Imaginary time and the Landau method of calculating quasiclassical matrix elements

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In a number of problems of quantum mechanics, particularly in problems of quantum chemistry, the problem arises of calculating matrix elements of a physics quantity f between states which can be described quasiclassically. (For simplicity we shall have in mind a one dimensional case and consider that f is simply a function of the coordinates $f(x)$.)

This problem is in actual fact more difficult than might appear from first glance. The point is that in the case of a sufficiently large difference between the energies of the initial and the final states the matrix element turns out to be exponentially small. And the quasiclassical wave functions in the classically accessible region are not small and the exponential smallness of the integral arises as a result of rapid oscillations of the integrand. In such a case even a relatively small difference of the quasiclassical wave functions from the exact ones can lead to a large error in the matrix element. And, furthermore, a significant contribution to the integral is made by the region near the classical turning point, where the asymptotic quasiclassical expression of the wave function is inapplicable.

The situation turns out to be relatively simple in the case that the energy of the initial and final states are sufficiently close that in accordance with the general principle of correspondence between classical and quantum mechanics the matrix element turns out to be equal to the Fourier component with respect to time of the corresponding classical quantity $f[x(t)]$ with the frequency equal to the "transition frequency":

$$f_{12} \approx \int f[x(t)] \exp(-i\omega_{21}t)\mathrm{d}t, \qquad \hbar\omega_{21} = E_2 - E_1. \tag{1}$$

In this case the difference between the energies can still be sufficiently great that the Fourier component (and consequently also the matrix element) would be exponentially small.

In this case the Fourier component can be estimated by shifting the contour of integration with respect to the time into the upper half-plane of the complex variable t. (Here and subsequently we assume for the sake of definiteness that $E_2 > E_1$). Such a shift is restricted by the necessity of going around singularities. As a result the matrix element can be estimated with exponential accuracy as[1]

$$f_{12} \sim \exp(-i\omega_{21}t_c), \tag{2}$$

where t_c is the singular point of the integrand (1) closest to the real axis. In order to estimate the integral with respect to its modulus it is sufficient of course, to know the imaginary part t_c, $|f_{12}| \sim \exp(-\omega_{21}\,\mathrm{Im}\,t_c)$.

If, as often occurs, the function $f(x)$ has no singularities, the singularities of the above expression are determined by the singularities of the potential energy $U(x)$. Then t_c represents "complex time", during which the particle reaches the singularity x_c of the potential energy:

$$t_c = \int_{x_0}^{x_c} \left[\frac{m}{2(E-U(x))}\right]^{1/2} \mathrm{d}x = \int_{x_0}^{x_c} \frac{\mathrm{d}x}{v(x)}; \tag{3}$$

here $v(x)$ is the velocity of the particle; and for E in the formula one can take either one of the two close values E_2 or E_1.

The case is typical when x_c occurs for real values of x, but in the classically forbidden region. (In such a case for the lower limit of integration x_0 one can take any arbitrarily chosen point in the classically allowed region; the imaginary part of the integral obviously does not depend on this choice.) Then the estimate (2), (3) requires an analytic continuation of the potential energy into this region. This procedure may turn out to be quite unpleasant in numerical calculations, if, for example, the potential energy is also specified numerically. Usually, however, there is no need of an analytic continuation. The modern numerical methods of Fourier-analysis enable one to calculate the integral (1) directly with the required accuracy without employing a preliminary analytical continuation of expression (1) with the aid of (2). (Of course, in such a case one requires a sufficiently accurate specification of the potential $U(x)$.) On the other hand in accordance with (2) the dependence of the integral (1) on ω_{21} must be exponential. Having found this dependence over a sufficiently wide interval of variation of ω_{21} we can make the obtained values of f_{12} fit formula (2) and thus to determine the complex time t_c as a function of E. One can say that by a sufficiently accurate calculation of the integral (1) we in fact constructed the required analytical continuation to complex values of time. We emphasize in connection with this the trivial, but important circumstance, that for finding $t_c(E)$ by this method it is necessary to know the potential energy $U(x)$ only in the classically allowed (at the energy E) range of values of the coordinates.

We now note that the limiting formula (2) for the matrix element is valid under the conditions:

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$$E_2,\ E_1 \gg |E_2-E_1| \gg \hbar/t_c. \tag{4}$$

Relinquishing the lefthand inequality dramatically complicates the problem since now the calculation of the matrix element no longer reduces to the calculation of the Fourier component.

The object of this note consists of showing that in retaining the righthand inequality, i.e., under the conditions when the matrix element is exponentially small, in order to estimate it with an exponential accuracy it is sufficient to calculate the Fourier component of the classical quantity in the range of energies between E_1 and E_2.[2,3]

The problem of estimating f_{12} under such conditions was solved in general form by Landau in 1932,[4] but a sufficiently detailed derivation of the result was published only in "Quantum Mechanics" by Landau and Lifshitz; see Ref. 5, §51. A sufficiently complete justification of Landau's result leads to interesting mathematical problems. Some of them are discussed in Ref. 6.

The expression obtained by Landau for the matrix element has the form

$$|f_{12}| \sim \exp\left[-\frac{1}{\hbar}\,\mathrm{Im}\left\{\int_{x_0}^{x_c}[2m(E_2-U)]^{1/2}\mathrm{d}x - \int_{x_0}^{x_c}[2m(E_1-U)]^{1/2}\mathrm{d}x\right\}\right]. \tag{5}$$

We note that the matrix element (5) is broken up into a product of two factors. One of them is exponentially great, and the other is exponentially small. But the product as a whole is exponentially small. (The square roots in the forbidden region must be interpreted as being positive.)

Expression (5) can be written in the form:

$$|f_{12}| \sim \exp\left[-\frac{1}{\hbar}\,\mathrm{Im}\,(S(x_c,x_0,E_2)-S(x_c,x_0,E_1))\right], \tag{6}$$

where $S(X_c,x_0,E)$ is the abbreviated action calculated along the classical trajectory with energy E joining the points x_0 and x_c. Since the point x_c lies in the classically forbidden region the time corresponding to motion along such trajectories turns out to be complex.

Expression (6) has a simple physical interpretation as the transition from the state 1 to the state 2 through the point x_c at which in view of the infinity of the potential energy U the difference between the energies E_2 and E_1 is not significant, so that the classical transition becomes possible. A similar expression can also be written for the system with several degrees of freedom, although the justification of such a formal expression requires in each specific case additional arguments.

The central point for the present note is the remark that the time of motion between the end points of the trajectory is equal to the derivative of the abbreviated action with respect to energy (see Ref. 7, §44, equation (44,11)). This assertion is valid, naturally, also for motion with "complex time" in the classically inaccessible region. Thus,

$$t_c(E)=\frac{\partial S(x_c,x_0,E)}{\partial E}. \tag{7}$$

Integrating this equation with respect to the energy from $E_1$to E_2, we obtain

$$\int_{E_1}^{E_2} t_c(E)\mathrm{d}E = S(x_c,x_0,E_2)-S(x_c,x_0,E_1),$$

i.e., just the expression defining the exponent of the exponential function in (6). This enables one finally to rewrite the quasiclassical matrix component in the Landau approximation as

$$|f_{12}| \sim \exp\left[-\frac{1}{\hbar}\,\mathrm{Im}\int_{E_1}^{E_2} t_c(E)\mathrm{d}E\right]. \tag{8}$$

Formula (8) solves, in principle, the problem posed by us to express the matrix element in the Landau approximation in terms of the classical Fourier component, since the quantity t_c can be defined in accordance with (2) if one knows the dependence of these components on frequency. The method opens up a conventional procedure of a numerical determination of the Landau matrix element since, as we have already said, the modern programs of numerical calculations enable one to calculate the Fourier component with a high accuracy. And the integration with respect to energy in (8) does not present any difficulty. When the difference E_2-E_1 is small the expression (8) goes over in a natural manner into (2).

Formula (8) defines the matrix element with exponential accuracy. As regards the factor preceding the exponential, in view of its weak dependence on the frequency of the transition it can be taken equal to the value which it has for the Fourier component for the "average" energy $(E_2+E_1)/2$.

We also note the following: from what has been said above one can easily see that the matrix element in the Landau approximation together with the corresponding Fourier components depends only on the values of the potential in the classically allowed (for the greater energy E_2) region. The matrix element is not altered if we change the behavior of the potential in the forbidden region. (In such a case the potential, of course, will become nonanalytic.) This, however, can be understood also from the Landau derivation, since he uses the analytic continuation of the potential from the allowed region into the forbidden one (and not the potential itself in the forbidden region).

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[1] L. Landau and E. Teller, Phys. Z. Sowjetunion **10**, 34 (1936); L. D. Landau, *Collected Works* (in Russian), Article 21, Nauka, M., 1969, Vol. 1, p. 181.
[2] E. E. Nikitin, C. Noda, and R. N. Zare, J. Chem. Phys. **98**, 47 (1993).
[3] E. E. Nikitin, A. J. Jortner, L. P. Pitaevskiĭ, and R. N. Zare, Preprint, 1993.
[4] L. Landau, Phys. Z. Sowjetunion 1, 1 (1932); L. D. Landau *Collected Works* (in Russian), Article 6, Nauka, M., Vol. 1, p. 71.
[5] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, 3rd Ed., Pergamon Press, Oxford, 1977 [Russ. original, Nauka, M., 1972, 1974, 1989].
[6] E. E. Nikitin, in *Mode Selective Chemistry*, Kluwer Academic Publ., Amsterdam, 1991, p. 401.
[7] L. D. Landau and E. M. Lifshitz, *Mechanics*, 3rd Ed., Pergamon Press Oxford, 1976 [Russ. original, Nauka, M., 1973 and 1988].

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