Tale 6
The Kramers' Phase and Laplace's Method

The Balmer's formula paradox

We will start with a paradox. Consider a hydrogen atom. The enery of its s-wave bound states is given by the Balmer's formula, which in the atomic units, has the form

$$E_n = -\frac{1}{2n^2}, \tag{1}$$

where n is the principal quantum number. The states with high values of this number ($n \gg 1$) obey condition of the WKB-approximation. Conventional for semi-classics the Bohr-Sommerfeld (BS) quantization rule ($\hbar = 1$)

$$\int_0^{r(E)} p(r, E)dr = \pi(n + 1/2) \tag{2}$$

contains the standard $n + 1/2$ in its right hand side. One can see that the energies E_n given by Eq (2) are functions of $n+1/2$ in an evident contradiction to the Balmer's formula (1).
The solution of this paradox must come from the analysis the conditions under which the WKB approximation is valid. It is valid,as we know if the electron wave vector $p(r, E) = \sqrt{E - U(r)}$ changes only slightly over the wave length $\lambda \sim 1/p$ in comparison with the wave vector itself, i.e if

$$\frac{dp}{dr} \ll p^2 \tag{3}$$

This condition becomes invalid at the points of the electron trajectory, where p vanishes (the regular turning points). In the case of the Coulomb potential there is a turning point at $r = r(E)$. Validity of the WKB approximation near the lower limit in the integral in BS-condition Eq(2) $r = 0$ requires an extra analysis. At $r \to 0$ the wave vector $p \sim r^{-1/2}$ and

$$\frac{d}{dr}\frac{1}{\sqrt{r}} \sim r^{-3/2} \gg p^2 \sim \frac{1}{r^2} \tag{4}$$

Therefore, as $r \to 0$ the WKB approximation also becomes invalid.

It is known that the regular turning points $r(E)$ add an extra phase $\pi/4$. Two turnin points lead to the BS condition in the form of Eq (2). In a general case, the extra phases must be reexamined in order to obtain a correct BS quantization condition. Therefore, the correct strategy is to solve the Schroedinger equation exactly near $r \to 0$ and $r = r(E)$ and match the WKB wave function to these exact solutions. This way allows to derive the extra phase in the BS condition without any uncertainties.

The regular turning point

Consider a regular turning point of the classical motion. It corresponds to the equation

$$-y'' + xy = 0 \tag{5}$$

which we are going to solve exactly to find the asymptotes at $x \to \pm\infty$. Using the Laplace method, we are looking for the solution of Eq (5) in the integral form.

$$y(x) = \int_C dt\phi(t)e^{xt} \tag{6}$$

The contour C in the complex plane t must be chosen so, that the integrated terms after the partial integration vanishes. The integral representation implies the following relations between the operations of the multiplication of the function by its argument and calculation of the derivatives.

$$\frac{dy(x)}{dx} \rightarrow t\phi(t), \quad xy(x) \rightarrow -\frac{d\phi(t)}{dt}. \tag{7}$$

Using these relations, we can rewrite Eq (5) in the form

$$-\frac{d\phi}{dt} - t^2\phi = 0. \tag{8}$$

Its solution is

$$\phi(t) = e^{-t^3/3}$$

so that

$$y(x) = \int_C dt \exp[xt - \frac{t^3}{3}]. \tag{9}$$

The integrand must vanish at both ends of this contour C. These ends must, therefore go to infinity in those sectors of complex t-plane, where $\mathrm{Re}t^3 > 0$ (the shaded sectors in Fig 1). Three different passes with the ends going to infinity in shadowed sectors of Fig 1 generate three sulutions of Eq (5), which correspond to linear combinations of two independent solutions. Solution which we need decays at $x \rightarrow +\infty$. We will see hat this condition is obeyed if the path of integration C is parallel to imaginary axis. If it is taking just along the imaginary axis, Eq (9) gives the Airy function:

$$\Phi(x) = Ai(x) = \frac{1}{\sqrt{\pi}} \int_0^\infty du \cos{(ux + \frac{u^3}{3})}. \tag{10}$$

The asymptoti expression for $\Phi(x)$ for large values of x is obtained by calculating the integral (5) by the steepest descent method. In the course of this method the integrand must be written in the form $\exp[-h(t)]$ and the minimum of $h(t)$ must be found. For $x > 0$ the minimum condition

$$0 = h'(z) = -x + t_0^2 \tag{11}$$

gives us two solutions $t_0 = \pm\sqrt{x}$. The values of the function $\exp[-h(t_0)]$ at these points are equal respectively to $\exp[\mp 2x^{3/2}/3]$. Therefore, the branch, which decays exponentially at $x \to +\infty$, corresponds to $t_0 = -\sqrt{x}$. Shifting the path of integration to pass through this point and calculation the integral by the steepest descent method, we obtain

$$\Phi(x) = \frac{1}{2x^{1/4}} \exp\left[-2x^{3/2}3\right]. \tag{12}$$

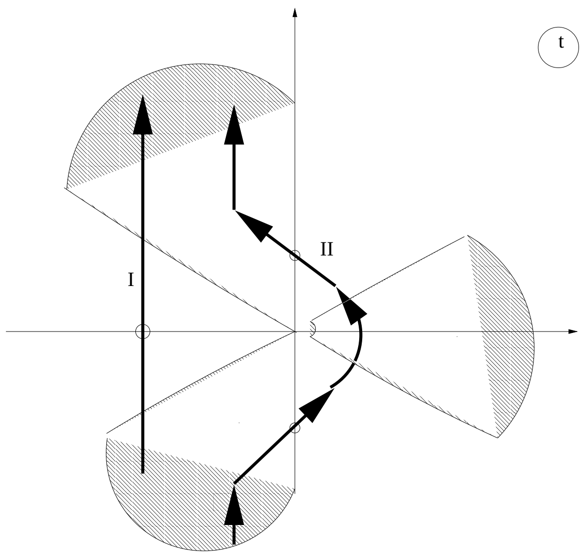

Figure 1: Plane of complex variable t and contours of integration. Saddle points are marked by circles on contour I (at x ¿ 0 and on contour II at x ¡ 0.

This shows that the chosen path of integration, indeed, gives solution, which decays exponentially at $x \to +\infty$. For $x < 0$, solutions of Eq (11) gives for the saddle-points

$$t_0 = \pm i\sqrt{|x|} \tag{13}$$

The values of the function at these two point are $\exp[\pm i2x^{3/2}/3]$, while second derivation of the phase is $h''(\pm i\sqrt{|x|}) = \pm i\sqrt{|x|}$. Therefore the steepest descent path of integration must go as it is shown by line II in Fig 1 , having the angles of $\pm 3\pi/4$ with the real axis. Integration gives:

$$\Phi(x)|_{x\to-\infty} = \frac{1}{|x|^{1/4}} \sin\left(\frac{2|x|^{3/2}}{3} + \frac{\pi}{4}\right). \tag{14}$$

The phase $\pi/4$ (the Kramers phase) appears in asymptotic expression (14).

Origin

Near the origin the potential is so large, that it possible to put the energy E in Schroedinger's equation at zero. Then the quation for the radial part $\chi(r)$ of the wave function becomes:

$$-\frac{d^2\chi}{dr^2} - \frac{\chi}{r} = 0 \qquad \chi(0) = 0, \quad \psi(r) = \frac{\chi(r)}{r}. \tag{15}$$

Using again Laplace's method, we seek the solution in the form

$$\chi(r) = \int_C dz X(z) e^{rz} \tag{16}$$

Solving the differential equation for $X(z)$

$$-\frac{d}{dz}(z^2 X) + X = 0 \tag{17}$$

we have

$$\chi(r) = \int_C \frac{dz}{z^2} e^{zr-1/z}. \tag{18}$$

Since $\chi(0) = 0$, we must chose the path C in the form of a closed loop around the origin in the complex z-plane. Then the result of integration vanishes at $r = 0$. Therefore, the solution near the origin has the form

$$\chi(r) = \oint_{|z|=1} \frac{dz}{z^2} \; e^{zr-1/z} \tag{19}$$

One could recognize the Bessel function $J_1(\sqrt{r})$ in this integral representation

$$\chi(r) \propto \sqrt{r} \; J_1(\sqrt{r}), \tag{20}$$

but we, really, do not need this. For large positive r ($r \gg 1$), the exponent has an extremum for

$$z_0 = \pm \frac{i}{\sqrt{r}}, \tag{21}$$

and, after standard evaluation we obtain

$$\chi(r) \sim r^{1/4} \sin(\sqrt{r} - \frac{\pi}{4}) \tag{22}$$

Thus, the point $r = 0$ gives rise to the extra phase $-\pi/4$ in the WKB expression for the wave functions in the Coulomb potential. This extra phase cancels one, genrated by the regular point $r = r(E)$. As the result the quantization rule takes the form

$$\int_0^{r(E)} p(r, E) dr = 2\pi\hbar n \tag{23}$$

which does not contradict Balmer's formula.

Appendix 1. Laplace Method

In order to demonstrate the power of the Laplace method, we solve two well known problem from Quantum mechanics in a quadratic potential.
Consider first the Schroedinger equation for the linear oscillator

$$-y'' + x^2 y = \lambda y \tag{24}$$

The asymptote of its solution at $|x| \to \infty$ is

$$y \sim \exp\left(-\frac{x^2}{2}\right) \tag{25}$$

The substitution

$$y(x) = H_\lambda(x) \exp\left(-\frac{x^2}{2}\right) \tag{26}$$

into Eq (24) leads to the following equation for $H_\lambda(x)$:

$$\left\{-\frac{d^2}{dx^2} + 2x\frac{d}{dx} - \lambda + 1\right\} H_\lambda(x) = 0 \tag{27}$$

Using the Laplace method, we can find an integral representation for $H_\lambda(x)$.

$$H_\lambda(x) = \frac{1}{2\pi i} \oint_{|z|=1} \exp\left(xz - \frac{z^2}{2}\right) \frac{dz}{z^{(\lambda+1)/2}} \tag{28}$$

This function is a polynomial of power n if and only if

$$\frac{\lambda+1}{2} = n+1; \quad \lambda = 2n+1; \quad n = 0, 1, 2, ... \tag{29}$$

Under these conditions, these polynomia (Hermite Polynomia) are the coefficients in the power expansion:

$$\exp\left(xz - \frac{z^2}{2}\right) = \sum_{n=0}^{\infty} H_n(x) z^n, \tag{30}$$

which give a general formula

$$H_n(x) = (-1)^n \exp\left(\frac{z^2}{2}\right) \frac{d^n}{dx^n} \exp\left(-\frac{z^2}{2}\right). \tag{31}$$

Another example comes from the problem about the particle passing through the barrier, which has a shape of inverted parabola. So, let us consider equation

$$-y'' - x^2 y = \epsilon y, \tag{32}$$

with the boundary conditions

$$y(x) = \frac{1}{\sqrt{p(x)}} \begin{cases} \exp[-i \int_0^x p(x')dx'] + r \exp[i \int_0^x p(x')dx'], \; x \to -\infty; \\ t \exp[i \int_0^x p(x')dx'], \; x \to +\infty. \end{cases} \tag{33}$$

Here

$$p(x) = \sqrt{\epsilon + x^2} \cong x + \frac{\epsilon}{2x}, \quad S(x) = \int_0^x dx' p(x') \cong \frac{x^2}{2} + \frac{\epsilon}{2} \log x$$

and, therefore,

$$y(x) = \frac{|x|^{i\epsilon/2} e^{\pi\epsilon/2}}{\sqrt{p(x)}} \begin{cases} e^{-ix^2/2} + r|x|^{-2i\epsilon/2} e^{i\left(x^2 - 2\pi\epsilon\right)/2}, \; x \to -\infty \\ t e^{i\left(x^2 - \pi\epsilon\right)/2}, \; x \to +\infty \end{cases} \tag{34}$$

The problem is to find the transmission and reflection amplitudes t and r and transmission and reflection coefficients $T = |t|^2$ and $R = |r|^2$.
Our strategy will the following:
1. using the Laplace method we will construct an integral representation for solution of Eq (32);
2. the contour in of integration we will chose to satisfy the condition at infinity (34);
3. we will find asymptotes of that integral at $x \to \pm\infty$ and find from these asymptotes the walues of t and r.

Appendix 2. Maslov Index

Question about extra phase in the semi-classical quantization condition has an interesting generalization, valid also for multidimensional systems.
General calssical Hamilton system is characterized by the Hamilton function $H(x_i, p_i)$, where coordinates and momentums obey the canonical equation. If, in particular,

$$H = \frac{p^2}{2} + U(x),$$

we have a particle in a potential in a space of an arbitrary dimension.