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ORIGINAL PAPER

Heavy-particle resonance phase shifts: an improved amplitude–phase formula

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Abstract An improved amplitude–phase formula suitable for non-relativistic heavy-particle resonance phase shifts is derived. The present formula makes use of two amplitude functions instead of one for a central potential; an inner amplitude which is non-oscillatory in the well region of the effective potential, and an outer amplitude function which is non-oscillatory far away from the origin of the effective potential. The low-energy limit is discussed in connection with Levinson's theorem. Numerical computations at resonance energies and graphical illustrations are presented. Numerical comparisons with an existing single-amplitude formula are made.

Keywords Elastic molecular scattering · Resonances · Phase shifts · Amplitude–phase method

1 lntroduction

A study of scattering resonances need reliable computations of phase shifts [1–4]. Absolute values of phase shifts with correct multiples of π plays an important role in connection with Levinson's theorem and the correct number of bound states in a given effective potential [2,5], as well as for calculations of virial coefficients [3,4]. Numerical methods and algorithms do not automatically provide phase shifts with correct multiples of π [3,4,6–8], partly because calculations of cross sections do not require correct multiples of π. For use of methods other than amplitude–phase methods, Wei and Le Roy (2006) [3,4] present a quantal/semiclassical method to calculate absolute

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phase shifts (rather than relative phase shifts modulo π) that improves standard quantal methods [9,10]. This method is general and not specific to resonance scattering.

In cases of heavy-particle scattering, resonances often appear in tiny energy intervals and require accurate phase shift computations. The amplitude–phase method using a single amplitude function turns out to miscount the correct multiple of π in such cases. The improvement presented here (a two-amplitude method) is specific for potentials supporting extremely sharp resonances, having 'thick barriers' causing exponential behaviors of wave functions. For non-resonance scattering of heavy particles one can rely on the single-amplitude method of calculating phase shift. Both amplitude–phase methods automatically provide absolute phase shifts.

The amplitude–phase method sees a fundamental quantum wave function as composed of a real-valued amplitude function and a real-valued phase function in exponential form [11,12]. The idea of subdividing a wave function of quantum theory into a phase function and an amplitude function has been introduced also in semiclassical approximations; see [1,2,13,14]. It was implemented as an exact numerical method by Milne [11] and Wheeler [12], and later improved by others; often referred to as the 'amplitude-phase method'. Because of a suitable exact relation between the phase and the amplitude, the basic quantity of computation is the amplitude function.

There may be several 'local' representations of a solution obtained by an amplitude–phase method, being formally exact in all space. However, their numerical efficiencies may differ significantly. A typical case is the problem of calculating bound-state solutions and energies in double-well potantials [15]. Another case is the reflection/transmission solutions in the presence of thick potential barriers [16]; see also [17]. Therefore, like semiclassical representations of the Wentzel–Kramers–Brillouin (WKB) type [16], the amplitude–phase representations of a wave can be seen as 'locally valid' and connections between them are useful in the present study. As yet, connections of 'local' amplitude–phase representations occur only between regions of oscillating waves [15]. In the present derivations, two representations of the scattering solution are obtained and made to agree at a convenient matching point between the two oscillatory regions. The resulting phase shift formula is valid also when the inner and outer regions merge at energies above the barrier.

A typical effective radial potential of interest here is illustrated in Fig. 1. For scattering energies above the minimum of the well one can use fixed potential characteristics to define two amplitude functions; the local (inner) minimum position r_i and any sufficiently large value of the relative distance. The barrier maximum position r_m of the effective potential is used to match the two representations of the wave.

In cases of no or small angular momenta there there may be no centrifugal barrier in the effective potential. In the absence of a barrier one may choose r_m equal to the potential range parameter. This is the case treated by Mott and Massey [5] for phase shifts due to an attractive radial rectangular well potential. In that case r_i can be chosen anywhere in the well, e.g. at the origin, and r_m is chosen at the discontinuity where the well vanishes. This is demonstrated in one of the sections.

Section 2 reviews the radial Schrödinger equation of potential scattering and the definition of the partial-wave phase shifts. Section 3 presents a derivation of the well used single-amplitude amplitude–phase formula. This section also introduces a second amplitude function and derives a new formula for phase shifts suitable at resonance

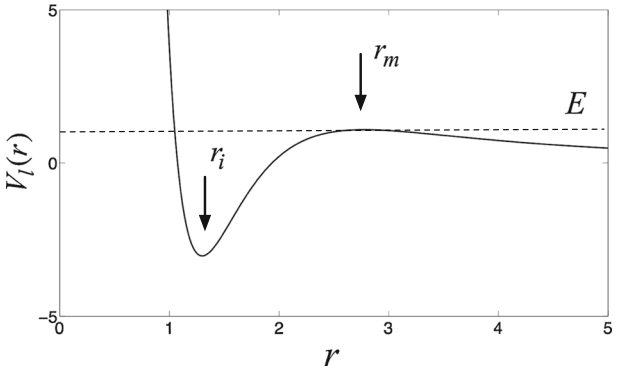

Fig. 1 Schematic illustration in arbitrary units of an effective potential $V_l(r)$ and a scattering energy E near the potential barrier maximum

conditions. Levinson's theorem is discussed in the light of the new phase-shift formula in Sect. 4. Numerical applications to carbon–oxygen scattering with a simplified potential model are found in Sect. 5. Conclusions are stated in Sect. 6.

2 The radial Schrödinger equation and scattering solutions

The radial Schrödinger equation can be written as

$$\Psi_l''(r) + K_l^2(r)\Psi_l(r) = 0, \quad \Psi_l(0) = 0, \tag{2.1}$$

where $\Psi_l(r)$ is the radial wave function being regular at the origin. A prime ($'$) denotes the derivative along an r-axis and l denotes the orbital angular momentum quantum number. The potential $V(r)$ and the scattering energy E are contained in the real-valued coefficient function $K_l^2(r)$. The regular radial wave function is normalized here to satisfy

$$\Psi_l \approx k^{-1/2} \sin\left(kr - l\pi/2 + \delta_l\right), \quad r \to \infty, \tag{2.2}$$

where δ_l is the scattering phase shift. The wave number k is defined by

$$k = \sqrt{K_l^2(+\infty)}. \tag{2.3}$$

It is assumed that the potential vanishes as $r \to \infty$. The asymptotic expression (2.2) is assumed at far distances where centrifugal barrier is negligible. These distances are typically far beyond the distance where the potential is negligible.

With standard quantum computations one wants to extract the phase shift at a wave node as close as possible to the range of the potential by fitting the quantal wave to a linear combination of spherical Bessel functions. In that way one obtains '$\tan\delta_l$' and may then miss some multiple of π in the phase shift 'δ_l' [3,4]. To overcome this problem one interpolates phases of the waves, without the potential (spherical Bessel function) and/or with the potential, between nodes using semiclassical approximations.

This method is robust if the algorithm to count and localize nodes of the numerical wave function is robust. The method is not limited to resonance scattering. However, the number of oscillations of a quantal wave increases as scattering energy increases. Accurate numerical integrations would then become more demanding, in particular for large angular momenta.

The influence of a partial-wave phase shift δ_l on cross sections is proportional to the transition factor defined here as

$$T_l = 2\mathrm{i}\mathrm{e}^{2\mathrm{i}\delta_l} \sin \delta_l. \tag{2.4}$$

Total cross-sections are obtained from

$$\sigma = \sum_{\ell=0}^{\infty} \sigma_l = \frac{\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \left|T_l\right|^2, \tag{2.5}$$

where σ_l is the 'partial cross section'. A maximum value $|T_l|^2 = 4$ usually occurs in a single term at a time and this happens when the phase shift is close to an odd multiple of $\pi/2$. The correct multiple of π in the phase shift is not needed.

3 Amplitude phase method

The improved amplitude–phase formula presented in Sect. 3.2 is specific for potentials supporting extremely sharp resonances, having thick barriers causing exponential behaviors of wave functions. In other cases calculations using the single-amplitude method in Sect. 3.1 are reliable. Both formulas automatically provides the absolute phase shift.

The use of a single amplitude function to determine the (regular) scattering wave function is reviewed and followed by an improved method in sharp-resonance situations using two amplitude functions.

3.1 Method with one amplitude function

This method applies if there is a single classically allowed interval of the r-axis, say $r > R$, with R being a classical turning point [12,19]. It also applies if there are tiny barriers and there is no radial turning point at all. In the latter case the method may meet numerical complications if the attraction surrounding the origin is too strong.

A non-normalized wave function $\Psi_l(r)$, regular at $r = 0$, can be represented in terms of an amplitude $u(r)$ and a phase $\phi(r)$ along the *entire* r-axis as [12,19]

$$\Psi_l(r) = u(r) \sin \phi(r). \tag{3.1}$$

The phase $\phi(r)$ is obtained from the amplitude function $u(r)$ by

$$\phi(r) = \int_0^r u^{-2}(r')\mathrm{d}r', \quad \phi(0) = 0. \tag{3.2}$$

Amplitude and phase functions depend on the angular momentum ('l'), which is formally suppressed in the notation here.

In case of a classically forbidden region ($0 < r < R$) the phase contribution becomes small because $u(r)$ always increases strongly there, if defined as below. The amplitude function $u(r)$ is a solution of a non-linear (Milne/Wheeler-type) differential equation [11,12,19]

$$u''(r) + K_l^2(r)u(r) = u^{-3}(r), \tag{3.3}$$

where $K_l^2(r)$ is the coefficient function in (2.1). As explained in references [17,19] expression (3.1) is an oscillating function only in classically allowed regions, where $K_l^2(r) > 0$. If two classically allowed regions are significant in the problem, but separated, one can find slowly varying amplitude functions in each classically allowed region but not in both of them. In scattering problems the asymptotic region ($r \to +\infty$) is classically allowed and the slowly varying amplitude may be chosen with the boundary conditions

$$u(+\infty) = {K_l}^{-1/2}(+\infty) = k^{-1/2},\ u'(+\infty) = 0. \tag{3.4}$$

Note that $u(r) = k^{-1/2}$ and $\phi(r) = kr$+const. for all values of r in case of a vanishing effective potential. k is the asymptotic (angular) wave number.

The nonlinear differential equation (3.3) is integrated with the boundary condition (3.4) towards the origin $r = 0$. In that integration process the function $u^{-2}(r)$ (as an integrand) can be added as a separate component in the first-order vector solution. If the effective potential is repulsive in a region containing the origin (see Fig. 1) the amplitude function will increase exponentially [16,17]. This behavior is illustrated in Fig. 2. As a result $u^{-2}(r) \to 0$ so that the phase integral in (3.2) becomes convergent as $r \to +0$.

In the asymptotic region the amplitude–phase solution becomes

$$\Psi_l(r) \approx k^{-1/2} \sin\phi(r), \quad r \to +\infty, \tag{3.5}$$

and by comparison with (2.2) the phase shift formula is

$$\delta_l = \lim_{r\to+\infty} (\phi(r) - kr) + l\pi/2, \quad \phi(0) = 0. \tag{3.6}$$

The single-amplitude method is reliable for calculating most partial wave phase shifts of light scattering systems, but meets numerical problems under semiclassical conditions in the presence of a barrier and a well in the effective potential. As illustrated in Fig. 2 the amplitude function tends to oscillate as the scattering energy approaches that of the barrier maximum (here $E \approx 1$).

Single-amplitude computations are limited by the choices of the limits of integration of the phase function. The lower limit is chosen as a suitable fraction of the inner classical turning point and the outer limit is chosen sufficiently far out in the asymptotic region where the asymptotic forms of the spherical Bessel functions are sufficiently accurate.

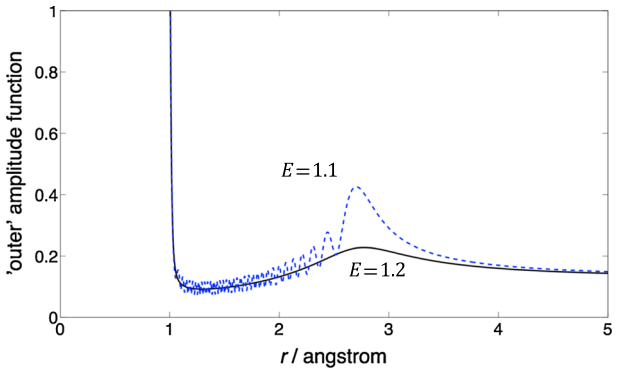

Fig. 2 Illustration of an 'outer' amplitude function $u(r)$, defined in the limit $r \to +\infty$ with $l = 200$ in the CO model [18], as scattering energy becomes comparable to a potential barrier energy. For $E = 1.1$ eV $u(r)$ tends to oscillate inside the barrier region. These oscillations can have exponentially large amplitudes in heavy-particle scattering involving a barrier and a well in the effective potential

3.2 Method with two amplitude functions

The aim here is to find an algorithm or equation that determines the precise value of the phase shift from a single computation given l and energy E (or k) as well as potential parameters. The effective potential is assumed to be sufficiently attractive so that the radial wave function is subject to two classically allowed regions for the relevant energies; the inner region of the r-axis and the outer region. In each region it is possible to construct a slowly varying amplitude function and a well-behaved amplitude–phase representation of the physical wave.

The two representations are matched at a matching point r_m, typically chosen inside the barrier region; see Fig. 1. In energy regions of sharp resonances the barrier region is classically forbidden. At a matching point inside a barrier region both inner and outer amplitude functions may be large and positive. Since they approach the barrier region from the left respectively from the right along the r-axis they will have different directions of their slopes; see Fig. 3. Each amplitude function is generally non-oscillatory but exponentially increasing in the surrounding 'classically forbidden' regions.

Both inner and outer representations of the same scattering wave function are matched at $r = r_m$ in Fig. 1, or anywhere between the two main oscillating regions. In case of a discontinuous potential with one discontinuity one has to choose r_m at this discontinuity position.

3.2.1 Inner region

The radial wave function vanishes at $r = 0$ and can be represented by the amplitude–phase representation

$$\Psi_l(r) = A u_i(r) \sin \phi_i(r), \quad \phi_i(r) = \int_0^r u_i^{-2}(r')\mathrm{d}r', \tag{3.7}$$

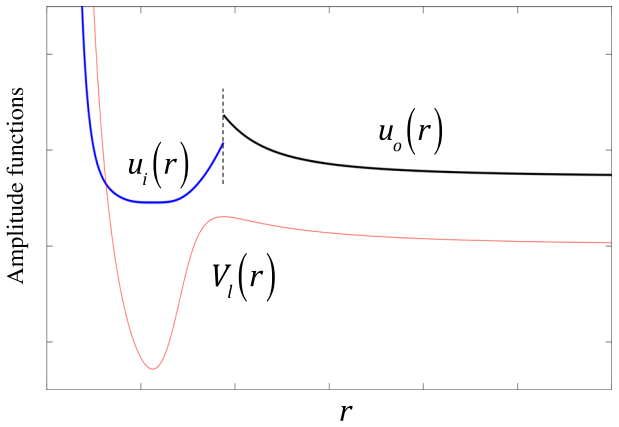

Fig. 3 Illustration of inner and outer amplitude functions $u_i(r)$ respectively $u_o(r)$ in the presence of a barrier in the effective potential $V_l(r)$. Units are arbitrary

where the lower limit of the phase integral in (3.7) implies $\phi_i(0) = 0$, as in (3.2). The r-independent factor A (> 0) is an amplitude of the inner wave *relative* to the outer wave, the outer wave being determined from the amplitude–phase representation as $r \to +\infty$ and normalized as in (2.2).

To calculate $u_i(r)$ and $\phi_i(r)$ one needs boundary conditions in the inner, classically allowed region. These are conveniently taken at a local minimum $r = r_i$ of the effective potential where the derivative of the coefficient $K_l(r)$ is zero. Hence,

$$u_i(r_i) = {K_l}^{-1/2}(r_i), \quad u_i'(r_i) = 0. \tag{3.8}$$

From $r = r_i$ one integrates the amplitude Eq. (3.3) in two directions; towards the origin and towards the matching point r_m. With this amplitude function the solution (3.7) is evaluated at the matching point $r = r_m$. The same solution can then be expressed in terms of a (shifted) phase function ϕ_{im} having a lower limit of integration at $r = r_m$. One obtains the inner wave expression

$$\Psi_l(r) = A u_i(r) \left[a_i \cos \phi_{im}(r) + b_i \sin \phi_{im}(r)\right], \quad \phi_{im}(r_m) = 0. \tag{3.9}$$

The lower limit of ϕ_{im} is thus taken at $r = r_m$ and satisfies $\phi_{im}(r) = \phi_i(r) - \phi_i(r_m)$. Constants a_i and b_i are determined at $r = r_m$, where both 'inner' representations, (3.7) and (3.9), provide equivalent expressions of Ψ_l. At $r = r_m$

$$a_i = \sin \phi_i(r_m), \quad b_i = \cos \phi_i(r_m). \tag{3.10}$$

Hence, from (3.9)

$$\Psi_l(r_m) = A U_i a_i, \quad \Psi'(r_m) = A(U_i' a_i + U_i^{-1} b_i), \tag{3.11}$$

with $U_i = u_i(r_m)$ and $U_i' = u_i'(r_m)$.

Following the treatment in [5], note that in case of a constant potential with $l = 0$ one would have $U_i = k_i^{-1/2}$ and $U_i' = 0$, where k_i is the relevant wave number inside the attractive rectangular well potential.

3.2.2 Outer region and the phase shift formula

In the outer region an amplitude function u_o is defined with boundary conditions similar to those in (3.4) and (3.8), i.e.

$$u_o(+\infty) = K_l{}^{-1/2}(+\infty) = k^{-1/2}, \quad u_0'(+\infty) = 0, \tag{3.12}$$

leading to a phase function defined as

$$\phi_{om}(r) = \int_{r_m}^{r} u_o^{-2}(r')\mathrm{d}r', \tag{3.13}$$

where the lower limit r_m being the matching point. The 'outer' amplitude-phase representation of $\Psi_l(r)$ is

$$\Psi_l(r) = u_o(r)\left[a_o \cos\phi_{om}(r) + b_o \sin\phi_{om}(r)\right], \quad \text{with} \quad \phi_{om}(r_m) = 0, \tag{3.14}$$

where a_o and b_o are constants to be determined by the matching at $r = r_m$. One finds from (3.14)

$$\Psi_l(r_m) = U_o a_o, \quad \Psi_l'(r_m) = (U_o' a_o + U_o^{-1} b_o), \tag{3.15}$$

with $U_o = u_o(r_m)$ and $U_o' = u_o'(r_m)$.

With reference to the treatment in [5], a vanishing potential in the region $r \geq r_m$ and $l = 0$ imply $\phi_{om}(r) = k(r - r_m)$, $U_o = k^{-1/2}$ and $U_o' = 0$, where k is the asymptotic wave number.

By equating Ψ_l and Ψ_l' from the inner and outer representations with the same phase-reference point at $r = r_m$, one obtains

$$a_o = U_i U_o^{-1} A a_i, \quad b_o = U_o U_i^{-1} A b_i + \left(U_o U_i' - U_i U_o'\right) A a_i. \tag{3.16}$$

The outer wave (3.14) satisfies

$$\Psi_l(r) \approx k^{-1/2}\left[a_o \cos\phi_{om}(r) + b_o \sin\phi_{om}(r)\right], \quad r \to +\infty, \tag{3.17}$$

since by boundary conditions of the outer amplitude function

$$u_o(r) \to k^{-1/2}, \quad r \to +\infty. \tag{3.18}$$

By writing the wave (3.17) in a form similar to (2.2), i.e.

$$\Psi_l(r) \approx k^{-1/2} \sin(\phi_{om}(r) + \eta), \quad r \to +\infty, \tag{3.19}$$

$$= k^{-1/2}\left[\sin\eta \, \cos\phi_{om}(r) + \cos\eta \sin\phi_{om}(r)\right], \quad r \to +\infty, \tag{3.20}$$

one can express the extra phase η as

$$\eta = \arctan\left(a_o/b_o\right) \pmod{\pi}. \tag{3.21}$$

Of less interest in the present context one realizes from (3.20)

$$\sqrt{a_o^2 + b_o^2} = 1, \tag{3.22}$$

which determines the inner/outer relative amplitude factor A, i.e.

$$A = \left\| \left[U_i U_o^{-1} a_i\right]^2 + \left[U_o U_i^{-1} b_i + \left(U_o U_i' - U_i U_o'\right) a_i\right]^2 \right\|^{-1/2}. \tag{3.23}$$

The phase-shift formula is obtained by comparing equations (2.2) and (3.19), i.e.

$$\delta_l = \lim_{r \to +\infty} \left(\phi_{om}(r) - kr\right) + l\pi/2 + \eta. \tag{3.24}$$

Because of the sign of a_o/b_o it is natural to define η as

$$\eta = \arctan(a_o/b_o) + H[-\arctan(a_o/b_o)]\pi + n\pi, \tag{3.25}$$

where the Heaviside function is just zero respectively one, depending on the positive respectively negative sign of a_o/b_o; see [20]. It follows that

$$0 \leq \arctan(a_o/b_o) + H[-\arctan(a_o/b_o)]\pi < \pi. \tag{3.26}$$

The integer 'n' in (3.25) remains to be analyzed and understood. It turns out from the analysis in the subsequent section that

$$n = \mathrm{Int}\left[\phi_i(r_m)/\pi\right]. \tag{3.27}$$

3.2.3 Analyzing the integer n

The integer 'n' is related to the inner phase accumulation $\phi_i(r_m)$ in (3.19)–(3.21) through the connection (3.16). A basic relation between the coefficient sets $\{a_i, b_i\}$ and $\{a_o, b_o\}$ is

$$\frac{a_o}{b_o} = \frac{U_i U_o^{-1} \tan\phi_i(r_m)}{U_o U_i^{-1} + \left(U_o U_i' - U_i U_o'\right)\tan\phi_i(r_m)}. \tag{3.28}$$

The various jumps of the inner function '$\tan\phi_i(r_m)$' are understood from the monotonically increasing behavior of $\phi_i(r_m)$ as function of energy (or k). The U-functions are functions of the energy as well. However, one can think of the U-functions as being less dependent on energy compared to the energy dependence of $\phi_i(r_m)$. Furthermore, the amplitudes U_i and U_o are always positive, while $U_i' \geq 0$ and $U_o' \leq 0$ at all energies

as long as there is a barrier in the effective potential. Recall that the amplitude functions always increase monotonically in the direction towards the barrier center; see Fig. 3. Hence, in case of a classically forbidden region separating the two classically allowed regions one can write (3.28) as

$$\frac{a_o}{b_o} = \frac{|U_i U_o^{-1}| \tan\phi_i(r_m)}{|U_o U_i^{-1}| + \left(|U_o U_i'| + |U_i U_o'|\right) \tan\phi_i(r_m)}. \tag{3.29}$$

or

$$\frac{a_o}{b_o} = \frac{|U_i U_o^{-1}|^2 \tan\phi_i(r_m)}{1 + |U_i U_o^{-1}| \left(|U_o U_i'| + |U_i U_o'|\right) \tan\phi_i(r_m)}. \tag{3.30}$$

Whenever $\phi_i(r_m) = 0, \pi, 2\pi, \cdots$, say $\phi_i(r_m) = n\pi$, then $a_o/b_o (= \tan\eta) = 0$. In order η accounts for the inner oscillations it is clear that η contains the same multiple of π as $\phi_i(r_m)$ does. Therefore equation (3.25) becomes $\eta = 0 + \mathrm{Int}[\phi_i(r_m)/\pi]\pi = n\pi$. 'Int' stands for the integer part of its argument.

Assuming instead $n\pi < \phi_i(r_m) < (n+1)\pi$, there are two possibilities. As long as $\tan\phi_i(r_m) > 0$, then $a_o/b_o > 0$, implying $0 < \arctan(a_o/b_o) < \pi/2$ in (3.25). The same implication results from $\tan\phi_i(r_m) < 0$ while a_o/b_o still being positive. However, if $\tan\phi_i(r_m) < 0$ *and* $a_o/b_o < 0$ it is required that a π is added to the $\arctan(a_o/b_o)$-value in the expression (3.25) for η. This is taken care of by the Heaviside function in equation (3.25) now read as $\eta = [\arctan(a_o/b_o) + \pi] + \mathrm{Int}[\phi_i(r_m)/\pi]\pi$. The extra '$\pi$' just added by the Heaviside function to $\arctan(a_o/b_o)$ (while being negative) is *replaced* by the increase of π in the term $\mathrm{Int}[\phi_i(r_m)/\pi]\pi$ as the inner phase becomes $\phi_i(r_m) = (n+1)\pi$.

The above scenario is repeated again and again as energy increases for a given effective potential. All possible cases of $\phi_i(r_m) \pmod\pi$ result in the following computation formula of the integer 'n':

$$n = \mathrm{Int}\left[\phi_i(r_m)/\pi\right]. \tag{3.31}$$

The main additional disadvantage of the two-amplitude method is the need of approximate locations of maxima and minima of the effective potential when such exist.

4 Levinson's theorem and the number of bound states

To understand the relation between the phase shift formula and the number of bound states one makes use of Levinson's theorem. The direct way is to read the calculated value of the phase shift as $E \to +0$. With the present approach it is also interesting to consider how the inner phase (or η) relates to the number of bound states of the effective potential.

If $V_l(r_i) > 0$, proper bound states ($E < 0$) *do not* exist. Formula (3.24) is valid only for energies above the (effective) potential minimum $E \geq V_l(r_i) > 0$. In case $E = V_l(r_i)$, then $n = 0$, $\tan\phi_i(r_m) = 0$ and $\eta = 0$. As $E > V_l(r_i)$ formula (3.31) applies and the 'n'-formula only counts the number of completed π-intervals by $\phi_i(r_m)$.

If $V_l(r_i) < 0$, proper bound states may exist and $\phi_i(r_m)$ has a finite non-negative value. In this limit (3.24) satisfies

$$\delta_l \to \eta, \quad E \to +0, \tag{4.1}$$

since the outer phase will be totally dominated by the classically allowed region outside the classical turning point for the centrifugal potential. The outer phase will behave as for a 'free' partial wave $\phi_{om} \to kr - l\pi/2$, as $kr \to +\infty$ (while $E \to +0$).

Suppose one has the integer $s = \mathrm{Int}\,[\phi_i(r_m)/\pi]$ in the limit $E \to +0$. Then $H(-\arctan(a_o/b_o))$ has two alternative values, 0 or 1, depending on the sign of a_o/b_o. The two alternative values of η are

$$\eta = \arctan(a_o/b_o) + s\pi, \quad a_o/b_o > 0, \tag{4.2}$$

and

$$\eta = \pi + \arctan(a_o/b_o) + s\pi, \quad a_o/b_o < 0. \tag{4.3}$$

Occasionally it may happen that $\arctan(a_o/b_o) \to \pm\pi/2$, as $E \to +0$. In both cases of sign, (4.2) and (4.3) result in

$$\eta \to \left(s + \frac{1}{2}\right)\pi, \quad E \to +0. \tag{4.4}$$

It is customary to say that the partial wave satisfying (4.4) has a resonance (since all resonances occur for odd multiples of $\pi/2$) in the zero-energy limit and the effective potential supports 's' proper bund states (Fig. 4).

However, if $\arctan(a_o/b_o) \to \pm 0$, since $U_o \to +\infty$ as $E \to +0$, one finds the two alternative limits

$$\eta =\to s\pi, \quad a_o/b_o \to +0, \quad E \to +0, \tag{4.5}$$

and

$$\eta \to (s+1)\pi, \quad a_o/b_o \to -0, \quad E \to +0. \tag{4.6}$$

The number of bound states is given by 's' if $a_o/b_o \to +0$ and by '$s+1$' if $a_o/b_o \to -0$.

The ratio a_o/b_o is a rather complicated function of the inner phase $\phi_i(r_m)$ and the inner/outer amplitude values U_i/U_o and r_m. Therefore the exact limits corresponding to $\phi_i(r_m)$ as $E \to +0$ are not studied in detail here. This inconvenience is simplified for rectangular potential wells. Next subsection may clarify further the low-energy limit (Levinson's theorem [1,2,5]) in such cases.

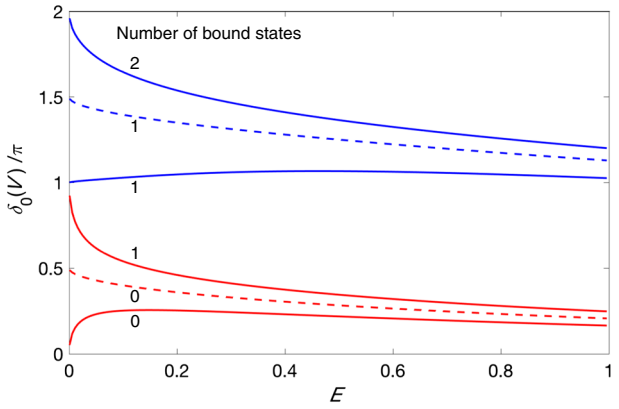

Fig. 4 Illustration of phase shift behaviors, as $E \to +0$ for a sequence of rectangular potentials $V_{l=0}(r)$ with increasing well depths (from bottom curve to top curve). Arbitrary units are used

4.1 Radial rectangular well with $l = 0$ and $E \to +0$

This case is treated by Mott and Massey [5] in great detail. The radial potential consists of two constant parts (in arbitrary units)

$$V(r) = -V_0, \quad 0 \le r < R, \qquad V(r) = 0, \quad R \le r < +\infty, \tag{4.7}$$

with a discontinuity at $r = R$, where R is the radius of the well. No effective barrier is present and one can choose $r_i = 0$ and $r_m = R$ in formula (3.24) and its derivation.

The potential is locally constant. The coefficient $K^2_{l=0}(r)$ in (2.1) has two constant values $K_i^2 = 2\mu(E + V_0)/\hbar^2$ and $K_o^2 = 2\mu E/\hbar^2$ with μ the reduced mass and $\hbar$ being Planck's reduced constant. The corresponding (local) wave numbers are $k_i = K_i$ respectively $k = K_o$ with $k_i > k > 0$. Here k is the asymptotic scattering wave number.

The outer amplitude function remains constant by the defining Eqs. (3.3) and (3.4), yielding $U_o = k^{-1/2}$ and $U_o' = 0$ at the matching point $r = R$. Similarly, the inner amplitude function remains constant with values at $r = R$ being $U_i = k_i^{-1/2}$ and $U_i' = 0$. The inner phase is $\phi_i(r) = k_i r$, but restricted to $0 \le r \le R$. The outer phase is $\phi_{om}(r) = k(r - R)$ and restricted to $R \le r < +\infty$ for r.

As $E \to +0$ one has $k \to +0$ and $k_i \to k_i^{(0)} = \sqrt{2\mu V_0}/\hbar > 0$. Furthermore, the inner wave number k_i satisfies

$$k_i = \sqrt{(k_i^{(0)})^2 + k^2} \approx k_i^{(0)} + \frac{1}{2}\frac{k^2}{k_i^{(0)}}, \quad k \to +0. \tag{4.8}$$

Because of the locally constant potential, equations (3.28)–(3.30) become

$$\frac{a_o}{b_o} = U_i^2 U_o^{-2} \tan\phi_i(R) \approx \frac{k}{k_i^{(0)}} \tan\left[\left(k_i^{(0)} + \frac{1}{2}\frac{k^2}{k_i^{(0)}}\right) R\right], \quad k \to +0. \tag{4.9}$$

As $E \to +0$ there are the two limits $(a_o/b_o) \to \pm 0$, unless the potential is such that the limit of the inner phase is $k_i^{(0)} R = \pi/2 + s\pi$ with $s = 0, 1, \ldots$. In all, there are three limits of (a_o/b_o) to consider.

Studying the particular case $k_i^{(0)} R = \pi/2 + s\pi$ of (4.9), one has

$$\tan\left[\frac{\pi}{2} + s\pi + \frac{1}{2}\frac{k^2}{k_i^{(0)}}R\right] = \tan\left[\frac{\pi}{2} + \frac{1}{2}\frac{k^2}{k_i^{(0)}}R\right] \to -\infty, \quad k \to +0. \tag{4.10}$$

Furthermore, from reference [20], one has

$$\tan\left[\frac{\pi}{2} + \frac{1}{2}\frac{k^2}{k_i^{(0)}}R\right] = -\cot\left[\frac{1}{2}\frac{k^2}{k_i^{(0)}}R\right] = -\frac{1}{\tan\left[\frac{1}{2}\frac{k^2}{k_i^{(0)}}R\right]} \approx -\frac{2k_i^{(0)}}{k^2 R}, \quad k \to +0. \tag{4.11}$$

Inserted into (4.9) one obtains

$$\frac{a_o}{b_o} \approx -\frac{2}{kR}, \quad k \to +0, \tag{4.12}$$

implying

$$\arctan\left(\frac{a_o}{b_o}\right) \approx \arctan\left(-\frac{2}{kR}\right) \to -\pi/2, \quad k \to +0. \tag{4.13}$$

Since $\arctan(a_o/b_o)$ is negative and approaching $-\pi/2$ one has $H(-\arctan(a_o/b_o)) = 1$ in equation (3.31). The phase shift formula (3.24) with $l = 0$ and $\eta = (s + 1/2)\pi$ gives

$$\delta_{l=0} = \lim_{r \to +\infty} (\phi_{om}(r) - kr) + (s + 1/2)\pi \to -kR + (s + 1/2)\pi \to (s + 1/2)\pi, \quad E \to +0. \tag{4.14}$$

This result is consistent with the analysis in [5].

Next consider the two other possible limiting cases as $E \to +0$: $0 \le k_i^{(0)} R < \pi/2 + s\pi$, respectively $\pi/2 + s\pi \le k_i^{(0)} R < \pi + s\pi$. According to (4.9) the former case corresponds to $(a_o/b_o) \to +0$ and the latter case corresponds to $(a_o/b_o) \to -0$. These cases are different. One finds the phase shift limits

$$\delta_l \to -kR + s\pi \to s\pi, \quad \text{for } 0 \le k_i^{(0)} R < \pi/2 + s\pi, \quad E \to +0, \tag{4.15}$$

respectively

$$\delta_l \to -kR + (s + 1)\pi \to (s + 1)\pi, \quad \text{for } \pi/2 + s\pi \le k_i^{(0)} R < \pi + s\pi, \quad E \to +0. \tag{4.16}$$

Levinson's theorem then provides an interpretation of these limits: If the inner phase limit satisfies $(\tan\phi_i =) \tan k_i^{(0)} R > 0$ and $(\mathrm{Int}[\phi_i/\pi] =) \mathrm{Int}[k_i^{(0)} R/\pi] = s$, then '$s$' is the number of proper bound states, whereas if $(\tan\phi_i =) \tan k_i^{(0)} R < 0$ and

Table 1 Phase shift results (in units of π) for the CO-potential with $l = 250$ and selected scattering energies

The local minimum of the effective barrier is ≈ 1.153 eV and the barrier maximum is ≈ 2.248 eV. For scattering energies between the potential minimum and maximum the single-amplitude formula generally differ from the two-amplitudes formula by several integers of π. No bound states are possible for $l = 250$. The 'tol'-parameter in MatLab is 10^{-7}

E	$\delta_l/\pi(AP1)$	δ_l(AP2)
1.20	0.4432	0.4432
1.30	0.6129	1.6129
1.40	0.8213	2.8213
1.50	1.0730	4.0730
1.60	1.3738	5.3738
1.70	1.7310	6.7310
1.80	2.1546	8.1546
1.90	2.6592	9.6592
2.00	3.2686	11.2686
2.10	4.0278	13.0278
2.20	16.0608	16.0607
–	–	–
2.30	19.8107	19.8107

(Int$[\phi_i/\pi] =$)Int$[k_i^{(0)}R/\pi] = s$ the number of proper bound states is '$s + 1$'. This agrees with the more general cases in (4.5) and (4.6).

5 Application to a CO-potential model

The model potential used for numerical calculations is [18]

$$V(r) = D\left(1 - \frac{e^{\alpha r_e} - 1}{e^{\alpha r} - 1}\right)^2 - D, \tag{5.1}$$

with

$$D = 11.225528 \text{ eV}, \ \alpha = 2.2994 \text{ Å}^{-1}, \ r_e = 1.1283 \text{ Å}. \tag{5.2}$$

Also

$$\frac{2\mu}{\hbar^2} = 3282.4691 \text{ eV}^{-1}\text{Å}^{-2}, \tag{5.3}$$

with μ being the reduced mass of the scattering CO-system. The model is primarily used to illustrate resonances typical for heavy-particle systems.

In numerical applications the theoretical limits $r \to 0$ and $r \to +\infty$ must be replaced by something more practical. Thereby it is important that phase-shift results must be unaffected by significant variations of the lower respectively upper limits explored.

Both amplitude–phase methods are applicable for scattering energies well above the barrier maximum. Below the well minimum of positive energy only the single-amplitude method is applicable. Table 1 shows phase-shift values for $l = 250$ in the energy range where the effective potential affects the wave function with its barrier and its well. Both methods agree at energies near the well minimum and barrier maximum and at higher energies (not shown). For the numerical accuracy used in the integrator

Table 2 Phase shifts (in units of π) as related to numerical integration accuracies ('tol') for the two amplitude–phase methods ('AP1' and 'AP2')

l	tol	δ_l/π(AP1)	δ_l/π(AP2)
200	exp(−5)	42.6883	42.6883
200	exp(−7)	42.688453	42.688453
200	exp(−9)	42.68845447	42.68845447
250	exp(−5)	1.0731	4.0731
250	exp(−7)	1.0729960	4.0729960
250	exp(−9)	1.07299640	4.07299640

The energy is $E = 1.5$ eV and the CO-potential is used. The 'tol'-parameter in MarLab controls the absolute and relative errors in the computations

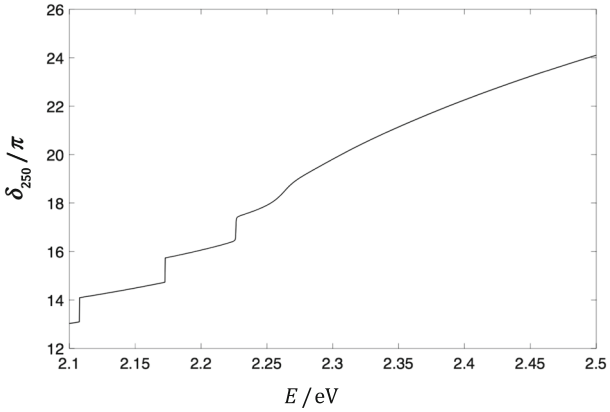

Fig. 5 Phase shift behavior as function of energy for $l = 250$. The CO potential is used, which has an effective barrier maximum at $E = 2.248$ eV

the method with one amplitude happens to miss integers of π in its phase shifts between the barrier maximum and the well minimum. Note that this 'defect' implies that that any cross section computations (involving hundreds or thousands of partial waves) would be unaffected. This result is surprising and not completely understood.

Table 2 illustrates the numerical values of the phase shifts (in units of π) as the accuracy of the integrator ('ode45' in MatLab) is varied. Except for the missing integers of π in the phase shifts of the single-amplitude method, the decimals agree for both formulas.

Figure 5 shows that the phase shift (in units of π) for $l = 250$ has sharp integer jumps below the barrier maximum energy $E = 2.248$ eV. Each sudden jump is related to a resonance resulting in an unstable CO-molecule with a life time proportional to the slope of the curve. This indicates long-lived unstable CO molecules with large angular momentum quantum numbers.

Figure 6 shows details of one of the phase–shift jumps in Fig. 5. To illustrate its appearance in a cross section the energy-dependent transition factor, $|T_{l=250}|^2 = 4\sin^2\delta_{l=250}$, is shown in the right-hand subplot. A resonance occurs as the phase shift

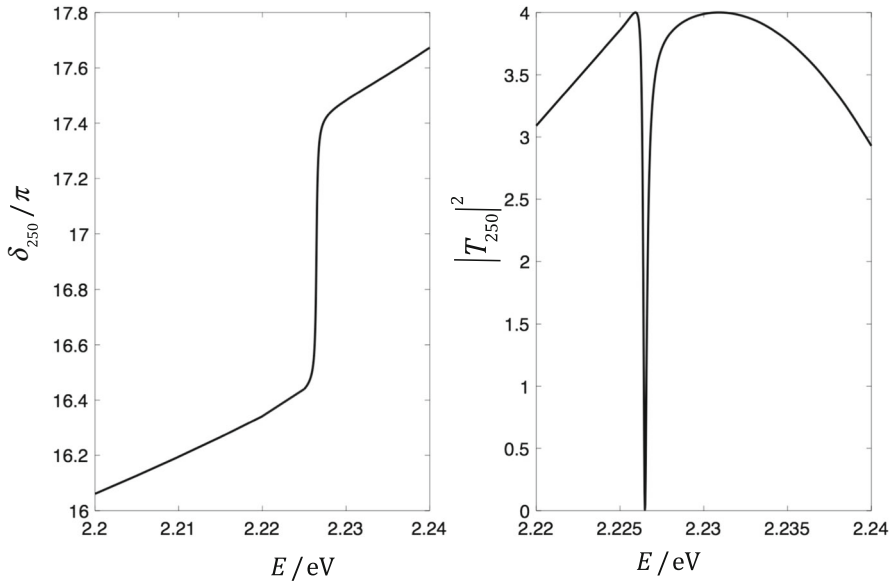

Fig. 6 Magnification of one of the phase shift jumps for $l = 250$ and its transition behavior; see Fig. 6

is an odd multiple of $\pi/2$. The phase shift in Fig. 6 passes through two such values. The two resonance peaks are separated by a tiny deep minimum in the transition curve in the right subplot.

6 Conclusions

A two-amplitude formula for resonance phase shifts is derived within the amplitude–phase method. The effective central potential is assumed real valued with a well and a barrier. The phase-shift formula applies to scattering energies between the well minimum or the potential threshold energies and the barrier maximum energy. It accounts for the absolute phase of the wave function and calculates phase shifts with correct multiples of π. The formula is particularly suitable for resonance studies of heavy-particle scattering and complementary to an already existing phase-shift formula using a single amplitude function.

Levinson's theorem directly connects the phase-shift values to the total number of proper bound states supported by the effective potential. Thereby the quantities of the formula in the limit $E \to 0$ provide additional conditions for the number of proper bound states.

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