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Non-adiabatic transitions at a continuum edge

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Abstract. We consider interaction of a single level with a broad, tending to semi-infinite continuum. In an example of two exactly solvable problems, we show that for time dependent quantum systems the probability of the irreversible transition from a discrete level to a continuum is strongly inhibited or even completely suppressed by the presence of a discrete adiabatic level near the continuum edge.

PACS. 03.65.-w Quantum mechanics – 34.10.+x General theories and models of atomic and molecular collisions and interactions (including statistical theories, transition state, stochastic and trajectory models, etc.) – 36.40.-c Atomic and molecular clusters

A quantum system which consists of a level interacting with a semi-infinite continuum has a remarkable property: for any coupling strength and for an arbitrary level position at the energy scale it possesses a discrete energy eigenstate that is separated from the continuous spectrum by a gap. Non-adiabatic transfer of population from this discrete state to the continuum, resulting from a time dependence of the coupling and the level position, is the subject of this paper. This problem is a natural generalization of the well-known Landau-Zener model [1] which is widely used for description of chemical reactions [2], atomic collisions [3], charge transfer at a surface [4] or in the course of cluster collisions [5], as well as in a number of other fields [6]. Here we show that this problem has an exact analytical solution at least for the two particular cases of time dependencies.

Note that interaction of a quantum level with a uniform infinite continuum results in an irreversible decay of the level population. This effect has already been considered in a number of publications [7], including the case of longitudinal relaxation in a two-level system with linear time dependence of the level position [8]. We concentrate here on another aspect of the problem, which is related to the presence of the continuum edge, inhibiting the irreversible decay of the level population. We note that the sharp edge of the continuum does not allow to consider the problem either with the help of Fermi Golden Rule, or by employing WKB or Stueckelberg methods.

Consider a level-band system shown in Figure 1 at a finite time. The Schrödinger equation for the probability amplitude Ψ_0 to be at the level $|0\rangle$ of energy $\Delta(t)$, and the

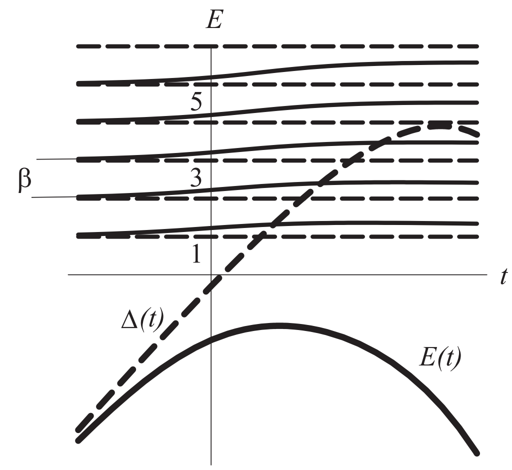

Fig. 1. Level-band system with time dependent parameters. Diabatic states (dashed lines) differ from the adiabatic ones (solid lines). A discrete adiabatic state of energy $E(t)$ remains below the band even when the corresponding diabatic state of the energy $\Delta(t)$ enters the band. We consider the continuum limit $\beta \to 0$.

band states amplitudes Ψ_n reads

$$\mathrm{i}\,\dot{\Psi}_0 = \Delta(t)\Psi_0 + V(t)\sum_{n=1}^{N}\Psi_n,$$
$$\mathrm{i}\,\dot{\Psi}_n = n\beta\Psi_n + V^*(t)\Psi_0, \quad (1)$$

where $\hbar = 1$ and index n numerates the states of a broad band, resulting in a continuum at the limit $\beta \to 0$. In this limit, the discrete eigenvalue $E(t)$ of the Hamiltonian corresponds to the adiabatic level underneath the continuum edge. For a given time t, the energy $E(t)$ is given by the

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negative root of the algebraic equation

$$E(t) - \varDelta(t) = \sum_{n=1}^{N} \frac{|V(t)|^2}{E(t) - n\beta} = W(t) \ln \left(\frac{-E(t)}{X - E(t)} \right), \tag{2}$$

where $W(t) = |V(t)|^2 / \beta$ is the instantaneous value of the static resonant transition rate in the level-band system, suggested by the Fermi golden rule, while $X = N\beta$ is a large bandwidth. The corresponding adiabatic state is given as

$$|\varPsi_{\mathrm{ad}}\rangle = \frac{1}{A} \left(|0\rangle + \sum_{n=1}^{N} \frac{V(t)}{E(t) - n\beta} |n\rangle \right), \tag{3}$$

with

$$A = \sqrt{1 + \sum_{n=1}^{N} \frac{|V(t)|^2}{|E(t) - n\beta|^2}} = \sqrt{1 - \frac{W(t)}{E(t)}}, \tag{4}$$

where we have replaced summation by integration and extended the upper integration limit to infinity. The first order perturbation theory suggests the explicit form for the coefficients of the sum equation (3) in the limit of a dense spectrum and a small individual coupling.

We first consider the case of a constant coupling $V(t) = V$ and a linear time dependence $\varDelta(t) = \alpha t$ of the level position, which belongs to the Demkov-Osherov [9] class of problems exactly solvable by the Laplace contour integral method [10]. For the initial condition $\varPsi_0(t = -\infty) = 1$ the solution reads [11]

$$\varPsi_0 = \frac{1}{\sqrt{2\pi}} \int\limits_C \mathrm{e}^{\mathrm{i}y\left[T + w \ln(-y/xe) - \frac{y}{2}\right]} \mathrm{d}y,$$
$$\varPsi_n = \frac{1}{\sqrt{2\pi}} \int\limits_C \frac{V \mathrm{e}^{\mathrm{i}y\left[T + w \ln(-y/xe) - \frac{y}{2}\right]}}{y - n\beta} \mathrm{d}y, \tag{5}$$

where e is the base of natural logarithms, $T = t\sqrt{\alpha}$ is dimensionless time, $w = W/\sqrt{\alpha}$ is an adiabaticity parameter, $\varepsilon = E(t)/\sqrt{\alpha}$ and $x = X/\sqrt{\alpha}$ are scaled time dependent detuning of the adiabatic state and the bandwidth respectively. The integration contour C which extends from $-\infty$ to $+\infty$ should be rotated counterclockwise by the angle $\pi/4$ in order to ensure rapid convergence of the integral. Projection of the state vector $|\varPsi\rangle = \sum_{n=0}^{N} \varPsi_n |n\rangle$ to the adiabatic state equation (3) with the allowance of equation (4) after the integration over states of the continuum yields

$$\langle\varPsi_{\mathrm{ad}}|\varPsi\rangle = \int\limits_C \mathrm{e}^{\mathrm{i}y\left[T + w \ln(-y/xe) - \frac{y}{2}\right]} \frac{\left(y - \varepsilon + w \ln \frac{-\varepsilon}{y}\right) \mathrm{d}y}{(y - \varepsilon)\sqrt{2\pi(1 - \frac{w}{\varepsilon})}}. \tag{6}$$

In Figure 2 we depict the probability $|\varPsi_{\mathrm{ad}}|^2 = |\langle\varPsi_{\mathrm{ad}}|\varPsi\rangle|^2$ as function of T and w. Along with decay of the adiabatic state at a rate decreasing with an increase of the interaction w, one sees a remainder of the oscillatory behavior typical of coherent processes. The stationary phase analysis of the integrals equations (5) leads to a negligible contribution. The dominating contribution comes from a singularity near the point $y = \varepsilon$ for the integral equation (6). Employing the asymptotic solution $\varepsilon = -x\mathrm{e}^{-T/w}$ of equation (2) for long T yields

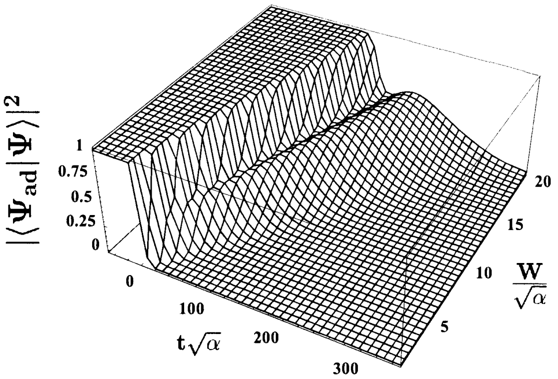

Fig. 2. Probability to stay on the discrete adiabatic level as a function of dimensionless parameters $t\sqrt{\alpha}$ and $W/\sqrt{\alpha}$ for time-independent coupling and a bandwidth $X/\sqrt{\alpha} = 700$.

$$|\varPsi_{\mathrm{ad}}|^2 \simeq 2\pi^3 wx\mathrm{e}^{-T/w},$$
$$|\varPsi_0|^2 \simeq \mathrm{e}^{-2\pi wT}, \tag{7}$$

which shows that for a slow motion, $\alpha \to 0$ (that is $w \to \infty$), the asymptotic population of the adiabatic state decays much slower than the population $|\varPsi_0|^2$ of the diabatic state $|0\rangle$. From equation (7) one see that for $T/w > \ln\left(2\pi^3 wx\right)/(1 - 2\pi w^2)$ the adiabatic state population indeed exceeds the diabatic one, and the decay time of the adiabatic state linearly increases with the interaction W.

We now consider another case of a constant detuning $\varDelta$ and an exponentially rising [12] coupling $V(t) = V\mathrm{e}^{\gamma t}$. For a large bandwidth X the problem can be solved exactly up to the first order perturbation theory over a small parameter $a = 1/\ln X$ in terms of a non-standard type of special functions. These functions depend only on two arguments: the properly scaled time and the detuning. By the exact solution we mean that the functions can be given either in the form of an explicit and strongly converging power series or with the help of an explicit integral representation, which allow one to compute efficiently the value of the function for all values of the arguments.

In order to make calculations more compact, we choose $1/2\gamma$ as a time unit, denote $W = \mathrm{e}^t V^2/\beta$, and set the energy reference point at the level energy – such that the band starts at the point $\varDelta > 0$ and ends at the point X. We look for the solution of equation (1) in a form of the series

$$\varPsi_0(t) = \sum_{k=0}^{\infty} \frac{a_k (-\mathrm{i}W)^k}{k!}, \tag{8}$$

which for the initial condition $\Psi_0(t=-\infty)=1$ implies $a_0=1$. Direct substitution of this ansatz to equation (1) after performing the integration over the continuum results in the recurrent relation for the coefficients

$$a_k = a_{k-1}\ln\left(\frac{\mathrm{i}\Delta + k - \frac{1}{2}}{\mathrm{i}X + k - \frac{1}{2}}\right) = a_{k-1}\ln\left(\frac{\mathrm{i}\Delta + k - \frac{1}{2}}{\mathrm{i}X}\right), \tag{9}$$

where in the last equality we have taken into account that the bandwidth $X = \mathrm{e}^{1/a}$ is very large.

We therefore obtain an exact series

$$\Psi_0(t) = 1 + \sum_{k=1}^{\infty}\frac{(-\mathrm{i}W)^k}{k!}\prod_{p=1}^{k}\ln\left(\frac{\mathrm{i}\Delta + p - \frac{1}{2}}{\mathrm{i}\mathrm{e}^{1/a}}\right), \tag{10}$$

which can be approximated with high precision by

$$\Psi_0(t) = \sum_{k=0}^{\infty}\frac{(\mathrm{i}W/a)^k}{k!}\frac{(\Delta - \mathrm{i}k - \mathrm{i}/2)^{-a(k+\mathrm{i}\Delta)}}{(\Delta - \mathrm{i}/2)^{a\mathrm{i}\Delta}} \tag{11}$$

for small a. In order to obtain this approximation, one has to write the product in equation (10) in the form of an exponent of the sum

$$\sum_{p=1}^{k}\ln\left[\ln\frac{\mathrm{i}\Delta + p - \frac{1}{2}}{\mathrm{i}\exp 1/a}\right] \simeq \ln\frac{-1}{a^k} + a\ln\prod_{p=1}^{k}\frac{\mathrm{i}}{\mathrm{i}\Delta + p - \frac{1}{2}}, \tag{12}$$

express the product in the logarithm in terms of Γ-functions, and make use of the asymptotic formula [13] for $\ln\Gamma(z)$. Both series equations (10, 11) are rapidly converging and are equally efficient for computation at small and moderate values of the argument W.

In order to find a representation suitable for computation at large W, we note that the sum equation (11) can be given in the form of a contour integral

$$\Psi_0(t) = \int_C \left(\frac{W}{\mathrm{i}a}\right)^{-y}\Gamma(y)\frac{(\Delta + \mathrm{i}y - \mathrm{i}/2)^{a(y-\mathrm{i}\Delta)}}{2\pi\mathrm{i}\,(\Delta - \mathrm{i}/2)^{-a\mathrm{i}\Delta}}\mathrm{d}y \tag{13}$$

along a contour C circumventing all the negative integer points $y=-k$, at which the Γ-function has residuals $(-1)^k/k!$. Employing the asymptotic of $\Gamma(z)$, one obtains the expression

$$\Psi_0(t) \simeq \int_C \frac{(\Delta - \mathrm{i}/2)^{a\mathrm{i}\Delta}\,(\mathrm{i}ay/We)^y}{\mathrm{i}\sqrt{2\pi y}\,(\Delta + \mathrm{i}y - \mathrm{i}/2)^{a(\mathrm{i}\Delta - y)}}\mathrm{d}y, \tag{14}$$

convenient for the saddle-point calculation [14] at moderate and large W. The saddle point locates near $y=-\mathrm{i}W/a$ and can easily be found numerically along with the second derivative giving the integrand width. For an extremely large W/a one finds a simple analytic expression for the probability

$$|\Psi_0|^2 \simeq \exp\left[-\frac{2W + a\Delta}{W/a + \Delta} + 2a\Delta\arctan\frac{1}{2\Delta}\right]. \tag{15}$$

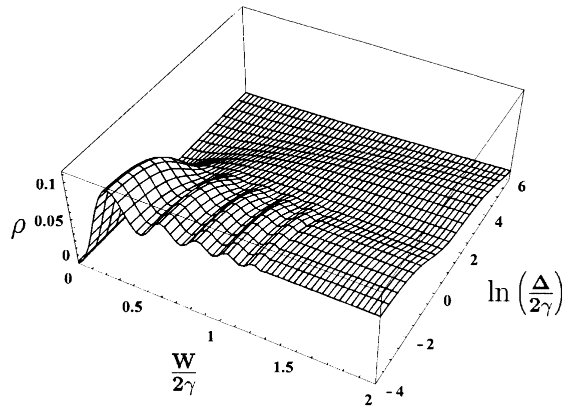

Fig. 3. Exponentially increasing interaction $V(t) = V\mathrm{e}^{\gamma t}$. Transition probability $\rho = 1 - |\langle\Psi_{\mathrm{ad}}|\Psi\rangle|^2$ as a function of dimensionless parameters $W/2\gamma$ and the scaled detuning $\Delta/2\gamma$ for $\ln(X/2\gamma) = 20$. For $W/2\gamma > 1.3$ we employ the asymptotic formula, suggested by equation (14). At large W one also sees the asymptotic two-step dependence $\rho(\Delta)$ suggested by equation (15).

The results of the calculation are shown in Figure 3. One sees that at short times and for small detunings the population as a function of W experiences dying oscillation at a "cooperative" Rabi frequency $\sim 1/a$, which is typical of the process of coherent damping [15]. The asymptotic value of the transition probability is small and amounts to $2a$ at most. Far from the resonance at $\Delta \gg \gamma$ the transition probability is zero until the exponentially rising coupling reaches the detuning by the order of magnitude, that is $W \sim \Delta$. After that it approaches the asymptotic value a. We also note that for the exponentially rising coupling the adiabatic state practically coincides with the level $|0\rangle$, and the normalization constant equation (4) is close to unity.

For a double passing of resonance, which is typical of collisions, the classical Landau-Zener formula ignores the phase correlation between the forward and the back passages. It yields the transition probability $P_{\mathrm{tr}} = 2\mathrm{e}^{-2\pi V^2/\alpha}(1 - \mathrm{e}^{-2\pi V^2/\alpha})$ that has a maximum, when the relative velocity α of the levels displacement is of the order of the squared levels coupling V^2. For large and small velocities P_{tr} vanishes as $1/v$ for the upper limit, and as $\mathrm{e}^{-1/v}$ for the lower one. For the double non-adiabatic transitions at the continuum edge the similar transition probability behaves in the same way; it also has a maximum, and it vanishes at the extremes as well, although with different asymptotics.

In Figure 4 we show these dependencies for both problems considered. Here we have employed the relation $P_{\mathrm{tr}} = 1 - |\Psi_0|^4$ for the second model, valid for $|\Psi_0|$ close to $|\Psi_{\mathrm{ad}}|$, whereas for the first model we have taken into account that the return of population may occur *via* the adiabatic as well as *via* the diabatic states that are not orthogonal. In the last case the transition probability reads $P_{\mathrm{tr}} = 1 - |\Psi_0|^4 - |\Psi_{\mathrm{ad}}|^4 + |\Psi_0|^2|\Psi_{\mathrm{ad}}|^2/A^2$, where the probability amplitudes are given by equations (5, 6)

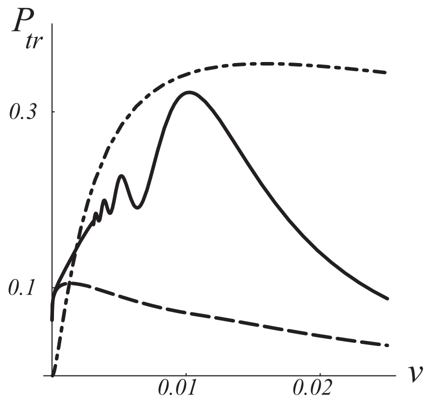

Fig. 4. Transition probability P_{tr} after double passage of the continuum edge in function of the collision velocity v (in atomic units). Exponentially rising interaction for small detuning $\Delta = \mathrm{e}^{-7}$ a.u. (solid line), and for large $\Delta = \mathrm{e}^{-4}$ a.u. detunings (dashed line), as compared to the coupling $W = 0.001$ a.u., for the band width $X \sim 1$ a.u. is shown in contrast with the case of a linear dependence of the detuning (dot-dash line). In the last case the reverse of the linear time dependence occurs at time moment τ_{r} corresponding to the adiabatic level at the position $\Delta = -W/e$ underneath the band edge.

and the normalization constant by equation (4). We note that the asymptotic behavior is very different for the two considered models: the linearly changing detuning results in a power dependence at small velocity and gives a slow decrease for fast collisions, whereas the exponentially increasing coupling manifests $1/(-\log v)$ behavior for slow interactions and an inverse power law for high speeds.

We conclude by summarizing the main results. We have considered two particular cases of time dependent quantum systems consisting of a level interacting with a broad continuous band: the case of a linearly changing detuning of the level with a constant coupling, and the case of an exponentially rising coupling at a fixed detuning. In both processes one can observe some elements of coherent behavior which manifests itself in non-exponential and under certain conditions even oscillatory behavior of the populations. In both processes the finite width X of the continuum is important, although it enters the result in a "weak" way *via* the combination $\log X$. As in the classical Landau-Zener problem, in both cases the transition probability in the course of sequential direct and reversed process decorrelated in phase behaves qualitatively in the same way. It has a maximum at a certain rate of the parameter variation and vanishes at the extremes of small and high rates. However, the asymptotic behavior of the probability for high and slow collisions are quite different. The most interesting feature of the process is the inverse logarithmic dependence on the velocity, which occurs when the coupling growth rate is slow. The most important fact common to both cases is that the exponential decay given by Fermi's Golden Rule in the case of a linearly moving level is strongly inhibited by the presence of the continuum edge and is completely suppressed for the exponentially rising interaction.

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