A QUASICLASSICAL APPROXIMATION IN THE TWO-CENTER PROBLEM

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The problem of two Coulomb centers is investigated in the quasiclassical approximation. Interpolation quantization formulas are obtained which are valid for any distance between the centers, and expressions for the wave functions are also obtained. Comparison with the results of an exact calculation shows that the quasiclassical approximation is quite accurate even for terms with low quantum numbers.

SEVERAL quantum-mechanical problems lead to the so-called two center problem, i.e., to the determination of the wave functions and the energy levels of a charged particle moving in the field of two fixed Coulomb centers with charges Z_1 and Z_2.

A particular case of this problem—the hydrogen molecular ion—has been investigated by many authors. (We note that even prior to the creation of quantum mechanics this problem has been investigated in Pauli's dissertation[1] on the basis of the old Bohr theory.) At present there exist numerical calculations of several low lying terms (cf., [2,3] and the references given there). Moreover, there exist many approximate methods of solving this problem (LCAO, UA, the variational method, perturbation theory), which, however, are valid only for $R \gg 1$ or $R \ll 1$ (R is the distance between the centers).

In this paper the two-center problem is discussed by means of a quasiclassical approximation. It is well known that the WKB method is effective for large quantum numbers, but one might expect that quasiclassical considerations will in this case give good results also in the case of small quantum numbers, since it is well known that in the field of one Coulomb center the quasiclassical energy levels coincide with the exact ones not only for $n \gg 1$, but also for $n = 1$, while the two-center problem in the limits $R \to 0$ and $R \to \infty$ reduces to the problem under consideration.

The use of the WKB method in the earlier papers encountered peculiar difficulties associated with the divergence of the phase integral for σ-terms. The reason for these difficulties lies, essentially, in the incorrect choice of the quasimomentum[4], which, as is well known, is not determined uniquely and admits the so called Langer transformation[5]. Different authors[6] have surmounted these difficulties in different ways, sometimes very cleverly,[1)] but no single unifying method has been proposed and, probably, as a result of this the WKB method has not been applied to this problem subsequently.

In the present paper it is shown that if the quasimomentum is chosen correctly the difficulties mentioned above do not arise and, therefore, we succeed in obtaining a closed solution of the problem over the whole range of variation of R with sufficiently good accuracy.

1. BASIC EQUATIONS

The Schrödinger equation for the two center problem has the form in atomic units $\hbar = e = m = 1$

$$-\frac{1}{2}\Delta\psi + \left(-\frac{Z_1}{r_1} - \frac{Z_2}{r_2}\right)\psi = E\psi. \tag{1}$$

In extended elliptic coordinates

$$\xi = \frac{r_1 + r_2}{R}, \quad \eta = \frac{r_1 - r_2}{R}, \quad \varphi = \operatorname{arc\,tg}\frac{y}{x} \qquad (2)^*$$

the equation is separable, and the normalized solution can be obtained in the form

$$\psi = NX(\xi)Y(\eta)e^{im\varphi}. \tag{3}$$

In this case we have

$$\frac{d}{d\xi}(\xi^2 - 1)\frac{dX}{d\xi} + \left(-p^2\xi^2 + b'\xi + A - \frac{m^2}{\xi^2 - 1}\right)X = 0, \tag{4}$$

[1)]For example, Kramers has utilized a rather unique method of regularization of the phase integral. It is of interest to note that the idea of the method is in general terms analogous to the idea of regularization in quantum field theory.

*arctg = tan^{-1}.

$$\frac{d}{d\eta}(1-\eta^2)\frac{dY}{d\eta}+\left(p^2\eta^2+b\eta-A-\frac{m^2}{1-\eta^2}\right)Y=0, \quad (5)$$

where A is the separation constant,

$$p^2=-R^2E/2=R^2\varkappa/4, \quad b=R(Z_2-Z_1),$$

$$b'=R(Z_2+Z_1).$$

The total energy is given by

$$W=E+Z_1Z_2/R. \quad (6)$$

An equation of the form

$$\frac{d}{dx}p(x)\frac{dy}{dx}+r(x)y=0 \quad (7)$$

by a change in the independent variable and in the dependent function

$$t=\chi(x), \quad y=u/[p(x)\chi'(x)]^{1/2} \quad (8)$$

is brought to a form convenient for the application of quasiclassical considerations:

$$d^2u/dt^2+q(t)u=0. \quad (7')$$

Since $\chi(x)$ is an arbitrary function such a reduction is not unique.

As has been shown previously [4], in the case when $p(x)$ has simple zeros [which are singular points of equation (7)] one should utilize the transformation

$$t=\int dx/p(x), \quad y(x)=u(t). \quad (8')$$

Such a replacement by removing the singular points of equation (7) to $t=\pm\infty$ guarantees the correct behavior of the quasiclassical solutions at the singular points and the correct phase far from the turning points. Moreover, as we shall show, (8′) also gives the correct behavior of the terms for $R\to 0$ and $R\to\infty$. Utilizing (8′) and returning to the original variables we obtain the quasiclassical solutions of (4) and (5) in the form

$$Y(\eta)=\frac{C_\pm}{[(1-\eta^2)Q(\eta)]^{1/2}}\exp\left\{\pm i\int_{\eta_1}^{\eta}Q(\eta)d\eta\right\}, \quad (9)$$

$$Q(\eta)=\left[\frac{p^2\eta^2+b\eta-A}{1-\eta^2}-\frac{m^2}{(1-\eta^2)^2}\right]^{1/2}$$

$$=\left[-p^2+\frac{p^2-A+b\eta}{1-\eta^2}-\frac{m^2}{(1-\eta^2)^2}\right]^{1/2}, \quad (9')$$

$$X(\xi)=\frac{C_\pm'}{[(\xi^2-1)R(\xi)]^{1/2}}\exp\left\{\pm i\int_{\xi_1}^{\xi}R(\xi)d\xi\right\}, \quad (10)$$

$$R(\xi)=\left[\frac{-p^2\xi^2+b'\xi+A}{\xi^2-1}-\frac{m^2}{(\xi^2-1)^2}\right]^{1/2}. \quad (10')$$

It can be easily seen that this form of quasimomenta coincides with their classical expressions in the Hamilton-Jacobi method [7].[2)]

The quantization conditions for the quasimomenta $R(\xi)$ and $Q(\eta)$ yield respectively the separation constants A_ξ and A_η as functions of the quantum numbers n_ξ, n_η, m and of the parameters p^2 and R, while the equation $A_\xi = A_\eta$ yields the electronic terms $E = E_{n_\xi n_\eta m}(R)$.

2. QUANTIZATION CONDITIONS

In Eq. (4) the function $[Q(\eta)]^2$ plays the role of an effective potential for zero quantization energy. Depending on the values of the parameters p^2 and A for $m \neq 0$ the potential can have the form I or II corresponding to the curves I and II shown in the lower part of Fig. 1.

In case I there exist two regions of classical motion $\eta_1 < \eta < \eta_2$ and $\eta_3 < \eta < \eta_4$ separated by a potential barrier. For $p^2 \gg 1$ this corresponds to the separated atom approximation. Case II for $p^2 \ll 1$ corresponds to the united atom approximation. (The special case $m = 0$ is shown in the upper part of Fig. 1. In this case $\eta_1 = -1$, $\eta_4 = 1$ become the extreme "turning points.")

Utilizing the expressions for A for $R \gg 1$ and $R \ll 1$ given, for example in [11], it can be shown that in these two limiting cases the motion is quasiclassical in case I ($p^2 \gg 1$, $A \gg 1$) correspondingly in the left hand side and the right hand side potential well if

$$m^2/(p^2-A\mp b)\ll 1-\eta^2\ll(p^2-A\mp b)/p^2, \quad (11)$$

i.e.,

$$(p^2-A-b)/p\approx 2(2n_2+|m|+1)\gg 1,$$

$$(p^2-A+b)/p\approx 2(2n_2'+|m|+1)\gg 1 \quad (11')$$

(n_2 and n_2' are the numbers of zeros of the wave function in each of the two wells); and in case II ($p^2 \ll 1$, $A < 0$) if

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2)Usually in the WKB method one utilizes the transformation

$$t=x, \quad y=u/\sqrt{p(x)}, \quad (8'')$$

and this leads in the present problem to quasimomenta which differ from (9′) and (10′) by the replacement $m^2 \to m^2 - 1$. In early papers [6] it is this particular circumstance that led to the difficulties mentioned in the Introduction. Similarly (8″) gave $m^2 - 1$ instead of m^2 in the quasiclassical discussion of the Stark effect in the hydrogen atom [8], and it was empirically established that the correct result is obtained by neglecting unity [9]. In exactly the same manner one proceeded by replacing $l(l+1) \to (l+\frac{1}{2})^2$ in the radial equation prior to the appearance of Langer's paper [10].

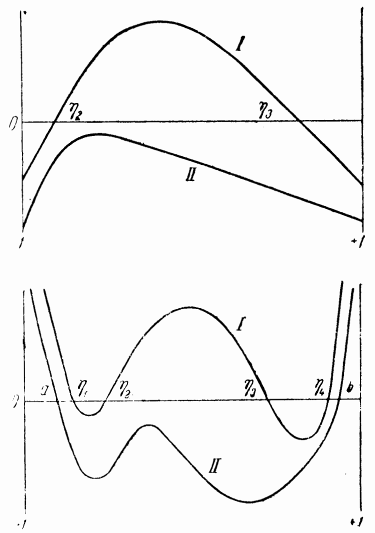

FIG. 1

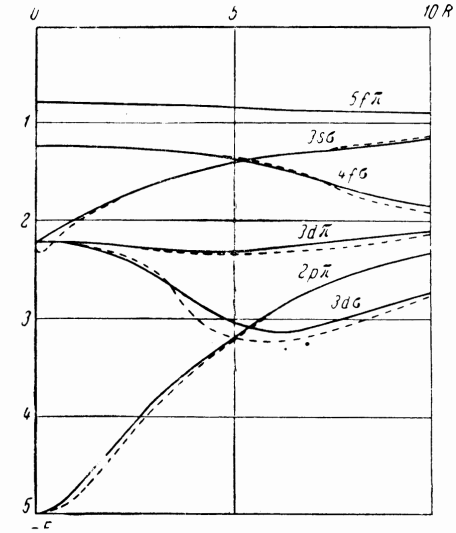

FIG. 2. The terms of the H_2^+ system. Solid lines-values from [3], dotted lines-values calculated according to (20). The $5f\pi$ term is calculated according to formulas (20).

$$1-\eta^2 \gg \frac{m^2}{p^2-A\mp b}, \qquad \frac{p^2}{p^2-A\mp b} \ll 1, \tag{12}$$

i.e.,

$$|A| \approx (n_\eta + |m|)(n_\eta + |m| + 1) \gg 1 \tag{12'}$$

(n_η is the number of zeros of the function in the common well).

In these limiting cases the quantization conditions can be simply written as conditions on the phase integrals over the range of quasiclassical motion in each of the wells (case I) or in the common well (case II). For each given term $E_{n_\xi n_\eta m}$ as R is varied case I goes over continuously into II. However, the usual quantization conditions are in this case, naturally, not "smoothly connected" at the top of the potential barrier since in this region they are not applicable at all. This is related to the fact that in the derivation of these conditions in case II reflection in the case of energy above the barrier is not taken into account, while in case I transmission at energies below the barrier is neglected. The two corrections being exponentially small far from the top of the barrier become quite significant near the top of the barrier. By utilizing successively the method of going around the turning points in the complex plane proposed by Zwaan[12], and the equation of continuity of current (as was done by Kemble[13]), one can easily obtain (cf., Appendix) interpolation formulas valid right up to the top of the barrier. We have in case I:

$$\cos(\omega_2 + \omega_2') = -\cos\lambda \cdot \cos(\omega_2 - \omega_2') \tag{13}$$

or*

$$\operatorname{ctg}\omega_2 \cdot \operatorname{ctg}\omega_2' = \operatorname{tg}^2(\lambda/2);$$

in case II

$$\cos\omega_0 = -\sin\varepsilon \cdot \cos(\omega - \omega') \tag{14}$$

or

$$\operatorname{ctg}\omega \cdot \operatorname{ctg}\omega' = \operatorname{tg}^2(\pi/4 - \varepsilon/2).$$

All the notation is defined in the Appendix.

For $R \to \infty$ the quantity $\lambda \to 0$ and for $R \to 0$ the quantity $\epsilon \to 0$. Therefore, formulas (13) and (14) go over into the usual quantization formulas. At the top of the barrier $\lambda = \epsilon = \pi/4$ [cf., (A.11)], i.e., formulas (13) and (14) become smoothly joined and coincide at that point with the exact quantization conditions obtained in this limiting case in the paper of Kramers and Ittman[14] 3) (cf., Figs. 2–4; the points of intersection of the exact and the quasiclassical terms correspond to the position of the top of the barrier). Thus, formulas (13) and (14) give an interpolation of the quantization conditions right up to the top of the barrier.

The effective potential $[R(\xi)]^2$ of equation (5) has the form of an ordinary well, and, therefore, the quantization conditions can be written down immediately:

$$\omega_1 = \pi(n_1 + 1/2), \qquad \omega_1 = \int_{\xi_1}^{\xi_2} R(\xi)\, d\xi. \tag{15}$$

*ctg = cot, tg = tan.

3)For energies lying near the top of the barrier ($|E - U_0| = S \to 0$) the latter can be approximated by a parabola. In this case the problem can be solved exactly in terms of parabolic cylinder functions. In this case the exact quantization conditions give $|\lambda - \pi/4| \approx S \ln S$, while formulas (A.11) (cf., below) yield $|\lambda - \pi/4| \sim S$, i.e., the results agree with logarithmic accuracy. However, far from the barrier the quantization formulas (13) and (14) go over into the usual formulas, while the "exact" ones are valid only near the top of the barrier.

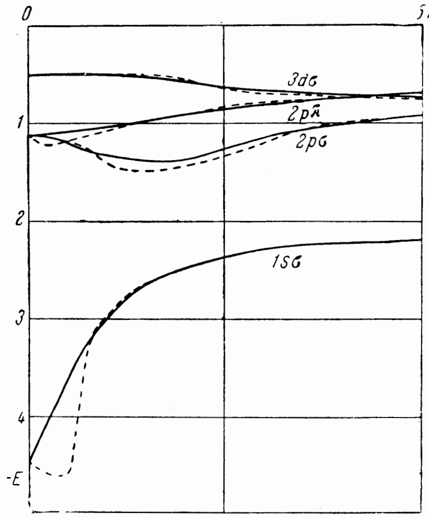

FIG. 3. The terms of the system $Z_1 = 1$, $Z_2 = 2$. Solid lines-according to [3], dotted lines-according to (13) and (14).

At the same time in the case $m \neq 0$ we always have $\xi_1 > 1$ (ξ_1 is the smallest positive root of the equation $R(\xi) = 0$). If $m = 0$, then $\xi_1 \to -1$ for $p^2 \to \infty$. For $\xi_1 < 1$ the lower limit in (15) must be set equal to unity. (We note that for values of parameters corresponding to $\xi_1 = 1$, the quasiclassical and the exact σ-terms coincide [with the exception of 1sσ, (cf., Figs. 2–4)].

3. EVALUATION OF E AND A IN LIMITING CASES

All the quantities in (13) and (14) are expressed in terms of complete elliptic integrals. But in the limiting cases $R \to 0$ and $R \to \infty$ it is simpler to start with the definitions utilizing for expansions into series relations (11) and (12). (In particular, sometimes it is very convenient to utilize Sommerfeld's method [15]).

For $R \to \infty$ one can quantize independently in each well; conditions (13) reduce to

$$\omega_2 = \pi(n_2 + 1/2), \quad \omega_2' = \pi(n_2' + 1/2). \qquad (13')$$

Then deep below the barrier we obtain as a result of quantization in the left hand well (up to fourth order terms):

$$\begin{aligned} A_\xi = {} & p^2 + 2p(2n_1 + |m| + 1) - R(Z_1 + Z_2) \\ & + 1/2\,(2n_1 + 1)(2n_1 + |m| + 1) - 1/2\,p^{-1}R(Z_1 + Z_2) \\ & \times(2n_1 + |m| + 1) - 1/16\,p^{-3}R^2(Z_1 + Z_2)^2(2n_1 + |m| + 1) \\ & - 1/8\,p^{-1}(2n_1 + 1)(2n_1 + |m| + 1)(2n_1 + 2|m| + 1) \\ & + 3/16\,p^{-2}R(Z_1 + Z_2)(2n_1 + |m| + 1)^2, \end{aligned} \qquad (16)$$

$$\begin{aligned} A_\eta = {} & p^2 - 2p(2n_2 + |m| + 1) - R(Z_2 - Z_1) \\ & + 1/2\,(2n_2 + 1)(2n_2 + |m| + 1) + 1/2\,p^{-1}R(Z_2 - Z_1) \\ & \times(2n_2 + |m| + 1) + 1/16\,p^{-3}R^2(Z_2 - Z_1)^2(2n_2 + |m| + 1) \\ & + 1/8\,p^{-1}(2n_2 + 1)(2n_2 + |m| + 1)(2n_2 + 2|m| + 1) \\ & + 3/16\,p^{-2}R(Z_2 - Z_1)(2n_2 + |m| + 1)^2. \end{aligned} \qquad (16')$$

Similar formulas are obtained for the right hand side well by replacing $Z_1 \to Z_2$, $n_2 \to n_2'$.

Expressions (16) and (16′) differ very little from those obtained in [16] even when $n_1 = n_2 = m = 0$. However, for the energy levels condition $A_\xi = A_\eta$ yields ($n = n_1 + n_2 + |m| + 1$)

$$E = -\frac{Z_1^2}{2n^2} - \frac{Z_2}{R} + \frac{3}{2}n(n_1 - n_2)\frac{Z_2}{Z_1 R^2}, \qquad (17)$$

i.e., the correct expression for the linear Stark effect [9] for arbitrary n.

For $R \to 0$ we obtain ($l = n_0 + |m|$, $N = n_1 + l + 1$)

$$\omega_0 = \pi(n_0 + 1/2), \qquad (14')$$

$$A_\eta = -\left(l + \frac{1}{2}\right)^2 + \frac{1}{2}p^2\left[1 - \frac{m^2}{(l + 1/2)^2}\right] - \frac{1}{8}\frac{R^2(Z_2 - Z_1)^2}{N^2} \times\left[1 - \frac{3m^2}{(l + 1/2)^2}\right], \qquad (18)$$

$$\sqrt{A_\xi} = \frac{Z_1 + Z_2}{\sqrt{-2E}} - \left(n_1 + \frac{1}{2}\right) - \frac{1}{4}\frac{p^2}{l + 1/2}\left[1 - \frac{m^2}{(l + 1/2)^2}\right] - \frac{1}{16}\frac{R^2(Z_1 + Z_2)^2}{(l + 1/2)^3}\left[1 - \frac{3m^2}{(l + 1/2)^2}\right], \qquad (18')$$

$$E = -\frac{(Z_1 + Z_2)^2}{2N^2} - \frac{R^2}{4}\frac{Z_1 Z_2 (Z_1 + Z_2)^2}{N^3(l + 1/2)^3}\left[1 - 3\frac{m^2}{(l + 1/2)^2}\right], \qquad (19)$$

in good agreement with [9].

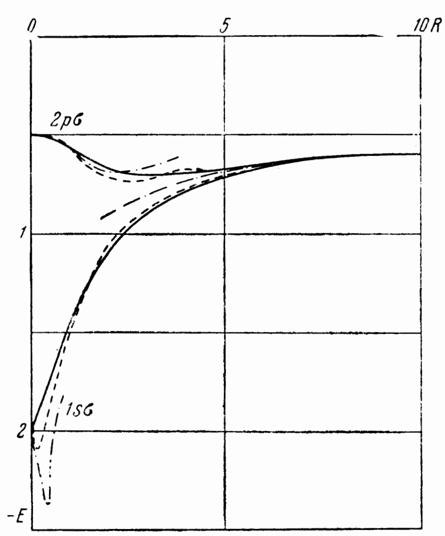

FIG. 4. The lower terms of H_2^+. Solid lines-values from [3], dotted lines-values calculated according to (20). Dot-dashed lines-calculations according to the usual quasiclassical formulas.

4. THE CASE $Z_1 = Z_2 = 1$

For the hydrogen molecular ion the quantization conditions (13) and (14) become greatly simplified:

$$\omega_0 = \pi(n_0 + 1/2) + (-)^{n_0}\varepsilon, \qquad \omega_1 = \pi(n_1 + 1/2),$$
$$\omega_2 = \pi(n_2 + 1/2) + (-)^{n_0}\lambda/2. \tag{20}$$

$n_0 = 2n_2$ for the symmetric term, $n_0 = 2n_2 + 1$ for the antisymmetric term. We obtain the splitting of these levels below the barrier for $m = 0$. From (20) we obtain

$$\Delta\omega_2 = \frac{\partial\omega_2}{\partial p}\Delta p + \frac{\partial\omega_2}{\partial A}\Delta A = \lambda,$$
$$\Delta\omega_1 = \frac{\partial\omega_1}{\partial p}\Delta p + \frac{\partial\omega_1}{\partial A}\Delta A = 0; \tag{21}$$

$$\Delta p = \lambda\frac{\partial\omega_1}{\partial A} \Big/ \frac{\partial(\omega_2, \omega_1)}{\partial(p, A)}; \tag{22}$$

$$\frac{\partial\omega_1}{\partial A} \approx \frac{\pi}{4p}, \quad \frac{\partial(\omega_2, \omega_1)}{\partial(p, A)} \approx -\frac{\pi^2}{4}\frac{n}{p^2}, \quad K = 2\frac{A}{p}B\left(\frac{\sqrt{A}}{p}\right), \tag{22'}$$

where B(k) is an elliptic integral [11].

Utilizing (6), (16′), and the properties of elliptic integrals we obtain

$$\Delta E = \frac{1}{\pi}\frac{\varkappa}{n}\left(\frac{8pe}{2n_2+1}\right)^{2n_2+1} e^{-2p} \tag{23}$$

and with the same degree of accuracy as in Stirling's formula

$$\sqrt{2\pi}\left(\frac{n_2 + 1/2}{e}\right)^{n_2+1/2} = n_2!,$$

we obtain for $n_2 \gg 1$ the formula from the paper of Smirnov [17] ($\kappa = -2E$)

$$\Delta E = -\frac{2\varkappa}{n}\frac{(4p)^{2n_2+1}}{n_2!n_2!}e^{-2p}. \tag{24}$$

Formula (24) is valid for $R \gg 1$ and for arbitrary n_2, formula (23) is valid for arbitrary R (up to the barrier) and $n_2 \gg 1$. For the ground state (23) yields

$$\Delta E = 4\pi^{-1}Re^{-R}, \tag{23'}$$

and formula (24) yields

$$\Delta E = 4e^{-1}Re^{-R}. \tag{24'}$$

For $R = 9$ it follows from (23′) that $\Delta E = 2.0 \times 10^{-3}$, while from (24′) we obtain $\Delta E = 2.3 \times 10^{-3}$. An exact calculation [3] leads to $\Delta E = 1.7 \times 10^{-3}$; without going to the limit ($n_2 \gg 1$) we obtain in accordance with formula (23) $\Delta E = 1.9 \times 10^{-3}$; an exact calculation in accordance with equations (20) yields $\Delta E = 1.5 \times 10^{-3}$. The fact that (24′) gives worse agreement with exact calculations compared to (23′) is apparently explained by the fact that for $R = 9$ the asymptotic region has not yet been reached.

5. COMPARISON WITH EXACT CALCULATIONS

The systems of transcendental equations (13), (15) and (14), (15) were solved numerically by an electronic computer by the method of minimization, for the first eight terms of the hydrogen molecular ion and for the system $Z_1 = 1$, $Z_2 = 2$. The results are shown in Figs. 2 and 3. We have also given there for comparison the exact results of the work of Bates et al. [3] It can be seen that the results agree well for $R \ll 1$ and $R \gg 1$, and also exactly at the barrier for $R = R_0$ (the agreement is better for $R > R_0$). In the immediate neighborhood of the barrier the agreement is worse, it is better for π-terms than for σ-terms, and among the latter it is better for p- and d-terms, than for s-terms, as should be expected from quasiclassical considerations. However, the relative error nowhere exceeds 5% (with the exception of the $1s\sigma$ term, $Z_1 = 1$, $Z_2 = 2$ where the error reaches 10%).

Figure 4 also shows the $2p\sigma$ and $1s\sigma$ terms of the H_2^+ system evaluated by three different methods: 1) exact calculation from [3], 2) calculation in accordance with formulas (20), 3) calculation using ordinary quasiclassical formulas. It can be seen that quantization in accordance with formulas (20) gives the best approximation.

6. WAVE FUNCTIONS

Utilizing the results in [4] we write out the normalized wave functions for the two center problem in the region of quasiclassical motion for the limiting cases of potentials I and II.

In case I far below the barrier we have in the left hand well ($\kappa = -2E$)

$$\psi_{n_1 n_2 m}(\xi, \eta, \varphi) = \frac{2}{\pi^{3/2}}\frac{\varkappa^{3/4}}{n^{1/2}}\frac{\cos(I_1(\xi) - \pi/4)}{[(\xi^2-1)R(\xi)]^{1/2}}\frac{\cos(I_2(\eta) - \pi/4)}{[(1-\eta^2)Q(\eta)]^{1/2}}, \tag{25}$$

where

$$I_1(\xi) = \int_{\xi_1}^{\xi} R(\xi)d\xi, \qquad I_2(\eta) = \int_{\eta_1}^{\eta} Q(\eta)d\eta.$$

Correspondingly in the right hand well we have obtained the same expression with the replacement $\kappa \to \kappa'$, $n \to n'$, $\eta_1 \to \eta_3$.

In case II far above the barrier we have

$$\psi_{Nlm}(\xi, \eta, \varphi) = \frac{2}{\pi^{3/2}}\frac{\varkappa^{3/4}(-A)^{1/4}}{[R(Z_2 + Z_1)]^{1/2}} \times \frac{\cos(I_1(\xi) - \pi/4)}{[(\xi^2-1)R(\xi)]^{1/2}}\frac{\cos(I_2(\eta) - \pi/4)}{[(1-\eta^2)Q(\eta)]^{1/2}}. \tag{26}$$

It can be shown that as $R \to 0$ Eq. (26) coincides with the normalized wave functions of a hydrogen-like atom of charge $Z_1 + Z_2$, while as $R \to \infty$ Eq. (25) coincides with the asymptotic expression for the wave function of an electron of an isolated atom in parabolic coordinates.

The functions (25) and (26) for $\xi \to 1$ and $\eta \to \pm 1$ have the correct behavior:

$$\psi(\xi, \eta, \varphi) \sim (\xi^2 - 1)^{m/2}(1 - \eta^2)^{m/2}.$$

Similarly for the wave functions of the continuous spectrum normalized to a δ-function of k (k is the electron momentum) we obtain (after replacing $p^2 \to -s^2$, $s = Rk/2$):

$$X(\xi) = \left(\frac{2s}{\pi}\right)^{1/2} \frac{2}{R} \frac{\cos(I_1(\xi) - \pi/4)}{[(\xi^2 - 1)R(\xi)]}, \tag{27}$$

$$Y(\eta) = \left(\frac{2}{\pi}\right)^{1/2} (-A)^{1/4} \frac{\cos(I_2(\eta) - \pi/4)}{[(1 - \eta^2)Q(\eta)]^{1/2}} \tag{28}$$

APPENDIX

We shall derive the quantization conditions for potential II (cf., Fig. 1) taking into account reflection above the barrier, and for potential I taking into account transmission below the barrier. A problem of this type has an exact meaning near the top of the barrier, where the coefficient of reflection above the barrier (and correspondingly the coefficient of transmission below the barrier) is not small, and taking it into account does not exceed the accuracy of the quasiclassical approximation. However, as long as the formulas obtained high above the barrier (and correspondingly deep below the barrier) go over into the usual quantization rules they can be regarded as interpolation formulas.

In the case under consideration of energy above the barrier there exist two real and two complex conjugate "turning points" $Q(\eta) = 0$; $\eta_1 = a$, $\eta_4 = b$, $\eta_{2,3} = \alpha \pm i\beta$ (cf., Fig. 1). Utilizing the complex turning point method proposed by Pokrovskiĭ and Khalatnikov[18] we can establish the connection between the quasiclassical solutions taken from different turning points:

$$\frac{1}{\sqrt{Q}} \exp\left\{i\int_a Q\,d\eta\right\} - ie^{2i\varphi_0}\frac{1}{\sqrt{Q}}\exp\left\{-i\int_a^\eta Q\,d\eta\right\} \leftarrow$$

$$\leftarrow e^{i(\varphi_0+\varphi_0')}\frac{1}{\sqrt{Q}}\exp\left\{i\int_b^\eta Q\,d\eta\right\}; \tag{A.1}$$

$$\varphi_0 = \int_a^{\eta_2} Q\,d\eta, \qquad \varphi_0' = \int_{\eta_2}^{b} Q\,d\eta \tag{A.2}$$

(a similar relation for the wave reflected to the right is obtained if we utilize the complex conjugate turning point η_3).

Formula (A.1) does not take into account the fact that the coefficient of the transmitted wave differs from unity, since this difference, being an exponentially small quantity of the second order far from the barrier, cannot be determined correctly. However, as Kemble has noted[13] the use of the condition of conservation of current enables one to extrapolate the quasiclassical formulas right up to the top of the barrier where the reflection coefficient is no longer small. Introducing the coefficient g into the incident wave (A.1) and determining it from the condition of the conservation of current we obtain finally for the waves travelling respectively to the right and to the left above the barrier:

$$g\frac{1}{\sqrt{Q}}\exp\left\{i\int_a^\eta Q\,d\eta\right\} - ie^{2i\omega}e^{-\delta}\frac{1}{\sqrt{Q}}\exp\left\{-i\int_a^\eta Q\,d\eta\right\} \leftarrow$$

$$\leftarrow e^{i(\omega+\omega')}\frac{1}{\sqrt{Q}}\exp\left\{i\int_b Q\,d\eta\right\}, \tag{A.3}$$

$$e^{i(\omega+\omega')}\frac{1}{\sqrt{Q}}\exp\left\{-i\int_a^\eta Q\,d\eta\right\} \to g\frac{1}{\sqrt{Q}}\exp\left\{-i\int_b^\eta Q\,d\eta\right\}$$

$$- ie^{2i\omega'}e^{-\delta}\frac{1}{\sqrt{Q}}\exp\left\{i\int_b Q\,d\eta\right\}, \tag{A.3'}$$

where

$$\omega = \int_a^\alpha Q\,d\eta - \int_0^\beta \operatorname{Im} Q(\alpha + it)\,dt,$$

$$\omega' = \int_\alpha^b Q\,d\eta + \int_0^\beta \operatorname{Im} Q(\alpha + it)\,dt, \quad \delta = \int_{-\beta} \operatorname{Re} Q(\alpha + it)\,dt,$$

$$g = (1 + e^{-2\delta})^{1/2}, \qquad \omega_0 = \omega + \omega' = \int_a Q\,d\eta. \tag{A.4}$$

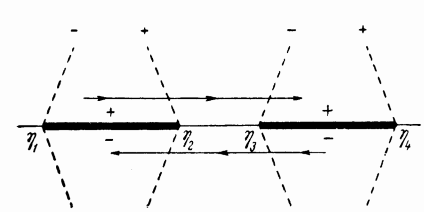

FIG. 5. Cuts in the complex plane shown by heavy lines. Dotted lines show the Stokes lines, i.e., lines along which the coefficients $a_\pm$ in the asymptotic solution at the turning points η_i:

$$\psi = \frac{1}{\sqrt{Q}}[a_+ \exp\{-it^{3/2}\} + a_- \exp\{it^{3/2}\}] \quad (t = |\eta - \eta_i|\, e^{i\varphi})$$

undergo a discontinuous change.

In the case of energy below the barrier there exist four turning points (cf., Fig. 1). By defining the cuts $Q(\eta)$ in the complex η-plane as in Fig. 5 and by continuing the solutions from the left hand "well" into the right hand "well" along the upper edge of the cut, and from the right hand "well" into the left hand "well" along the lower edge of the cut (again taking conservation of current into account) we obtain

$$e^{i(\omega_2+\omega_2')}e^{-K}\frac{1}{\sqrt{Q}}\exp\left\{-i\int_{\eta_1}^{\eta}Q\,d\eta\right\}\to h\frac{1}{\sqrt{Q}}\exp\left\{-i\int_{\eta_4}^{\eta}Q\,d\eta\right\}$$
$$-ie^{2i\omega_2'}\frac{1}{\sqrt{Q}}\exp\left\{i\int_{\eta_4}^{\eta}Q\,d\eta\right\}, \qquad (A.5)$$

$$h\frac{1}{\sqrt{Q}}\exp\left\{i\int_{\eta_1}^{\eta}Q\,d\eta\right\}-ie^{2i\omega_2}\frac{1}{\sqrt{Q}}\exp\left\{-i\int_{\eta_1}^{\eta}Q\,d\eta\right\}\leftarrow$$
$$\leftarrow e^{i(\omega_2+\omega_2')}e^{-K}\frac{1}{\sqrt{Q}}\exp\left\{i\int_{\eta_4}^{\eta}Q\,d\eta\right\}, \qquad (A.5')$$

where

$$\omega_2=\int_{\eta_1}^{\eta_2}Q\,d\eta,\quad \omega_2'=\int_{\eta_3}^{\eta_4}Q\,d\eta,\quad K=\int_{\eta_2}^{\eta_3}|Q|\,d\eta,$$
$$h=(1+e^{-2K})^{1/2}. \qquad (A.6)$$

It can be easily seen that (A.3) and (A.3′) coincide with (A.5) and (A.5′) after the replacement

$$\omega_2\to\omega,\quad \omega_2'\to\omega',\quad e^{-K}\to e^{\delta}. \qquad (A.7)$$

Therefore, in subsequent discussion we shall consider in detail only the pair (A.5) and (A.5′).

From the requirement of exponential damping of the solution outside the region of quasiclassical motion near the turning points η_1 and η_4 we must respectively choose the solutions

$$\cos\left(\int_{\eta_1}^{\eta}Q\,d\eta-\frac{\pi}{4}\right),\qquad C\cos\left(\int_{\eta_4}^{\eta}Q\,d\eta+\frac{\pi}{4}\right).$$

Apart from normalization we can obtain from (A.5) and (A.5′) the following correspondence between the solutions at the turning points η_1 and η_4:

$$\begin{pmatrix}\cos\left(\int_{\eta_1}^{\eta}Q d\eta-\frac{\pi}{4}\right)\\ \sin\left(\int_{\eta_1}^{\eta}Q d\eta-\frac{\pi}{4}\right)\end{pmatrix}\sim e^{K}\begin{pmatrix}h\sin(\omega_2+\omega_2')-\sin(\omega_2-\omega_2') & h\cos(\omega_2+\omega_2')+\cos(\omega_2-\omega_2')\\ -h\cos(\omega_2+\omega_2')+\cos(\omega_2-\omega_2') & h\sin(\omega_2+\omega_2')+\sin(\omega_2-\omega_2')\end{pmatrix}\begin{pmatrix}\cos\left(\int_{\eta_4}^{\eta}Q d\eta+\frac{\pi}{4}\right)\\ \sin\left(\int_{\eta_4}^{\eta}Q d\eta+\frac{\pi}{4}\right)\end{pmatrix}. \qquad (A.8)$$

For the required correspondence of the solutions

$$\cos\left(\int_{\eta_1}^{\eta}Q\,d\eta-\frac{\pi}{4}\right)\longrightarrow C\cos\left(\int_{\eta_4}^{\eta}Q\,d\eta+\frac{\pi}{4}\right)$$

it is necessary to set

$$h\cos(\omega_2+\omega_2')+\cos(\omega_2-\omega_2')=0. \qquad (A.9)$$

Similarly for the pair (A.3) and (A.3′)

$$g\cos(\omega+\omega')+e^{-\delta}\cos(\omega-\omega')=0. \qquad (A.10)$$

Introducing the notation

$$\operatorname{tg}\lambda=e^{-K},\qquad \operatorname{tg}\varepsilon=e^{-\delta}, \qquad (A.11)$$

we obtain formulas (13) and (14) given in the text. For $\delta\to\infty$ and $K\to\infty$ they reduce to the well-known ones.

The constant C is determined [utilizing (A.5), (A.5′) and (A.9)] from the condition

$$C^2=\frac{h+\cos^2\omega_2}{h+\cos 2\omega_2'}=\frac{\sin 2\omega_2}{\sin 2\omega_2'}. \qquad (A.12)$$

For the case $E > U_0$ (U_0 is the energy corresponding to the top of the potential barrier) we have an analogous formula with the replacement (A.7).

From (A.12) it can be seen that for $E \ll U_0$ the wave function of the level corresponding to the left hand well falls off exponentially towards the interior of the right hand well, since in that case

$$h\approx 1+{}^1/_2e^{-2K},\qquad \cos 2\omega_2\approx -1,$$
$$h+\cos 2\omega_2'\approx 1+\alpha,\qquad C\sim\pm e^{-K}.$$

In the case $E \gg U_0$ after the replacement (A.7) has been made we shall have $h\to(1+e^{2\delta})^{1/2}$. It can be see that $C\approx\pm 1$; the sign of C is determined in accordance with the rules given in [16].

[1] W. Pauli, Ann. Physik **68**, 177 (1922).

[2] E. Teller, Z. Physik **61**, 458 (1930). A Hylleraas, Z. Physik **71**, 739 (1931). S. K. Chakravarty, Phil. Mag. **28**, 423 (1939).

[3] Bates, Ledsham, and Stewart, Phil. Trans. Roy. Soc. London **A246**, 215 (1953). D. R. Bates and T. R. Carson, Proc. Roy. Soc. (London) **A234**, 207 (1954).

[4] L. I. Ponomarev, JINR Preprint P-1815, 1964.

[5] R. Langer, Trans. Am. Math. Soc. **37**, 397 (1935).

[6] M. Willstätter, Ann. Physik **10**, 873 (1931). E. M. Engers and H. A. Kramers, Z. Physik **82**, 328 (1933). E. Hellmig, Z. Physik **94**, 361 (1935).

[7] L. D. Landau and E. M. Lifshitz, Mekhanika (Mechanics), Gostekhizdat, 1958.

[8] C. Lanczos, Z. Physik **65**, 431 (1930).

[9] H. Bethe, Quantum Mechanics of the Simplest Systems (Russ. Transl. ONTI, 1935).

[10] R. E. Langer, Phys. Rev. **51**, 669 (1937).

[11] E. Jahnke and F. Emde, Tables of Functions (Russ. Transl. Fizmatgiz, 1959).

[12] A. Zwaan, Arch. Nederl. des Sciences **12**, 33 (1929).

[13] E. C. Kemble, Phys. Rev. **48**, 549 (1935); The Fundamental Principles of Quantum Mechanics, New York, Dover, 1958.

[14] H. A. Kramers and G. P. Ittman, Z. Physik **58**, 217 (1929).

[15] A. Sommerfeld, Atombau und Spektrallinien **1** (Russ. Transl. Gostekhizdat, Moscow, 1956).

[16] S. S. Gershteĭn and V. D. Krivchenkov, JETP **40**, 1491 (1961), Soviet Phys. JETP **13**, 1044 (1961).

[17] B. M. Smirnov, JETP **46**, 1017 (1964), Soviet Phys. JETP **19**, 692 (1964).

[18] V. L. Pokrovskiĭ and I. M. Khalatnikov, JETP **40**, 1713 (1961), Soviet Phys. JETP **13**, 1207 (1961).

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