Quantal Two-Centre Coulomb Problem treated by means of the Phase-Integral Method I. General Theory

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The present paper concerns the derivation of phase-integral quantization conditions for the two-centre Coulomb problem under the assumption that the two Coulomb centres are fixed. With this restriction we treat the general two-centre Coulomb problem according to the phase-integral method, in which one uses an *a priori* unspecified *base function*. We consider base functions containing three unspecified parameters $C, \tilde{C}$ and Λ. When the absolute value of the magnetic quantum number m is not too small, it is most appropriate to choose $\Lambda = |m| \neq 0$. When, on the other hand, $|m|$ is sufficiently small, it is most appropriate to choose $\Lambda = 0$. Arbitrary-order phase-integral quantization conditions are obtained for these choices of Λ. The parameters C and $\tilde{C}$ are determined from the requirement that the results of the first and the third order of the phase-integral approximation coincide, which makes the first-order approximation as good as possible.

In order to make the paper to some extent self-contained, a short review of the phase-integral method is given in the Appendix.

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1. INTRODUCTION

The two-centre Coulomb problem, that is, the problem of solving the Schrödinger equation for the motion of an electron with the charge $-e$ $(e > 0)$ in the field of two fixed Coulomb centres with charges $Z_1 e$ and $Z_2 e$ at the distance r_{12} from each other, plays an important role in several fields of theoretical physics, for example in the theory of diatomic molecules, in scattering theory, and in the three-body problem. The two-centre Coulomb problem has therefore been the subject of extensive studies both by numerical and by approximate analytical methods, and hence the literature on this problem is very comprehensive. In spite of this fact it is still of interest to continue the treatment of this problem for arbitrary values of Z_1, Z_2 and r_{12}. One reason for this is that the numerically exact solution of the problem meets with difficulties when $|Z_1 - Z_2|$ increases. There appear also numerical difficulties for large values of r_{12}. For a general review of the problem we refer to Eyring *et al.* [1], Herzberg [2], Slater [3] and Rosen [4].

Ignoring the finiteness of the mass of the protons, Bates *et al.*[5] obtained important numerical results for the hydrogen molecule ion. Corresponding numerical results were obtained by Wallis and Hulburt [6] for the homonuclear one-electron two-centre problem, by Bates and Carson [7] for the ion $HeH^{2+}(Z_1 = 1, Z_2 = 2)$, by Wind [8] for the ground state of the hydrogen molecule ion, by Peek [9] for the states $1s\sigma_g$ and $2p\sigma_u$ of the hydrogen molecule ion, and by Ponomarev and Puzynina [10, 11] for several states of the Coulomb two-centre system with $Z_1 = 1$ and $Z_2 = 2, 3, ..., 8$. Hunter and Pritchard[12] used a numerical procedure to compute nonadiabatic energies for the first few rotation-vibration levels of $^2\Sigma_g H_2^+$, $^2\Sigma HD^+$ and $^2\Sigma_g D_2^+$. For the hydrogen molecule ion Rosenthal and E. Bright Wilson, Jr., [13] calculated an accurate value of the ground state energy which is in agreement with the values obtained by Wind [8] and Peek[9]. For different internuclear distances Bates and Reid [14], Murai [15] and Murai and Takatsu [16] calculated electronic energies for various states of the hydrogen molecule ion under the assumption of infinite proton mass. For a large range of internuclear distances Winter *et al.*[17] made very accurate calculations for the lowest 20 states of the molecule ion HeH^{2+}. Klaus[18] studied the electronic energy of the ground state of the hydrogen molecule ion for small internuclear separation r_{12} and confirmed the remarkable discovery by Byers Brown and Steiner [19] that the electronic energy cannot be expanded in powers of r_{12} alone, but that powers of $\ln r_{12}$ must also be included. Klaus [18] also obtained for the hydrogen molecule ion further terms in the series given by Byers Brown and Steiner [19] for the general two-centre Coulomb problem.

There exist also various approximate analytical methods for solving the quantal two-centre Coulomb problem. In one of them one uses the quasiclassical approximation, that is, the first order of the phase-integral approximation. In using this method, one encountered in the early papers difficulties associated with the divergence of the phase-integral

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due to an inappropriate choice of the phase-integrand (also called the quasimomentum), which is not determined quite uniquely. Different authors have mastered these difficulties in different ways, but no single unifying method has until now been proposed for the two-centre Coulomb problem. An essential feature in our method is the use of the phase-integral approximation generated from an unspecified base function; see the Appendix.

The semiclassical quantization of the low-lying electronic states of the hydrogen molecule ion was treated by Strand and Reinhardt [20]. Pajunen [21] calculated the energy levels of the hydrogen molecule ion (under the assumption of infinitely heavy nuclei) in the first and the third order of the phase-integral approximation. Although he refers to one of the papers (his reference 10) in which the phase-integral approximation generated from an unspecified base function was introduced, he does not use the freedom to choose optimal expressions for the functions that he denotes by $Q_{mod}(\mu)$ and $Q_{mod}(\nu)$, and that in the present paper correspond to the more general base functions $\tilde{Q}(\xi)$ and $Q(\eta)$, respectively. In the present paper we shall make full use of the possibility to choose $\tilde{Q}(\xi)$ and $Q(\eta)$ most conveniently.

The phase-integral method, in which one uses the phase-integral approximation generated from an unspecified base function [22], offers a method for mastering the previously mentioned difficulties in a unified way for an arbitrary order of the phase-integral approximation. In the present paper we shall apply this method to the quantal two-centre Coulomb problem with fixed Coulomb centres.

For the convenience of the reader a short review of the phase-integral method and formulas to be used are given in the Appendix.

The present paper will be the basis for further work, in which convenient transformations to complete elliptic integrals will be used, analogously as in papers by Lakshmanan and Kaliappan[23] and Lakshmanan *et al.*[24, 25]. Thereby the contour integrals, occurring in the quantization conditions, will be expressed in terms of complete elliptic integrals.

2. SEPARATION OF THE SCHRÖDINGER EQUATION IN ELLIPTIC COORDINATES

We start by quoting some well-known results. The time-independent Schrödinger equation for the motion of an electron of mass μ and charge $-e$ ($e > 0$) in the field of two fixed Coulomb centres with charges Z_1e and Z_2e takes the following form

$$\left(-\frac{\hbar^2}{2\mu}\Delta_{\vec{r}} - \frac{Z_1e^2}{r_1} - \frac{Z_2e^2}{r_2}\right)\Psi(\vec{r}) = E\Psi(\vec{r}), \tag{2.1}$$

where r_1 and r_2 are the distances of the electron from the two centres, $\vec{r}$ is the position vector of the electron, and E is the electronic energy. To obtain the total energy one must add the potential energy of the two fixed charges, getting

$$E_{total} = \frac{Z_1Z_2e^2}{r_{12}} + E, \tag{2.2}$$

where r_{12} is the distance between the two centres. The differential equation (2.1) is separable in elliptic coordinates. If one introduces the variables

$$\xi = \frac{r_1 + r_2}{r_{12}}, \quad 1 \le \xi < +\infty, \tag{2.3a}$$

$$\eta = \frac{r_1 - r_2}{r_{12}}, \quad -1 \le \eta \le +1, \tag{2.3b}$$

and puts

$$\Psi(\vec{r}) = X(\xi)Y(\eta)e^{im\phi}, \tag{2.4}$$

where m is the magnetic quantum number (positive or negative integer or zero), and ϕ is the corresponding angle, the separation yields, in atomic units ($\hbar = e = \mu = 1$), the two differential equations

$$\frac{d}{d\xi}\left((\xi^2-1)\frac{dX}{d\xi}\right) + \left(-p^2\xi^2 + b'\xi + A - \frac{m^2}{\xi^2-1}\right)X = 0, \tag{2.5a}$$

$$\frac{d}{d\eta}\left((1-\eta^2)\frac{dY}{d\eta}\right) + \left(p^2\eta^2 + b\eta - A - \frac{m^2}{1-\eta^2}\right)Y = 0, \tag{2.5b}$$

where A is the separation constant and

$$p^2 = -\frac{1}{2} r_{12}^2 E, \tag{2.6a}$$

$$b' = r_{12}(Z_2 + Z_1), \tag{2.6b}$$

$$b = r_{12}(Z_2 - Z_1). \tag{2.6c}$$

Putting

$$X(\xi) = \frac{f(\xi)}{(\xi^2 - 1)^{\frac{1}{2}}}, \tag{2.7a}$$

$$Y(\eta) = \frac{g(\eta)}{(1 - \eta^2)^{\frac{1}{2}}}, \tag{2.7b}$$

we can transform the differential equations (2.5) into

$$\left(\frac{d^2}{d\xi^2} + \tilde{R}(\xi)\right) f(\xi) = 0, \tag{2.8a}$$

$$\left(\frac{d^2}{d\eta^2} + R(\eta)\right) g(\eta) = 0, \tag{2.8b}$$

where

$$\tilde{R}(\xi) = -p^2 + \frac{b'\xi + A'}{\xi^2 - 1} - \frac{m^2 - 1}{(\xi^2 - 1)^2}, \tag{2.9a}$$

$$R(\eta) = -p^2 + \frac{b\eta - A'}{1 - \eta^2} - \frac{m^2 - 1}{(1 - \eta^2)^2}, \tag{2.9b}$$

with

$$A' = A - p^2. \tag{2.10}$$

The differential equations (2.8) are of the Schrödinger type. By solving them simultaneously under the boundary conditions that $f(+1) = f(+\infty) = 0$ and $g(-1) = g(+1) = 0$, one can obtain the energy and the separation constant as functions of the distance r_{12} and the quantum numbers.

When $Z_1 = Z_2$ every bound-state wave function $Y(\eta)$ is either an even or an odd function of η, and when $\vec{r}$ is reflected at the centre of symmetry for the two-centre Coulomb problem, the wave function (2.4) remains unchanged when $Y(\eta)$ and m are both even or both odd, while the wave function (2.4) changes sign when one of $Y(\eta)$ and m is even and the other is odd.

3. APPLICATION OF THE PHASE-INTEGRAL METHOD

The essential features of the phase-integral method are briefly sketched in the Appendix. The phase-integral solutions of the differential equations (2.8a) and (2.8b), respectively, are linear combinations of the phase-integral functions

$$\tilde{q}^{-\frac{1}{2}}(\xi)\exp\left\{\pm i \int^{\xi} \tilde{q}(\xi) d\xi\right\} \tag{3.1a}$$

and

$$q^{-\frac{1}{2}}(\eta)\exp\left\{\pm i \int^{\eta} q(\eta) d\eta\right\}, \tag{3.1b}$$

respectively, where $\tilde{q}(\xi)$ and $q(\eta)$, respectively, are generated according to (A5a,b), (A6a,b,c), (A3) and (A2) in the Appendix, with $R(z), Q(z)$ replaced by the appropriate functions $\tilde{R}(\xi), \tilde{Q}(\xi)$ and $R(\eta), Q(\eta)$, respectively, the quantities pertaining to the ξ-equation being characterized by a tilde.

3.1. Base functions generating phase-integral solutions

As is seen from (2.9a,b), the functions $\tilde{R}(\xi)$ and $R(\eta)$ have poles at $\xi = \pm 1$ and $\eta = \pm 1$, respectively; these poles are of the second order if $m \neq \pm 1$, but of the first order if $m = \pm 1$. Furthermore, we note that when $m \neq 0$ the coefficients of the second-order poles differ from $\frac{1}{4}$, while for $m = 0$ they are equal to $\frac{1}{4}$.

There are two main alternatives, discussed in the Appendix for the case of the radial Schrödinger equation, for choosing the base functions generating the phase-integral functions (3.1a) and (3.1b). Unifying these two alternatives, we choose the squares of the base functions to be

$$\tilde{Q}^2(\xi) = -p^2 + \frac{A' - \tilde{C} + b'\xi}{\xi^2 - 1} - \frac{\Lambda^2}{(\xi^2 - 1)^2}, \tag{3.2a}$$

$$Q^2(\eta) = -p^2 + \frac{-A' + C + b\eta}{1 - \eta^2} - \frac{\Lambda^2}{(1 - \eta^2)^2}, \tag{3.2b}$$

where $C, \tilde{C}$ and Λ are parameters, the choice of which we shall discuss below. The introduction of these parameters increases essentially the flexibility of the phase-integral formulas to be obtained.

By choosing $C = \tilde{C} = 1/4$ one obtains in the limit when $r_{12} \to 0$ the energy E and the reduced separation constant A' correctly from the first-order phase-integral quantization conditions (to be derived in Section 3.2). For arbitrary values of r_{12} it is most appropriate to determine C and $\tilde{C}$ as functions of r_{12} such that one obtains the same value of p^2 (i.e., of the energy) and also of A' in the first and in the third order of the phase-integral approximation. One thereby achieves the optimal accuracy obtainable from the first-order quantization conditions. We emphasize that this can be achieved by the use of the phase-integral approximation generated from an unspecified base function (described in the Appendix), but cannot be achieved by means of the JWKB approximation. The decisive properties of the phase-integral approximation in question versus the JWKB approximation have been explained in some detail by Dammert and P.O. Fröman [26] and by Fröman and Fröman [22].

When $|m|$ is not too small, we choose $\Lambda = |m| \neq 0$, but when $|m|$ is sufficiently small we choose $\Lambda = 0$. For $m = 0$ one should always choose $\Lambda = 0$. The two alternatives $\Lambda = |m| \neq 0$ and $\Lambda = 0$ yield solutions with different properties. When $\Lambda = |m| \neq 0$ the phase integral solutions of the differential equations (2.8a) and (2.8b) remain valid as $\xi \to \pm 1$ and $\eta \to \pm 1$, respectively. When $\Lambda = 0$ the phase-integral solutions of the differential equations in question break down as $\xi \to \pm 1$ and $\eta \to \pm 1$, respectively, but the regular solutions of the ξ- and η-equations can be obtained at some distances from those points by the use of the connection formula described in subsection A.2.b of the Appendix, when one there replaces l by $(|m| - 1)/2$; cf. (2.9a,b). The wave functions obtained in that way are expected to be the more accurate the stronger the Coulomb singularities of $\tilde{R}(\xi)$ and $R(\eta)$ at $\xi = \pm 1$ and $\eta = \pm 1$ are. However, even if the Coulomb singularities are strong, these wave functions are not expected to be good if $|m|$ is too large, in which case one should use $\Lambda = |m| \neq 0$, as mentioned in the beginning of this paragraph.

Using the terminology classically allowed region and classically forbidden region in a generalized sense, *viz.* to characterize regions where $\tilde{Q}^2(\xi)$ or $Q^2(\eta)$ is larger than zero and less than zero, respectively, we shall now discuss the wave functions pertaining to the ξ-equation and the η-equation.

3.1.1. Wave functions pertaining to the ξ-equation

According to (3.2a) the function $-\tilde{Q}^2(\xi)$, where $1 \leq \xi < +\infty$, always corresponds to a single-well potential.

For $\Lambda = |m| \neq 0$ there are four zeros of $\tilde{Q}^2(\xi)$, which we denote by ξ_1, ξ_2, ξ_3 and ξ_4; see Fig. 1(a). The zeros ξ_1 and ξ_2 may be real and both less than 1, or they may be complex conjugate. The zeros $\xi_3(> 1)$ and $\xi_4(> \xi_3)$ are real. There is thus a classically allowed region between ξ_3 and ξ_4, but classically forbidden regions for $1 < \xi < \xi_3$ and $\xi > \xi_4$. The phase-integral wave functions generated from $\tilde{Q}(\xi)$ are good at $\xi = 1$, and we can use the arbitrary-order connection formula, given by (A13) and (A14) in the Appendix, for tracing the physically acceptable wave function from the classically forbidden region between 1 and ξ_3 to the classically allowed region, that is, the region between ξ_3 and $\xi_4(> \xi_3)$ where $\tilde{Q}^2(\xi) > 0$; see Fig. 1(a).

For $\Lambda = 0$ there are two zeros of $\tilde{Q}^2(\xi)$, which we denote by $\xi_3(< \xi_4)$ and $\xi_4(> 1)$. The classically allowed region lies between ξ_3 and ξ_4 when $\xi_3 > 1$, but between 1 and ξ_4 when $\xi_3 < 1$; see Fig. 1. The phase-integral wave function is not good at $\xi = 1$, but for the physically acceptable wave function one can obtain a phase-integral expression in the interior of the classically allowed region, when $\xi_3 > 1$ and the classically forbidden region between 1 and ξ_3 is sufficiently large, by means of the arbitrary-order connection formula given by (A13) and (A14) in the Appendix, and when $\xi_3 < 1$ by means of the connection formula presented in subsection A.2.b of the Appendix.

Both when $\Lambda = |m| \neq 0$ and when $\Lambda = 0$ the wave function, obtained in the classically allowed region to the left of ξ_4 as described above, can be joined to the physically acceptable wave function traced from the classically forbidden region to the right of ξ_4 into the classically allowed region to the left of ξ_4 with the aid of the arbitrary-order connection formula given by (A13) and (A14) in the Appendix. In this way alternative quantization conditions, corresponding to $\Lambda = |m| \neq 0$ and $\Lambda = 0$, can be obtained. They can be combined into one quantization condition. Fig. 1 illustrates the two possible situations that the classically allowed region is delimited either by ξ_3 and ξ_4 [Fig. 1(a)] or by the pole at $\xi = +1$ and the turning point at $\xi = \xi_4$ [Fig. 1(b)].

3.1.2. Wave functions pertaining to the η-equation

The function $-Q^2(\eta)$ may correspond either to a single-well potential or to a double-well potential.

For $\Lambda = |m| \neq 0$ the phase-integral solution is valid at the poles $\eta = \pm 1$ (which delimit classically forbidden regions) and can be traced into the classically allowed region closest to the pole in question with the aid of the connection formula given by (A13) and (A14) in the Appendix. When there is only one classically allowed region, one obtains the quantization condition by identifying the two expressions for the wave function in that region. This case applies when $-Q^2(\eta)$ is a single-well potential (Fig. 2), or when the energy lies so far above the top of an underdense barrier [Fig. 4(b)] that it is appropriate to disregard the presence of the complex conjugate zeros η_2 and η_3 of $Q^2(\eta)$. When $-Q^2(\eta)$ corresponds to a double-well potential, the wave function can be traced from the region on one side of the barrier to the region on the other side with the aid of the arbitrary-order connection formula for a barrier described in Section A.3 of the Appendix; see Fig. 3 and Fig. 4. Joining the two expressions for the wave function thus obtained to each other, one obtains the quantization condition.

When $\Lambda = 0$ [Fig. 2 or Fig. 4(b)] the phase-integral wave function is not good at $\eta = \pm 1$, but at some distance from these points physically acceptable solutions can be obtained in the same classically allowed region by the use of the connection formulas presented in Sections A.2 and A.3 of the Appendix. Thus one obtains two expressions for the wave function, and by identifying these expressions one obtains a quantization condition.

3.2. Quantization conditions

3.2.1. Quantization conditions pertaining to the ξ-equation

For the differential equation (2.8a) the physically relevant interval is $1 < \xi < \infty$. The phase-integral quantization condition for the situation in Fig. 1(a) involves a contour integral in the complex ξ-plane encircling ξ_3 and ξ_4, while the phase-integral quantization condition for the situation in Fig. 1(b) involves a contour integral encircling the simple pole at $\xi = 1$ and the generalized classical turning point ξ_4. The quantization condition (A31) in the Appendix applies to the first situation, and the quantization condition (A32) in the Appendix applies to the second situation. Introducing the notations

$$\tilde{L} = \sum_{n=0}^{N} \tilde{L}^{(2n+1)}, \tag{3.3a}$$

$$\tilde{L}^{(2n+1)} = \frac{1}{2}\int_{\Lambda_{\tilde{L}}} \tilde{q}^{(2n+1)}(\xi)d\xi, \tag{3.3b}$$

$$\tilde{L}' = \sum_{n=0}^{N} \tilde{L}'^{(2n+1)}, \tag{3.4a}$$

$$\tilde{L}'^{(2n+1)} = \frac{1}{2}\int_{\Lambda_{\tilde{L}'}} \tilde{q}^{(2n+1)}(\xi)d\xi, \tag{3.4b}$$

where $\tilde{q}(\xi)$ is obtained according to (A5a,b), (A6a,b,c), (A3) and (A2) in the Appendix, and $\Lambda_{\tilde{L}}$ and $\Lambda_{\tilde{L}'}$ are the appropriate contours of integration pertaining to $\xi_3 > 1$ and $\xi_3 < 1$, respectively, and shown in Fig. 1(a) and Fig. 1(b), respectively, we can write the two quantization conditions corresponding to $\xi_3 > 1$ and $\xi_3 < 1$ as follows

$$\tilde{L} = \left(\tilde{s} + \frac{1}{2}\right)\pi, \quad \xi_3 > 1, \tag{3.5a}$$

$$\tilde{L}' = \left(\frac{|m|}{2} + \tilde{s} + \frac{1}{2}\right)\pi, \quad \xi_3 < 1, \tag{3.5b}$$

where $\tilde{s}$ is an integer. If, when $\Lambda = |m| \neq 0$ and hence $\xi_3 > 1$, we enlarge the contour of integration $\Lambda_{\tilde{L}}$ in Fig. 1(a), so that the new contour $\Lambda_{\tilde{L}'}$ encloses the turning points ξ_3 and ξ_4 as well as the pole at $\xi = 1$, and if we compensate in (3.5a) along with (3.3a,b) for this change by taking the residue of the integrand at $\xi = 1$ into account, we obtain a general quantization condition, valid for both cases $\xi_3 > 1$ and $\xi_3 < 1$, i.e., for both situations depicted in Fig. 1, *viz.*

$$\tilde{L}' = \left(\frac{|m|}{2} + \tilde{s} + \frac{1}{2}\right)\pi, \qquad \xi_3 > 1 \text{ or } \xi_3 < 1. \tag{3.6}$$

Besides condensing the two alternative quantization conditions (3.5a) and (3.5b) nicely into one formula, the quantization condition (3.6) has the further merit that, if the integration along the contour is made numerically (in cases where expressions in terms of complete elliptic integrals are not available), it may be advantageous to use the contour $\Lambda_{\tilde{L}'}$ instead of $\Lambda_{\tilde{L}}$ when $\xi_3 > 1$.

The quantization condition (3.6) yields the value of the reduced separation constant A' as a function of p^2 and $\tilde{C}$; see (3.2a).

3.2.2. Quantization conditions pertaining to the η-equation

In the physically relevant interval $-1 < \eta < 1$ the function $-Q^2(\eta)$ may correspond to a single-well potential (Fig. 2) or to a double-well potential with a superdense (Fig. 3) or underdense (Fig. 4) barrier. When, in the case of an underdense barrier, the energy lies sufficiently far above the top of the barrier, it may be preferable to disregard the barrier and to treat the double-well potential problem as a single-well potential problem.

When $\Lambda = |m| \neq 0$ or $\Lambda = 0$, and $-Q^2(\eta)$ is or can be considered as a single-well potential, and the classically allowed region is delimited by two simple zeros of $Q^2(\eta)$, as shown in Fig. 2 and in Fig. 4(a), we obtain from (A31) the single-well quantization condition

$$L = \left(s + \frac{1}{2}\right)\pi, \quad s = \text{non-negative integer}, \tag{3.7}$$

where by definition

$$L = \frac{1}{2}\int_{\Lambda_L} q(\eta)d\eta, \tag{3.8}$$

Λ_L being a closed contour encircling the generalized classical turning points. Note that in the derivation of (3.7) we have considered the classically forbidden regions to be thick also when $\Lambda = 0$ (Fig. 2). When $\Lambda = |m| \neq 0$ we can with the aid of residue calculus write (3.7) along with (3.8) as

$$L' = \left(|m| + s + \frac{1}{2}\right)\pi, \tag{3.9}$$

where L' is defined by

$$L' = \frac{1}{2}\int_{\Lambda_{L'}} q(\eta)d\eta, \tag{3.10}$$

$\Lambda_{L'}$ being a closed contour encircling -1 and $+1$; see Fig. 2 and Fig. 4(a).

When $\Lambda = 0$, and the classically allowed region is delimited by two first-order poles of $Q^2(\eta)$, as shown in Fig. 4(b), and the energy lies far above the top of the barrier, one can consider $-Q^2(\eta)$ as a single-well potential. From (A33) one then obtains the quantization condition (3.9) with L' defined by (3.10), where $\Lambda_{L'}$ is now the contour in Fig. 4(b).

We disregard the possibility that $\Lambda = 0$ and the residues of $Q^2(\eta)$ at $\eta = -1$ and $\eta = +1$ have different signs, since this case has so far not appeared in the applications.

When $-Q^2(\eta)$ corresponds to a double-well potential (Fig. 3 and Fig. 4), which is usually the case, the quantization condition (A39) gives

$$\cos(\alpha+\beta+\tilde{\phi}-2a)=\frac{\cos(\alpha-\beta)}{[1+\exp(-2\pi\bar{K})]^{\frac{1}{2}}}, \tag{3.11}$$

where

$$a=\frac{\pi}{2} \quad \text{when} \quad \Lambda=|m|\neq 0, \tag{3.12a}$$

$$a=(|m|+1)\frac{\pi}{2} \quad \text{when} \quad \Lambda=0, \tag{3.12b}$$

$$\alpha=\sum_{n=0}^{N}\alpha^{(2n+1)}, \tag{3.13a}$$

$$\alpha^{(2n+1)}=\mathrm{Re}\frac{1}{2}\int_{\Lambda_\alpha}q^{(2n+1)}(\eta)d\eta, \tag{3.13b}$$

$$\beta=\sum_{n=0}^{N}\beta^{(2n+1)}, \tag{3.14a}$$

$$\beta^{(2n+1)}=-\mathrm{Re}\frac{1}{2}\int_{\Lambda_\beta}q^{(2n+1)}(\eta)d\eta, \tag{3.14b}$$

$$\bar{K}=\sum_{n=0}^{N}\bar{K}_{2n}, \tag{3.15a}$$

$$\bar{K}_{2n}=\frac{i}{2\pi}\int_{\Lambda_K}q^{(2n+1)}(\eta)d\eta. \tag{3.15b}$$

For the super-barrier case (Fig. 4) we can instead of (3.15b) use the alternative formula

$$\begin{aligned}\bar{K}_{2n}&=-2\mathrm{Im}\frac{1}{2\pi}\int_{\Lambda_\alpha}q^{(2n+1)}(\eta)d\eta\\&=-2\mathrm{Im}\frac{1}{2\pi}\int_{\Lambda_\beta}q^{(2n+1)}(\eta)d\eta,\end{aligned} \tag{3.15b'}$$

which is useful in connection with the transformation to complete elliptic integrals. With the use of (3.13a,b), (3.14a,b) and (3.15a,b') each one of the quantities α,β and $\bar{K}$ is then obtained as the real or imaginary part of an integral over the contour Λ_α or Λ_β. The contours of integration $\Lambda_\alpha,\Lambda_\beta$ and Λ_K for sub-barrier and super-barrier energies are shown in Fig. 3 and Fig. 4. The analytic expressions for the quantity $\tilde{\phi}$ are given in terms of $\bar{K}$ and $\bar{K}_{2n}$ by (A28) and (A29a,b,c) in the Appendix. The quantity $\tilde{\phi}$ is of decisive importance for energies in the neighbourhood of the top of the barrier. The quantities α and β are positive. The quantity $\bar{K}_0$ is positive when η_2 and η_3 are real, it is equal to zero when η_2 and η_3 coincide, and it is negative when η_2 and η_3 are complex conjugate. The quantity $\bar{K}_2$ may be positive or negative irrespectively of whether η_2 and η_3 are real or complex conjugate.

Analogously as we changed the original contour $\Lambda_{\tilde{L}}$ into $\Lambda_{\tilde{L}'}$, when dealing with the quantization condition (3.5a), we can, when $\Lambda=|m|\neq 0$, change the contours Λ_α and Λ_β depicted in Fig. 3(a) and Fig. 4(a), so that, instead of letting them enclose only η_1,η_2 and η_3,η_4, respectively, we make each one of them enclose also a pole, $\eta=-1$ or $\eta=+1$, respectively. Calling the new contours $\Lambda_{\alpha'}$ and $\Lambda_{\beta'}$ [see Fig. 3(a) and Fig. 4(a)] and defining

$$\alpha'=\sum_{n=0}^{N}\alpha'^{(2n+1)}, \tag{3.16a}$$

$$\alpha'^{(2n+1)} = \mathrm{Re}\frac{1}{2}\int_{\Lambda_{\alpha'}} q^{(2n+1)}(\eta)d\eta, \tag{3.16b}$$

$$\beta' = \sum_{n=0}^{N} \beta'^{(2n+1)}, \tag{3.17a}$$

$$\beta'^{(2n+1)} = -\mathrm{Re}\frac{1}{2}\int_{\Lambda_{\beta'}} q^{(2n+1)}(\eta)d\eta, \tag{3.17b}$$

and recalling that the functions Y_{2n} are regular analytic at $\eta = \pm 1$ when $\Lambda = |m| \neq 0$, we find with the use of residue calculus that for $\Lambda = |m| \neq 0$

$$\begin{aligned} \alpha' - \alpha &= \beta' - \beta \\ &= \Lambda\pi/2, \end{aligned} \tag{3.18a}$$

$$\begin{aligned} \alpha' - \beta' &= \alpha - \beta \\ &= -\frac{b\pi}{2p}. \end{aligned} \tag{3.18b}$$

With the aid of (3.18a,b) we obtain from (3.11) along with (3.12a) for $\Lambda = |m| \neq 0$ the following quantization condition

$$\cos[\alpha' + \beta' + \tilde{\phi} - (|m| + 1)\pi] = \frac{\cos[b\pi/(2p)]}{[1 + \exp(-2\pi\bar{K})]^{\frac{1}{2}}}, \tag{3.19}$$

which has the same merits, relative to the original form of the quantization condition, i.e., (3.11) with (3.12a), as were mentioned in connection with the quantization condition (3.6), pertaining to the ξ-equation. When $\Lambda = 0$ we define

$$\alpha' = \sum_{n=0}^{N} \alpha'^{(2n+1)}, \tag{3.20a}$$

$$\alpha'^{(2n+1)} = \alpha^{(2n+1)}, \tag{3.20b}$$

$$\beta' = \sum_{n=0}^{N} \beta'^{(2n+1)}, \tag{3.21a}$$

$$\beta'^{(2n+1)} = \beta^{(2n+1)}, \tag{3.21b}$$

and note that (3.18a) is obviously valid also for $\Lambda = 0$. With the use of the theory of complex integration one finds that also (3.18b) is valid for $\Lambda = 0$. Then it follows from (3.11), (3.12b) and (3.18a,b) that the quantization condition (3.19) is valid also when $\Lambda = 0$. The quantization condition (3.19) thus covers in a unified and convenient form both cases $\Lambda = |m| \neq 0$ and $\Lambda = 0$.

The quantization condition (3.19) can be rewritten as

$$\begin{aligned} &\alpha' + \beta' + \tilde{\phi} - (|m| + 1)\pi \\ &\qquad = \pm\arccos\frac{\cos[b\pi/(2p)]}{[1 + \exp(-2\pi\bar{K})]^{\frac{1}{2}}} + 2s'\pi, \end{aligned} \tag{3.22}$$

where s' is an integer. As already mentioned, (3.18b) is valid for $\Lambda = |m| \neq 0$ as well as for $\Lambda = 0$. When the plus sign in (3.22) applies, we use (3.18b) to express β' in terms of α', and when the minus sign in (3.22) applies, we use (3.18b) to express α' in terms of β'. Replacing s' by s_α or s_β, we thus obtain from (3.22) and (3.18b) the two quantization conditions

$$\begin{aligned}\alpha' &= \left(\frac{|m|}{2}+s_\alpha+\frac{1}{2}\right)\pi-\frac{\tilde{\phi}}{2}-\frac{b\pi}{4p}\\ &\quad+\frac{1}{2}\arccos\frac{\cos\left(\frac{b\pi}{2p}\right)}{[1+\exp(-2\pi\bar{K})]^{\frac{1}{2}}},\end{aligned} \tag{3.23a}$$

$$\begin{aligned}\beta' &= \left(\frac{|m|}{2}+s_\beta+\frac{1}{2}\right)\pi-\frac{\tilde{\phi}}{2}+\frac{b\pi}{4p}\\ &\quad-\frac{1}{2}\arccos\frac{\cos\left(\frac{b\pi}{2p}\right)}{[1+\exp(-2\pi\bar{K})]^{\frac{1}{2}}},\end{aligned} \tag{3.23b}$$

where we choose the branch of arccos such that the last two terms on the right-hand side of (3.23a,b) cancel in the limit $\bar{K}\to+\infty$, that is, when the barrier becomes infinitely thick. In this limit, the formulas (3.23a,b) simplify to

$$\alpha' = \left(\frac{|m|}{2}+s_\alpha+\frac{1}{2}\right)\pi, \tag{3.24a}$$

$$\beta' = \left(\frac{|m|}{2}+s_\beta+\frac{1}{2}\right)\pi. \tag{3.24b}$$

For the particular case that we have a symmetric two-centre Coulomb problem, i.e., that $Z_1 = Z_2$, as is the case for the ion H_2^+, the double-well potential pertaining to the η-equation becomes symmetric ($b = 0$), and the quantization conditions (3.23a,b) can be simplified:

$$\begin{aligned}\alpha' &= \left(\frac{|m|}{2}+s_\alpha+\frac{1}{2}\right)\pi-\frac{\tilde{\phi}}{2}\\ &\quad+\frac{1}{2}\arctan\exp(-\pi\bar{K}),\end{aligned} \tag{3.25a}$$

$$\begin{aligned}\beta' &= \left(\frac{|m|}{2}+s_\beta+\frac{1}{2}\right)\pi-\frac{\tilde{\phi}}{2}\\ &\quad-\frac{1}{2}\arctan\exp(-\pi\bar{K}).\end{aligned} \tag{3.25b}$$

The reduced separation constant A', obtained from (3.23a,b) in the general case and from (3.25a,b) in the symmetric case, is a function of p^2 and C.

3.2.3. Comments on the quantization conditions

In the existing semi-classical treatments, the quantization conditions derived on assumptions valid for $m \neq 0$ are in general extrapolated to $m = 0$ (corresponding to a particularization of our case $\Lambda = 0$) without any motivation. It is, however, not allowed to obtain a quantization condition corresponding to $m = 0$ from a quantization condition corresponding to $m \neq 0$ by letting m take continuous values and tend to zero by a limiting procedure. That the formulas obtained by such an extrapolation are valid is an *a posteriori* conclusion. The correct justification of the quantization conditions for $\Lambda = 0$ rests on the use of the connection formula in subsection A.2.b of the Appendix.

For given values of r_{12}, m and E one can, as already mentioned, obtain the possible values of the reduced separation constant A' in the differential equation (2.8a) with (2.9a) by applying phase-integral quantization conditions for a single-well potential, while to obtain the possible values of the reduced separation constant A' in the differential equation (2.8b) with (2.9b) one has to use quantization conditions either for a single-well potential or for a double-well potential. The appropriate quantization condition for the ξ-equation determines A' as a function of p^2 and $\tilde{C}$. The appropriate quantization condition for the η-equation determines A' as a function of p^2 and C. The eigenvalues of p^2, and hence the energy eigenvalues E, are obtained from the requirement that these two expressions for A' must be equal to each other. One then obtains A' from the quantization condition for the ξ-equation or the η-equation. The value thus obtained for A' depends obviously on the choice of C and $\tilde{C}$. One should choose these parameters as funcitons of r_{12} in such a way that very accurate values of p^2 and A' are obtained already in the first order of the phase-integral approximation. A practically useful criterion for this can be formulated as follows. For every value of r_{12} one determines C and $\tilde{C}$ such that the first-order approximation gives the same value as the third-order approximation for p^2(and hence for the energy) as well as for A'. In this way one can make all calculations within the framework of the phase-integral method.

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APPENDIX A: PHASE-INTEGRAL METHOD

Since the present paper is based on phase-integral formulas that are scattered in different publications, we collect in this Appendix the background material that is necessary for reading the paper.

The phase-integral method for solving differential equations of the type

$$\frac{d^2\psi}{dz^2} + R(z)\psi = 0 \tag{A1}$$

involves the following items:

1. Arbitrary-order phase-integral approximation generated from an unspecified base function $Q(z)$, as described in Chapter 1 of [22]; see also Dammert and P.O. Fröman [26].
2. The method for solving connection problems developed by Fröman and Fröman [27], generalized to apply to the phase-integral approximation referred to in the above item.
3. Supplementary quantities, expressed analytically in terms of phase-integrals. An example is the quantity $\tilde{\phi}$, which is a new notation for the quantity -2σ in Fröman *et al.*[28], and which is of decisive importance, when two transition zeros lie close to each other.

We shall first briefly describe the phase-integral approximation referred to in item 1. Then we collect connection formulas pertaining to a single transition point [first-order zero or first-order pole of $Q^2(z)$] and to a real potential barrier, which can be derived by means of the method mentioned in item 2 combined with comparision equation technique for obtaining the supplementary quantity $\tilde{\phi}$ mentioned in item 3 and appearing in the connection formula for a real barrier. Finally we present quantization conditions for single-well and double-well potentials, which can be derived by means of the connection formulas just mentioned. These quantization conditions are used in our treatment of the two-centre Coulomb problem.

1. Phase-integral approximation generated from an unspecified base function

For a detailed description of the phase-integral approximation generated from an unspecified base function we refer to chapter 1 in [22]. A brief description is given below.

In the arbitrary-order phase-integral approximation in question there appears an unspecified function $Q(z)$ called the *base function.* This function is often chosen to be equal to $R^{\frac{1}{2}}(z)$, but in many physical problems it is important to use the possibility of choosing $Q(z)$ differently when there exist certain exceptional points, for example the origin in connection with the radial Schrödinger equation, and, correspondingly, the poles of $\tilde{Q}^2(\xi)$ and $Q^2(\eta)$ at $\xi = 1$ and $\eta = \pm 1$ in the two-centre Coulomb problem. In the present paper we introduce in the base functions a parameter Λ, chosen such that either $\Lambda = |m| \neq 0$ or $\Lambda = 0$, and two parameters C and $\tilde{C}$ to be determined such that the first- and third-order results coincide, in order that the first-order approximation be as good as possible.

To be able to write the phase-integral approximation generated from an unspecified base function in condensed form one introduces the new independent variable

$$\zeta = \int^{z} Q(z)dz \tag{A2}$$

and the function

$$\varepsilon_0 = Q^{-\frac{3}{2}}(z)\frac{d^2}{dz^2}Q^{-\frac{1}{2}}(z) + \frac{R(z) - Q^2(z)}{Q^2(z)}. \tag{A3}$$

It can be shown that in a local region of the complex z-plane, where the absolute value of ε_0 is small, the differential equation (A1) has the approximate solutions

$$\psi = q^{-\frac{1}{2}}(z)\mathrm{exp}[\pm iw(z)], \tag{A4a}$$

$$w(z) = \int_{z_0}^{z} q(z)dz, \tag{A4b}$$

where the lower limit of integration z_0 is an unspecified constant, and the function $q(z)$, pertaining to the phase-integral approximation of the order $2N + 1$, is given by

$$q(z) = \sum_{n=0}^{N} q^{(2n+1)}(z), \tag{A5a}$$

$$q^{(2n+1)}(z) = Q(z)Y_{2n}, \tag{A5b}$$

with the first few functions Y_{2n} given by

$$Y_0 = 1, \tag{A6a}$$

$$Y_2 = \frac{1}{2}\varepsilon_0, \tag{A6b}$$

$$Y_4 = -\frac{1}{8}\varepsilon_0^2 - \frac{1}{8}\frac{d^2\varepsilon_0}{d\zeta^2}. \tag{A6c}$$

The choice of the function $Q(z)$ does not affect the expressions for Y_{2n} in terms of ε_0 and ζ; only the expressions for ε_0 and ζ as functions of z are affected.

It is an essential advantage of the phase-integral approximation described above versus the Carlini[29] (JWKB) approximation in higher order that the former approximation contains the unspecified base function $Q(z)$, which one can take advantage of in several ways. A criterion for the determination of the base function is that the function ε_0 be in some sense small in the region of the complex z-plane that is relevant for the problem under consideration. However, this criterion does not determine the base function $Q(z)$ uniquely; it turns out that, within certain limits, the results are not very sensitive to the choice of $Q(z)$, when the approximation is used in higher orders. With a convenient choice of $Q(z)$ already the first-order approximation can be very good. On the other hand an inconvenient, but possible, choice of $Q(z)$ introduces in the first-order approximation an unnecessarily large error that, however, in general becomes corrected already in the third-order approximation.

The freedom that one has in the choice of the base function $Q(z)$ will be illuminated in a concrete way below. For a radial Schrödinger equation the usual choice of $Q^2(z)$ is

$$Q^2(z) = R(z) - \frac{1}{4z^2}. \tag{A7a}$$

However, the replacement of (A7a) by

$$Q^2(z) = R(z) - \frac{1}{4z^2} - \frac{\mathrm{const}}{z}, \tag{A7b}$$

where the coefficient of $\frac{1}{z}$ should be comparatively small, does not destroy the great accuracy of the results usually obtained with the phase-integral approximation in higher orders. There is thus a whole set of base functions that may be used, and there are various ways in which one can take advantage of this nonuniqueness to make the choice of the base function well adapted to the particular problem under consideration. For instance, by adapting the choice of $Q^2(z)$ to the analytical form of $R(z)$ one can sometimes achieve the result that the integrals occurring in the phase-integral approximation can be evaluated analytically. To give an example we assume that $R(z)$ contains only $\exp(z)$ but not z itself. In this case it is convenient to replace the choice (A7b) by the choice

$$Q^2(z) = R(z) - \frac{1}{4(e^z-1)^2} - \frac{\text{const}}{e^z-1}. \tag{A7c}$$

By a convenient choice, for instance of the unspecified coefficient in (A7b) or (A7c), one can sometimes attain the result that, for example, eigenvalues or phase-shifts are obtained exactly for some particular parameter value in every order of the phase-integral approximation. By making this exactness fulfilled in the limit of a parameter value, for which the phase-integral result without this adaptation would not be good, one can actually extend the region of validity of the phase-integral treatment; see p. 12 in [30]. When the differential equation contains one or more parameters, the accurate calculation of the wave function may require different choices of the base function $Q(z)$ for different ranges of the parameter values. To illustrate this fact we consider the radial Schrödinger equation. For sufficiently large values of the angular momentum quantum number l we obtain an accurate phase-integral approximation (valid also close to $z = 0$) if we choose $Q^2(z)$ according to (A7a) or (A7b). If the value of l is too small, this phase-integral approximation is not good. It can be considerably improved (except close to $z = 0$), when the absolute value of the coefficient of $\frac{1}{z}$ in $R(z)$ is sufficiently large, if one chooses instead

$$Q^2(z) = R(z) + \frac{l(l+1)}{z^2}. \tag{A7d}$$

The corresponding phase-integral approximation is not valid close to $z = 0$, but the wave function that is regular and tends to z^{l+1} as $z \to 0$ can be obtained sufficiently far away from $z = 0$ by means of the connection formula that will be presented in subsection A.2.b of this Appendix.

The appearance of the unspecified base function $Q(z)$ in the phase-integral approximation is thus very important from several points of view. In our treatment of the two-centre Coulomb problem we use two essentially different kinds of base function [corresponding to $\Lambda = |m| \neq 0$ and $\Lambda = 0$ in (3.2a,b)], which yield approximate solutions with different regions of validity.

When the first-order approximation is used, it is often convenient to choose the constant lower limit of integration z_0 in (A4b) to be a zero or a first-order pole of $Q^2(z)$. This is, however, in general not possible when a higher-order approximation is used, since the integral in (A4b) would then in general be divergent. If z_0 is an odd-order zero or an odd-order pole of $Q^2(z)$, it is therefore convenient to replace the definition (A4b) of $w(z)$ by the definition

$$w(z) = \frac{1}{2}\int_{\Gamma_{z_0}(z)} q(z)dz, \tag{A8}$$

where $\Gamma_{z_0}(z)$ is a path of integration that starts at the point corresponding to z on a Riemann sheet adjacent to the complex z-plane under consideration, encircles z_0 in the positive or in the negative sense, and ends at z. It is immaterial for the value of the integral in (A8) if the path of integration encircles z_0 in the positive or in the negative sense, but the endpoint must be z. For the first-order approximation the definitions (A4b) and (A8) are identical.

It is useful to introduce a short-hand notation for the integral in the right-hand member of (A8) by the definition

$$\int_{(z_0)}^{z} q(z)dz = \frac{1}{2}\int_{\Gamma_{z_0}(z)} q(z)dz. \tag{A9}$$

For the first order of the phase-integral approximation one can replace (z_0) by z_0 in the left-hand member of (A9) and thus get an ordinary integral from z_0 to z instead of half of the integral along the contour $\Gamma_{z_0}(z)$. In analogy to (A9) one defines a short-hand notation for an integral in which the upper limit of integration is an odd-order zero or an odd-order pole of $Q^2(z)$. When one has two transition points of that kind as limits of integration, the definition of the short-hand notation with both limits within parentheses implies that the integral is equal to half of the integral along a closed loop enclosing both transition points. The simplified notation in the left-hand member of (A9) for the integral in the right-hand member of (A9) was introduced by Fröman *et al.* [31], pp 160-161. It makes it possible to use, for an arbitrary order of the phase-integral approximation, a similar simple notation and almost the same simple language (although in a generalized sense) as for the first order of the phase-integral approximation. One thus achieves a great formal and practical simplification in the treatment of concrete problems, when an arbitrary order of the phase-integral approximation is used.

We remark that the notations used above differ from the notations in the original papers published up to the beginning of the eighties in the respect that $Q^2(z)$ and $Q^2_{mod}(z)$ in those papers correspond in the present paper to $R(z)$ and $Q^2(z)$, respectively.

2. Connection formulas associated with a single transition point

a. Connection formulas pertaining to a first-order, real transition zero

Before the phase-integral approximation generated from an unspecified base function had been introduced, N. Fröman [32] derived arbitrary-order connection formulas associated with a turning point for the particular phase-integral approximation of arbitrary order corresponding to $Q^2(z) = R(z)$. After the phase-integral approximation generated from an unspecified base function had been introduced, it turned out that these connection formulas remain valid also when $Q^2(z) \neq R(z)$. Below we shall present the general connection formulas.

The functions $R(z)$ and $Q^2(z)$ are assumed to be real on the real z-axis (the x-axis). On this axis there is a generalized classical turning point t, i.e., a simple zero of $Q^2(z)$, and there is, in a generalized sense, a classically allowed region on one side of t, i.e., a region where $Q^2(x) > 0$, and a classically forbidden region on the other side of t, i.e., a region where $Q^2(x) < 0$. Defining

$$w(x) = \int_{(t)}^{x} q(z)dz, \tag{A10}$$

we can write the connection formula for tracing a phase-integral solution of (A1) from the classically allowed to the classically forbidden region as

$$\begin{aligned} A\left|q^{-\frac{1}{2}}(x)\right| \exp\left\{i\left[|w(x)| + \frac{\pi}{4}\right]\right\} \\ +B\left|q^{-\frac{1}{2}}(x)\right| \exp\left\{-i\left[|w(x)| + \frac{\pi}{4}\right]\right\} \longrightarrow \\ \longrightarrow (A+B)\left|q^{-\frac{1}{2}}(x)\right| \exp\left[|w(x)|\right], \end{aligned} \tag{A11}$$

where A and B are constants, which are arbitrary except for the requirement that $\frac{A+B}{|A|+|B|}$ must not be too close to zero. As a consequence of (A11) we have the connection formula

$$\begin{aligned} \left|q^{-\frac{1}{2}}(x)\right| \cos\left[|w(x)| + \delta - \frac{\pi}{4}\right] \rightarrow \\ \rightarrow \sin\delta\left|q^{-\frac{1}{2}}(x)\right| \exp\left[|w(x)|\right], \end{aligned} \tag{A12}$$

where δ is a real phase constant that must not be too close to zero. The connection formula for tracing a phase-integral solution of (A1) from the classically forbidden to the classically allowed region is

$$\begin{aligned} \left|q^{-\frac{1}{2}}(x)\right| \exp\left[-|w(x)|\right] + C\left|q^{-\frac{1}{2}}(x)\right| \exp\left[|w(x)|\right] \rightarrow \\ \rightarrow 2\left|q^{-\frac{1}{2}}(x)\right| \cos\left[|w(x)| - \frac{\pi}{4}\right], \end{aligned} \tag{A13}$$

and it is valid provided that the condition

$$C\exp\left[|w(x)|\right] \lesssim \exp\left[-|w(x)|\right], \tag{A14}$$

is fulfilled. For a numerical study of the accuracy and the properties of the connection formula (A13) with $C = 0$ we refer to N. Fröman and Mrazek[33]. We emphasize the one-directional character of the connection formulas (A11), (A12) and (A13), which means that the tracing of a solution must always be made in the direction of the arrow. This property of the connection formulas has been thoroughly investigated and even illustrated numerically by N. Fröman [34] for the first order of the Carlini [29] (JWKB) approximation. The whole discussion in [34] applies in principle to the connection formulas for the higher orders of the phase-integral approximation as well. The above connection formulas for the phase-integral approximation of any order may in many cases be used for obtaining very accurate solutions of physical problems, when the classical turning points are well separated, and when there are no other transition points near the real axis in the region of the complex z-plane of interest. Within their range of applicability the connection formulas are very useful because of their simplicity and the great ease with which they can be used.

b. *Connection formula pertaining to a first-order transition pole*

Now we assume that in a certain region of the complex z-plane around a first-order transition pole t, i.e., a first-order pole of $Q^2(z)$, we have

$$R(z) = -\frac{l(l+1)}{(z-t)^2} + \frac{B}{z-t} + \text{ a regular function of } z, \tag{A15}$$

$$Q^2(z) = \frac{\bar{B}}{z-t} + \text{ a regular function of } z, \tag{A16}$$

where $2l+1$ is a non-negative integer. We assume that the absolute values of B and $\bar{B}$ are sufficiently large, while the absolute value of $B-\bar{B}$ and the absolute value of the difference between the two regular functions in (A15) and (A16) are sufficiently small. There is one particular curve on which $w(z)$, defined as

$$w(z) = \int_{(t)}^{z} q(z)dz, \tag{A17}$$

is real. For the first order of the phase-integral approximation this is the anti-Stokes line that emerges from t. Therefore we use, also when a higher order of the phase-integral approximation is used, the terminology an *anti-Stokes line that emerges from* t in a generalized sense to denote the anti-Stokes line on which $w(z)$, defined in (A17), is real. For the first-order approximation (and under certain unnecessarily restrictive assumptions) Fröman and Fröman [27] obtained a phase-integral formula [their eq.(7.28)], valid sufficiently far away from t on the anti-Stokes line that emerges from t, for the particular solution $\psi(z)$ of (A1) that fulfils the condition

$$\lim_{z\to t} \frac{\psi(z)}{(z-t)^{l+1}} = 1. \tag{A18}$$

This formula can be generalized to be valid for an arbitrary order of the phase-integral approximation generated from an unspecified base function and can then be formulated as follows. On the lip of the anti-Stokes line emerging from t, where *arg* $w(z)$ is smallest, the solution of (A1) that fulfils the condition (A18) is, sufficiently far away from t, given by the phase-integral formula

$$\psi(z) = \left(\pi c \frac{w(z)}{|w(z)|}\right)^{-\frac{1}{2}} q^{-\frac{1}{2}}(z) \cos\left[|w(z)| - \left(l + \frac{3}{4}\right)\pi\right], \tag{A19}$$

where c is the residue of $[\psi(z)]^{-2}$ at $z=t$ and is thus determined by the expansion of $\psi(z)$ in powers of $z-t$, and the sign of $\left[\pi c \frac{w(z)}{|w(z)|}\right]^{-\frac{1}{2}}$ has to be chosen conveniently. For the special case that $l=0$ one finds that $c=B$. Formula (A19) can easily be particularized to the case that $R(z)$ and $Q^2(z)$ are real on the real z-axis (the x-axis) and t lies on that axis.

3. Connection formula for a real, smooth, single-hump potential barrier

Our starting point is a paper by Fröman and Fröman [35]. Although it was assumed in the treatment there that $Q^2(z) = R(z)$ with the notations in the present paper, the results obtained are valid also when $Q^2(z) \neq R(z)$. In the present paper it is convenient to introduce partly other notations than in [35]. Thus we now denote by t' and t'' the two relevant zeros of $Q^2(z)$, i.e., the two generalized classical turning points in the sub-barrier case ($t' < t''$) and the two complex conjugate transition zeros in the super-barrier case ($\text{Im } t' \leq 0, \text{Im } t'' \geq 0$). Let x', called x_1 in [35], be a point in the classically allowed region of the real z-axis to the left of the barrier, and let x'', called x_2 in [35], be a point in the classically allowed region of the real z-axis to the right of the barrier. We introduce the notations

$$\theta = |F_{22}| \exp(K), \tag{A20a}$$

$$\vartheta = \arg F_{22}, \tag{A20b}$$

$$\tilde{\phi} = -2\sigma = \frac{\pi}{2} - \arg F_{12}, \tag{A20c}$$

where F_{12} and F_{22} are defined in [35], and K is defined by eq.(12) in [35]. In the definitions (A20a,b,c) it is assumed that the phase of $q^{\frac{1}{2}}(z)$ is chosen as shown in Fig.1 in [35]. We shall, however, in the following write the formulas in such a way that they remain unchanged if one changes the phase of $Q^{\frac{1}{2}}(z)$ and hence the phase of $q^{\frac{1}{2}}(z)$; see (A5a,b). The quantity K in (A20a) is then given by

$$\begin{aligned} K &= \frac{1}{2} i \int_{\Lambda} q(z) dz \\ &= i \int_{(t')}^{(t'')} q(z) dz, \end{aligned} \tag{A21}$$

where Λ [not to be confused with the parameter Λ in the base function $Q(\eta)$] is a closed contour of integration encircling both t' and t'', but no other transition point, and the integration is performed in the direction that in the *first-order approximation* yields $K > 0$ for energies below the top of the barrier and $K < 0$ for energies above the top of the barrier. If higher-order approximations are used, the quantity K may become negative also for energies below (but not too far from) the top of the barrier; see Table I in [36]. We have replaced σ, defined by eq. (28) in [35], by $-\frac{\tilde{\phi}}{2}$ [cf. (A20c)] in order to get better agreement with a notation used by other authors; see for instance Child [37]. Now we define

$$B' = A_1 \exp\left(-i\frac{\pi}{4}\right), \tag{A22a}$$

$$A' = B_1 \exp\left(+i\frac{\pi}{4}\right), \tag{A22b}$$

where the notations in the right-hand members are those used in [35]. Using the short-hand notation defined in (A9), we obtain from eqs. (25a) and (9a), with x_1 replaced by x', in [35] and (A22a,b) in the present paper

$$\begin{aligned} \psi(x') &= A' \left| q^{-\frac{1}{2}}(x') \right| \exp\left(+i \left| \mathrm{Re} \int_{(t')}^{x'} q(z) dz \right| \right) \\ &\quad + B' \left| q^{-\frac{1}{2}}(x') \right| \exp\left(-i \left| \mathrm{Re} \int_{(t')}^{x'} q(z) dz \right| \right), \end{aligned} \tag{A23a}$$

and from eqs. (25b) and (23), with x_2 replaced by x'', in [35] and (A20a,b,c) and (A22a,b) in the present paper

$$\begin{aligned} \psi(x'') &= A'' \left| q^{-\frac{1}{2}}(x'') \right| \exp\left(+i \left| \mathrm{Re} \int_{(t'')}^{x''} q(z) dz \right| \right) \\ &\quad + B'' \left| q^{-\frac{1}{2}}(x'') \right| \exp\left(-i \left| \mathrm{Re} \int_{(t'')}^{x''} q(z) dz \right| \right), \end{aligned} \tag{A23b}$$

where

$$\begin{pmatrix} A'' \\ B'' \end{pmatrix} = \tilde{M} \begin{pmatrix} A' \\ B' \end{pmatrix}, \tag{A24}$$

$$\tilde{M} = \begin{pmatrix} \theta \exp\left[-i(\frac{\pi}{2} + \vartheta)\right] & (\theta^2 + 1)^{\frac{1}{2}} \exp(+i\tilde{\phi}) \\ (\theta^2 + 1)^{\frac{1}{2}} \exp(-i\tilde{\phi}) & \theta \exp\left[+i(\frac{\pi}{2} + \vartheta)\right] \end{pmatrix}, \tag{A25a}$$

$$\det \tilde{M} = -1. \tag{A25b}$$

It is seen from (A23a,b) that the coefficients A' and A'' are associated with waves travelling away from the barrier, while the coefficients B' and B'' are associated with waves incoming towards the barrier. From (A25a,b) we obtain

$$\tilde{M}^{-1} = \begin{pmatrix} \theta \exp\left[-i(\frac{\pi}{2} - \vartheta)\right] & (\theta^2 + 1)^{\frac{1}{2}} \exp(+i\tilde{\phi}) \\ (\theta^2 + 1)^{\frac{1}{2}} \exp(-i\tilde{\phi}) & \theta \exp\left[+i(\frac{\pi}{2} - \vartheta)\right] \end{pmatrix}. \tag{A26}$$

One thus obtains $\tilde{M}^{-1}$ from $\tilde{M}$ by replacing ϑ by $-\vartheta$. We emphasize that the above formulas are in principle exact, provided that one knows the quantities θ, ϑ and $\tilde{\phi}$, which depend slightly on x' and x''. Furthermore, the two transition zeros associated with the potential barrier need not lie far away from other possibly existing transition points; see [35]. However, when one introduces for θ, ϑ and $\tilde{\phi}$ the approximate values that will be given below, the barrier is assumed to be well separated (in the sense just described) from all transition points that are not associated with the barrier.

When A' and B' are given constants, associated with a wave function that is given at the point x', the coefficients A'' and B'', which are obtained from (A24) along with (A25a), depend slightly on x' and x'' via the quantities θ, ϑ and $\tilde{\phi}$. One obtains the derivatives of $\psi(x')$ and $\psi(x'')$ from (A23a,b) by considering A', B', A'' and B'' *formally* as constants.

When the transition points that are *not* associated with the barrier lie sufficiently far away from t' and t'', it follows from eq.(43a) in [35] and (A20a,b) that

$$\theta \approx \exp(K), \tag{A27a}$$

$$\vartheta \approx 0. \tag{A27b}$$

The quantity $\tilde{\phi}$ is particularly important when the energy is close to the top of the barrier, but it is important also for energies well below the top, if one with the use of higher orders of the phase-integral approximation wants to obtain very accurate results. In practice one cannot obtain useful expressions for $\tilde{\phi}$ from the exact formula (A20c). Under the assumption that $\frac{d^2R(z)}{dz^2}$ is not too close to zero at the top of the barrier, Fröman *et al.* [38] derived by means of comparision equation technique, adapted to yield formulas for supplementary quantities in the phase-integral method, an approximate, but very accurate, formula in the $(2N+1)$th order of the phase-integral approximation [their eqs. (5.5.30), (5.5.25a-g), (5.4.23) and (5.4.21)], from which we can obtain the formula

$$\tilde{\phi} = \arg\Gamma\left(\frac{1}{2} + i\bar{K}\right) - \bar{K}\ \ln|\bar{K}_0| + \sum_{n=0}^{N} \phi^{(2n+1)}, \tag{A28}$$

where

$$\phi^{(1)} = \bar{K}_0, \tag{A29a}$$

$$\phi^{(3)} = -\frac{1}{24\bar{K}_0}, \tag{A29b}$$

$$\phi^{(5)} = -\frac{7}{2880\bar{K}_0^3} + \frac{\bar{K}_2}{24\bar{K}_0^2} - \frac{\bar{K}_2^2}{2\bar{K}_0}, \tag{A29c}$$

with

$$\bar{K}_{2n} = \frac{1}{2\pi i}\int_{\Lambda} Y_{2n} Q(z) dz, \quad n = 0, 1, 2, ...N, \tag{A30a}$$

$$\bar{K} = \sum_{n=0}^{N} \bar{K}_{2n} = \frac{K}{\pi}, \tag{A30b}$$

Λ being the previously described contour of integration encircling t' and t'' but no other transition point, with the integration performed in the direction that makes $\bar{K}_0$ positive when t' and t'' are real, i.e., when the barrier is superdense, but negative when t' and t'' are complex conjugate, i.e., when the barrier is underdense. (Note that we perform the integrations in (A21) and (A30a) in opposite directions in order to make these formulas to agree with eq. (12) in [35] and eq. (5.4.21) in [38], respectively.) The result given by (A28), (A29a,b,c) and (A30a,b) can also be obtained from [28], where -2σ is the same as our $\tilde{\phi}$.

We emphasize again that for the validity of (A28) with the expressions (A29a-c) for $\phi^{(2n+1)}$ the essential restriction is that $\left|\frac{d^2R(z)}{dz^2}\right|$ must not be too small at the top of the barrier, which means that close to its top the barrier is approximately parabolic. However, when the energy is close to the top of the barrier, it is the slight deviation from parabolic shape close to the top of the barrier that determines the values of the quantities $\bar{K}_{2n}, n > 0$, and one needs accurate values of these quantities for obtaining accurate values of $\tilde{\phi}$ in higher orders of the phase-integral approximation.

The barrier connection formula presented in this section is valid uniformly for all energies, below and above the top of the barrier. We would also like to emphasize that while the connection formulas pertaining to an isolated turning point (N. Fröman [32]) are one-directional, the barrier connection formula (A23a,b) with (A24) and (A25a), which is valid when the barrier is well isolated and has an approximately parabolic top, is bi-directional. However, the neighbourhood of an energy that corresponds to a resonance requires a careful discussion.

4. Quantization conditions for single-well and double-well potentials

In this section we shall present quantization conditions for general single-well potentials [39, 40, 41] and double-well potentials [28, 41, 42, 43], valid for any conveniently chosen order of the phase-integral approximation, in forms especially adapted to the two-centre Coulomb problem. In the quantization conditions pertaining to the double-well potential there appears the supplementary quantity $\tilde{\phi}$, which was discussed in Section A.3, and which is of particular importance for energy eigenvalues in the neighbourhood of the top of the barrier; cf. numerical results in [28], where Q^2, Q^2_{mod} and σ correspond to R, Q^2 and $-\frac{\tilde{\phi}}{2}$, respectively, in the present paper. Comparision with numerical results [28] shows that all energy eigenvalues, also the low-lying ones and those in the neighbourhood of the top of the barrier, are obtained very accurately from the phase-integral quantization conditions when the third- or fifth-order approximation is used.

Since arbitrary-order phase-integral quantization conditions for the single-well and for the double-well potential problem have been given in previous work, we restrict ourselves to quoting those results and taking into account the fact that we are dealing with the special potentials pertaining to the two-centre Coulomb problem.

a. Quantization conditions for single-well potentials

We assume that $R(z)$ and $Q^2(z)$ are real on the real z-axis (the x-axis) and that there are two transition points t' and t'' $(> t')$ on this axis, each one of which may be either a first-order transition zero, i.e., a first-order zero of $Q^2(z)$, or a first-order transition pole, i.e., a first-order pole of $Q^2(z)$. These transition points are assumed to lie far away from all other transition points. On the real axis between t' and t'' it is assumed that $Q^2(x)$ is positive. With the aid of the connection formulas in Section A.2 we can derive the quantization conditions that will be presented below.

When both t' and t'' are first-order transition zeros, we obtain the quantization condition [39, 40]

$$\left| \int_{(t')}^{(t'')} q(z)dz \right| = \left(s + \frac{1}{2} \right) \pi, \quad s = 0, 1, 2... \tag{A31}$$

When one of the transition points t' and t'' is a first-order transition zero, and the other is a first-order transition pole in the neighbourhood of which $R(z)$ and $Q^2(z)$ can be expanded according to (A15) and (A16) with $l = \frac{|m|-1}{2}$, i.e., $l(l+1) = \frac{m^2-1}{4}$, we obtain under the assumptions introduced below those expansions the quantization condition [40]

$$\left| \int_{(t')}^{(t'')} q(z)dz \right| = \left(\frac{|m|}{2} + s + \frac{1}{2} \right) \pi, \tag{A32}$$

where m is an integer (positive, negative or zero), and s is also an integer.

When both transition points t' and t'' are first-order transition poles, in the neighbourhood of which $R(z)$ and $Q^2(z)$ can be expanded according to (A15) and (A16) with $l = \frac{|m|-1}{2}$, i.e., $l(l+1) = \frac{m^2-1}{4}$ for both transition poles but possibly with different coefficients B and $\bar{B}$ for the two transition poles, we obtain under the assumptions introduced below (A15) and (A16) the quantization condition [30]

$$\left| \int_{(t')}^{(t'')} q(z)dz \right| = \left(|m| + s + \frac{1}{2} \right) \pi, \tag{A33}$$

where m is an integer (positive, negative or zero), and s is also an integer.

b. *Quantization conditions for double-well potentials*

We assume that $R(z)$ and $Q^2(z)$ are real on the real z-axis (the x-axis) and that there are either two generalized classical turning points t' and t'' $(> t')$ [real, simple zeros of $Q^2(z)$] associated with a superdense potential barrier or two complex conjugate simple transition zeros t' and t'' [simple zeros of $Q^2(z)$; Im $t' < 0$, Im $t'' > 0$] associated with an underdense potential barrier. The classically allowed region to the left of the barrier is to the left delimited by a transition point t_- (on the real axis), and the classically allowed region to the right of the barrier is to the right delimited by a transition point t_+ (on the real axis), where t_- and t_+ are both either generalized classical turning points, i.e., simple zeros of $Q^2(z)$, or first-order transition poles, i.e., first-order poles of $Q^2(z)$. The points t_- and t_+, as well as other possibly existing transition points that are not associated with the barrier, are assumed to lie far away from t' and t''. When t_- and t_+ are simple transition poles we assume that in the neighbourhood of $t_\pm$ we have

$$R(z) = \frac{(1-m^2)}{4(z-t_\pm)^2} + \frac{B_\pm}{z-t_\pm} + \text{ a regular function of } z, \tag{A34}$$

$$Q^2(z) = \frac{\bar{B}_\pm}{z-t_\pm} + \text{a regular function of } z, \tag{A35}$$

where m is an integer (positive, negative or zero), $B_\pm$ and $\bar{B}_\pm$ are sufficiently large to their absolute values, while the absolute values of $B_\pm - \bar{B}_\pm$, as well as the difference between the regular functions in (A34) and (A35), is not too large. Under the above assumptions we obtain with the aid of connection formulas in Section A.2 and Section A.3 the quantization condition

$$\begin{aligned}\tan\left(\left|\mathrm{Re}\int_{(t_-)}^{(t')} q(z)dz\right| + \frac{\tilde{\phi}}{2} - a\right) \tan\Bigg(\left|\mathrm{Re}\int_{(t_+)}^{(t'')} q(z)dz\right| \\ + \frac{\tilde{\phi}}{2} - a\Bigg) = \frac{[1+\exp(-2K)]^{\frac{1}{2}} - 1}{[1+\exp(-2K)]^{\frac{1}{2}} + 1},\end{aligned} \tag{A36}$$

where

$$K = \frac{1}{2i}\int_\Lambda q(z)dz, \tag{A37}$$

Λ being a closed contour, enclosing t' and t'', along which the integration is performed in the direction that makes the first-order contribution to K positive when the barrier is super-dense but negative when the barrier is under-dense, and

$$a = \begin{cases} \frac{\pi}{2} & \text{when } t_- \text{ and } t_+ \text{ are transition zeros,} \\ (|m|+1)\frac{\pi}{2} & \text{when } t_- \text{ and } t_+ \text{ are transition poles.} \end{cases} \tag{A38}$$

The quantization condition (A36) can be rewritten into the form

$$\begin{aligned}\cos\left(\left|\mathrm{Re}\int_{(t_-)}^{(t')} q(z)dz\right| + \left|\mathrm{Re}\int_{(t_+)}^{(t'')} q(z)dz\right| + \tilde{\phi} - 2a\right) \\ = \frac{\cos\left(\left|\mathrm{Re}\int_{(t_-)}^{(t')} q(z)dz\right| - \left|\mathrm{Re}\int_{(t_+)}^{(t'')} q(z)dz\right|\right)}{[1+\exp(-2K)]^{\frac{1}{2}}}.\end{aligned} \tag{A39}$$

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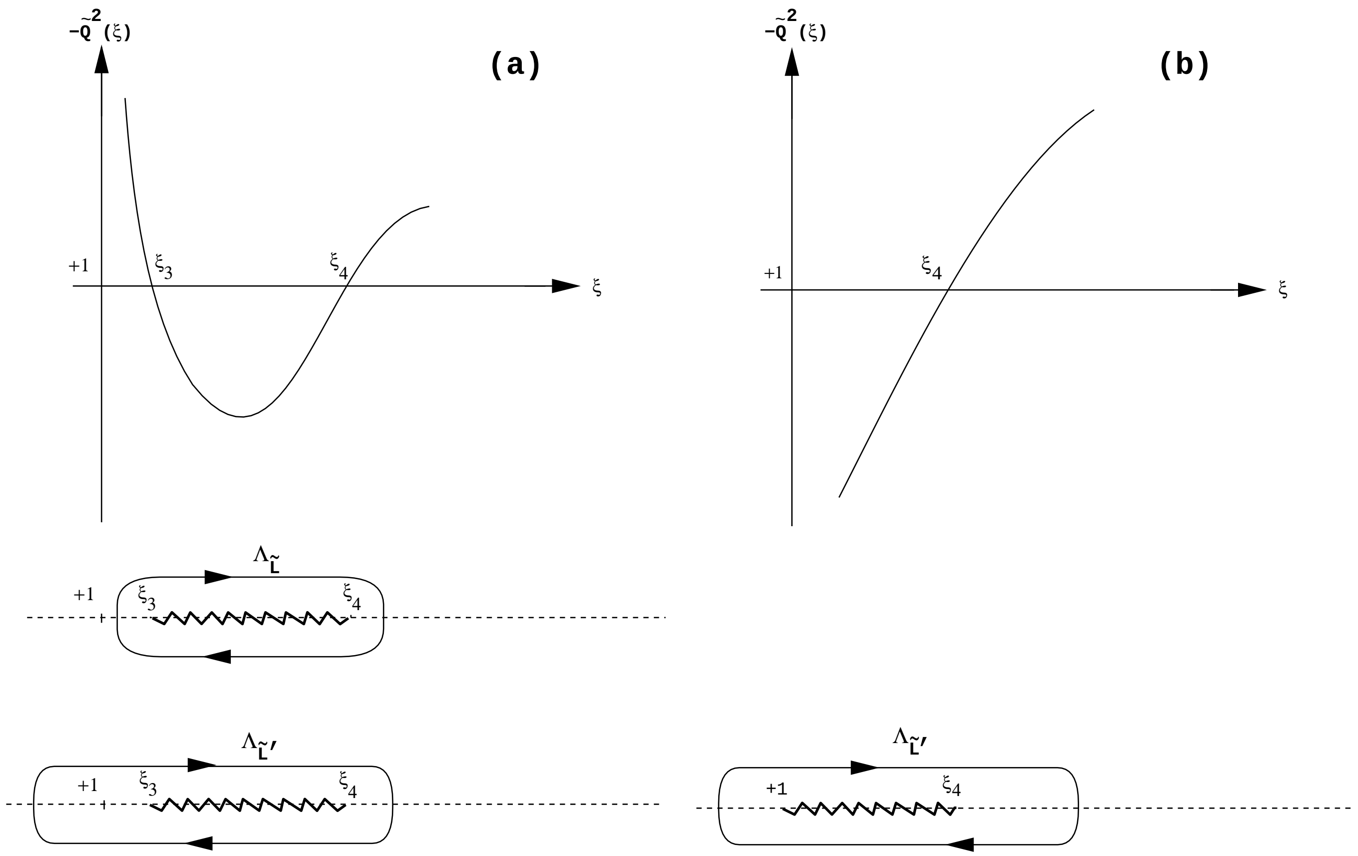

FIG. 1: The figure gives schematic pictures of $-\tilde{Q}^2(\xi)$ for $\xi > 1$ and of the contours of integration in the complex ξ-plane. The cuts are indicated by wavy lines. On the upper lip of the cut $\tilde{Q}(\xi)$ is positive. Only those zeros of $\tilde{Q}^2(\xi)$ that are relevant for the contours of integration are shown. For $\Lambda = |m| \neq 0$ (a) always applies, and the relation between the integrals associated with the contours $\Lambda_{\tilde{L}}$ and $\Lambda_{\tilde{L}'}$ is $\tilde{L}' = \tilde{L} + \frac{|m|}{2}$; the zeros ξ_1 and ξ_2 of $\tilde{Q}^2(\xi)$, which are not shown in the figure, may be real or complex conjugate. For $\Lambda = 0$ there are only two zeros, ξ_3 and ξ_4, of $\tilde{Q}^2(\xi)$, and either (a) or (b) may apply.

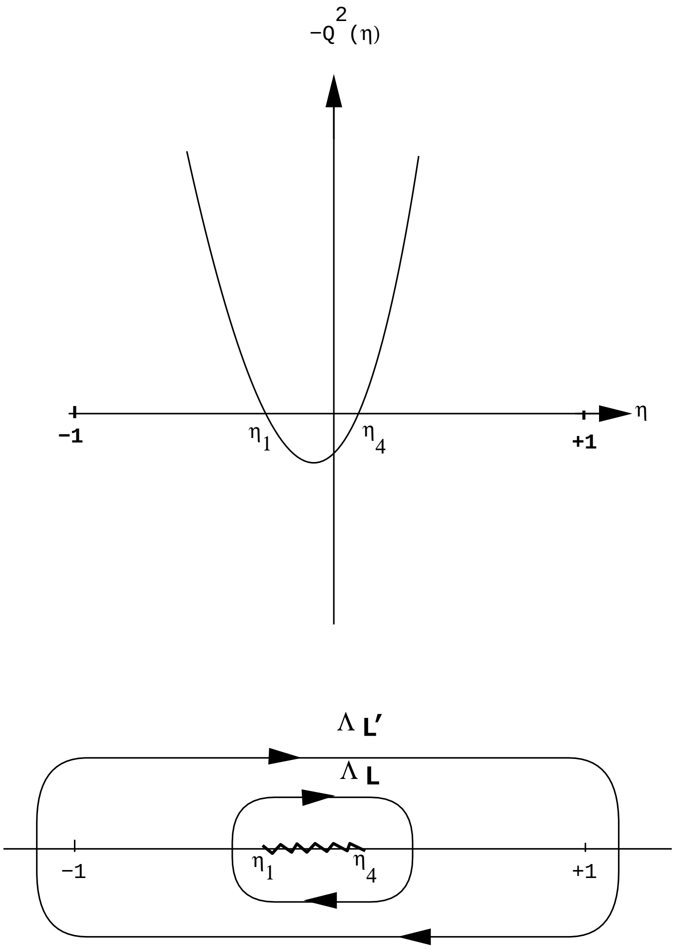

FIG. 2: The figure gives schematic pictures of $-Q^2(\eta)$ for $-1 < \eta < 1$ and of the contours of integration when $-Q^2(\eta)$ in the interval $-1 < \eta < 1$ is a single-well potential, which may occur for $\Lambda = |m| \neq 0$ as well as for $\Lambda = 0$. The cut is indicated by a wavy line, on the upper lip of which $Q(\eta)$ is positive. The contour $\Lambda_{L'}$ can be used only when $\Lambda = |m| \neq 0$, and the relation between the integrals associated with the contours Λ_L and $\Lambda_{L'}$ is then $L' = L + |m|$. The quantization conditions, expressed in terms of complete elliptic integrals, for the situation in this figure with $\Lambda = |m| \neq 0$ are the same as the corresponding quantization conditions for the situation in Fig. 4(a). The quantization condition for the case in the present figure with $\Lambda = 0$ has so far not appeared in the applications.

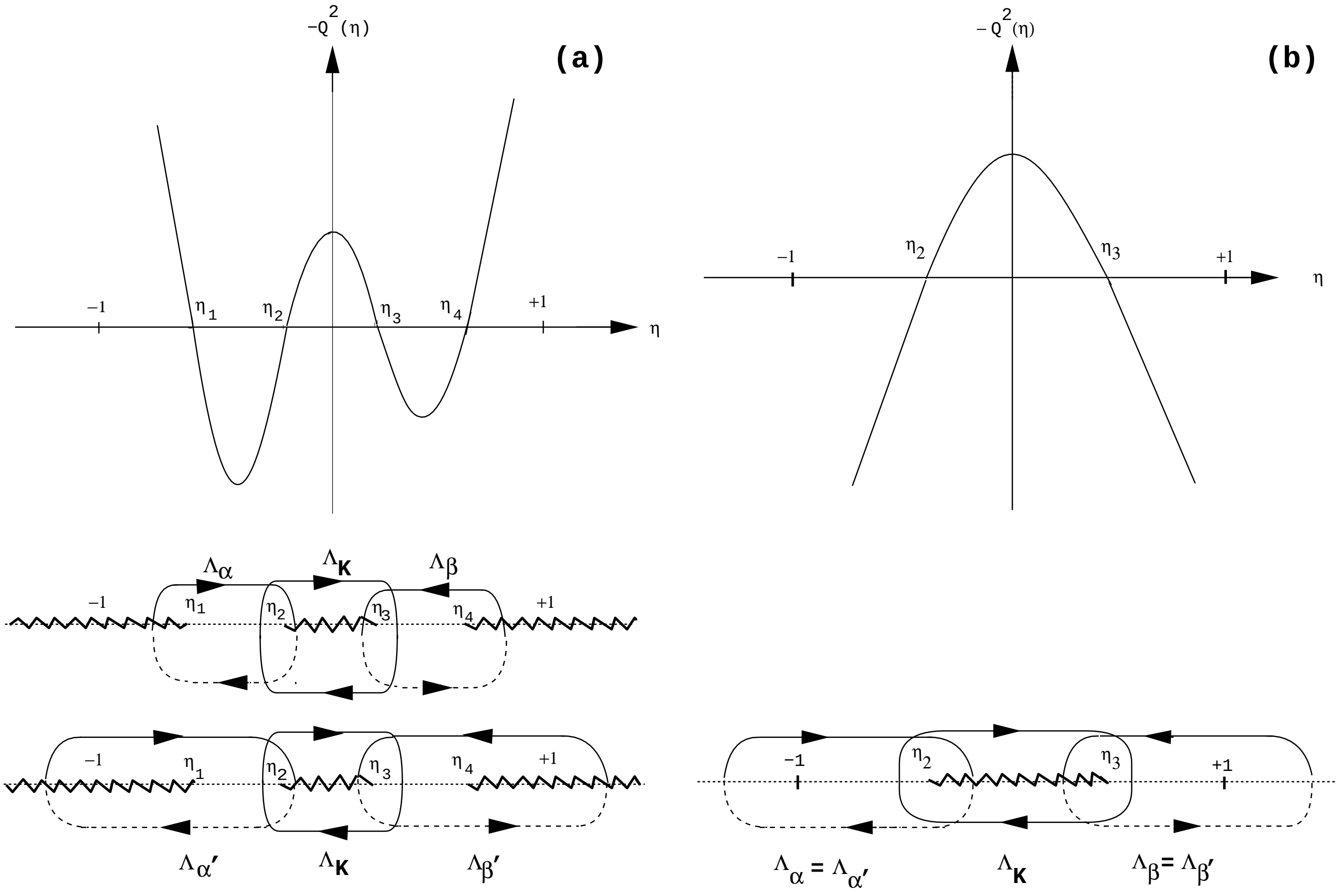

FIG. 3: The figure gives schematic pictures of $-Q^2(\eta)$ for $-1 < \eta < 1$ and of the contours of integration in the complex η-plane, when $-Q^2(\eta)$ corresponds to a double-well potential with a super-dense barrier. In (a) $\Lambda = |m| \neq 0$ and in (b) $\Lambda = 0$. The cuts are indicated by wavy lines, and the parts of the contours of integration that lie on Riemann sheets adjacent to the complex η-plane under consideration are dashed. In the left-hand classically allowed region $Q(\eta)$ is positive. Only those zeros of $Q^2(\eta)$ that are relevant for the contours of integration are shown. We recall the relations (3.18a) which mean that $\alpha' = \alpha + \frac{\Lambda\pi}{2}$ and $\beta' = \beta + \frac{\Lambda\pi}{2}$.

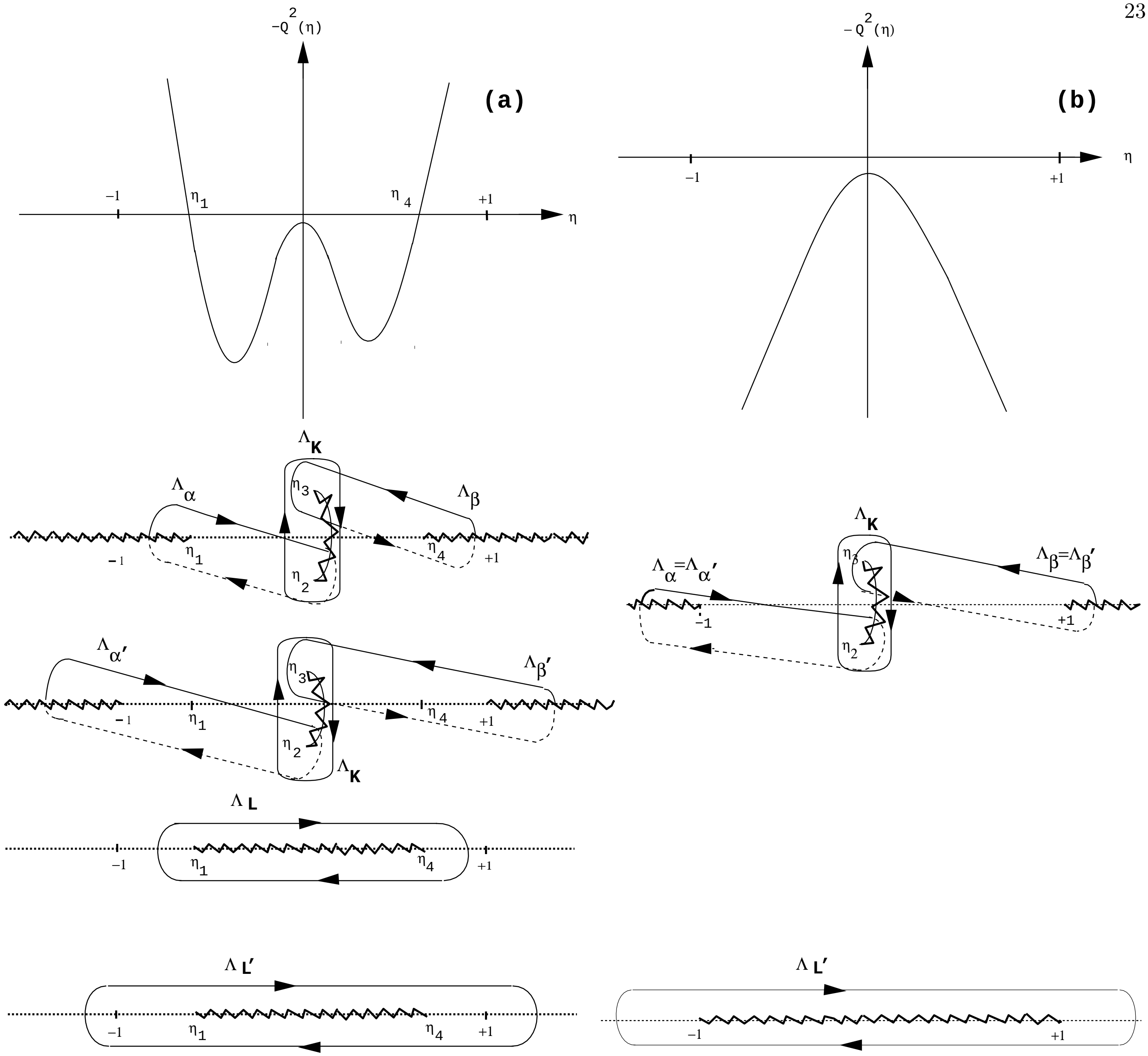

FIG. 4: The figure gives schematic pictures of $-Q^2(\eta)$ for $-1 < \eta < 1$ and of the contours of integration in the complex η-plane, when $-Q^2(\eta)$ corresponds to a double-well potential with an under-dense barrier. In (a) $\Lambda = |m| \neq 0$ and in (b) $\Lambda = 0$. The cuts are indicated by wavy lines, and the parts of the contours of integration that lie on Riemann sheets adjacent to the complex η-plane under consideration are dashed. In the left-hand classically allowed region $Q(\eta)$ is positive. Only those zeros of $Q^2(\eta)$ that are relevant for the contours of integration are shown. If the energy lies sufficiently far above the top of the barrier, one may treat the double-well potential problem as a single-well potential problem with the classically allowed region between η_1 and η_4 in (a) and between the poles at $\eta = -1$ and $\eta = +1$ in (b). One introduces then new cuts [between η_1 and η_4 in (a) and between -1 and $+1$ in (b)], on the upper lips of which $Q(\eta)$ is positive, and uses the contours Λ_L and $\Lambda_{L'}$. In (a) the relation between the corresponding integrals is $L' = L + |m|$. In both (a) and (b) L is related to α and β by the relation $L = \alpha + \beta$.