Quasiclassical expression for parameters which determine nonadiabatic transitions in a Z_1eZ_2 basis

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An asymptotic theory of quasiclassical type is constructed for the quasistationary states and branch points of terms in the problem of two Coulomb centers. In the adiabatic approximation of atomic collision theory, the branch points and the parameters of quasistationary states, respectively, determine the electron transitions between two bound states and between a bound state and the continuous spectrum.

I. INTRODUCTION

The probabilities of nonadiabatic transitions in diatomic quasimolecular systems are determined by the parameters of the branch points of $E(R)$ potential curves in the complex plane of the internuclear spacing R and also, for transitions into a continuous spectrum, by the parameters of quasistationary states.[1,2] An extremely topical question in this area is the study of the branch points and quasistationary states of the simplest diatomic system—the problem of two Coulomb centers Z_1eZ_2. For one thing, this model brings out some basic general features of term behavior in the complex plane R which are also characteristic of more complex systems; for another, the Hamiltonian of the Z_1eZ_2 system is frequently used as an adiabatic in the solution of actual cases. A very important and useful property of the Z_1eZ_2 system is the possibility of separating the variables,[3,4] which greatly simplifies its theoretical study.

Complex branch points of potential curves in the Z_1eZ_2 system were first found numerically, and the earliest studies of them are in Refs. 5–7; their quasistationary states were studied in Refs. 8 and 9. In the present paper it is shown that their occurrence in the quantum problem Z_1eZ_2 is closely bound up with cases of what is called *limiting motion* in the classical description of this system. They have, in fact, been studied by Legendre and are described in monographs on celestial mechanics (cf., e.g., Ref. 10) with the sole limitation that celestial mechanics, unlike atomic physics, treats both centers as centers of attraction. The special cases indicated occur on confluence of the turning points of the equations of motion. On the basis of classical analysis we have obtained uniform asymptotic formulas for the wave function in the problem of two Coulomb centers, corresponding in particular to the limiting trajectories, and also formulas for branch points and quasistationary states. Comparison with results obtained numerically shows that these formulas have high accuracy over a fairly wide range of variation of the parameters of the problem.

II. LIMITING MOTION IN THE PROBLEM OF TWO COULOMB CENTERS

The problem of the motion of a particle with unit mass and charge $e=-1$ in the field of two charges Z_1eZ_2 which are separated by a distance R permits separation of the variables in prolate spheroidal coordinates:

$$\xi=(r_1+r_2)/R,\quad 1\le\xi\le\infty$$

$$\eta=(r_1-r_2)/R,\quad 1\le\eta\le-1$$

$$\phi=\arctan(y/x),\quad 0\le\phi\le2\pi\ ,$$

where r_1, r_2 are the distances of the particle from centers 1 and 2. Separation of the variables is possible because, in addition to the Hamiltonian

$$H=\tfrac{1}{2}p^2-\frac{Z_1}{r_1}-\frac{Z_2}{r_2} \tag{1}$$

and the projection L_z of the moment of the internuclear axis, the problem contains a further integral of motion, the separation constant Λ (Ref. 3):

$$\Lambda = L^2 + ZR\left[\frac{Z_1}{r_1} - \frac{Z_2}{r_2}\right] + \tfrac{1}{4}R^2(p_z^2 - 2H) \ . \qquad (2)$$

In the quantum-mechanical description, the wave function, which is the eigenfunction of the three commuting observables H, Λ, L_z, is expressed as a product

$$\Psi(\mathbf{r}) = [(\xi^2-1)(1-\eta^2)]^{-1/2}U(\xi)V(\eta)\exp(im\phi)$$

(m being the azimuthal quantum number) in which the "radial" function $U(\xi)$ and the "angular" function $V(\eta)$ satisfy the following system of equations:[4]

$$\left[\frac{d^2}{d\xi^2} + \frac{1}{\hbar^2}\left[c^2 + \frac{a\xi-\lambda}{\xi^2-1}\right] + \frac{1-m^2}{(\xi^2-1)^2}\right]U(\xi) = 0 \ , \qquad (3)$$

$$\left[\frac{d^2}{d\eta^2} + \frac{1}{\hbar^2}\left[c^2 + \frac{b\eta+\lambda}{1-\eta^2}\right] + \frac{1-m^2}{(1-\eta^2)^2}\right]V(\eta) = 0 \ , \qquad (4)$$

subject to the condition of their being finite for $\xi = 1$, and $\eta = -1, +1$. In Eqs. (3) and (4) we have used the definitions

$$c^2 = \tfrac{1}{2}ER^2, \quad a = (Z_1+Z_2)R, \quad b = (Z_2 - Z_1)R \ ,$$

where E is the total energy and λ is an eigenvalue of the operator Λ in (2). If the energy is negative we replace c^2 by $p^2 = -c^2 = -ER^2/2$.

In this paper we study asymptotics of quasiclassical type ($\hbar \to 0$) for the solutions of the system (3),(4) where c^2, a, b, and λ are of order $O(1)$, $L_z = O(\hbar)$, i.e., $m = O(1)$. It is therefore suitable to write dependences on $\hbar$ in explicit form, not using a system of units in which $\hbar = 1$. The case we are studying is most important in practical applications. In the classical limit ($\hbar \to 0$) it corresponds to motion with zero projection of moment on the internuclear axis ($L_z = \hbar m \to 0$) where all trajectories lie in a plane passing through this axis. The classical equations of motion in terms of the variables ξ, η can then be written as functions of the corresponding generalized velocities on ξ and η:

$$v_\xi = \frac{d\xi}{dt} = \frac{4(\xi^2-1)}{R^2(\xi^2-\eta^2)}[c^2 - Q(\xi)]^{1/2} = \frac{4\{(\xi^2-1)[c^2(\xi^2-1)+a\xi-\lambda]\}^{1/2}}{R^2(\xi^2-\eta^2)} \ , \qquad (5)$$

$$v_\eta = \frac{d\eta}{dt} = \frac{4(1-\eta^2)}{R^2(\xi^2-\eta^2)}[c^2 - P(\eta)]^{1/2} = \frac{4\{(1-\eta^2)[c^2(1-\eta^2)+b\eta+\lambda]\}^{1/2}}{R^2(\xi^2-\eta^2)} \ , \qquad (6)$$

where the effective angular potential $P(\eta)$ and radial potential $Q(\xi)$ have the form

$$P(\eta) = -\frac{b\eta+\lambda}{1-\eta^2} = \frac{b-\lambda}{2(1+\eta)} - \frac{b+\lambda}{2(1-\eta)} \ , \qquad (7)$$

$$Q(\xi) = -\frac{a\xi-\lambda}{\xi^2-1} = \frac{-(a+\lambda)}{2(\xi+1)} - \frac{(a-\lambda)}{2(\xi-1)} \ . \qquad (8)$$

To the principal order in $\hbar$ the effective potentials of the quantum equations (3),(4) agree with $Q(\xi)$ and $P(\eta)$. Figures 1–3 show them for different relations between a, b, and λ.

These figures clearly illustrate the special cases of which the quasiclassical analysis is the subject of this work. These all involve confluence of the roots of the fourth-degree polynomials appearing under radical signs in the expressions (5) for v_ξ and (6) for v_η. It is a special feature of the generalized velocities v_ξ and v_η that they vanish not only at the classical turning points $\xi_1, \xi_2, \eta_1, \eta_2$ where the generalized moments $p_\xi = [c^2 - Q(\xi)]^{1/2}$ and $p_\eta = [c^2 - P(\eta)]^{1/2}$ vanish, but also at $\xi = -1, +1$ and $\eta = -1, +1$. These roots are not dependent on the parameters. Unlike them the roots $\xi_1, \xi_2, \eta_1, \eta_2$ vary with the parameters and can merge, both with one another and the roots ± 1. We shall consider four cases of confluence of these roots: case I, confluence of η_1 and η_2, corresponding to motion at an energy coinciding with the top of the potential barrier in the angular equation (Fig. 1, curve 5); case II, convergence of η_2 to -1, corresponding to coincidence of the top of the barrier with the $\eta = -1$ pole in the angular equation (Fig. 1, curve 4); and the analogous cases for the radial equation: case III, confluence of ξ_1 and ξ_2 (Fig. 2, curve 3); case IV, convergence of ξ_2 to the $\xi = 1$ pole (Fig. 2, curve 2 and Fig. 3, curve 2). Cases of triple confluence will not be considered in this work.

Case I. Confluence of η_1 and η_2 occurs if $\lambda > b$ in the angular equation. $P(\eta)$ then has a maximum at an internal point of the interval $[-1,1]$, at $\eta = \eta_m$:

$$\eta_m = -\frac{b}{\lambda + (\lambda^2 - b^2)^{1/2}} \ ,$$

$$P(\eta_m) = -\tfrac{1}{2}[\lambda + (\lambda^2 - b^2)^{1/2}] \ .$$

Since $P(\eta_m) < 0$ the analysis of this case requires us to

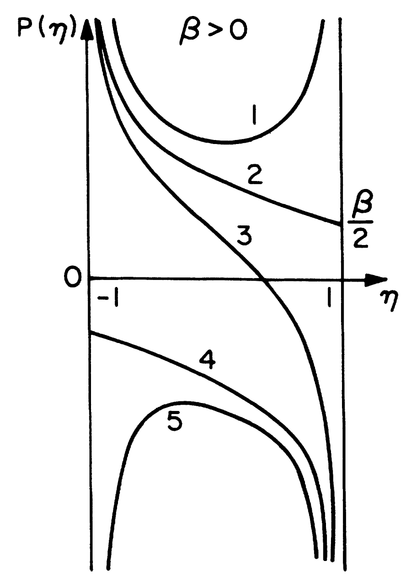

FIG. 1. Effective angular potential $P(\eta)$ (7) at $b > 0$ in the cases (1) $\lambda < -b$, (2) $\lambda = -b$, (3) $-b < \lambda < b$, (4) $\lambda = b$, (5) $\lambda > b$.

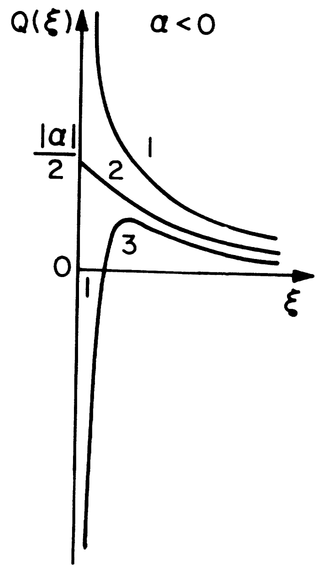

FIG. 2. Effective radial potential $Q(\xi)$ (8) for $a<0$ in the cases (1) $\lambda<a$, (2) $\lambda-a$, (3) $\lambda<a$.

consider only motion with negative energy, $p^2=-ER^2/2>0$. The roots η_1,η_2 are given by the expression

$$\eta_{1,2}=-\frac{b}{2p^2}\pm\left[1+\frac{b^2}{4p^2}-\frac{\lambda}{p^2}\right]^{1/2} . \tag{9}$$

They are real if the energy is less than the potential maximum $[p^2+P(\eta_m)>0]$ and complex for motion above the barrier $[p^2+P(\eta_m)<0]$. At $p^2=-P(\eta_m)=\frac{1}{2}[\lambda+(\lambda^2-b^2)]^{1/2}$ the roots coincide, $\eta_1=\eta_2=\eta_m$. The classical trajectory then has the form shown in Fig. 4: the particle oscillates about a ξ coordinate and in terms of η

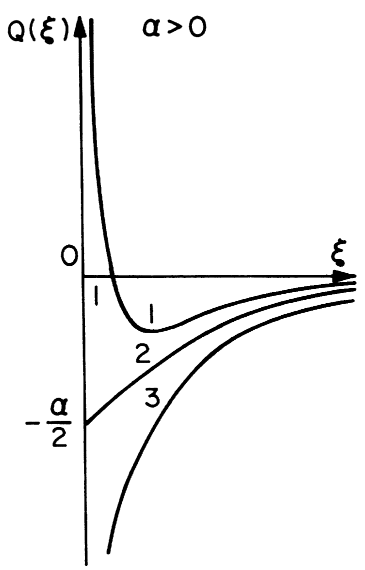

FIG. 3. Effective radial potential $Q(\xi)$ (8) for $a>0$ in the cases (1) $\lambda>a$, (2) $\lambda=a$, (3) $\lambda<a$.

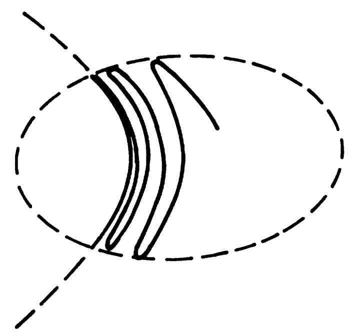

FIG. 4. Classical trajectory of the particle at an energy coinciding with the top of the potential barrier in the angular equation.

infinitely slowly approaches the value $\eta=\eta_m$ while, as follows from the equations of motion (5),(6), the time diverges logarithmically as $\eta(t)\to\eta_m$: $t\sim\ln|\eta-\eta_m|$. In the quantum case (see Sec. III) this situation is expressed by the occurrence of general branch points at potential curves having the same quantum number n_ξ. These occur in the complex plane R at distances of order $O(\bar{h})$ from the real axis.

Case II. The top of the barrier coincides with the $\eta=-1$ end of the interval when $\lambda=b$. One of the roots η_1,η_2 then coincides with the root $\eta=-1$ and the Coulomb potential singularity $P(\eta)$ vanishes at this point (Fig. 1, curve 4). Of physical relevance are the negative energies for which the point $\eta=-1$ is classically attainable and coincides with the greater root η_2, while the lesser root η_1 lies in the nonphysical region $\eta<-1$. This occurs at values of p satisfying $0<p^2<b/2$ (when $p^2\to b/2$ we have triple confluence). The corresponding classical trajectory is shown in Fig. 5. Motion of this trajectory is such that the particle oscillates about a ξ coordinate and in terms of η infinitely slowly approaches the value $\eta=-1$ $[t\sim\ln(1+\eta)]$. In the quantum case (Sec. IV) this situation, as in case I, leads to the appearance of general branch points at potential curves having the same n_ξ in the complex plane R at distances of order $O(\bar{h})$ from the real axis.

Case III. In the radial equation the barrier exists only at $\lambda<a$ and $a<0$, where the total charge corresponds to repulsion (Fig. 2, curve 3). The potential $Q(\xi)$ then has a maximum at the point

$$\xi_m=\frac{a}{\lambda+(\lambda^2-a^2)^{1/2}}$$

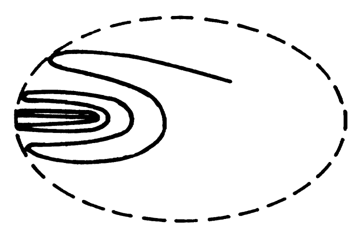

FIG. 5. Classical trajectory of the particle when the top of the potential barrier in the angular equation coincides with the $\eta=1$ pole.

and has the value

$$Q(\xi_m)=\tfrac{1}{2}[\lambda+(\lambda^2-a^2)^{1/2}] \ .$$

Since $Q(\xi_m)>0$ the turning points ξ_1,ξ_2 coincide only at positive energies $c^2=1/2ER^2>0$, i.e., in the case of scattering. The roots ξ_1,ξ_2 are given by the expression

$$\xi_{1,2}=-\frac{a}{2c^2}\pm\left[1+\frac{a^2}{4c^4}-\frac{\lambda}{c^2}\right]^{1/2} . \qquad (10)$$

They are real if $c^2-Q(\xi_m)<0$, complex if $c^2-Q(\xi_m)>0$, and equal if $c^2=Q(\xi_m)=-\frac{1}{2}[\lambda+(\lambda^2-a^2)^{1/2}]$, in which case $\xi_1=\xi_2=\xi_m$. The classical trajectory is shown in Fig. 6. Moving on this curve, the particle rebounds an infinite number of times from a hyperbola corresponding to the turning point in the angular equation. During this process it approaches, in terms of ξ, the value $\xi=\xi_m$ in such a way that the time diverges logarithmically. In the quantum treatment of the scattering problem in this case (Sec. V) a series of quasistationary states appear with lifetimes of order $O(\hbar^{-1})$.

Case IV. With $\lambda=a$ in the radial equation one of the roots ξ_1,ξ_2 merges with the pole $\xi=1$ and the Coulomb potential singularity $Q(\xi)$ vanishes at this point.

If the total charge corresponds to repulsion, $Z_1+Z_2<0$, $a<0$, singularities at $\lambda=a$ occur only in the scattering problem, and then at an energy for which $c^2>|a|/2$. The particle rebounds infinitely many times either from the two hyperbolae $\eta=\eta_1$, $\eta=\eta_2$ corresponding to turning points in the angular equation (this occurs when the changes Z_1,Z_2 are both negative, cf. Fig. 7), or from one hyperbola if in the angular equation there is only one turning point inside $(-1,1)$ (i.e., if $Z_2>0>-Z_2>Z_1$, (cf. Fig. 8). The ξ coordinate of the particle then approaches the value $\xi=1$ at infinite length. In the quantum treatment of the problem this leads to the occurrence of quasistationary states (Sec. VI).

If the total charge corresponds to attraction $Z_1+Z_2>0$ then with $\lambda=a$ and positive energy the trajectory appears in the case $Z_1>0$, $Z_2>0$ as a spiral with an infinite number of turns enclosing a segment of a straight line joining the nuclei (Fig. 9), and in the case $Z_2>0>Z_1>-Z_2$ as the curve shown in Fig. 8 and al-

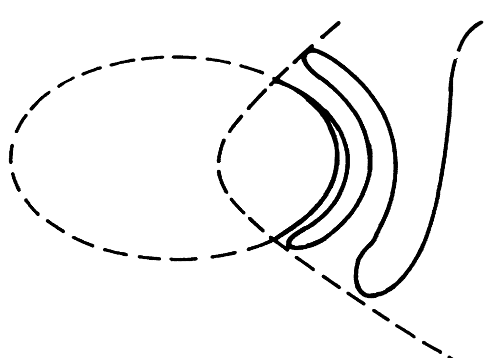

FIG. 6. Classical trajectory of the particle at an energy coinciding with the top of the potential barrier in the radial equation.

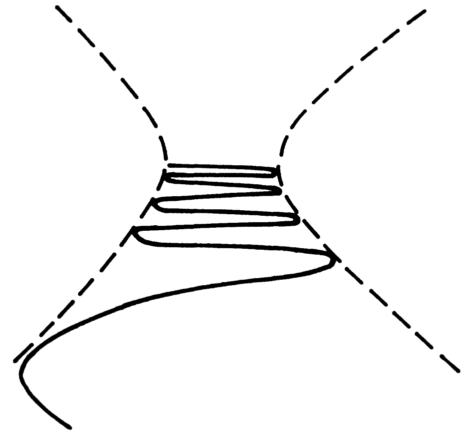

FIG. 7. Classical trajectory of the particle when the turning point z_1 coincides with the pole $\zeta=1$ in the radial equation at $0>Z_2\geq Z_1$ and $c^2>0$.

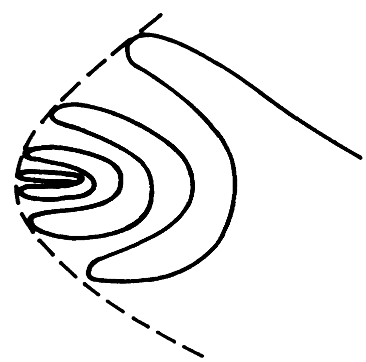

FIG. 8. Same as Fig. 7 at $Z_2>0>-Z_2>Z_1$ and $c^2>0$.

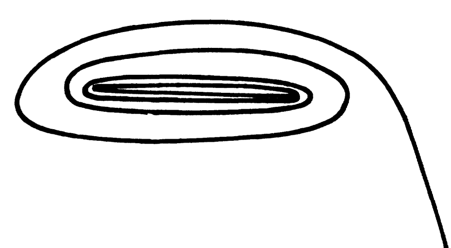

FIG. 9. Same as Fig. 7 at $Z_2\geq Z_1>0$ and and $c^2>0$.

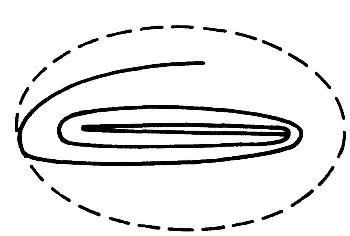

FIG. 10. Same as Fig. 7 at $Z_2\geq Z_1>0$ and and $c^2<0$.

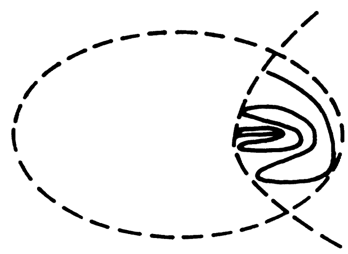

FIG. 11. Same as Fig. 7 at $Z_2>0>-Z_2>Z_1>0$ and $c^2<0$.

ready discussed. In the quantum treatment such limiting trajectories are also associated with quasistationary states (Sec. VII).

If $Z_1+Z_2>0$ then limiting trajectories exist even at negative energies. They correspond to finite motion and are shown in Fig. 10 for $Z_1>0$, $Z_2>0$ and in Fig. 11 for $Z_2>0>Z_1>-Z_2$. In the quantum problem (Sec. VI) these singularities appear as general branch points at potential curves having the same angular quantum number n_η.

At parameter ratios corresponding to confluence of roots in the classical equations of motion the quasiclassical formulas obtained for the problem of two Coulomb centers in Ref. 11 are not usable, and neither is the standard technique for constructing quasiclassical solutions. In this paper a reference equation method is used instead which makes it possible to construct a uniform asymptotics around a singularity and to describe the branch points or quasistationary states produced by this singularity.

III. UNIFORM QUASICLASSICAL ASYMPTOTICS OF SOLUTIONS OF THE ANGULAR PROBLEM NEAR THE TOP OF THE BARRIER

Let us write the angular equation (4) in the form

$$V''(\eta)+\left[\frac{1}{\hbar^2}q(\eta)+\frac{1-m^2}{(1-\eta^2)^2}\right]V(\eta)=0\ ,$$
$$q(\eta)=p^2(\eta-\eta_1)(\eta-\eta_2)/(1-\eta^2)\ . \qquad (11)$$

The classical turning points are given by the formula (9). In this case the reference equation, with two turning points which can merge and become complex on variation of the parameter ν, is the equation for the parabolic cylinder function:

$$W''(z)+\frac{1}{\hbar^2}(\tfrac{1}{4}z^2-\nu)W(z)=0\ .$$

Its solution is expressed by the Whittaker function[12]

$$W_{1,2}(z)=z^{1/2}M_{i(\nu/2\hbar),\mp 1/4}\left[i\frac{z^2}{2\hbar}\right]$$

with $W_1(z)$ even and $W_2(z)$ odd as $z\to -z$.

Following the usual scheme of the comparison equation method[4] we construct the solution of the initial equation (11) in the central region containing both turning points in the form

$$V(\eta)=\alpha V_1(\eta)+\beta V_2(\eta)\ ,$$
$$V_i(\eta)=[z'(\eta)]^{-1/2}W_i(z(\eta))\ ,$$

where α and β have to be determined by matching with solutions satisfying the boundary conditions at $\eta=\pm 1$. The scale function $z(\eta)$ is found from the equations

$$[z'(\eta)]^2(\tfrac{1}{4}z^2-\nu)=q(\eta)+\hbar^2\frac{1-m^2}{(1-\eta^2)^2}-\tfrac{1}{2}\hbar^2\{z,\eta\}\ ,$$
$$\{z,\eta\}\equiv-\frac{3}{2}\left[\frac{z''}{z'}\right]^2+\frac{z'''}{z'}\ . \qquad (12)$$

It must also satisfy conditions of smoothness, which amounts to saying that the turning points of the initial and reference equations must coincide and permit a reliable choice of the parameter ν. Subject to these requirements $z(\eta,p,\lambda,b,m)$ and $\nu(p,\lambda,b,m)$ are found from Eqs. (12) as expansions in $\hbar^2$. In the highest order we obtain for ν an expression in terms of the elliptic integral

$$\nu=\frac{1}{\pi}\int_{\eta_1}^{\eta_2}\sqrt{-q(\eta)}d\eta\ . \qquad (13)$$

$z(\eta)$ is defined by the transcendental equation

$$\int_{2\sqrt{\nu}}^{z(\eta)}(\tfrac{1}{4}\tilde{z}^2-\nu)^{1/2}d\tilde{z}=\int_{\eta_2}^{\eta}[q(\tilde{\eta})]^{1/2}d\tilde{\eta}\ . \qquad (14)$$

Having obtained the asymptotic Whittaker function for a large argument[12] and also the formula (14) for $z(\eta)$ we can obtain expressions for $V_1(\eta)$ and $V_2(\eta)$ in the classically permitted regions far away from the turning points. To the right of the barrier ($z>0$)

$$V_{1,2}(\eta)=A_{1,2}q^{-1/4}\sin\left[\frac{1}{\hbar}\int_{\eta_2}^{\eta}[q(\tilde{\eta})]^{1/2}d\tilde{\eta}+\varphi_{1,2}\right]\ ,$$
$$\varphi_{1,2}=\frac{\nu}{2\hbar}\left[1-\ln\frac{\nu}{2\hbar}\right]+\arg\Gamma\left[\frac{1}{2}\pm\frac{1}{4}+\frac{i\nu}{2\hbar}\right]+\frac{\pi}{4}\pm\frac{\pi}{8}\ , \qquad (15)$$
$$A_{1,2}=\text{const}\ .$$

To the left of the barrier ($z<0$)

$$V_{1,2}(\eta)=\pm A_{1,2}q^{-1/2}\sin\left[\frac{1}{\hbar}\int_{\eta}^{\eta_1}[q(\tilde{\eta})]^{1/2}d\tilde{\eta}+\varphi_{1,2}\right]\ . \qquad (16)$$

In these formulas the estimate of the discarded term $O(\hbar)$ is uniform in ν, i.e., the formulas are valid both for finite ν and for ν close to zero. The Γ functions are nontrivial terms with respect to conventional quasiclassics and provide uniform asymptotics in the given region. In the formulas (15),(16) they are isolated in explicit form. And since these Γ functions have poles in the complex ν plane at $\nu=i\hbar/2$ and $\nu=3i\hbar/2$, the quasiclassical phase in the variation of ν in the neighborhood of $\nu=0$ changes very sharply. These poles are the cause of the occurrence of branch points on the potential-energy surfaces, which will be considered below.

The solution $V_-(\eta)$ which satisfies the boundary condition at $\eta=-1$ is constructed by using a Bessel equation as the reference equation. This enables us to take good account of the existence of a second-order pole caused by a centrifugal term not containing a large parameter. As the standard form we obtain

$$V_-(\eta)=[y'(\eta)/y(\eta)]^{-1/2}J_m\left[\frac{2}{\hbar}\sqrt{y(\eta)}\right],$$

where $J_m(x)$ is a Bessel function of the first kind[12] and the scale function $y(\eta)$ is defined to the first order by the formula

$$2\sqrt{y(\eta)}=\int_{-1}^{\eta}[q(\tilde\eta)]^{1/2}d\tilde\eta\ .$$

Far from the poles, in the left-hand region the asymptotic $V_-(\eta)$ has the form

$$V_-(\eta)=\text{const}\times q^{-1/4}\times\sin\left[\frac{1}{\hbar}\int_{-1}^{\eta}[q(\tilde\eta)]^{1/2}d\tilde\eta-\frac{\pi m}{2}+\frac{\pi}{4}\right].\qquad(17)$$

A function $V_+(\eta)$ which is finite for $\eta=1$ is obtained from $V_-(\eta)$ by the transformation $\eta\to-\eta$, $b\to-b$, which does not change the angular equation but relocates the end point of the interval. In this way we obtain in the right-hand region of connection

$$V_+(\eta)=\text{const}\times q^{-1/4}\sin\left[\frac{1}{\hbar}\int_{\eta}^{1}[q(\tilde\eta)]^{1/2}d\tilde\eta-\frac{\pi m}{2}+\frac{\pi}{4}\right].\qquad(18)$$

On connecting the solution $V(\eta)=\alpha V_1(\eta)+\beta V_2(\eta)$ to $V_-(\eta)$ and $V_+(\eta)$ and then eliminating α and β we obtain a quantization condition in the form of an equality of ratios of Wronskians:

$$\frac{[V_+,V_2]}{[V_+,V_1]}=\frac{[V_-,V_2]}{[V_-,V_1]}\ .$$

The Wronksians $[V_-,V_1],[V_-,V_2]$ are calculated using the asymptotic formulas (16),(17) for the left-hand region, while $[V_+,V_1],[V_+,V_2]$ are calculated using the asymptotic formulas (15),(18) for the right-hand region. The final version of the condition of quantization is

$$F(p,\sigma,\lambda)=\Phi_++\Phi_-+(-1)^{n_\eta}\arcsin\frac{\cos(\Phi_+-\Phi_1)}{[1+\exp(-2\pi\nu/\hbar)]^{1/2}}-\pi(n_\eta+\tfrac{1}{2})=0\ ,\qquad(19)$$

where n_η is the number of zeros of the angular function within the interval $[-1,1]$, and $\Phi_+(p,b,\lambda),\Phi_-(p,b,\lambda)$ are given by the following asymptotic formulas, which are uniform in a neighborhood of $\nu=0$:

$$\Phi_+=\frac{1}{\hbar}\int_{\eta_2}^{1}[q(\tilde\eta)]^{1/2}d\tilde\eta+\Phi_0\ ,$$

$$\Phi_-=\frac{1}{\hbar}\int_{-1}^{\eta_1}[q(\tilde\eta)]^{1/2}d\tilde\eta+\Phi_0\ ,\qquad(20)$$

$$\Phi_0\equiv\frac{\nu}{2\hbar}\left[1-\ln\frac{\nu}{\hbar}\right]+\tfrac{1}{2}\arg\Gamma\left[\frac{1}{2}+i\frac{\nu}{\hbar}\right]-\frac{\pi m}{2}\ .$$

Here η_1, η_2, and ν are given by the expressions (9) and (13).

These uniform asymptotic formulas take simpler forms both for energies far from the top of the barrier $[\nu=O(1)]$ and for energies close to it $[\nu=O(\hbar)]$.

Far away from the barrier, either above it or below, when $\eta_2-\eta_1$ and ν take values of unit order, Stirling's formula[12] can be used for the Γ function in (20) and the quantization condition (19) then coincides with the ones obtained in Ref. 11.

If, on the other hand, the energy is close to the barrier, $\eta_2-\eta_1$ and ν take small values and Striling's approximation for the Γ function is not usable. In that case we can simplify the elliptic integrals in the expressions (20) for Φ_+ and Φ_-. We introduce the notation

$$\eta_0=\tfrac{1}{2}(\eta_1+\eta_2)=-\frac{b}{2p^2}\ ,$$

$$\delta=\frac{p(\eta_2-\eta_1)^2}{8\hbar(1-\eta_0^2)^{1/2}}=\frac{p^2(1+\eta_0^2)-\lambda}{2p\hbar(1-\eta_0^2)^{1/2}}\ ,\qquad(21)$$

and consider the range of parameter values in which $\delta=O(1)$, that is, $\eta_2-\eta_1=O(\hbar^{-1/2})$, $\nu=O(\hbar)$. Substituting (21) in (18) and (20) and expanding the elliptic integrals into asymptotic series with $\hbar\to0$, $\eta_0=O(1)$, $\delta=O(1)$ we obtain

$$\nu=\hbar\delta(1+O(\hbar))\ ,\qquad(22)$$

$$\Phi_\pm=\frac{p}{\hbar}[(1-\eta_0^2)^{1/2}+\eta_0\arcsin\eta_0]-\tfrac{1}{2}\delta\ln\frac{8p}{\hbar}(1-\eta_0^2)^{3/2}+\tfrac{1}{2}\arg\Gamma(\tfrac{1}{2}+i\delta)\pm\frac{\pi p\eta_0}{2\hbar}-\frac{\pi m}{2}\ ,\qquad(23)$$

for $\Phi_\pm$. An important point to note is that (23) can be obtained more simply than from (20) by directly constructing an asymptotic solution of the angular problem by the comparison equation method for the range of parameters where $\eta_2-\eta_1=O(\hbar^{1/2})$. This is done in the Appendix.

All these formulas can be simplified for identical centers, $Z_1=Z_2$, $b=0$. In this case we have $\eta_1=\eta_2$, $\eta_0=0$, $\Phi_+=\Phi_-$ and the quantization condition (19) can be written in the form

$$\int_{\eta_2}^{1}\sqrt{q(\eta)}d\eta+\frac{1}{2}V\left[1-\ln\frac{V/\hbar}{2}\right]+\hbar\arg\Gamma\left[\frac{1}{2}\pm\frac{1}{4}+i\frac{V/\hbar}{2}\right]=\pi\hbar\left[\eta_2+\frac{m+1}{2}\pm\frac{1}{8}\right],\qquad(24)$$

where

$$\delta=\frac{2}{\pi}\int_0^{\eta_2}\sqrt{-q(\eta)}d\eta,\quad \eta_2=(1-\lambda/p^2)^{1/2}\ ,$$

n_2 being the parabolic quantum number. The upper sign in (24) corresponds to u symmetry, the lower sign to g symmetry. If the energy is close to the top of the barrier (23) is converted to the form

$$p-\tfrac{1}{2}\delta\hbar\ln\left[\frac{4p}{\hbar}\right]+\hbar\arg\Gamma\left[\frac{1}{2}\pm\frac{1}{4}-\frac{i\delta}{2}\right]=\pi\hbar\left[n_2+\frac{m+1}{2}\pm\frac{1}{8}\right] \quad (25)$$

and $\delta=(p^2-\lambda)/2\hbar p$.

The potential curves $E(R)$ of the two Coulomb center problem are obtained from the quantization condition (19), in which we have to substitute the quasiclassical solution of the radial spectral problem $\lambda=\lambda_{n_\xi,m}(p,a)$:

$$F(b,p,\lambda_{n_\xi,m}(p,a))=0\ . \quad (26)$$

At branch points we obviously have

$$\frac{dp}{dR}=\frac{d}{dR}[\tfrac{1}{2}R\sqrt{-2E(R)}]\to\infty \quad (26a)$$

(because near a branch point $-R_B$, $E=E_B+\text{const}\times\sqrt{R-R_B}$). This condition leads to the equation

$$\frac{\partial F}{\partial p}+\frac{dF}{\partial\lambda}\frac{\partial}{\partial p}\lambda_{n_\xi,m}(p,a)=0\ . \quad (27)$$

The branch points are found as roots of the system of transcendental equations (26),(27) and, as analysis shows, they lie at a distance of the order of $O(\hbar)$ from the real R axis. It is found that the T and P series of branch points (to use a terminology introduced in Ref. 6) are respectively associated with the poles of the Γ function and the poles of the argument of the arccos function in Eq. (19).

IV. UNIFORM QUASICLASSICAL ASYMPTOTICS OF SOLUTIONS OF THE ANGULAR PROBLEM IN THE NEIGHBORHOOD OF $\lambda=b$

In this case, as was shown in Sec. III, the negative energies for which $p^2<b/2$ are also of interest. The situation is characterized by the fact that with $\lambda=b$ the Coulomb singularity of the angular potential $P(\eta)$ changes sign at the point $\eta=-1$. This causes a jump of $\pi/4$ in the phase of the quasiclassical function.[1] The true phase does not have this jump. Its uniform quasiclassical asymptotic in the neighborhood of $\lambda=b$ is constructed by the comparison equation method.

In the neighborhood of $\eta=-1$ the reference equation has to be the Whittaker equation

$$W''(z)+\left[\frac{1}{\hbar^2}\left[-p^2+\frac{b}{2}+\frac{k}{z}\right]+\frac{1-m^2}{4z^2}\right]W(z)=0\ . \quad (28)$$

which enables us to allow properly for the turning point η_2, which passes through the value $\eta=-1$ at $\lambda=b$, and for the influence of the second-order pole associated with the centrifugal term not containing $\hbar$. The Whittaker function is a solution of (28) which is regular at $z=0$.

In accordance with Ref. 4 we construct a solution of the angular equation which is finite at $\eta=-1$ in the form

$$V_-(\eta)=[z'(\eta)]^{-1/2}M_{-ik/\hbar\gamma,m/2}\left[\frac{i}{\hbar}\gamma z(\eta)\right]\ ,\qquad \gamma\equiv(2b-4p^2)^{1/2}\ . \quad (29)$$

The scale function $z(\eta)$ and the parameter κ are found as usual in the form of power series in $\hbar^2$ from an equation analogous to (12) allowing for the requirements of smoothness of $z(\eta)$. To the first order κ is given by

$$\kappa=-\frac{\gamma}{\pi}\int_{-1}^{y_2}\sqrt{-q(y)}dy\ , \quad (30)$$

while the function $z(\eta)$ is implicitly defined by

$$\int_{-4\kappa/\gamma^2}^{z(\eta)}\left[\frac{\gamma^2}{4}+\frac{\kappa}{z'}\right]^{1/2}dz'=\int_{\eta_2}^{\eta}\sqrt{q(y')}dy'\ . \quad (31)$$

The formulas (30) and (31) are valid from large negative $\lambda-b$ to large positive $\lambda-b$, including $\lambda=b$, at which the turning point passes through the value $\eta=-1$. For $\lambda>b$ we have $\eta_2<-1$, $\kappa>0$, and for $\lambda<b$ we find $\eta_2>-1$, $\kappa<0$.

Using the relations (29)–(31) and the asymptotic formula for the Whittaker function with large argument[12] we obtain an asymptotic expression, uniform in the neighborhood of $\lambda=b$, for $V_-(\eta)$ in the classically permitted region—the region in which it has to match with the solution $V_+(\eta)$ which satisfies the boundary condition at $\eta=1$. We have

$$V_-(\eta)=\text{const}\times q^{-1/4}\sin\left[\frac{1}{\hbar}\int_{\eta_2}^{\eta}\sqrt{q}\,dy+\chi-\frac{\pi}{4}(m-1)\right]\ ,$$
$$\chi\equiv-\frac{\kappa}{\hbar\gamma}\left[1-\ln\left[-\frac{\kappa}{\hbar\gamma}\right]\right]+\arg\Gamma\left[\frac{m+1}{2}-\frac{i\kappa}{\hbar\gamma}\right]\ . \quad (32)$$

An asymptotic expression for $V_+(\eta)$ was constructed in the preceding section and is given in the matching relation by (18).

On matching the solutions $V_-(\eta)$ (32) and $V_+(\eta)$ (18) we obtain a quantization condition in the form

$$\frac{1}{\hbar}\int_{\eta_2}^{1}\sqrt{q(y)}dy+\chi-\pi\left[n_\eta-\frac{3m-2}{4}\right]=0\ . \quad (33)$$

This asymptotic formula simplifies in the case that $\lambda-b$ is of the same order as λ and b [$\lambda-b=O(1)$], and also in the case that the order of $\lambda-b$ is less than that of λ and b [$\lambda-b=O(\hbar)$].

If $\lambda-b=O(1)$ the turning point η_2 lies at a finite distance from -1 and κ is of order $O(1)$. The condition (33) then becomes the usual condition[11] both for $\lambda>b$ ($\kappa>0$) and for $\lambda<b$ ($\kappa<0$).

If λ is close to b, however, suitable formulas can be obtained by assuming $\lambda-b=O(\hbar)$ and using the notation

$$\mu=(b/2p^2)^{1/2},\quad \epsilon=(b-\lambda)/2\hbar(b+\lambda-4p^2)^{1/2}$$

[ϵ is of order $O(1)$]. The elliptic integral in (33) then simplifies and the quantization condition takes the form

$$\frac{2}{\hbar}p[(\mu^2-1)^{1/2}+\mu^2\arcsin\mu^{-1}] -\epsilon\ln\left[\frac{16p}{\mu^2\hbar}(\mu^2-1)^{3/2}\right] +\arg\Gamma\left[\frac{m+1}{2}+i\epsilon\right]-\pi\left[n_\eta+\frac{3m-2}{4}\right]=0 . \quad (34)$$

The potential curves of the Z_1eZ_2 system are found from (33) or (34) after substitution in these equations of the quasiclassical solution on the boundary-value problem for the radial equation, i.e., $\lambda=\lambda_{n_\xi,m}(p,a)$. As in case I (Sec. III), the confluence of the roots η_2 and $\eta=-1$ is associated with the occurrence of general branch points on therms with different n_η in the complex R plane. These lie in the neighborhood of poles of $\Gamma((m+1)/2+i\epsilon)$ and are found from the system of equations (26),(27) using as the function $F(p,b,\lambda)$ the left-hand side of (33) or (34).

V. UNIFORM QUASICLASSICAL ASYMPTOTICS OF SOLUTIONS OF THE RADIAL PROBLEM NEAR THE TOP OF THE BARRIER

The technique used for constructing a uniform asymptotic expansion of the solution of the radial equation near the top of the barrier (Sec. II, case III, Fig. 2, curve 3) is basically the same as in the analogous equation for the angular equation (Sec. III). The difference lies in the fact that in the radial case motion near the top of the barrier corresponds to a continuous spectrum function ($E>0$) which in the region to the right of the barrier does not have to satisfy the conditions of matching as in the angular equation. In this region we are now required to calculate an asymptotic of the radial function as $\xi\to\infty$.

We write the radial equation (3) in the form

$$U''(\xi)+\left[\frac{1}{\hbar^2}r(\xi)+\frac{1-m^2}{(\xi^2-1)^2}\right]U(\xi)=0 , \quad (35)$$

where

$$r(\xi)=c^2(\xi-\xi_1)(\xi-\xi_2)/(\xi^2-1)$$

and the classical turning point are given by (10). The solution in the region containing both turning points is constructed exactly as in Sec. III. We have

$$U(\xi)=\alpha U_1(\xi)+\beta U_2(\xi) ,$$

$$U_{1,2}(\xi)=[z'(\xi)z(\xi)]^{-1/2}M_{i\mu/2\hbar,\pm1/4}\left[\frac{i}{2\hbar}z^2(\xi)\right] ,$$

where α and β are constants whose ratio α/β is determined from the conditions of matching with a solution regular at $\xi=1$, and $M_{\kappa,m}(\chi)$ is a Whittaker function.[12] The index μ and the scale function $z(\xi)$ are defined to the first order by

$$\mu=\frac{1}{\pi}\int_{\xi_1}^{\xi_2}[-r(\tilde\xi)]^{1/2}d\tilde\xi , \quad (36)$$

$$\int_{2\sqrt{\mu}}^{z(\xi)}(\tfrac{1}{4}\tilde z^2-\mu)^{1/2}=\int_{\xi_2}^{\xi}\sqrt{r(\xi')}d\xi' . \quad (37)$$

These formulas are valid both below the top of the barrier ($\mu>0$, ξ_1,ξ_2 real), and above it ($\mu>0$, ξ_1,ξ_2 complex), and also when the roots ξ_1,ξ_2 coincide ($\mu=0$).

In classically permitted regions far from the turning points the asymptotics of the functions $U_1(\xi)$ and $U_2(\xi)$ are given by formulas analogous to (15) and (16). On the right of the barrier ($z>0$)

$$U_{1,2}(\xi)=C_{1,2}r^{-1/4}\sin\left[\frac{1}{\hbar}\int_{\xi_2}^{\xi}\sqrt{r(\xi')}d\xi'+\phi_{1,2}\right] ,$$
$$\phi_{1,2}=\frac{\mu}{2\hbar}\left[1-\ln\frac{\mu}{2\hbar}\right]+\arg\Gamma\left[\tfrac{1}{2}\pm\tfrac{1}{4}+\frac{i\mu}{2\hbar}\right]+\frac{\pi}{4}\pm\frac{\pi}{8} , \quad (38)$$

and on the left of the barrier ($z<0$)

$$U_{1,2}(\xi)=\pm C_{1,2}r^{-1/4}\sin\left[\frac{1}{\hbar}\int_{\xi}^{\xi_1}\sqrt{r(\xi')}d\xi'+\Phi_{1,2}\right] , \quad (39)$$

where C_1 and C_2 are constants.

A solution $U_-(\xi)$ regular at $\xi=1$ is constructed by means of a Bessel function like $U_-(\xi)$ in Sec. III. In the sewing region—between the pole $\xi=1$ and the ξ_1 turning point—the $U_-(\xi)$ asymptotic has the form

$$U_-=\text{const}\times r^{-1/4}\sin\left[\frac{1}{\hbar}\int_1^{\xi}\sqrt{r(\xi')}d\xi'-\frac{\pi m}{2}+\frac{\pi}{4}\right] . \quad (40)$$

On sewing the functions $U(\xi)=\alpha U_1(\xi)+\beta U_2(\xi)$ and $U_-(\xi)$ together, using Eqs. (39) and (40) for them, we obtain, for the ratio α/β,

$$\frac{\alpha}{\beta}=-\frac{[U_2,U_-]}{[U_1,U_-]}=\frac{\sin[\phi+\arg\Gamma(\frac{3}{4}+i(\mu/2\hbar))+\frac{3}{8}\pi]}{\sin[\phi+\arg\Gamma(\frac{1}{4}+i(\mu/2\hbar))+\frac{5}{8}\pi]}\frac{C_2}{C_1} ,$$

where

$$\phi=\frac{1}{\hbar}\int_1^{\xi_1}\sqrt{r(\xi)}d\xi+\frac{\mu}{2\hbar}\left[1-\ln\frac{\mu}{2\hbar}\right]-\frac{\pi m}{2} . \quad (41)$$

The spheroidal phase Δ is defined by means of an asymptotic expression for $U(\xi)$ as $\xi\to\infty$ (Ref. 4):

$$U(\xi)\xrightarrow[\xi\to\infty]{}\text{const}\times\sin\left[\frac{c}{\hbar}\xi+\frac{a}{2c\hbar}\ln\frac{2c\xi}{\hbar}+\Delta-\frac{\pi}{2}(n_\eta+m)\right] . \quad (42)$$

Using the results obtained for $U_1(\xi)$, $U_2(\xi)$ (38), and for (41), it is not hard to obtain an expression for the S matrix:

$$e^{2i\Delta}=e^{2i(\chi+\phi)}\frac{\Gamma^{-1}(\frac{1}{2}-i(\mu/\hbar))+(2\pi)^{-1/2}\exp[-2i\phi+\pi\mu/2\hbar+(i\mu/\hbar)\ln 2]}{\Gamma^{-1}(\frac{1}{2}+i(\mu/\hbar))+(2\pi)^{-1/2}\exp[2i\phi+\pi\mu/2\hbar-(i\mu/\hbar)\ln 2]}\ , \tag{43}$$

where

$$\chi=\frac{\pi}{4}+\frac{1}{\hbar}\left[\int_{\xi_2}^{\infty}\left[\sqrt{r_\xi}-c-\frac{a}{2c\xi}\right]d\xi+\frac{\mu}{2}\left[1-\ln\frac{2\mu}{\hbar}\right]-c\xi_2-\frac{a}{2c}\ln\left[\frac{2c\xi_2}{\hbar}\right]\right]\ . \tag{44}$$

This asymptotic expression is uniform in the neighborhood of $\mu=0$. It simplifies both for μ of unit order and for small μ. When μ is of order $O(1)$ we can use Stirling's formula for $\Gamma(\frac{1}{2}\pm i\mu/\hbar)$ and (43) becomes the usual quasiclassical expression.[11] For small μ suitable formulas can be obtained by treating μ as of order $O(\hbar)$, which corresponds to a short distance between the roots, $\xi_2-\xi_1=O(\hbar^{1/2})$. Introducing the notation

$$\xi_0=\tfrac{1}{2}(\xi_1+\xi_2)=-\frac{a}{2c^2}\ ,$$
$$\rho=\frac{c(\xi_2-\xi_1)^2}{8\hbar(\xi_0^2-1)^{1/2}}=\frac{c^2(\xi_0^2+1)+\lambda}{2\hbar c(\xi_0^2-1)^{1/2}}\ , \tag{45}$$

and expanding the elliptic integrals in (36), (41), and (43) in asymptotic series with $\hbar\to 0$, $\xi_0=O(1)$, $p_0=O(1)$ we obtain

$$\mu=\hbar\rho\ , \tag{46}$$

$$\phi=\frac{c}{\hbar}\{\xi_0\ln[\xi_0+(\xi_0^2-1)^{1/2}]-(\xi_0^2-1)^{1/2}\}$$
$$-\rho\ln\left[\frac{2c}{\hbar}(\xi_0^2-1)^{3/4}\right]-\frac{\pi m}{2}\ , \tag{47}$$

$$\chi=\frac{c}{\hbar}\left[\xi_0\ln\frac{c}{\hbar}[\xi_0-(\xi_0^2-1)^{1/2}]-(\xi_0^2-1)^{1/2}\right]$$
$$-\rho\ln\left[\frac{4c}{\hbar}(\xi_0^2-1)^{3/4}[\xi_0-(\xi_0^2-1)^{1/2}]\right]+\frac{\pi}{4}\ . \tag{48}$$

From (43) we see that the S matrix has poles at complex values of the parameters for which the denominator in (43) becomes zero. These occur close to the poles of $\Gamma(\frac{1}{2}+i\mu/\hbar)$—where the exponential becomes equal to $\Gamma(\frac{1}{2}+i\mu/\hbar)$. The equation defining the poles of the S matrix thus has the form

$$\frac{1}{\sqrt{2\pi}}\Gamma\left[\tfrac{1}{2}+\frac{i\mu}{\hbar}\right]\exp\left[\frac{\pi\mu}{2\hbar}+i\left[2\phi-\frac{\mu}{\hbar}\ln 2\right]\right]=-1\ . \tag{49}$$

To find the positions of the poles in the three-dimensional (3D) Z_1eZ_2 problem, i.e., the relation between c,a,b (or between E,R,Z_1,Z_2) for which the S matrix has a pole, we need to solve (49) together with the quasiclassical quantization condition.

VI. UNIFORM QUASICLASSICAL ASYMPTOTICS OF SOLUTIONS OF THE RADIAL PROBLEM IN THE NEIGHBORHOOD OF $\lambda=a$

In the case of positive energies (when with $a<0$ the inequality $c^2>|a|/2$ must be satisfied), with $\lambda=a$ the greater of the roots ξ_1,ξ_2 (10) coincide with the $\xi=1$ pole, i.e., the root ξ_2, so that there are no other turning points in the physical region $\xi>1$ (Fig. 2, curve 2; Fig. 3, curve 2). A uniform asymptotic of the solution of the radial equation, regular at $\xi=1$, is then constructed by means of the Whittaker function exactly as in the case $\lambda=b$ for the angular equations (Sec. IV):

$$V(\xi)=[z'(\xi)]^{-1/2}M_{i(\gamma/\hbar),m/2}\left[\frac{i}{\hbar}(4c^2+a+\lambda)^{1/2}z(\xi)\right]\ . \tag{50}$$

To the first order in $\hbar$ the index γ is equal to

$$\gamma=\frac{1}{\pi}\int_1^{\xi_2}\left[\frac{\lambda-a\xi}{\xi^2-1}-c^2\right]^{1/2}d\xi \tag{51}$$

and the scale function $z(\xi)$ is defined implicitly by

$$\int_0^{z(\xi)}\left[c^2+\frac{a+\lambda}{4}-(4c^2+a+\lambda)^{1/2}\frac{\gamma}{z'}\right]^{1/2}dz'$$
$$=\int_1^{\xi}\left[c^2+\frac{a\tilde{\xi}-\lambda}{\tilde{\xi}^2-1}\right]^{1/2}d\tilde{\xi}\ . \tag{52}$$

In this approximation the phase Δ defined by (42) is equal to

$$\Delta=\lim_{\xi'\to\infty}\frac{1}{\hbar}\int_{\xi_0}^{\xi'}\left[c^2+\frac{a\xi-\lambda}{\xi^2-1}\right]^{1/2}d\xi-c\xi'$$
$$-\frac{a}{2c}\ln\frac{2c\xi'}{\hbar}+\frac{\gamma}{\hbar}\left[1-\ln\frac{\gamma}{\hbar}\right]+\arg\Gamma\left[\frac{m+1}{2}+i\frac{\gamma}{\hbar}\right]$$
$$+\frac{\pi}{4}(2n_\eta+m+1)\ . \tag{53}$$

It is uniform in the neighborhood of $\lambda=a$ and is valid for both positive and negative a (in the latter case, however, only for $|a|<2c^2$—as $c^2\to-|a|/2$ we have triple confluence of the roots in the classical problem—Sec. II). The expression (53) simplifies both for large and for small $|\lambda-a|$.

If $\lambda-a$ is small compared with λ and a, suitable formulas can be obtained if we suppose that $\lambda-a$ is of order $O(\hbar)$. Introducing the notation

$$q=\frac{\lambda-a}{c},\quad \rho=\left[1+\frac{\lambda+a}{4c^2}\right]^{1/2},$$

and expanding the elliptic integrals (51) and (53) with $\hbar\to 0$, $p=O(1)$, $q=O(\hbar)$, we obtain

$$\Delta=\frac{c}{\hbar}(1-2\rho)-\frac{a}{2c\hbar}\ln\frac{c}{\hbar}(1+\rho)^2-\frac{q}{4\hbar\rho}\ln\frac{c}{\hbar}\frac{16\rho^3}{(1+\rho)^2}+\arg\Gamma\left[\frac{m+1}{2}+i\frac{\gamma}{\hbar}\right]+\frac{\pi}{4}(2n_\eta+m+1)\,, \tag{54}$$

$$\gamma=\frac{q}{4\rho}-\frac{1}{32c\rho}\left[\frac{3q^2}{4\rho^4}(1-\rho^2)-\hbar^2(1-m^2)\left[3+\frac{1}{\rho^2}\right]\right]. \tag{55}$$

From (53) and (54) we see that the S matrix contains a factor of

$$\Gamma\left[\frac{m+1}{2}+i\frac{\gamma}{\hbar}\right]\Big/\Gamma\left[\frac{m+1}{2}-i\frac{\gamma}{\hbar}\right]$$

which has poles at pure imaginary γ.

$$\gamma=i\hbar\left[n'+\frac{m+1}{2}\right],\quad n'=0,1,2,\ldots . \tag{56}$$

These poles correspond to quasistationary states and are the quantum-mechanical expression of the singularities of classical motion at $\gamma=a$ (Sec. II, Figs. 7–11). To obtain the relation between E,R,Z_1,Z_2 which correspond to a quasistationary state we have to solve Eq. (56) with γ given by (51) or (55) and in place of γ the quasiclassical solution of the spectral problem for the angular equation, $\gamma=\gamma_{n_\eta,m}(c,b)$. The results of calculation of quasistationary states by the quasiclassical formulas, and the corresponding results of accurate numerical calculation, are shown in Fig. 12.

An important feature of these quasistationary states is that they occur in the fully 3D Z_1eZ_2 problem. In the isolated radial problem, considered with fixed real λ, the poles of the S matrix in the complex c plane are pure imaginary. In our case they are shifted towards the real axis because of the 3D problem λ is not an independent parameter but is dependent on c in a way determined by the solution of the angular problem.

The width of these quasistationary states is proportional to $\hbar$. In this respect they differ from the usual quasistationary states caused by the particles being locked into a region enclosed by the potential barrier, the width of which becomes exponentially small as $\bar{h}\to 0$.

When the total charge corresponds to attraction ($a>0$) the singularities associated with confluence of the roots at $\lambda=a$ occur not only in the continuous but also in the discrete spectrum, for energies such that $p^2<a/2$ (Fig. 3, curve 2). A quantization condition uniform in the neighborhood of $\lambda=a$ then has the form[7]

$$G(p,a,\lambda)=\frac{1}{\hbar}\int_{\xi_1}^{\xi_2}\left[-p^2+\frac{a\xi-\lambda}{\xi^2-1}\right]^{1/2}d\xi+g-\frac{\pi}{2}\left[2n\kappa_\xi+\frac{m}{2}-1\right], \tag{57}$$

where

$$g=\frac{\gamma}{\hbar}\left[1-\ln\frac{\gamma}{\hbar}\right]+\arg\Gamma\left[\frac{m+1}{2}+i\frac{\gamma}{\hbar}\right],$$

$$\gamma=\frac{1}{\pi}\int_1^{\xi_1}\left[\frac{\lambda-a\xi}{\xi^2-1}+p^2\right]^{1/2}d\xi\,,$$

ξ_1 being the left-hand turning point (Fig. 3, curve 2). As in all the other cases considered, this equation simplifies both for large $\lambda-a$ [$\gamma=O(1)$] and for small $\lambda-a$ [$\gamma=O(\hbar)$]. For $\gamma=O(1)$ the formula (57) becomes the usual quantization condition[11] both for $\gamma>0$ and for $\gamma<0$.

For $\gamma\approx\lambda-a=O(\hbar)$ it is convenient to introduce the notation

$$\xi_0=(a/2p^2)^{1/2},\quad \epsilon=\tfrac{1}{2}(\lambda-a)(a+\lambda-4p^2)^{-1/2}\,.$$

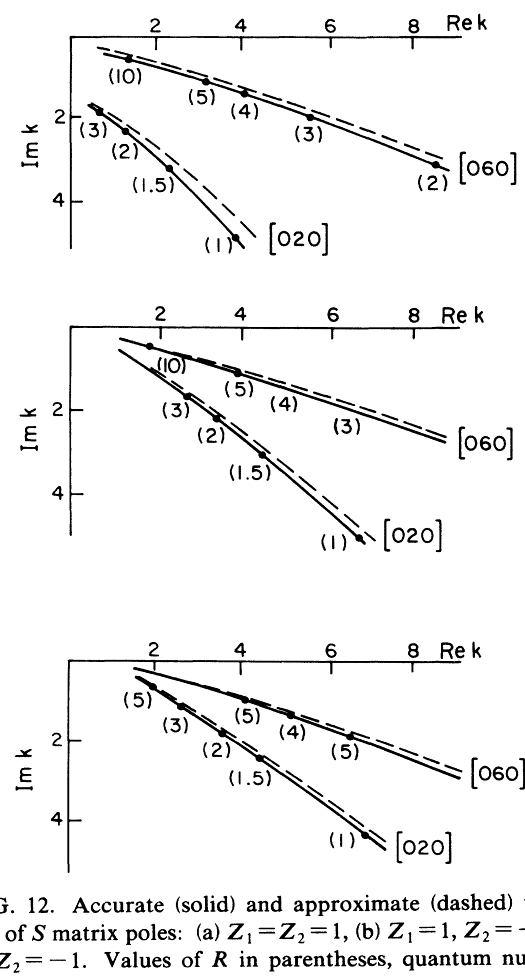

FIG. 12. Accurate (solid) and approximate (dashed) trajectories of S matrix poles: (a) $Z_1=Z_2=1$, (b) $Z_1=1$, $Z_2=-1$, (c) $Z_1=Z_2=-1$. Values of R in parentheses, quantum numbers n,l,m in square brackets.

Proceeding as in the derivative of (54) and expanding the elliptic integral in (57) with $\hbar \to 0$, $\epsilon = O(\hbar)$, $\xi_0 = O(1)$, we obtain a quantization condition in the form

$$p[-(\xi_0^2-1)^{1/2}+\xi_0^2 \arccos \xi_0^{-1}] - \epsilon \ln \left[\frac{16p}{\hbar \xi_0^2} (\xi_0^2 - 1)^{3/2} \right] + \hbar \arg \Gamma \left[\frac{m+1}{2} + i\frac{\epsilon}{\hbar} \right] = \bar{h} \pi \left[n_\xi + \frac{m}{4} - \frac{1}{2} \right] . \quad (58)$$

In complete analogy with the case considered in Sec. IV the Γ function in (57) and (58) is responsible for potential branch points in the complex R plane, but in this case they join energy curves having different radial quantum numbers n_ξ and the same angular quantum number n_η; these are known as the S series of branch points.[6] The position of such branch points is calculated from a system of equations similar to (26) and (27) except that in $G(p,a,\lambda)$ we have to substitute the solution of the angular spectral problem $\lambda = \lambda_{n_\eta,m}(p,b)$:

$$G(p,a,\lambda_{n_\eta,m}(p,b)) = 0 , \quad (59)$$

$$\frac{\partial G}{\partial p} + \frac{\partial G}{\partial \lambda} \frac{\partial \lambda_{n_\eta,m}(p,b)}{\partial p} = 0 . \quad (60)$$

VII. ENERGY SPECTRUM OF OUTGOING ELECTRONS

The quasiclassical formulas obtained for the S matrix in the preceding section permit analytical description not only of the quasistationary levels but also of the energy spectrum of electrons emitted in the process of ionization. The probability density of the electron energy distribution is expressed by the quantity $C_{nlm}^2(E)$ (Ref. 8), which is an analytic extension to positive E of the normalization constant of the bound state:

$$C_j^2 = 2\pi\kappa_j \int \Psi_j^2 d\mathbf{r} , \quad (61)$$

where the bound-state function at large r satisfies the condition

$$\Psi_j \xrightarrow[r \to \infty]{} Y(\hat{\mathbf{r}}) r^{[-1+(Z_1+Z_2)]/\kappa_j} e^{-\kappa_j r} ,$$

where $\kappa_j = \sqrt{-2E_j(R)}/\hbar$ and $Y(\hat{r})$ is an angular function normalized to unity on a sphere.

It is not difficult to find the relation of the C_j^2 to the residue of the S matrix at the pole $k = i\kappa_j$ corresponding to the bound state. It is entirely similar to the one which exists in the spherically symmetric case[13,14] and has the form ($k = \sqrt{2E}$)

$$C_j^2 = \pi (2i\kappa_j)^{2(Z_1+Z_2)/\kappa_j} \lim_{k \to i\kappa_j} (k - i\kappa_k) e^{2i\Delta} . \quad (62)$$

The quasistationary states which we have considered are an analytic continuation of the potential-energy curves $E_j(R)$ to the half axis $E > 0$ (Ref. 8). Furthermore, in this analytic continuation the relation (62) between $C^2(E)$ and the residue of the S matrix is maintained. Using this fact Eq. (62) [rather than (61)] enables us to determine C^2 in the complex R plane and with expression (53) for Δ we find

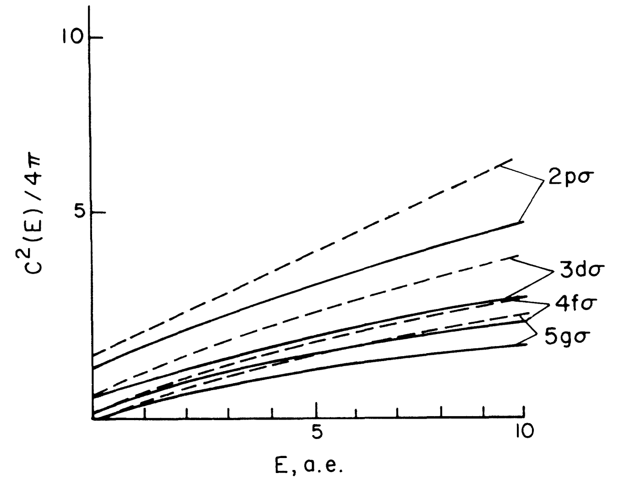

FIG. 13. Accurate values (solid) and values approximated by (63) (dashed) of $C^2(E)$ for the $H_2{}^+$ system. Classification of n,l,m states is the same as in Ref. 8.

$$\begin{aligned} C^2(E) &= 2\pi \left[\hbar^2 (n_\eta + m)! \frac{\partial \gamma}{\partial E} \right]^{-1} (2k)^{2i(Z_1+Z_2)/k} \times \exp(2i\Delta') , \\ \Delta' &= \Delta - \arg \Gamma \left[\frac{m+1}{2} + i\frac{\gamma}{\hbar} \right] , \\ \gamma &= \frac{1}{\pi} \int_1^{\xi_0} \left[\frac{\lambda - a\xi}{\xi^2 - 1} - c^2 \right]^{1/2} d\xi , \\ \xi_0 &= -\frac{a}{2c^2} + \left[\frac{a^2}{4c^2} + \frac{\lambda}{c^2} + 1 \right]^{1/2} . \end{aligned} \quad (63)$$

In Fig. 13 we compare the results of calculation of the $C_j(E)$ by the quasiclassical formula (63) with those of numerical calculation.

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APPENDIX

To construct an asymptotic solution close to the top of the barrier, in the range of parameters where $\eta_2 - \eta_1 = O(\hbar^{1/2})$ it is convenient to use the notation of (21) and rewrite the angular equation of the form

$$V''(\eta) + \left[\frac{p^2(\eta-\eta_0)^2 - 2p\hbar\delta(1-\eta_0^2)^{1/2}}{\hbar^2(1-\eta)^2} + \frac{1-m^2}{(1-\eta^2)^2} \right] V(\eta) = 0 . \quad (A1)$$

Here δ,η,m,p are quantities of the order of unity. The absolute value of ν is then of order $O(\hbar)$, so that the comparison equation for the central region containing both turning points can be written in the form

$$W''(z)+\frac{1}{\hbar^2}(\tfrac{1}{4}z^2-\hbar\kappa)W(z)=0\ , \tag{A2}$$

where κ can vary from zero to a value of the order of unity. The odd and even solutions of (A2) are given by the expression

$$W_{1,2}(z)=z^{-1/2}M_{i\kappa/2,\pm1/4}\left[i\frac{z^2}{2\hbar}\right]\ . \tag{A3}$$

As in Sec. III we construct the solution of Eq. (A1) in the central region in the form

$$\begin{aligned}&V(\eta)=\alpha V_1(\eta)+\beta V_2(\eta)\ ,\\ &V_i(\eta)=[z'(\eta)]^{-1/2}W_i(z(\eta))\ ,\end{aligned} \tag{A4}$$

where α and β have to be found from the condition of matching to solutions regular at $\eta=\pm1$. The scale function $z(\eta)$ satisfies the equation

$$\begin{aligned}(z')^2(\tfrac{1}{4}z^2-\hbar\kappa)-[p^2(\eta-\eta_0)^2-2p\delta\hbar(1-\eta_0^2)^{1/2}\\ +\hbar^2(1-m^2)/(1-\eta^2)]/(1-\eta^2)+\tfrac{1}{2}\hbar^2\{z,\eta\}=0\ ,\end{aligned} \tag{A5}$$

which is obtained by substituting (A4) in (A1) and using (A2). The function $z(\eta)$ and the index κ are constructed in the form of asymptotic series in powers of $\hbar$:

$$\begin{aligned}&z(\eta)=z_0(\eta)+\hbar z_1(\eta)+\hbar^2z_2(\eta)\ldots\ ,\\ &\kappa=\kappa_0+\hbar\kappa_1+\hbar^2\kappa_2\ldots\ .\end{aligned} \tag{A6}$$

Equation (A6) is substituted into Eq. (A5), and the coefficients of successive powers of $\hbar$ are compared. This leads to a recursive system of equations which must be solved under the condition that $Z(\eta)$ has no singularities. For the principal terms in the expansion (A6) we obtain

$$\kappa_0=\delta\ ,$$

$$z_0^2=4p[(1-\eta_0^2)^{1/2}-(1-\eta^2)^{1/2}+\eta_0(\arcsin\eta_0-\arcsin\eta)]\ , \tag{A7}$$

$$z_0z_1=2\delta\ln\left[\frac{\{1-\eta\eta_0+[(1-\eta^2)(1-\eta_0^2)]^{1/2}\}z_0}{2\sqrt{2p}\,(\eta-\eta_0)(1-\eta_0^2)^{3/4}}\right]\ .$$

Using the asymptotic expressions for the Whittaker function with large argument,[12] i.e., the expressions (A6) and (A7) for $z(\eta)$ and κ, we obtain expressions for $V_1(\eta)$ and $V_2(\eta)$ in the classically permitted regions far from the turning points. On the right of the barrier, with $\eta>\eta_0$,

$$\begin{aligned}V_1(\eta)&=\text{const}\times(\eta-\eta_0)^{-1/2}(1-\eta^2)^{1/4}\\ &\quad\times\sin\left[\varphi(\eta)+\arg\Gamma\left[\frac{1}{4}+\frac{i\delta}{2}\right]+\frac{3\pi}{8}\right]\ ,\\ V_2(\eta)&=\text{const}\times(\eta-\eta_0)^{-1/2}(1-\eta^2)^{1/4}\\ &\quad\times\sin\left[\varphi(\eta)+\arg\Gamma\left[\frac{3}{4}+\frac{i\delta}{2}\right]+\frac{\pi}{8}\right]\ ,\end{aligned} \tag{A8}$$

where

$$\varphi(\eta)=\frac{z_0^2}{4\hbar}-\delta\ln\left|\left[\frac{p}{\hbar}\right]^{1/2}\frac{2(1-\eta_0^2)^{3/4}(\eta-\eta_0)}{(1-\eta\eta_0)+[(1-\eta_0^2)(1-\eta^2)]^{1/2}}\right|\ . \tag{A9}$$

On the left of the barrier, with $\eta<\eta_0$, the expression for $V_1(\eta)$ is the same as in (A8) while for $V_2(\eta)$ the sign changes.

A solution $V_-(\eta)$ satisfying the boundary condition at $\eta=-1$ is constructed as in Sec. III using as reference equation the Bessel equation

$$W''(y)+\left[\frac{p^2}{\hbar^2}\frac{1}{y}+\frac{1-m^2}{4y^2}\right]W(y)=0\ , \tag{A10}$$

$$W(y)=\sqrt{2}J_m(^2p\sqrt{y}\,/\hbar),\quad V_-=[y'(\eta)]^{-1/2}W(y(\eta))\ , \tag{A11}$$

where $J_m(x)$ is a Bessel function of the first kind. Substitution of (A11) in (A1) and using (A10) leads to an equation for the scale function $y(\eta)$:

$$(y')^2\left[\frac{p^2}{\hbar^2y}+\frac{1-m^2}{4y^2}\right]=\frac{p^2(\eta-\eta_0)^2-2p\hbar\delta(1-\eta_0^2)^{1/2}}{\hbar^2(1-\eta^2)}+\frac{1-m^2}{(1-y^2)^2}+\tfrac{1}{2}\{y,\eta\}\ . \tag{A12}$$

Its solution is constructed as an asymptotic series

$$y(\eta)=y_0(\eta)+\hbar y_1(\eta)+\hbar^2y_2(\eta)\ldots\ , \tag{A13}$$

in which the coefficients satisfy the boundary condition $y_i(-1)=0$. For the principal terms of (A13) we obtain

$$\begin{aligned}&\sqrt{y_0}=\frac{1}{2}\left[(1-\eta^2)^{1/2}+\eta_0+\left[\frac{\pi}{2}+\arcsin\eta\right]\right]\ ,\\ &y_1=p^{-1}\delta\sqrt{y_0}\ln\{|1-\eta\eta_0-\sqrt{[1-\eta^2)(1-\eta_0^2)]}|\eta-\eta_0|\}\ .\end{aligned} \tag{A14}$$

Using these expressions and the asymptotic form of the Bessel function[12] we obtain an asymptotic expression for $V_-(\eta)$ far from the pole, in the region where the solution $\alpha V_1+\beta V_2$ must be matched

$$V_-\approx\frac{(1-\eta^2)^{1/4}}{|\eta-\eta_0|^{1/2}}\sin\left\{\varphi+\delta\ln\left[2\left[\frac{p}{\hbar}\right]^{1/2}(1-\eta_0^2)^{3/2}\right]-\frac{z_0^2(0)+p(4+2\pi\eta_0)}{4\hbar}+\frac{\pi}{4}(2m-1)\right\} \tag{A15}$$

with $\varphi(\eta)$ given by (A9). A solution $V_+(\eta)$ satisfying the boundary condition at $\eta=+1$ is obtained from $V_-(\eta)$ by the transformation $\eta\to-\eta$, $\eta_0\to-\eta_0$. Far from the pole at $\eta=1$ the asymptotic of the solution for $V_+(\eta)$ has the form

$$V_+\approx\frac{(1-\eta^2)^{1/4}}{|\eta-\eta^0|^{1/2}}\sin\left\{\varphi+\delta\ln\left[2\left[\frac{p}{\hbar}\right]^{1/2}(1-\eta_0^2)^{3/4}\right]-\frac{z_0^2(0)+p(4-2\pi\eta_0)}{4\hbar}+\frac{\pi}{4}(2m-1)\right\}. \tag{A16}$$

When the solution $\alpha V_1+\beta V_2$ has been matched with the solution $V_-(\eta)$ on the left and with the solution $V_+(\eta)$ on the right, and α and β have been eliminated, the quantization condition has the form ($[A,B]$ is the Wronksian $A'B-AB'$)

$$[V_-,V_1][V_+,V_2]=[V_+,V_1][V_-,V_2]\ .$$

On calculating the Wronksians in this formula by means of the asymptotic expressions (A8), (A9), (A15), and (A16) we obtain the quantization condition in the form (19) with $\Phi_\pm$ given by (23)

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