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Uniform approximation for potential scattering involving a rainbow

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Abstract. In scattering situations characterized by the appearance of a rainbow, the scattering sum converges very slowly. To calculate the differential cross section in such cases the sum is transformed by the Poisson summation formula into a series of integrals, each of which is evaluated by the method of stationary phase. Previous work along these lines, reviewed here, has led to the classical, 'crude semi-classical' and Airy approximations. Using a method due to Chester, Friedman and Ursell a uniform approximation is derived, valid for all angles irrespective of whether they are near or far from the rainbow angle. This new approximation involves only those quantities needed to solve the equivalent purely classical problem; it also reduces to the earlier results in appropriate limiting cases. For a particular numerical example of scattering by a Lennard-Jones potential the uniform approximation is found to agree very well with the results of an exact calculation by Hundhausen and Pauly.

1. Introduction

When a plane wave is scattered by a spherically symmetric disturbance, there often exists a scattering angle θ_r (reckoned from the forward direction) for which the differential cross section $\sigma(\theta)$ is large. On one side of θ_r (the shadow region) the scattering drops rapidly to zero, or to a very low value, while on the other side (the lit region) $\sigma(\theta)$ oscillates. This effect occurs when light from the Sun (or, occasionally, the Moon) encounters water droplets in the atmosphere, giving rise to rainbows; accordingly, Ford and Wheeler (1959 a) gave the name 'rainbow scattering' to the effect whenever it appears in other scattering situations. θ_r (if it is not near 0 or π) is called the rainbow angle. Rainbow scattering also occurs in the intermolecular collisions arising in molecular beam experiments; potentially, these molecular rainbows are a source of information concerning intermolecular forces, and considerable effort has recently gone into calculations of the cross sections in this case (see, for example, Munn and Smith 1966, Hundhausen and Pauly 1965, Mason and Monchick 1964).

The rapidly varying differential cross sections under discussion arise only if a large number of partial waves contribute to the scattering; this occurs when the scattering disturbance is considerably larger than the wavelength of the incident beam. Under these conditions one is near the classical limit of quantum mechanics and the geometrical optics limit of electromagnetism. Despite this similarity, the calculations for optical rainbows (van der Pol and Bremmer 1937, Rubinow 1961) and molecular rainbows (Ford and Wheeler 1959 b) are different; this is because in the optical case the refractive index of a droplet is discontinuous in the sense that in some regions it changes considerably over a distance much smaller than a wavelength (even though this is itself small), whereas for intermolecular collisions the potential is continuous. In this paper only the case of an analytic potential will be considered.

Previous approximations to the rainbow scattering cross section are as follows:

(i) The classical approximation: this can be obtained by smoothing out the oscillations in the asymptotic form of the exact cross section for angles far from θ_r and analytically continuing the result to angles near θ_r ; this approximation, which for the case of the optical rainbow originates from the theory of Descartes, diverges at θ_r .

(ii) The 'crude semi-classical' approximation: this is the *unsmoothed* asymptotic form of $\sigma(\theta)$ far from θ_r , and it also diverges if analytically continued to θ_r .

(iii) The Airy approximation: this is the application by Ford and Wheeler (1959 a) to continuous potentials of the famous Airy (1838) theory of light intensity near a caustic; it gives the form of $\sigma(\theta)$ very close to θ_r but fails badly even when $|\theta - \theta_r|$ is only a few degrees.

The reason for the existence of different approximations, each valid in a restricted angular domain, is that the asymptotic expansion of the scattering amplitude $f(\theta)$ with respect to the small parameter \hbar changes its form from a series in powers of $\hbar^{1/2}$ (when $|\theta - \theta_r|$ is large) to a series in powers of $\hbar^{1/3}$ (when $\theta - \theta_r = 0$). This phenomenon is well known for functions defined by an ordinary differential equation: what we have called the 'crude semi-classical' approximation is the WKB or Green-type approximation, and the Airy approximation is called a transitional approximation. Uniform approximations, valid for all values of the variable, were derived by Langer (1937, for further references and discussion see Jorna 1964). Now $f(\theta)$ is not definable by an ordinary differential equation, so these methods fail for it; however, Chester *et al.* (1957, to be referred to as I) have devised an analogous method for finding uniform approximations to functions defined by definite integrals.

In § 2 of this paper the eigenfunction expansion of $f(\theta)$ is transformed by the Poisson sum formula to give a series of integrals. This device has already been used by Rubinow (1961) and others for the discontinuous problem, and it has been suggested by Pekeris (1950) that the Poisson formula is the natural mathematical tool to use when considering a modal or eigenfunction expansion in a region where ray or classical concepts are appropriate. In § 3 the asymptotic evaluation of the integrals is discussed, and the method of I is used to obtain a uniform approximation to the rainbow amplitude, valid for all relevant values of $\theta_r - \theta$; this result, in the form of equations (29) and (30), is the main conclusion of this paper. In § 4 a numerical example is given for which the uniform approximation gives results very close to an exact calculation made using the partial wave sum. The conclusions are summarized in § 5.

2. Transformation of the eigenfunction expansion for scattering amplitude

We start from the Faxen-Holtmark formula for the scattering amplitude for non-forward angles (see Mott and Massey 1949):

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

In this formula, m and E are the mass and energy of the incident particle, and η_l is the phase shift of the l th partial wave, obtained by solving the Schrödinger equation for the incident particle moving in a potential $V(r)$ representing its interaction with the scatterer.

Although the series (1) is exact, the terms in it converge extremely slowly whenever rainbow scattering occurs; many thousands of partial waves are often involved in cases of practical interest. We therefore transform (1) using a modification of the Poisson sum formula (Lighthill 1958); this gives

$$f(\theta) = -i \left(\frac{\hbar^2}{2mE} \right)^{1/2} \sum_{m=-\infty}^{\infty} \exp(-im\pi) \int_0^{\infty} d\lambda \lambda \exp(2i\eta_{\lambda - \frac{1}{2}} + 2m\pi i\lambda) P_{\lambda - \frac{1}{2}}(\cos \theta) \quad (2)$$

where $\eta_{\lambda-\frac{1}{2}}$ and $P_{\lambda-\frac{1}{2}}(\cos \theta)$ are any convenient functions which reduce to η_l and $P_l(\cos \theta)$ when $\lambda - \frac{1}{2}$ is integral. In § 3 we shall see that there are familiar cases where it is wrong to approximate (2) by ignoring all terms except that for $m = 0$ (this would amount to replacing the sum in (1) by an integral); nevertheless, such cases are fairly rare and, in general, only a few terms contribute with more or less equal magnitude, the rest being negligible.

Rainbows occur only under quasi-classical conditions, and since we shall be finding not a complete asymptotic expansion but only its first term we require $\eta_{\lambda-\frac{1}{2}}$ and $P_{\lambda-\frac{1}{2}}(\cos \theta)$ to lowest order in \hbar . To do this consistently we must use the relation

$$L = \lambda \hbar \quad (3)$$

giving the angular momentum in terms of the variable λ corresponding to the quantum number l , and then regard L as being of zero order in \hbar ; this will only be justified if it turns out (as it does) that the scattering can be described using the values of L occurring if the same collision is treated classically. The lowest-order expression for the phase shift is then

$$\begin{aligned} \eta_{\lambda-\frac{1}{2}} &= \frac{\bar{\eta}(L)}{\hbar} + O(\hbar) \\ &= \frac{(2mE)^{1/2}}{\hbar} \left[\int_{r_0}^{\infty} \left\{ \left(1 - \frac{V(r)}{E} - \frac{L^2}{2mEr^2} \right)^{1/2} - 1 \right\} dr - r_0(L) + \frac{L\pi}{2} \right] \end{aligned} \quad (4)$$

where $r_0(L)$ is the outermost zero of the square root; this means that

$$\exp(2i\eta_{\lambda-\frac{1}{2}}) = \exp\left\{ \frac{2i}{\hbar} \bar{\eta}(L) \right\} \{1 + O(\hbar)\}. \quad (5)$$

For the interpolated Legendre polynomials, the analogous formula is

$$P_{\lambda-\frac{1}{2}}(\cos \theta) = \left(\frac{2\hbar}{\pi L \sin \theta} \right)^{1/2} \left\{ \cos \left(\frac{L\theta}{\hbar} - \frac{\pi}{4} \right) + O(\hbar) \right\} \quad (6)$$

valid for $\hbar/L \ll \theta \ll \pi - \hbar/L$, a condition which is satisfied for rainbow scattering if the range $0 < L < \hbar$ does not contribute significantly to the integrals in (2).

When the substitutions (4), (5) and (6) and the change of variable (3) are made, the Poisson representation (2) becomes

$$\begin{aligned} f(\theta) &= \frac{-i}{2(\pi \hbar m E \sin \theta)^{1/2}} \sum_{m=-\infty}^{\infty} \exp(-im\pi) \left\{ \exp\left(-\frac{i\pi}{4}\right) \right. \\ &\quad \times \int_0^{\infty} L^{1/2} \exp\left[\frac{i}{\hbar} \{2\bar{\eta}(L) + L(\theta + 2\pi m)\} \right] dL + \exp\left(\frac{i\pi}{4}\right) \\ &\quad \times \int_0^{\infty} L^{1/2} \exp\left[\frac{i}{\hbar} \{2\bar{\eta}(L) + L(-\theta + 2\pi m)\} \right] dL \left. \right\} \{1 + O(\hbar)\}. \end{aligned} \quad (7)$$

3. Evaluation of integrals

3.1. General considerations

We now have to evaluate a number of integrals, which may be defined as follows:

$$I_m^{\pm} = \int_0^{\infty} L^{1/2} \exp\left[\frac{i}{\hbar} \{2\bar{\eta}(L) + L(\pm\theta + 2m\pi)\} \right] dL. \quad (8)$$

In terms of these, the scattering amplitude (7) is simply

$$f(\theta) = \frac{-i}{2(\pi\hbar mE \sin \theta)^{1/2}} \sum_{m=-\infty}^{\infty} \exp(-im\pi) \left\{ \exp\left(-\frac{i\pi}{4}\right) I_m^+ + \exp\left(-\frac{i\pi}{4}\right) I_m^- \right\} \times \{1 + O(\hbar)\}. \quad (9)$$

When evaluating I_m^\pm , \hbar will be considered small and only the leading term of the resulting series will be retained, in accordance with the approximations already made.

The integrands of I_m^\pm are rapidly oscillating functions (because of the smallness of \hbar in comparison with $2\bar{\eta}(L) + L(\pm\theta + 2m\pi)$ under quasi-classical conditions) and it is well known (see e.g. Copson 1965) that the main contributions to the integrals arise from stationary points on the positive real axis, whenever these exist. The stationary points in this case are those values of L satisfying

$$2 \frac{d\bar{\eta}}{dL} = \pi - \left(\frac{2}{mE}\right)^{1/2} L \int_{r_0}^x \frac{dr}{\{1 - V(r)/E - L^2/2mEr^2\}^{1/2}} \\ = \Theta(L) = \mp\theta - 2m\pi \quad (10)$$

where the upper and lower signs refer to I_m^+ and I_m^- respectively. Following Ford and Wheeler (1959 a) we have here noted the equality of $2(d\bar{\eta}/dL)$ with the classical deflection function $\Theta(L)$, which gives the *total* angle (positive for net repulsion, negative for net attraction) with the forward direction made by the classical paths of particles hitting the target with angular momentum L . Since $\Theta(L) \leq +\pi$ (this is fairly obvious on dynamical grounds as well as from (10)), the integrals I_m^\pm for $m < 0$ have no stationary points on the path of integration, and are thus negligible in comparison with those of the other integrals which do have such points. The particular one of the set of integrals (8) which contains the contribution of a given classical path depends, according to (10), on the manner in which the path encircles the target particle before emerging at the scattering angle θ .

Apart from the classical paths, which are solutions of (10) for real positive L , there will also be stationary points off the real axis. These complex angular momenta, corresponding to 'complex classical paths', give exponentially small contributions to the integrals and, unless L is very close to the real axis, are negligible under quasi-classical conditions if there are any competing real paths. If there are no real paths, the scattering is very small, depends entirely on the complex paths, and is very difficult to calculate since it depends on the fine analytical details of the potential (see Patashinskii *et al.* 1964).

Rainbow scattering arises whenever $\Theta(L)$ has an extremum (Ford and Wheeler 1959 a). For definiteness, let us consider the case of figure 1, where $|\Theta(L)|$ never exceeds π and where the extremum occurs at $L = L_r$ when $\Theta(L_r) = -\Theta_r$.

In this situation only I_0^\pm contribute to $f(\theta)$, which can be written

$$f(\theta) = f_0(\theta) + f_r(\theta) = \frac{-i}{2(\pi\hbar mE \sin \theta)^{1/2}} \left\{ \exp\left(-\frac{i\pi}{4}\right) I_0^- + \exp\left(-\frac{i\pi}{4}\right) I_0^+ \right\} \quad (11)$$

where $f_r(\theta)$, the term involving I_0^+ (and hence the negative branch of the deflection curve—the part with the minimum), is called the rainbow amplitude. All the characteristic features of rainbow scattering arise from $f_r(\theta)$, since the interference term between it and $f_0(\theta)$ in the scattering cross section contains oscillations so rapid that experiments cannot usually detect them (see Munn and Smith 1966). We can therefore write, for

the measured cross section,

$$\sigma(\theta) = |f_o(\theta)|^2 + |f_r(\theta)|^2.$$

We shall only find $f_r(\theta)$, since the semi-classical form of $f_o(\theta)$ is simple and has been discussed adequately before (Ford and Wheeler 1959 a).

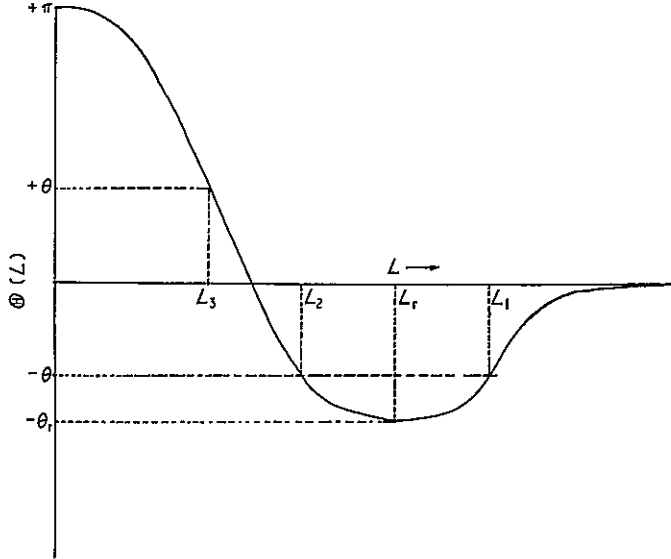


Figure 1. Classical deflection function for a case of rainbow scattering.

3.2. 'Crude semi-classical' approximation

By (11), the rainbow scattering depends on

$$I_0^+ = \int_0^\infty L^{1/2} \exp\left[\frac{i}{\hbar}\{2\bar{\eta}(L) + L\theta\}\right] dL. \tag{12}$$

Consider first the case $\theta < \theta_r$. There are two stationary points, $L_1(\theta)$ and $L_2(\theta)$ ($L_1 > L_2$), where $\Theta(L) = -\theta$ (the one at $L_3(\theta)$, where $\Theta(L) = +\theta$, does not contribute to I_0^+ or to the rainbow effect). We have, from figure 1,

$$\begin{aligned} 2 \frac{d^2\bar{\eta}(L_1)}{dL^2} &= \frac{d\Theta(L_1)}{dL} > 0 \\ 2 \frac{d^2\bar{\eta}(L_2)}{dL^2} &= \frac{d\Theta(L_2)}{dL} < 0 \end{aligned} \tag{13}$$

and the method of stationary phase (Copson 1965) can be applied to (12) in a straightforward way, giving, to lowest order in \hbar ,

$$\begin{aligned} I_0^+ &= \left\{ \frac{2\pi L_1(\theta)\hbar}{|\Theta'(L_1)|} \right\}^{1/2} \exp\left[i \left\{ \frac{\pi}{4} + \frac{2\bar{\eta}(L_1) + L_1\theta}{\hbar} \right\} \right] \\ &\quad + \left\{ \frac{2\pi L_2(\theta)\hbar}{|\Theta'(L_2)|} \right\}^{1/2} \exp\left[i \left\{ -\frac{\pi}{4} + \frac{2\bar{\eta}(L_2) + L_2\theta}{\hbar} \right\} \right] \end{aligned} \tag{14}$$

(primes denote differentiation with respect to L). From (11) the rainbow cross section

is given, in this approximation, by

$$\sigma_r(\theta) = \frac{1}{2mE \sin \theta} \left(\frac{L_1}{|\Theta'(L_1)|} + \frac{L_2}{|\Theta'(L_2)|} + 2 \left\{ \frac{L_1 L_2}{|\Theta'(L_1)\Theta'(L_2)|} \right\}^{1/2} \right) \times \sin \left[\frac{1}{\hbar} \{ 2\bar{\eta}(L_2) - 2\bar{\eta}(L_1) + L_2\theta - L_1\theta \} \right]. \quad (15)$$

The first two terms do not involve \hbar and represent the classical result that the cross section contains two independent contributions, one for each path that emerges at θ . The third term is the typical quasi-classical modification of classical mechanics, that the two paths interfere as waves with a phase difference equal to the action difference between them divided by \hbar . At the rainbow angle this approximation diverges, because $\Theta'(L)$ is zero there. The reason for this is that we have treated the two stationary points as independent; as θ approaches θ_r , however, L_1 and L_2 get closer together until, when $\theta = \theta_r$, they coalesce to form a third-order stationary point, and the above theory is inappropriate.

When $\theta > \theta_r$ there are no real stationary points (see figure 1); instead there are two saddle points off the real axis, with complex conjugate L values; only one of these contributes to I_0^+ . Its contribution is exponentially small when $\theta \gg \theta_r$, and can be neglected in comparison with that from L_3 contributing to the non-rainbow amplitude $f_0(\theta)$. When θ exceeds θ_r only slightly, $f_r(\theta)$ is appreciable, but cannot be calculated by the simple saddle-point method because L_1 and L_2 are close together and the result would diverge like (15).

3.3. Airy approximation

The direction θ_r is a caustic direction of the outgoing classical paths far from the target (see figure 2), and the coalescence of the two saddle points as $\theta \rightarrow \theta_r$ is just a reflection of the well-known failure of simple semi-classical approximations near such caustics (see e.g. Keller 1962).

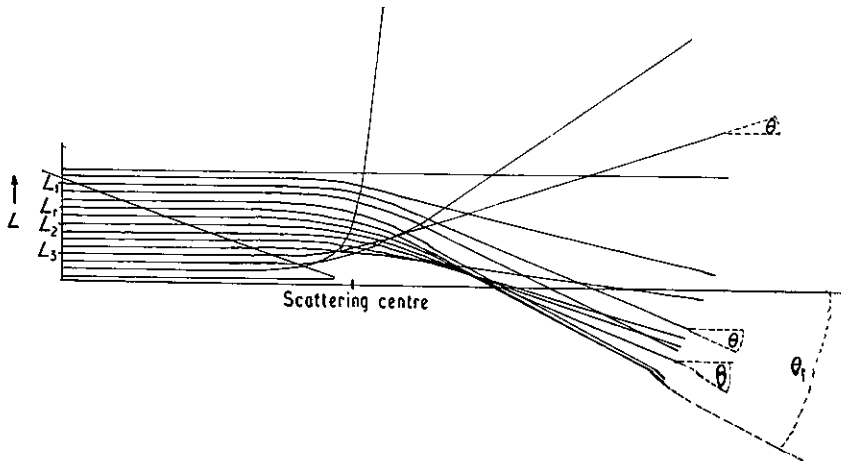


Figure 2. Sketch of classical paths for the case of figure 1, showing the caustic at the rainbow angle.

The analysis by Airy (1838) of light intensity near a caustic applies to this case, and proceeds by assuming that near θ_r the two stationary points can be treated as coincident as far as the slowly varying parts of the integrand are concerned, so that these

can be expanded about L_r . Defining a new variable u by

$$L = u + L_r$$

and taking the limits of u as $-\infty$ to $+\infty$ (on the grounds that the main contribution to I_0^+ comes from the two stationary points near $u = 0$), we can write

$$\begin{aligned} I_0^+ &= \int_{-\infty}^{\infty} L_r^{1/2} \left(1 + \frac{u}{2L_r} + \dots \right) \exp \left[\frac{i}{\hbar} \left\{ 2\bar{\eta}(L_r) + 2\bar{\eta}'(L_r)u + \frac{\bar{\eta}''}{3}(L_r)u^3 \right\} \right] \{ 1 + O(u^4) \} du \\ &= L_r^{1/2} \exp \left[\frac{i}{\hbar} \{ 2\bar{\eta}(L_r) + L_r\theta \} \right] \int_{-\infty}^{\infty} \left\{ 1 + \frac{u}{2L_r} + O(u^2) \right\} \\ &\quad \times \exp \left[\frac{i}{\hbar} \left\{ (\theta_r - \theta)u + \frac{\eta''(L_r)u^3}{3} \right\} \right] du \end{aligned}$$

where we have used the fact that $2\eta''(L_r) = \Theta'(L_r) = 0$. The integrals can be easily evaluated in terms of Airy functions (*Handbook of Mathematical Functions* 1964), and the result is

$$\begin{aligned} I_0^+ &= \frac{2\pi L_r^{1/2} \hbar^{1/3}}{[\bar{\eta}''(L_r)]^{1/3}} \exp \left[\frac{i}{\hbar} \{ 2\bar{\eta}(L_r) + L_r\theta \} \right] \left(\text{Ai} \left[\frac{\theta - \theta_r}{\{\hbar^2 \bar{\eta}''(L_r)\}^{1/3}} \right] \right. \\ &\quad \left. + \frac{\hbar^{1/3}}{2i L_r \{\bar{\eta}''(L_r)\}^{1/3}} \text{Ai}' \left[\frac{\theta - \theta_r}{\{\hbar^2 \bar{\eta}''(L_r)\}^{1/3}} \right] \right). \end{aligned} \tag{16}$$

The first of these terms is the Airy approximation, giving rise to the cross section

$$\sigma_r(\theta) = \frac{\pi L_r \text{Ai}^2(\theta - \theta_r) / \{\hbar^2 \bar{\eta}''(L_r)\}^{1/3}}{\hbar^{1/3} m E \sin \theta \{\bar{\eta}''(L_r)\}^{2/3}}. \tag{17}$$

For non-zero \hbar this does not diverge at $\theta = \theta_r$ (as the classical approximation does). Near θ_r the first term of (16) dominates the second, which is then of order $\hbar^{1/3}$ with respect to it. As $|\theta - \theta_r|$ increases, however, and the Airy functions can be represented by their asymptotic approximations, the two terms become of equal order in \hbar , but then the approximation fails because of the omission of the higher terms which involve powers of $\theta - \theta_r$.

3.4. Uniform approximation

The correct short-wavelength approximation to I_0^+ has to be uniform in θ ; that is, it must agree with (14) far from θ_r , and with (16) near θ_r , as well as providing the behaviour for intermediate angles. The method of I, referred to in § 1, enables us to obtain such an approximation; instead of treating the stationary points separately, as in § 3.2, or as though they were both very near to L_r , as in § 3.3, this method maps their exact behaviour onto that of the stationary points in the integrand of the Airy function. Although this technique would seem to be potentially very useful in diffraction theory, it does not seem to have been widely applied (in fact, the only application so far seems to have been to Bessel functions—a case where the uniform approximation was already known from the differential equation); therefore we review it briefly here in a slightly specialized form (mathematical details will be found in I).

We introduce into I_0^+ the new variable x , by the substitution

$$2\bar{\eta}(L) + L\theta = \zeta(\theta)x + \frac{1}{3}x^3 + A(\theta) \tag{18}$$

so that

$$I_0^+ = \exp\left\{\frac{iA(\theta)}{\hbar}\right\} \int_{-\infty}^{\infty} \{L(x)\}^{1/2} \frac{dL(x)}{dx} \exp\left\{\frac{i}{\hbar}(\zeta x + \frac{1}{3}x^3)\right\} dx \quad (19)$$

where the limits can be taken as written because only the region near the stationary points, now at $x = \pm i\zeta^{1/2}$, is considered to contribute to the integral. The mapping $L \rightarrow x$ can be made 1-1 by stipulating that the stationary points of the two integrands must be made to correspond by the relations

$$\begin{aligned} x &= -i\zeta^{1/2}(\theta) \leftrightarrow L = L_1(\theta) \\ x &= +i\zeta^{1/2}(\theta) \leftrightarrow L = L_2(\theta). \end{aligned} \quad (20)$$

When inserted successively into (18), these relations yield the values of $A(\theta)$ and $\zeta(\theta)$, as

$$A(\theta) = \frac{1}{2}\{2\bar{\eta}(L_1) + L_1\theta + 2\bar{\eta}(L_2) + L_2\theta\} \equiv \bar{S}(\theta) \quad (21)$$

where $\bar{S}(\theta)$ is the mean value of the classical actions (measured with respect to that along a straight-line path in the absence of a potential) along the two paths emerging at θ , and

$$\frac{4}{3}i\zeta^{3/2} = 2\bar{\eta}(L_2) + L_2\theta - 2\bar{\eta}(L_1) - L_1\theta \equiv \Delta S(\theta) \quad (22)$$

where $\Delta S(\theta)$ is the difference between the classical actions along these same two paths. In the lit region ($\theta < \theta_c$), L_1 and L_2 are both real, whereas in the shadow region they are complex conjugates. Thus $A(\theta)$ is always real. An examination of the possible choices of phase for ζ shows that we can always take ζ real, and that it must be positive in the shadow region where

$$\zeta_{\text{shadow}} = \left|\frac{3}{2}\mathcal{I}S(\theta)\right|^{2/3} \quad (23)$$

($S(\theta)$ is the action along either complex path), and negative in the lit region where

$$\zeta_{\text{lit}} = -\left|\frac{3}{4}\Delta S(\theta)\right|^{2/3}. \quad (24)$$

In order to evaluate (19) it is necessary to expand the factor $L^{1/2}(x)\{dL(x)/dx\}$ in a systematic way. A series of powers of x is not appropriate because higher terms of the resulting series will not tend to decrease if \hbar is small. The authors of I show that a suitable expansion, which moreover includes the desired dependence on the stationary points, is

$$L^{1/2}(x) \frac{dL(x)}{dx} = \sum_{m=0}^{\infty} \{x^2 + \zeta(\theta)\}^m (p_m + q_m x). \quad (25)$$

The question of the difference between this and a series in powers of x will not arise for us, since the lowest-order approximation to the integral (19) involves only the $m = 0$ term of (25). To find p_0 and q_0 we introduce the relations (20) into (25), to obtain

$$L_1^{1/2} \left(\frac{dL}{dx}\right)_{L_1} = p_0 - iq_0 \zeta^{1/2}$$

$$L_2^{1/2} \left(\frac{dL}{dx}\right)_{L_2} = p_0 + iq_0 \zeta^{1/2}$$

so that

$$\begin{aligned} p_0 &= \frac{1}{2} \left\{ L_1^{1/2} \left(\frac{dL}{dx}\right)_{L_1} + L_2^{1/2} \left(\frac{dL}{dx}\right)_{L_2} \right\} \\ q_0 &= \frac{1}{2i\zeta^{1/2}} \left\{ L_2^{1/2} \left(\frac{dL}{dx}\right)_{L_2} - L_1^{1/2} \left(\frac{dL}{dx}\right)_{L_1} \right\}. \end{aligned} \quad (26)$$

The values of the derivatives dL/dx at the two stationary points can be found by two successive differentiations of the mapping relation (18) with respect to x . The first gives

$$(2\bar{\eta}' + \theta) \frac{dL}{dx} = \zeta + x^2$$

and the second gives

$$\Theta' \left(\frac{dL}{dx} \right)^2 + (\Theta + \theta) \frac{dL}{dx} = 2x.$$

The second term of this vanishes at the stationary points (where $dL/dx \neq \infty$ because the mapping is regular), and we have

$$\begin{aligned} \left(\frac{dL}{dx} \right)_{L_1} &= \left\{ - \frac{2i\zeta^{1/2}}{\Theta'(L_1)} \right\}^{1/2} \\ \left(\frac{dL}{dx} \right)_{L_2} &= \left\{ + \frac{2i\zeta^{1/2}}{\Theta'(L_2)} \right\}^{1/2}. \end{aligned} \tag{27}$$

The higher coefficients p_m and q_m , and the higher derivatives of $L(x)$ involved, can be derived in a straightforward way by simple differentiation of (25) and (18).

By inserting (27) into (26), (26) into (25), (25) into (19) and integrating, we finally obtain the uniform approximation to I_0^+ :

$$\begin{aligned} I_0^+ &= \pi 2^{1/2} \exp\left\{ \frac{i\bar{S}(\theta)}{\hbar} \right\} \left\{ i \left[\left\{ \frac{L_1}{\Theta'(L_1)} \right\}^{1/2} + \left\{ \frac{L_2}{-\Theta'(L_2)} \right\}^{1/2} \right] (-\zeta)^{1/4} \hbar^{1/3} \text{Ai} \left(\frac{\zeta}{\hbar^{2/3}} \right) \right. \\ &\quad \left. + \left[\left\{ \frac{L_2}{-\Theta'(L_2)} \right\}^{1/2} - \left\{ \frac{L_1}{\Theta'(L_1)} \right\}^{1/2} \right] \frac{\hbar^{2/3}}{(-\zeta)^{1/4}} \text{Ai}' \left(\frac{\zeta}{\hbar^{2/3}} \right) \right\}. \end{aligned} \tag{28}$$

This means that in the lit region ($\theta < \theta_r$), where $\zeta < 0$, the rainbow cross section is

$$\begin{aligned} \sigma_r(\theta) &= \frac{\pi}{2mE \sin \theta} \left\{ \left[\left\{ \frac{L_1}{|\Theta'(L_1)|} \right\}^{1/2} + \left\{ \frac{L_2}{|\Theta'(L_2)|} \right\}^{1/2} \right]^2 \frac{|\zeta|^{1/2}}{\hbar^{1/3}} \text{Ai}^2 \left(\frac{-|\zeta|}{\hbar^{2/3}} \right) \right. \\ &\quad \left. + \left[\left\{ \frac{L_2}{|\Theta'(L_2)|} \right\}^{1/2} - \left\{ \frac{L_1}{|\Theta'(L_1)|} \right\}^{1/2} \right]^2 \frac{\hbar^{1/3}}{|\zeta|^{1/2}} \text{Ai}'^2 \left(\frac{-|\zeta|}{\hbar^{2/3}} \right) \right\}. \end{aligned} \tag{29}$$

Far from θ_r the difference in action between the two contributing paths is many units of \hbar ; hence, from (22), ζ is large and the Airy functions can be replaced by their known asymptotic approximations (*Handbook of Mathematical Functions* 1964). When this is done, the two terms of (29) are both of zero order in \hbar and their sum reduces exactly to the crude semi-classical result (15). Very near the caustic ζ is small and the first term of (29) dominates the second, which is smaller by a factor of order $\hbar^{2/3}$; also, $\bar{\eta}(L)$ may be approximated by a cubic expression as in § 3.3 and (29) then reduces exactly to the Airy approximation (17).

On the dark side of θ_r , we have

$$\begin{aligned} L_1(\theta) &= |L(\theta)| e^{i\alpha(\theta)}, & L_2(\theta) &= |L(\theta)| e^{-i\alpha(\theta)} \\ \Theta'(L_1) &= |\Theta'(\theta)| e^{i\beta(\theta)}, & \Theta'(L_2) &= |\Theta'(\theta)| e^{-i\beta(\theta)}; \end{aligned}$$

if these expressions are used in (28), the resulting rainbow cross section is

$$\begin{aligned} \sigma_r(\theta) &= \frac{\pi |L(\theta)|}{mE \sin \theta |\Theta'(\theta)|} \left\{ [1 - \sin\{\alpha(\theta) - \beta(\theta)\}] \frac{\zeta^{1/2}}{\hbar^{1/3}} \text{Ai}^2 \left(\frac{\zeta}{\hbar^{2/3}} \right) \right. \\ &\quad \left. + [1 + \sin\{\alpha(\theta) - \beta(\theta)\}] \frac{\hbar^{1/3}}{\zeta^{1/2}} \text{Ai}'^2 \left(\frac{\zeta}{\hbar^{2/3}} \right) \right\}. \end{aligned} \tag{30}$$

There is no point in evaluating this far from the caustic, since it is then exponentially small. Very near to θ_r , L_1 and L_2 are both nearly real and equal to L_r , and $\alpha \simeq 0$; $\Theta'(L)$ is nearly zero, and it is a simple matter to show that $\beta \simeq \frac{1}{2}\pi$. Using these values, and the cubic approximation to $\bar{\eta}(L)$ near L_r , it is possible to show that (30), like (29), reduces to the Airy approximation (17).

The equations (29) and (30) together constitute the desired uniform approximation to the rainbow cross section.

4. Numerical example

It is interesting to make a numerical comparison between the uniform approximation to $\sigma_r(\theta)$ and an exact calculation, based on summing the terms in the partial-wave series (1). Hundhausen and Pauly (1965) have performed such exact calculations for the Lennard-Jones potential used to describe intermolecular forces; this is

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

where ϵ is the depth of the potential minimum, and r_m the radial distance at which it occurs (r_m is a measure of the size of the scatterer). The case to be considered is defined by the parameter values

$$\frac{E}{\epsilon} = 4.7$$

$$\frac{(2mE)^{1/2}r_m}{\hbar} = 346.$$

The ratio E/ϵ defines the classical problem; the appropriate energy relationship is sketched in figure 3.

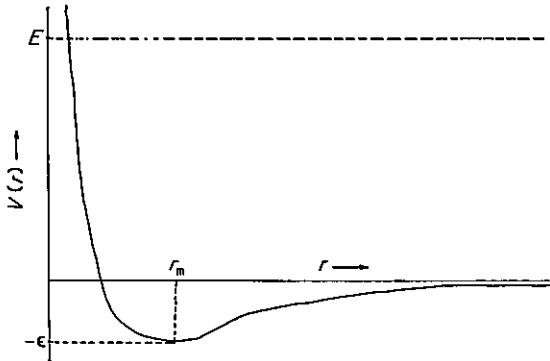


Figure 3. Energy relationships for scattering in Lennard-Jones potential.

The quantity $(2mE)^{1/2}r_m/\hbar$ is a measure of the wave-likeness of the problem, and in this case indicates that about 346 de Broglie wavelengths of the incident particle fit into the space occupied by the scatterer.

The rainbow cross section, calculated from our formula (29), is shown in figure 4, which also shows the classical approximation, the Airy approximation and the result of the exact calculation of Hundhausen and Pauly. The uniform approximation has not been used into the shadow because it only differs from the Airy approximation at angles

where $\sigma_r(\theta)$ is negligible in comparison with its values in the lit region. The calculations of $\sigma_r(\theta)$ are presented in units of πr_m^2 , the projected area of the scatterer. Because it was not possible to interpret the scale of the ordinates for the curves in the paper of Hundhausen and Pauly, these are drawn in figure 4 with the height of the maximum near $\theta = 12^\circ$ being made to agree with that calculated using (29); this is of course a somewhat arbitrary step.

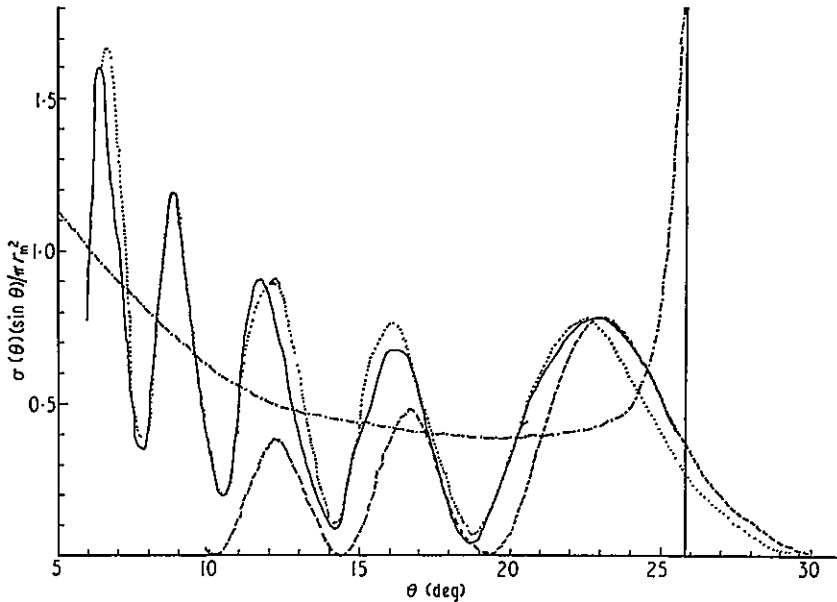


Figure 4. Comparison of different approximations for the rainbow cross section. Full curve, uniform approximation (equation (29) of text); dotted curve, exact calculation of Hundhausen and Pauly; broken curve, Airy approximation; chain curve, classical approximation.

It is clear that the uniform approximation mirrors the exact behaviour rather well. The worst discrepancies occur very close to the rainbow angle; these could well be errors of calculation, since our calculations of the classical and Airy approximations disagree in this angular region from those of Hundhausen and Pauly.

5. Conclusions

The Poisson sum formula seems to be the appropriate mathematical device to use in problems involving sums over discrete values of a variable which classically can assume any value. In the present problem it expresses in a simple way the interference between classical paths emerging at the same observation angle after making different numbers of complete circuits of the scatterer.

The method of I for the uniform asymptotic expansion of integrals in situations where two stationary points come together and separate again indicates that, even near a caustic, the scattering can be considered as coming only from the classical paths. Numerical calculations showed that the uniform approximation for the cross section is very close to the exact value calculated in the particular case considered by Hundhausen and Pauly.

Extension of the results of this paper to include more terms in the *formal* asymptotic expansion of $\sigma(\theta)$ would be straightforward but tedious: the integrand would have to include further terms in the expansions for $P_l(\cos \theta)$ and $\exp(2i\eta_l)$ with respect to \hbar , and the evaluation of the integral would involve higher coefficients p_m and q_m (equation (25)). The result would not be the *complete* asymptotic expansion; to obtain that, we should have to include contributions from (i) complex stationary points in addition to L_1 and L_2 (this would involve all the other integrals of the set I_m^\pm), (ii) the interaction of these stationary points with L_1 and L_2 , (iii) the fact that the integration contours end at $L = 0$ instead of including the whole real axis, and (iv) complex turning points in the potential $V(r)$ (these would alter the terms in the asymptotic expansion of the factor $\exp(2i\eta_l)$).

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