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FOUR-STATE (TWO-SPIN) NON-STATIONARY MODELS

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Quantum dynamical non-stationary 4-state systems with potential curve crossings are analyzed. Special emphasis is made on the semi-classical description in terms of transition paths that join initial and final states. Exact solutions (when available), approximate approaches and numerical results are considered. It is shown that the Multi-state Landau-Zener theory (MLZ) accounts very well for the time-dependent state populations and final transition probabilities even in cases when multiple crossings appear in close vicinity of each other. This is also true for multiple paths systems when the adiabatic and dynamic phases are accounted appropriately for. It is found that transitions may take place also between diabatic states that do not couple directly and that the dynamics of such crossings may be accurately described within the multichannel Landau-Zener theory.

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I. INTRODUCTION

Transitions in composite systems of interacting spins exposed to time-dependent magnetic fields are considered in an immense number of publications. The demagnetization of magnetic molecules and nanomagnets is one of the physical realizations, see, for instance, [1–9]. Mathematically similar problems emerge in the theory of quantum logic operations with very different physical realizations such as ion traps or coupled Josephson junctions [13]. From a more general perspective the matter concerns solving the time-dependent Schrödinger equation in a finite basis of N states, which is one of generic problems in quantum mechanics.

The dynamics of 4 state (two spin-$\frac{1}{2}$) systems was considered in early applications to nuclear magnetic resonance problems, see, e.g. Ref. [14]. They became particularly important as two coupled two-state systems serve as a basic model of entanglement in spin $\frac{1}{2}$ systems [15]. In the theory of quantum computation such systems are needed to obtain logic quantum gates such as, e.g., the Cnot gate [16]. Their analytic are especially significant with respect to long time dispersion [17] or decoherence which are sources to reduce the efficiency of the quantum processor. Various aspects of two-spin systems were studied intensively, see, e.g., Ref. [10–12, 18].

Very often linear time dependence of the magnetic field is presumed, which links the problem to the well-known two-state Landau-Zener (LZ) model and its multi-state generalizations. For systems of non-interacting spins the non-stationary quantum problem is effectively factorized, which makes the solution simple. The case of interacting spins corresponds to a special realization of the generalized Multi-state Landau-Zener model (MLZ). It is appropriate now to introduce the major notions and concepts of this model which are extensively used in the present paper.

In the MLZ model the $N \times N$ Hamiltonian matrix has linear dependence on time

$$\mathbf{H}(t) = \mathbf{A} + \mathbf{B}t \ . \tag{1.1}$$

The basis of states in which this representation holds is called *diabatic basis*. It is presumed to be time-independent. Without loss of generality one can presume that the matrix $\mathbf{B}$ is diagonal, $\mathbf{B} = \mathrm{diag}\{\beta_j\}$. The diagonal and non-diagonal elements of matrix $\mathbf{A}$ have different status. This is stressed by new notations: $A_{jj} = \varepsilon_j$, $A_{jk} = V_{jk}$. The diagonal elements of the $\mathbf{H}(t)$ matrix, $\mathcal{E}_j(t) = \beta_j t + \varepsilon_j$, are known as *diabatic potential curves* and V_{jk} are *couplings* between the diabatic states j and k. The diabatic potential curves form a rectilinear network. One can consider propagation along this network as following diabatic potential curves with hopping from one curve to another at the instances of time when the two curves cross. In this way the propagation path is introduced; it is implied that the propagation proceeds only forward in the time variable. In general several paths join prechosen initial and final states. The contributions are coherent, which implies summation of the amplitudes. In turn, this means interference and oscillations in the state-to-state transition probabilities as the parameters of the problem (ε_j, for instance) are varied. Along with such *multi-path* transitions, *single-path* transitions are always present. The obvious examples correspond to survival in the initial diabatic state j in the case when the latter has extremal (maximum or minimum) *slope* β_j; other single-path transitions are also possible.

The description in terms of propagation paths is approximate and has heuristic significance; but it could be easily put in a more quantitative form. Below, in Section III, we provide a brief overview of the two-state Landau-Zener model (Section III A) and then describe how it is generalized and applied to systems of many states in the MLZ model (Section III B).

Exact solutions of the N-state MLZ model has been obtained for some special cases: the SO(3) model [19], the Demkov-Osherov model [20], the bow-tie model [21] and its generalization [22]. Among numerical studies of three- and four-state models we indicate Refs. [23, 24].

The objective of this paper is to analyze the relation between four-state models that allow exact analytical solution and the cases when such solutions are not available and apparently do not exist. The important issue here is the distinction between single-path and multiple-path transitions. In most cases when exact solutions exist they describe single-path transitions although some exceptions are known. On the other hand, not all single-path models allow exact solution. We reveal the reason for this by demonstrating that the single-path property is not absolute because analytical continuation over model parameters may link single-path and multiple-path models.

In Section II we start with formulating the theory of two spin $\frac{1}{2}$-particles in separate magnetic fields, at first for noninteracting particles (Section II A) and then with allowance for interaction in some restricted form (Section II B). The MLZ theory of Section III is applied to the two-spin model in Section IV; the results are compared with direct numerical solutions of the Schrödinger equation. Single- and multi-path transitions and exactly solvable four-state models are considered. Another object of interest is the case of second-order interaction, i.e. when potential curves i and j cross, but direct coupling is absent ($V_{ij} = 0$). Some mathematical derivations are provided in Appendix A. The conclusions are drawn in Section V. Atomic units ($\hbar = e = m_e = 1$) are used throughout.

II. FOUR-STATE MODEL OF TWO SPIN-$\frac{1}{2}$ PARTICLES

A. Model of non-interacting spins

We start by considering a simple case of a system of two non-interacting spins. To a significant extent we follow the ideas suggested originally by Mayorana [25] and Hioe [19] and recently reformulated by Sinitsyn [26]. However, our context is somewhat different.

Consider a particle a with spin $s_a = 1/2$ in a time-dependent magnetic field $\boldsymbol{B}(t)$. The two-state matrix Hamiltonian is

$$\mathbf{H}_a(t) = \frac{1}{2}\,\boldsymbol{B}(t)\cdot\boldsymbol{s}_a = \frac{1}{2}\begin{pmatrix} B_z(t) & B_x(t)+iB_y(t) \\ B_x(t)-iB_y(t) & -B_z(t) \end{pmatrix}. \tag{2.1}$$

We re-parameterize this Hamiltonian in an apparently general form

$$\mathbf{H}_a(t) = \begin{pmatrix} E_{1a}(t) & V_a(t) \\ V_a^*(t) & E_{2a}(t) \end{pmatrix}, \tag{2.2}$$

where $E_{1a}(t)$, $E_{2a}(t)$, $V_a(t)$ are some functions of time.

Consider now the system consisting of two particles a and b with spin $\frac{1}{2}$ and denote the spin operators as $\boldsymbol{s}_a$ and $\boldsymbol{s}_b$. The one-particle basis states are

$$|\alpha_j\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |\beta_j\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{2.3}$$

where subscript $j = a,\ b$ labels the particles. Assume that the second particle interacts with a magnetic field which generally *differs* from the magnetic field acting on the first particle. The interaction Hamiltonian $\mathbf{H}_b(t)$ is parameterized similarly to $\mathbf{H}_a(t)$, Eq. (2.2):

$$\mathbf{H}_b(t) = \begin{pmatrix} E_{1b}(t) & V_b(t) \\ V_b^*(t) & E_{2b}(t) \end{pmatrix}. \tag{2.4}$$

Suppose at first that there are no interaction between the particles. Then the Hamiltonian of the two-particle system is $H(t) = H_a(t) \oplus H_b(t)$. It is operative on the two-particle states. The two-particle basis states are obtained as products of one-particle basis states; we label them as

$$\begin{aligned} |1\rangle &= |\alpha_a\rangle\,|\alpha_b\rangle\,, \qquad |2\rangle = |\alpha_a\rangle\,|\beta_b\rangle\,, \\ |3\rangle &= |\beta_a\rangle\,|\alpha_b\rangle\,, \qquad |4\rangle = |\beta_a\rangle\,|\beta_b\rangle\,. \end{aligned} \tag{2.5}$$

In this basis the matrix of the two-particle Hamiltonian is

$$\mathbf{H}(t) = \begin{pmatrix} E_{1a}+E_{1b} & V_b & V_a & 0 \\ V_b^* & E_{1a}+E_{2b} & 0 & V_a \\ V_a^* & 0 & E_{2a}+E_{1b} & V_b \\ 0 & V_a^* & V_b^* & E_{2a}+E_{2b} \end{pmatrix}, \tag{2.6}$$

where time-dependence is implicit in the right hand side. Since each particle is subject to its own magnetic field $\boldsymbol{B}^{(a)}(t)$ and $\boldsymbol{B}^{(b)}(t)$, the total spin S and its projection S_z ($\boldsymbol{S} = \boldsymbol{s}_a + \boldsymbol{s}_b$) are not integrals of motion, in distinction to the commonly met case in which both magnetic fields are identical. The relations between V_i, $\mathcal{E}_{ij}$ and $\boldsymbol{B}^{(a)}(t)$, $\boldsymbol{B}^{(b)}(t)$ reads

$$\begin{aligned} V_a &= \frac{1}{2}\left(B_x^{(a)} + iB_y^{(a)}\right), \qquad E_{1a} = -E_{2a} = \frac{1}{2}B_z^{(a)} \ , \\ V_b &= \frac{1}{2}\left(B_x^{(b)} + iB_y^{(b)}\right), \qquad E_{1b} = -E_{2b} = \frac{1}{2}B_z^{(b)} \ . \end{aligned} \tag{2.7}$$

The diagonal elements of the matrix H, Eq. (2.6), satisfy the condition

$$H_{11} - H_{22} = H_{33} - H_{44} \ . \tag{2.8}$$

This implies that by a simple common phase transformation one can always achieve $H_{11} = -H_{44}$, $H_{22} = -H_{33}$.

One possible physical realization of the situation of different fields appears for a hydrogen Rydberg atom treated within the pseudo-spin approach, see, e.g., [27][28]. A dynamical problem emerges when such an atom is subject to external (generally time-dependent) electric and magnetic fields. Linear combinations of these fields can be equivalently considered as two different effective magnetic fields (it is presumed here that the fields are treated in the linear approximation). The role of the spin of the total system is played by the atom orbital momentum $\boldsymbol{L}$. This magnitude is generally not conserved under combined action of the fields.

Another realization of a four-state system emerges in the theory of two coupled superconducting flux qubits. The structure of the Hamiltonian provided in [13] is similar to Eq. (2.6) although condition Eq. (2.8) is not satisfied.

The matrix $\mathbf{H}$ has zeroes on the *cross-diagonal*, which goes via elements $\{1,4\}$, $\{2,3\}$, $\{3,2\}$ and $\{4,1\}$. The matrix is symmetrical under reflection in the cross diagonal. This is due to the fact that the two spins are not coupled to each other, so that there is no interaction responsible for simultaneous spin flip. The presence of terms bilinear in components of $\mathbf{s}_a$ and $\mathbf{s}_b$ in the Hamiltonian would in general eliminate these special properties of the $\mathbf{H}$ matrix.

When both magnetic fields coincide, the following relations hold: $E_{1a} = E_{1b}$, $E_{2a} = E_{2b}$, $V_a = V_b$, and the total spin $\boldsymbol{S} = \boldsymbol{s}_a + \boldsymbol{s}_b$ is integral of motion. Therefore the four-dimensional Hilbert space with the basis Eq. (2.5) is split into two invariant subspaces: a one-dimensional subspace corresponding to $S = 0$ and a three-dimensional subspace with $S = 1$. All this is embedded into well-known SO(3) model ascending to Majorana [19, 25]. If different magnetic field acts on each of the two particles, we obtain what could be named *generalized* SO(3) *model*. In the latter, the total spin S is not integral of motion. In fact such a generalized SO(3) model was considered by Sinitsyn [26] in the context of condensed matter physics.

If we know the one-particle time-propagators $U_a(t,t')$ and $U_b(t,t')$, the two-particle propagator is straightforwardly obtained as $U_a(t,t') \otimes U_b(t,t')$. In particular, if we know the probabilities of non-adiabatic transitions (or spin-flips) p_a, p_b (i. e. probabilities of diabatic evolution), the related probabilities of adiabatic development are $q_a = 1 - p_a$, $q_b = 1 - p_b$. Then the probabilities P_{ij} of transitions from ith to jth two-particle basis states comprise to a 4×4 matrix [26]:

$$\mathbf{P} = \begin{pmatrix} p_a p_b & p_a q_b & q_a p_b & q_a q_b \\ p_a q_b & p_a p_b & q_a q_b & q_a p_b \\ q_a p_b & q_a q_b & p_a p_b & p_a q_b \\ q_a q_b & q_a p_b & p_a q_b & p_a p_b \end{pmatrix} . \tag{2.9}$$

The element P_{jk} gives probability of transition from the initial state j to the final state k. Note that this matrix is symmetrical not only with respect to its principal diagonal, but also with respect to its cross-diagonal.

B. Model of two interacting spins

Now we turn to a model of spins that interact with the external fields and with each other, albeit the latter interaction is not of the most general form.

Non-zero elements on the cross-diagonal of matrix H are obtained if one includes the bilinear terms $s_{a+}\, s_{b-} + s_{a-}\, s_{b+}$ where we use the standard definitions $s_{a\pm} = s_{ax} \pm i s_{ay}$, $s_{b\pm} = s_{bx} \pm i s_{by}$. Such terms lead to simultaneous flip of both the spins. In the following we will not consider such terms, but allow for bilinear terms of the form

$$W_{\rm int} = 4\left(c_1 s_{az} s_{bx} + c_2 s_{az} s_{by} + c_3 s_{bz} s_{ax} + c_4 s_{bz} s_{ay} + b s_{az} s_{bz}\right), \tag{2.10}$$

with some coefficients c_j. In the basis Eq. (2.5) the matrix of this interaction reads

$$\mathbf{W}_{\rm int} = \begin{pmatrix} b & c_1 - ic_2 & c_3 - ic_4 & 0 \\ c_1 + ic_2 & -b & 0 & -c_3 + ic_4 \\ c_3 + ic_4 & 0 & -b & -c_1 + ic_2 \\ 0 & -c_3 - ic_4 & -c_1 - ic_2 & b \end{pmatrix} . \tag{2.11}$$

This leads to the *generalized four-state model* with the Hamiltonian [29]

$$\mathbf{H}_{\rm g}(t) = \begin{pmatrix} \tilde{\mathcal{E}}_1(t) & V_{12} & V_{13} & 0 \\ V_{12}^* & \tilde{\mathcal{E}}_2(t) & 0 & V_{24} \\ V_{13}^* & 0 & \tilde{\mathcal{E}}_3(t) & V_{34} \\ 0 & V_{24}^* & V_{34}^* & \tilde{\mathcal{E}}_4(t) \end{pmatrix} \tag{2.12}$$

with the following relations between V_{ij}, V_i and c_i:

$$\begin{aligned} V_{12} &= V_b + c_1 - ic_2 \ , \qquad V_{13} = V_a - c_3 + ic_4 \ , \\ V_{24} &= V_a + c_3 - ic_4 \ , \qquad V_{34} = V_b - c_1 + ic_2 \ , \\ \tilde{\mathcal{E}}_1(t) &= \mathcal{E}_1(t) + b \ , \qquad \tilde{\mathcal{E}}_2(t) = \mathcal{E}_2(t) - b \ , \\ \tilde{\mathcal{E}}_3(t) &= \mathcal{E}_3(t) - b \ , \qquad \tilde{\mathcal{E}}_4(t) = \mathcal{E}_4(t) + b \ . \end{aligned} \tag{2.13}$$

Compared to the Hamiltonian Eq. (2.6), $\mathbf{H}_{\rm g}$ retains zeroes on the cross-diagonal, albeit the symmetry with respect to it is lifted.

III. GENERAL LANDAU-ZENER THEORY

For multi-state systems featuring crossing *diabatic* potential curves, the generic case is the situation of pairwise crossing when only two curves cross at a time. In the *adiabatic* representation one has to consider the instantaneous eigenvalues $\epsilon_j(t)$ of the Hamiltonian $\mathbf{H}(t)$, which depends parametrically on time. It is well known from the Neumann-Wigner theorem that crossing of diabatic potential curves correspond to pseudo-crossings (or avoided crossings) of *adiabatic potential curves* $\epsilon_j(t)$. Exceptions to this generic correspondence may occur for special sparse structures of Hamiltonian when adiabatic curves cross.

The LZ model provides a very attractive way of finding the probability of transitions between the two states involved in a pairwise crossing. Furthermore, the amplitudes of the crossing states are subject to a phase-shift, which is also known analytically in the LZ case. If we assume that the dynamics in the vicinity of a crossing, or rather an avoided crossing, only involves the two (almost) crossing states, these expressions may, in principle, be used to estimate the dynamics of any system of arbitrary number of states with arbitrary number of crossings. Such ideas are used in quasi-molecular theory of atomic collisions, see, e.g., [30]. In the following, we will briefly outline this theory and also elaborate on the validity of the approach employed.

The presence of several paths gives raise to interference effects. The importance of one path compared to the others is governed not only by the transition probabilities, but also the phase differences between the relevant states. These phases may be divided into three categories: the adiabatic phase $\int^t \epsilon_j(t')\,dt'$, the instantaneous (Stokes) phase shift experienced at each crossing and finally signs arising from "book keeping" arguments. All of these are crucial, and must be considered carefully.

In outlining the theory, it is useful to define the relevant concepts and parameters of the LZ model in its original two state form.

A. The two state Landau-Zener case

Within some diabatic basis $\mathcal{B}_{\rm D} = \{|1\rangle, |2\rangle\}$, the Hamiltonian may be expressed as

$$H_{\rm D} = \begin{pmatrix} -\frac{1}{2}bt & V \\ V^* & \frac{1}{2}bt \end{pmatrix} , \tag{3.1}$$

where the constant b is the difference in the slopes of the diagonal energies of state 1 and 2, and the coupling V is assumed to be constant and real. We label the diabatic diagonal energies (potential curves) as $\mathcal{E}_{1,2} = \mp\frac{1}{2}bt$. For a

spin $\frac{1}{2}$-particle in a magnetic field, this situation may be realized with $B_z = -bt$, $B_x = V$ and $B_y = 0$, referring to Eq. (2.2). In this form the problem was solved by Majorana [25] in the same year as by Landau [31], Zener [32] and Stueckelberg [33]. A comparative discussion of physical motivations and the technical treatments used was provided recently by Di Giacomo and Nikitin [34]. However, the author's claim that "the Majorana name is never mentioned in connection with formula" (3.10) is an exaggeration; some of counter-examples are given by Refs. [21, 22, 35, 36].

The adiabatic basis $\mathcal{B}_{\rm A} = \{|\chi_1\rangle, |\chi_2\rangle\}$ is defined by the eigenvectors of the matrix Eq. (3.1). We order them corresponding to increasing energy, and choose the signs such that

$$\begin{aligned} |\chi_1\rangle &\equiv C\left\{\left(bt/2+\sqrt{(bt/2)^2+V^2}\right)|1\rangle - V|2\rangle\right\}\ , \\ |\chi_2\rangle &\equiv C\left\{V|1\rangle + \left(bt/2+\sqrt{(bt/2)^2+V^2}\right)|2\rangle\right\}\ , \end{aligned} \tag{3.2}$$

where C is a positive normalization factor. Note that the signs of the coefficients $\langle 2|\chi_1\rangle$ and $\langle 1|\chi_2\rangle$ depend on the sign of the coupling V, whereas the other ones, $\langle 1|\chi_1\rangle$ and $\langle 2|\chi_2\rangle$, are always positive.

The Hamiltonian H_D, Eq. (3.1), being transformed to the adiabatic basis, becomes a diagonal matrix. The diabatic basis states are considered as time-independent, while time-dependence of the adiabatic states (3.2) generates coupling through the matrix element $\langle\chi_1|(d/dt)|\chi_2\rangle$. The effective Hamiltonian in the adiabatic basis reads:

$$H_{\rm A} = \begin{pmatrix} -\sqrt{(bt/2)^2+V^2} & i\frac{bV}{b^2t^2+4V^2} \\ -i\frac{bV}{b^2t^2+4V^2} & \sqrt{(bt/2)^2+V^2} \end{pmatrix}. \tag{3.3}$$

The adiabatic diagonal energies (potential curves),

$$\epsilon_j = \mp\sqrt{(bt/2)^2+V^2}, \tag{3.4}$$

coincide with the diabatic ones in the limit $|t| \to \infty$. At the instant when the diabatic curves cross, the splitting of the adiabatic ones gives the magnitude of the coupling:

$$\Delta\epsilon(t=0) = 2|V|\ . \tag{3.5}$$

From the above expressions of the effective Hamiltonian matrices in the two bases, Eqs. (3.1) and (3.3), it is evident that the adiabatic basis is more stable in the sense that the state-to-state couplings are localized in time. The coupling has a Lorentzian shape in this basis, whereas it is constant in the diabatic one. We may estimate the length of the time interval in which transitions take place in the adiabatic basis as the width of the Lorentzian in Eq. (3.3) at 1/10 of its maximal value. We label this time τ, and define it by $1/(b^2\tau^2+4V^2) = \frac{1}{10}\cdot 1/(4V^2)$, which gives

$$\tau = 6\left|\frac{V}{b}\right|\ . \tag{3.6}$$

In the adiabatic basis we are able to describe the dynamics through propagators in the form of 2×2 matrices:

$$\mathbf{c}(t_f) = J(t_f,0)SJ(0,t_i)\mathbf{c}(t_i), \tag{3.7}$$

where $\mathbf{c}(t) = (c_1,c_2)^T$ is defined by $|\Psi(t)\rangle = c_1(t)|\chi_1(t)\rangle + c_2(t)|\chi_2(t)\rangle$. The initial and final times, t_i and t_f, are to be chosen well separated from the crossing.

Intuitively, we may think of the system as undergoing an instantaneous transition at the time the diabatic potential curves cross ($t=0$). Before and after the crossing, the only time-evolution is the one corresponding to the adiabatic phase, given by the J-matrices:

$$J(t_2,t_1) \equiv \mathrm{diag}\left\{\int_{t_1}^{t_2}\epsilon_1(t')dt', \int_{t_1}^{t_2}\epsilon_2(t')dt'\right\}. \tag{3.8}$$

The "instantaneous" transition matrix S reads

$$S^{(\pm)} = \begin{pmatrix} \sqrt{1-p}e^{i\alpha} & \pm\sqrt{p} \\ \mp\sqrt{p} & \sqrt{1-p}e^{-i\alpha} \end{pmatrix}, \tag{3.9}$$

where p is the probability of a non-adiabatic transition [25, 30–33],

$$p \equiv \exp\left(-2\pi\delta\right), \quad \delta \equiv V^2/|\,b|\ , \tag{3.10}$$

and α is the Stokes (instantaneous) phase [30]:

$$\alpha \equiv \frac{1}{4}\pi + \delta(\ln\delta - 1) - \arg[\Gamma(1+i\delta)] \ . \tag{3.11}$$

The sign in Eq. (3.9) is far from arbitrary; care must be taken when choosing the right expression. When both the parameters b and V are positive, $S^{(+)}$ applies. By considering the expressions of the adiabatic basis vectors, Eq. (3.2), and the form of the Schrödinger equation in the diabatic basis, Eq. (3.1), we find that when the product bV is positive, one should use $S^{(+)}$, and $S^{(-)}$ is to be used when bV is negative.

The picture is complicated further when multi-path transitions are operative. In this case it may not be possible to insist on our adiabatic basis to follow the same sign convention as in Eq. (3.2) in all (avoided) crossings; we must make sure that our basis vectors are continuous in time. One is easily convinced that when one – and only one – of the basis vectors differ from Eq. (3.2), the S-matrix must be transposed.

In summary, $S^{(+)}$ applies when the product bV is positive and both basis vectors have the same sign relative to Eq. (3.2) or when bV is negative and one of the basis vectors differs by a sign. If this is not the situation, $S^{(-)}$ applies.

B. The multi state Landau-Zener case

The expression Eq. (3.7) is easily generalized to a system of more than two states with more than one crossing. Suppose a system of N states is subject to m crossings:

$$\begin{pmatrix} c_1(t_f) \\ c_2(t_f) \\ \vdots \\ c_N(t_f) \end{pmatrix} = J(t_f,t_m)\, S_m\, J(t_m,t_{m-1})\, S_{m-1} \cdots J(t_3,t_2)\, S_2\, J(t_2,t_1)\, S_1\, J(t_1,t_i) \begin{pmatrix} c_1(t_i) \\ c_2(t_i) \\ \vdots \\ c_N(t_i) \end{pmatrix} \tag{3.12}$$

with

$$t_i \le t_1 \le t_2 \le \ldots t_{m-1} \le t_m \le t_f \ . \tag{3.13}$$

The S-matrices are constructed by inserting the elements of the 2×2 matrix Eq. (3.9) in the entries corresponding to the adiabatic states involved in the avoided crossing. It is imperative to maintain the ordering of the adiabatic basis vectors such that the energy order is unchanged. The rest of the matrix should correspond to the identity matrix. The J-matrices are constructed by a straightforward generalization of Eq. (3.8). Alternatively, through the Dirac-picture formulation, $|\chi_k\rangle \to \exp\left(-i\int_{t_i}^{t_f}\epsilon_k(t')dt'\right)|\chi_k\rangle$, the dynamics may be expressed as a pure product of S-matrices. In this case, a phase shift originating from the adiabatic phases must be imposed on the off-diagonal elements.

The simplest way to obtain the adiabatic diagonal energies that enter into the J-matrix, is usually numerical solution of the eigenvalue equation with the diabatic Hamiltonian matrix. Of course, in doing so, the model is no longer purely analytical. Alternatively one may try and find approximate eigenenergies analytically. One way of doing this would be to use the two state energies given by Eq. (3.4) in the vicinity of a crossing and diabatic energies elsewhere.

As mentioned, the underlying assumption is that in the vicinity of an avoided crossing, the multi-state system may be treated as a two level system. Equation (3.6) may serve as a criterion for this; the time separation between two consecutive crossings must be such that their Lorentzian couplings does not overlap considerably. In other words,

$$t_{n+1} - t_n > \frac{1}{2}(\tau_{n+1} + \tau_n) \quad \forall n \ . \tag{3.14}$$

Logically, we have assumed that the system locally may be considered a two level system in order to justify that very same idea, so technically it is a necessary condition, not a sufficient one. Still, the criterion should serve at least as an estimate.

From Eq. (3.12) we may predict the dynamical *evolution* of the system – not just the final state – by only multiplying by the propagators corresponding to crossings that have taken place at the instant in question. Of course, such a prediction should be compared with the actual evolution expressed in the adiabatic basis rather than the diabatic one. Although the diabatic and adiabatic basis vectors coincide when well separated from crossings, there are oscillations in the populations of states undergoing a crossing or an avoided crossing, which obviously die out much faster in the adiabatic basis than in the diabatic one [37].

C. Second order crossings

From Eq. (3.10) it seems reasonable to assume that no transition will occur between two diabatic states that do not couple. To some extent this is true – but not completely. When there are more than two states, there may be a finite coupling between two adiabatic states for which the corresponding diabatic states does not couple directly. This manifests itself in the fact that the adiabatic potential curves do exhibit an avoided crossing rather than an exact one. With the Hamiltonian Eq. (2.12), we may find a diabatic "*pseudo*-coupling" $\tilde{V}$ as

$$|\tilde{V}_{k\ell}| = \left| \sum_{j\neq k,\,\ell} \frac{V_{kj}V_{j\ell}}{\mathcal{E}_j(t_{k\ell}) - \mathcal{E}_k(t_{k\ell})} \right|, \tag{3.15}$$

where $\mathcal{E}_j$ is the potential curve of the diabatic state j, and $k\ell$ label a set of two diabatic, uncoupled states ($V_{k\ell} = 0$) that cross at time $t = t_{k\ell}$ [that means $\mathcal{E}_k(t_{k\ell}) = \mathcal{E}_\ell(t_{k\ell})$]. This formula, which has been checked numerically by comparing it to half the energy splitting at avoided crossings, is derived in Appendix A. In this way, also second order transition may be studied. Seen from a "diabatic point of view", this phenomenon is quite puzzling; the transition takes place through instantaneous hops to states that do *not* take part in the crossing, then, at the same instant, onto the other crossing state that and no shifts in the populations of the "intermediate" states are seen. Similar dynamical phenomenon in the theoretical description of two-level atoms in an ion trap was described as "mindboggling" [15].

IV. APPLICATION OF LANDAU-ZENER THEORY TO THE TWO SPIN-$\frac{1}{2}$ SYSTEM

In Section II we have made no assumption about the time dependence of the elements of the Hamiltonian matrices Eqs. (2.6), (2.12) of the system of the two spin particles. In the following we will assume that the couplings are constant and the diagonal energies are linear in time. Hence, our basis, Eq. (2.5), coincides with the time-independent basis of the LZ model. This situation is certainly physically realizable. Morover, it may be considered as an approximation to systems of more complex time dependence.

In the following, we wish to investigate the applicability of the MLZ model to various situations met in the case of the Hamiltonian Eq. (2.12). We start out with the simple case of two non-interacting spins Eq. (2.12).

A. Dynamics in the case of non interacting particles

The formula Eq. (2.9) remains valid for any time-dependence in the matrix elements of the Hamiltonian H, Eq. (2.6). The specific character of this time dependence governs the values of p_a and p_b but the general form remains the same. In the particular choice of time-dependence corresponding to the LZ model, expressions for the two-state transition probabilities p_a and p_b are known, Eq. (3.10).

The diabatic potential curves for the Hamiltonian H are identified with the diagonal elements of the matrix Eq. (2.6)

$$\begin{aligned} \mathcal{E}_1(t) &= E_{1a}(t) + E_{1b}(t)\ , \qquad \mathcal{E}_2(t) = E_{1a}(t) + E_{2b}(t)\ , \\ \mathcal{E}_3(t) &= E_{2a}(t) + E_{1b}(t)\ , \qquad \mathcal{E}_4(t) = E_{2a}(t) + E_{2b}(t)\ . \end{aligned} \tag{4.1}$$

Referring to the adiabatic basis, the non-adiabatic transitions are located in the vicinities of crossings between the diabatic potential curves. Four types of crossings are located at the instants of time where the single-particle diabatic potential curves cross, namely:

$$\begin{aligned} \mathcal{E}_1(t) &= \mathcal{E}_2(t) \ \Rightarrow\ E_{1b}(t) = E_{2b}(t)\ , \\ \mathcal{E}_3(t) &= \mathcal{E}_4(t) \ \Rightarrow\ E_{1b}(t) = E_{2b}(t)\ , \\ \mathcal{E}_1(t) &= \mathcal{E}_3(t) \ \Rightarrow\ E_{1a}(t) = E_{2a}(t)\ , \\ \mathcal{E}_2(t) &= \mathcal{E}_4(t) \ \Rightarrow\ E_{1a}(t) = E_{2a}(t)\ . \end{aligned} \tag{4.2}$$

We denote the time of the crossing of the diabatic potential curves $\mathcal{E}_i(t)$ and $\mathcal{E}_j(t)$ as t_{ij}. From Eq. (4.2) one sees that two pairs of diabatic potential curves, $\{\mathcal{E}_1(t),\ \mathcal{E}_2(t)\}$ and $\{\mathcal{E}_3(t),\ \mathcal{E}_4(t)\}$, cross at the same instant of time denoted as t_1 in Fig. 1 ($t_1 = t_{12} = t_{34}$). Similarly, two other pairs of diabatic potential curves, $\{\mathcal{E}_1(t),\ \mathcal{E}_3(t)\}$ and $\{\mathcal{E}_2(t),\ \mathcal{E}_4(t)\}$, cross simultaneously at some other instant of time $t_2 = t_{13} = t_{24}$. Note that for the crossing discussed above the couplings are non-zero, $V_{ij} \equiv H_{ij} \neq 0$ (see Fig. 1).

The conditions for two other types of crossing cannot be reduced to single-particle crossings:

$$\begin{aligned} \mathcal{E}_1(t) &= \mathcal{E}_4(t) \;\Rightarrow\; E_{1a}(t) + E_{1b}(t) = E_{2a}(t) + E_{2b}(t) \;, \\ \mathcal{E}_2(t) &= \mathcal{E}_3(t) \;\Rightarrow\; E_{1a}(t) + E_{2b}(t) = E_{2a}(t) + E_{1b}(t) \;. \end{aligned} \tag{4.3}$$

Note however that here the crossing potential curves are not coupled directly, which corresponds to the zero elements of the Hamiltonian matrix Eq. (2.6), $V_{14} = V_{23} = 0$. As discussed in Section III C, in the general case, such *second-order* crossings manifest a typical pseudo-crossing pattern of adiabatic potential curves, although with small splitting ($\sim V^2$ as compared to $\sim V$ splittings in the generic case, see Eq. (3.5) and Appendix A). However, in the special case of the Hamiltonian Eq. (2.6), due to its specific structure, the adiabatic curves cross exactly. This correlates with the fact that formula (A12) gives zero second-order splitting in this case. For the generalized Hamiltonian Eq. (2.12) the splittings are non-zero.

The remarkable features of the model of non-interacting spins is that only *single path* connects any initial state to any final state via two-state crossings of the type in Eqs. (4.2) with non-zero couplings; it is assumed that the crossings with zero couplings, Eqs. (4.3), do not lead to transitions. It is worthwhile to remind here that, as discussed in the Introduction, by definition, a *path* is composed of segments of diabatic potential curves; it can switch from one curve to the other at the point where diabatic potential curves cross, *provided* there is a non-zero direct coupling between these two curves. A path always corresponds to propagation in positive direction of time t.

When checking the single-path property, it is convenient to assume that, in the spirit of the MLZ model, the diabatic potential curves are linear functions of time, with some constants β_{1j}, β_{2j}, α_{1j}, α_{2j},

$$\begin{aligned} E_{1a}(t) &= \beta_{1a} t + \alpha_{1a} \;, \qquad E_{2a}(t) = \beta_{2a} t + \alpha_{2a} \;, \\ E_{1b}(t) &= \beta_{1b} t + \alpha_{1b} \;, \qquad E_{2b}(t) = \beta_{2b} t + \alpha_{2b} \;, \end{aligned} \tag{4.4}$$

and the couplings V_a and V_b are time independent. Within this assumption, the pairwise transition probabilities are given by Eq. (3.10) as

$$p_j = \exp\left(-\frac{2\pi |V_j|^2}{|\beta_{1j} - \beta_{2j}|} \right) \;, \qquad q_j = 1 - p_j \;, \tag{4.5}$$

where $j = a, b$. The path-following arguments lead to the state-to-state probability matrix (2.9) which is exact for the non-interacting spins model. We emphasize once again that the validity of formula (2.9) does not necessarily require presumption (4.4).

Figure 2 shows the solution of the Schrödinger equation using the Hamiltonian of Eq. (2.6) with diagonal energies given by Eq. (4.4) and constant couplings. In this particular case, we have in atomic units $\beta_i = \{-2.0, -0.50, 0.50, 2.0\}$, $\alpha_i = \{0.0, -7.0, 7.0, 0.0\}$, $(i = 1, 2, 3, 4)$, $V_{12} = V_{34} = 0.5$, and $V_{24} = V_{13} = 0.3$. The figure shows the population of each of the diabatic states as a function of time along with the MLZ prediction. The inset shows diabatic potential curves, and the horizontal lines are the predictions of the LZ model. One can clearly see that redistribution of populations is localized in time around the crossings, Eq. (4.2) (of course, at least one of two interacting states is to be populated prior to the crossing). The exact crossings, Eq. (4.3) (that are not replaced by pseudo-crossings in the adiabatic picture) do not lead to any redistribution of population. The final LZ probabilities are given by the second column of the matrix in Eq. (2.9). We find that they agree rather well with the numerical solution of the Schrödinger equation.

B. Dynamics within the interacting spins model

In the following we will refer to the more general Hamiltonian of Eq. (2.12). This model also normally has 4 crossings of diabatic potential curves with non-zero coupling (first-order crossings) and 2 crossings with zero couplings (second-order crossings). One can again suggest linear time-dependence of the diabatic potential curves $\tilde{\mathcal{E}}_j(t)$ with some constants A_j and B_j:

$$\tilde{\mathcal{E}}_j(t) = B_j t + A_j \;, \tag{4.6}$$

and time-independence of the couplings V_{jk}.

In general, all crossings occur at different instants of time t_{ij}. Two qualitatively different situations are met. In case of the time ordering

$$t_{34} < t_{12} < t_{14} < t_{24} < t_{13} < t_{23}, \tag{4.7}$$

the generalized model has single-path property, as seen from Fig. 3*a*. In case of the time ordering

$$t_{24} < t_{12} < t_{14} < t_{13} < t_{34} < t_{23}, \tag{4.8}$$

the single-path property is absent, as seen in Fig. 3*b*. These conclusions can be drawn through direct inspection of the generic Figures 3.

In the single-path case, when the ordering Eq. (4.7) is valid, by considering paths that connect initial and final states, one obtains a matrix of all state-to-state transition probabilities

$$\mathbf{P} = \begin{pmatrix} p_{12}p_{13} & p_{24}q_{12} & p_{12}q_{13} & q_{12}q_{24} \\ p_{13}q_{12} & p_{12}p_{24} & q_{12}q_{13} & p_{12}p_{24} \\ p_{34}q_{13} & q_{24}q_{34} & p_{13}p_{34} & p_{24}q_{34} \\ q_{13}q_{34} & p_{34}q_{24} & p_{13}q_{34} & p_{24}p_{34} \end{pmatrix} . \tag{4.9}$$

Here p_{jk} is the probability of non-adiabatic transition at the crossing between the jth and the kth diabatic potential curves, i.e. the probability of remaining in the same diabatic state. Within the Landau-Zener model one has

$$p_{jk} = \exp\left(-\frac{2\pi|V_{jk}|^2}{|B_j - B_k|}\right). \tag{4.10}$$

Note that the matrix in Eq. (4.9) generally is non-symmetrical.

The formula (2.9) is exact within the related 'generalized SO(3)' model. In distinction, the formula (4.9) for the model Eq. (2.12) is derived from 'path-following' arguments of semi-classical type. As numerical calculation shows, this formula is not valid within the general model Eq. (2.12). As an example one can consider the model with the diabatic potential curves as drawn in Fig. 1. By rotating potential curve 4 around the point of its crossing with the potential curve 1 and keeping all other parameters unchanged we thereby turn from Hamiltonian (2.6) to the more general model of Eq. (2.12). Let us consider a transition probability P_{32} as a function of the slope B_4 as obtained by the rotation described. Other Hamiltonian parameters used in numerical calculations are, in atomic units: $B_1 = -4$, $B_3 = 2 = -B_2$, $A_1 = A_4 = 0$, $A_3 = 1 = -A_2$, with the couplings $V_{12} = V_{34} = 0.65$, $V_{13} = V_{24} = 0.8$, $V_{23} = V_{14} = 0$.

At $B_4 < -2$ the transition $3 \to 2$ can be realized via two different paths, while at $B_4 > -2$ only a single path is available. Formula (4.9) suggests that the probability P_{32} does not depend on B_4 at all. Figure 4 shows that it is not true not only when several transition paths exist, but also when there is only one path connecting the initial and final states.

Some special cases of the generalized model Eq. (2.12) are known in which exact solutions are available.

The first case appears when the model Eq. (2.12) reduces to the model Eq. (2.6). In this case $V_{12} = V_{34}$, $V_{31} = V_{42}$ and $\tilde{\mathcal{E}}_1 - \mathcal{E}_2 = \tilde{\mathcal{E}}_3 - \mathcal{E}_4$. From the latter property it follows that $B_1 - B_2 = B_3 - B_4$, $B_3 - B_1 = B_1 - B_2$ and formula (4.10) leads to $p_{12} = p_{34} \equiv p_b$, $p_{13} = p_{24} \equiv p_a$. The transition probabilities, Eq. (4.9), are reduced to (2.9), which are *exact*.

Generally, four linear adiabatic curves experience 6 avoided crossings, although at some crossings the couplings would turn zero, as in the case of model Eq. (2.12). In the special case when three diabatic curves are parallel, they are crossed by the fourth one at 3 points. This is the well known Demkov-Osherov model [20]. In the following, we will consider some special cases with 5 (section IV B 1) and 4 (section IV B 3) crossings, and finally we will study the general case including interference effects and second order crossings.

1. Four-state generalized bow-tie model

The case when semi-classical considerations are exact stems from the generalized bow-tie model [22]. Exact solution of this model is available for any N, but the simplest case, $N = 4$, was not yet considered in detail. The original bow-tie model [21] is covered by the generalized one as a special case. Our four-state model, Eq. (2.12), is reduced to the generalized bow-tie model provided that some restrictions on its parameters are imposed. One claim is that two diabatic potential curves are parallel; by an appropriate phase transformation they could be made horizontal. Let these curves have labels 2 and 3. Then one has $B_2 = B_3 = 0$. The state 1 interacts with 2 and 3 so that the couplings are identical, i.e. $V_{12} = V_{13}$. The same refers to the state 4, namely, $V_{24} = V_{34}$. Besides this, the generalized bow-tie model presumes that within the pairs 2, 3 and 1, 4 the couplings are absent: $V_{23} = V_{32} = 0$, $V_{14} = V_{41} = 0$. The latter properties are intrinsic in the Hamiltonian operator in Eq. (2.12). The additional condition is that the diabatic potential curves cross half-way between the curves 2 and 3. Denoting the instant of crossing as t_0 we obtain

$$B_1 t_0 + A_1 = B_4 t_0 + A_4 = \frac{1}{2}(A_2 + A_3) . \tag{4.11}$$

By choosing $t_0 = 0$ and the energy zero half-way between the horizontal potential curves 2 and 3, we have $A_1 = A_4 = 0$ without any loss of generality. Within these conventions the model Hamiltonian is

$$\mathbf{H}_{\rm gb}(t) = \begin{pmatrix} B_1 t & V_{12} & V_{12} & 0 \\ V_{12}^* & A_2 & 0 & V_{24} \\ V_{12}^* & 0 & -A_2 & V_{24} \\ 0 & V_{24}^* & V_{24}^* & B_4 t \end{pmatrix} . \tag{4.12}$$

At first we consider the case when the slopes B_1 and B_4 have opposite signs (for definiteness we assume below that $B_1 < 0$ and $B_4 > 0$, see Fig. 5*a*. For a special symmetric case of matrix (4.12) with $B_4 = -B_1$,

$$\mathbf{H}_{\rm gb1}(t) = \begin{pmatrix} B_1 t & V_{12} & V_{12} & 0 \\ V_{12}^* & A_2 & 0 & V_{24} \\ V_{12}^* & 0 & -A_2 & V_{24} \\ 0 & V_{24}^* & V_{24}^* & -B_1 t \end{pmatrix} , \tag{4.13}$$

it is particularly easy to write down the related spin-Hamiltonian:

$$\begin{aligned} H_{\rm gb1}(t) \;&=\; B_1 t(s_{az} + s_{bz}) + A(s_{az} - s_{bz}) + 2G_1(s_{ax} + s_{bx}) + 2G_2(s_{ay} + s_{by}) \\ &\quad + 4c_1(s_{az}s_{bx} + s_{bz}s_{ax}) + 4c_2(s_{az}s_{by} + s_{bz}s_{ay}) \; , \end{aligned} \tag{4.14}$$

with $V_{12} = G_1 - iG_2 + c_1 - ic_2$, $V_{24} = G_1 - iG_2 - c_1 + ic_2$. Note that the Hamiltonian (4.14) is symmetric under permutation of spins a and b, except for the term $A(s_{az} - s_{bz})$. The case when this term turns zero, i.e. $A \to 0$, corresponds to transition from the generalized bow-tie model [22] to the original one [21], as described in detail in [22].

According to the results of *exact* analytical calculations (carried out in [22] for an arbitrary number of states N), the matrix of transition probabilities reads

$$\mathbf{P} = \begin{pmatrix} p_1^2 & p_1 q_1 & p_4 q_1 & q_1 q_4 \\ p_4 q_1 & p_1 p_4 & q_4^2 & p_4 q_4 \\ p_1 q_1 & q_1^2 & p_1 p_4 & p_1 q_4 \\ q_1 q_4 & p_1 q_4 & p_4 q_4 & p_4^2 \end{pmatrix} , \tag{4.15}$$

where

$$p_1 = \exp\left(-\frac{2\pi|V_{12}|^2}{|B_1|}\right) , \quad p_4 = \exp\left(-\frac{2\pi|V_{24}|^2}{|B_4|}\right) , \qquad q_1 = 1 - p_1 \; , \quad q_4 = 1 - p_4 \; . \tag{4.16}$$

The matrix of Eq. (4.15) is generally non-symmetrical. This is a special case of formula (4.9) (with $p_{13} = p_{12} = p_1$, $p_{24} = p_{34} = p_4$). Only single-path transitions are operative in this case.

Figure 6 shows the dynamics of a system with Hamiltonian of the form Eq. (4.12) with parameters $B_1 = -0.5$, $B_4 = 1$, $B_2 = B_3 = A_1 = A_4 = 0$, $A_2 = 5$, $= -A_3$, $V_{12} = V_{13} = 0.2$, $V_{24} = V_{34} = 0.15$. Initially, the system is prepared in state 1 (see Fig. 5 *a*), so the diabatic populations should converge towards the probabilities in the first column of the matrix in Eq. (4.15). This is the case to a high degree of accuracy. The remaining small discrepancy is a measure of precision of the numerical procedure employed.

We now turn to the case when the slopes B_1 and B_4 have the same sign; for definiteness we assume that $B_4 > B_1 > 0$, see Fig. 5*b*. Again we use the *exact* results of [22], which give the matrix of transition probabilities

$$\mathbf{P} = \begin{pmatrix} (1 - p_4 q_1)^2 & p_4 q_1 & \underline{p_1 p_4^2 q_1} & \underline{\underline{q_1 q_4 p_4}} \\ \underline{q_1 p_1 p_4^2} & p_1 p_4 & (1 - p_1 p_4)^2 & \underline{\underline{p_1 p_4 q_4}} \\ p_4 q_1 & \underline{\underline{0}} & p_1 p_4 & q_4 \\ \underline{\underline{q_1 q_4 p_4}} & q_4 & \underline{\underline{p_1 p_4 q_4}} & \underline{\underline{p_4^2}} \end{pmatrix} . \tag{4.17}$$

This matrix does not have form of Eq. (4.9). In this case both single- and multi-path transitions are operative. Actually above *multi-* means *double-*; such transition probabilities are underlined in the matrix in Eq. (4.17). The doubly underlined matrix elements correspond to transitions that in principle could be multi-path ones in the generalized bow-tie model for an arbitrary N (cf. [22]), but in fact are single-path in the particular $N = 4$ realization considered here.

Figure 7 shows the dynamics for the same system as in Fig. 6 except for the sign of B_1, which now is positive. The initial state is still diabatic state number 1. Once again, we find that the final probabilities coincide rather well with the phase independent LZ-prediction given in the first row of the matrix in Eq. (4.17).

The intermediate case emerges when $B_1 = 0$. Here we obtain the single-path Demkov-Osherov model [20] with three parallel horizontal diabatic potential curves (1, 2, 3) crossed by a slanted curve (4) under the particular condition $V_{14} = 0$. The state-to-state transition probability matrix reads ($B_4 > 0$)

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & p_4 & q_4^2 & p_4 q_4 \\ 0 & 0 & p_4 & q_4 \\ 0 & q_4 & p_4 q_4 & p_4^2 \end{pmatrix} . \tag{4.18}$$

The condition $V_{14} = 0$ means that the state 1 is completely decoupled from all other states, i.e. $p_1 \to 1$, $q_1 \to 0$. Both the matrices in Eqs. (4.15), (4.17) tends to Eq. (4.18) in this limit. Although the transition from Eq. (4.15) via Eq. (4.18) to Eq. (4.17) is continuous, it is not smooth and analytical, i.e. there is no analytical formula that embraces all these expressions.

Thus, a change of sign of the slopes B_1, B_4 alters the character of the model (from single- to multiple- path) and drastically changes the expressions for the state-to-state transition probabilities. For instance, if B_1 and B_4 are both positive, transition $2 \to 3$ becomes impossible, $P_{23} \equiv 0$. The generalized bow-tie model provides a so far unique case in which exact solutions are available also in the situation when multi-path transitions are operative. The important specific feature of the model is that the multi-path transitions do not result in interference oscillations, as discussed in detail in Ref. [22].

2. Survival on a diabatic curve with extreme slope

Consider now the case when all the slopes B_j are different. Let B_1 be largest of all the slopes B_j, and B_4 be the smallest of all the slopes B_j

$$B_1 = \max\{B_j\} , \qquad B_4 = \min\{B_j\} . \tag{4.19}$$

Then, according to conjecture of Brundobler and Elser [38], recently proved by Shytov [39] and Volkov and Ostrovsky [35], some transition probabilities are known exactly

$$P_{11} = p_{12} p_{13} p_{14} , \qquad P_{44} = p_{14} p_{24} p_{34} . \tag{4.20}$$

For our particular model with $V_{14} = 0$ one has to put $p_{14} = 1$. For the generalized bow-tie model additional relations are $p_{12} = p_{13} = p_1$ and $p_{24} = p_{34} = p_4$. This reduces formulas (4.20) to

$$P_{11} = p_1^2 , \qquad P_{44} = p_4^2 , \tag{4.21}$$

in agreement with Eqs. (4.15), (4.17).

3. Crossing of two parallel bands of diabatic states

Usuki [40] considered crossing of two parallel bands of diabatic states [41]. The case of two states in each band corresponds in our terms to $B_1 = B_4$, $B_2 = B_3$. With an appropriate choice of zeroes on the energy and time axes the Hamiltonian takes the form

$$\mathbf{H}_{\rm band}(t) = \begin{pmatrix} B_1 t + A_1 & V_{12} & V_{13} & 0 \\ V_{12}^* & B_2 t + A_2 & 0 & V_{24} \\ V_{13}^* & 0 & B_2 t - A_2 & V_{34} \\ 0 & V_{24}^* & V_{34}^* & B_1 t - A_1 \end{pmatrix} . \tag{4.22}$$

Within each band coupling is absent, but inter-band coupling persist. For definiteness we assume $B_1 > 0$, $B_2 < B_1$.

Again, only some state-to-state transition probabilities are known exactly [36, 40, 42]

$$\begin{aligned} P_{11} &= p_{12} p_{13} , \qquad P_{44} = p_{24} p_{34} , \\ P_{22} &= p_{24} p_{12} , \qquad P_{33} = p_{34} p_{13} , \end{aligned} \tag{4.23}$$

Two more probabities have exact expressions, depending on sign of A_1 and A_2

$$P_{41} = 0 , \ A_1 > 0 ; \qquad P_{14} = 0 , \ A_1 < 0; \tag{4.24}$$

$$P_{23} = 0 , \ A_2 > 0 ; \qquad P_{32} = 0 , \ A_2 < 0; \tag{4.25}$$

Within the general MLZ, Eq. (1.1), one can distinguish the case of degenerate slopes, where $\beta_i = \beta_j$ and the case of complete degeneracy, where in addition $\varepsilon_i = \varepsilon_j$. A number of cases of slope degeneracy appeared above: Demkov-Osherov model, bow-tie model, band-crossing model. The situation with complete degeneracy generally requires a special treatment, to be carried out elsewhere. As an illustrative example we consider here only the limit of band-crossing model with complete pairwise degeneracy of diabatic potential curves. Presuming additionally that the couplings are pairwise equal we obtain Hamiltonian matrix for *degenerate band* case as

$$\mathbf{H}_{\rm db}(t) = \begin{pmatrix} B_1 t & V_a & V_b & 0 \\ V_a^* & B_2 t & 0 & V_a \\ V_b^* & 0 & B_2 t & V_b \\ 0 & V_a^* & V_b^* & B_1 t \end{pmatrix} . \tag{4.26}$$

There is only one, albeit degenerate crossing of diabatic potential curves at $t = 0$. To simplify the problem we introduce new orthonormal basis set:

$$\begin{aligned} |I\rangle &= \frac{1}{\sqrt{2}}(|1\rangle - |4\rangle) \ , \\ |II\rangle &= \frac{1}{\sqrt{2}}(|1\rangle + |4\rangle) \ , \\ |III\rangle &= \frac{1}{h}(V_a|2\rangle + V_b|3\rangle) \ , \\ |IV\rangle &= \frac{1}{h}(V_b|2\rangle - V_a|3\rangle) \end{aligned} \tag{4.27}$$

with $h = \sqrt{|V_a|^2 + |V_b|^2}$. In the new basis the Hamiltonian (4.26) is transformed to

$$\tilde{\mathbf{H}}_{\rm db}(t) = \begin{pmatrix} B_1 t & 0 & 0 & 0 \\ 0 & B_1 t & \sqrt{2}h & 0 \\ 0 & \sqrt{2}h & B_2 t & 0 \\ 0 & 0 & 0 & B_2 t \end{pmatrix} . \tag{4.28}$$

Thus the states $|I\rangle$ and $|IV\rangle$ are fully decoupled while the remaining pair of states $|II\rangle$ and $|III\rangle$ provide standard two-state Landau-Zener model. Accordingly, S-matrix (i.e. matrix of state-to-state transition amplitudes) is

$$\tilde{\mathbf{S}}_{\rm db} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & s_{22} & s_{23} & 0 \\ 0 & s_{32} & s_{33} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} , \tag{4.29}$$

where

$$s_{22} = s_{33}^* = p_0 e^{i\varphi} \ , \quad s_{23} = s_{32}^* = e^{i\theta}\sqrt{1-p_0^2} \ , \tag{4.30}$$

$$p_0 = \exp\left(-\frac{2\pi h^2}{|B_1 - B_2|}\right) \ , \tag{4.31}$$

where the phase θ is insignificant (see below), and the phase of the diagonal elements, $\pm\varphi$, vanishes when the interaction time before and after the crossing is about the same. Note that the effective coupling in the Hamiltonian (4.28) is $\sqrt{2}h$ which is responsible for extra factor of 2 in the exponent (4.31) [cf. expression (4.10)]. Returning to the original basis of states we get

$$\mathbf{S}_{\rm db} = \begin{pmatrix} \frac{1}{2}(s_{22}+1) & (V_a/\sqrt{2}h)s_{23} & (V_b/\sqrt{2}h)s_{23} & \frac{1}{2}(s_{22}-1) \\ (V_a/\sqrt{2}h)s_{32} & (V_a^2/h^2)s_{33} + V_b^2/h^2 & (V_a V_b/h^2)(s_{33}-1) & (V_a/\sqrt{2}h)s_{32} \\ (V_b/\sqrt{2}h)s_{32} & (V_a V_b/h^2)(s_{33}-1) & (V_b^2/h^2)s_{33} + V_a^2/h^2 & (V_b/\sqrt{2}h)s_{32} \\ \frac{1}{2}(s_{22}-1) & (V_a/\sqrt{2}h)s_{23} & (V_b/\sqrt{2}h)s_{23} & \frac{1}{2}(s_{22}+1) \end{pmatrix} \tag{4.32}$$

that corresponds to the transition probabilities

$$\mathbf{P}_{\rm bd} = \begin{pmatrix} \frac{1}{4}(1+p_0)^2 & (V_a/2h^2)(1-p_0^2) & (V_b^2/2h^2)(1-p_0^2) & \frac{1}{4}(1-p_0)^2 \\ V_a^2(1-p_0^2)/(2h^2) & (V_a^2 p_0 + V_b^2)^2/h^4 & V_a^2 V_b^2(1-p_0)^2/h^4 & V_a^2(1-p_0^2)/(2h^2) \\ V_b^2(1-p_0^2)/(2h^2) & V_a^2 V_b^2(1-p_0)^2/h^4 & (V_b^2 p_0 + V_a^2)^2/h^4 & V_b^2(1-p_0^2)/(2h^2) \\ \frac{1}{4}(1-p_0)^2 & V_a^2(1-p_0^2)/(2h^2) & V_b^2(1-p_0^2)/(2h^2) & \frac{1}{4}(1+p_0)^2 \end{pmatrix} . \tag{4.33}$$

This result does not depend on the phase θ in formula (4.30); nor φ when $|t_i| \sim t_f$. No state-to-state transition probability coincides with that from the matrix (4.9).

C. The general multiple path case

In the general case systems are subject to both interference effects and possibly also second order transitions. The question of exact solutions remains a difficult one, but we do expect that if the crossings are separated well enough, the MLZ model should give satisfactory predictions.

When the couplings are very strong, and when the crossings are not very well separated in time, the LZ model may not describe the dynamics very well. This may be attributed to the fact that the populations oscillate with decreasing amplitude after an avoided crossing. It should be re-emphasized, however, that figures demonstrated here do not give a very accurate idea of these oscillations; in the MLZ model we are always referring to the adiabatic basis, in which the oscillations die out much faster than in the diabatic one. The figures, however, display the populations in the diabatic basis. Hence, the actual situation is not as unstable as suggested by the figures, and the agreement between the final transition probabilities and the LZ prediction is far from as coincidential as it may seem.

Figure 8 shows the dynamics corresponding to the Hamiltonian of Eq. (2.12) with parameters $B_i = \{-3,\, 0.5,\, 5,\, 0\}$, $A_i = \{0,\, 4,\, -5,\, 1.5\}$ $(i = 1,\, 2,\, 3,\, 4)$, $V_{12} = 0.5$, $V_{13} = 0.3$, $V_{24} = 0.1$ and $V_{34} = 0.4$. This is a realization of the system displayed generically in Fig. 3*b*. The initial state is the diabatic state 2. Referring to the diabatic basis, the transitions to e.g. the final state 4 can take place trough various paths, and hence the transition probabilities are strongly phase-dependent. If second order transitions are considered, the picture becomes even more complex. Even though the crossings appear rather close, the condition (3.14) is satisfied, and, as we see, the MLZ model describes the dynamics quite well.

Figure 9 shows essentially the same as Fig. 8 but with parameters corresponding to a slightly longer time scale. In this case we have $B_i = \{-3,\, 1,\, 5,\, 0\}$, $A_i = \{0,\, 50,\, -80,\, 16\}$, $V_{12} = 0.6$, $V_{13} = 0.5$, $V_{24} = 0.45$ and $V_{34} = 0.4$. Again we find that the agreement between the numerical calculations and Eq. (3.12) is rather good. Furthermore, by focusing on what happens at $t_3 \approx -5$, we discover a rather striking phenomena; there is a significant shift in the populations at the time of the crossing between two states that do not couple directly. This is quite surprising considering the very low probability of an adiabatic transition. In this particular case, the LZ model, Eq. (3.15), predicts this probability to be $1 - p_3 < 10^{-4}$, which leads us to suspect that the populations of the crossing diabatic states are practically unaltered. However, when both diabatic states are initially populated, the shift in population may be orders of magnitude larger. In order to trace this amplification effect, consider the transition matrix S_3 corresponding to $t = t_3$:

$$S_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & \sqrt{1-p_3}\,e^{i\alpha_3} & \sqrt{p_3} & 0 \\ 0 & -\sqrt{p_3} & \sqrt{1-p_3}\,e^{-i\alpha_3} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{4.34}$$

Suppose that the state immediately before the crossing is given by $(0, 1, e^{i\varphi}, 0)/\sqrt{2}$. Then the populations of adiabatic states 2 and 3 immediately after the crossing are $1/2 \pm \sqrt{p_3(1-p_3)}\cos(\alpha_3 - \varphi)$. This amounts to a maximum shift of populations of $\sqrt{p_3(1-p_3)}$, which may be orders of magnitude larger than $1 - p_3$. Consequently, second order transitions may be quite significant – even for very small diabatic transition probabilities. This is demonstrated in Fig. 10 in which the particular case treated above is demonstrated using the same parameters as in Fig. 9.

V. CONCLUSIONS

In this paper we have studied in detail the analytic properties of quantum mechanical four-state systems. The particular case of crossings of time dependent diagonal elements of the Hamiltonian leads to semi-analytical expressions for the state probabilities determined by the LZ model. We have demonstrated that the MLZ model in many cases gives accurate transition probabilities tested by parallel numerical solution of the four-state system. Furthermore, it has been demonstrated that by carefully taking phase interference effects into account, the general case in which multiple paths are encountered may also be treated adequately within the Landau-Zener model.

It is found that transitions may take place also between diabatic states that does not couple directly. These transitions, which are induced by the presence of the states that are not involved directly in the (avoided) crossing, can strongly influence the dynamics. An analytical expression for such effective coupling strengths has been derived and verified by numerical calculations.

The known analytically solvable four-state models have been analyzed with focus on their single- and multi-path properties. In particular, the four-state generalized bow-tie model has been explored in detail for two qualitatively different realizations. Transition between the two cases has been shown to go through the Demkov Osherov model.

APPENDIX A: SECOND-ORDER PSEUDO-CROSSINGS

1. Four-state model

At first we consider the special case of our four-state model by analyzing the characteristic equation for the eigenvalues λ of the Hamiltonian matrix $\mathbf{H}_{\rm g}$ of Eq. (2.12)

$$\begin{aligned}(\mathcal{E}_1-\lambda)(\mathcal{E}_2-\lambda)(\mathcal{E}_3-\lambda)(\mathcal{E}_4-\lambda)-(\mathcal{E}_3-\lambda)(\mathcal{E}_4-\lambda)V_{12}^2-(\mathcal{E}_2-\lambda)(\mathcal{E}_4-\lambda)V_{13}^2\\ -(\mathcal{E}_1-\lambda)(\mathcal{E}_3-\lambda)V_{24}^2-(\mathcal{E}_1-\lambda)(\mathcal{E}_2-\lambda)V_{34}^2+\left(V_{13}V_{24}-V_{12}V_{34}\right)^2=0\ .\end{aligned} \tag{A1}$$

The special case of the Hamiltonian of Eq. (2.6) is obtained by putting $V_{13}=V_{24}=V_a$, $V_{12}=V_{34}=V_b$, $\mathcal{E}_4=-\mathcal{E}_1$, $\mathcal{E}_3=-\mathcal{E}_2$. In this case, the characteristic equation (A1) reduces to

$$\begin{aligned}(\mathcal{E}_1^2-\lambda^2)(\mathcal{E}_2^2-\lambda^2)-(\mathcal{E}_2+\lambda)(\mathcal{E}_1+\lambda)V_b^2+(\mathcal{E}_2-\lambda)(\mathcal{E}_1+\lambda)V_a^2\\ +(\mathcal{E}_1-\lambda)(\mathcal{E}_2+\lambda)V_a^2-(\mathcal{E}_1-\lambda)(\mathcal{E}_2-\lambda)V_b^2+\left(V_a^2-V_b^2\right)^2=0\ .\end{aligned} \tag{A2}$$

It could be rewritten as bi-quadratic equation

$$\mathcal{E}_1^2\mathcal{E}_2^2+2\mathcal{E}_1\mathcal{E}_2\left(V_a^2-V_b^2\right)+\left(V_a^2-V_b^2\right)^2-\left(\mathcal{E}_1^2+\mathcal{E}_2^2+2V_a^2+2V_b^2\right)\lambda^2+\lambda^4=0\ . \tag{A3}$$

Now we consider the second-order crossing of a pair of potential curves 2 and 3; at the crossing of diabatic curves one obtains $\mathcal{E}_2=\mathcal{E}_3\equiv\mathcal{E}$. Assuming $(\mathcal{E}-\lambda)\sim V_{ij}^2\ll 1$ and retaining terms of order $\sim V_{ij}^4$, we reduce Eq. (A1) to

$$\begin{aligned}(\mathcal{E}_1-\mathcal{E})(\mathcal{E}_4-\mathcal{E})(\mathcal{E}-\lambda)^2-(\mathcal{E}-\lambda)\left[(\mathcal{E}_4-\mathcal{E})\left(V_{12}^2+V_{13}^2\right)+(\mathcal{E}_1-\mathcal{E})\left(V_{24}^2+V_{34}^2\right)\right]\\ +\left(V_{13}V_{24}-V_{12}V_{34}\right)^2=0\ .\end{aligned} \tag{A4}$$

This is a quadratic equation over $(\mathcal{E}-\lambda)$ with discriminant

$$\begin{aligned}D&=\left[(\mathcal{E}_4-\mathcal{E})\left(V_{12}^2+V_{13}^2\right)+(\mathcal{E}_1-\mathcal{E})\left(V_{24}^2+V_{34}^2\right)\right]^2-4(\mathcal{E}_1-\mathcal{E})(\mathcal{E}_4-\mathcal{E})\left(V_{13}V_{24}-V_{12}V_{34}\right)^2\\ &=\left[(\mathcal{E}_4-\mathcal{E})\left(V_{12}^2-V_{13}^2\right)-(\mathcal{E}_1-\mathcal{E})\left(V_{24}^2-V_{34}^2\right)\right]^2+4\left[(\mathcal{E}_4-\mathcal{E})V_{12}V_{13}+(\mathcal{E}_1-\mathcal{E})V_{24}V_{34}\right]^2\end{aligned} \tag{A5}$$

presented as a sum of two squared (i.e. positive) quantities. The first of these quantities turns zero upon adjustment of the system parameters (in our case this parameter is the time t). Then splitting of the two eigenvalues governed by Eq. (A4) equals

$$\Delta\lambda=2\left|\frac{V_{12}V_{13}}{\mathcal{E}_1-\mathcal{E}}+\frac{V_{24}V_{34}}{\mathcal{E}_4-\mathcal{E}}\right|. \tag{A6}$$

We remind that this is splitting at the second-order pseudo-crossing of potential curves 2 and 3; it is quadratic over V_{ij}. It can be compared with the splitting at conventional (or the first-order) pseudo-crossing of curves i and j; it is linear over V_{ij}, Eq. (3.5):

$$\Delta\lambda=2\left|V_{ij}\right|. \tag{A7}$$

The formula (A6) has structure typical for the second-order quantities in the perturbation theory: the states 2 and 3 are coupled via intermediate states 1 and 4, with the characteristic energy denominators. By fitting of parameters, the expression (A6) can be made equal zero. Then the splitting $\Delta\lambda$ is of higher order over V_{ij}. In special cases it might turn zero exactly; this occurs in the model of non-interacting spins.

2. Model with an arbitrary number of states

Consider now an $N \times N$ Hamiltonian matrix $\mathbf{H}_{\rm t}$ with diagonal elements $\mathcal{E}_j$ and non-diagonal elements V_{ij} (for brevity we assume that matrix $\mathbf{H}_{\rm t}$ is real). We consider the second-order crossing of potential curves 2 and 3: $\mathcal{E}_2 = \mathcal{E}_3 \equiv \mathcal{E}$, $V_{23} = 0$. Let λ be eigenvalue of $\mathbf{H}_{\rm t}$, and column vector $\mathbf{c}$ be an eigenvector. Then the standard set of equations is

$$\begin{aligned} \sum_{k\neq 2,\,3}^{N} (\mathbf{h} - \lambda \mathbf{I})_{jk} c_k + V_{j2} c_2 + V_{j3} c_3 = 0 \ , \\ \sum_{k\neq 2,\,3}^{N} V_{2k} c_k + (\mathcal{E}_2 - \lambda) c_2 = 0 \ , \\ \sum_{k\neq 2,\,3}^{N} V_{3k} c_k + (\mathcal{E}_3 - \lambda) c_3 = 0 \ , \end{aligned} \tag{A8}$$

where $\mathbf{h}$ is an $(N-2)\times(N-2)$ submatrix of $\mathbf{H}_{\rm t}$, and $\mathbf{I}$ is the $(N-2)\times(N-2)$ unit matrix. Denote $\mathbf{R}(\lambda) = (\mathbf{h} - \lambda)^{-1}$ the resolvent for the matrix $\mathbf{h}$. Then the first equation of Eqs. (A8) gives $c_k = -\sum_{k\neq 2,\,3}^{N} R_{kj}(V_{j2}c_2 + V_{j3}c_3)$ and two other equations are reduced to

$$\begin{aligned} -\sum_{j,\,k\neq 2,\,3}^{N} V_{2k} R_{kj}(\lambda) V_{j2} c_2 - \sum_{j,\,k\neq 2,\,3}^{N} V_{2k} R_{kj}(\lambda) V_{j3} c_3 + (\mathcal{E} - \lambda) c_2 = 0 \ , \\ -\sum_{j,\,k\neq 2,\,3}^{N} V_{3k} R_{kj}(\lambda) V_{j2} c_2 - \sum_{j,\,k\neq 2,\,3}^{N} V_{3k} R_{kj}(\lambda) V_{j3} c_3 + (\mathcal{E} - \lambda) c_2 = 0 \ . \end{aligned} \tag{A9}$$

We approximately put $\lambda = \mathcal{E}$ in the argument of the resolvent and obtain for the splitting of two eigenvalues of interest (which are degenerate in the limit $V \to 0$):

$$\Delta\lambda = 2 \left| \sum_{j,\,k\neq 2,\,3}^{N} V_{2k} R_{kj}(\mathcal{E}) V_{j3} \right| . \tag{A10}$$

In the particular case when $N = 4$, a simple analytical expression for the reslovent is available that allows to rewrite expression (A10) as

$$\begin{aligned} \Delta\lambda &= \frac{2}{|(h_{11} - \mathcal{E})(h_{44} - \mathcal{E}) - h_{14}^2|} \, |V_{21}(h_{44} - \mathcal{E}) V_{13} + V_{24}(h_{11} - \mathcal{E}) V_{43} - 2 V_{21} h_{14} V_{43}| \\ &= \frac{2}{|(\mathcal{E}_1 - \mathcal{E})(\mathcal{E}_4 - \mathcal{E}) - V_{14}^2|} \, |V_{21}(\mathcal{E}_4 - \mathcal{E}) V_{13} + V_{24}(\mathcal{E}_1 - \mathcal{E}) V_{43} - 2 V_{21} V_{14} V_{43}| \, , \end{aligned} \tag{A11}$$

where we have simply switched to alternative notations in the second line. In this paper we considered 4×4 Hamiltonian matrices, Eq. (2.12), with zeroes on the cross-diagonal, i.e. with $V_{14} = 0$. Then

$$\begin{aligned} \Delta\lambda &= \frac{2}{|(\mathcal{E}_1 - \mathcal{E})(\mathcal{E}_4 - \mathcal{E})|} \, |V_{21}(\mathcal{E}_4 - \mathcal{E}) V_{13} + V_{24}(\mathcal{E}_1 - \mathcal{E}) V_{43}| \\ &= 2 \left| \frac{V_{21} V_{13}}{\mathcal{E}_1 - \mathcal{E}} + \frac{V_{24} V_{43}}{\mathcal{E}_4 - \mathcal{E}} \right| , \end{aligned} \tag{A12}$$

which coincides with Eq. (A7).

If the submatrix $\mathbf{h}$ is diagonal, the formula (A10) reduces to

$$\Delta\lambda = 2 \left| \sum_{k\neq 2,\,3}^{N} \frac{V_{3k} V_{k2}}{\mathcal{E}_k - \mathcal{E}} \right| . \tag{A13}$$

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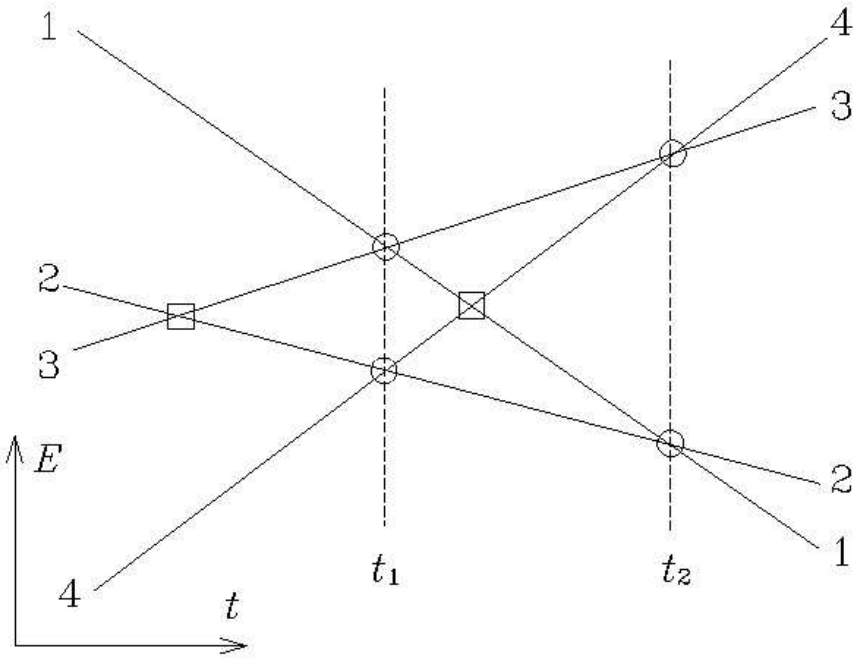

FIG. 1: Diabatic potential curves for the four-state model with the Hamiltonian of Eq. (2.6). In the generic case, there are no parallel curves. Altogether 6 curve crossings take place. Open circles mark crossings between curves i and j with non-zero couplings V_{ij}. Open boxes mark crossings between non-interacting curves, $V_{ij} = 0$. Due to the specific form of the model Hamiltonian H (2.6), two pairs of curves cross simultaneously at instants of time t_1 and t_2.

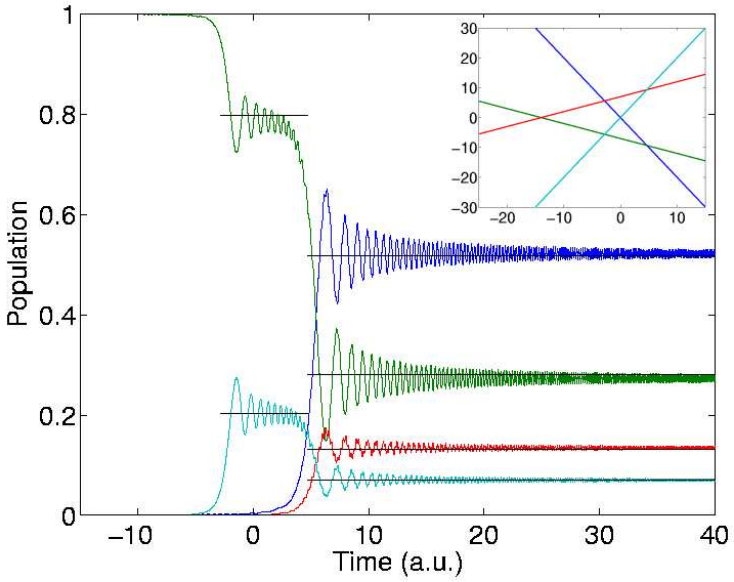

FIG. 2: (Color online) Dynamics of a particular system with the Hamiltonian of the form of Eq. (2.6), with the diabatic diagonal energies displayed in Fig. 1. The parameters are listed in the text. The initial state is diabatic state 2 (green in the color version), so the final LZ transition probabilities are given by the second column of the matrix in Eq. (2.9) with the transition probabilities at each crossing given in Eq. (4.5).

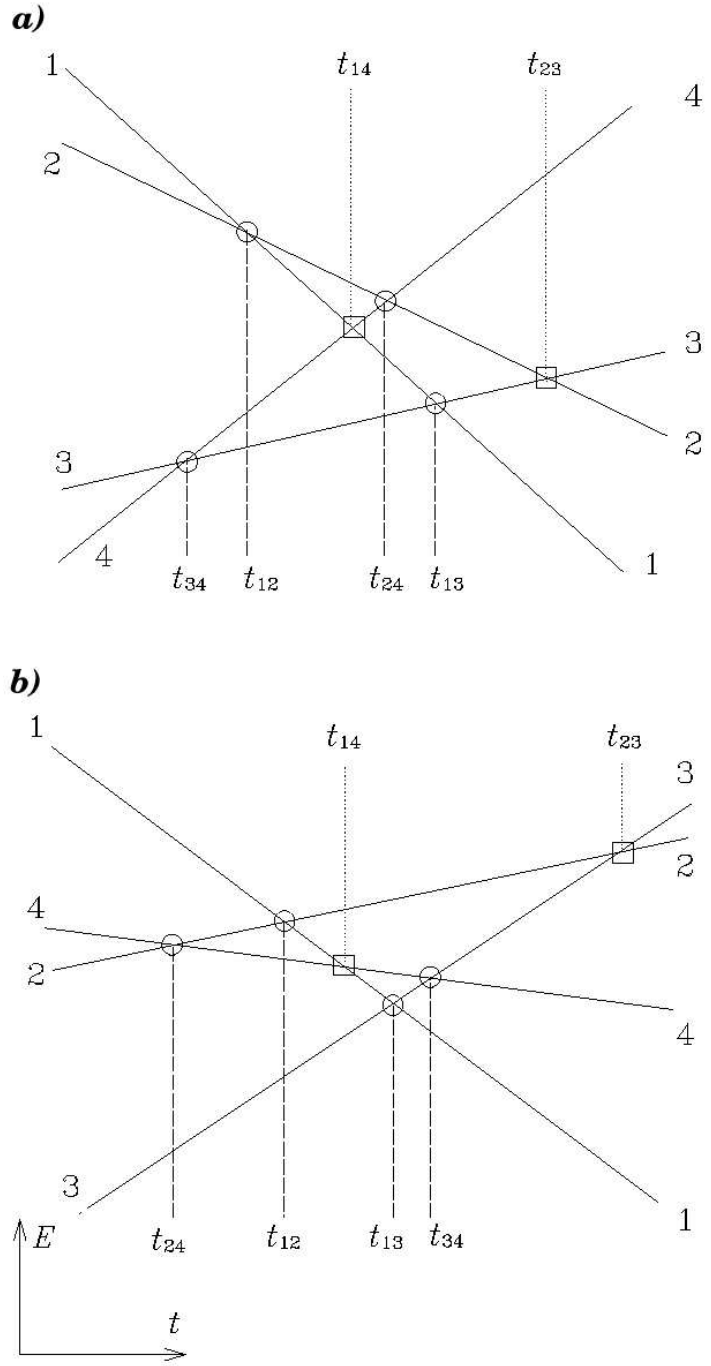

FIG. 3: Same as in Fig. 1, but for the more general model Hamiltonian $H_{\rm g}$ (2.12). All curve crossings occur at different instants of time. In case (a), neglecting second order transitions, all the state-to-state transitions occur via single paths, while in case (b), this property is absent.

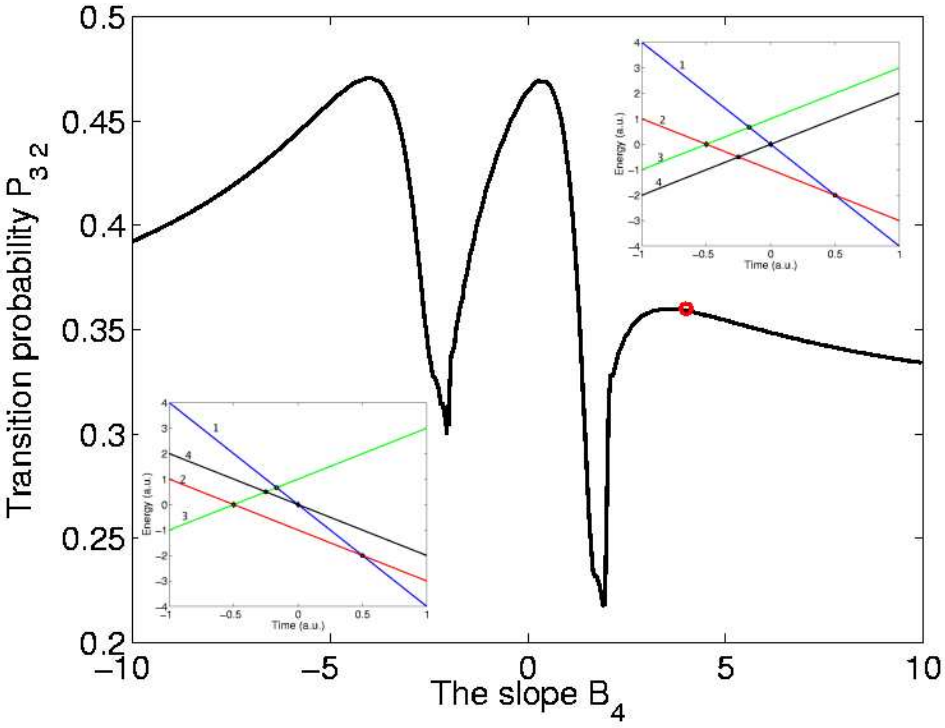

FIG. 4: (Color online) Transition probability P_{32} depending on the slope parameter B_4. It is implied that the variation of B_4 is achieved by rotating the potential curve 4 in Fig. 1 around the point of its crossing with the potential curve 1. The inserted plots corresponds to the special cases $B_4 = \pm 2$. The Hamiltonian parameters are listed in the text. Exact result for P_{32} is available only at $B_4 = 4$ (red circle).

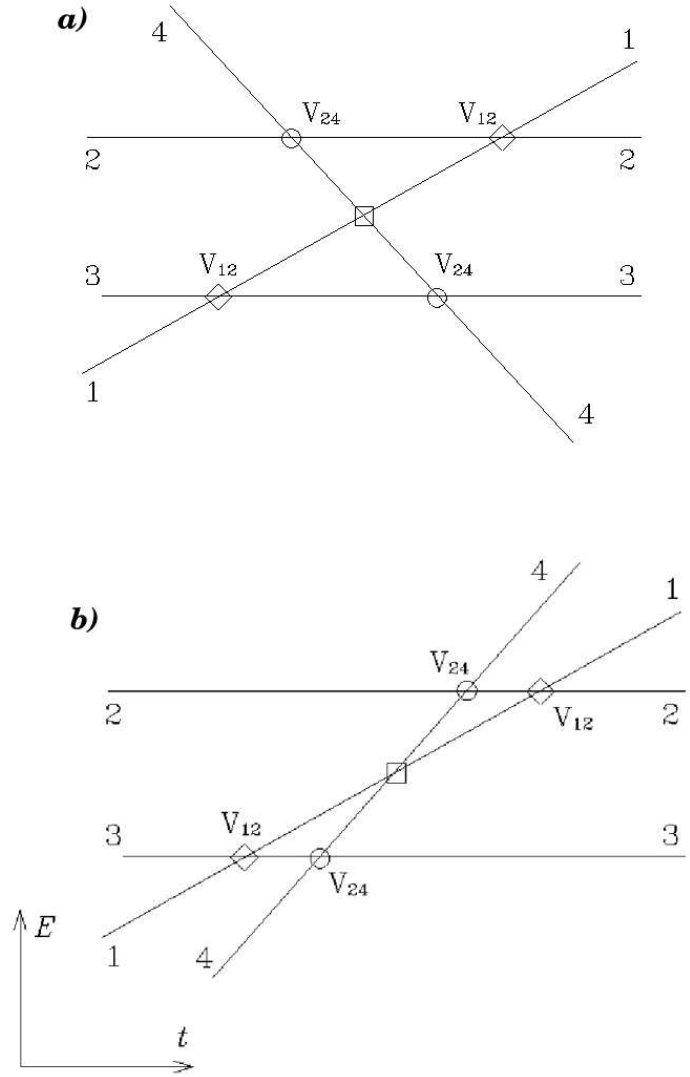

FIG. 5: Diabatic potential curves in the four-state generalized bow-tie model with the Hamiltonian (4.9). Open circles and diamonds mark crossings with pairwise identical couplings; open box marks crossing of non-interacting potential curves. In case (a) the slopes B_1 and B_2 have opposite signs ($B_1 > 0$, $B_2 < 0$) and all the state-to state transitions occur via single paths, while in case (b) ($B_4 > B_1 > 0$) two paths are allowed for the transitions $1 \to 1$, $1 \to 3$, $2 \to 1$ and $2 \to 3$.

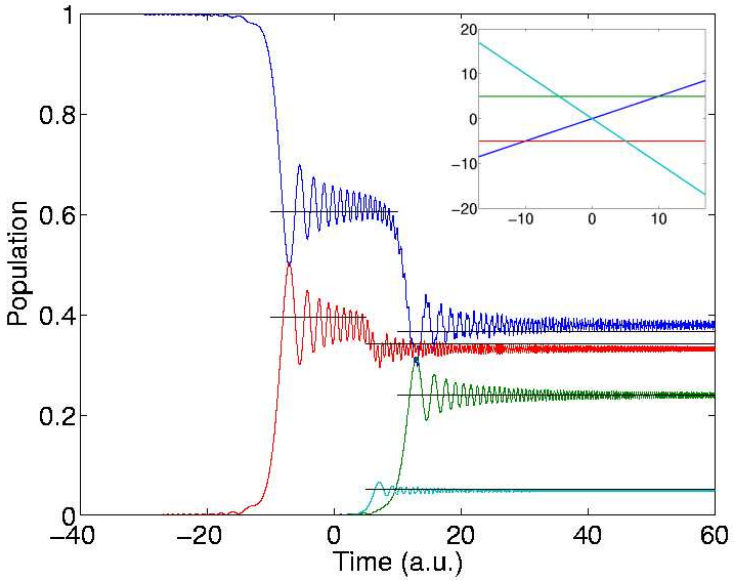

FIG. 6: (Color online) Dynamics corresponding to a Hamiltonian of the form of Eq. (4.12) where the slopes of the non-parallel potential curves have opposite signs (see Fig. 5*a*). The diabtic energy curves specific of this case are shown in the inserted figure. The system is initially prepared in diabatic state 1 (blue in the color version). The final probabilities coincide with the first row of the matrix in Eq. (4.15).

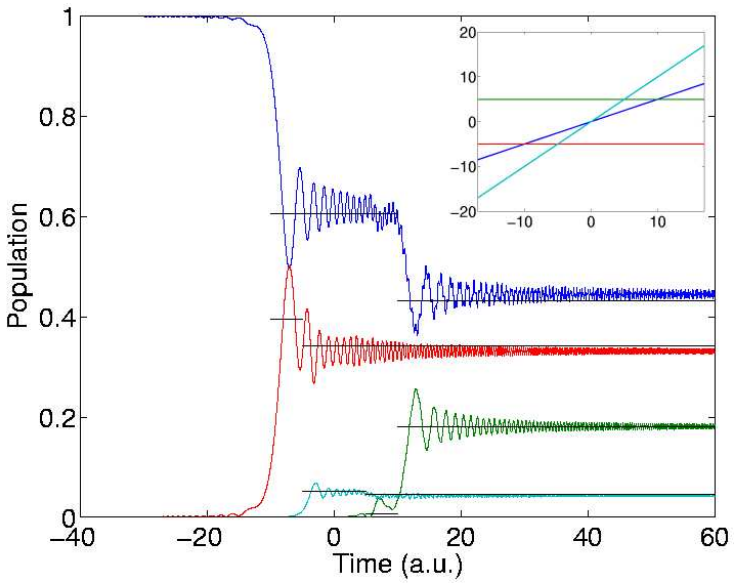

FIG. 7: (Color online) The same as in Fig. 6 except for the signs of the slopes of the non-parallel potential curves, which are the same in this case. This removes the single path nature of the system. However, in this particular case, the final transition probabilities are still independent of the adiabatic phases, as explained in detail in Ref. [22]. The final LZ-probabilities (the horizontal lines) corresponds to the first row in Eq. (4.17).

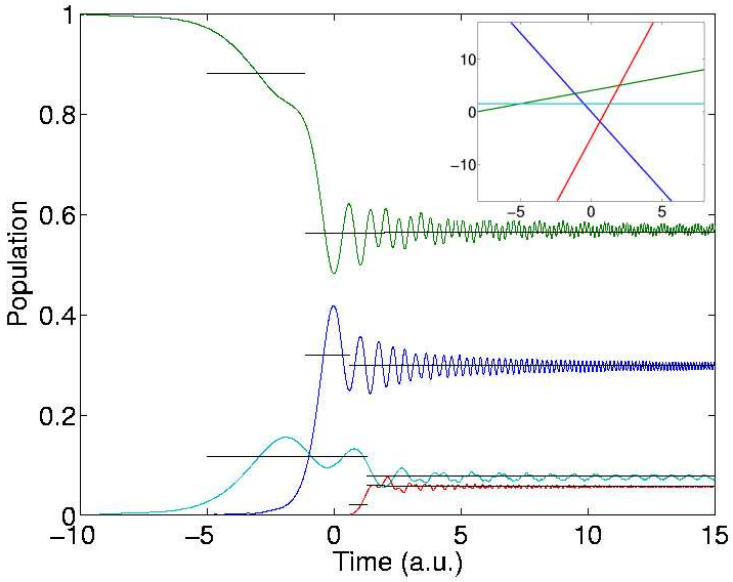

FIG. 8: (Color online) Dynamics given by the general 4-state Hamiltonian in Eq. (2.12) (see Fig. 3) when starting out in diabatic state 2 (green in the color version), which initially is adiabatic state number 2 as well. The LZ transition probabilities are found by Eq. (3.12), which includes the effect of the adiabatic phase. Furthermore, the instantaneous transition matrices at the second order crossings (crossings number 3 and 6) takes into account the possibility of transitions. The diagonal energies are indicated by the inserted figure, and the couplings are in this case $V_{12} = 0.5$, $V_{13} = 0.3$, $V_{24} = 0.1$ and $V_{34} = 0.4$. The strong oscillations in the diabatic populations may give the impression that the agreement of the MLZ-predictions with the final probabilities is somewhat coincidental. However, if the dynamic populations of the *adiabatic* states were displayed, we would see that the oscillations would die out much more rapidly in this basis.

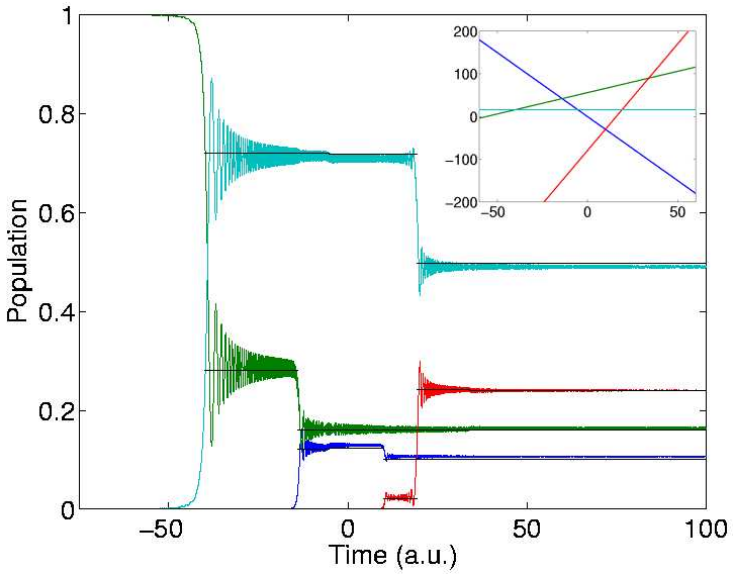

FIG. 9: (Color online) Dynamics of a system with the same generic structure as Fig. 8, but on a different time scale. Here the couplings are $V_{12} = 0.6$, $V_{13} = 0.5$, $V_{24} = 0.45$ and $V_{34} = 0.4$. As in the prior figure, the accuracy of the model is fully relying on the inclusion of the adiabatic and dynamic phases and the use of correct signs in the S-matrices. Since the oscillations in the populations of the diabatic states following each crossings has had time to die out, second order transitions at $t = -5.3$ can be seen in the figure.

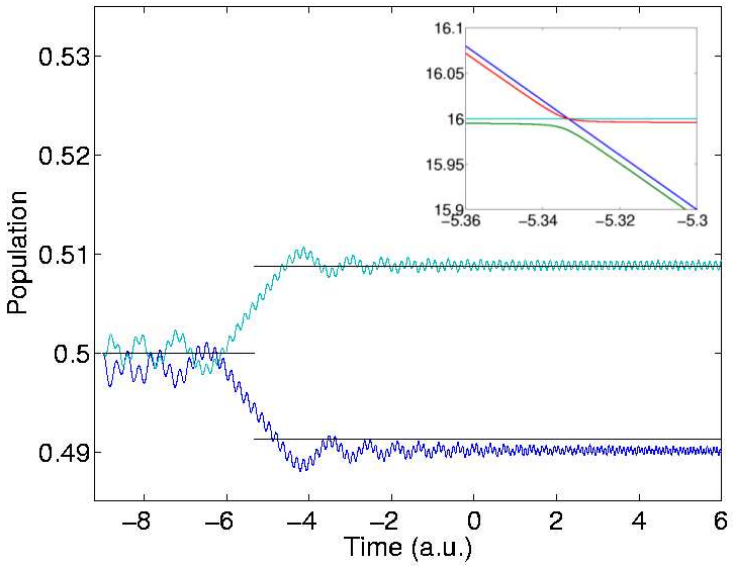

FIG. 10: (Color online) This figure demonstrates the significance of second order transitions. The parameters are the same as in Fig. 9, and the initial state is a mix of equal populations of the crossing diabatic states at a time shortly before the second order crossing. In this case, both diabatic and adiabatic diagonal energies are shown in the vicinity of the second order (avoided) crossing in the upper right corner. As we see, both populations are shifted approximately by 1 % although the probability of a diabatic transition is very low; $1 - p_3 = 8.3 \cdot 10^{-5}$.