Semiclassical and Adiabatic Approximation in Quantum Mechanics

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Contents

I. INTRODUCTION

In this notes we consider the semiclassical approximation (SA) in Quantum Mechanics. Though this approximation is presented in the most of textbooks on Quantum Mechanics, there is hardly any other topic which arises so many confusions. Often the authors know the correct result, but the derivation is impossible to understand. Even such brilliant textbooks as Landau and Lifshitz (1) and by Merzbacher (2) did not avoid substantial omissions and inaccuracies. Some special questions, especially related to the multi-dimensional version of the SA can be found in the book by Zeldovich and Perelomov (3). There exists a waste mathematical literature on the subject from which I can recommend the book by Maslov and Fedoryuk (4). Unfortunately this literature is not very useful for physicists because of excessive mathematical rigor and abundance of notations.

On the other hand, the SA plays a special role in Quantum Mechanics since it demonstrates in a simple analytical form basic phenomena: energy quantization, quantum tunnelling, resonance scattering and tunnelling, overbarrier reflection, Aharonov-Bohm effect. Its time-dependent modification, adiabatic approximation, allows to solve many problems in atomic and molecular physics and leads to mportant notions such as the Berry's phase. L. Landau and C. Zener proposed a simple theory of transitions at avoided two-level crossing, which plays fundamental role in theory of chemical reactions, atomic scattering, interaction of atoms with the resonant laser field, dynamics of disordered systems, quantum computing etc.

Besides that, the SA gives the energy spectrum with a reasonable accuracy even in the range where its validity is not guaranteed. It allows to calculate energy density for many systems including deterministic systems with chaotic spectrum and random systems. It is worthwhile to remind that the initial form of quantum theory of the atom by N. Bohr can be treated just as semiclassical approximation from the point of view of modern Quantum Mechanics.

In these notes we use the following system of references: equations inside a subsection are enumerated by the letter of the subsection and their numbers. An equation from another section is referred additionally by the section number.

A. Historical remarks.

Semiclassical approximation in Quantum Mechanics was formulated independently by G. Wentzel (Germany), H. Kramers (Holland) and L. Brilloin (France) in 1927 and was coined as the WKB approximation. In many books and articles this abbreviation is appended by the letter J from the left, honoring an English mathematician H. Jeffrys, who developed the approximation in 20th century. However, essential ideas of this approximation were formulated in the beginning of the XIX century by the famous mathematicians Cauchy and Bessel. Very important features of the SA were discovered by Stokes, who studied properties of the so-called Airy equation in the middle of the 19th century. The SA was applied to physical acoustic by Lord Rayleigh in the end of the XIX century. H. Poincare has formulated the SA as a series expansion and Borel proposed a general method of summation for these divergent series in the beginning of the 20th century. Thus, the question already had a long history when Quantum Mechanics was formulated

in 1925-1926.

The semiclassical approximation was developed by many people afterwards. The names of G.Gamov, H. Furry, E. Kemble, V. Fock, L. Landau, C. Zener, V. Maslov, I. Keller, M. Berry, M. Kruskal, M. Gutzwiller must be mentioned. The semiclassical approximation is still not exhausted. New essential results were obtained quite recently.

II. SEMICLASSICAL APPROXIMATION

A. Definition and criterion of validity

This is approximation of a short de Broglie wave-length λ. Namely, the necessary condition for this approximation reads: $\lambda << L$, where L is a characteristic length for variation of potential $V(\mathbf{r})$. In classical mechanics it is possible to determine the dependence of the momentum modulus p on coordinate $\mathbf{r}$ at a fixed value of energy E: $p(\mathbf{r}) = \sqrt{2m(E - V(\mathbf{r}))}$. The local value of the de Broglie wavelength is $\lambda(\mathbf{r}) = 2\pi\hbar/p(\mathbf{r})$. In terms of the local wavelength the explicit validity criterion for semiclassical approximation reads:

$$| \nabla \lambda | = \frac{\lambda | \nabla V |}{|(E - V(\mathbf{r}))|} << 1 \qquad (A1)$$

It means that the variation of the potential energy at the wavelength is small in comparison to the kinetic energy. It is clear from the inequality (1) that the semiclassical approximation regularly fails near classical turning points at which $E = V(\mathbf{r})$. The semiclassical approximation (SA) often allows to study qualitatively and even quantitatively effects, otherwise hopeless for an analytical solution.

B. One-dimensional case: Intuitive consideration.

We start with the simple case of one dimension. As we discussed in subsection A, the wavelength λ or momentum p varies slowly in space. If it does not change at all, the wave-function for a wave propagating to the right (left) would be $\psi_\pm(x) = Ce^{\pm ipx/\hbar}$. Since $p(x)$ changes slowly, this dependence is valid only locally. It means that on passing a distance Δx, small in comparison to L, but possibly larger than λ, the phase of the wave-function is changed by $\pm p(x)\Delta x/\hbar$. Summing up many such contributions, we arrive at wave-functions of the type:

$$\psi_\pm = C(x) \exp(\pm i \int_{x_0}^{x} p(x')dx'/\hbar) \qquad (B1)$$

It can be shown that, at varying $p(x)$, the former constant $C(x)$ becomes also a slowly varying function of x. Indeed for the wave-functions B1 the current j reads:

$$j_\pm = \frac{\hbar}{2mi} \left(\psi_\pm^* \frac{d\psi_\pm}{dx} - \psi_\pm \frac{d\psi_\pm^*}{dx} \right) = \pm \frac{p(x)}{m} \mid C^2(x) \mid \qquad (B2)$$

For stationary Schrödinger equation (SE) the current is constant. Therefore $C(x) = C/\sqrt{p(x)}$. Thus, we have found two independent solutions corresponding to propagating waves as

$$\psi_\pm(x) = \frac{1}{\sqrt{p(x)}} e^{\pm i \int_{x_0}^{x} p dx'/\hbar}; \; p = \sqrt{2m(E - V(x))} \qquad (B3)$$

A general solution of the SE must be an arbitrary linear combination of the two independent solutions (B1). Looking at them, we see that they formally diverge at classical turning points, at which $V(x) = E$ and $p(x) = 0$. Note, that they are regular points of the SE and the solutions have no singularity at them. It is the approximation that becomes invalid near them.

Sometimes we will use the wave-vector $k(x) = p(x)/\hbar$ to simplify formulae:

$$\psi_\pm(x) = \frac{1}{\sqrt{k(x)}} e^{\pm i \int_{x_0}^{x} k dx} \qquad (B4)$$

C. One-dimensional case: Formal derivation

It is useful to derive the asymptotic equation (B3) formally to estimate their precision. Let us right down the Schrödinger equation (SE) in the form:

$$\hbar^2 \frac{d^2\psi}{dx^2} + p^2(x)\psi = 0; \; p^2(x) = 2m(E - V(x)) \qquad (C1)$$

We introduce a new sought function $S(x)$ by a following substitution: $\psi(x) = e^{iS/\hbar}$. Then equation (C1) reads:

$$\left(\frac{dS}{dx}\right)^2 - i\hbar \frac{d^2S}{dx^2} = p^2(x) \qquad (C2)$$

This nonlinear differential equation is equivalent to the linear SE (C1). We solve it approximately by expanding S into a formal power series in $\hbar$:

$$S = S_0 + \hbar S_1 + \hbar^2 S_2 + ... \qquad (C3)$$

Plugging (C3) into (C2) and keeping only terms independent on $\hbar$, we find:

$$\left(\frac{dS_0}{dx}\right)^2 = p^2(x); \quad \frac{dS_0}{dx} = \pm p(x) \qquad (C4)$$

or:

$$S_0 = \pm \int\limits_{x_0}^{x} p\,dx \qquad (C5)$$

This is the classical action for one-dimensional motion. Retaining in the next approximation terms linear in $\hbar$, we find:

$$2\frac{dS_0}{dx}\frac{dS_1}{dx} = i\frac{d^2S_0}{dx^2} \qquad (C6)$$

or:

$$S_1 = \frac{i}{2}\ln p(x) + c \qquad (C7)$$

Substituting (C5) and (C7) into $\psi = e^{iS(x)/\hbar}$, we arrive again at the solution (B3). To estimate a correction to it, we find S_2. In the same way:

$$\frac{dS_2}{dx} = \left[-\left(\frac{dS_1}{dx}\right)^2 + i\frac{d^2S_1}{dx^2}\right] \Big/ \left(2\frac{dS_0}{dx}\right)$$

The correction to action is:

$$\hbar S_2 = \hbar \int_{x_0}^{x} \frac{3p'^2 - 2pp''}{8p^3}dx = o\left(\frac{\hbar}{pL}\right) = o\left(\frac{\lambda}{L}\right)$$

(We accepted that each derivative contributes $1/L$, the integration contributes L). Thus, the second correction is small.

D. Quantum penetration into classically forbidden region

A classical particle can not penetrate into the region in which $V(x) > 0$ since it violates the energy conservation. The quantum particle can be found in classically forbidden range because the coordinate is not compatible with the energy. When coordinate is fixed the energy is uncertain. The effect of penetration is incorporated in the semiclassical approximation. Indeed at $V(x) > E$ the square of momentum $p^2(x)$ becomes imaginary. But still the two solutions (B3) are valid. One of them exponentially decreases in the classically forbidden region, for example:

$$\psi_- = \frac{1}{\sqrt{|\,p\,|}}\exp\left(-\int\limits_{x_0}^{x} |\,p\,|\,dx'/\hbar\right) \qquad (D1)$$

This solution corresponds to the quantum penetration of a particle. Another solution ψ_+ grows exponentially with x growing. Often it can be rejected from a physical point
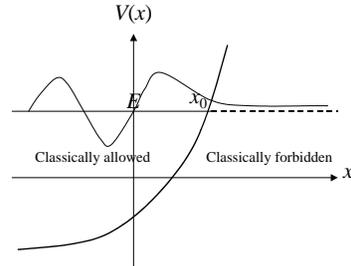

FIG. 1 Quantum penetration into classically forbidden area.

of view. Still it is the second independent solution of the linear differential equation (C1) and plays an important role in the general treatment. Sometimes it contributes to the solution of a specific physical problem. Note that in the classically forbidden region the increasing solution (ψ_+) is exponentially large and an admixture of the decreasing solution with a not too large coefficient can be neglected on its background. On the other hand, a similar addition of the increasing solution ψ_+ to a decreasing one changes the latter drastically.

E. Passing the turning point

A semiclassical solution may be chosen in such a way that it decreases exponentially, to say, right from a turning point x_0 and oscillates left from the turning point (see Fig. 1). Since it is real and its normalization is free, we can choose it in a form:

$$\psi(x) = \frac{1}{\sqrt{|\,k\,|}}e^{-\int\limits_{x_0}^{x}|k(x')|dx'}; \qquad x > x_0 \quad (E1a)$$

$$\psi(x) = \frac{A}{\sqrt{k}}\cos\left(\int\limits_{x_0}^{x} k(x')dx' + \varphi\right); \; x < x_0 \quad (E1b)$$

The problem is to find the constants A and φ. It can not be done by direct matching of two expressions for $\psi(x)$ at the point x_0 since both are invalid in a close vicinity $|\,x - x_0\,| \leq \left(\frac{\hbar^2}{2mV_0'}\right)^{1/3} \sim (\lambda^2 L)^{1/3}$, where $V_0' = |dV/dx|_{x=x_0}$[1]. A standard way of finding A and

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[1] Please, check that the semiclasiccal approximation is invalid in-

φ proposed first by Kramers and accepted by most textbooks consists of approximation of the local kinetic energy $E - V(x)$ near x_0 by the linear function $V_0'(x_0 - x)$. The SE with the linear potential is called Airy equation. It allows an exact solution in terms of special functions (Airy functions) which can be reduced to Bessel functions with the index 1/3. This solution, valid in a vicinity of the turning point $|x - x_0| \ll L$, should be matched with the asymptotic (1a) and then it gives A and φ in the asymptotic (E1b)[2]. This way seems, however, to be too complicated given such a simple answer ($A = 2$, $\varphi = \pi/4$). We prefer another way due to H. Furry, in which no other functions besides the semiclassical asymptotics are involved. The price for this simplicity is that the solution must be considered in the complex plane of the variable x.

The idea is to pass around the "dangerous" turning point x_0 in the complex plane of coordinate x along a sufficiently remote circle $|x - x_0| \gg \left(\frac{\hbar^2}{2mV_0'}\right)^{1/3}$, so that the semiclassical approximation is valid everywhere on this path. The potential $V(x)$ is assumed to be an analytical function in a vicinity of the turning point x_0. We still can choose $|x - x_0| \ll L$ to retain the linear expansion $E - V(x) = V_0'(x_0 - x)$. The value $k \approx \frac{\sqrt{2mV_0'}}{\hbar}\sqrt{x_0 - x}$ is imaginary at $x > x_0$ and real at $x < x_0$ on the real axis x. Let us consider the function

$$S(x) = \int_{x_0}^{x} k(x')dx' = \frac{\sqrt{2mV_0'}}{\hbar} \cdot \frac{2}{3}(x_0 - x)^{3/2}$$

It is real on 3 rays $\arg(x - x_0) = \pm\pi/3, \pi$ (solid lines on Fig. 2) and imaginary on another 3 rays, the bisectors of angles formed by the first 3 rays (dashed lines on Fig. 2). The latter are called Stokes lines. They are lines of the fastest decrease (or increase) of the solutions (steepest descent lines in topographical terms). On the solid three rays the solutions oscillate. We will call them anti-Stokes lines.

We start with the solution (E1), which decreases exponentially along the Stokes line 1. On the Stokes line 1 it can be written as an analytic function:

$$\psi(x) = \frac{e^{i\pi/4}}{\sqrt{k}} \exp\left(i \int_{x_0}^{x} kdx'\right) \qquad \text{(E2)}$$

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side the interval determined by this inequality and that it is valid outside.

[2] Two regions defined by inequalities $|x - x_0| \ll L$ and $|x - x_0| \gg (\lambda^2 L)^{1/3}$ overlap. Inside the overlapping region both approximation are valid and should match.
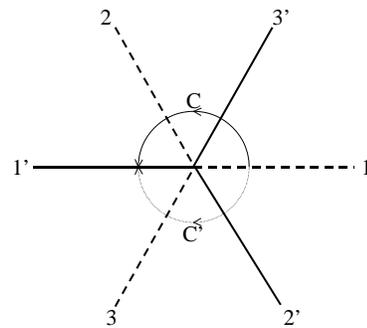

FIG. 2 Stokes lines near a turning point.

We assumed that $\arg k = \pi/2$ along the Stokes line 1. The phase factor $e^{i\pi/4}$ makes the solution (E2) real on the real axis. Let the point x pass around the turning point x_0 along the contour C in the upper half-plane of the complex variable. Until the contour crosses Stokes line 2, the solution (E2) grows exponentially and an admixture of the second, decreasing exponent on its background is negligible. However, in the interval between the Stokes line 2 and real axis at $x < x_0$ the exponent (E2) decreases and uncontrolled appearance of the second exponent is possible. Thus, on the real axis at $x < x_0$ (the anti-Stokes line 1') the solution is a superposition of the solution (E2) multiplied by a constant and the complex conjugated solution multiplied by a complex conjugated constant (both are oscillating solutions). We will argue that both above mentioned constant factors are equal to 1. Indeed the exponent (E2) (right-propagating wave) grows when moving from the anti-Stokes line 1' toward the Stokes line 2. Therefore, only this wave determines the asymptotic on the Stokes line 2 and they must coincide. Let us now make a similar operation passing along the contour C' in the lower half-plane. We arrive at the Stokes line 3 with the same solution (E2) and can guarantee that it will contribute to the solution on the real half-axis $x < x_0$ with the same coefficient 1. But this solution differs from that obtained by passing along the contour C. Indeed, near the turning point $k(x) \sim \sqrt{x_0 - x} = e^{i\pi/2}\sqrt{x - x_0}$. We assumed that $\arg k = \pi/2$ at $x > 0$. Then $\arg k = \pi$ when arriving $x < x_0$ along the contour C and $\arg k = 0$ when arriving $x < x_0$ along the contour C'. Thus, we have found both waves, traveling right and left in classically allowed region $x < x_0$. Collecting them, we obtain:

$$\psi(x) = \frac{2}{\sqrt{k}} \cos\left(\int_{x_0}^{x} kdx' + \pi/4\right) \qquad \text{(E3)}$$

Equation (E3) establishes $A = 2$ and $\varphi = \pi/4$ for our solution (E1b). This was done for the case when the classically forbidden region is located right from the turning point. In the opposite case with the same method it can be found that $A = 2$, but $\varphi = -\pi/4$ (please, check it yourself). Note the meaning of the Stokes lines: they are the lines where the asymptotics change: instead of one exponent a linear combination of two exponents appears.

The rule of the circulation around the isolated turning point can be reformulated in the following way. Let a solution of the SE be an oscillating exponent $\psi(x) = k^{-1/2} \exp\left[i \int\limits_{x_0}^{x} k dx\right]$ on a ray along which the action $S(x) = \int\limits_{x_0}^{x} p dx$ is real (we will call them anti-Stokes lines). Then on a neighboring anti-Stokes ray it is the same exponent if it is exponentially small in a sector between these two rays. If the exponent is large between the two anti-Stokes rays, then on the second ray the solution is a linear combination of two oscillating exponents:

$$\psi(x) = \frac{1}{\sqrt{k}} \left[\exp(i\int\limits_{x_0}^{x} k(x')dx' \mp i \exp(-i\int\limits_{x_0}^{x} k(x')dx')\right]$$
(E4)

The sign in (4) depends on the direction of rotation. It is $-$ for counter-clockwise rotation.

F. The Bohr's quantization rule

Consider a particle confined in a potential well. Let a and b are classical turning points (see Fig. 3). The configuration of the Stokes and anti-Stokes lines for this case is shown in Fig. 4. The wave function $\psi(x)$ must decrease exponentially at $x < a$ and $x > b$. According to the general rule of passing the turning point, the wave function in the classically allowed region reads:

$$\psi(x) = \frac{2}{\sqrt{k}} \cos\left(\int\limits_{a}^{x} k(x')dx' - \frac{\pi}{4}\right)$$
(F1)

On the other hand, the same wave function can be written as

$$\psi(x) = C \cdot \frac{2}{\sqrt{k}} \cos\left(\int\limits_{b}^{x} k(x')dx' + \frac{\pi}{4}\right)$$
(F2)

Equations (F1) and (F2) can be valid simultaneously only if $C = \pm 1$ and

$$\int\limits_{a}^{x} k(x')dx' - \frac{\pi}{4} = \int\limits_{b}^{x} k(x')dx' + \frac{\pi}{4} + n\pi$$
(F3)
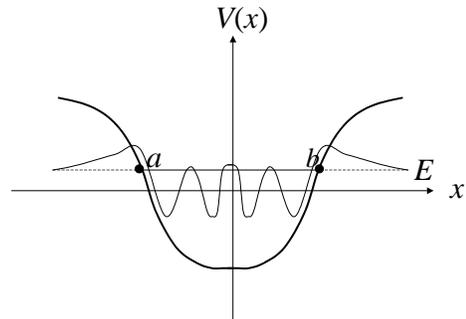
FIG. 3 Wave function of a particle in a potential well
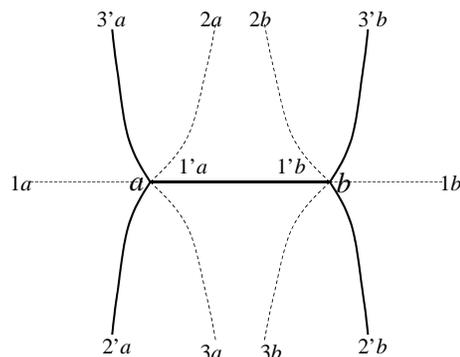
FIG. 4 Stokes lines at Bohr's quantization.

where n is an integer. From equation (F3) we immediately find:

$$\int\limits_{a}^{b} k(x)dx = (n + \frac{1}{2})\pi$$
(F4)

or:

$$\int\limits_{a}^{b} p(x)dx = (n + \frac{1}{2})\pi\hbar$$
(F4')

This is the famous *Bohr's quantization rule* which determines the energy of a level E_n as a function of its number n. Another meaning of the integer n is the number of half-waves between the turning points or the number of

zeros of the wave-function in the classically allowed region $a < x < b$. The semiclassical approximation is valid if $n >> 1$. But for practical purposes and for not too sophisticated potential the quantization rule (F4′) gives rather good approximation even for the ground-state energy ($n = 0$).

The doubled value of integral (F4′) is the action taken along the closed classical trajectory $S(E)$:

$$S(E) = \oint p(x)dx$$

Bohr conjectured in 1913 that the action $S(E)$ is quantized in units of the Planck constant $h = 2\pi\hbar$. He applied his conjecture to the spectrum of the Hydrogen atom and was able to reproduce the empirical Rydberg formula for frequencies:

$$\omega_{n,n'} = \frac{me^4}{2\hbar^3}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) \quad (n < n')$$

He quantized only circular orbits, but his answer for the Hydrogen spectrum was exact. It was discovered by A. Sommerfeld, who quantized elliptic orbits. The Bohr spectrum was derived rigorously by Schrödinger 13 years later, when he solved his equation for the Coulomb attractive potential.

G. An excursion to classical mechanics

The reciprocal to $S(E)$ function $E(S)$ can be considered as the Hamiltonian in terms of the variable action. It is straightforward to prove that

$$\frac{\partial H(S)}{\partial S} = \frac{\partial E(S)}{\partial S} = \frac{\omega}{2\pi} = \nu \qquad (G1)$$

where ω is the cyclic frequency of the orbital motion and ν is the ordinary frequency. Indeed, calculation of the inverse value gives:

$$\frac{\partial S}{\partial E} = \oint \frac{\partial p}{\partial E}dx = \oint \frac{mdx}{p} = \oint \frac{dx}{v(x)} = T \qquad (G2)$$

Here we used $p = \sqrt{2m(E - V(x))}$ and $p/m =$ v, where v(x) is the local velocity and T is the period of motion. Equation (G1) follows from (G2) and a trivial relationship $T = 1/\nu = 2\pi/\omega$. A very transparent form of equation (G1) is:

$$\frac{\partial E_n}{\partial n} = \hbar\omega \qquad (G3)$$

which simply means that the classical frequency of the periodic motion determines the energy difference between nearest levels.

What is a variable θ canonically conjugated to S ? In the Hamiltonian formulation of classical mechanics θ and S must satisfy canonical equations:

$$\dot{\theta} = \frac{\partial H}{\partial S}$$
$$\dot{S} = -\frac{\partial H}{\partial \theta} \qquad (G4)$$

Thus, for the Hamiltonian of a periodic 1-dimensional motion, the action S is the integral of motion and θ is the phase of motion which changes by 1 for a period. The variable $\varphi = 2\pi\theta$ is the cyclic phase. The pair of variables θ and S is similar to the pair of variables x and p. Therefore, their quantum commutator is the same:

$$[S, \theta] = \hbar/i \qquad (G5)$$

Keeping in mind that $S \approx 2\pi\hbar n$ and $\theta = \varphi/2\pi$, we find the commutator for n and φ:

$$[n, \varphi] = 1/i \qquad (G6)$$

It is identical with the commutator of the number of "phonons" n and the phase φ for the quantum oscillator problem. Thus, the energy and the phase can not be measured simultaneously.

In classical mechanics the action is an adiabatic invariant. It means that it is approximately invariant if parameters of the Hamiltonian, such as the mass m or the potential $V(x)$, vary slowly in time. We call a value $A(t)$ slowly varying if its variation for the period T is small in comparison to A, i.e., $\left|\dot{A}/A\right| << \nu$. When the Hamiltonian depends on time, it can not be function of S only since the energy is not more conserved. Therefore H depends on θ as well and the second equation of motion now reads:

$$\dot{S} = -\frac{\partial H}{\partial \theta} \qquad (G7)$$

However, H is necessarily a periodic function of θ with the period 1. It can be represented as a Fourier-series constructed by $\sin(2\pi n\theta)$ and $\cos(2\pi n\theta)$ with coefficients slowly varying in time. Averaging equation (G7) over one period of rotation, we find $\langle\dot{S}\rangle = 0$ since average of derivative of a periodic function is zero. Note that the phase θ is not an adiabatic invariant since the derivative of the Hamiltonian by S generally has zero harmonic, i.e. a term independent on θ. Its main part is given by $\int \omega(t)dt$, but in the case of slowly varying parameters there exists an additional part in zero harmonic proportional to the derivative $\frac{\partial^2 H}{\partial S \partial \mathbf{R}}$ (see section IV.C).
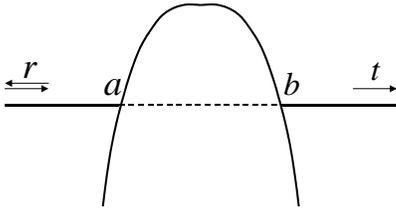
FIG. 5 Quantum tunneling under a barrier.

FIG. 6 Decay of a metastable state.

H. The under-barrier tunneling

A classical particle with the energy E, lower than the maximum of potential energy, would be fully reflected from the classical turning point a. Due to the under-barrier penetration the quantum particle can reach the second turning point b and then propagate to the right (Fig. 5).

Our purpose is to find the tunneling amplitude t. In the semiclassical approximation the wave function must be

$$\psi(x) \simeq \frac{t}{\sqrt{p}} \exp\left(\frac{i}{\hbar}\int\limits_{b}^{x} pdx\right) \qquad \text{(H1)}$$

at $x > b$ since right to the turning point b there is no wave propagating to the left. This wave function grows exponentially under the barrier, left to the turning point b, and it is expressed by the same equation (H1) under the barrier at $a < x < b$. But the same wave-function exponentially decreases under the barrier right to the turning point a. According to the general rule of passing the turning point (equation E4), the wave-function in the classically allowed region $x < a$ reads:

$$\psi(x) \simeq \frac{t}{\sqrt{p}}\left(e^{\frac{i}{\hbar}\int\limits_{a}^{x} pdx} - ie^{-\frac{i}{\hbar}\int\limits_{a}^{x} pdx}\right) \cdot e^{-\frac{i}{\hbar}\int\limits_{a}^{b} pdx} \qquad \text{(H2)}$$

The statement of the problem about tunneling requires that the amplitude of the incident wave to be equal to 1. It means that

$$t = \exp\left(\frac{i}{\hbar}\int\limits_{a}^{b} pdx\right) = \exp\left(-\frac{1}{\hbar}\int\limits_{a}^{b} |p(x)|dx\right)$$
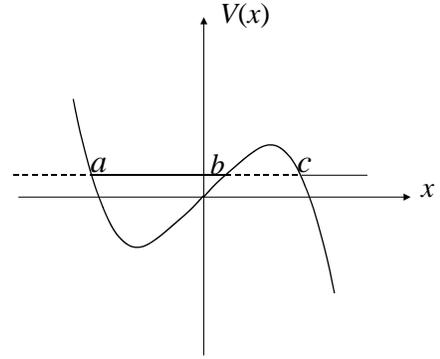
The probability of tunneling is:

$$P = |t|^2 = \exp\left(-\frac{2}{\hbar}\int\limits_{a}^{b} |p(x)|dx\right) \qquad \text{(H3)}$$

I. Decay of a metastable state

Let us consider a potential schematically depicted in Fig. 6:

A classical particle with the energy E between $V_{\min}$ and $V_{\max}$ is confined on a trajectory limited by turning points a and b. Quantum mechanics allows the particle to tunnel and escape when it reaches point b. The probability of this process is:

$$P = \exp\left(-\frac{2}{\hbar}\int\limits_{b}^{c} |p(x)|dx\right) \qquad \text{(I1)}$$

as it was established in previous subsection. Let particle was placed between a and b at an initial moment of time $t = 0$. The probability to find it in the potential well after time t much longer than the period of oscillations T is:

$$w(t) = (1 - P)^{t/T} \qquad \text{(I2)}$$

At small enough P the probability (I2) can be rewritten as:

$$w(t) = e^{-tP/T} = e^{-2t/\tau} \qquad \text{(I3)}$$

where we have introduced the life-time τ of the particle on the level E:

$$\tau = 2T(E)/P = 2T \exp\left(\frac{2}{\hbar}\int\limits_b^c |p(x)| \, dx\right) \qquad (I4)$$

Note, that the state of a particle in such a potential well is not stationary, it decays with time, but it can be considered as being quasistationary one. It means that the particle makes a large number τ/T oscillations before it leaves. The modulus of the wave-function is decreasing exponentially as $e^{-t/\tau}$. The wave-function has also the standard phase factor $\exp(-iEt/\hbar)$. In total the wave-function changes in time as $\exp\left(-\frac{i(E_n - i\gamma)t}{\hbar}\right)$, where $\gamma = \hbar/\tau$. Thus, the metastable state can be alternatively described as a state with a complex energy $E = E_n - i\gamma$. The wave-function of the metastable state can be expanded into Fourier-integral:

$$\psi(t) = \int \widetilde{\psi}(E) e^{-iEt/\hbar} dE \qquad (I5)$$

The square of modulus $|\widetilde{\psi}(E)|^2$ can be interpreted as the probability density to find our system with the energy E. A simple calculation shows that

$$|\widetilde{\psi}(E)| = \frac{const}{(E - E_n)^2 + \gamma^2} \qquad (I6)$$

This is the so-called Lorenz distribution or the Lorenzian. It has a shape of a peak of the width γ centered at $E = E_n$. Thus, the metastable state has uncertainty of energy ΔE or the width of the level equal to γ. On the other hand, its life-time τ can be considered as the uncertainty of time Δt. From the relation $\gamma = \hbar/\tau$ we find the energy-time uncertainty relation:

$$\Delta E \cdot \Delta t \geq \hbar \qquad (I7)$$

G. Gamov (1928) was the first to treat the α-decay of radioactive nuclei as the quantum tunnelling.

J. The resonance tunnelling and the Ramsauer effect

Consider a one-dimensional potential well separated by two barriers from zero level at $x \to \pm\infty$ (Fig. 7). At a proper condition, this potential has metastable levels. We will prove that the transmission of the particle through the potential has very sharp maxima at values of energy equal to the energies of metastable levels.
Let a, b, c and d are the turning points taken from the left to the right at some positive value of energy E. We will employ the fact that the two independent solutions of stationary Schrödinger equation can be always chosen to be real, due to the time reversal symmetry. Let denote
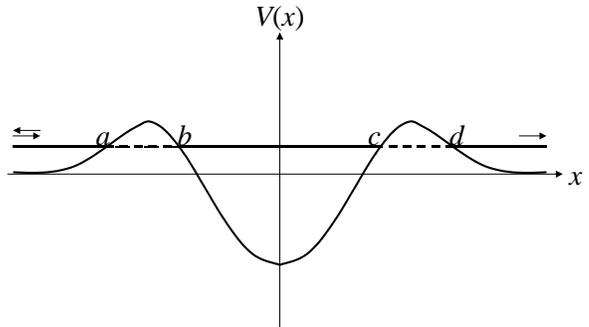

FIG. 7 Resonance transmission.

these solutions $\psi_1(x)$ and $\psi_2(x)$. Without loss of generality, we can choose them in such a way that, in classically allowed region between the turning points b and c, their semiclassical asymptotics are:

$$\psi_1(x) \approx \frac{2}{\sqrt{k(x)}} \cos\left(\int\limits_b^x k(x')dx' - \frac{\pi}{4}\right); \quad (J1a)$$

$$\psi_2(x) \approx \frac{2}{\sqrt{k(x)}} \cos\left(\int\limits_c^x k(x')dx' + \frac{\pi}{4}\right) \qquad (J1b)$$

Since the energy E is arbitrary and does not obey the Bohr's quantization rule, the two asymptotics given by eq. (J1a) represent different functions. According to the general rule of passing turning points, the first solution becomes exponentially small in the classically forbidden region between a and b, whereas the second one is exponentially small between c and d:

$$\psi_1(x) = \frac{1}{\sqrt{|k(x)|}} e^{\int\limits_b^x |k(x')|dx'} \qquad (a < x < b); \quad (J2a)$$

$$\psi_2(x) = \frac{1}{\sqrt{|k(x)|}} e^{-\int\limits_c^x |k(x')|dx'} \qquad (c < x < d). (J2b)$$

The first solution will be, generally speaking, exponentially large in the classically forbidden region between c and d, whereas the second solution is exponentially large between a and b. We must be very careful calculating these asymptotics, since the large exponents must vanish at values of energy corresponding to the Bohr quantization rule and by continuity they are small in close vicinity of the metastable levels. To catch this effect we present the asymptotics of $\psi_1(x)$ in the following form:

$$\psi_1(x) = \frac{2}{\sqrt{k(x)}} \sin\left(\int_c^x k(x')dx' - \frac{\pi}{4} + \alpha\right); \quad \text{(J3)}$$

where $\alpha = \int_b^c k(x)dx$. It must be a linear combination of two solutions formally represented by sine and cosine of the argument $\int_c^x k(x')dx' + \pi/4$. The first of them decreases in the classically forbidden region $c < x < d$, whereas the second one increases. Thus, the solution ψ_1 in the forbidden region $c < x < d$ reads:

$$\psi_1(x) = \frac{1}{\sqrt{|k(x)|}}\left[\sin\alpha \; e^{-\int_c^x |k(x')dx'|} + \cos\alpha \; e^{\int_c^x |k(x')dx'|}\right]$$
$$\text{(J4)}$$

Continuing the same solution into the right classically allowed region $x > d$, we find:

$$\psi_1(x) = \frac{2}{\sqrt{|k(x)|}}\left[\sin\alpha \; \Gamma_R^{-1} \sin\left(\int_d^x k(x')dx' - \frac{\pi}{4}\right)\right.$$
$$\left. + \cos\alpha \; \Gamma_R \cos\left(\int_d^x k(x')dx' - \frac{\pi}{4}\right)\right] \quad \text{(J5)}$$

where $\Gamma_R = \exp\left(\int_c^d |k(x)dx|\right)$. The same continuation for the solution ψ_2 is simpler, since in the interval $c < x < d$ it contains only one, decreasing exponent. Therefore, in the interval $x > d$ the asymptotic of ψ_2 is:

$$\psi_2(x) = \frac{2}{\sqrt{|k(x)|}}\Gamma_R^{-1} \sin\left(\int_d^x k(x')dx' - \frac{\pi}{4}\right) \quad \text{(J6)}$$

A linear combination of the solutions ψ_1 and ψ_2 which represents a wave propagating to the right at $x > d$ is:

$$\psi(x) = \frac{te^{i\pi/4}}{2\Gamma_R \cos\alpha}\left(\left[\psi_1 + \left(i\Gamma_R^2 \cos\alpha - \sin\alpha\right)\psi_2\right]\right.$$
$$\sim te^{i\int_d^x kdx'} \quad \text{(J7)}$$

Here we introduced an arbitrary coefficient t which occurs further to be the transmission amplitude. Continuing our solutions in an analogues way to the left allowed region $x < a$, we find:

$$\psi_1(x) = \frac{2}{\sqrt{|k(x)|}}\Gamma_L^{-1} \sin\left(\int_a^x k(y)dy + \frac{\pi}{4}\right)$$
$$\psi_2(x) = \frac{2}{\sqrt{|k(x)|}}\left[\sin\alpha \; \Gamma_L^{-1} \sin\left(\int_a^x k(y)dy + \frac{\pi}{4}\right)\right. \quad \text{(J8)}$$
$$\left. - \cos\alpha \; \Gamma_L \cos\left(\int_a^x k(y)dy + \frac{\pi}{4}\right)\right]$$

where $\Gamma_L = \exp\left(\int_a^b |k|dx\right)$. Now we are in position to construct the asymptotic of the wave function $\psi(x)$ (1) at $x < a$. Requiring the coefficient at the wave propagating to the right to be 1, we find the transmission amplitude:

$$t = \frac{2i\Gamma_L\Gamma_R}{(\Gamma_L\Gamma_R)^2 \cos\alpha + i(\Gamma_L^2 + \Gamma_R^2)\sin\alpha} \quad \text{(J9)}$$

Its square of modulus (the transmission coefficient) is:

$$|t|^2 = \frac{4(\Gamma_L\Gamma_R)^2}{(\Gamma_L\Gamma_R)^4 \cos^2\alpha + (\Gamma_L^2 + \Gamma_R^2)^2 \sin^2\alpha} \quad \text{(J10)}$$

Since $\Gamma_{L,R}$ are exponentially large values, the transmission coefficient (J10) reaches its maximum at $\cos\alpha = 0$, i.e. at energy satisfying the Bohr's condition $\alpha = (n + 1/2)\pi$. The maximum is equal to

$$|t|_{\max}^2 = \frac{4(\Gamma_L\Gamma_R)^2}{(\Gamma_L^2 + \Gamma_R^2)^2} \leq 1$$

The value 1 is reached at $\Gamma_L = \Gamma_R$. The peak is very sharp. The value $|t|^2$ decreases twice at $|\frac{\pi}{2} - \alpha| \approx \left(\Gamma_L^{-2} + \Gamma_R^{-2}\right)$. Thus, we demonstrated that the barrier is selectively transparent for particles with energy close to the metastable levels.

The phenomenon of selective transparency was found experimenatally in optics and electron beams propagation. It is known as the Ramsauer effect. It also known as the resonant tunneling. It plays an important role in semiconductor physics, especially in the devices called single-electron transistors.

K. The overbarrier reflection.

To find a small reflection coefficient for a particle with energy higher than the maximum potential energy, one can apply similar ideas passing the turning points x_0 in the complex plane of the coordinate x. There is no turning point on the real axis, but a general theorem of complex variables theory guarantees that an analytical function accepts any value in the complex plane. In particular, $V(x) = E$ at some point x_0 of the complex plane. We consider a simple situation when there is only one such a point. The asymptotics of a proper wave function are:

$$\psi(x) = \begin{cases} e^{ik_- x} + re^{-ik_- x} & x \to -\infty \\ te^{ik_+ x} & x \to +\infty \end{cases} \quad \text{(K1)}$$

where $k_\pm$ are limiting values of $k(x) = \sqrt{2m(E - V(x))}$ at $x \to \pm\infty$, r is the reflection amplitude, t is the transmission amplitude. Starting from the real axis x at $x \to +\infty$ it is possible to continue the solution into the complex
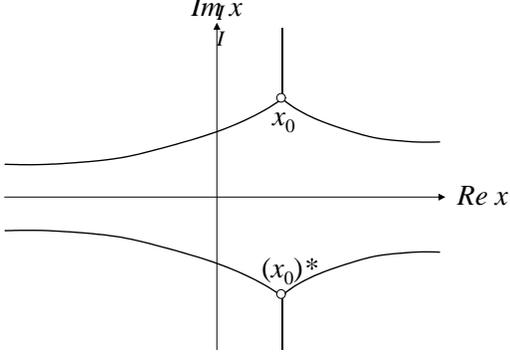
FIG. 8 Stokes lines at over-barrier reflection.

plane of x and arrive at the line 1 $\operatorname{Im} \int\limits_{x_0}^{x} k(x')dx' = 0$ which is parallel to the real axis at $\operatorname{Re} x \to \infty$ (Fig. 8). This is possible since the potential is constant with any desirable precision at $\operatorname{Re} x \to \infty$. The asymptotic solution (1) on the line 1 can be written as follows:

$$\psi(x) = te^{ik_+x} \approx \frac{tk_+}{\sqrt{k(x)}} \exp\left(i\int\limits_{x_0}^{x} k(x')dx' \right) \cdot \text{(K2)}$$

$$\cdot \exp\left(ik_+x_0 - i\int\limits_{x_0}^{\infty} (k(x') - k_+)dx' \right)$$

The solution in this form can be continued along the line 1 till the vicinity of the turning point. According to the general rule (E4), the asymptotic of the same solution on line 2 is

$$\psi(x) = \frac{tk_+}{\sqrt{k(x)}} \exp\left(ik_+x_0 - i\int\limits_{x_0}^{\infty} (k(x') - k_+)dx' \right) \text{ (K3)}$$

$$\cdot \left[\exp\left(i\int\limits_{x_0}^{x} k(x')dx' \right) - i\exp\left(-i\int\limits_{x_0}^{x} k(x')dx' \right) \right]$$

Passing along the line 2, we arrive at $\operatorname{Re} x \to -\infty$ and then descend to the real axis employing the fact that the potential is constant with any desirable precision. At $x \to -\infty$ the argument of exponents can be evaluated as follows:

$$\int\limits_{x_0}^{x} k(x')dx = k_-(x - x_0) + \int\limits_{x_0}^{x} (k(x') - k_-)\, dx' \text{ (K4)}$$

$$\approx k_-x - \int\limits_{-\infty}^{x_0} (k(x') - k_-)\, dx' - k_-x_0$$

Plugging (K4) into (K3) and comparing this result to the second line in (K1), we find:

$$t\frac{k_+}{k_-}e^{i\left[(k_+-k_-)x_0 - \int\limits_{-\infty}^{x_0} (k(x')-k_-)dx' - \int\limits_{x_0}^{\infty} (k(x')-k_+)dx' \right]} = 1$$
(K5)

$$-it\frac{k_+}{k_-}e^{i\left[(k_++k_-)x_0 + \int\limits_{-\infty}^{x_0} (k(x')-k_-)dx' - \int\limits_{x_0}^{\infty} (k(x')-k_+)dx' \right]} = r$$
(K6)

Eliminating t from (K5) and (K6), we find:

$$r = i\exp\left[2ik_-x_0 + 2i\int\limits_{-\infty}^{x_0} (k(x) - k_-)\, dx \right] \text{ (K7)}$$

The integration in the argument of the exponent in (K7) can be performed along real axis x from $-\infty$ till $\operatorname{Re} x_0$ and parallel to the imaginary axis from this point till x_0. The part of argument

$$2ik_- \operatorname{Re} x_0 + 2i\int\limits_{-\infty}^{\operatorname{Re} x_0} (k(x) - k_-)\, dx$$

is purely imaginary. It contributes to the phase factor. The remaining contribution is:

$$-2k_- \operatorname{Im} x_0 - 2\int\limits_{0}^{\operatorname{Im} x_0} (k(\operatorname{Re} x_0 + iy) - k_-)\, dy$$

$$= -2\int\limits_{0}^{\operatorname{Im} x_0} k(\operatorname{Re} x_0 + iy)dy$$

It has real and imaginary parts. Its imaginary part again contributes to the phase factor only. Its real part determines the modulus of r:

$$|r| = \exp\left(-2\int\limits_{0}^{\operatorname{Im} x_0} \operatorname{Re} k(\operatorname{Re} x_0 + iy)dy \right) \text{ (K8)}$$
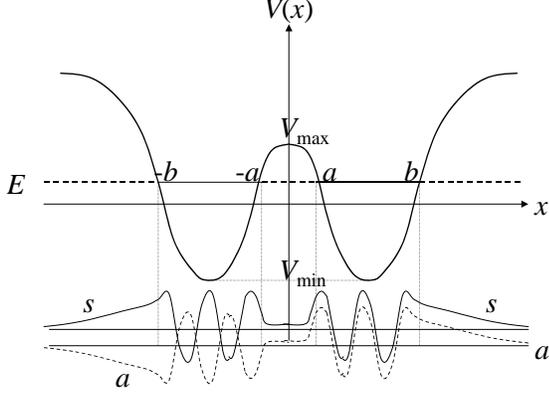
FIG. 9 Wave functions in a double potential well.

The last equation can be simplified taking in account that $k(x)$ is real on the real axis, and therefore $k(x^*) = k^*(x)$ for complex x. Thus:

$$-2\int\limits_{0}^{\operatorname{Im} x_0} \operatorname{Re} k(x_0+iy)dy = -\int\limits_{-\operatorname{Im} x_0}^{\operatorname{Im} x_0} k(\operatorname{Re} x_0+iy)dy = i\int\limits_{x_0^*}^{x_0} k(x)dx \quad (K9)$$

and

$$|\,r\,| = \exp\left(i\int\limits_{x_0^*}^{x_0} k(x)dx\right) \qquad (K10)$$

The reflection amplitude is exponentially small and can not be found in any power approximation over the small parameter (λ/L). This method of calculation was proposed by Pokrovsky and Khalatnikov (1961).

L. Splitting of levels in a symmetric double well.

Let us consider energy levels in a symmetric double potential well schematically depicted on Fig 9.
For energies E between the double degenerate absolute minimum of the potential $V_{\min}$ and its maximum, $V_{\max}$, the energy levels are double degenerate if the tunnelling between the wells is neglected. This degeneration is lifted by the tunnelling. To find the splitting of the levels we start with Schrödinger equations for symmetric and anti-symmetric wave functions ψ_s, ψ_a with close energies E_s and E_a:

$$\frac{\hbar^2}{2m}\frac{d^2\psi_s}{dx^2} + (E_s - V(x))\psi_s = 0 \qquad (L1)$$

$$\frac{\hbar^2}{2m}\frac{d^2\psi_a}{dx^2} + (E_a - V(x))\psi_a = 0 \qquad (L2)$$

Let multiply equation (L1) by $\psi_a(x)$, equation (L2) by $\psi_s(x)$ and subtract the second equation from the first. The result reads:

$$\frac{\hbar^2}{2m}\frac{d}{dx}\left(\psi_a\frac{d\psi_s}{dx} - \psi_s\frac{d\psi_a}{dx}\right) + (E_s - E_a)\psi_s\psi_a = 0 \quad (L3)$$

After integration of equation (L3) from $x = 0$ to infinity, we find:

$$E_a - E_s = \frac{\hbar^2}{2m}\cdot\frac{\psi_s(0)\frac{d\psi_a(0)}{dx}}{\int\limits_{0}^{\infty}\psi_s(x)\psi_a(x)dx} \qquad (L4)$$

We have employed the fact that $\psi_a(0) = \psi_a(\infty) = \psi_s(\infty) = 0$. The asymptotics of the symmetric wave function can be chosen as follows:

$$\psi_s(x) = \begin{cases} \dfrac{1}{\sqrt{|p(x)|}}\dfrac{\cosh\left(\int_0^x|p(x')|dx'/\hbar\right)}{\cosh\left(\int_0^a|p(x')|dx'/\hbar\right)} & |\,x\,| < a \\[3mm] \dfrac{2}{\sqrt{|p(x)|}}\cos\left(\dfrac{1}{\hbar}\int_a^x p(x')dx' - \pi/4\right) & a < |\,x\,| < b \\[3mm] \dfrac{1}{\sqrt{|p(x)|}}\exp\left(-\dfrac{1}{\hbar}\int_b^x |\,p(x')\,|\,dx'\right) & |\,x\,| > b \end{cases}$$

$$(L5)$$

The normalization of the function $\psi_s(x)$ is chosen in such a way that it decreases as $\psi_s(x) \approx \frac{1}{\sqrt{|p(x)|}}\exp\left(-\int\limits_x^a |\,p(x')\,|\,dx'\right)$ for $x < a$ and $|\,a - x\,| >> (\hbar^2/mV'(a))^{1/3}$. For the antisymmetric wave-function $\psi_a(x)$ the asymptotic reads:

$$\psi_a(x) = \begin{cases} \dfrac{1}{\sqrt{|p(x)|}}\dfrac{\sinh\left(\int_0^x|p(x')|dx'/\hbar\right)}{\sinh\left(\int_0^a|p(x')|dx'/\hbar\right)} & |\,x\,| < a \\[3mm] \pm\dfrac{2}{\sqrt{|p(x)|}}\cos\left(\dfrac{1}{\hbar}\int_a^x p(x')dx' - \pi/4\right) & a < |\,x\,| < b \\[3mm] \pm\dfrac{1}{\sqrt{|p(x)|}}\exp\left(-\dfrac{1}{\hbar}\int_b^x |\,p(x')\,|\,dx'\right) & |\,x\,| > b \end{cases}$$

$$(L6)$$

With the accepted precision the asymptotics differ only in the region $|\,x\,| < a$ for positive x. From (L5) and (L6) the product $\psi_s(0)\frac{d\psi_a(0)}{dx}$ occurring in equation (L4) can be easily found:

$$\psi_s(0)\frac{d\psi_a(0)}{dx} = \frac{1}{\hbar\left[\sinh\left(2\int_0^a |\,p(x')\,|\,dx'/\hbar\right)\right]} \qquad (L7)$$

Let calculate the integral:

$$\int\limits_0^\infty \psi_s(x)\psi_a(x)dx \approx \int\limits_a^b \psi_s(x)\psi_a(x)dx \approx$$

$$\approx 4\int\limits_a^b \cos^2\left[\int\limits_0^x p(x')dx'/\hbar - \pi/4\right]\frac{dx}{p(x)}$$

Substituting quickly oscillating $\cos^2$ by its average value $1/2$, we arrive at a following result:

$$\int\limits_0^\infty \psi_s(x)\psi_a(x)dx \approx 2\int\limits_a^b \frac{dx}{p(x)} = \frac{1}{m}T(E) \qquad \text{(L8)}$$

where $T(E)$ is the period of motion along the classical trajectory. Plugging (L7) and (L8) into equation (L4), we obtain:

$$E_a - E_s = \frac{\hbar}{T(E)\left[\sinh\left(2\int\limits_0^a |p(x')|\,dx'/\hbar\right)\right]} \approx \text{(L9)}$$

$$\approx \frac{\hbar\omega}{\pi}\exp\left(-\int\limits_{-a}^a |p(x')|\,dx'/\hbar\right)$$

where ω is the classical frequency of motion ($\hbar\omega$ is the distance between levels in each well). Again we obtain exponentially small value, specific for a classically forbidden effect. Note that the antisymmetric state has always higher energy than the symmetric one.

M. Semiclassical approximation for the radial wave equation

The radial SE for spherically symmetric potential reads:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) + \left(k^2 - v(r) - \frac{l(l+1)}{r^2}\right)\psi = 0 \quad \text{(M1)}$$

where as usual $k^2 = 2mE/\hbar^2$ and $v(r) = 2mV(r)/\hbar^2$. The last term is proportional to centrifugal potential; the integer l is the dimensionless total orbital momentum. We assume $l \gg 1$. To trasform this equation to the standard one-dimensional form we introduce a new function $\chi(r) = r\psi(r)$. The wave equation for the function χ reads:

$$\frac{d^2\chi}{dr^2} + \left(k^2 - v(r) - \frac{l(l+1)}{r^2}\right)\chi = 0 \qquad \text{(M2)}$$

General condition of semiclassical approximation also requires that

$$\frac{dk(r)}{dr} \ll k^2(r); \quad k(r) = \sqrt{k^2 - v(r) - \frac{(l+1/2)^2}{r^2}} \tag{M3}$$

Note that the centrifugal term in expression (M3) for $k(r)$ differs from that in equation (M2) by a comparatively small term $1/4r^2$. We will show later that this choice allows to obtain an interpolation formula which works well at large and small values of r. Indeed, if the potential varies slowly enough and $r \geq k/l$, the requirement (M3) is satisfied. At $r \ll k/l$ the centrifugal term dominates. Then $k(r)$ becomes purely imaginary $k(r) \approx \pm i(l+1/)/r$. The wave function χ decreasing in the classically forbidden area $r < r_0$ reads:

$$\chi(r) = \frac{e^{i\pi/4}}{\sqrt{k(r)}}\exp\left(i\int\limits_{r_0}^r k(r')dr'\right) \qquad \text{(M4)}$$

where r_0 is the classical turning point. For $r \ll l + 1/2$ the approximate estmate is

$$\chi(r) \approx \sqrt{\frac{r}{l+1/2}}\exp\left((l+1/2)\ln\frac{r}{l+1/2}\right) = \left(\frac{r}{l+1/2}\right)^{l+1}$$

For the initial radial wave function in the same region we find an asymptotic:

$$\psi(r) \approx \frac{r^l}{(l+1/2)^{l+1}}$$

which agrees with the general analysis. Then in classically allowed region $r > r_0$ the semiclassical approximation reads:

$$\chi(r) = \frac{2}{\sqrt{k(r)}}\sin\left(\int\limits_{r_0}^r k(r')dr' + \frac{\pi}{4}\right) \qquad \text{(M5)}$$

Problems:
1. Find asymptotics of spherical Bessel functions $j_l(x)$ at large values of l.
2. The same problem for standard Bessel functions.
3. Find the roots $x_{n,m}$ of Bessel functions $J_m(x)$ with large m or with large n or both.

III. SEMICLASSICAL APPROXIMATION IN 3 DIMENSIONS

A. Hamilton-Jacobi equation

Solving Schrödinger equation in 3 dimensions for the case when $|\nabla\lambda| = (\lambda|\nabla V|/K) << 1$, we apply the same
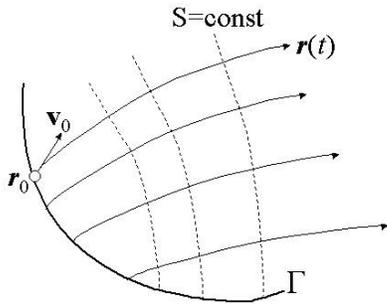
FIG. 10 Family of classical trajectories.

trick representing ψ as $\psi = e^{iS/\hbar}$. Equation for $S(\mathbf{r},E)$ reads:

$$\frac{1}{2m}(\nabla S)^2 + V(\mathbf{r}) - \frac{i\hbar}{2m}\Delta S = E \qquad (A1)$$

Again we expand formally S into a power series over $\hbar$:

$$S = S_0 + \hbar S_1 + \hbar^2 S_2 + ... \qquad (A2)$$

Then in the leading approximation we find equation for S_0:

$$\frac{1}{2m}(\nabla S_0)^2 + V(\mathbf{r}) = E \qquad (A3)$$

This equation is well-known in classical mechanics as the stationary Hamilton-Jacobi equation. It can be considered as one of possible formulations of classical mechanics, equivalent to other important formulations: Newton laws, Hamilton canonical equations and Lagrange-Hamilton variational principle. As it is seen from equation (3), the value $\frac{1}{2m}(\nabla S_0)^2$ is the kinetic energy of a particle. Therefore, the absolute value of ∇S_0 is equal to the absolute value of momentum at the point $\mathbf{r}$ for a particle with the total energy E. To understand what is the physical meaning of the function $S_0(\mathbf{r})$ consider a family of trajectories for particles with fixed energy passing through a point $\mathbf{r}_0$ of a surface Γ with the direction of velocity $\mathbf{n}_0 = \mathbf{v}_0/|\mathbf{v}_0|$ normal to the surface (see Fig. 10). The modulus of the velocity for each starting point $\mathbf{r}_0$ is uniquely defined as $p(\mathbf{r}_0)/m$.

One can imagine the surface Γ as a set of points $\mathbf{r}_0$ passed by a beam of particles at some initial moment of time t_0. These conditions determine a family of trajectories $\mathbf{r}(t) =$

$\mathbf{r}(t, \mathbf{r}_0, E)$ unambiguously. The classical action along this trajectories is:

$$S(\mathbf{r},E) = \int\limits_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{p}(\mathbf{r}')d\mathbf{r}' \qquad (A4)$$

At a fixed surface Γ the point $\mathbf{r}_0$ is determined by the point $\mathbf{r}$ [3]. Therefore, $S(\mathbf{r},E)$ is a function of $\mathbf{r}$ only. Its gradient is equal to the momentum of a particle on a trajectory starting on Γ in the point $\mathbf{r}_0$ with the velocity perpendicular to Γ. The surface $S(\mathbf{r},E) = const$ is normal to the family of trajectories intersecting this surface. In optics the surface perpendicular to the light rays is called the wave front. A close analogy between the Hamilton-Jacobi formulation of classical mechanics and the diffraction theory of optical waves inspired W.R. Hamilton to develop his particle-wave analogy which anticipated the Quantum Mechanics more than half a century prior its creation.

Equation (A4) shows how to construct a general solution of the Hamilton-Jacobi equation [4]. One should fix a surface Γ in $3d$ space (or a line in $2d$ space) and find the unit vector of normal $\mathbf{n}_0(\mathbf{r}_0)$ at each point of this surface, then calculate classical trajectories passing through Γ with the direction of velocity $\mathbf{n}_0(\mathbf{r}_0)$, find a trajectory passing through the point $\mathbf{r}$ and integrate momentum along this trajectory. It is clear that the general solution $S(\mathbf{r},E)$ depends on the choice of initial surface Γ, which is completely determined by an arbitrary function of 3 (or 2) variables. On the other hand, any particular solution of Hamilton-Jacobi equation (A3) corresponds to a family of classical trajectories which can be found as solution of ordinary differential equation:

$$\dot{\mathbf{r}}(t) = \frac{1}{m}\nabla S(\mathbf{r}) \qquad (A5)$$

As an example, consider free particles ($V(\mathbf{r}) = 0$). A simplest solution of equation (3) in this case is

$$\nabla \mathbf{S}_0 = \mathbf{p} = const; \quad \mathbf{S}_0 = \mathbf{p} \cdot \mathbf{r} \qquad (A6)$$

It corresponds to a family of straight-lined trajectories parallel to the constant vector $\mathbf{p}$. The initial surface Γ is the plane perpendicular to $\mathbf{p}$. The wave-function corresponding to this solution is the plane-wave $\psi(\mathbf{r}) = e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$. This result seems quite natural. A spherically symmetric

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[3] Actually, it can happen that several trajectories starting at different $\mathbf{r}_0$ pass through the same point $\mathbf{r}$. We consider this situation later.

[4] The method described here is well known in theory of differential equations with partial derivatives as "Method of characteristics".

solution of Hamiltonian-Jacobi equation for a free particle is:

$$S = p \cdot r \qquad (A7)$$

where p is a constant and r is the spherical radius. Its gradient $\nabla S = p\hat{\mathbf{r}}$ is directed along the radius and its modulus is constant. The initial surface Γ is a sphere. In classical mechanics this solution corresponds to a beam of particles moving from the origin with a permanent velocity. In quantum mechanics it is an outgoing spherical wave $\psi(\mathbf{r}) = \frac{\exp\left(\frac{ipr}{\hbar}\right)}{r}$. The origin of the factor r in denominator is explained in the next subsection. The reader can construct cylindrical wave in a similar way. Note that trajectories in both cases have no intersections.

B. The caustics and tubes of trajectories

A less trivial situation arises when trajectories intersect. As an example consider trajectories of free particles in 2 dimensions starting from a parabola $y = kx^2$ in the direction normal to the parabola in the starting point (Fig. **??**) .

If the coordinates of starting point are $y_0 = kx_0^2$ and x_0 , equation of the trajectory is:

$$y - kx_0^2 = -\frac{1}{2kx_0}(x - x_0) \qquad (B1)$$

Equation (B1) can be considered as equation for x_0 at fixed x and y. It has only one root for any point between the initial parabola $y = kx^2$ and a curve

$$x = \pm\frac{2(2ky - 1)^{3/2}}{3\sqrt{6}k} \qquad (B2)$$

For any point (x, y) inside the latter curve ("semicubic parabola") there exist three trajectories passing through it (try to prove this statement). The curve (B2) is the envelope of classical trajectories, the so-called caustic. Even visually it is seen as a line where classic trajectories become dense. Therefore, one can expect that the stationary density increases near caustics. This anticipation will be supported by the direct calculation later.

As a second example let us consider particles in 2 dimensions subjected to an external potential $V(x)$ depending on coordinate x only. The family of trajectories is characterized by the total energy and the angle θ which they form with the x-axis at $x \to -\infty$ where $V(x)$ can be neglected. The components of momentum in this asymptotic region are $p_x = \sqrt{2mE}\cos\theta$ and $p_y = \sqrt{2mE}\sin\theta$. The value p_y is conserved. Therefore

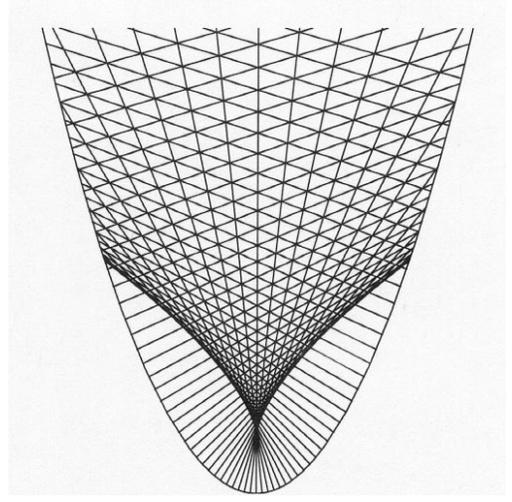$$p_x^2 = 2mE - p_y^2 - 2mV(x) = 2m(E\cos^2\theta - V(x)) \quad (B3)$$

FIG. 11 Trajectories of particles and caustics in a parabolic billiard.
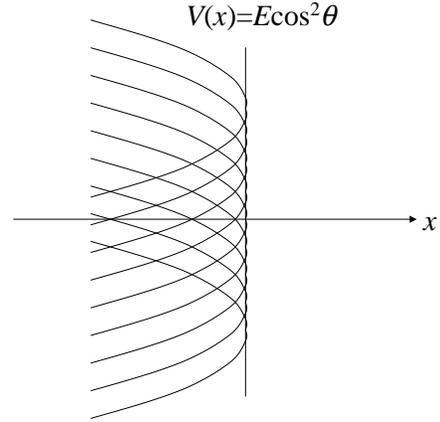
FIG. 12 Caustics for a 2d particles in 1d potential.

It becomes zero at $V(x) = E\cos^2\theta < E$. This is again the envelope of classical trajectories for this case, i.e. the caustic (Fig. 12).

Note, that the energy remains larger than the potential energy, but the region behind the caustic $V(x) > E\cos^2\theta$ is classically forbidden. Thus, the caustics can be also considered as boundaries of classically allowed regions. The classically forbidden region behind a caustic is the shadow region in optics and common life.

Now we proceed to construction of the next after the leading semiclassical approximation. Returning to equation (A1), we retain in it terms proportional to $\hbar$. The result reads:

$$2\nabla S_0 \nabla S_1 = i\Delta S_0 \qquad (B4)$$

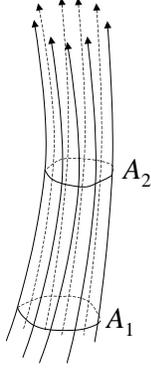FIG. 13 Tube of trajectories.

Remembering that $\nabla S_0 = \mathbf{p}$, equation (B4) can be rewritten as follows:

$$(\mathbf{p}\nabla)S_1 = \frac{i}{2}\nabla \cdot \mathbf{p} \qquad (B5)$$

Let us introduce a coordinate along a classical trajectory. As the most natural choice for the coordinate along the trajectory we accept its length l from some initial point to the current point. Then equation (B5) can be rewritten in an equivalent form:

$$\frac{dS_1}{dl} = \frac{i}{2p}\nabla \cdot \mathbf{p} \qquad (B6)$$

To solve it explicitly, we need to elucidate the geometrical meaning of $\nabla \cdot \mathbf{p}$. Consider a tube limited by a family of trajectories and cut it by two close cross-sections 1 and 2, normal to trajectories (Fig. 13).
The flux of the vector $\mathbf{p}$ through a surface composed by these cross-sections and the tube of trajectories connecting them is equal to $p_1 A_1 - p_2 A_2$ where $p_{1,2}$ are values of the momentum at the cross-sections 1 and 2 and $A_{1,2}$ are the cross-section areas. Since $\mathbf{p}$ is directed along trajectories, there is no flux through the side part of the surface. The volume limited by our surface is approximately equal to $A \cdot \Delta l$ where Δl is the distance along the trajectories between the cross-sections. Therefore:

$$\nabla \cdot \mathbf{p} = \lim_{\Delta l \to 0} \frac{p_1 A_1 - p_2 A_2}{A \Delta l} = \frac{1}{A}\frac{d(pA)}{dl} \qquad (B7)$$

Substituting (B7) into (B6) and integrating both parts by l, we find:

$$S_1 = \frac{i}{2}(\ln pA - \ln C) \qquad (B8)$$

where C is a constant. To make S_1 finite, this constant must be proportional to a cross-section area A_0 at some point. Then equation (B8) acquires a finite limit when the tube of trajectories becomes infinitely thin: the ratio of cross-sections at different points of trajectory is finite. Plugging S_0 and S_1 into the wave function $\psi = e^{iS/\hbar}$, we find:

$$\psi(x) = \frac{C}{\sqrt{pA}} \exp\left(\frac{i}{\hbar}\int\limits_{\mathbf{x}_0}^{\mathbf{x}} \mathbf{p}\,d\mathbf{x}\right) \qquad (B9)$$

where the integration proceeds along a classical trajectory. The pre-exponential factor ensures that the flux of particles through the cross-section of a narrow tube of trajectories does not change from one cross-section to another, i.e. that the number of particles or their probability is conserved. In particular, for spherical way $A \sim r^2$ leading to the factor r in denominator.

Since a narrow tube of trajectories merges into a point on a caustic, equation of the caustic can be formulated as $A = 0$. Equation (B9) shows that the semiclassical wavefunction has a singularity near caustics and the density grows as $1/A$. Actually, equation (B9) is invalid in a small vicinity of the caustic. In terms of a coordinate ξ perpendicular to the caustic and equal to zero exactly on it, the validity of semiclassical approximation (B9) requires that $|\xi| >> \hbar^{2/3}/(m \mid \nabla V \mid)^{1/3}$, similar to what was found in $1d$ case. Close inspection reveals the rule of passing through the caustic also similar to that we found for passing the turning point in $1d$. In particular, the wave-function decreases exponentially in classically forbidden region (shadow region). If several classical trajectories pass through the point $\mathbf{x}$, as it has happened in above considered examples, equation (B9) must be generalized:

$$\psi(\mathbf{x}) = \sum_j \frac{C_j}{\sqrt{p_j A_j}} \exp\left(\frac{i}{\hbar}S_j(\mathbf{x})\right) \qquad (B10)$$

where j enumerates the trajectories.

C. Bohr's quantization in 3 dimensions. Deterministic chaos in classical and quantum mechanics

Generalization of the Bohr's quantization rule (1.F4') is obvious:

$$S(E) = \oint \mathbf{p}\,d\mathbf{x} = (n+\boldsymbol{\gamma})\hbar \qquad (C1)$$

where integral is taken along a closed trajectory and γ is a constant of the order of one. The necessary conditions for such a quantization is the existence of classical periodic trajectory.

How restrictive is this limitation? This problem is very important for classical mechanics. There exist few exceptional systems which allow the exact solution of the Newton or Hamilton equations due to their high symmetry. One of the most important is the Kepler (or Coulomb) problem. In this case the periodic solutions are found explicitly. But how do they relate to reality? Real systems always are subject to perturbations which destroy the symmetry. For example, the Earth rotates in the gravitational field of the Sun, just the Kepler problem. But it is also effected by the moon and other planets. Can it happen that in the course of time these perturbations are accumulated and destroy the Keplerian periodicity?

The answer to this question was given by French matematician A. Poincare and later by A. Kolmogorov, V. Arnold and A. Mozer. They have found that a weak periodic perturbation does not destroy periodic trajectory if the ratio of the perturbation frequency to the frequency of motion on the trajectory is not close to a rational number with sufficiently small nominator and denominator, i.e. they are not in resonance. If, on contrary, the perturbation frequency is close to a low-order resonance or its amplitude is large, the initial classical trajectory can be destroyed. It becomes aperiodic, though it can be limited in space. In this situation two trajectories with very close initial conditions diverge very far in the course of time. It means, that the coordinates and momenta become unpredictable. The motion becomes chaotic, despite of the fact that equations of motion are completely deterministic. This is the so-called deterministic chaos, the main problem of the modern non-linear mechanics.

How the deterministic chaos displays itself in the quantum mechanics? One can conjecture that the randomness of trajectories lead to the randomness of phase factors for wave-functions and transition amplitudes. Not only phase factors, but the moduli of transition amplitudes become random since the caustics also are chaotic. Thus, in quantum mechanics the matrix of transition amplitudes is random. The transition amplitudes are matrix elements of the evolution operator $U(t)$. Since $U(t) = \exp(iHt/\hbar)$, it also means that the Hamiltonian H can be considered as a random matrix. Theory of random matrices was created by E. Wigner and F. Dyson. It shows that the distance Δ between nearest energy levels is a random value. Its average $\bar{\Delta}$ is equal to inverse density of levels $(\partial n/\partial E)^{-1}$, but its fluctuations are of the same order of magnitude. The probability density to find the inter-level distance Δ occurs an universal function of the ratio $\Delta/\bar{\Delta}$. This function is now reliably established. It plays the central role in so remote areas as spectra of atomic nuclei, spectroscopy of highly excited (Rydberg) atoms in external magnetic field and properties of disordered conductors of small size (the so-called mesoscopic).

Among numerous books and reviews on classical and quantum deterministic chaos I can recommend the book by M. Gutzwiller (5).

IV. ADIABATIC APPROXIMATION

A. Definition and main problems

This approximation is similar to the semiclassical one, but it deals with time-dependent problems. It works if coordinates of a system can be divided into two groups: fast varying $\mathbf{r}$ and slowly varying $\mathbf{R}$, where both $\mathbf{r}$ and $\mathbf{R}$ are multicomponent variables. A popular example is the molecular motion. Any molecule consists of heavy ions and light electrons. According to the virial theorem, their kinetic energy must be of the same order of magnitude, i.e. $Mv_i^2 \approx mv_e^2$, or $v_e = \sqrt{M/m}v_i$. Thus, the electron velocity is typically $\sqrt{M/m} \sim 10^3$ times larger than the ion velocity. It means that the quantum problem for electrons can be solved in the leading approximation at fixed positions $\mathbf{R}_i$ of ions. The total Hamiltonian for a molecule reads

$$H = H_{ei} + H_i \qquad (A1)$$

where $H_{ei}(\mathbf{R}_i)$ is the Hamiltonian for electrons at fixed positions of ions and H_i is the part of the Hamiltonian containing coordinates of ions only. To be specific, we write:

$$
\begin{aligned}
H_{ei} &= \sum_k \frac{p_k^2}{2m} + e^2 \sum_{k<l} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} - e^2 \sum_{k,i} \frac{Z_i}{|\mathbf{r}_k - \mathbf{R}_i|} \\
H_i &= \sum_i \frac{P_i^2}{2M_i} + e^2 \sum_{i<j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}
\end{aligned}
\qquad (A2)
$$

where capitals relate to ions, lower cases relate to electrons. The adiabatic or Born-Oppenheimer approximation works well for a bound state of electronic system $|n, \mathbf{R}\rangle$ obeying the Schrödinger equation:

$$H_{ei}(\mathbf{R}_i) \, | \, n, \mathbf{R}_i\rangle = E_n(\mathbf{R}_i) \, | \, n, \mathbf{R}_i\rangle \qquad (A3)$$

Electrons follow adiabatically the motion of ions as long as the transition frequency ω is large in comparison to a characteristic frequency of ion motion $\Omega = L/v_i$, where L is a characteristic size of the ionic motion. For molecules $\Omega \sim \sqrt{m/M}\omega << \omega$. The adiabatic parameter $\sqrt{m/M}$ is really small. It means that the ion motion does not produce transitions between electronic levels. The effective Hamiltonian for ions then can be intuitively found by averaging of the Hamiltonian (1) over a fixed electronic state $| \, n, \mathbf{R}_i\rangle$. Thus, we find:

$$H_{eff}^{(i)} = H_i + E_n(\mathbf{R}_i) \qquad (A4)$$

The electronic term $E_n(\mathbf{R}_i)$ plays the role of an additional potential energy for ions. Note that the complete vector of state in this approximation is the direct product of the ionic state $|i\rangle$ and electronic state dependent on the ionic coordinates as parameters $| \, n, \mathbf{R}_i\rangle$.

Another example is delivered by a particle with spin $1/2$ moving slowly in varying in space magnetic field B. Then the transition frequency is $\omega = g\mu_B B/\hbar$ where $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton, g is the gyromagnetic ratio (2 for a free electron). The adiabaticity condition reads:

$$v/L << \omega \qquad (A5)$$

where v is the particle velocity. In this case the direction of spin follows adiabatically the local direction of magnetic field being either parallel or antiparallel to it.

One more example is delivered by a quantum rotator , i.e. a particle with large spin or total angular moment J, placed into external electric or magnetic fields. The centre of the particle must be fixed. Classical rotator is characterized by its two spherical coordinates θ and φ. They play role of slow coordinates. The fast coordinates determine quantum fluctuations of the rotator near the classical position. We will return to this example in some details later.

General formulation of the adiabatic approximation is as follows. Let the Hamiltonian of a system $H(\mathbf{R})$ depend on a set of parameters $\mathbf{R}$ which vary in time. Let $\mid n, \mathbf{R}\rangle$ is a stationary state of this Hamiltonian at a fixed set $\mathbf{R}$:

$$H(\mathbf{R}) \mid n, \mathbf{R}\rangle = E_n(\mathbf{R}) \mid n, \mathbf{R}\rangle \qquad (A3')$$

The process is called adiabatic if

$$\frac{\mid \dot{\mathbf{R}} \mid}{\mid \mathbf{R} \mid} << \frac{E_{n+1} - E_n}{\hbar} = \omega \qquad (A4)$$

Since transitions are suppressed in the adiabatic process, it is obvious that the system will follow the same state $\mid n, \mathbf{R}\rangle$ as long as adiabaticity condition (4) is satisfied. Two main problems must be solved to complete the picture.

i) The adiabatic approximation definitely is invalid in points where two or more levels cross, since transition frequency ω turns into zero. Then the transition between levels become probable. The problem is to find the transition amplitudes. This is the so-called Landau-Zener problem. Points of levels crossing in the adiabatic problem are similar to the classical turning points in the semiclassical approximation.

ii) The electronic state $\mid n, \mathbf{R}\rangle$ persists if $\mathbf{R}$ vary very slowly with time, but it does not exclude a time-dependent phase factor $e^{i\gamma(t)}$ accompanying the adiabatic change of parameters $\mathbf{R}$. This phase is called the Berry's phase. It plays very important role in numerous interference phenomena. It also changes the effective Hamiltonian for slow variables $\mathbf{R}$.
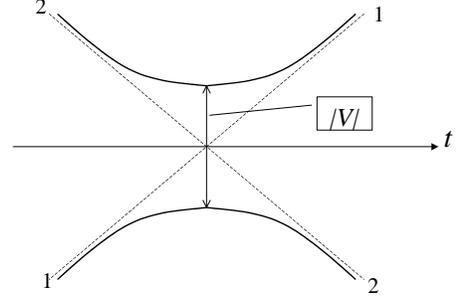

FIG. 14 Two levels crossing. Dashed lines show levels in the absence of interlevel matrix element. Solid lines show levels in adiabatic approximation.

B. Transitions at avoided two-level crossing (Landau-Zener problem)

Though sometimes more than two levels can cross simultaneously, two-levels crossing is the most common situation. At two-level crossing we can neglect all other levels and consider two-level system. We start with the consideration of the most general two-level system with the time-independent Hamiltonian. Stationary Schrödinger equations for such a system are:

$$\begin{cases} E_1 a_1 + V a_2 = E a_1 \\ V^* a_2 + E_2 a_2 = E a_2 \end{cases} \qquad (B1)$$

where $a_{1,2}$ are the amplitudes of the states, $E_{1,2}$ are their energies and V is the transition matrix element. Solution of secular equation for the system (1) reads:

$$E_\pm = \frac{E_1 + E_2}{2} \pm \sqrt{\frac{(E_1 - E_2)^2}{4} + \mid V \mid^2} \qquad (B2)$$

If $\mid E_1 - E_2 \mid >> V$, the two solutions (2) are approximately $E_+ = E_1 + \frac{|V|^2}{E_1 - E_2}$, $E_- = E_2 - \frac{|V|^2}{E_1 - E_2}$, very close to initial levels E_1, E_2. In the opposite limiting case $\mid E_1 - E_2 \mid << V$, we find $E_\pm \approx \frac{E_1 + E_2}{2} \pm \mid V \mid$. It means that energy levels do not cross, they repulse each other and the minimal distance between them is $2 \mid V \mid$. This phenomenon is called the Wigner-Teller level repulsion. If E_1 and E_2 are driven by some parameter t, a schematic picture of levels near the crossing looks like it is shown on Fig. 14. At infinitely slow variation the system follows the static level which it occupied initially. It means that the state 1 transits with the probability 1 to the state 2 and vice versa. Most naturally one can choose t to

be real time. The time-dependent Schrödinger equations must be solved. They are:

$$\begin{cases} i\hbar\dot{a_1} = E_1(t)a_1 + Va_2 \\ i\hbar\dot{a_2} = E_2(t)a_2 + V^*a_1 \end{cases} \qquad (B3)$$

By the change of variables:

$$a_{1,2} = \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}\frac{E_1(t') + E_2(t')}{2}dt'\right)\tilde{a}_{1,2} \qquad (B4)$$

the system (3) is reduced to a following one:

$$\begin{aligned} i\dot{\tilde{a}}_1 &= \frac{\omega(t)}{2}\tilde{a}_1 + v\tilde{a}_2 \\ i\dot{\tilde{a}}_2 &= -\frac{\omega(t)}{2}\tilde{a}_2 + v^*\tilde{a}_1 \end{aligned} \qquad (B5)$$

where $\omega(t) = (E_1(t) - E_2(t))/\hbar$ is the time-dependent transition frequency and $v = V/\hbar$. We are interested in a vicinity of the levels crossing point only. Accepting $t = 0$ in this point, let expand the frequency up to a linear term: $\omega(t) = \dot{\omega}_0 t$, where $\dot{\omega}_0$ is the time derivative of the frequency at the crossing point. The time dependence of v can be neglected. In this approximation the system (5) can be rewritten as:

$$\begin{cases} i\dot{a_1} = \frac{\dot{\omega}_0 t}{2}a_1 + va_2 \\ i\dot{a_2} = v^*a_1 - \frac{\dot{\omega}_0 t}{2}a_2 \end{cases} \qquad (B5')$$

Here and further we omit tilde over $a_{1,2}$. In terms of a dimensionless variable $\tau = \sqrt{\dot{\omega}_0}t$ equation (5') reads:

$$\begin{cases} \left(i\frac{d}{d\tau} - \frac{\tau}{2}\right)a_1 = \gamma a_2 \\ \left(i\frac{d}{d\tau} + \frac{\tau}{2}\right)a_2 = \gamma^* a_1 \end{cases} \qquad (B6)$$

These equations depend on one dimensionless parameter $\gamma = \frac{v}{\sqrt{\dot{\omega}_0}} = \frac{V}{\hbar\sqrt{\dot{\omega}_0}}$ which was first introduced by Landau (without loss of generality v can be taken real, ascribing its phase factor to a_2). It is possible to eliminate the amplitude a_2 from the system (6) and reduce it to a second order differential equation for a_1:

$$\left(i\frac{d}{d\tau} + \frac{\tau}{2}\right)\left(i\frac{d}{d\tau} - \frac{\tau}{2}\right)a_1 = |\gamma|^2 a_1 \qquad (B7)$$

or

$$\frac{d^2 a_1}{d\tau^2} + \left(\frac{i}{2} + \frac{\tau^2}{4} + |\gamma|^2\right)a_1 = 0 \qquad (B8)$$

This is the so-called equation of parabolic cylinder. Its two independent solutions are expressed in terms of the confluent hypergeometric functions, but our purpose can

be achieved without knowledge of these special functions. We look for a solution which corresponds to the filled state 1 and empty state 2 at $t \to -\infty$, i.e. $|a_1| = 1$ and $a_2 = 0$ at $\tau \to -\infty$. Neglecting $|\gamma|^2$ in equation (8) at large $|\tau|$, we find two independent solutions of equation (8): $a_1^{(1)} \approx e^{-i\tau^2/4}$, $a_1^{(2)} \approx \frac{e^{i\tau^2/4}}{\tau}$. Only the first one corresponds to our initial condition at $\tau \to -\infty$, the second one leads to a finite a_2 according to (6). To find what happens with this solution at $\tau \to +\infty$, we apply the same trick we have used already for passing the classical turning point: we pass the crossing point $\tau = 0$ along a big circle in the upper half-plane of the complex plane τ. To understand why the contour of circulation must be chosen in the upper half-plane, let us consider the asymptotic behavior of the solution $a_1 \approx e^{-i\tau^2/4}$. This solution decreases exponentially on the Stokes line $\arg\tau = 3\pi/4$. Therefore, it definitely is represented by the same exponent on the ray $\arg\tau = \pi$ and on a large arc in the complex plane τ until it crosses the second Stokes ray $\arg\tau = \pi/4$. After this line a second asymptotic solution must be added with the coefficient $-i$, but the coefficient at the first one does not change till the next Stokes line $\arg\tau = -\pi/4$ and the second solution vanishes on the real axis at $\tau \to +\infty$. Due to the additional term $|\gamma|^2 a_1$ in equation (7), the modulus of the solution a_1 is not more equal to 1 at $\tau \to +\infty$. Indeed, representing a_1 as $a_1 = e^{iS(\tau)}$ in the spirit of the semiclassical approximation, we find equation for $S(\tau)$:

$$\left(\frac{dS}{d\tau}\right)^2 - i\frac{d^2S}{d\tau^2} = \left(\frac{\tau^2}{4} + \frac{i}{2} + |\gamma|^2\right) \qquad (B9)$$

At large τ we expand $\frac{dS}{d\tau}$ in a series over $\frac{1}{\tau}$. In the leading approximation we find:

$$\frac{dS_0}{d\tau} = -\frac{\tau}{2}; \; S_0 = -\frac{\tau^2}{4} \qquad (B10)$$

Next approximation reads:

$$2\frac{dS_0}{d\tau}\frac{dS_1}{d\tau} = |\gamma|^2 ; \; S_1 = -|\gamma|^2\ln\tau + const \qquad (B11)$$

If the constant in equation (11) is chosen to make S_1 real at $\arg\tau = +\pi$, then $\text{Im}\,S_1 = \pi|\gamma|^2$ at $\arg\tau = 0$. Therefore,

$$|a_1| = e^{-\pi|\gamma|^2} \text{at } \tau \to +\infty \qquad (B12)$$

Pay attention to the fact that, if we formally perform a circulation in the lower half-plane of τ, we obtain an erroneous answer for asymptotic value $a_1 = e^{\pi|\gamma|^2}$ ($|a_1|$ can not be more than 1). This asymmetry stems from the exponential growth of the solution $e^{-i\tau^2/4}$ along the Stokes line $\arg\tau = -i3\pi/4$. It acquires another exponent

on the line $\arg \tau = -i\pi/2$ which further grows exponentially, while the initial exponent becomes uncontrollably small. The result (12) was first obtained independently by Landau and Zener in 1932.

Landau has added to this consideration a feature specific for electronic transitions at a collision of two atoms or ions. In this case the adiabatic parameter is the distance R between colliding particles. Let the level crossing takes place at some value $R = R_0$. Then it happens twice during the collision process provided the minimal distance between the particles $R_{\min}$ is less than R_0. Let the crossing proceeds at moments of time t_1 and t_2. If the change of phase $\int\limits_{t_1}^{t_2}\omega(t)dt$ between the crossing is large, the interference effects are negligibly small at small averaging over energy or other quantum numbers. Then not the amplitudes, but the probabilities of different versions of electronic transitions become additive. The transition probability at one crossing is $P = 1 - \mid a_1 \mid^2$. The transition probability at the collision P_{col} is the sum of probabilities that the transition happens at the first crossing and does not happen at the second one and vice versa, i.e.

$$P_{col} = 2P(1-P) = 2e^{-2\pi|\gamma|^2}\left(1 - e^{-2\pi|\gamma|^2}\right) \quad \text{(B13)}$$

An interesting problem of interference between two successive transitions is not yet solved.

C. Berry's phase, Berry's connection

1. Definition of the geometrical phase

Let us consider again a system with adiabatically varying parameters $\mathbf{R}(t)$ and with the Hamiltonian $H(\mathbf{R})$. Let $E_n(\mathbf{R})$ and $\mid n, \mathbf{R}\rangle$ are the eigenvalues and corresponding eigenstates of the Hamiltonian $H(\mathbf{R})$. We will look for a solution of the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\mid \alpha, t\rangle = H(\mathbf{R}(t))\mid \alpha, t\rangle \quad \text{(C1)}$$

considering $\overset{\bullet}{\mathbf{R}}(t)$ as small values: $\frac{|\overset{\bullet}{\mathbf{R}}(t)|}{\mathbf{R}} << \omega_{n,n\pm1}$. Then, as it was already argued, the interlevel transitions are suppressed and time-dependent states presumably follow stationary states $\mid n, \mathbf{R}(t)\rangle$ corresponding to instantaneous values of the parameters. Thus, a solution of equation (C1) generically associated with $\mid n, \mathbf{R}(t)\rangle$ can be represented as

$$\mid n, t\rangle = e^{-i\varphi(t)}\mid n, \mathbf{R}(t)\rangle \quad \text{(C2)}$$

By such an ansatz we automatically provide a correct normalization of the state $\mid n, t\rangle$. Substituting (2) to (1), we arrive at equation:

$$\hbar\frac{\partial\varphi}{\partial t}\mid n, \mathbf{R}(t)\rangle + i\hbar\frac{\partial}{\partial t}\mid n, \mathbf{R}(t)\rangle = E_n(\mathbf{R}(t))\mid n, \mathbf{R}(t)\rangle \quad \text{(C3)}$$

What is lost in this approach is the admixture of other eigenstates $\mid n', \mathbf{R}(t)\rangle$ $(n' \neq n)$ generated by the derivative

$$\frac{\partial}{\partial\mathbf{R}}\mid n, \mathbf{R}\rangle = \sum_{n'}\langle\mid n', \mathbf{R}\rangle\langle n', \mathbf{R}\mid\frac{\partial}{\partial\mathbf{R}}\mid n, \mathbf{R}\rangle$$

It determines the transition amplitudes, i.e. the Landau-Zener problem. In this section we assume that the trajectory $\mathbf{R}(t)$ passes sufficiently far from the level crossing points and neglect the transitions. Note, that even if it passes the crossing point, the Landau-Zener parameter

$$\gamma^2 = \frac{V^2}{\hbar^2|\overset{\bullet}{\omega}|} \simeq \frac{\overset{\bullet}{\mathbf{R}}^2\mid\langle n', \mathbf{R}\mid\frac{\partial}{\partial\mathbf{R}}\mid n, \mathbf{R}\rangle\mid^2}{\hbar^2\mid\partial\omega/\partial\mathbf{R}\mid\mid\overset{\bullet}{\mathbf{R}}\mid}\sim\overset{\bullet}{\mathbf{R}}$$

goes to zero when $\left|\overset{\bullet}{\mathbf{R}}\right|$ goes to zero. Thus, the transition amplitudes are zero in adiabatic limit, whereas the Berry's phases are finite. Let multiply equation (C3) by $\langle n, \mathbf{R}(t)\mid$ to find:

$$\frac{\partial\varphi}{\partial t} = \frac{1}{\hbar}E_n(\mathbf{R}(t)) - i\langle n, \mathbf{R}(t)\mid(\frac{\partial}{\partial t}\mid n, \mathbf{R}(t)\rangle) \quad \text{(C4)}$$

We prove that the second term in the r.-h.s. of equation (C4) is real. Indeed, from the normalization condition $\langle n, \mathbf{R}(t)\mid n, \mathbf{R}(t)\rangle = 1$ it follows that

$$\langle n, \mathbf{R}(t)(\frac{\partial}{\partial t}\mid n, \mathbf{R}(t)\rangle) + (\frac{\partial}{\partial t}\langle n, \mathbf{R}(t)\mid)\mid n, \mathbf{R}(t)\rangle = 0$$

On the other hand, according to general relations:

$$(\frac{\partial}{\partial t}\langle n, \mathbf{R}(t)\mid)\mid n, \mathbf{R}(t)\rangle = \langle n, \mathbf{R}(t)\mid(\frac{\partial}{\partial t}\mid n, \mathbf{R}(t)\rangle^*$$

Thus, the matrix element $\langle n, \mathbf{R}(t)\mid(\frac{\partial}{\partial t}\mid n, \mathbf{R}(t)\rangle)$ is a number equal to its complex conjugated taken with the sign minus and, therefore, it is purely imaginary. Returning to equation (C4), let integrate it:

$$\varphi(t) = \frac{1}{\hbar}\int\limits_{t_0}^{t}E_n(\mathbf{R}(t'))dt' + \gamma(t, t_0) \quad \text{(C5)}$$

where

$$\gamma(t, t_0) = -i\int\limits_{t_0}^{t}\langle n, \mathbf{R}(t')\mid\frac{\partial}{\partial t'}\mid n, \mathbf{R}(t')\rangle dt' \quad \text{(C6)}$$

The first part of the phase $\varphi(t)$ is what we could expect from the naive arguments similar to those used for explanation of the semiclassical limit. But the second part $\gamma(t, t_0)$ is not trivial. It is called the Berry's phase in honor of the author, Michael Berry, who has discovered it in 1983. This is an example of a simple phenomenon which was overlooked by numerous researchers during almost 50 years after discovery of Quantum Mechanics.

We will simplify equation (6). First, let us note that

$$\langle n, \mathbf{R}(t) \mid \frac{\partial}{\partial t} n, \mathbf{R}(t) \rangle = \frac{d\mathbf{R}}{dt} \cdot \langle n, \mathbf{R}(t) \mid \frac{\partial}{\partial \mathbf{R}} \mid n, \mathbf{R}(t') \rangle$$

Thus, equation (6) can be rewritten as follows:

$$\gamma(t, t_0) = \int_{t_0}^{t} \mathbf{A}(\mathbf{R}(t)) \frac{d\mathbf{R}}{dt} \cdot dt \qquad (C7)$$

where we have introduced the so-called Berry's connection:

$$\mathbf{A}(\mathbf{R}) = -i \langle n, \mathbf{R} \mid \frac{\partial}{\partial \mathbf{R}} \mid n, \mathbf{R} \rangle \qquad (C8)$$

Since $\frac{d\mathbf{R}}{dt} \cdot dt = d\mathbf{R}$, the integral in (C6) can be transformed into a linear integral along a trajectory $\mathbf{R}(t)$:

$$\gamma(t, t_0) = \gamma(\mathbf{R}, \mathbf{R}_0) = \int_{\mathbf{R}_0}^{\mathbf{R}} \mathbf{A}(\mathbf{R}'(t)) d\mathbf{R}' \qquad (C9)$$

The last equation demonstrates that the Berry's phase is a geometrical phase in the meaning that it depends on the shape of trajectory and its endpoints, but it does not depend on the dynamics on the trajectory. Any time dependence $\mathbf{R}(t)$ at passing a fixed curve in $\mathbf{R}$-space leads to the same Berry's phase. Therefore, the Berry's phase is also called the geometrical phase.

An important peculiarity of the Berry's phase C9 is that the Planck constant is dropped out of it. It means that the Berry's phase is a purely classical effect. Its physical meaning can be easily explained for a simple example of the Foucault pendulum. It is well known that its oscillation is followed by a slow rotation of the oscillation plane due to the Coriolis force induced by the Earth rotation around its axis. The Berry's phase is the phase of this rotation for this specific problem.

More generally, the classical adiabatic motion is a fast oscillation with slowly varying parameters. The frequency of this motion is a given function of time, but its phase and amplitude also vary slowly (see section II.G).

2. Gauge transformations

The geometrical phase $\gamma(\mathbf{R}, \mathbf{R}')$ is not defined uniquely even if the contour of integration is fixed together with
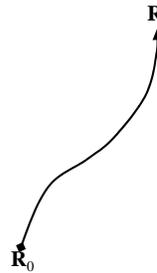

FIG. 15 Trajectory of a system in R-space.

its ends. Multiplication of the ket $\mid n, \mathbf{R} \rangle$ by a phase factor $e^{-if(\mathbf{R})}$ depending on $\mathbf{R}$ and the simultaneous gauge transformation of the Berry's connection:

$$\mathbf{A}(\mathbf{R}) \rightarrow \mathbf{A}(\mathbf{R}) + \boldsymbol{\nabla}_{\mathbf{R}} f(\mathbf{R}) \qquad (C10)$$

does not change the time dependence of the state $\mid n, t \rangle$. The gauge transformation of the Berry's phase reads:

$$\gamma(\mathbf{R}, \mathbf{R}) \rightarrow \gamma(\mathbf{R}, \mathbf{R}') + f(\mathbf{R}) - f(\mathbf{R}') \qquad (C11)$$

The gauge transformation of the Berry's connection (10) is similar to the gauge transformation of the vector-potential in electricity and magnetism theory. It is not surprising since both fields belong to the class of the Yang-Mills gauge fields compensating the local $U(1)$ transformation[5]. An essential difference between them is that the electromagnetic vector-potential depends on real coordinates $\mathbf{r}$, whereas the Berry's connection depends on parameters $\mathbf{R}$ which can be identified with slow variables. Thus, the Hamiltonian for slow variables must include $\mathbf{A}(\mathbf{R})$ in a gauge-invariant combination $\nabla_{\mathbf{R}} = \frac{1}{i} \partial/\partial \mathbf{R} - \mathbf{A}$ which is proportional to the quantum operator of velocity $\dot{\mathbf{R}}$. Indeed, according to the adiabatic assumption, a state of the complete system $|S, F\rangle$ including fast and slow variables is a direct product of the type: $|S, F\rangle = |S\rangle \otimes |n, \mathbf{R}\rangle$ in which the first ket determines the state of slow subsystem and the second ket is the state of the fast subsystem parametrically

---

[5] In terms of topological fiber-bundles theory the gauge potential realises connection (parallell translation) between $U(1)$ layers belonging to different points of the base (the manifold of points labeled by $\mathbf{R}$). It justifies the notation "Berry's connection", but may be "Berry' vector-potential" would be not worse.

dependent on slow coordinates. Applying the translation generator $-i\,\partial/\partial\mathbf{R}$ to this state and multiplying the resulting state by the bra $\langle\mathbf{R}|\otimes\langle n,\mathbf{R}|$ where $\langle\mathbf{R}|$ is the vector of a state with a fixed coordinate, we arrive at the gauge invariant derivative:

$$\frac{1}{i}\frac{\partial\psi(\mathbf{R})}{\partial\mathbf{R}}-i\psi(\mathbf{R})\cdot\langle n,\mathbf{R}|\frac{\partial}{\partial\mathbf{R}}\mid n,\mathbf{R}\rangle=(\frac{1}{i}\frac{\partial}{\partial\mathbf{R}}-\mathbf{A}(\mathbf{R}))\psi(\mathbf{R})$$

Here $\psi(\mathbf{R})=\langle\mathbf{R}\mid S\rangle$ is the Schrödinger wave-function for slow coordinates.

3. Invariant Berry's phase

Though generally the Berry's phase is not invariant under the gauge transformation, it becomes invariant for any closed contour C. In this case the gauge phases $f(\mathbf{R})$ and $f(\mathbf{R}')$ coincide and cancel each other (see equation (C11). Thus, for a closed contour the geometrical phase depends only on the contour: $\gamma=\gamma(C)$. Here we find this dependence in some important cases.

We start with the case of a particle with spin $1/2$ moving in an inhomogeneous magnetic field. The spin Hamiltonian for such a system is:

$$H_{\mathbf{B}}(\mathbf{B})=g\mu_{\mathbf{B}}\mathbf{s}\cdot\mathbf{B}\qquad(C12)$$

and $\mathbf{B}$ is an arbitrary slow function of time t. Slow here means that $|\,\dot{\mathbf{B}}\,|\,/B\ll g\mu_{\mathbf{B}}B/\hbar$. The vector $\mathbf{B}$ plays the role of slow parameters which was denoted in previous sections $\mathbf{R}$. The spin adiabatically follows the direction of magnetic field $\mathbf{B}$. The instantaneous stationary states are spinors $\mid\pm,\hat{\mathbf{B}}\rangle$ obeying equations:

$$\hat{\mathbf{B}}\cdot\mathbf{s}\mid\pm,\hat{\mathbf{B}}\rangle=\pm\frac{1}{2}\mid\pm,\hat{\mathbf{B}}\rangle\qquad(C13)$$

($\hat{\mathbf{B}}$ is unit vector along magnetic field $\mathbf{B}$). Let us expand them in a fixed base $\mid\pm1/2,z\rangle$ of states with spin projections $\pm1/2$ onto a fixed axis z:

$$\mid\pm,\hat{\mathbf{B}}\rangle=\alpha_{\pm}(\hat{\mathbf{B}})\mid+,z\rangle+\beta_{\pm}(\hat{\mathbf{B}})\mid-,z\rangle\qquad(C14)$$

Substituting (3) into (2) and solving corresponding equations, we find: $\alpha_{+}=\cos\theta/2$; $\beta_{+}=\sin\theta/2\ e^{-i\varphi}$; $\alpha_{-}=\sin\theta/2\ e^{i\varphi}$; $\beta_{-}=\cos\theta/2$ where θ and φ are spherical angles determining the direction of $\hat{\mathbf{B}}$. It is convenient to express $\alpha_{\pm}$ and $\beta_{\pm}$ directly in terms of Cartesian components of the vector $\mathbf{B}$:

$$\alpha_{+}=\sqrt{\frac{B+B_z}{2B}};\ \beta_{+}=\sqrt{\frac{B-B_z}{2B}}\frac{B_x-iB_y}{\sqrt{B_x^2+B_y^2}}\quad(C15)$$

$$\alpha_{-}=\sqrt{\frac{B-B_z}{2B}}\frac{B_x+iB_y}{\sqrt{B_x^2+B_y^2}};\ \beta_{-}=\sqrt{\frac{B+B_z}{2B}}$$

where $B=\sqrt{B_x^2+B_y^2+B_z^2}$ is the modulus of the vector $\mathbf{B}$. Now the differentiation of the amplitudes (15) by B_j $(j=x,y,z)$ is straightforward and, according to the general prescription, components of the Berry's connection are:

$$A_j^{(\pm)}=-i\,\langle\pm,\mathbf{B}|\frac{\partial}{\partial B_j}\mid\pm,\mathbf{B}\rangle\qquad(C16)$$

We leave this calculation as an exercise for a reader. The result for state " + " is:

$$A_z^{(+)}=0;\ A_x^{(+)}=-\frac{1-\cos\theta}{2\sin\theta}\frac{\sin\varphi}{B};\ A_y^{(-)}=\frac{1-\cos\theta}{2\sin\theta}\frac{\sin\varphi}{B}$$
$$(C17)$$

Transformation of the Berry's connection vector to spherical components simplifies it remarkably:

$$A_r=A_\theta=0;\ A_\varphi=\frac{1}{2B}\frac{1-\cos\theta}{\sin\theta}\qquad(C18)$$

Pay attention that the vector $\mathbf{A}$ has a singularity on the line $\theta=\pi$. If we consider $\mathbf{B}$ as the radius-vector in $\mathbf{B}$-space, the Berry's connection (7) coincides formally with the vector-potential of the Diracs monopole with the magnetic charge $1/2$. It is useful to introduce the representing field $\mathcal{B}=\nabla\times\mathbf{A}$. Do not confuse it with the real magnetic field $\mathbf{B}$. Its calculation from equation (7) is straightforward:

$$\mathcal{B}=\frac{1}{2}\frac{\mathbf{B}}{B^3}\qquad(C19)$$

The calculation of the invariant Berry's phase can be performed explicitly using the Stokes theorem:

$$\gamma(C)=\oint_C\mathbf{A}d\mathbf{B}=\int_{\Gamma(C)}\mathcal{B}d\mathbf{S_B}=\frac{\Omega(C)}{2}\qquad(C20)$$

Here $\Gamma(C)$ is any surface in the $\mathbf{B}$-space subtended by the contour C and $\Omega(C)$ is the solid angle at which this surface is seen from the origin. This answer has a direct experimental consequence determining the quantum interference of two spin-1/2-particle sub-beams, one of which passes a region of varying in space magnetic field.

The extremely simple geometrical phase (C20) has a more general meaning. It relates to an adiabatic quantum system if all points of the contour C are close to a

two-level crossing points. Near this point the time derivatives of all states $| n, \mathbf{R} \rangle$, except of the two which cross, can be neglected. The problem is effectively reduced to the 2-level problem which in turn is reduced to that of spin-1/2 in an external field.

The above described problem allows generalization to higher spins $S > 1/2$. In analogy with the states $| \pm \hat{\mathbf{B}} \rangle$ determined by equation (C14), we introduce $| m, \hat{\mathbf{B}} \rangle$ the eigenstates of the operator $\mathbf{S} \cdot \hat{\mathbf{B}}$:

$$\mathbf{S} \cdot \hat{\mathbf{B}} \mid m, \hat{\mathbf{B}} \rangle = m \mid m, \hat{\mathbf{B}} \rangle; \; m = -S, -S+1 \ldots S \quad \text{(C20)}$$

They can be obtained from the state $\mid m, \hat{z} \rangle$ applying to it first the rotation $R_x(\theta)$ by the angle θ around the x-axis and then the rotation $R_z(\varphi)$ around the z (namely these two rotations transform the unit vector $\hat{z}$ into the unit vector $\hat{B}$, see Fig.):

$$\mid m, \hat{B} \rangle = R_z(\varphi) R_x(\theta) R_z^{-1}(\varphi) \mid m, \hat{z} \rangle \quad \text{(C21)}$$

The operator $R_z^{-1}(\varphi)$ does not change the state $\mid m, \hat{z} \rangle$, it simply multiplies it by the factor $e^{im\varphi}$, but it ensures that the state $\mid m, \hat{B} \rangle$ coincides with $\mid m, \hat{z} \rangle$ at $\theta = 0$. The rotation operators are:

$$R_z(\varphi) = e^{-iS_z \varphi}; \; R_x(\theta) = e^{-iS_x \theta}$$

Substituting them into (11) and differentiating, we find:

$$
\begin{aligned}
A_\theta &= -\frac{i}{B} \times \\
& \langle m, \hat{z} | e^{iS_x\theta} e^{iS_z\varphi} \frac{\partial}{\partial \theta} \left(e^{-iS_z\varphi} e^{-iS_x\theta} \right) | m, \hat{z} \rangle \\
&= -\frac{1}{B} \langle m, \hat{z} \mid S_x \mid m, \hat{z} \rangle = 0 \\
A_\varphi &= -\frac{i}{B \sin\theta} \times \quad \text{(C22)} \\
& \langle m, \hat{z} | e^{iS_z\varphi} e^{iS_x\theta} e^{iS_z\varphi} \frac{\partial}{\partial \theta} \left(e^{-iS_z\varphi} e^{-iS_x\theta} e^{iS_z\varphi} \right) | m, \hat{z} \rangle \\
&= -\frac{1}{B \sin\theta} \langle m, \hat{z} \mid e^{iS_x\theta} S_z e^{-iS_x\theta} - m \mid m, \hat{z} \rangle \\
&= \frac{m(1 - \cos\theta)}{B \sin\theta}
\end{aligned}
$$

This answer differs from that of equation (C20) only by substitution of m instead 1/2. Therefore, for the state with a fixed projection of spin m the Berry's phase reads

$$\gamma(C, m) = m\Omega(C) \quad \text{(C23)}$$

An experimental verification of equation (C20) has been performed by T. Bitter and D. Dublers (Phys. Rev. Lett.
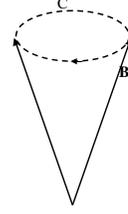

FIG. 16 Closed contour formed by rotating magnetic field.

59, 251, 1987). They have used a neutron beam in the magnetic field slowly rotating in space around the direction of the beam propagation. Neutrons were polarized perpendicularly to the field and remained perpendicularly polarized due to the adiabaticity along their trajectory. We know that in the homogeneous field spin precesses with the angular velocity $\omega = \frac{g\mu B}{\hbar}$ and turns over the angle $\Phi_0(t) = \omega t$. But in the rotating field the Berry's phase must be added:

$$\Phi = \Phi_0(t) + 2\gamma(C)$$

where C is a contour in $\mathbf{B}$-space formed by the vector $\hat{B}$ along the beam path (Fig. 16).

Assuming that projection B_z of $\mathbf{B}$ to the beam direction is fixed $B_z/\mathbf{B} = \cos\theta = const$, the solid angle subtended by the contour C is $\Omega = 2\pi(1 - \cos\theta)$ and

$$2\gamma(C) = \Omega = 2\pi(1 - \cos\theta) \quad \text{(C24)}$$

This deviation of the rotation angle from the standard precession $\Phi_0(t)$ was confirmed by the experiment.

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