UNIVERSITY OF MARYLAND

UNIVERSITY OF MARYLAND 1807-1856-1920

INSTITUTE FOR MOLECULAR PHYSICS

HIGHER-ORDER STATIONARY PHASE APPROXIMATIONS IN SEMICLASSICAL SCATTERING

N66 33384 (ACCESSION NUMBER) — 1 (THRU)

29 (PAGES) — 1 (CODE)

CR-59822 (NASA CR OR TMX OR AD NUMBER) — 24 (CATEGORY)

FACILITY FORM 602

Francis J. Smith, E. A. Mason, and J. T. Vanderslice

[redacted]

GPO PRICE $ ______

CFSTI PRICE(S) $ ______

Hard copy (HC) 2.00

Microfiche (MF) .50

ff 653 July 65

IMP-NASA-43

November 30, 1964

HIGHER-ORDER STATIONARY PHASE APPROXIMATIONS IN SEMICLASSICAL SCATTERING*

Francis J. Smith,† E. A. Mason, and J.T. Vanderslice

Institute for Molecular Physics, University of Maryland
College Park, Maryland

ABSTRACT

Higher-order stationary phase approximations are used to calculate corrections to the classical expression for the differential cross section for elastic scattering. An expansion for the cross section as a series in $\hbar^2$ is obtained, whose first term is the classical result. An oscillating term is also present, whose "wavelength" is approximately $\Delta\theta \approx 2\pi/kb$. Both the "wavelength" and the amplitude of this term vary as $\hbar$. It is shown that the classical differential cross section is valid for angles as small as the critical angle defined by Massey and Mohr.

A similar technique is used to obtain corrections to Ford and Wheeler's semiclassical expression for the differential cross section at a rainbow angle. An expansion as a series

---

* Supported in part by the National Aeronautics and Space Administration (Grant NsG-5-59).

† On leave from the Department of Applied Mathematics, The Queen's University of Belfast, Northern Ireland.

in $\hbar^{2/3}$ is derived, whose first term varies as $\hbar^{-1/3}$ and hence diverges in the classical limit. It is shown that the leading term agrees with Ford and Wheeler's result, and that the first correction term is very small for a 12-6 potential.

AUTHOR

I. INTRODUCTION

The classical expression for the differential cross section for elastic scattering of heavy particles is known to be invalid at small angles.[1] The usual criterion for the validity of the classical theory, as given by Massey and Mohr,[1,2] is that the deflection angle θ should be greater than a critical angle θ_c, given by

$$\theta_c \approx \pi/kr_o, \tag{1}$$

where k is the wave number of the relative motion and r_o is the distance of closest approach. More recently it has been shown that the classical description can also be inaccurate at large angles. Ford and Wheeler[3] have found such inaccuracies in the vicinity of rainbow angles; Munn, Mason, and Smith[4] have found that the quantal differential cross section oscillates about the classical cross section at angles greater than θ_c.

This paper has two objectives. One is to find an accurate criterion for the prediction of the angle at which deviations from the classical approximation become important; in other words, to give a more quantitative result than the Massey-Mohr value of θ_c. A second objective is to try to reproduce some of the other quantal results with a semiclassical approximation. The mathematical procedure by which both objectives are approached is the stationary phase approximation carried to higher orders. The first objective has already been discussed in detail in a previous paper,[5] using some of the present results without discussion of the mathematical steps involved. Hence the present paper can be limited to an outline of the mathematical procedure as far as the first objective is concerned.

In the quantum theory the differential cross section $\sigma(\theta)$ for scattering by a central force is given as the square of the scattering amplitude $f(\theta)$,

$$\sigma(\theta) = \left|f(\theta)\right|^2 , \tag{2}$$

$$f(\theta) = (2ik)^{-1} \sum_{\ell=0}^{\infty} (2\ell+1) \left[\exp(2i\delta_\ell)-1\right] P_\ell(\cos\theta) , \tag{3}$$

where δ_ℓ is the phase shift for angular momentum quantum number ℓ, k is the wave number, and $P_\ell(\cos\theta)$ is a Legendre polynomial of order ℓ in $\cos\theta$. There are three distinct parts to a semiclassical approximation for $\sigma(\theta)$, as discussed by Ford and Wheeler.[3] The JWKB approximation is used for δ_ℓ; asymptotic formulas are used for $P_\ell(\cos\theta)$; and the summation in Eq.(3) is replaced by an integration. An additional approximation may be to evaluate the resulting integral by some procedure like the method of stationary phase.[3] The asymptotic expressions for $P_\ell(\cos\theta)$ are

$$P_\ell(\cos\theta) \approx J_0\left[(\ell+\tfrac{1}{2})\theta\right] \quad \text{for } \sin\theta \lesssim 1/\ell, \tag{4a}$$

$$P_\ell(\cos\theta) \approx \left[\tfrac{1}{2}\pi(\ell+\tfrac{1}{2})\sin\theta\right]^{-\frac{1}{2}} \sin\left[(\ell+\tfrac{1}{2})\theta+\tfrac{1}{4}\pi\right]$$

$$\text{for } \sin\theta \gtrsim 1/\ell. \tag{4b}$$

In previous work on semiclassical scattering for angles greater than θ_c, the second of these expressions for $P_\ell(\cos\theta)$ was used for all values of ℓ and the resulting integral expression for $f(\theta)$ was evaluated by the lowest order stationary phase approximation. This yielded the classical differential cross section.

In this paper $P_\ell(\cos\theta)$ is correctly approximated for all values of ℓ and the resulting integrals are evaluated with higher-order stationary phase approximations. This gives rise to three corrections to the classical differential cross section. The first is a small non-oscillating term which falls off monotonically as θ grows larger than θ_c. This arises from the use of higher-order stationary phase approximations at the point of stationary phase. The second is a larger oscillatory term which arises from the contribution at small values of ℓ, and the third is another non-oscillatory term from small ℓ values. These corrections are discussed separately in the following section.

In the last section the higher-order stationary phase approximations are applied to rainbow angle scattering. A rainbow angle is a special case because its point of stationary phase is stationary to a higher order of derivative than at an ordinary scattering angle.

II. HIGHER-ORDER STATIONARY PHASE APPROXIMATIONS

The application of the stationary phase approximation to physical problems is seldom carried beyond the lowest order of approximation.[6] However, a general asymptotic series expansion has been given by Erdélyi[7] (who quotes earlier references). It is applicable to integrals of the form

$$I = \int_{\alpha}^{\beta} g(t)\,(t-\alpha)^{\lambda-1}(\beta-t)^{\mu-1} \exp\left[\,i\,x\,h(t)\right]\,dt, \qquad (5)$$

in which all the variables are real, $\alpha \leqslant t \leqslant \beta$, $\lambda > 0$, $\mu \leqslant 1$, and the functions $g(t)$ and $h(t)$ are differentiable. The function $h(t)$ is also assumed to be monotonically increasing from α to β. Erdélyi shows that in the limit as the scale parameter x approaches infinity the integral can be expressed as an asymptotic series of which the first N terms are given by

$$I = B_N - A_N \,, \qquad (6)$$

where

$$A_N = -\sum_{n=0}^{N-1} \frac{k^{(n)}(0)}{n!\,\rho}\,\Gamma\!\left(\frac{n+\lambda}{\rho}\right) x^{-(n+\lambda)/\rho} \exp\left[\frac{\pi i(n+\lambda)}{2\rho}\right] \exp\left[\,ixh(\alpha)\right],$$

$$B_N = -\sum_{n=0}^{n-1} \frac{\ell^{(n)}(0)}{n!\,\sigma}\,\Gamma\!\left(\frac{n+\mu}{\sigma}\right) x^{-(n+\mu)/\sigma} \exp\left[-\frac{\pi i(n+\mu)}{2\sigma}\right] \exp\left[\,ixh(\beta)\right],$$

and

$$u^{\rho} = h(t) - h(\alpha), \qquad v^{\sigma} = h(\beta) - h(t),$$

$$k(u) = g_1(t)\,u^{1-\lambda}\,\frac{dt}{du}\,, \qquad \ell(v) = g_1(t)\,v^{1-\mu}\,\frac{dt}{dv}\,,$$

$$g_1(t) = g(t)\,(t-\alpha)^{\lambda-1}\,(\beta-t)^{\mu-1}.$$

The integers ρ and σ are equal to one plus the orders of the stationary points at α and β, respectively. The order of a stationary point is just a number one less than the order of the first non-vanishing derivative of h(t) at that point. An ordinary point is a stationary point of order zero; the usual stationary phase approximation corresponds to a stationary point of order one; rainbow angle scattering corresponds to a stationary point of order two.

The approximation used in previous work on the differential cross section was limited to the first term of this series $(N = 1)$. Higher terms are more complicated to calculate because of the necessity of calculating the higher derivatives $k^{(n)}(u)$ and $\ell^{(n)}(v)$ as functions of u and v. Several more terms are used in the following discussion, but first the zero-order approximation is described. For simplicity the discussion is limited to monotonic potentials, not because non-monotonic potentials present any greater difficulty in principle, but because the mathematical analysis for monotonic potentials is less laborious. Only repulsive potentials are considered; attractive potentials can be treated in exactly the same manner. Explicit results are obtained for the inverse power and exponential potentials.

A. Zero-Order Approximation

Before replacing the summation in (3) by an integral we first note that $\Sigma(2\ell+1)P_\ell(\cos\theta) = 0$. We also assume at this stage that θ is large enough that there are few phase shifts between 0 and $1/\theta$, so that the approximation for $P_\ell(\cos\theta)$ valid for $\ell > 1/\theta$ can be used for all values of ℓ. It follows that $f(\theta)$

becomes

$$f(\theta) = -(2\pi \sin\theta/k)^{-\frac{1}{2}} (I^{+} - I^{-}) \quad , \tag{7}$$

where

$$I^{\pm} = \int_{0}^{\infty} \beta^{\frac{1}{2}} \exp\left[i(2\delta \pm \beta k\theta \pm \tfrac{1}{4}\pi)\right] d\beta \quad ,$$

the variable of integration having been changed from ℓ to $\beta = (\ell + \frac{1}{2})/k$. For a repulsive potential I^{+} has no stationary phase point of order higher than zero, and I^{-} has one stationary point of order one when $\theta = (2/k)(d\delta/d\beta) = 2(d\delta_{\ell}/d\ell)$. In previous calculations of these integrals contributions from the end points were neglected and it was assumed that the only contribution to $f(\theta)$ arose from the stationary phase point of order one in I^{-}. This contribution was evaluated by the lowest-order stationary phase approximation $(N = 1)$ of (6), and the result is

$$\sigma_{c\ell}(\theta) = \left| \frac{\beta}{\sin\theta} \frac{d\beta}{d\theta} \right|_{\beta = b} \quad , \tag{8}$$

where b, the classical impact parameter, is the value of β at the stationary phase point of I^{-}.

B. Higher-Order Approximations

Because of the difficulty of eliminating the apparent singularities at $\beta = \infty$ in I^{+} and I^{-}, it is convenient to replace the summation in (3) by an integration without setting $\Sigma(2\ell + 1)P_{\ell}(\cos\theta) = 0$. The scattering amplitude $f(\theta)$ then becomes

$$f(\theta) = (2\pi \sin \theta/k)^{-\frac{1}{2}} (I_1 e^{-i\pi/4} - I_2 e^{+i\pi/4}), \tag{9}$$

where

$$I_1 = \int_0^\infty \left[e^{2i\delta(\beta)} - 1\right] e^{-ik\beta\theta} \beta^{\frac{1}{2}} d\beta,$$

$$I_2 = \int_0^\infty \left[e^{2i\delta(\beta)} - 1\right] e^{ik\beta\theta} \beta^{\frac{1}{2}} d\beta.$$

We consider first the integral I_2 because it contains no stationary point of order higher than zero.

The integral I_2 is conveniently written in the form

$$I_2 = \lim_{\gamma \to \infty} \left[\int_0^\gamma e^{2i\delta(\beta)+ik\beta\theta} \beta^{\frac{1}{2}} d\beta - \int_0^\gamma e^{ik\beta\theta} \beta^{\frac{1}{2}} d\beta \right]. \tag{10}$$

Because both $[2\delta(\beta) + k\beta\theta]$ and $k\beta\theta$ are increasing functions of β between 0 and γ, the two integrals in (10) can be directly evaluated by the asymptotic expansion in (6). There are two contributions, one from the point $\beta = 0$ and the other from $\beta = \gamma$. We first consider the point at $\beta = \gamma$ and show that it makes no contribution. The point at $\beta = 0$ requires a special discussion, which we defer to Sec. IID, because the Bessel function approximation for $P_\ell \cos(\theta)$ needs to be used there. In other words we first consider only the B_N part of I_2. The first term is

$$I_2 : B_1 = \lim_{\gamma \to \infty} \left[\frac{i\gamma^{\frac{1}{2}} e^{2i\delta(\gamma)+ik\gamma\theta}}{k(\theta+\theta_\gamma)} - \frac{i\gamma^{\frac{1}{2}} e^{ik\gamma\theta}}{k\theta} \right], \tag{11}$$

where $\theta_\gamma = (2/k)(d\delta/d\beta)_{\beta=\gamma}$. In the limit as $\gamma \to \infty$, both $\delta(\gamma) \to 0$ and $\theta_\gamma \to 0$ for any potential that falls to zero as $r \to \infty$. It follows that $B_1 = 0$ for I_2. If higher terms in the expansion are also used, they too can be shown to be zero in the limit $\gamma \to \infty$. Thus $B_N = 0$ for I_2. This is a physically plausible result, stating that collisions with infinitely great impact parameters cannot affect the scattering amplitude.

A similar procedure can be used in the elimination of the apparent singularity at $\beta = \infty$ in I_1, but some preliminary manipulation is required to put the integral into the standard form of Eq.(5). The integral is first written in the form

$$I_1 = \lim_{\gamma \to \infty} \left[\int_0^\gamma e^{2i\delta(\beta) - ik\beta\theta} \beta^{\frac{1}{2}} \, d\beta - \int_0^\gamma e^{-ik\beta\theta} \beta^{\frac{1}{2}} \, d\beta \right]. \tag{12}$$

The first integral must be split into two parts at the first-order stationary phase point at $\beta = b$, and the integration variable changed so that $h(t)$ is monotonically increasing in both parts. A similar variable change must be made in the second integral in (12). On substituting $\beta = -\zeta$, we obtain

$$I_1 = \lim_{\gamma \to \infty} \left[\int_0^b e^{2i\delta(\beta) - ik\beta\theta} \beta^{\frac{1}{2}} \, d\beta + \int_{-\gamma}^{-b} e^{2i\delta(-\zeta) + ik\zeta\theta} (-\zeta)^{\frac{1}{2}} d\zeta \right.$$
$$\left. - \int_{-\gamma}^{0} e^{ik\zeta\theta} (-\zeta)^{\frac{1}{2}} \, d\zeta \right] . \tag{13}$$

As before we postpone the discussion of the contributions at $\beta = 0$ and $\zeta = 0$ to Sec.IID. The contribution from $\zeta = -\gamma$ is again zero in the limit $\gamma \to \infty$. The only other contribution to I_1 comes from the first two integrals in (13) at $\beta = b$ and $\zeta = -b$. These can be evaluated from Eq. (16), a straightforward but tedious process. The result out to five terms in the series is

$$f(\theta) = i\left[\sigma_{cl}(\theta)\right]^{\frac{1}{2}} e^{i\left[2\delta(b)-kb\theta\right]}\left[1 + \frac{A_1}{(k\theta')^{\frac{1}{2}}} e^{-i\pi/4} + \right.$$

$$\left. + \frac{A_2}{(k\theta')} e^{-i\pi/2} + \frac{A_3}{(k\theta')^{3/2}} e^{-3i\pi/4} + \frac{A_4}{(k\theta')^2} e^{-i\pi} + \cdots\right], \tag{14}$$

where $\sigma_{cl}(\theta)$ is the classical differential cross section in (8), $\theta' = (d\theta/d\beta)_{\beta=b}$, and the odd-numbered coefficients A_1, A_3, etc. are identically zero because the contributions to them from the two sides of the stationary point cancel. Since k is inversely proportional to Planck's constant, Eq. (14) is a series in ascending powers of $\hbar^{\frac{1}{2}}$ with the odd powers missing. The even-numbered non-zero coefficients are

$$A_2 = (1/8b^2)\left[b^2(\theta'''/\theta') - \frac{5}{3} b^2(\theta''/\theta')^2 + 2b(\theta''/\theta') + 1\right],$$

$$A_4 = -(1/8b^4)\left[\frac{1}{6} b^4(\theta^{v}/\theta') - \frac{7}{6} b^4(\theta^{iv}/\theta')(\theta''/\theta')\right.$$

$$- \frac{35}{48} b^4(\theta'''/\theta')^2 + \frac{35}{8} b^4(\theta'''/\theta')(\theta''/\theta')^2 - \frac{385}{144} b^4(\theta''/\theta')^4$$

$$+ \frac{1}{2} b^3(\theta^{iv}/\theta') - \frac{35}{12} b^3(\theta'''/\theta')(\theta''/\theta') + \frac{35}{12} b^3(\theta''/\theta')^3$$

$$\left. - \frac{5}{8} b^2(\theta'''/\theta') + \frac{35}{24} b^2(\theta''/\theta')^2 + \frac{5}{4} b(\theta''/\theta') + \frac{15}{16}\right],$$

where $\theta'' = (d^2\theta/d\beta^2)_{\beta=b}$, etc.

When $f(\theta)$ is squared, the final series for $\sigma(\theta)$ is in powers of k^{-2} or $\hbar^2$, because the non-zero terms in $f(\theta)$ are alternately real and imaginary. The result is

$$\sigma(\theta)/\sigma_{cl}(\theta) = 1 + (2kb^2\theta')^{-2}\Big[\tfrac{1}{6} b^4(\theta^{v}/\theta') - \tfrac{7}{6} b^4(\theta^{iv}/\theta')(\theta''/\theta')$$
$$- \tfrac{2}{3} b^4(\theta'''/\theta')^2 + \tfrac{25}{6} b^4(\theta'''/\theta')(\theta''/\theta')^2 - \tfrac{5}{2} b^4(\theta''/\theta')^4$$
$$+ \tfrac{1}{2} b^3(\theta^{iv}/\theta') - \tfrac{8}{3} b^3(\theta'''/\theta')(\theta''/\theta') + \tfrac{5}{2} b^3(\theta''/\theta')^3$$
$$- \tfrac{1}{2} b^2(\theta'''/\theta') + \tfrac{3}{2} b^2(\theta''/\theta')^2 + \tfrac{3}{2} b(\theta''/\theta') + 1\Big]$$
$$+ O(k^{-4}) + \cdots . \qquad (15)$$

This result was quoted from our work by Mason, Vanderslice, and Raw.[5]

C. Results for the Inverse Power and Exponential Potentials

Two of the most common monotonic potentials are the inverse power potential, $V(r) = K/r^s$, where K and s are positive constants, and the exponential potential, $V(r) = Ae^{-\alpha r}$, where A and α are positive constants. If we restrict ourselves to small-angle scattering, we can find θ as an explicit function of b for both these potentials. For the inverse power potential we find[8]

$$\theta = KC_s / Eb^s, \qquad (16)$$

where E is the relative kinetic energy and

$$C_s = \pi^{\frac{1}{2}}\, \Gamma(\tfrac{1}{2}s + \tfrac{1}{2}) \Big/ \Gamma(\tfrac{1}{2}s) .$$

For the exponential potential we find[8,9]

$$\theta = (A/E)(\alpha b)\; K_o(\alpha b), \tag{17}$$

where $K_o(\alpha b)$ is the zero-order modified Bessel function of the second kind.

On substituting these results into Eq. (15), we obtain

$$\sigma(\theta)/\sigma_{cl}(\theta) = 1 + (2kb\theta)^{-2} + \cdots , \tag{18}$$

$$\sigma(\theta)/\sigma_{cl}(\theta) = 1 - (\alpha b/3)(2kb\theta)^{-2} + \cdots , \tag{19}$$

for the inverse power and exponential potentials, respectively. It is surprising that the result does not depend on the potential parameter s of the inverse power potential, but does depend on the parameter α of the exponential. Furthermore, the sign of the correction term is different for the two cases. As previously shown,[5] the correction amounts to about 2.5% at θ_c for He-He collisions at E = 250 eV. This correction happens to be small because of cancellation between the terms of $f(\theta)$, and not because the individual correction terms in $f(\theta)$ are small. Higher terms in the expansions of (18) and (19) are not significant since higher terms in the asymptotic expansion (4b) for the Legendre polynomials are estimated to be of larger magnitude than these.[5]

D. Correction for Small Angular Momentum Collisions

We now consider the correction that must be included in a complete semiclassical analysis to take account of the asymptotic form of $P_\ell(\cos\theta)$ for small angular momenta, namely

$P_\ell(\cos\theta) \approx J_o(\ell\theta)$ for $\ell\theta \leqslant 1$. To do this we write the semiclassical expression for $f(\theta)$ as

$$f(\theta) = (k/i) \int_0^{1/k\theta} \left[e^{2i\delta(\beta)} - 1\right] J_o(k\beta\theta)\beta\, d\beta$$

$$+ (k/i) \int_{1/k\theta}^{\infty} \left[e^{2i\delta(\beta)} - 1\right] P_\ell(\cos\theta)\, \beta\, d\beta. \quad (20)$$

Using the same procedure as that adopted in the previous discussion, we replace the Legendre polynomial $P_\ell(\cos\theta)$ in the second integral by its asymptotic expansion (4b) for $\ell\theta \geqslant 1$ and can then show that the contribution from $\beta = \infty$ is zero. The only other contribution besides that giving rise to the classical differential cross section at $\beta = b$ comes from the end point at $\beta = 1/k\theta$. Writing out explicitly the contribution from $\beta = b$ as found previously, we can reduce Eq.(20) to

$$f(\theta) = i\left[\sigma_{cl}(\theta)\right]^{\frac{1}{2}} e^{i[2\delta(b) - kb\theta]} \left[1 - i\frac{A_2}{k\theta'} - \frac{A_4}{(k\theta')^2} + \cdots\right] +$$

$$+ I_1 + I_2 - I_3 - I_4, \quad (21)$$

where the first part is the contribution from $\beta = b$ given in Eq.(14), and

$$I_1 = (k/i) \int_0^{1/k\theta} e^{2i\delta(\beta)} J_o(k\beta\theta)\beta\, d\beta,$$

$$I_2 = (k/i) \int_{1/k\theta} e^{2i\delta(\beta)} P_\ell(\cos\theta)\beta\, d\beta,$$

$$I_3 = (k/i) \int_0^{1/k\theta} J_o(k\beta\theta)\,\beta\, d\,\beta,$$

$$I_4 = (k/i) \int_{1/k\theta} P_\ell(\cos\,\theta)\,\beta d\,\beta.$$

Using the stationary phase approximation to any order we can readily show that the contributions to I_1 and I_2 from $\beta = 1/k\theta$ should cancel to within the order of accuracy of Eq.(4), since $P_\ell(\cos\,\theta) \approx J_o(k\beta\,\theta)$ at $\beta = 1/k\theta$ or $\ell\theta = 1$, and the point $\beta = 1/k\theta$ is a point of order zero. The contribution to I_1 at $\beta = 0$ can also be straightforwardly determined by the stationary phase method. The total contribution of I_1 and I_2 is thus

$$I_1 + I_2 = (i/k\pi^2)\ e^{2i\delta(0)} + \cdots\ . \tag{22}$$

The same procedure can be used on I_3 and I_4 if $J_o(k\beta\,\theta)$ and $P_\ell(\cos\,\theta)$ can be written in imaginary exponential notation. This is accomplished for $P_\ell(\cos\,\theta)$ by using the approximation (4b) and then writing the sine function in exponential form. Examination of the series expansion for $J_o(x)$ shows that the following approximation is quite accurate for $x \lesssim 1$:

$$J_o(x) \approx \cos\ (x/\sqrt{2})\,. \tag{23}$$

Writing the cosine in exponential form, we see that the contributions to I_3 and I_4 from $\beta = 1/k\theta$ cancel within the order of accuracy of Eqs.(4) and (23). The remaining contribution is

$$I_3 + I_4 = (k/2i)\left[\int_0 e^{ik\beta\theta/\sqrt{2}}\ \beta\, d\,\beta + \int_0\ e^{-ik\beta\theta/\sqrt{2}}\ \beta\, d\,\beta\ \right]. \tag{24}$$

These integrals are readily evaluated by the stationary phase method, giving

$$I_3 + I_4 = 2i/k\theta^2, \tag{25}$$

which is correct to all orders, the higher terms being identically zero.

For small-angle scattering the contribution from $I_1 + I_2$ is much smaller than that from $I_3 + I_4$ and can be neglected. Combining Eqs. (21) and (25) we obtain

$$f(\theta) = i\left[\sigma_{cl}(\theta)\right]^{\frac{1}{2}} e^{i[(2\delta(b)-kb\theta]}\left[1 - i\frac{A_2}{k\theta'} + \cdots\right] + \frac{2i}{k\theta^2}, \tag{26}$$

so that the final result is

$$\sigma(\theta) = \sigma_{cl}(\theta)\left[1 + \frac{(A_2^{\,2}-2A_4)}{(k\theta')^2} + O(k^{-4}) + \cdots\right] + \frac{4}{(k\theta^2)^2} +$$

$$+ \frac{4}{k\theta^2}\left[\sigma_{cl}(\theta)\right]^{\frac{1}{2}}\left[1 + \frac{(A_2^{\,2}-2A_4)}{(k\theta')^2} + O(k^{-4}) + \cdots\right]^{\frac{1}{2}} \cos(\phi+\phi_o), \tag{27}$$

where

$$\phi = 2\delta(b) - kb\theta, \tag{28}$$

$$\tan\phi_o = -\left[\frac{A_2}{k\theta'} + O(k^{-3}) + \cdots\right]\left[1 - \frac{A_4}{(k\theta')^2} + O(k^{-4}) + \cdots\right]^{-1}. \tag{29}$$

The first term in brackets in Eq. (27) is the contribution from $\beta = b$, and is the same as given by Eq. (15). Neither A_2 nor A_4 is individually small, but the combination $(A_2^{\,2}-2A_4)$ is fortuitously very small, at least for inverse power and exponential repulsive potentials. The next term, $4/(k\theta^2)^2$, is a non-oscillatory correction term arising from $\beta = 0$; it is of the same order in $\hbar$ as the correction arising from $\beta = b$. The magnitudes of these two non-oscillatory corrections are most easily compared for small-angle scattering by an inverse power potential, for which

$$\sigma_{cl}(\theta) = b^2/s\theta^2. \tag{30}$$

For this case Eq.(27) can therefore be written as

$$\sigma(\theta)/\sigma_{cl}(\theta) = 1 + (2kb\theta)^{-2} + (16s)(2kb\theta)^{-2} + \cdots$$
$$+ \text{ oscillatory term,} \tag{31}$$

and the non-oscillatory quantum correction from $\beta = 0$ is seen to be much larger than the one from $\beta = b$. A similar result holds for the exponential potential, for which

$$\sigma_{cl}(\theta) \approx b^2/\alpha b\theta^2 \tag{32}$$

$$\sigma(\theta)/\sigma_{cl}(\theta) = 1-(\alpha b/12)(kb\theta)^{-2} + (4\alpha b)(kb\theta)^{-2} + \cdots$$
$$+ \text{ oscillatory term.} \tag{33}$$

The large magnitude of the non-oscillatory correction from $\beta = 0$ is due entirely to the use of the J_o approximation for P_ℓ given in Eq.(4a); if the approximation (4b) had been used, the correction would have been zero.

E. Numerical Calculations

It is of interest to compare the present results with other approximations and with exact calculations for different molecular models. The present results are not expected to be good at very small angles, where a classical description breaks down completely. A different semiclassical approximation than the method of stationary phase can be used to obtain an expression for $\sigma(\theta)$ valid at very small angles.[5] For inverse power potentials this expression is

$$\sigma(\theta) = \left(\frac{kS}{4\pi}\right)^2 \left[1 + \tan^2\left(\frac{\pi}{s-1}\right)\right] \exp\left[-\frac{f(s)k^2S\theta^2}{8\pi}\right], \qquad (34)$$

where S is the total scattering cross section and f(s) is a numerical constant of magnitude unity.

A number of quantum scattering phenomena were first noticed by Massey and Mohr[2] in their study of rigid sphere scattering, and we therefore consider this case first. For rigid spheres of diameter σ, the total cross section is[2] $S = 2\pi\sigma^2$ and the classical differential cross section is[8] $\sigma_{cl}(\theta) = \sigma^{2}/4$. Substituting these results into Eq.(34) and passing to the limit $s \to \infty$, for which $f(s) \to 1$, we find the small-angle result

$$\sigma(\theta)/\sigma_{cl}(\theta) = (k\sigma)^2 \exp\left[-(k\sigma\theta/2)^2\right]. \qquad (35)$$

The classical deflection angle for rigid spheres is[8] $\cos(\theta/2) = b/\sigma$. Using this result and the semiclassical equivalence formula $\theta = (2/k)(d\delta/d\beta)_{\beta=b}$, we obtain $\phi = -2k\sigma \sin(\theta/2)$. The present semiclassical formula of Eq.(27) can then be written to sufficient accuracy for rigid spheres as

$$\sigma(\theta)/\sigma_{cl}(\theta) = 1 + (4/k\sigma\theta^2)^2 + (8/k\sigma\theta^2)\cos\left[2k\sigma\sin(\theta/2)\right] . \qquad (36)$$

Numerical results from Eq.(35) and (36) are shown in Fig. 1 for the case $k\sigma = 20$, for which $\theta_c = 0.157$ according to Eq.(1). Although the two results do not overlap, they come fairly near to each other. The value of θ_c predicted from Eq.(1) is seen to give a fair prediction of the angle above which the classical result is accurate in an average sense. The oscillations in the curve are in qualitative agreement with the exact results, as can be seen by comparison of Fig. 1 with Massey and Mohr's corresponding figure (also reproduced in reference 1, p.39), but do not damp out fast enough at larger angles.

The semiclassical formula of Eq.(27) can also be compared with the quantum calculations by Munn, Mason, and Smith[4] for the potential $V(r) = 4\epsilon(\sigma/r)^{12}$ at an energy $E/\epsilon = 45$, and for the de Boer parameter $\Lambda^* = h/\sigma(2\mu\epsilon)^{\frac{1}{2}}$ having values of 0.50 and 2.67. These energy and parameter values are equivalent to $k\sigma = 84.30$ and $k\sigma = 15.79$, respectively. To check the accuracy of the JWKB approximation in such cases the JWKB and quantum cross sections were also compared. The JWKB phase shifts and the classical deflection angles were evaluated by Gauss-Mehler quadratures.[10] The JWKB and quantum differential cross sections agree very well for $\Lambda^* = 0.50$, but not so well for $\Lambda^* = 2.67$, as shown in Figs. 2 and 3. The small-angle result of Eq.(34) was calculated with the exact value of S.[4] The exact value of $\sigma_{cl}(\theta)$ was also used,[10] but for $\Lambda^* = 0.50$ the correction terms of Eq.(27) were calculated with small-angle approximations, for which

$$\phi = -\frac{skb\theta}{s-1}\,, \tag{37}$$

$$\frac{A_2}{k\theta'} = \frac{2s^2+7s+2}{skb\theta}\;. \tag{38}$$

Within the accuracy of these approximations it is also reasonable to take $A_2^2 = 2A_4$, so that Eq.(37) becomes

$$\sigma(\theta) \approx \sigma_{cl}(\theta) + \frac{4}{(k\theta^2)^2} + \left(\frac{4}{k\theta^2}\right)\left[\sigma_{cl}(\theta)\right]^{\frac{1}{2}} \cos(\phi+\phi_o)\,, \tag{39}$$

with $\phi + \phi_o \approx -kb\theta$ when $s = 12$. This same formula was used for $\Lambda^* = 2.67$, but with $\phi + \phi_o \approx 2\delta(b) - kb\theta$ because these calculations extend to large angles. The results are shown in Figs. 2 and 3, where it can be seen that the small-angle result of Eq.(34) is remarkably accurate out to θ_c, but that the nearly classical result of Eq.(39) gives only a qualitative representation of the exact calculations. In particular, the oscillations of Eq.(39) are not sufficiently damped as θ increases. It should also be remarked in passing that θ_c from Eq.(1) gives an accurate prediction of the angle above which $\sigma_{cl}(\theta)$ is accurate in an average sense, and that θ_c is nearly the angle at which the small-angle formula (34) intersects $\sigma_{cl}(\theta)$ for the second time.[4]

III. APPROXIMATIONS AT A RAINBOW ANGLE

When the potential contains a minimum, a classical plot of θ against b will also show a minimum, so that $d\theta/db = 0$. According to the classical formula (8), there is a singularity in $\sigma_{cl}(\theta)$ at this minimum angle.[11] Semiclassically, at such a point $d^2\delta/d\beta^2$ is zero and hence the stationary phase point is of order two rather than one. This means that the zero-order approximation leading to the classical formula (8) is inherently incorrect, since it is based on the assumption that the stationary point is of order one. The angle at which this occurs has been called by Ford and Wheeler[3] the rainbow angle, θ_r, on the basis of the optical analogy. Ford and Wheeler have used a semiclassical approximation, without recourse to the method of stationary phase, to discuss the behavior of $\sigma(\theta)$ in the vicinity of θ_r. It is thus of interest to calculate $\sigma(\theta_r)$ by the method of stationary phase for comparison with the Ford and Wheeler approximation.

We consider just the contribution from the stationary point and ignore the contributions from the origin, which can be added on at the end by the method given in Sec.IID. As before, there is no contribution from the limit at infinity. We have thus to evaluate the integrals

$$f(\theta) = (2\pi \sin\theta/k)^{-\frac{1}{2}} \left[\int^{b} e^{2i\delta(\beta)-ik\beta\theta} \beta^{\frac{1}{2}} d\beta + \right.$$

$$\left. + \int_{b} e^{2i\delta(\beta)-ik\beta\theta} \beta^{\frac{1}{2}} d\beta \right]. \qquad (40)$$

The application of Eq. (16) is again straightforward but tedious, and yields

$$f(\theta_r) = -\frac{2}{3}\left(\frac{k}{2\pi \sin\theta_r}\right)^{\frac{1}{2}} e^{i(\phi_r - \pi/4)}\left[\frac{B_1}{(k\theta_r'')^{1/3}}\cos\left(\frac{\pi}{6}\right) - \right.$$

$$\left. -i\frac{B_2}{(k\theta_r'')^{2/3}}\sin\left(\frac{2\pi}{6}\right) + \frac{B_3}{(k\theta_r'')}\cos\left(\frac{3\pi}{6}\right) - i\frac{B_4}{(k\theta_r'')^{4/3}}\sin\left(\frac{4\pi}{6}\right) + \cdots\right] \tag{41}$$

where $\phi_r = 2\delta(b_r) - k\, b_r\, \theta_r$, $\theta_r'' = (d^2\theta/d\beta^2)_{\beta=b_r}$, and the sines and cosines have been written explicitly to show how every third term vanishes instead of every second term as at a first-order stationary point. This is a series in $\hbar^{1/3}$ with every third term missing, starting as $\hbar^{-1/6}$, $\hbar^{1/6}$, $\cdots$.

The foregoing formula has only limited application; it is valid just at the rainbow angle θ_r and gives no information about $f(\theta)$ or $\sigma(\theta)$ on either the bright or the shadow side of θ_r. Its main function would be to check the accuracy of other rainbow approximations, and so only the first two coefficients have been evaluated explicitly:

$$B_1 = -\,2b_r^{\frac{1}{2}}\,(3/2)^{1/3}\,\Gamma(1/3),$$

$$B_2 = -\,2b_r^{-\frac{1}{2}}\,(3/2)^{2/3}\,\Gamma(2/3)\,\left[(b_r/3)(\theta_r'''/\theta_r'') - 1\right].$$

Since the terms in Eq. (41) for $f(\theta_r)$ are alternately real and imaginary, the final series for $\sigma(\theta_r)$ is in powers of $\hbar^{2/3}$, starting as $\hbar^{-1/3}$, $\hbar^{1/3}$, $\cdots$, as follows:

$$\sigma(\theta_r) = \frac{(2/3)^{1/3}\left[\Gamma(1/3)\right]^2 k b_r}{\pi \sin\theta \; (k\theta_r'')^{2/3}} \left\{ 1 + \frac{(3/2)^{2/3}}{b_r^2 (k\theta_r'')^{2/3}} \left[\frac{\Gamma(2/3)}{\Gamma(1/3)}\right]^2 \left[\frac{b_r}{3}\left(\frac{\theta_r'''}{\theta_r''}\right) - 1\right]^2 + \cdots \right\}. \tag{42}$$

This expression may be compared with Ford and Wheeler's result. Rather than keep a general expression for $\delta(\beta)$ or $\theta(\beta)$ and evaluate the integral approximately, Ford and Wheeler use an approximate expression for $\delta(\beta)$ or $\theta(\beta)$ and evaluate the integral exactly. The approximate expression is obtained by expanding $\theta(\beta)$ in a Taylor series about the rainbow point and dropping the terms beyond the quadratic,

$$\theta(\beta) = \theta_r + \tfrac{1}{2}\,\theta_r''\,(\beta - b_r)^2 . \tag{43}$$

The integral over β then becomes an Airy integral whose argument is $\left[q^{-1/3}(\theta_r - \theta)\right]$, where $q = \theta_r''/2k^2$. We therefore expect that our result with all higher derivatives of θ_r set to zero should be an asymptotic series representation of Ford and Wheeler's result at exactly the rainbow angle. The first term of Eq.(42) does in fact agree with Ford and Wheeler, who quote only the first term of the appropriate series for the Airy function.

To check the magnitudes of the correction terms, we use the example of K^+ scattered by Ar at a relative energy of 0.17 eV, discussed by Ford and Wheeler in terms of the Lennard-Jones (12-6) potential. If we use the parameters given by Ford and Wheeler and take $\theta_r''' = 0$, we find the ratio of the second to the first term of Eq.(42) is only 1.5×10^{-4}. From calculations[12] of θ_r'' and θ_r''' for the (12-6) potential we find that $b_r(\theta_r'''/\theta_r'')$ is about 15 to 25, so that the ratio is raised to a little less than 10^{-2}. Thus the neglect of higher derivatives of θ is more serious than neglect of higher terms in the series for the Airy function, but neither is very important at the rainbow angle, and the first approximation given by Ford and Wheeler is entirely adequate. Unfortunately, the Ford and Wheeler approximation is not so accurate farther away from θ_r, because of the inadequacy of a quadratic representation of $\theta(\beta)$, and does not give the angular locations of the oscillations on the bright side of the rainbow (the supernumerary rainbows[13]) with sufficient accuracy for the quantitative interpretation of molecular beam scattering experiments. Accurate expressions could be obtained through the Ford and Wheeler procedure by keeping more terms in the Taylor expansion of $\theta(\beta)$. However, the necessary numerical computations are so involved that it is probably both easier and more accurate to go back to the original formulation, calculate phase shifts by the JWKB approximation, and integrate over ℓ or β by numerical techniques.

IV. DISCUSSION

In summary, the main contribution to $f(\theta)$ in the stationary phase approximation comes from the point of stationary phase of order one or higher. There is no contribution from the point of order zero at infinity, but there is a contribution from the point of order zero at the origin. The contribution from the origin and from the higher-order terms at the stationary point lead to quantum corrections to $\sigma_{cl}(\theta)$ which vanish at large angles as θ^{-4}. The interference between the contributions from the stationary point and from the origin adds an oscillatory term to $\sigma_{cl}(\theta)$, whose "wavelength" is approximately

$$\Delta\theta \approx 2\pi/kb, \tag{44}$$

and whose amplitude is of order of magnitude

$$\Delta\sigma/\sigma_{cl} \approx (k\sigma_{cl}^{\frac{1}{2}}\,\theta^2)^{-1}. \tag{45}$$

This oscillatory term is in only qualitative agreement with accurate quantum calculations, and it may be conjectured that the convergence of the higher-order stationary phase asymptotic series is not very good. The convergence for $\sigma(\theta)$ seems to be better than for $f(\theta)$, due partly to an apparently fortuitous near cancellation of higher terms.

In contrast, the small-angle result obtained by Mason, Vanderslice, and Raw is surprisingly accurate, and leads to a precise prediction of θ_c which is in good agreement with the Massey-Mohr value.

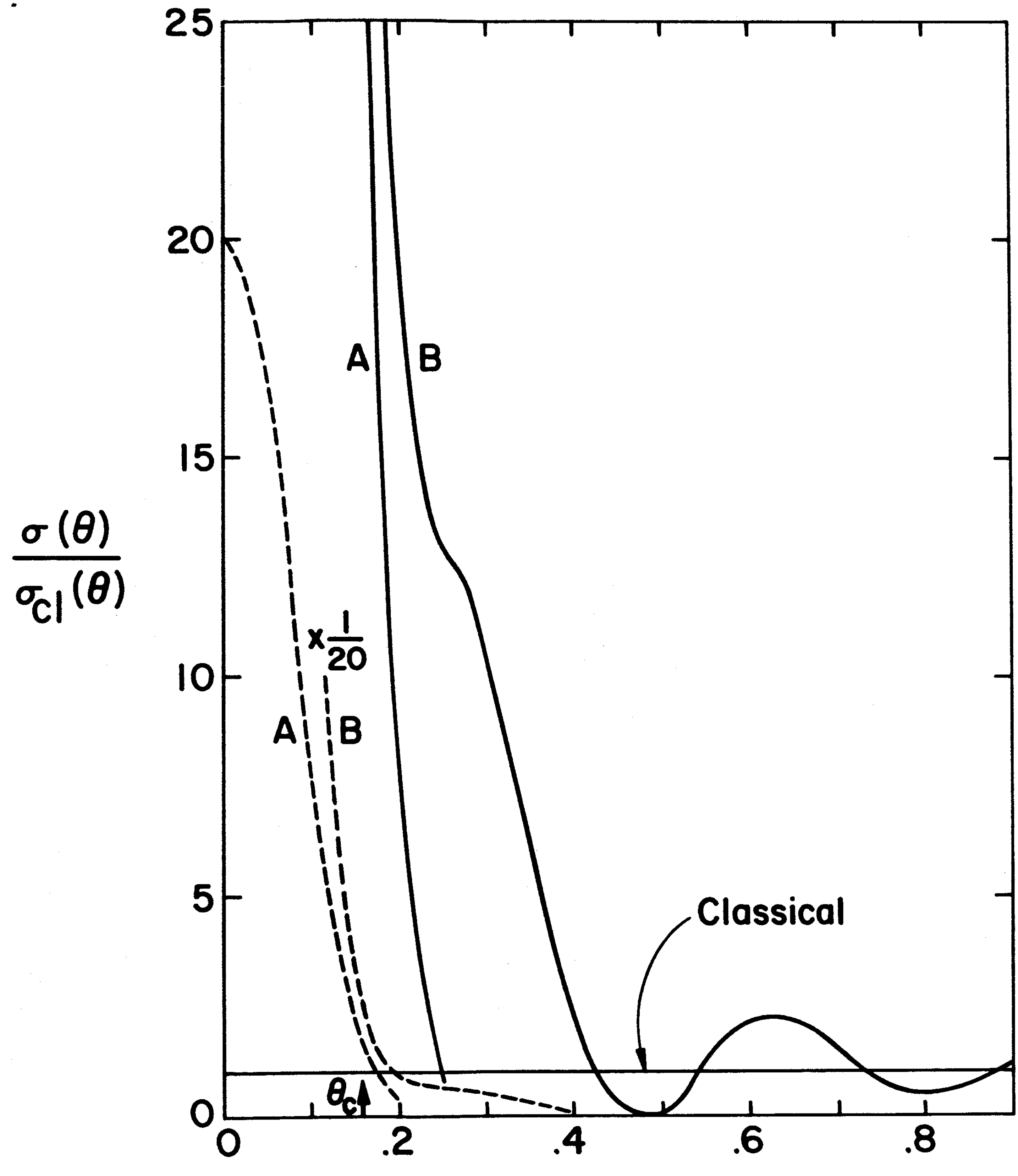
It is interesting to investigate the convergence of the stationary phase asymptotic series as the system approaches the classical limit, especially at a rainbow angle. Classical behavior is approached by letting k become large; this can be thought of either as the mass of the system increasing, or as the value of $\hbar$ decreasing. For non-rainbow scattering the non-oscillatory quantum terms vanish as k^{-2} or $\hbar^2$. The oscillatory term changes both in amplitude and "wavelength" as k^{-1} or $\hbar$; classical behavior is approached by the oscillations becoming more numerous and decreasing in amplitude. The decrease in wavelength means that any attempt to follow such oscillations in detail by accurate quantal or JWKB phase-shift calculations may meet severe numerical difficulties because of large numbers of oscillations. For rainbow scattering every term of the series involves k or $\hbar$, the series going as $k^{-2/3}$ or $\hbar^{2/3}$ with the first term being of order $k^{1/3}$ or $\hbar^{-1/3}$. This means there is no proper classical limit, since the leading term diverges as classical behavior is approached, even though the higher terms vanish. From this point of view it is not surprising that quantum effects are observable in molecular-beam scattering near a rainbow angle, although the scattering may be classical almost everywhere else.

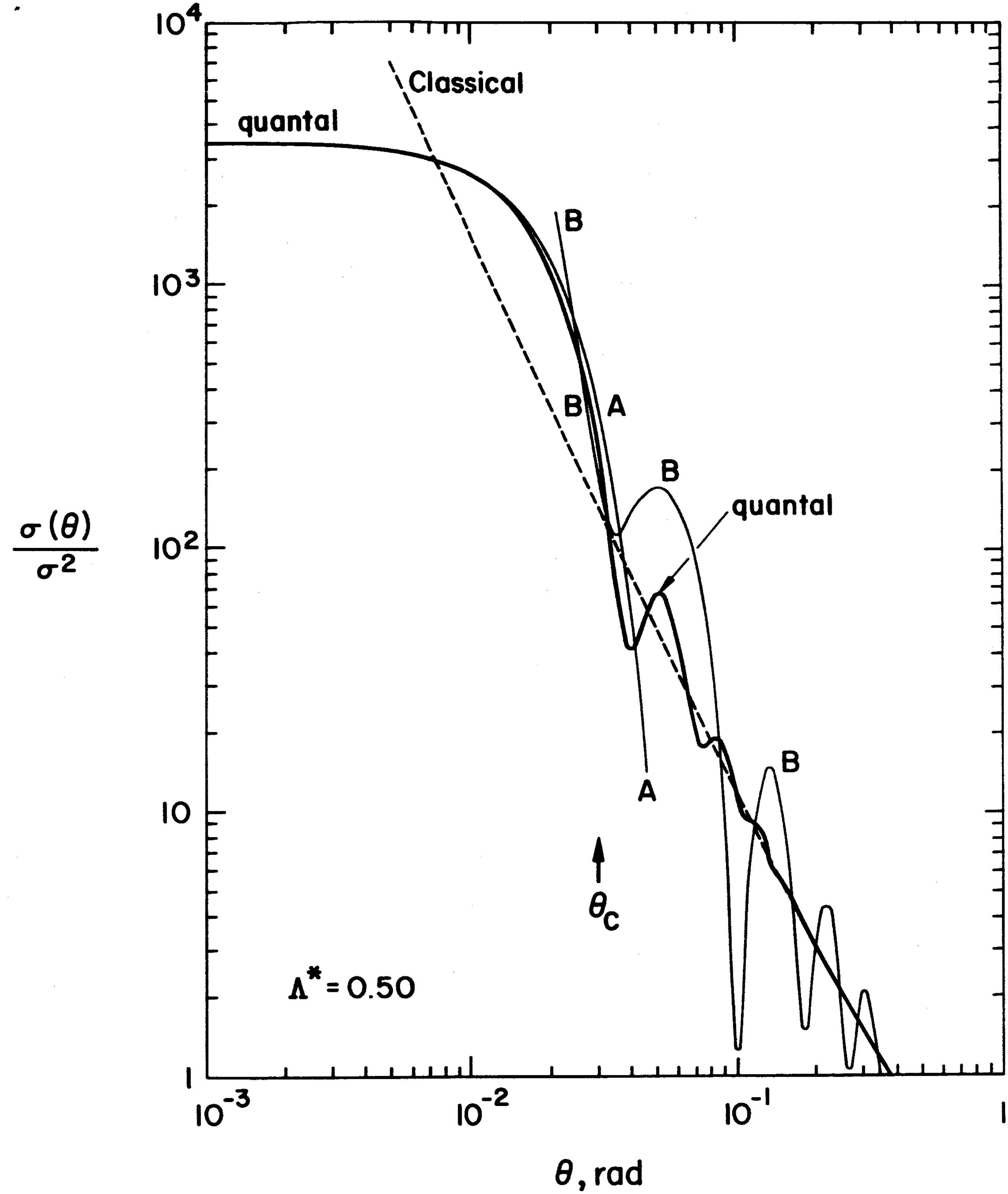
FIGURE CAPTIONS

Fig. 1. Differential cross section for scattering by a rigid sphere for $k\sigma = 20$. Curve A is from Eq. (35) and curve B from Eq. (36).

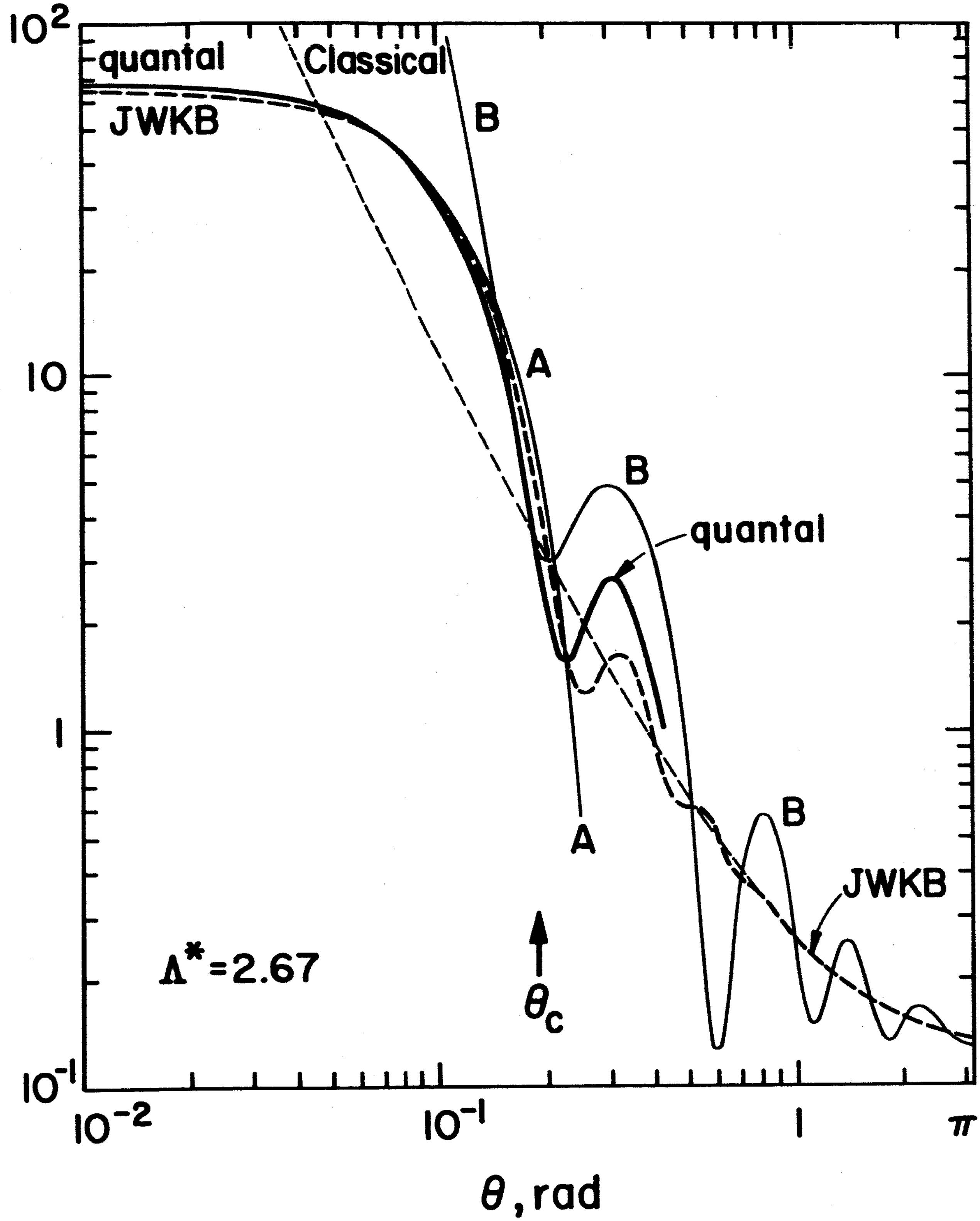
Fig. 2. Differential cross section for scattering by an inverse 12th power repulsive potential, $\varphi(r) = 4\epsilon(\sigma/r)^{12}$, with $E/\epsilon = 45$ and $\Lambda^* = 0.50$, corresponding to $k\sigma = 84.30$. The heavy curve is the exact quantal result, which is indistinguishable from the JWKB result. Curve A is from Eq. (34) and curve B from Eq. (39).

Fig. 3. Differential cross section for scattering as in Fig. 2, but with $\Lambda^* = 2.67$, corresponding to $k\sigma = 15.79$. The heavy dashed curve is the JWKB result, which differs appreciably from the exact quantal result.


25
20
15
10
5
0
σ (θ)
σ_Cl (θ)
A
B
x 1/20
A
B
Classical
θc
0
.2
.4
.6
.8
θ, rad



Classical
quantal
B
B
A
B
quantal
A
B
θ_c
$\Lambda^* = 0.50$
$\frac{\sigma(\theta)}{\sigma^2}$
10^4
10^3
10^2
10
1
10^{-3}
10^{-2}
10^{-1}
1
θ, rad



quantal
Classical
JWKB
B
A
B
quantal
A
B
JWKB
$\Lambda^* = 2.67$
θ_c
$\frac{\sigma(\theta)}{\sigma^2}$
10^2
10
1
10^{-1}
10^{-2}
10^{-1}
1
π
θ, rad

REFERENCES

1 N.F. Mott and H.S.W. Massey, The Theory of Atomic Collisions (Oxford University Press, London, 1949), Chap. 7.

2 H.S.W. Massey and C.B.O. Mohr, Proc. Roy. Soc. (London) A141, 434(1933); A144, 188(1934).

3 K.W. Ford and J.A. Wheeler, Ann. Phys. (N.Y.) 7, 259, 287(1959).

4 R.J. Munn, E.A. Mason, and F.J. Smith, J. Chem. Phys. 41, 0000 (1964).

5 E.A. Mason, J.T. Vanderslice, and C.J.G. Raw, J. Chem. Phys. 40, 2153(1964).

6 C. Eckart, Rev. Mod. Phys. 20, 399(1948).

7 A. Erdélyi, Asymptotic Expansions (Dover Publications, Inc., New York, 1956), pp.51-56.

8 E.H. Kennard, Kinetic Theory of Gases (Mc Graw-Hill Book Company, Inc., New York, 1938), pp.118-120.

9 R.B. Bernstein, J. Chem. Phys. 38, 515(1963).

10 F.J. Smith, Physica 30, 497(1964); F.J. Smith and R.J. Munn, J. Chem. Phys. 41, 0000(1964).

11 E.A. Mason, J. Chem. Phys. 26, 667(1957).

12 R.J. Munn, F.J. Smith, and E.A. Mason, to be published.

13 E.A. Mason and L. Monchick, J. Chem. Phys. 41, 2221(1964).