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Abstract

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QUASISTATIONARY STATES IN A CONICAL POTENTIAL WELL

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Statement of the problem. As is known, for many-atomic systems there exists a fundamental possibility of intersection of adiabatic electronic terms of the same symmetry ([1]). The simplest situation of this kind is realized in a system of three identical atoms in the ^2S state in the configuration of an equilateral triangle. In two coordinates x and y, describing the deviation of this system from the symmetric configuration, the adiabatic electronic terms corresponding to the lowest and the first excited doublet states have the form of two circular cones touching at their vertices. In the conical potential well (the upper term) there exist quasistationary states, whose decay is possible owing to the nonadiabatic coupling of electronic and nuclear motions. It is known ([2,3]) that near the vertex of the double cone the adiabatic electronic functions ψ_i depend mainly on the polar angle $\varphi = \operatorname{arc\,tg}(y/x)$ relative to the vertex, and the relation between ψ_i and certain basis functions ψ_i^0, assumed not to depend on x and y, is given by the relations

$$\psi_1 = \psi_1^0 \cos(\varphi/2) + \psi_2^0 \sin(\varphi/2), \qquad \psi_2 = -\psi_1^0 \sin(\varphi/2) + \psi_2^0 \cos(\varphi/2). \quad (1)$$

When going around the point of intersection of the surfaces along one of its branches, the corresponding function changes sign, which indicates the existence of a singularity of the term inside the contour of traversal.

In the basis of two electronic functions $\psi_i(\xi, \varphi)$ (ξ is the set of electronic coordinates), the nonadiabatic electron-nuclear function Φ is written in the form

$$\Phi = \psi_1(\xi,\varphi)\eta_1(r,\varphi) + \psi_2(\xi,\varphi)\eta_2(r,\varphi), \quad (2)$$

where r, φ are the polar coordinates of the vector x, y. In the usual way one obtains for the functions η_i a system of coupled equations. With the substitution $\eta_i = \sqrt{r}\chi_i(r)\exp(im\varphi)$, the angular variable is separated, and for χ_i one obtains a coupled pair of wave equations of a one-dimensional case. The requirement that Φ be single-valued when going around the point $r = 0$ admits in (2) only half-integer values of m. This quantization condition for the angular momentum is a dynamical reflection of the existence of the singularity of the terms at the origin.

Radial equations and nonadiabatic coupling. In what follows the dimensionless energy ε and the dimensionless coordinate ρ are introduced,

$$\varepsilon = E(\mu/F^2\hbar^2)^{1/3}, \qquad \rho = r(F\mu/\hbar^2)^{1/3}, \tag{3}$$

where μ denotes the mass of the particle, and F the force acting on the particle on the lower cone. The system of radial equations takes the form:

$$\frac{1}{2}\frac{d^2\chi_1}{d\rho^2}+\left(\varepsilon-\frac{m^2}{2\rho^2}-\rho\right)\chi_1=\frac{im}{2\rho^2}\chi_2, \qquad \frac{1}{2}\frac{d^2\chi_2}{d\rho^2}+\left(\varepsilon-\frac{m^2}{2\rho^2}+\rho\right)\chi_2=-\frac{im}{2\rho^2}\chi_1. \tag{4}$$

Here the energy ε is measured from the vertex of the cone. The stationary solutions of equations (4) describe, for $\varepsilon > 0$, scattering of a wave by a conical po-

potential barrier with allowance for resonant capture into the conical well. If the widths of the resonances are small in comparison with the distances between levels in the upper well, then the entire scattering characteristic is given by the complex values of the energy ε corresponding to quasistationary states in the well. In particular, near a resonance caused by an incident and reflected flux on the lower term normalized to unity, the square of the amplitude $|A(\varepsilon)|^2$ of the function χ_1 on the upper term is given by the well-known formula (4)

$$|A(\varepsilon)|^2 = \gamma_{sm}/\left[(\varepsilon-\varepsilon_{sm})^2+\gamma_{sm}^2/4\right], \tag{5}$$

where $\varepsilon_{sm} - \frac{i}{2}\gamma_{sm}$ are the eigenvalues of the quasistationary states in the conical well. They are found by solving system (4) with the boundary conditions: finiteness of the functions χ_i at zero, decrease of χ_1 as $\rho \to \infty$, and absence of an incident wave in the function χ_2. The energy levels ε_{sm} and widths γ_{sm} are calculated below in the quasiclassical approximation.

Energy levels. The eigenvalues ε_{sm} are found by solving the equation

$$\frac{1}{2}\frac{d^2}{d\rho^2}\chi_{1,sm}+\left(\varepsilon_{sm}-\frac{m^2}{2\rho^2}-\rho\right)\chi_{1,sm}=0 \tag{6}$$

with the usual boundary conditions. The quasiclassical quantization rule states:

$$\pi\frac{(s+1/2)}{m} = \int_{x_1}^{x_2}\left(1-\frac{1}{x^2}-\lambda_{sm}x\right)^{1/2}dx, \qquad \lambda_{sm}=\frac{2m}{(2\varepsilon_{sm})^{3/2}}, \tag{7}$$

where x_1 and x_2 are the smaller and larger roots of the expression under the radical. To take into account the violation of quasiclassicality at small ρ for small m, the replacement $m^2 \to m^2 + 1/4$ must be made in the integral (see (1), p. 207). Everywhere below (if accuracy so requires) by m we shall mean the angular momentum value modified in this way. Of special interest are the lower levels (initial values of the sequence of the radial quantum number $s = 0, 1, 2, ...$) for a given m. To calculate them, we approximate the effective potential energy U in the vicinity of the minimum by a fourth-degree polynomial and use the known result for the energy levels of an anharmonic oscillator (see (1), p. 165):

$$U(\rho) = \frac{3}{2}m^{2/3} + \frac{3}{2}m^{-2/3}(\Delta\rho)^2 - 2m^{-4/3}(\Delta\rho)^3 + \frac{5}{2}m^{-6/3}(\Delta\rho)^4,$$

$$\Delta\rho = \rho - m^{2/3}; \tag{8a}$$

$$\varepsilon_{sm} = \frac{3}{2}m^{2/3} + \sqrt{3}\,m^{-1/3}(s+1/2) - \frac{15}{36}m^{-4/3}(s^2+s+1/12). \tag{8b}$$

Approximation (8b) is sufficiently accurate for $s \ll \sqrt{3}\,m$.

Level width. The level width γ_{sm}, under the condition $\gamma_{sm} \ll \Delta\varepsilon_{sm}$, can be calculated in terms of the probability of transition from the conical well to states on the conical peak. In the case under consideration, the smallness of γ_{sm} is due only to the small velocity of the particle; therefore, in calculating the probability, adiabatic perturbation theory (1) must be used. In order to extend the applicability of the quasiclassical method as much as possible, when calculating γ_{sm} we proceed as follows. At the first stage, γ_{sm} is found with exponential accuracy by the Landau method (1)

$$\gamma_{sm} \sim \exp\left[-2\,\mathrm{Im}\left(\int_{\rho_1}^{\rho_c} p_1(\rho)\,d\rho - \int_{\rho_2}^{\rho_c} p_2(\rho)\,d\rho\right)\right], \tag{9}$$

where p_i are the momenta of the particle on each of the adiabatic terms; ρ_i are the turning points and ρ_c is the singular point of the momenta in the complex ρ-plane. On

at the second stage one passes to classical mechanics, within which a single trajectory $\rho = \rho(t)$ is introduced. By comparison with the known classical expression

$$\gamma = B \exp\left[-2\ \mathrm{Im}\int^{t_c} \Delta U[\rho(t)]\, dt\right], \tag{10}$$

in which ΔU denotes the adiabatic splitting of the terms, the pre-exponential factor is found. Finally, at the third stage, for γ_{sm} an approximate expression is written down with a classical pre-exponential factor and a quasiclassical exponential multiplier, which takes into account the spreading of the wave packet. Thus it is assumed that the quantum character of the system manifests itself primarily in the magnitude of the exponential multiplier.

With this definition of γ_{sm}, it is possible to consider also those cases in which the condition $\gamma_{sm} \ll \Delta\varepsilon_{sm}$ is violated, but the motion is quasiclassical in character. Then from the expression for γ_{sm} one must single out the transition probability P and assign it to those portions of the trajectory where this transition is most probable. On this portion the classical trajectory bifurcates, and each of its continuations must then be followed along one of the adiabatic terms until the next arrival at a nonadiabatic portion.

The exponent in (9) has the form

$$f = 2\int_{\rho_1}^{\rho_c}\left[2\varepsilon - \frac{m^2}{\rho^2} - 2\rho\right]^{1/2} d\rho - 2\int_{\rho_i}^{\rho_c}\left[2\varepsilon - \frac{m^2}{\rho^2} + 2\rho\right]^{1/2} d\rho, \tag{11}$$

where the singular point corresponds to the apex of the cone, $\rho_c = 0$. After transformations, for f one obtains the following expression, containing no divergent integrals:

$$f = m\int_0^{\lambda} d\lambda' \int_{x_1}^{x_2} \frac{x^2\, dx}{[1 - x^2 + \lambda x^3]^{1/2}} = \frac{\pi}{2} m\lambda\left(1 + \frac{35}{32}\lambda^2 + \dots\right). \tag{12}$$

On the right is given the expansion of f for small λ ($\lambda < \lambda_{\max} = 2/3\sqrt{3}$). The classical approximation is obtained from (12) in the case when one can restrict oneself to the first term of the expansion. In this case the transition probability must coincide, and does coincide, with the Landau–Zener formula (1), in which the pre-exponential factor is equal to unity. Thus, taking account of the expansion (12), we have

$$\gamma_{sm} = \nu_{sm} P_{sm}; \tag{13a}$$

$$\nu_{sm} = \frac{1}{2\pi}\left[3m^{-1/3} - \frac{15}{18} m^{-4/3}(s + 1/2)\right]; \qquad (13\ )$$

$$P_{sm} = \exp\left[-\frac{\pi}{2} m\lambda_{sm}\left(1 + \frac{33}{32}\lambda_{sm}^2 + ...\right)\right]. \quad (13\ )$$

Together with (8b), these formulas solve the problem of calculating γ_{sm} under quasiclassical conditions. They make it possible, in particular, to describe the most interesting region, where the resonances no longer overlap but are still sufficiently broad.

Classification of states in a conical well. The accuracy of the calculation of the level widths by the quasiclassical method can be estimated by comparing formulas (13) with the results of the numerical calculation of the capture time τ, given in work (5) for a number of lower states. The quantities $\tau(\varepsilon)$, introduced in (5), in the notation adopted here are equal to $\tau(\varepsilon) = \frac{1}{4}|A(\varepsilon)|^2$, so that the resonance values $\tau_{sm} = \tau(\varepsilon_{sm})$ coincide with the reciprocal level widths $1/\gamma_{sm}$. Such a comparison shows that for $s = 3$ (the highest value of s for which the numerical calculation was performed (5)) approximation (13) gives an accuracy of about 5% for $m = 13/2$ and $m = 11/2$. A discrepancy of about 40% is obtained when m is decreased to 7/2, while the for-

formulas (13) give overestimated values of τ_{sm}. This is to be expected, since the approximation used does not take into account the decay of the system far from the turning point closest to the apex of the cone. For a constant angular momentum m, formulas (13) give a correct description of the change of γ_{sm} when the radial quantum number is changed. For $m = 13/2$ (the highest value of m for which the numerical calculation was performed [5]), formulas (13) give a very good approximation to τ_{sm} for all calculated states ($s = 0, 1, 2, 3$), if the correction term in (13c) is completely neglected. For the lower states ($s = 0$ and 1), inclusion of the correction worsens the agreement, leading to an excess of the quasiclassical time τ ($s = 0, m = 13/2$) over the exact value by a factor of one and a half. This, however, is connected with the fact that for the lower states the frequency factor in the expression for γ_{sm} must, of course, differ from the quasiclassical expression (13b).

Formulas (13) make it possible to carry out the following classification of states in a conical potential well. The phase plane of the system in the coordinates m, ε, in the region of positive radial energies $\varepsilon > 3/2m^{2/3}$, is divided by the two curves $\varepsilon = m^{4/3}$ and $\varepsilon = 4 + m^{8/9}/2$ into four regions A, B, C, and D, characterized as follows:

A. $3/2m^{2/3},\ m^{4/3} < \varepsilon < 4 + \frac{1}{2}m^{8/9}$. Quantum states, broad levels. The expressions derived for γ_{sm} are not applicable here.

B. $m^{4/3},\ 4 + \frac{1}{2}m^{8/9} < \varepsilon$. Quasiclassical states, broad levels. A description of capture is possible in terms of the transition probabilities (13c) (without allowance for the correction), referred to the turning points.

C. $4 + \frac{1}{2}m^{8/9} < \varepsilon < m^{4/3}$. Quasiclassical states, narrow levels. For γ_{sm}, expressions (13) are valid; moreover, in (13c) the correction term in curly brackets may be disregarded.

D. $3/2m^{2/3} < \varepsilon < 4 + \frac{1}{2}m^{8/9}$. Quantum states, narrow levels. For γ_{sm}, formulas (13) are valid; moreover, in (13c) the correction should be taken into account either in the form of the first term of the expansion or in the integral form (12). In this region the energy levels ε_{sm} are given by formula (8b).

The quasistationary states considered above may arise under optical excitation of symmetric triatomic molecules, upon charge exchange of symmetric triatomic ions, and may also manifest themselves in the resonance scattering of an atom by a diatomic molecule consisting of atoms of the same kind.

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Note: Figure translations are in progress. See original paper for figures.