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Abstract

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On the Correspondence Between Quantum and Classical Equations for a System of Two Linear Terms

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Nonadiabatic transitions in slow collisions of atoms and molecules are conveniently considered by expressing the complete wave function of the system as a series in electronic adiabatic functions. In this case the coefficients of this series, which play the role of nuclear functions, satisfy a system of coupled wave equations ([1]). In most cases, for transitions, the regions of nonadiabaticity where the levels approach one another are essential; therefore the problem is often reduced to a two-level problem. However, even for this problem the solution of the wave equations is difficult, and the usual semiclassical approximation consists in treating the motion of the nuclei classically ([2]). In doing so, however, an ambiguity arises in the determination of the nuclear trajectory, since it cannot be assigned to any single electronic state. It is therefore of interest to clarify the correspondence between the results of solving the quantum-mechanical equations and the semiclassical approximation.

In this work both methods are compared for calculating the probability of a nonadiabatic transition for a system of two linear terms with slopes F_1, F_2 and a constant interaction V_{12} between them. Such a system was considered in ([3]) in a semiclassical approximation justified only under the condition $|F_1 - F_2|/F_1 \ll 1$. The wave function, expanded in the electronic eigenfunctions of the zero Hamiltonian, has the form

$$\Psi = u_1(x)\Psi_1^e + u_2(x)\Psi_2^e. \tag{1}$$

The wave functions of the nuclear motion $u_j(x)$ satisfy the system of equations

$$u_1''(x) + (E + F_1 x)u_1 = V_{12}u_2,$$

$$u_2''(x) + (E + F_2 x)u_2 = V_{12}u_1, \tag{2}$$

where E is the energy of the system, measured from the value of the potential energy at the point of intersection of the terms. Here and below the system of units $\hbar = 1,\ m = {}^1/_2$ is used.

Owing to the linearity of the terms, the wave functions in the momentum representation satisfy first-order equations, just as do the time-dependent amplitudes $A_i(t)$ of the semiclassical approximation. Therefore it is expedient to pass to the momentum representation

$$u_j(x) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{1}{\sqrt{|F_j|}} \exp\left\{ikx - \frac{i}{F_j}\left(\frac{k^3}{3} - Ek\right)\right\} A_j(k)\, dk. \tag{3}$$

For the functions $A_j(k)$ one obtains the equations:

$$\begin{aligned} i\frac{dA_1}{dk} &= \frac{V_{12}}{\sqrt{|F_1F_2|}} \exp\left\{-\frac{i\Delta F}{F_1F_2}\left(\frac{k^3}{3} - Ek\right)\right\} A_2(k), \\ i\frac{dA_2}{dk} &= \pm\frac{V_{12}}{\sqrt{|F_1F_2|}} \exp\left\{\frac{i\Delta F}{F_1F_2}\left(\frac{k^3}{3} - Ek\right)\right\} A_1(k). \end{aligned} \tag{4}$$

The sign $+(-)$ in the second equation corresponds to the case when the slopes F_1, F_2 have the same (different) signs.

Let us consider the first case: $F_1F_2 > 0$. Then system (4), by the simple substitution

$$k = \frac{\sqrt{F_1F_2}}{\hbar}\, t$$

is reduced to the equations of the semiclassical approximation (3), if in them, as the mean force determining the trajectory, one takes $F = \sqrt{|F_1F_2|}$. To find the transition probability in the quantum-mechanical formulation of the problem, one must trace the specification of the boundary conditions for the solution of system (2). First of all, any physical solution must decrease as $x \to -\infty$ (in the classically inaccessible region). As $x \to +\infty$, the solution must correspond to the presence of a unit incident flux from $+\infty$ on level 1 and outgoing fluxes on both levels. Thus, one must know the asymptotics of $u_j(x)$ as $|x| \to \infty$, which are related to the asymptotics of $A_j(k)$ as $|k| \to \infty$ (owing to the rapidly oscillating character of e^{ikx} as $|x| \to \infty$). But as $k \to \pm\infty$, as is seen from equations (4), $A_j(k)$ tend to constants $A_j(\pm\infty) = C_j^{\pm}$. Using in (3) the saddle-point method and the asymptotic values $A_j(k)$ as $|k| \to \infty$, it is not difficult to verify that $u_j(x) \to 0$ as $x \to -\infty$, while for $x \to +\infty$ we obtain

$$u_j(x) = iC_j^{+}(F_{jx} + E)^{-1/4} \exp\left\{\frac{2}{3}\, i\, \frac{1}{F_j}(F_{jx} + E)^{3/2} - i\pi/4\right\} +$$

$$+iC_j^-(F_{jx}+E)^{-1/4}\exp\left\{-\frac{2i}{3F_j}(F_{jx}+E)^{3/2}+i\pi/4\right\}. \tag{5}$$

The boundary conditions formulated above correspond to $|C_1^-| = 1$, $|C_2^-| = 0$, $P_{12} = |C_2^+|^2$. Thus, the boundary conditions for system (4) become exactly the same as in the semiclassical approximation, namely: $|A_1(-\infty)| = 1$, $|A_2(-\infty)| = 0$. The answer is expressed identically as well: $P_{12} = |A_2(+\infty)|^2$.

Thus, for the given problem it proves possible to introduce the classical trajectory of the nuclei, determined by the force $F = \sqrt{F_1F_2}$, in such a way that the result coincides with the result of the exact quantum-mechanical problem. This fact, for the case when the transition probability is exponentially small, was noted in work ([4]). As is clear from the preceding discussion, it proves valid for any value of the transition probability. Such a reformulation of the problem makes it possible to investigate the properties of P_{12} in more detail. This was done in work ([7]) using the method proposed in work ([5]).

The case when the slopes of the terms have different signs ($F_1F_2 < 0$) is encountered in calculating the widths of quasistationary molecular states. The problem may also be of interest for estimating the role of nonadiabaticity in chemical reactions. Indeed, when calculating the probability of passage through an activation barrier, one usually considers only the lower adiabatic surface, without taking into account the fact that there is always a second potential surface "overhanging" the first ([6]). Taking the upper adiabatic potential surface into account may, as shown below, change the tunneling corrections to the probability of passage through the lower barrier.

A one-dimensional model of such a system may be the system under consideration of two terms, linear in the zero approximation, with slopes F_1, F_2 of different signs and a constant interaction between them. The Schrödinger equation (2) of such a system, after passage to the momentum representation according to (3), leads to system (4) with a minus sign in the second equation. Such a system, in contrast to the case $F_1F_2 > 0$, is non-Hermitian. This corresponds to the impossibility of introducing a classical trajectory (simultaneous passage through and reflection from the barrier). In connection with this, the flux-conservation condition also changes. It is not difficult to verify that for $F_1F_2 < 0$

we have $|A_1(k)|^2 - |A_2(k)|^2 = \text{const}$ instead of the relation $|A_1(k)|^2 + |A_2(k)|^2 = \text{const}$ for the case $F_1F_2 > 0$.

By reasoning analogous to the preceding one, relating the asymptotics $u_j(x)$ as $|x| \to \infty$ to the asymptotics $A_j(k)$ as $|k| \to \infty$, we obtain for the reflection coefficient Q and transmission coefficient P the expressions

$$Q = \left|\frac{1}{A_1(+\infty)}\right|^2, \qquad P = \left|\frac{A_2(+\infty)}{A_1(+\infty)}\right|^2, \tag{6}$$

if for $k \to -\infty$ we have $A_1(-\infty) = 1,\ A_2(-\infty) = 0$.

As P_{12} in the preceding problem, the reflection and transmission coefficients Q and P turn out to depend only on the same two parameters ε and b. Let us find the probabilities of reflection and transmission for two cases: large energies $\varepsilon \gg 1$ (above-barrier reflection) and very small $\varepsilon \ll -1$ (subbarrier transmission).

For $\varepsilon \gg 1$, two regions near $k = \pm\sqrt{E}$ are essential for integrating system (4). Solving system (4) exactly in neighborhoods of these points and matching, we obtain

$$P = \frac{1+\cos\varphi}{1+d+\cos\varphi}, \qquad Q = \frac{d}{1+d+\cos\varphi}, \qquad d = \frac{\frac{1}{2}e^{-4\pi\delta}}{1-e^{-2\pi\delta}}, \tag{7}$$

where, as before, $\delta = b/8\sqrt{\varepsilon}$ is the Massey parameter for the present problem; φ is a large phase. Near $\varphi = \pi(2n+1)$ we have resonant reflection. It is not difficult to see that this is resonant reflection on quasistationary states of the upper adiabatic curve, since the resonance shape near a level

$$Q = \frac{\Gamma^2/4}{(\Delta E)^2 + \Gamma^2/4}$$

is determined by the width Γ, related to the lifetime of the quasistationary state,

$$\Gamma = \frac{1}{\tau} = \frac{\hbar|F_1F_2|}{v\Delta F}\, e^{-2\pi\delta}.$$

The reflection coefficient averaged over a small energy interval has the form

$$\overline{Q} = \int_0^{2\pi} Q(\varphi)\, d\varphi = \frac{\frac{1}{2}e^{-2\pi\delta}}{1-e^{-2\pi\delta}}. \tag{8}$$

From formula (8) one sees a substantial difference between reflection from a single-level barrier and from a barrier with an upper adiabatic curve. If in the first case $Q \to 0$ as $E \to \infty$, then here, owing to the nonadiabaticity of the motion as $E \to \infty$, $Q \to 1$, $P \to 0$ (motion along the terms of the zero approximation).

Finally, in the case of subbarrier penetration $E < -V$. The exponentially small probability of transmission in this system, found in the same way as in (7), is equal to

$$P = Be^{-2\chi},$$

$$\chi = \int_{a_1}^{a_2} \left[|E| + \frac{F_1 + F_2}{2} x - \left\{ \left(\frac{\Delta F}{2} x \right)^2 + V^2 \right\}^{1/2} \right]^{1/2} dx =$$

$$= \frac{\pi\sqrt{2}}{4} b(|\varepsilon| - 1) = F\left(-\frac{1}{2}, \frac{3}{2}, 2, \frac{1 - |\varepsilon|}{2} \right),$$

where a_1, a_2 are the roots of the expression under the integral sign. The pre-exponential factor B, which in the case of a single adiabatic curve is equal to unity, has the form

$$B = \frac{2\pi}{\delta(\Gamma(\delta))^2} e^{-\delta} (\delta)^{\delta/2}.$$

For the case of a small splitting between the terms ($\delta \ll 1$), $B = 2\pi\delta$, which differs substantially from 1. For $\delta \gg 1$, $B = 1$, and the penetration proceeds as through a one-level barrier. The influence of the second adiabatic curve becomes apparent at $\delta \sim 1$. To find the tunneling corrections to passage through the barrier, one must numerically integrate the system (4).

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REFERENCES CITED

1. E. G. Stueckelberg, *Helv. Phys. Acta*, **5**, 370 (1932).
2. L. D. Landau, E. M. Lifshitz, *Quantum Mechanics*, 1963, p. 368.
3. E. E. Nikitin, *Optics and Spectroscopy*, **9**, 452 (1961).
4. Yu. S. Sayasov, *ZhETF*, **46**, 561 (1963).
5. V. L. Pokrovsky, I. P. Khalatnikov, *ZhETF*, **40**, 1713 (1963).
6. S. Glasstone, K. Laidler, H. Eyring, *The Theory of Absolute Reaction Rates*, IL, 1948.
7. V. K. Bykhovsky, E. E. Nikitin, M. Ya. Ovchinnikova, *ZhETF*, **47**, 750 (1964).