mathrm{A}) = \lim_{n\to\infty} \int \mathrm{d}\boldsymbol{q}_1 \ldots \int \mathrm{d}\boldsymbol{q}_{n-1} \prod_{i=0}^{n-1} K(i+1,i). \tag{7.7}$$

The integrand of this infinite-dimensional integral depends on a set of values $\boldsymbol{q}_i$ at each of the times t_i, and thus represents a possible path between $(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A})$ and $(\boldsymbol{q}_\mathrm{B}, t_\mathrm{B})$. Equation (7.7) is therefore an expression of the Green function as an *integral over all paths* between the specified end points: the significance of the particular path taken by a classical system is not yet apparent.

In order for the expression (7.7) to be useful, it is necessary to calculate the Green function for infinitesimal times which is involved in each of the factors K; in other words, we need an explicit expression for $\langle\boldsymbol{q}_\mathrm{B}\,|\,\hat{U}(t_\mathrm{A}+\epsilon, t_\mathrm{A})\,|\,\boldsymbol{q}_\mathrm{A}\rangle$ when ϵ is very small. It is easy to solve (7.2) for small ϵ, and express the result in a form which preserves the vital unitarity property of $\hat{U}$:

$$\langle\boldsymbol{q}_\mathrm{B}\,|\,\hat{U}(t_\mathrm{A}+\epsilon, t_\mathrm{A})\,|\,\boldsymbol{q}_\mathrm{A}\rangle \underset{\epsilon\to 0}{=} \langle\boldsymbol{q}_\mathrm{B}\,|\exp\{-(\mathrm{i}\epsilon/\hbar)H(\hat{\boldsymbol{q}}, \hat{\boldsymbol{p}}, t_\mathrm{A})\}\,|\,\boldsymbol{q}_\mathrm{A}\rangle. \tag{7.8}$$

The contribution of higher powers of ϵ vanishes, even after taking n factors K in (7.7) and passing to the limit $n\to\infty$. To proceed further we restrict ourselves for the moment to cartesian coordinates q^α, and hamiltonians that are quadratic in the momenta with a velocity-independent potential, namely

$$\hat{H} = \sum_{\alpha=1}^{N} \frac{(\hat{p}^\alpha)^2}{2m_\alpha} + V(\hat{\boldsymbol{q}}, t). \tag{7.9}$$

This hamiltonian is very general; it could, for instance, describe $N/3$ particles of different masses, interacting among themselves and with an external potential field; but it does not include magnetic forces. The noncommutativity of the terms containing $\hat{p}^\alpha$ and $\hat{q}^\alpha$ gives rise to terms of order ϵ^2 in the expansion of the operator exponential in (7.8), so that we may write

$$\begin{aligned}
&\langle\boldsymbol{q}_\mathrm{B}\,|\,\hat{U}(t_\mathrm{A}+\epsilon, t_\mathrm{A})\,|\,\boldsymbol{q}_\mathrm{A}\rangle \\
&\quad \underset{\epsilon\to 0}{=} \langle\boldsymbol{q}_\mathrm{B}\,|\exp\{-(\mathrm{i}\epsilon/\hbar)\textstyle\sum_\alpha (\hat{p}^\alpha)^2/2m_\alpha\}\exp\{-\mathrm{i}V(\hat{\boldsymbol{q}}, t)\,\epsilon/\hbar\}\,|\,\boldsymbol{q}_\mathrm{A}\rangle \\
&\quad = \frac{\prod_{\alpha=1}^{N} m_\alpha^{1/2}}{(2\pi\mathrm{i}\hbar\epsilon)^{N/2}} \exp\left[\frac{\mathrm{i}\epsilon}{\hbar}\left\{\sum_{\alpha=1}^{N} \frac{m_\alpha}{2}\left(\frac{q_\mathrm{A}^\alpha - q_\mathrm{B}^\alpha}{\epsilon}\right)^2 - V(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A})\right\}\right].
\end{aligned} \tag{7.10}$$

If $\boldsymbol{q}_\mathrm{A}$ and $\boldsymbol{q}_\mathrm{B}$ are not close together—more exactly, if the condition

$$|\,q_\mathrm{A}^\alpha - q_\mathrm{B}^\alpha\,| < \mathrm{O}\left(\left(\frac{\epsilon\hbar}{m_\alpha}\right)^{1/2}\right) \quad \text{for all } \alpha \tag{7.11}$$

is violated—then (7.10) is an infinitely rapidly oscillating function of the end points $\boldsymbol{q}_\mathrm{A}$ and $\boldsymbol{q}_\mathrm{B}$, and its average value is therefore zero. It is thus a matter of indifference

whether the argument of V in (7.10) is $\boldsymbol{q}_A$ or $\boldsymbol{q}_B$ or any intermediate value (this is in any case implied by the derivation). When the potential is velocity-dependent, the place at which it is evaluated does matter, and it can be shown that we must take the midpoint $(\boldsymbol{q}_A+\boldsymbol{q}_B)/2$.

The phase and amplitude of the result (7.10) can be expressed in terms of quantities characterizing the *classical* path from $\boldsymbol{q}_A$ to $\boldsymbol{q}_B$, using the fact that for short times ϵ this path is a straight line. The α component of velocity is $(q_B{}^\alpha - q_A{}^\alpha)/\epsilon$, so that the summation in the exponent of (7.10) is the kinetic energy of the system, while the second term represents the potential energy, which is constant to order ϵ in view of (7.11). We may thus write, to order ϵ

$$\begin{aligned}\epsilon\left(\sum_{\alpha=1}^{N}\frac{m_\alpha}{2}\left(\frac{q_A^\alpha - q_B^\alpha}{\epsilon}\right)^2 - V(\boldsymbol{q}_A, t_A)\right)&\\ = \epsilon L(\boldsymbol{q}_A, \dot{\boldsymbol{q}}_A, t_A)&\\ = \int_{t_A}^{t_B} \mathrm{d}t\, L(\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t), t) \equiv W(\boldsymbol{q}_A, t_A;\, \boldsymbol{q}_B, t_A+\epsilon) \equiv W_{AB} &\qquad (7.12)\end{aligned}$$

where L is the 'classical lagrangian function', $\boldsymbol{q}(t)$ and $\dot{\boldsymbol{q}}(t)$ represent the coordinates and velocities of the system as functions of time along the classical path, while W and W_{AB} are alternative notations for 'Hamilton's principal function' connecting the two states A and B (see Synge 1960 p117), also known as the 'classical action function'. The amplitude occurring in (7.10) can be expressed in a symmetrical way in terms of the second derivatives of W with respect to the end points $\boldsymbol{q}_A$ and $\boldsymbol{q}_B$, simply by inspection of (7.12); the relation is

$$\begin{aligned}\frac{\prod_{\alpha=1}^{N} m_\alpha{}^{1/2}}{\epsilon^{N/2}} &= \left[(-1)^N \det{}_{\alpha\beta}\left(\frac{\partial^2 W(\boldsymbol{q}_A, t_A;\, \boldsymbol{q}_B, t_B)}{\partial q_A^\alpha\, \partial q_B^\alpha}\right)\right]^{1/2}\\ &\equiv [(-1)^N D_{AB}]^{1/2} \qquad (7.13)\end{aligned}$$

where $t_B = t_A + \epsilon$. The required infinitesimal propagator (7.10) is thus given by

$$\langle \boldsymbol{q}_B | \hat{U}(t_A + \epsilon, t_A) | \boldsymbol{q}_A \rangle \underset{\epsilon\to 0}{=} \left[\frac{(-1)^N D_{AB}}{(2\pi i\hbar)^N}\right]^{1/2} \mathrm{e}^{iW_{AB}/\hbar}. \qquad (7.14)$$

It was shown by Morette (1951) by means of the unitarity property of $\hat{U}$ that this is in fact the *general* formula correct to order ϵ for arbitrary coordinates and velocity-dependent potentials (see also de Witt 1957). Choquard (1955) gives a very detailed discussion of the form of the right-hand member of (7.14) as $\epsilon \to 0$, in which he shows that if there is more than one classical path from $(\boldsymbol{q}_A, t_A)$ to $(\boldsymbol{q}_A, t_A+\epsilon)$, then it is only the *direct* path that need be counted in (7.14).

We are now able to write an expression for the finite-time propagator $K(B, A)$ in terms of the path-integral (7.7), using (7.14); the result is

$$K(B, A) = \lim_{n\to\infty} \frac{1}{(2\pi i\hbar)^{Nn/2}} \int \mathrm{d}\boldsymbol{q}_1 \ldots \int \mathrm{d}\boldsymbol{q}_{n-1} \left\{\prod_{i=1}^{n-1} [(-1)^N D_{i,i+1}]^{1/2}\right\} \exp\left(\frac{i}{\hbar}\sum_{i=0}^{n-1} W_{i,i+1}\right) \qquad (7.15)$$

or

$$K(B, A) = \int \mathrm{d}[\boldsymbol{q}(t)] \exp\left\{\frac{i}{\hbar}\int_{t_A}^{t_B} L(\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t), t)\, \mathrm{d}t\right\}. \qquad (7.16)$$

The second of these equations is a purely symbolic way of writing the 'integral-over-all-paths'—$\boldsymbol{q}(t)$ (the paths are continuous because of the restriction (7.11), but the velocities may be infinite, as discussed by Feynman (1948), and Feynman and Hibbs (1965)); the profound mathematical difficulties associated with these functional integrals are reviewed by Gel'fand and Yaglom (1960).

Various alternative formulations of Feynman's integral (7.15) are possible. For instance, the integration may be taken over all paths in phase space, rather than configuration space (Davies 1963). In the case of time-independent hamiltonians, functions other than $K(\mathrm{B},\mathrm{A})$ may be calculated, for instance the energy-dependent Green function

$$G^{+}(\boldsymbol{q}_{\mathrm{B}},\boldsymbol{q}_{\mathrm{A}},E)\equiv\langle\boldsymbol{q}_{\mathrm{B}}|\frac{1}{E+\mathrm{i}\epsilon-\hat{H}}|\boldsymbol{q}_{\mathrm{A}}\rangle$$

$$=-\frac{\mathrm{i}}{\hbar}\int_{0}^{\infty}\mathrm{d}t\exp\left\{\frac{\mathrm{i}(E+\mathrm{i}\epsilon)t}{\hbar}\right\}\langle\boldsymbol{q}_{\mathrm{B}}|\hat{U}(t_{\mathrm{A}}+t,t_{\mathrm{A}})|\boldsymbol{q}_{\mathrm{A}}\rangle \qquad (7.17)$$

where ϵ is a positive infinitesimal, or the spectral function

$$n(\boldsymbol{q}_{\mathrm{B}},\boldsymbol{q}_{\mathrm{A}},E)\equiv\langle\boldsymbol{q}_{\mathrm{B}}|\,\delta(E-\hat{H})\,|\boldsymbol{q}_{\mathrm{A}}\rangle=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\mathrm{d}t\exp(\mathrm{i}Et/\hbar)\langle\boldsymbol{q}_{\mathrm{B}}|\hat{U}(t_{\mathrm{A}}+t,t_{\mathrm{A}})|\boldsymbol{q}_{\mathrm{A}}\rangle$$

$$=-\frac{1}{\pi}\operatorname{Im}G^{+}(\boldsymbol{q}_{\mathrm{B}},\boldsymbol{q}_{\mathrm{A}},E) \qquad (7.18)$$

(see Garrod 1966, Gutzwiller 1967).

7.2. *Semiclassical evaluation of the path integral*

Although the Feynman propagator (7.15) is fully quantum mechanical (it can easily be seen by direct differentiation (Feynman and Hibbs 1965 §4.1) that it satisfies Schrödinger's equation), the infinitesimal-time Green functions which go to make it up are themselves dependent on simple classical quantities (see (7.12) and (7.13)). The formulation is therefore particularly convenient for discussing the semiclassical aspects of quantum mechanics. First of all we discuss the extreme classical limit; the probability amplitude $K(\mathrm{B},\mathrm{A})$ has then no meaning, and we must deal instead with the *probability density* $P(\boldsymbol{q}_{\mathrm{B}},t_{\mathrm{B}};\boldsymbol{q}_{\mathrm{A}},t_{\mathrm{A}})$ defined in (7.3). To find out what boundary conditions to apply to the classical problem, we realize that in the initial quantum state the position $\boldsymbol{q}_{\mathrm{A}}$ is perfectly well defined; thus the distribution in momentum space is uniform, the probability that the momentum lies in a range $\mathrm{d}\boldsymbol{p}_{\mathrm{A}}$ being (see Dirac 1947 p97)

$$|\langle\boldsymbol{p}_{\mathrm{A}}|\boldsymbol{q}_{\mathrm{A}}\rangle|^{2}\,\mathrm{d}\boldsymbol{p}_{\mathrm{A}}=\left|\frac{\exp(\mathrm{i}\boldsymbol{p}_{\mathrm{A}}\cdot\boldsymbol{q}_{\mathrm{A}}/\hbar)}{(2\pi\hbar)^{N/2}}\right|^{2}\mathrm{d}\boldsymbol{p}_{\mathrm{A}}=\frac{\mathrm{d}\boldsymbol{p}_{\mathrm{A}}}{(2\pi\hbar)^{N}}. \qquad (7.19)$$

In the classical problem, therefore, copies of the system (particles if $N=3$) emerge from $(\boldsymbol{q}_{\mathrm{A}},t_{\mathrm{A}})$ with momenta $\boldsymbol{p}_{\mathrm{A}}$ uniformly distributed according to this law. At the time t_{B} some of these copies may, after travelling along classical trajectories, have reached the neighbourhood $\mathrm{d}\boldsymbol{q}_{\mathrm{B}}$ of the final point $\boldsymbol{q}_{\mathrm{B}}$ (see figure 21). In the general case the point $\boldsymbol{q}_{\mathrm{B}}$ itself may be reached by several different routes, which we distinguish with a suffix r. The paths of type r which end in $\mathrm{d}\boldsymbol{q}_{\mathrm{B}}$ at time t_{B} started out from $\boldsymbol{q}_{\mathrm{A}}$ at time t_{A} with momenta in a certain range, which we denote by $\mathrm{d}\boldsymbol{p}_{\mathrm{A}r}$.

Therefore the total number of systems arriving in $\mathrm{d}\boldsymbol{q}_\mathrm{B}$ at t_B which will give us the required probability (7.3) is, from (7.19)

$$P^{\text{classical}}(\boldsymbol{q}_\mathrm{B}, t_\mathrm{B};\, \boldsymbol{q}_\mathrm{A}, t_\mathrm{A})\,\mathrm{d}\boldsymbol{q}_\mathrm{B} = \sum_r \frac{\mathrm{d}\boldsymbol{p}_{\mathrm{A}r}}{(2\pi\hbar)^N} \tag{7.20}$$

so that the classical solution to our problem is

$$\begin{aligned} P^{\text{classical}}(\boldsymbol{q}_\mathrm{B}, t_\mathrm{B};\, \boldsymbol{q}_\mathrm{A}, t_\mathrm{A}) &= \frac{1}{(2\pi\hbar)^N}\sum_r \frac{\mathrm{d}\boldsymbol{p}_{\mathrm{A}r}}{\mathrm{d}\boldsymbol{q}_\mathrm{B}} \equiv \frac{1}{(2\pi\hbar)^N}\sum_r \left|\frac{\partial p^\alpha_{\mathrm{A}r}(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A};\, \boldsymbol{q}_\mathrm{B}, t_\mathrm{B})}{\partial q^\alpha_\mathrm{B}}\right| \\ &= \frac{1}{(2\pi\hbar)^N}\sum_r \left|\det{}_{\alpha\beta}\left(\frac{\partial p^\alpha_{\mathrm{A}r}(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A};\, \boldsymbol{q}_\mathrm{B}, t_\mathrm{B})}{\partial q^\beta_\mathrm{B}}\right)\right| \end{aligned} \tag{7.21}$$

where we have introduced in the third member the notation for the jacobian of the transformation from $\boldsymbol{p}_\mathrm{A}$ to $\boldsymbol{q}_\mathrm{B}$. (If there are no classical paths joining $(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A})$ with $(\boldsymbol{q}_\mathrm{B}, t_\mathrm{B})$, then P is zero.)

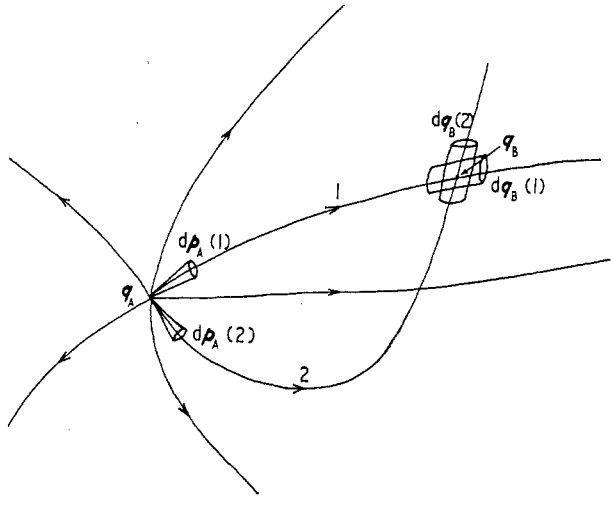

Figure 21. Classical paths along which systems have travelled from $(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A})$ at the time t_B.

The various possible contributing initial momenta $\boldsymbol{p}_{\mathrm{A}r}$ must be found by solving for the classical motion, either directly from Newton's or Hamilton's equations, or by finding Hamilton's principal function $W_r(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A};\, \boldsymbol{q}_\mathrm{B}, t_\mathrm{B})$ for the rth path. If this function is known, then $\boldsymbol{p}_\mathrm{A}$ follows immediately because of the relation (Synge 1960 p119)

$$p^\alpha_{\mathrm{A}r} = -\frac{\partial W}{\partial q^\alpha_\mathrm{A}}. \tag{7.22}$$

The determinant in (7.21) now becomes

$$\det{}_{\alpha\beta}\left(-\frac{\partial^2 W_r(\boldsymbol{q}_\mathrm{A}, t_\mathrm{A};\, \boldsymbol{q}_\mathrm{B}, t_\mathrm{B})}{\partial q^\beta_\mathrm{B}\,\partial q^\alpha_\mathrm{A}}\right) \equiv (-1)^N D_{\mathrm{AB},r} \tag{7.23}$$

so that, finally

$$P^{\text{classical}}(\boldsymbol{q}_\mathrm{B}, t_\mathrm{B};\, \boldsymbol{q}_\mathrm{A}, t_\mathrm{A}) = \frac{1}{(2\pi\hbar)^N}\sum_r |D_{\mathrm{AB},r}|. \tag{7.24}$$

The only difference between this purely classical formula and the square of the quantum formula (7.14) for the infinitesimal-time propagator is that for finite $t_B - t_A$ it is possible for there to be several contributing classical paths. The fundamental reason for the appearance of determinants like (7.21) or (7.24) in the classical limits of quantal problems is the uncertainty principle, which demands a total ignorance of the variable conjugate to one already known. A whole *family* of classical paths, involving all possible values of the conjugate variables, must therefore be considered; the transformation properties of this family appear in the form of the determinant D_{AB}, which represents the *density of paths* of this family at the point B. In the present problem, $\boldsymbol{q}_A$ is known precisely, so that the family consisting of paths from $\boldsymbol{q}_A$ with all possible $\boldsymbol{p}_A$ must be considered. In the potential scattering problem dealt with in § 6.1, it is the direction and energy of the incident particles, in other words the incident momentum $\boldsymbol{p}$ which is specified; the relevant family of trajectories therefore has fixed $\boldsymbol{p}$, but all possible values of starting position, specified by the impact parameter b in the spherically symmetrical case that we considered. The importance of the quantity D_{AB} was discussed in an early paper by Van Vleck (1928).

The first part of the derivation of the classical formula (7.24), and the related *semi*classical expression, starting from Feynman's integral (7.15) or (7.16), is to show that of all the possible paths over which the integration is taken, it is only the classical paths which contribute significantly. This is easy: the integrand in (7.16) is generally a very rapidly oscillating functional of the 'fictitious' path $\boldsymbol{q}(t)$ in semiclassical situations where the action integral along a path from $(\boldsymbol{q}_A, t_A)$ to $(\boldsymbol{q}_B, t_B)$ is large (when measured in units of $\hbar$), so that the contribution to $K(B, A)$ from a path $\boldsymbol{q}(t)$ is cancelled by the contribution from a nearby path $\boldsymbol{q}(t) + \delta\boldsymbol{q}(t)$. The only exception to this rule occurs when we have chosen a path $\boldsymbol{q}^c(t)$ for which

$$\delta \int_{t_A}^{t_B} L(\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t), t)\, dt = 0. \tag{7.25}$$

This equation is of course Hamilton's principle, and $\boldsymbol{q}^c(t)$ represents a possible classical path, so that the basic connection with classical mechanics has been established in a very simple and beautiful way (see Feynman and Hibbs 1965 § 2.3). The actual value of the integral taken along the classical path is of course W_{AB}, the classical action function (cf equation (7.12)).

In order to work out the contribution made by a particular classical path $\boldsymbol{q}_r^c(t)$ to the functional integral, previous workers (Morette 1951, Gel'fand and Yaglom 1960, Abé (quoted in Brush 1961) and Gutzwiller 1967) have expanded the exponent functional in (7.16) to second order in the departure $\delta\boldsymbol{q}(t)$ from the classical path, and evaluated the resulting $(n-1)N$-dimensional gaussian integral by using the formula (see Bellman 1960 p96, Gutzwiller 1967)

$$\int dx_1 \dots \int dx_m \exp\left(-i \sum_{j,k=1}^{m} a_{jk} x_j x_k\right) = \left(\frac{\pi}{i}\right)^{m/2} |\det_{jk} a_{jk}|^{-1/2} \exp(-iM\pi/2) \tag{7.26}$$

where M is the number of negative eigenvalues of the matrix a_{jk}, whose significance will appear in § 7.3. The work based on this procedure has foundered on the intractability of the determinant, which in our problem is (cf equations (7.15) and (7.12))

$$\Delta \equiv \det_{i\alpha, j\beta}\left(\frac{\partial^2(\sum_{k=0}^{n-1} W_{k,k+1})}{\partial q_i^\alpha\, \partial q_j^\beta}\right) \tag{7.27}$$

for $i, j = 1, \ldots, n-1$; and $\alpha, \beta = 1, \ldots, N$. It has so far been possible to evaluate Δ only in the following special cases: free particle in N dimensions, harmonic oscillator, particle in a one-dimensional potential, particle in a spherically symmetrical potential.

It is, however, possible to use a different approach, and perform the integrations over $\mathrm{d}\boldsymbol{q}_1 \ldots \mathrm{d}\boldsymbol{q}_{n-1}$ in (7.15) *successively* (rather than all at once) using the method of stationary phase to perform the N-dimensional integrations at each stage. Our method involves a very interesting classical relation, which we have not been able to find in the literature. To see how it arises, let us perform the integration over $\boldsymbol{q}_1$ in (7.15), keeping $\boldsymbol{q}_0, \boldsymbol{q}_2, \boldsymbol{q}_3, \ldots, \boldsymbol{q}_n$ constant. We have to evaluate

$$I \equiv \int \mathrm{d}\boldsymbol{q}_1 (D_{0,1} D_{1,2})^{1/2} \exp\{(\mathrm{i}/\hbar)(W_{0,1} + W_{1,2})\}. \tag{7.28}$$

The exponent is the action along the classical path from 0 to 1, plus the action along the classical path 1 to 2; it takes a stationary value whenever (cf equation (7.12) and Synge 1960 p119) the point $\boldsymbol{q}_1$ takes the value $\boldsymbol{q}_1^{\mathrm{c}}$, satisfying the equations

$$\left.\begin{aligned} &\frac{\partial}{\partial q_1^\alpha}(W(\boldsymbol{q}_0, t_0;\ \boldsymbol{q}_1, t_1) + W(\boldsymbol{q}_1, t_1;\ \boldsymbol{q}_2, t_2)) \\ &\qquad = p_1^\alpha(\boldsymbol{q}_0, t_0;\ \boldsymbol{q}_1, t_1) - p_1^\alpha(\boldsymbol{q}_1, t_1;\ \boldsymbol{q}_2, t_2) \\ &\qquad \equiv p_1^\alpha(01) - p_1^\alpha(12) = 0 \end{aligned}\right\} \tag{7.29}$$

where the last member introduces an obvious notation. The point $\boldsymbol{q}_1^{\mathrm{c}}$ is simply the configuration reached by the system at time t_1 on the classical path between

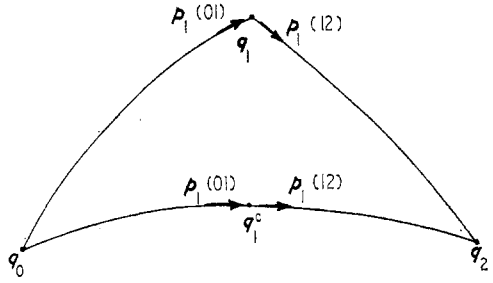

Figure 22. Classical paths joining $\boldsymbol{q}_0$, $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$.

$(\boldsymbol{q}_0 t_0)$ and $(\boldsymbol{q}_2 t_2)$ (see figure 22). For this value of $\boldsymbol{q}_1$ the phase in (7.28) is simply

$$W(\boldsymbol{q}_0, t_0;\ \boldsymbol{q}_1^{\mathrm{c}}, t_1) + W(\boldsymbol{q}_1^{\mathrm{c}}, t_1;\ \boldsymbol{q}_2, t_2) = W(\boldsymbol{q}_0, t_0;\ \boldsymbol{q}_2, t_2) \equiv W_{02} \tag{7.30}$$

and the N-dimensional method of stationary phase yields simply

$$I \simeq \left(\frac{2\pi\hbar}{-\mathrm{i}}\right)^{N/2} \left\{ \frac{(D_{01}(\boldsymbol{q}_1 = \boldsymbol{q}_1^{\mathrm{c}})\, D_{12}(\boldsymbol{q}_1 = \boldsymbol{q}_1^{\mathrm{c}})}{\det_{\alpha\beta}\left(\dfrac{\partial(p_1^\alpha(01) - p_1^\alpha(12))}{\partial q_1^\beta}\right)_{\boldsymbol{q}_1 = \boldsymbol{q}_1^{\mathrm{c}}}} \right\}^{1/2} \mathrm{e}^{\mathrm{i}W_{02}/\hbar} \tag{7.31}$$

The classical relation just mentioned concerns the quantity in $\{\ \}$. It states that, for arbitrary $(\boldsymbol{q}_0, t_0)$, $(\boldsymbol{q}_2, t_2)$ and t_1,

$$\frac{\partial(p_1^\alpha(01))/\partial(q_0^\alpha) \times \partial(p_2^\alpha(12))/\partial(q_1^\alpha)}{\partial(p_1^\alpha(01) - p_1^\alpha(12))/\partial(q_1^\alpha)} = (-1)^N \frac{\partial(p_2^\alpha(02))}{\partial(q_0^\alpha)} \tag{7.32}$$

provided $p_1^\alpha(01) - p_1^\alpha(12) = 0$. To show this we note that the equality of the two values of $\boldsymbol{p}_1$ implies a relation between $\boldsymbol{q}_1$ and $\boldsymbol{q}_0$ and $\boldsymbol{q}_2$ (and the times, but these

are fixed, so we ignore them); differentiation of this relation with respect to q_0^β, keeping q_2 fixed (see figure 23) gives the matrix equation

$$\frac{\partial p_1^\alpha(01)}{\partial q_0^\beta} + \sum_{\gamma=1}^{N} \frac{\partial(p_1^\alpha(01) - p_1^\alpha(12))}{\partial q_1^\gamma} \times \frac{\partial q_1^\gamma}{\partial q_0^\beta} = 0 \tag{7.33}$$

where we have made use of the fact that $p_1^\alpha(12)$ does not depend on q_0. Taking determinants, we get

$$\frac{\partial(p_1^\alpha(01))}{\partial(q_0^\alpha)} = (-1)^N \frac{\partial(p_1^\alpha(01) - p_1^\alpha(12))}{\partial(q_1^\alpha)} \times \frac{\partial(q_1^\alpha)}{\partial(q_0^\alpha)}. \tag{7.34}$$

The left-hand side of (7.32) now becomes

$$(-1)^N \frac{\partial(p_2^\alpha(12))}{\partial(q_1^\alpha)} \times \frac{\partial(q_1^\alpha)}{\partial(q_0^\alpha)}$$

which equals the right-hand side of (7.32) by virtue of the multiplication theorem for jacobians, thus proving the relation.

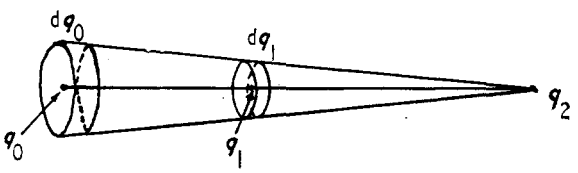

Figure 23. Sketch of transformation employed in deriving classical composition relation.

Our new relation (7.32), together with (7.30), constitute the classical equivalents of the basic quantum composition law (7.4). They enable us to express (7.31) as

$$I \simeq \left(-\frac{2\pi\hbar}{\mathrm{i}}\right)^{N/2} [(-1)^N D_{02}]^{1/2} \, \mathrm{e}^{\mathrm{i}W_{02}/\hbar}. \tag{7.35}$$

The basic Feynman integral (7.15) becomes

$$K(\mathrm{B},\mathrm{A}) = \lim_{n\to\infty} \frac{1}{(2\pi\mathrm{i}\hbar)^{(n-1)N/2}} \int \mathrm{d}q_2 \ldots \int \mathrm{d}q_{n-1} [(-1)^N D_{02}]^{1/2} \times \left\{ \prod_{i=2}^{n-1} [D_{i,i+1}(-1)^N]^{1/2} \right\} \exp\left\{ \frac{\mathrm{i}}{\hbar} \left(W_{02} + \sum_{i=2}^{n-1} W_{i,i+1} \right) \right\}.$$

It is clearly possible to evaluate the remaining $n-2$ integrations by iterating this process, since our evaluation of I did not make use of the smallness of the time interval $t_1 - t_0$. The resulting expression can be written down by inspection, once it is realized that, after any of the intermediate integrations, alternative classical paths might become available to the system; further, according to (7.26), a factor $\exp(-\mathrm{i}M\pi/2)$ (which can vary from path to path) is necessary in order to resolve the ambiguity inherent in the square root in, say (7.35). In §7.3 we shall discuss the value to be given to the index M. If we again denote the different possible classical paths by r, the final expression for the Green function is

$$K^{\mathrm{semiclassical}}(\mathrm{B},\mathrm{A}) = \frac{1}{(2\pi\mathrm{i}\hbar)^{N/2}} \sum_r |D_{\mathrm{AB},r}|^{1/2} \exp\left\{ \mathrm{i} \left(\frac{W_{\mathrm{AB},r}}{\hbar} - \frac{M_r \pi}{2} \right) \right\}. \tag{7.36}$$

It is worth noting that $W_{\mathrm{AB},r}$ need not be positive.

Starting from Schrödinger's equation and employing a generalized version of the WKB substitution (2.19 *et seq*), many authors (eg Brillouin 1926, Dirac 1947, Keller 1958a, Groenewold 1956) have derived formula (7.36), in which the amplitude $D_{AB,r}$ is given by the solution of a classical equation of continuity (see the remarks following (2.15) for a one-dimensional example). Van Vleck (1928), Choquard (1955) and Van Hove (quoted by Morette 1951) go further, and solve the continuity equation, to obtain the explicit determinantal form (7.23) for $D_{AB,r}$. Schiller (1962) and Motz (1962) generalize the Hamilton–Jacobi equation for the action function W, thus arriving at Schrödinger's equation.

When the hamiltonian is at most quadratic in the p^α and q^α, equation (7.36) is exact (see Jones and Papadopoulos 1971, Kilmister 1964 chap 3). Clutton-Brock (1965) claims that the equation is exact *for all cases*, basing his argument on Davies' (1963) phase-space representation of Feynman integrals, which he evaluates by transforming to new canonical coordinates Q^α, P^α for which the hamiltonian vanishes. The fallacy in his argument is to assume that, because the transformation

$$q^\alpha, p^\alpha \rightarrow Q^\alpha, P^\alpha$$

is canonical, the relation

$$\frac{\partial(q^\alpha, p^\alpha)}{\partial(Q^\alpha, P^\alpha)} = 1 \tag{7.37}$$

can be used when changing variables in the functional integral for $K(\mathrm{B}, \mathrm{A})$. But the transformation must be made *before* letting the discrete time intervals $\epsilon = t_{i+1} - t_i$ tend to zero, and the jacobian for each set of variables at each time t_i in this discrete case is not unity, but contains correction terms of order ϵ; these terms must be retained, since they accumulate to give a finite contribution when all $n-1$ factors are multiplied together. (For a general discussion of changes of variable in functional integration, see Gel'fand and Yaglom (1960.))

A beautiful application of functional integration has been made by Buslaev (1965), who considers the classical problem of the diffraction of free particles (or waves) by a smooth convex body. In the course of deriving the formulae describing the transition from light to shadow for such cases, he devises a method of extracting the asymptotic contribution to a functional integral from the end points of the range of the variables $\boldsymbol{q}_i$.

We now turn our attention to the *time-independent* Green function defined in (7.17). The simplest method for evaluating this semiclassically is shown by Gutzwiller (1967) to involve a straightforward application of the method of stationary phase to the integral over t, using the approximation (7.36) for the time-dependent propagator. Only those times $t_c(\boldsymbol{q}_A, \boldsymbol{q}_B, E)$ will contribute in which it is possible for the system to travel from $\boldsymbol{q}_A$ to $\boldsymbol{q}_B$ with energy E along a classical path; these satisfy

$$\frac{\partial}{\partial t} W(\boldsymbol{q}_A, t_A; \boldsymbol{q}_B, t_A + t) + E = 0. \tag{7.38}$$

Defining the energy-dependent action by

$$\begin{aligned} S_{AB} &\equiv S(\boldsymbol{q}_A, \boldsymbol{q}_B, E) \\ &\equiv W(\boldsymbol{q}_A, t_A; \boldsymbol{q}_B, t_A + t_c(\boldsymbol{q}_A, \boldsymbol{q}_B, E)) + E t_c(\boldsymbol{q}_A, \boldsymbol{q}_B, E) \end{aligned} \tag{7.39}$$

it is shown by Gutzwiller (1967) that

$$G^{+\text{semiclassical}}(\boldsymbol{q}_{\mathrm{B}}, \boldsymbol{q}_{\mathrm{A}}, E) = \frac{1}{\mathrm{i}\hbar(2\pi\mathrm{i}\hbar)^{(N-1)/2}} \sum_r |\Delta_{\mathrm{AB},r}|^{1/2} \exp\left\{\mathrm{i}\left(\frac{S_{\mathrm{AB},r}}{\hbar} - \frac{M_r\pi}{2}\right)\right\} \tag{7.40}$$

where r again distinguishes the different possible classical paths, and

$$\Delta_{\mathrm{AB}} \equiv -\left(\frac{\partial^2 S_{\mathrm{AB}}}{\partial E^2}\right)^{1-N} \det{}_{\alpha\beta}\left(\frac{\partial^2 S}{\partial E^2}\frac{\partial^2 S}{\partial q_{\mathrm{A}}^{\alpha}\partial q_{\mathrm{B}}^{\beta}} - \frac{\partial^2 S}{\partial q_{\mathrm{A}}^{\alpha}\partial E}\frac{\partial^2 S}{\partial q_{\mathrm{B}}^{\beta}\partial E}\right). \tag{7.41}$$

The simple form taken by these expressions in one dimension will be discussed in § 7.4. A simple example of a formula whose structure closely resembles (7.40) is the result (6.26) for scattering problems. The exponent M_r will be discussed in

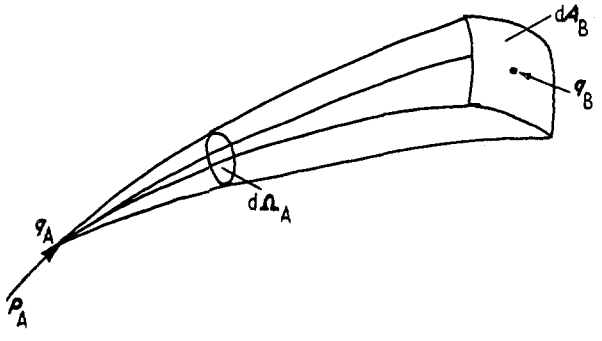

Figure 24. Tube of trajectories defining amplitude of energy-dependent Green function.

§ 7.3, along with the corresponding quantity for the time-dependent case. When the kinetic energy takes the simple 'isotropic' form $\sum_{\alpha=1}^{N}(p^{\alpha})^2/2m$ (so that the 'wave surfaces' on which $W(\boldsymbol{q}_{\mathrm{A}}, \boldsymbol{q}_{\mathrm{B}})$ is constant cut the paths perpendicularly), as in the case of a particle in three dimensions moving in a velocity-independent potential, it is easy to show that

$$\Delta_{\mathrm{AB}} = \frac{m^2|\boldsymbol{p}_{\mathrm{A}}|^{N-2}}{|\boldsymbol{p}_{\mathrm{B}}|}\frac{\mathrm{d}\boldsymbol{\Omega}_{\mathrm{A}}}{\mathrm{d}A_{\mathrm{B}}} \tag{7.42}$$

where $\mathrm{d}A_{\mathrm{B}}$ is the $(N-1)$-dimensional cross section at $\boldsymbol{q}_{\mathrm{B}}$ of the tube of trajectories of energy E which started out from $\boldsymbol{q}_{\mathrm{A}}$ within a solid angle ($(N-1)$-dimensional) $\mathrm{d}\boldsymbol{\Omega}_{\mathrm{A}}$ of the direction of $\boldsymbol{p}_{\mathrm{A}}$ (see figure 24). (The formula (7.42) is the time-independent analogue of the second member of (7.21).)

The reasoning leading to (7.40) breaks down when $\boldsymbol{q}_{\mathrm{A}}$ and $\boldsymbol{q}_{\mathrm{B}}$ are close together, because there is then always a direct classical path for which t_{c} is very small; in this case D_{AB} is very rapidly varying ($\sim t^{-N}$ cf (7.13)), whereas the method of stationary phase assumes it to be constant. To remedy this situation, a 'uniform approximation' must be devised, giving the correct (free-particle-like) form when $\boldsymbol{q}_{\mathrm{B}} \to \boldsymbol{q}_{\mathrm{A}}$ and reducing to (7.40) when the points are far apart. Using methods similar to those outlined in § 6.3, the following result is obtained:

$$G^{+\text{semiclassical}}(\boldsymbol{q}_{\mathrm{B}}, \boldsymbol{q}_{\mathrm{A}}, E) = \frac{1}{\mathrm{i}\hbar(2\pi\mathrm{i}\hbar)^{(N-1)/2}} \times \sum_r \left|\frac{\pi\Delta_{\mathrm{AB},r}S_{\mathrm{AB},r}}{2\hbar}\right|^{1/2} \mathrm{i}^{(N-1)/2}\,\mathrm{H}^{(1)}_{\mathrm{i}N-1}\left(\frac{S_{\mathrm{AB},r}}{\hbar} - \frac{M_r\pi}{2}\right). \tag{7.43}$$

(We must take the phase M_r to be zero for the direct paths; this will be discussed in § 7.3.) When $\boldsymbol{q}_A$ and $\boldsymbol{q}_B$ are far apart, this reduces to (7.40) by virtue of the asymptotic form of the Hankel function $H^{(1)}$. By what appears to be a lucky chance, based on the special forms of $H_{-\frac{1}{2}}^{(1)}$ and $H_{\frac{1}{2}}^{(1)}$, this new formula is identical with the simpler expression (7.40) in the two most common cases, of one and three dimensions.

In an important series of papers, Gutzwiller (1967, 1969, 1970, 1971) has applied (7.40) and the equivalent formula connecting two points $\boldsymbol{p}_A, \boldsymbol{p}_B$ in momentum space, to investigate in very great detail the case of a particle bound in a three-dimensional potential well; we shall return to this work in § 7.4 when we discuss quantization. Taking a different point of view, the papers of Norcliffe and Percival (1968a,b), and Norcliffe *et al* (1969a,b), consider the exactly soluble problems of the one-dimensional free particle (with various boundary conditions) and the three-dimensional Coulomb interaction (for both scattering and bound states); they show, by means of a detailed enumeration of the classical paths (real and complex—see § 7.3) in coordinate and momentum space, how known quantum solutions can be reconstructed exactly using classical path sums. An interesting paper by Pechukas (1969) is based on the derivation of the time-dependent semiclassical Green function (7.36) and its application to the potential scattering problem treated in § 6.

7.3. '*Sewing the wave flesh on the classical bones*'

Despite their generality, the basic semiclassical formula (7.36) and its time-independent equivalent (7.40) are crude by comparison with the expressions developed for simple particular problems in §§ 2–6. They suffer from three main defects. First, the formulae predict that the propagator is zero in regions not reached by classical trajectories, whereas the exact quantum $K(B, A)$ can be zero at most at isolated points (provided that $t_B - t_A$ is not zero, and there are no impenetrable potential barriers). Second, we have given no prescription for calculating the phase factors M_r which are associated with the classical paths. Third, the formulae contain the classical path-density factors $D_{AB,r}$ and $\Delta_{AB,r}$ which can become infinite in certain regions, whereas the exact propagators are regular functions of $\boldsymbol{q}_B$ if the hamiltonian is (unless $t_B = t_A$ or, in the time-independent case, $\boldsymbol{q}_B = \boldsymbol{q}_A$).

All of these deficiencies are related through one concept—the 'topological structure' of the family of classical paths which forms the skeleton on which the wave solution is built up. This structure arises because of the possible multiplicity of paths (of a given family) passing through a point, a fact which finds its mathematical reflection in the *multivaluedness* of the action function W_{AB} or S_{AB}, considered as a function of the endpoints $\boldsymbol{q}_A$ and $\boldsymbol{q}_B$ (with t or E fixed), the various branches being distinguished in our notation by the suffix r. The ordinary classical paths correspond to real values of the action function, but there is nothing in the principles of quantum mechanics to prevent the inclusion of *complex classical paths*, for which the action need not be real. In fact, as was shown by Keller (1958b) in his beautiful 'geometrical theory of diffraction', it is *necessary*, for a complete short-wavelength (semiclassical) description of the wave field, to include all the solutions of the extremum equation (7.25), or, what is equivalent, the

Hamilton–Jacobi equations

$$\left.\begin{aligned} H(\boldsymbol{q}_{\mathrm{B}}, \nabla_{\boldsymbol{q}_{\mathrm{B}}} W(\boldsymbol{q}_{\mathrm{A}}, t_{\mathrm{A}}; \boldsymbol{q}_{\mathrm{B}}, t_{\mathrm{B}}), t_{\mathrm{B}}) &= -\frac{\partial W}{\partial t_{\mathrm{B}}}(\boldsymbol{q}_{\mathrm{A}}, t_{\mathrm{A}}; \boldsymbol{q}_{\mathrm{B}}, t_{\mathrm{B}}) \\ H(\boldsymbol{q}_{\mathrm{A}}, \nabla_{\boldsymbol{q}_{\mathrm{A}}} W(\boldsymbol{q}_{\mathrm{A}}, t_{\mathrm{A}}; \boldsymbol{q}_{\mathrm{B}}, t_{\mathrm{B}}), t_{\mathrm{A}}) &= +\frac{\partial W}{\partial t_{\mathrm{A}}}(\boldsymbol{q}_{\mathrm{A}}, t_{\mathrm{A}}; \boldsymbol{q}_{\mathrm{B}}, t_{\mathrm{B}}) \end{aligned}\right\} \tag{7.44}$$

or

$$\left.\begin{aligned} H(\boldsymbol{q}_{\mathrm{B}}, \nabla_{\boldsymbol{q}_{\mathrm{B}}} S(\boldsymbol{q}_{\mathrm{A}}, \boldsymbol{q}_{\mathrm{B}}, E)) &= E \\ H(\boldsymbol{q}_{\mathrm{A}}, -\nabla_{\boldsymbol{q}_{\mathrm{A}}} S(\boldsymbol{q}_{\mathrm{A}}, \boldsymbol{q}_{\mathrm{B}}, E)) &= -E \end{aligned}\right\} \tag{7.45}$$

(see Synge 1960 §§72, 78). In addition to the complex solutions of immediate interest to us, Keller exhibits a variety of other types of 'diffracted rays' which arise from the impenetrable walls and discontinuous potentials encountered in classical diffraction problems. (For related work see Synge 1954, 1963, Popov *et al* 1967, Kotova *et al* 1968.)

By including complex paths it is possible to obtain at least one contribution for every value of $\boldsymbol{q}_{\mathrm{A}}$ and $\boldsymbol{q}_{\mathrm{B}}$, thus disposing of the first defect in the formulae (7.36) and (7.40). In one-dimensional time-independent problems the regions where real and complex paths contribute are clearly separated by the turning points, as we have seen in § 3, but in higher-dimensional cases it is possible for real and complex paths to coexist in the same region, as in the scattering problems dealt with in § 6.3 (beyond the rainbow angle).

In certain regions of dimensionality less than N, the values of the action function on two or more of its branches become equal, and the determinants D_{AB} and Δ_{AB} become infinite, being determined by the derivatives of W_{AB} and S_{AB} via equations (7.23) and (7.41). This behaviour represents a concentration of the rays in such regions, by virtue of the vanishing of the elements $\mathrm{d}\boldsymbol{q}_{\mathrm{B}}$ or $\mathrm{d}\boldsymbol{A}_{\mathrm{B}}$ in (7.21) or (7.42). A region where the dimensionality of the elements $\mathrm{d}\boldsymbol{q}_{\mathrm{B}}$ or $\mathrm{d}\boldsymbol{A}_{\mathrm{B}}$ is reduced by m is called 'a caustic of order m', the name arising from the surface on which the radiation is particularly intense behind a burning-glass illuminated by the sun; a 'focal line' in three dimensions is a caustic of order two, while a 'focal point' is a caustic of order three. Caustics are the *envelopes* of the families of classical paths; to see this, we distinguish the members of the family by the initial momentum $\boldsymbol{p}_{\mathrm{A}}$, and write the trajectories as

$$q_{\mathrm{B}}^{\alpha} = q_{\mathrm{B}}^{\alpha}(\boldsymbol{p}_{\mathrm{A}}, \boldsymbol{q}_{\mathrm{A}}, t_{\mathrm{A}}; t_{\mathrm{B}}). \tag{7.46}$$

The envelope is simply given by the determinantal condition

$$\partial(q_{\mathrm{B}}^{\alpha})/\partial(p_{\mathrm{A}}^{\alpha}) = (-1)^{N}/D_{\mathrm{AB}} = 0 \tag{7.47}$$

(similar considerations establish the divergence of Δ_{AB} in the time-independent case). Along its trajectory from $\boldsymbol{q}_{\mathrm{A}}$ to $\boldsymbol{q}_{\mathrm{B}}$, the system may pass through (or touch) several caustics, and if each is counted according to its order m the resulting integer is precisely the index M_r which fixes the phase of the semiclassical equations (7.36) and (7.40). As pointed out by Gutzwiller (1967), this follows from (7.26) together with a theorem due to Morse (1934 p61) relating the global aspects of the calculus of variations to the theory of the eigenvalues of quadratic forms. As a particular case, M_r is zero for the direct path if $\boldsymbol{q}_{\mathrm{A}}$ and $\boldsymbol{q}_{\mathrm{B}}$ are close together, because there are no caustics on the path.

The 'phase advance by $\pi/2$ on passing through a caustic', which this determination of M_r implies, is well known and can also be derived from integral representations of the field near the caustic (see eg Pechukas 1969, Kay and Keller 1954). The result is a generalization, to multi-dimensional systems and caustics of any order, of the simple connection formula (3.24) which led to the result $-\mathrm{i}$ (see (3.34) and (3.35)) for the reflection coefficient from a simple turning point, when the wave function decays exponentially into the forbidden region. The dependence of M_r on the caustics can be made plausible by the following simple argument: we consider the q_{B}^{α} to be N complex variables, and we cut the resulting $2N$-dimensional space with the caustic surfaces in such a way that W_{AB} and D_{AB} are single-valued functions of $\boldsymbol{q}_{\mathrm{B}}$. By staying on the appropriate 'sheet' it is possible to make the element $\mathrm{d}\boldsymbol{q}_{\mathrm{B}}$ change its phase by $+m\pi$ when passing through an mth order caustic, so that, from (7.47), D_{AB} changes by a factor $\mathrm{e}^{-\mathrm{i}m\pi}$; if we now omit the modulus signs in (7.36) and (7.40), and determine the phase of $D_{\mathrm{AB}}^{1/2}$ and $\Delta_{\mathrm{AB}}^{1/2}$ by analytic continuation along the classical path, the correct values M_r will follow automatically. This method, first stated in its general form by Keller (1958a), is attractive, but cannot be considered as a *proof* of the determination of M_r, because it ignores the fact that the journeys around the caustics in the complex space of the variables q_{B}^{α} involve crossing the multi-dimensional equivalents of the Stokes lines considered in § 3, on which the solution may change its character; indeed, if we had used the other sheet of the 'Riemann surface' and dealt instead with the solution which (when m is odd) *increases* exponentially into the shadow beyond the caustic, we would have got the wrong connection formula.

We must now discuss the third defect of the basic semiclassical formulae, namely their prediction that the Green functions become infinite on caustics. This matter forms the subject of an excellent review by Kravtsov (1968) (the title of this section comes from a remark due to Kinber, quoted there), while a descriptive account was given by Berry (1969b); therefore we shall not deal with it in detail, but merely summarize the main methods. Near a caustic, where the semiclassical expressions fail, it is possible to find an integral representation for the wave field, which remains finite on the caustic. We have met examples of such a procedure in § 6.2, where the integrals over angular momentum L gave a representation of the scattering amplitude which is valid semiclassically, for all angles θ, even near rainbows, etc, where the simple 'path' expressions diverge and also in § 7.2, where the integral over time represented the energy Green function accurately, even for small $\boldsymbol{q}_{\mathrm{B}}-\boldsymbol{q}_{\mathrm{A}}$ where the simple form (7.40) failed. A general method for finding such integrals (which are analogous to, though not identical with, the diffraction integrals of optics) was given by Maslov (1962), in important work of which an account is given in the review of Kravtsov (1968).

These integral representations cannot be said to solve the problem of finding useful semiclassical approximations, since their rapidly oscillating integrands make their behaviour difficult to understand or compute. To deal with this difficulty, the method of uniform approximation outlined in connection with scattering problems in § 6.3 can often be used, the principle being to find a new variable of integration in terms of which the integrand takes on as simple a form as possible, while retaining the same stationary-point structure as the old. This technique is useful only if the 'comparison integrals' are well understood in terms of the standard functions of analysis. It is not in fact necessary to start from an integral representation: uniform approximations can be derived directly from a differential equation (see § 4.1), or

even from a difference equation (Dingle and Morgan 1967a,b). Problems which have been solved in this manner include the pioneering work of Ludwig (1966) and Kravtsov (1968) on caustics of a variety of types (see also Khudyakov 1969, 1970), the classical diffraction problems of scattering from smooth convex bodies (Ludwig 1967) and waves creeping along smooth surfaces (Lewis *et al* 1967), the potential scattering problems discussed in § 6 (Berry 1966b, 1969a, Miller 1968a), bound states of potentials (Miller 1968a, Dickinson and Bernstein 1970), time-dependent Kirchhoff diffraction from a rough surface (Berry 1972) and water waves incident on a beach (Smith 1970).

It is worth stressing the physical content of the results of the various techniques of uniform approximation: under semiclassical conditions, quantum-mechanical wave fields can be described using *only quantities characterizing the appropriate family of classical paths* (including complex paths). In general, however, the action functions for the family of paths do not appear in sinusoidal or exponential functions (as in the simple semiclassical expressions (7.36) and (7.40)), but as the arguments of higher functions which are determined by the 'topological singularities', in other words the type of caustics, of the pattern of classical paths. This principle follows from the fact that the stationary-point structure of the integrands in Maslov's integral representations, and the turning-point structure of differential equations, on which the uniform approximations depend, are determined solely by the classical paths.

For the more complicated problems to which semiclassical and related methods have been applied, for example the motion of Bloch electrons in a magnetic field (Pippard 1969, Chambers 1969), and diffraction in crystals at high energies (Berry 1971), the mere analysis of the classical path structure presents such difficulties that no attempts have been made to deal with the behaviour of the wave field near the caustics. It is in these situations, where an enormous number of classical paths may contribute to the wave at a given point (particularly if $t_B - t_A$, or in the time-dependent case $|\boldsymbol{q}_B - \boldsymbol{q}_A|$, is large), that what appears to be a new difficulty of principle arises, threatening the very applicability of the semiclassical method. To make the problem clear, let us consider the pattern of paths (figure 25) produced when a parallel beam of particles of mass m and constant energy E, travelling along the x axis, is incident on a region where the potential varies sinusoidally along the y axis (this pattern arises when light is diffracted by ultrasound, see Berry 1966c p10 and references therein). As we move in the direction of increasing x we cross the caustics successively, and at each crossing two additional paths contribute; thus in the region A before the first caustic, only one path contributes, in region B three paths and in region C five paths, etc, the number growing without limit. But the *exact* solution of this problem is known (Berry 1966c chap 5) in terms of an eigenfunction series of Mathieu functions, of which a large but finite number of terms, say n, contributes significantly, n being independent of x, and of order $\hbar^{-1}$. For sufficiently large x the number of contributing classical paths will exceed n, and there seems little point in using a semiclassical theory at all. The question of what is the best type of asymptotic representation to use in the general case when such a clash of limits occurs ($n\hbar$ finite, $x\hbar \to \infty$) does not seem to have been investigated. It is related to the transition from Fresnel to Fraunhofer diffraction, and the transverse diffusion of solutions of the parabolic equation of diffraction theory (a point touched on by Kravtsov 1968 § 2.4); the problem also arises in the attempt to apply semiclassical methods to long-distance wave propagation in disordered media (to estimate the conductivity of liquid metals, for instance).

7.4. *Quantization and the density of states*

We have already (§ 6.2) discussed the quantization of angular momentum, and found it to originate in the topological properties of the angular coordinate θ. Now we focus attention on the more general and far harder problem of the structure of the *energy* spectrum for an arbitrary (time-independent) hamiltonian operator.

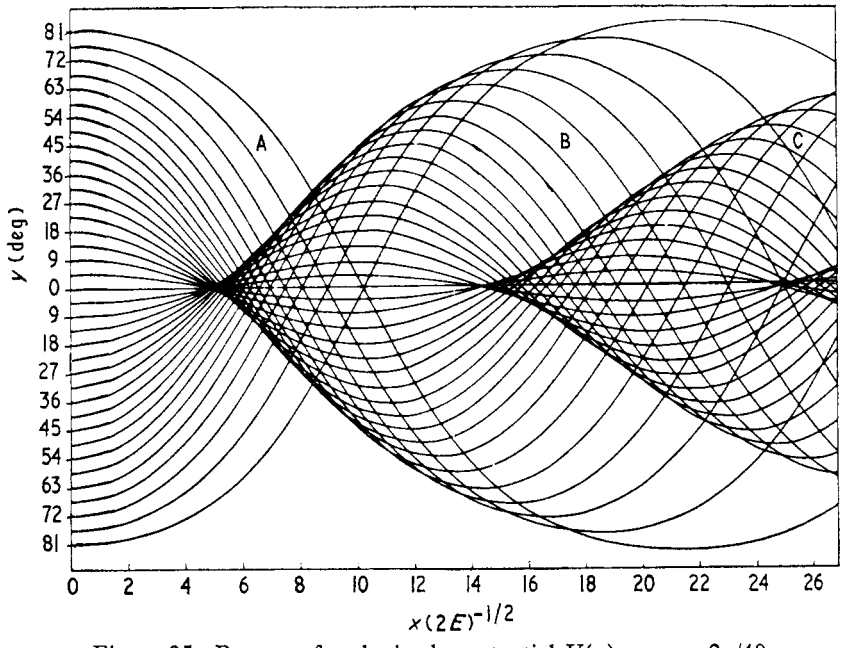

Figure 25. Pattern of paths in the potential $V(y) = -\cos 2y/40$.

In order to have a general formalism, capable of dealing with both bound and scattering states within the same framework, we aim to calculate the 'density of states' $n(E)$, defined as the trace of the spectral operator $\delta(E-\hat{H})$. Using an energy representation, we have

$$n(E) \equiv \mathrm{Tr}\,\delta(E-\hat{H}) = \sum_n \langle E_n|\,\delta(E-\hat{H})\,|E_n\rangle$$
$$= \sum_n \delta(E-E_n) \tag{7.48}$$

where the energy eigenstates are represented by the kets $|E_n\rangle$ in the notation of Dirac (1947). When the (N-dimensional) volume V of the system is very large, the spectrum may be quasicontinuous, and $n(E)$ is proportional to V; an example of this behaviour is provided by the system of $N/3$ noninteracting free particles, for which

$$\hat{H} = \sum_{\alpha=1}^{N} \frac{(p^\alpha)^2}{2m_\alpha} \tag{7.49}$$

where a direct evaluation of the trace in (7.48), using the momentum representation, yields

$$\left.\begin{aligned} n^{\text{free particles}}(E) &= \frac{V}{E}\left(\frac{E}{2\pi\hbar^2}\right)^{N/2} \frac{\prod_{\alpha=1}^{N} m_\alpha^{1/2}}{\Gamma(N/2)} \quad (E>0) \\ &= 0 \qquad\qquad\qquad\qquad\qquad\quad (E<0). \end{aligned}\right\} \tag{7.50}$$

In calculating $n(E)$ semiclassically, we lean heavily on the recent work of Gutzwiller (1971) (see also Miller 1972, Freed 1972), this being the most satisfactory general treatment to date although, as we shall see, it leaves some important questions unanswered. Using a position representation for the trace and the relation to the Green function provided by (7.18), we get

$$n(E) = -\frac{\mathrm{Im}}{\pi}\int \mathrm{d}\boldsymbol{q}\, G^{+}(\boldsymbol{q},\boldsymbol{q},E). \tag{7.51}$$

We know, however, that in the semiclassical approximation G^{+} is given by (7.40) or (7.43), expressions which involve the classical path from $\boldsymbol{q}_{\mathrm{A}}$ to $\boldsymbol{q}_{\mathrm{B}}$. Therefore, the semiclassical density of states depends only on the *classical paths which start and end at the same point.* These paths fall into two types: the 'path of zero length' which is the limit of the direct path as $\boldsymbol{q}_{\mathrm{B}} \to \boldsymbol{q}_{\mathrm{A}}$, and the looped paths which involve an excursion away from the point $\boldsymbol{q}$ before returning. We shall treat the two types separately.

The contribution to $n_0(E)$ from the paths of zero length must be calculated from (7.43) since that is the expression which is generally valid for paths which only take a short time to traverse. There are no caustics on the direct path, so the phase M_r is zero, and the limiting expression for the Hankel function for small argument gives

$$n_0(E) = \frac{2}{(2\pi\hbar^2)^{N/2}\,\Gamma(N/2)}\int_R \mathrm{d}\boldsymbol{q}\lim_{\epsilon\to 0}\left[\frac{\Delta_{q,q+\epsilon}}{2^N}\,S^{N-1}_{q,q+\epsilon}\right]^{1/2} \tag{7.52}$$

where the region R includes only those points where $E > V(\boldsymbol{q})$ since in other regions no direct path exists. It is difficult to work out the limit in the general case, but many situations of interest are covered if we restrict ourselves to an 'isotropic' hamiltonian, given by

$$H(\boldsymbol{q},\boldsymbol{p}) = \sum_{\alpha=1}^{N}\frac{(p^{\alpha})^2}{2m} + V(\boldsymbol{q}). \tag{7.53}$$

Then the action takes the simple form

$$S_{q,q+\epsilon} = \{2m(E - V(\boldsymbol{q}))\}^{1/2}\,|\,\boldsymbol{\epsilon}\,| \tag{7.54}$$

describing the isotropic divergence of the constant-energy trajectories in the immediate neighbourhood of $\boldsymbol{q}$. The determinant can best be evaluated with the aid of (7.42), since

$$\mathrm{d}A_{\mathrm{B}} = |\,\boldsymbol{\epsilon}\,|^{N-1}\,\mathrm{d}\boldsymbol{\Omega}_{\mathrm{A}} \tag{7.55}$$

and (7.52) becomes

$$n_0(E) = \left(\frac{m}{2\pi\hbar^2}\right)^{N/2}\int_R \mathrm{d}\boldsymbol{q}\,\frac{[E - V(\boldsymbol{q})]^{\frac{1}{2}N-1}}{\Gamma(N/2)}. \tag{7.56}$$

This formula reduces to the free-particle expression (7.50) when $V(\boldsymbol{q})$ is zero, since then the region R includes all space when $E > 0$, and is of zero measure when $E < 0$.

The contribution, $n_0(E)$, from the paths of zero length, has appeared in a variety of guises over the years (usually in a form less general than (7.56)). It is the first term of a formal series expansion of $n(E)$ in powers of $\hbar$ (Curtiss and Powers 1964, Choi and Ross 1964); it is the Thomas–Fermi formula, used in atomic theory (March and Plaskett 1956); finally, it is a direct consequence of the assumption that under semiclassical conditions each quantum state 'occupies' a volume h^N of the

classical phase space of the system (Landau and Lifshitz 1965 p241). Although (7.56) predicts a continuous spectrum even for classically bounded systems where it is well known that quantization occurs, we shall see later that it is nevertheless useful in that it gives correctly the 'average' density of states which is found when the system is not observed sufficiently closely to discriminate between the discrete energy levels.

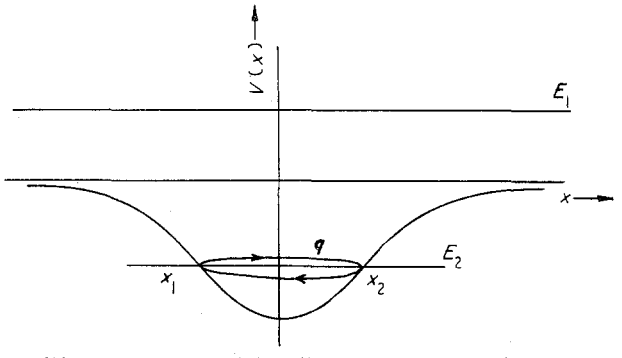

Figure 26. Potential well illustrating quantization.

When considering the paths that leave q and return, we may use the Gutzwiller (1967) formula (7.40), since these paths will not (generally) have small values of the action. Because of the large exponent in this expression for the Green function, most of these looped paths will have their contributions cancelled by neighbouring paths during the integration over q involved in taking the trace. The only exception to this rule occurs when

$$0 = \frac{\partial S_{q,q}}{\partial q^\alpha} = \lim_{q' \to q}\left(\frac{\partial S_{q,q'}}{\partial q^\alpha} + \frac{\partial S_{q,q'}}{\partial q'^\alpha}\right) = \lim_{q \to q'}(p'^\alpha - p^\alpha) \tag{7.57}$$

—in other words, when the system has the same *momenta* as well as the same coordinates at both ends of its trajectory, so that the orbit is *periodic*. It has long been known that the periodic orbits are of fundamental importance in semiclassical mechanics (Einstein 1917, Brillouin 1926, Keller 1958a), but their precise meaning is only now becoming clear as a result of this work of Gutzwiller (1971). Each periodic orbit contributes an infinite number of terms to $n(E)$, corresponding to returns to q after different numbers of traversals (in both directions); it is the *interference* between the waves making these successive circuits that gives rise to sets of quantized energy levels. Azbel (1961) applies these ideas to the problem of an electron in a magnetic field.

There are many kinds of possible periodic orbit in a general system each of which affects the density of states in a characteristic way; we start with the one-dimensional case, which is simplest. Consider the potential well $V(x)$ shown in figure 26. For positive energies, such as E_1, there are no periodic orbits, and $n(E)$ is given simply by the one-dimensional version of the Thomas–Fermi formula (7.56); it is convenient to express the result in terms of the density Δn of the new states which the potential introduces, and we get

$$\begin{aligned}\Delta n(E) &\equiv n_0(E) - n^{\text{free particle}}(E) \\ &= \frac{1}{\pi\hbar}\left(\frac{m}{2}\right)^{1/2}\int_{-\infty}^{\infty} dx \left\{\frac{1}{[E-V(x)]^{1/2}} - \frac{1}{E^{1/2}}\right\}.\end{aligned} \tag{7.58}$$

For negative energies such as E_2, periodic orbits are possible, due to the reflections from the classical turning points at x_1 and x_2. The action $S(E)$ for a single complete circuit is

$$S(E) = 2\int_{x_1}^{x_2}\{2m(E-V(x))\}^{1/2}\,\mathrm{d}x \tag{7.59}$$

while the amplitude Δ_{AB} occurring in the Green function (7.40) is easily worked out as

$$\Delta_{x,x} = \left(\frac{m}{p(x)}\right)^2 = \frac{m}{2(E-V(x))} \tag{7.60}$$

(where x lies between x_1 and x_2); this quantity remains the same after any number of circuits. During each circuit there are two reflections at the turning points (caustics) so that the phase loss is π per circuit. All the quantities in (7.40) are now known, and we can use (7.51) to get

$$n(E) = \frac{1}{\pi\hbar}\sum_{r=-\infty}^{\infty}\cos\left(\frac{rS(E)}{\hbar}-r\pi\right)\int_{x_1}^{x_2}\mathrm{d}x\left[\frac{m}{2(E-V(x))}\right]^{1/2} \tag{7.61}$$

where the negative values of r indicate traversals in the reverse sense, and $r = 0$ corresponds to the path of zero length. Interpreting the integral with the aid of (7.59) we get

$$2\int_{x_1}^{x_2}\mathrm{d}x\left(\frac{m}{2(E-V(x))}\right)^{1/2} = \frac{\partial S}{\partial E} = \tau(E) \tag{7.62}$$

where $\tau(E)$ is the time period of the orbit. The series can be summed exactly by the Poisson formula (cf § 6.1) to give

$$n(E) = \frac{\tau(E)}{\hbar}\sum_{n=-\infty}^{\infty}\delta\left(\frac{S(E)}{\hbar}-(2n+1)\pi\right) \tag{7.63}$$

$$= \sum_{n=0}^{\infty}\delta(E-E_n) \tag{7.64}$$

where E_n is given by

$$S(E_n)/\hbar = (2n+1)\pi. \tag{7.65}$$

This is precisely the Bohr–Sommerfeld quantization rule which we derived in § 3.3, using the complex method for dealing with one-dimensional differential equations with turning points (for another, very different, derivation see Argyres 1965). There is only a finite number of levels because the periodic orbit ceases to exist as E passes through zero. These simple arguments, involving the classical paths but not the eigenfunctions, have enabled us to derive all the essential features of the full quantum-mechanical energy spectrum. If we average $n(E)$ over a range ΔE sufficiently large to include a large number Δn of bound states (remembering that the states cluster together more thickly as $\hbar$ diminishes), we get

$$n^{\mathrm{av}}(E) = \tau(E)/2\pi\hbar \tag{7.66}$$

which is just the 'path-of-zero-length' expression (7.56), applied to this case. Different ways of treating one-dimensional problems are given by Kohn and Sham (1965) and Grover (1966).

In multi-dimensional cases, the periodic orbits for an energy E may be isolated, or they may form a *family* covering some part of the classically allowed region in the $\boldsymbol{q}$ space. For the Coulomb potential in three dimensions, *all* the trajectories (for $E<0$) are periodic, so that the family of periodic orbits covers the whole of the accessible $\boldsymbol{q}$ space; this is analogous to the one-dimensional case, and, as shown by Gutzwiller (1969), the integration over $\boldsymbol{q}$ for the periodic orbits produces the same amplitude factor as for the path of zero length, and the resulting topological sum reproduces the known spectrum precisely, including the n^2 degeneracy factor for the nth level (see also Norcliffe and Percival 1968a,b, Norcliffe *et al* 1969a,b). In all the separable problems for which the classical motion is well understood, the periodic orbits form a family, but in the general case, when the hamiltonian has no symmetry, there exist only *isolated* periodic orbits (see Whittaker 1927 p396).

Only the region of $\boldsymbol{q}$ space in the immediate neighbourhood of an isolated periodic orbit will contribute to the integral in the trace (7.51), so that it is natural to expand the S and Δ about their values on the orbit. This procedure is carried out in detail by Gutzwiller (1971), and we shall only quote his results. The isolated orbit may be stable or unstable, according to whether the determinant Δ_{AB} (which involves the expansion of the bundle of paths starting out almost parallel to the orbit—cf equation (7.42) and figure 24) grows without limit as the number r of circuits increases, or remains bounded. Elementary stability theory (Whittaker 1927) leads to the results

$$\left.\begin{aligned} &\Delta_{q,q}^{(r\ \text{circuits})} \propto \sin rv \qquad \text{(stable case)} \\ \text{or}\qquad &\\ &\Delta_{q,q}^{(r\ \text{circuits})} \propto \sinh ru \qquad \text{(unstable case)} \end{aligned}\right\} \tag{7.67}$$

for two-dimensional problems: v is the 'stability angle', and u the 'instability exponent'. In N dimensions there are $N-1$ quantities characterizing the stability of the orbit; we restrict ourselves to two dimensions.

For a stable orbit, the contribution to $n(E)$ from r circuits is shown by Gutzwiller to be

$$n_{(E)}^{(r\ \text{circuits})} = \frac{\tau(E)}{2\pi\hbar}\cos\left(\frac{rS(E)}{\hbar}-\frac{rv}{2}\right) \tag{7.68}$$

an expression which automatically takes care of the effects of the caustics which must occur at the zeros of $\Delta_{q,q}$. Summing over all the circuits is easy, after realizing that the 'path of zero length' does not correspond to setting $r=0$ in (7.68) and must be added in separately; the result in the two-dimensional case is

$$n(E) = n_0(E)+2\sum_{r=1}^{\infty} n_{(E)}^{(r\ \text{circuits})} = n_0(E)-\frac{\tau(E)}{2\pi\hbar}+\sum_{n=0}^{\infty}\delta(E-E_n). \tag{7.69}$$

E_n is given by

$$S(E_n)/\hbar = (2n\pi+\tfrac{1}{2}v) \tag{7.70}$$

which is a new quantization formula giving the location of a nondegenerate set of sharp levels which is superimposed on the continuous background over the energy range for which the periodic orbit (and hence $S(E)$) exists. In the extreme classical limit, the levels lie so close together that an average must be taken; then the second and third terms cancel in (7.69), leaving only the Thomas–Fermi contribution.

In the unstable case, the spreading out of the neighbouring trajectories implies that the contributions of successive orbits diminish, and Gutzwiller shows that

$$n_{(E)}^{(r\text{ circuits})} = \frac{\tau(E)}{2\pi\hbar}\cos\left(\frac{rS(E)}{\hbar} - \frac{rM\pi}{2}\right)\mathrm{e}^{-ru/2}$$

where M is the number of caustics traversed during a single circuit. The topological sum is a geometric series, which yields

$$n(E) = n_0(E) - \frac{\tau(E)}{2\pi\hbar} + \frac{\tau(E)\hbar u}{2\pi}\sum_{n=0}^{\infty}\left[\left\{S(E) - \left(n+\frac{M}{4}\right)2\pi\hbar\right\}^2 + \left(\frac{u\hbar}{2}\right)^2\right]^{-1} \quad (7.71)$$

so that the unstable orbits yield a set of Lorentz-broadened *resonances*, centred on the energies E_n given by

$$S(E_n) = (n + \tfrac{1}{4}M)\,2\pi\hbar. \quad (7.72)$$

The halfwidths of the resonances are $u\hbar/\tau(E_n)$. These resonances are therefore very different in form from those due to barrier penetration considered in §3.3 whose width/separation ratio diminishes as $\hbar\,\mathrm{e}^{-O(\hbar^{-1})}$ (an example of this new type of

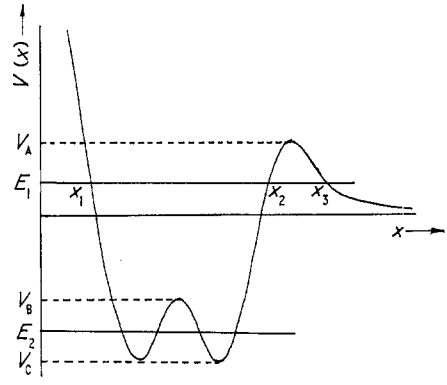

Figure 27. Potential for examining how the complex paths affect the spectrum.

resonance, due to unstable orbits, was discussed in §6.3 in connection with spiral scattering); nevertheless, barrier-penetration resonances can be included in Gutzwiller's scheme, as we shall presently see. Once again, the *average* density of states is simply given by the first term (Balian and Bloch (1971) derive what is essentially a Thomas–Fermi approximation from the Green function, with correction terms of 'Bremmer' type (cf §2.3) which vary smoothly with energy and thus do not represent the oscillatory effects due to periodic paths).

The effects of orbital stability on quantization have been neglected in the past; Keller (1958a), for instance, includes the effects of the phase M_r due to caustics, but treats the amplitude $|\Delta_{q,q}|$ as constant after successive circuits (see also Synge 1953). Nevertheless, the theory outlined above cannot tell the whole story of semiclassical quantization for it *always* predicts discrete states from stable orbits even when the energies concerned lie in the continuum of scattering states (ie the total classically accessible volume of $\boldsymbol{q}$ space is infinite), and it *always* predicts broadened resonances from unstable orbits even if the energies concerned lie in the region of discrete bound states (finite volume accessible in classical $\boldsymbol{q}$ space). At least part of this

difficulty with the theory originates in its neglect of *complex paths*, and the simple one-dimensional potential shown in figure 27 will help to show why this is so.

Consider first a positive energy such as E_1 in the region between 0 and V_A. The classical paths between the two turning points x_1 and x_2 are periodic and stable, so that Gutzwiller's theory predicts discrete levels, which is impossible since E_1 lies in the continuum. But if we include the effects of the complex path $x_2 \rightarrow x_3$ which enables particles to leak away through the barrier, we must regard the paths within the well as *unstable*, and reduce the amplitude by multiplying by the reflection

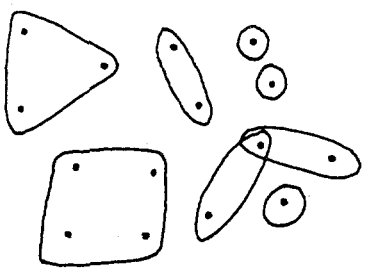

Figure 28. Some possible periodic orbits (at one energy) for an electron moving among attracting atoms (schematic).

coefficient $|R(E)|$ (cf §3.3) after each circuit. The topological sum then gives a series of resonant states (cf the third term in (7.71)) with exactly the right widths and positions, as may be seen by comparing with the phase shift (3.67). Considering now a negative energy such as E_2 among the discrete levels in the region of double-well potential between V_B and V_C, we observe that the classical paths are stable, so that if the two wells are identical in form, a doubly degenerate series of discrete states will occur. If we introduce the complex paths just discussed and treat the two wells separately each will produce a set of resonances in the spectrum, because the orbits are now unstable. However, if we consider both the wells and the barrier between them as a single unit, a careful evaluation of the sum over all the topologically different paths again yields discrete levels, but now the degeneracy is lifted and the splitting is correctly given (see Fröman 1966c).

It is clear that further work is needed before the precise nature of the effects of real and complex periodic paths is finally elucidated. However, in complicated problems where even the qualitative features of the variation of $n(E)$ are unknown, Gutzwiller's method may find immediate application. As an example, consider an electron moving among a disordered array of ions which attract it—in a liquid metal for instance (see figure 28 for a schematic two-dimensional representation). For energies above the asymptotic zero of the single-ion potential there are no classically forbidden regions. At a given such energy, say E, it may be possible to find a periodic orbit circling a small cluster of atoms; it is easy to see that such an orbit is unstable, and exists over a range of energies. As we have seen, this orbit will give rise to a series of resonances, and for the whole of the (effectively infinite) system $n(E)$ will consist of the sum of all the resonances due to the different orbits, plus the smooth background due to the 'paths of zero length'. These resonant contributions will add up to give a smooth variation of $n(E)$ unless many very similar orbits are distributed fairly densely throughout the system; we may expect this to occur for the smaller orbits (around just one or two or three atoms), and these will occur at lower energies. Thus $n(E)$ for energies not too far above the

asymptotic zero of the single-ion potential might be expected to show some resonant structure, each family of resonances indicating a different characteristic of the distribution of atoms. These remarks are frankly speculative, but they are justified because the nature of the electron states in a disordered system remains obscure, despite intensive study (see eg Ziman 1968, 1969a,b).

8. Conclusions

Despite the extensive investigations reviewed in this article, the body of techniques and formulae which constitute 'semiclassical mechanics' is by no means complete, and we would like to finish by listing a few areas where further research is needed. Only possible extensions of the *methods* are included in this list—we do not consider the numerous possible *applications* to new physical problems of the methods already in existence.

(i) It is possible that more information may be obtained from the complex method (§ 3) than has hitherto been thought possible, by taking full account of the necessary analyticity of phases, etc with respect to parameters such as energy. An elementary example of this was the determination in equation (3.62) of the form of the phase $\delta(E)$ of the transmission coefficient near a barrier top.

(ii) The study of more complicated comparison equations and integrals is necessary in order to provide the canonical descriptions required in the derivation of uniform approximations (§§ 4, 6.3, 7.3) for problems involving new configurations of stationary points and turning points.

(iii) The controversy over reversibility of connection formulae (§ 3.2) would be finally settled if approximations could be derived showing in detail how the Stokes constants change as a Stokes line is crossed. This would lead to a new type of asymptotic expansion in which, to take the case of a single turning point at $z = 0$, the wave function $\psi(z)$ is represented as

$$\psi(z) = b_+(z)\,\mathrm{e}^{\mathrm{i}w(z)} + b_-(z)\,\mathrm{e}^{-\mathrm{i}w(z)}$$

where $b_\pm(z)$ is represented as a series of descending powers of $|z|$ whose coefficients, which depend on $|z|$ and $\arg z$, are valid *uniformly* in $\arg z$.

(iv) The problem of how to treat the semiclassical limit when there is an enormous number of contributing classical paths (end of § 3.3) is important both from a fundamental point of view and also in applications to the theory of transport phenomena in disordered materials.

(v) Finally, the difficulties raised by Gutzwiller's (1971) theory of quantization (§ 7.4), which is perhaps the most exciting recent development in semiclassical mechanics, should be studied deeply in order to provide analytical insight into the properties of quantum states in those systems, previously almost intractable, where no separation of variables is possible.

Acknowledgments

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