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Semi-classical scattering phase shifts in the presence of metastable states

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Abstract. In a recent paper, Curtiss and Powers claim to have shown that the phase shift η_l, for the case when the effective potential presents three turning points, contains in the classical limit a contribution from the classically inaccessible potential well between the inner two turning points, but is independent of the form of the barrier between the outer two turning points. It is shown that what Curtiss and Powers calculated is the semi-classical form of the *average* of η_l over a small range of energies. If the correct semi-classical η_l is used, the contribution of classically inaccessible regions to the averages of observable quantities such as cross sections vanishes in the classical limit, as one would expect.

1. Introduction

When a particle of mass m and energy E moves in a spherically symmetric potential $V(r)$, the scattering phase shift η_l of the lth partial wave depends on the effective potential

$$U(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{1}$$

If $V(r)$ is attractive and sufficiently strong, the effective potential takes the form of a well near the origin, separated from the outside by a centrifugal barrier; if, in addition, E is less than the barrier maximum, then there are three 'turning points' (zeros of $E-U(r)$) at $r_1 > r_2 > r_3$ (see figures 1 and 3).

Under these circumstances the equivalent classical problem with angular momentum

$$L = \hbar\{l(l+1)\}^{1/2}$$

has two completely independent solutions, the bound states for $r_3 \leqslant r \leqslant r_2$ and the scattering states for $r_1 \leqslant r \leqslant \infty$. In quantum mechanics there are no bound states of positive energy; instead, there are 'metastable states' for certain energy ranges, where the particle is much more likely to be in unit volume inside the well than in unit volume outside (see Merzbacher 1961). Under semi-classical conditions, when $\hbar$ becomes very small while L remains constant, the properties of the system, in particular the phase shifts, should change, in accordance with the correspondence principle, from their quantum to their classical forms.

Curtiss and Powers (1964) have derived an expression for the semi-classical phase shifts, using a formalism based on the density of states. Their formula contains just two terms, one from the scattering region $r_1 \leqslant r \leqslant \infty$ and one from the potential well $r_3 \leqslant r \leqslant r_2$. Barker and Johnson (1965) point out that, according to this result, the contribution to the phase shift from the inner region is independent of the height and shape of the barrier separating it from the outside. They examine the special case of a square-well potential (for which the exact solution is known), and point out that Curtiss and Powers omitted to include in their calculations the effect of the density of the bound states which exist in the classical limit.

In this paper we use the WKB method to calculate the form of η_l under semi-classical conditions for a general potential $V(r)$; the calculation is different according as V is continuous or discontinuous, the latter case including the example of Barker and Johnson. Our result is that η_l increases sharply by π at certain energies E_n, and that its average value, taken over a range of energy, is the expression found by Curtiss and Powers. The average values of measurable quantities, however, contain in the classical limit no contributions from classically inaccessible regions; this result is physically obvious. E will be considered to be well below the barrier top; the complicated phenomena which arise when E is near the barrier maximum (so that this can be considered as parabolic) have been examined in great detail by Ford *et al.* (1959).

2. Calculation of the phase shift: continuous potential

In radial problems the boundary condition on the reduced radial wave function is that it is zero at the origin. It is not legitimate to satisfy this condition with the ordinary WKB solutions, since these are not valid near the origin where $U(r)$ varies rapidly.

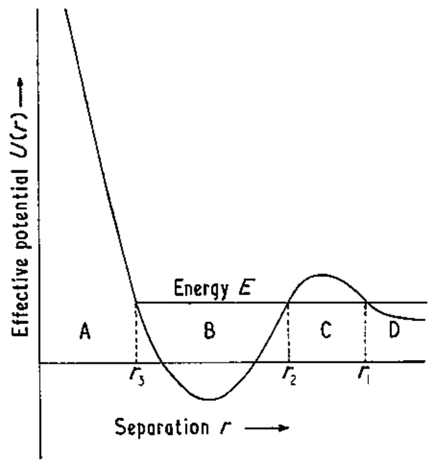

Figure 1. Effective potential; continuous case.

By means of a simple transformation (see Langer 1937, Bertocchi *et al.* 1965), however, it is possible to show that the WKB approximation can be used near the origin, provided the effective potential is replaced by $U'(r)$, which is identical with (1) except that $l(l+1)$ is replaced by $(l+\frac{1}{2})^2$.

The form of the reduced radial wave function given by this modified WKB approximation is

$$\psi(r) \propto \frac{\exp\left\{\pm i \int^r k(r)\, dr\right\}}{\{k(r)\}^{1/2}}$$

where

$$k^2(r) = \frac{2m}{\hbar^2}\{E - U'(r)\}.$$

This approximation fails at the turning points r_1, r_2 and r_3 (figure 1), and to keep track of the asymptotic form of a particular solution it is necessary to use a connection formula. In its most general form, required for this problem, the formula (see Langer 1937) states that there exists an exact solution of the radial equation whose asymptotic forms on either side of a turning point r_0 are

$$\frac{\cos\left(\left|\int_{r_0}^{r} k\,dr\right|-\frac{1}{4}\pi+\beta\right)}{k^{1/2}} \leftrightarrow \frac{\sin\beta\exp\left(\left|\int_{r_0}^{r} k\,dr\right|\right)}{|k|^{1/2}}+\frac{\cos\beta\exp\left(-\left|\int_{r_0}^{r} k\,dr\right|\right)}{2|k|^{1/2}}. \quad (2)$$

The trigonometric expression applies in the region $E > U'$, the exponential expression applies where $E < U'$, and β determines the particular solution involved.

We build up the wave function by starting with the region $0 \leqslant r < r_3$ (region A). In accordance with the boundary condition, ψ must decrease exponentially into A away from r_3, that is, it must take the form

$$\psi^{\mathrm{A}} = \frac{A\exp\left(-\int_{r}^{r_3} |k|\,dr\right)}{2|k|^{1/2}}$$

where A is a constant. In formula (2) β must be zero, so that the wave function in region B ($r_3 < r < r_2$) is

$$\psi^{\mathrm{B}} = \frac{A}{k^{1/2}}\cos\left(\int_{r_3}^{r} k\,dr-\frac{1}{4}\pi\right).$$

If we define the phase integral for the well as

$$\phi = \int_{r_3}^{r_2} k\,dr_1$$

we can rewrite this as

$$\psi^{\mathrm{B}} = \frac{A}{k^{1/2}}\cos\left\{\int_{r}^{r_2} k\,dr-\frac{1}{4}\pi-(\phi-\frac{1}{2}\pi)\right\}.$$

To connect this into region C ($r_2 < r < r_1$) we must take $\beta = -(\phi-\frac{1}{2}\pi)$ in (2), giving

$$\psi^{\mathrm{C}} = \frac{A}{|k|^{1/2}}\left\{-\sin(\phi-\tfrac{1}{2}\pi)\exp\left(\int_{r_3}^{r} |k|\,dr\right)+\tfrac{1}{2}\cos(\phi-\tfrac{1}{2}\pi)\exp\left(-\int_{r_2}^{r} |k|\,dr\right)\right\}.$$

If we define the phase integral for the barrier as

$$\gamma = \int_{r_2}^{r_1} |k|\,dr$$

we can rewrite this as

$$\psi^{\mathrm{C}} = \frac{A}{|k|^{1/2}}\left\{\tfrac{1}{2}\mathrm{e}^{-\gamma}\cos(\phi-\tfrac{1}{2}\pi)\exp\left(\int_{r}^{r_1} |k|\,dr\right)-\mathrm{e}^{\gamma}\sin(\phi-\tfrac{1}{2}\pi)\exp\left(-\int_{r}^{r_1} |k|\,dr\right)\right\}. \quad (4)$$

If we write the wave function in the final region D ($r > r_1$) as

$$\psi^{\mathrm{D}} = \frac{1}{k^{1/2}}\cos\left(\int_{r_1}^{r} k\,dr-\tfrac{1}{4}\pi+\alpha\right) \quad (5)$$

then to connect this with (4) in accordance with (2) we must have

$$\tfrac{1}{2}A\,\mathrm{e}^{-\gamma}\cos(\phi-\tfrac{1}{2}\pi) = \sin\alpha$$

and

$$-A\,\mathrm{e}^{\gamma}\sin(\phi-\tfrac{1}{2}\pi) = \tfrac{1}{2}\cos\alpha.$$

This implies that

$$\tan\alpha = -\tfrac{1}{4}\,\mathrm{e}^{-2\gamma}\cot(\phi-\tfrac{1}{2}\pi) \quad (6)$$

and

$$A^2 = \frac{1}{\frac{1}{4}\,\mathrm{e}^{-2\gamma}\cos^2(\phi-\frac{1}{2}\pi)+4\,\mathrm{e}^{2\gamma}\sin^2(\phi-\frac{1}{2}\pi)}. \quad (7)$$

The phase shift η_l is defined by requiring that the wave function very far from the origin takes the form

$$\psi^{D} \to \frac{1}{k_0^{1/2}} \sin(k_0 r - \tfrac{1}{2} l\pi + \eta_l)$$

where

$$k_0 = \left(\frac{2mE}{\hbar^2}\right)^{1/2}.$$

Together with (5) and (6), this means that the phase shift is

$$\begin{aligned}\eta_l &= \eta_l^{(0)} + \alpha \\ &= \int_{r_1}^{\infty} (k - k_0)\, dr + (l + \tfrac{1}{2})\tfrac{1}{2}\pi - k_0 r_1 - \tan^{-1}\{\tfrac{1}{4} e^{-2\gamma} \cot(\phi - \tfrac{1}{2}\pi)\}. \end{aligned} \quad (8)$$

3. Interpretation of the result

The expression (8) consists of two terms, whose variations with energy are sketched in figure 2 (we adopt the convention that the phase shift is a continuous function of

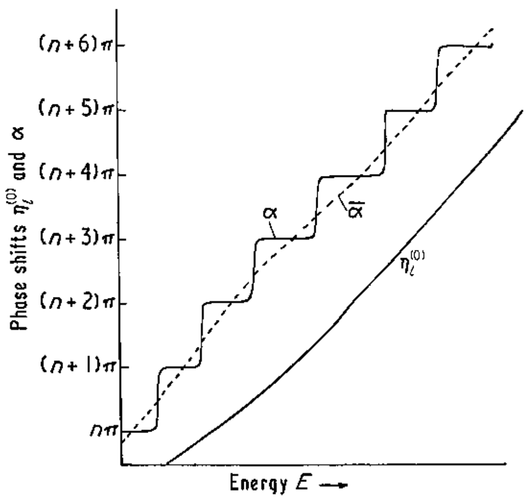

Figure 2. Variation with energy of contributions to phase shift.

energy). The first term $\eta_l^{(0)}$ is the usual semi-classical phase shift, derived by ignoring the inner region; it is a smooth function of energy. The second term α is the modification produced by the well and barrier. For most values of E the $e^{-2\gamma}$ factor ensures that α is almost an integral multiple of π; under these conditions the scattering from the potential, which depends on $\exp(i\eta_l) \sin \eta_l$ and not on the absolute value of η_l, is not affected by the inner region.

Resonances of tan α occur when E passes through one of the semi-classical positive energy levels E_n of the well; these are the zeros of $\sin(\phi - \tfrac{1}{2}\pi)$. Near such an energy, the approximate form of tan α is

$$-\tfrac{1}{4} e^{-2\gamma} \cot(\phi - \tfrac{1}{2}\pi) \simeq \frac{\Gamma_n}{2(E_n - E)}$$

where

$$\Gamma_n = \frac{\exp\{-2\gamma(E_n)\}}{2(\partial\phi/\partial E)_{E_n}}. \quad (9)$$

This expression is very easy to interpret: Γ_n is a level width equal to $\hbar$ times ω, the disintegration probability per unit time for the metastable state n. ω is the quotient of the barrier penetration probability $e^{-2\gamma}$ and the time $2\hbar(\partial\phi/\partial E)$ between successive impacts on the barrier of a particle moving classically inside the well. Near E_n the contribution to the scattering amplitude from the lth partial wave shows typical resonance behaviour (see Messiah 1961) of the form

$$\exp(i\eta_l)\sin\eta_l \simeq \exp(i\eta_l^{(0)})\sin\eta_l^{(0)} + \frac{\exp(2i\eta_l^{(0)})\frac{1}{2}\Gamma_n}{E_n - E - \frac{1}{2}i\Gamma_n}. \tag{10}$$

In order to observe these resonances it would be necessary to choose conditions which, while still semi-classical (in the sense that the expression (8) for the phase shift is qualitatively correct), are nevertheless rather far from the classical limit. There are two reasons for this. First, conditions must be such that only a few partial waves contribute to the scattering, otherwise the effect of the one undergoing resonance will be swamped by the others. Second, in all actual experiments the incident particle energy E is not precisely defined; it is essential that its spread does not exceed the separation of the resonances, and this is proportional to $\hbar$, vanishing in the classical limit (the width Γ decreases much faster, being proportional to $\hbar\exp(-c/\hbar)$).

If we wish to calculate the classical limit of a quantity involving the phase shift, we must average over a small range of energy, which is, however, large enough to include many resonances. In the special case of the phase shift itself, we have (denoting energy averages by bars)

$$\bar{\eta}_l = \bar{\eta}_l^{(0)} + \bar{\alpha}. \tag{11}$$

Now $\eta_l^{(0)}$ is a smooth function of E, and is therefore equal to its average $\bar{\eta}_l^{(0)}$. The average $\bar{\alpha}$ is obtained by replacing the staircase form of α (figure 2) by a smooth curve. The analytic form of this curve is very simple: the midpoints of the vertical steps of α lie at the values $(n+\frac{1}{2})\pi$, and correspond to energies E_n. But $(n+\frac{1}{2})\pi$ is just $\phi(E_n)$, so that for $\bar{\alpha}$ we can take the smooth function

$$\bar{\alpha}(E) = \phi(E).$$

Inserting this in (11) and using (8), we get

$$\bar{\eta}_l = \int_{r_1}^{\infty}(k-k_0)\,dr + (l+\tfrac{1}{2})\tfrac{1}{2}\pi - k_0 r_1 + \int_{r_3}^{r_2} k\,dr \tag{12}$$

which is just the expression, derived by Curtiss and Powers and not involving the barrier, which was criticized by Barker and Johnson.

Now the absolute phase shift is not a directly measurable quantity, so the average (12) seems to be without significance. A quantity which is frequently measured is the differential scattering cross section; this can be written

$$\overline{|f(\theta)|^2} = \frac{\int_E^{E+\Delta E}|f(\theta)|^2\,dE}{\Delta E} \tag{13}$$

where ΔE is small but finite. The partial wave expansion of $f(\theta)$ can be written in the following form, which separates the 'potential scattering' $f^{(0)}(\theta)$ from the scattering $f^{(\alpha)}(\theta)$ due to the resonances:

$$f(\theta) = f^{(0)}(\theta) + f^{(\alpha)}(\theta)$$

where

$$f^{(\alpha)}(\theta) = \frac{1}{k_0}\sum_l (2l+1)\mathrm{P}_l(\cos\theta)\frac{\tan\alpha}{1-i\tan\alpha}. \tag{14}$$

The summation is over $\Delta L/\hbar$ partial waves, where ΔL is the range of classical angular momenta for which the effective potential U' presents three turning points at the energy E; $\tan\alpha$ is given by (6). Near the classical limit, the separation of resonances for each partial wave is $b\hbar$ where b is a slowly varying classical function depending on the form of the well. The total number of resonances contributing to the integral (13) is thus approximately $\Delta L\Delta E/b\hbar^2$. It is obvious from (10) that the maximum contribution of each resonance to (14) is $(2l_{\max}+1)/k_0 \simeq 2L_{\max}/\hbar k_0$, where $L_{\max}$ is the largest angular momentum in the range ΔL. The width of each resonance is Γ, given by (9); this has the form $\hbar d\exp(-c/\hbar)$, where c and d are classical functions. We can now estimate the quantities involved in the average (13). We have

$$\begin{aligned}\overline{|f(\theta)|^2} &= \overline{|f^{(0)}(\theta)|^2}+\overline{|f^{(\alpha)}(\theta)|^2}+\overline{f^{(0)}(\theta)f^{(\alpha)*}(\theta)}+\overline{f^{(0)*}(\theta)f^{(\alpha)}(\theta)}\\ &= \overline{|f^{(0)}(\theta)|^2}+\overline{|f^{(\alpha)}(\theta)|^2}+\overline{f^{(0)}(\theta)}\;\overline{f^{(\alpha)*}(\theta)}+\overline{f^{(0)*}(\theta)}\;\overline{f^{(\alpha)}(\theta)}\end{aligned}$$

since any fluctuations $f^{(0)}(\theta)$ may exhibit with energy—and these can be very complicated in the classical limit (see Ford and Wheeler 1959)—are completely uncorrelated with those of $f^{(0)}(\theta)$, owing to the resonances. Now

$$\overline{f^{(\alpha)}(\theta)} < \frac{1}{\Delta E}\,\frac{\Delta L\Delta E}{b\hbar^2}\,\frac{2L_{\max}}{(2mE)^{1/2}}\,\hbar\, d\exp\left(-\frac{c}{\hbar}\right)$$

and

$$\overline{|f^{(\alpha)}(\theta)|^2} < \frac{1}{\Delta E}\,\frac{\Delta L\Delta E}{b\hbar^2}\left\{\frac{2L_{\max}}{(2mE)^{1/2}}\right\}^2\hbar\, d\exp\left(-\frac{c}{\hbar}\right)$$

and the right-hand sides of both of these inequalities vanish as $\hbar\to 0$. Thus

$$\overline{|f(\theta)|^2} = \overline{|f^{(0)}(\theta)|^2}$$

and the effects of the resonances are not observable in the classical limit. This result would not have been obtained if the average phase shift (12) had been used.

Curtiss (1965), in his reply to the criticisms of Barker and Johnson, considers the diffusion cross section

$$Q^{(1)} = \frac{4\pi}{k_0^{\,2}}\sum_{l=0}^{\infty}(l+1)\sin^2(\eta_{l+1}-\eta_l).$$

For η_l he uses the expression that we have found to be the average phase shift $\bar{\eta}_l$, given by (12). The sum is then replaced by an integral plus Euler–Maclaurin correction terms, and the result includes substantial contribution from the effective potential well. However, if the correct value (8) is used in $Q^{(1)}$, the same arguments apply as in the case of the differential scattering cross section: the resonances are so narrow that their contributions to $\int_E^{E+\Delta E} Q^{(1)}dE$ vanish in the classical limit, and the average cross section then involves no contributions from the well.

4. Calculation of the phase shift: discontinuous potential

The example given by Barker and Johnson of a square-well potential is a special case of the situation where $V(r)$ is quasi-classical except for one discontinuous part, the vertical outer wall of the well. The effective potential $U(r)$ then takes the form shown in figure 3. The calculation of η_l for this case is identical with that for the continuous case except that the quasi-classical expressions for the wave functions are valid right up to the discontinuity r_2, and are connected across it by joining slope and value there.

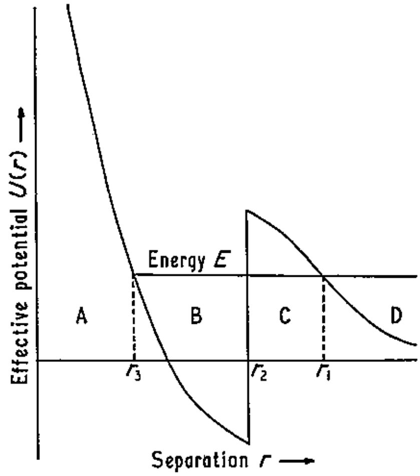

Figure 3. Effective potential; one discontinuity.

In region B, then, the wave function is given by (3), and in region D by (5). (5) is connected across r_1 into region C by the connection formula (2); this gives

$$\psi^C = \frac{1}{|k|^{1/2}}\left\{\sin\alpha\exp\left(\int_r^{r_1}|k|\,dr\right)+\tfrac{1}{2}\cos\alpha\exp\left(-\int_r^{r_1}|k|\,dr\right)\right\}$$

$$= \frac{1}{|k|^{1/2}}\left\{\sin\alpha\,e^{\gamma}\exp\left(-\int_{r_2}^{r}|k|\,dr\right)+\tfrac{1}{2}\cos\alpha\,e^{-\gamma}\exp\left(+\int_{r_2}^{r}|k|\,dr\right)\right\}.$$

Writing k_2 for $k(r_2-0)$ and K_2 for $|k(r_2+0)|$, we can write the continuity conditions on ψ at r_2 as

$$\frac{A}{k_2^{1/2}}\cos(\phi-\tfrac{1}{4}\pi) = \frac{1}{K_2^{1/2}}(\sin\alpha\,e^{\gamma}+\tfrac{1}{2}\cos\alpha\,e^{-\gamma})$$

and

$$Ak_2^{1/2}\sin(\phi-\tfrac{1}{4}\pi) = K_2^{1/2}(\sin\alpha\,e^{\gamma}-\tfrac{1}{2}\cos\alpha\,e^{-\gamma}).$$

Solving for α, we have that the phase shift is

$$\eta_l = \eta_l^{(0)}+\alpha$$

$$= \eta_l^{(0)}+\tan^{-1}\left[\frac{e^{-2\gamma}}{2}\left\{\frac{1+(k_2/K_2)\tan(\phi-\frac{1}{4}\pi)}{1-(k_2/K_2)\tan(\phi-\frac{1}{4}\pi)}\right\}\right]. \qquad (15)$$

This result has exactly the same meaning as (8): there are resonances whenever E is such that

$$\tan(\phi-\tfrac{1}{4}\pi) = \frac{K_2}{k_2};$$

this is just the condition for a semi-classical energy level in a well with one finite vertical side. The width of the resonance at E_n is

$$\Gamma_n = \frac{2\exp\{-2\gamma(E_n)\}K_2/k_2}{(\partial\phi/\partial E)_{E_n}(1+K_2^2/k_2^2)}$$

which has the same interpretation as (9), since the penetration probability of a barrier with the shape shown in figure 3 is

$$\frac{4e^{-2\gamma}K_2/k_1}{1+K_2^2/k_1^2}.$$

In the example of Barker and Johnson,

$$\begin{aligned} V &= 0 \qquad (r > a) \\ &= -D \qquad (r < a). \end{aligned}$$

The integrals involved in the functions $\eta_l^{(0)}$, ϕ and γ are all easily evaluated, and the final expression for η_l from (15) is identical with equation (17) of their paper except for a factor $\frac{1}{2}$ which they have omitted (some of the asymptotic expressions for Bessel functions of large order are also erroneously printed in their paper).

5. Conclusions

The phase shift, then, in the presence of three turning points is a function which increases sharply by π at certain energies E_n. This increase is a resonance phenomenon caused by metastable states in the potential well, and its sharpness depends on the form of the barrier. The average value of the phase shift is a smooth function which is independent of the form of the barrier. Measurable quantities, such as cross sections, exhibit resonance behaviour at the energies E_n, but their average values are smooth functions of energy which, in the classical limit, do not involve contributions from the well and barrier.

For this problem the classical solution is the limit, not simply of the appropriate solution of Schrödinger's equation, but of an average over a suitably chosen set of such solutions. This situation arises in all except the very simplest applications of the correspondence principle (in Ford and Wheeler (1959) many cases of scattering are examined where the averaging is taken over the angle of observation θ).

Acknowledgments

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