# Zhu-Nakamura theory and the superparabolic level-glancing models

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(Received 16 April 2013; published 3 October 2013)

We study the applicability of the Zhu-Nakamura theory to a class of time-dependent quantum mechanical level-crossing models called superparabolic level-glancing models. The phenomenon of a level glancing, being on the borderline between a proper crossing of energy levels and an avoided crossing, is also an important special case between the two different approximative expressions in the Zhu-Nakamura theory. It is seen that the application of the theory to these models is not straightforward. We discuss some possible causes of these difficulties and also compare the approximative formulas of Zhu-Nakamura theory to those obtained by the generalization of the Dykhne-Davis-Pechukas theory.

DOI: 10.1103/PhysRevA.88.043404 PACS number(s): 32.80.Xx, 03.65.Sq, 34.70.+e, 42.50.Ex

## I. INTRODUCTION

The level-crossing models form a paradigm in the study of quantum dynamics of nonadiabatic transitions [1]. These models describe quantum systems with coupled states for which the corresponding diabatic energy levels, i.e., the energies related to the system eigenstates when there is no coupling present, depend on some external parameter and cross so that the states in question become degenerate at some parameter values. Situations of this type appear in both time-independent and purely time-dependent settings. In collisional problems, for example, the nonadiabatic transitions happen effectively at the curve crossings of potentials that depend on a spatial coordinate [2], whereas in time-dependent problems the level crossings are induced by external time-dependent fields [3]. The proper frameworks for describing the dynamics in such situations are then the stationary and time-dependent Schrödinger equations, respectively.

The pioneering works on the subject were done by Landau, Zener, Stückelberg, and Majorana already in 1932 in their studies of the linear crossing problem in which the diabatic energies depend linearly on the external coordinate and the coupling between the diabatic states is constant [4–7]. This basic model is nowadays called the Landau-Zener (LZ) model. The relevance of this model, besides its relative simplicity, comes from the fact that the transitions are localized in the vicinity of the crossings so the above-mentioned behavior of the energy levels and the coupling often form a good approximation to describe the dynamics of many real physical systems. This and other level-crossing models have been widely applied over the years, for example, to the studies of atomic and molecular collisions [1,2], laser-atom interactions [8], and quantum information processing [9] and in attempts to understand the dynamics of quantum phase transitions [10,11].

One of the recent advances in the field of nonadiabatic transitions is the Zhu-Nakamura theory (ZNT) formulated by Nakamura and co-workers, which the authors claim to be a generally applicable and accurate approximate theory for any level-crossing model and, in this sense, to form a complete solution of the problem [1,12]. It is based on exact results obtained by Zhu and Nakamura for the linear curve-crossing problem, i.e., the time-independent LZ model [13]. By generalizing the coupled wave integral method introduced by Hinton [14], they were able to calculate the Stokes constants and thus to construct the scattering matrix for the problem. Unfortunately, the exact analytic expressions for the constants are very complicated and therefore not very useful. Because of this, they went on, starting from these exact results and working initially in the collisional setting, to build an approximate theory, i.e., ZNT, by introducing several phenomenological corrections to the final analytic formulas.

In the recent years, the purely time-dependent problems especially have gained a lot of importance because of the progress of experimental methods and laser technologies in particular. This has led to possibilities of controlling the state of a quantum system accurately, for example, by specifically tailored chirped laser pulses [15,16]. Therefore, it is natural that ZNT has been generalized to handle also these time-dependent problems [17]. This is due to the fact that the time-independent linear crossing model (i.e., LZ model) and the time-dependent quadratic crossing model (i.e., parabolic model [18–20]) both have the same analytical structure; namely, they both can be reduced to a triconfluent Heun equation [21]. This allows the same approximate formulas to be used in both settings. Despite the many different developments that are based on ZNT [22,23] and the claim that the theory comprises a complete solution to curve-crossing problems, there seems to be only few articles in the literature that deal with the basic characteristics of the theory. Also, the applicability of the theory must be, in principle, considered for each model independently due to the phenomenological character of the theory.

In this paper, we consider a simple class of time-dependent level-crossing models, namely, the superparabolic level-glancing models introduced in [24]. The parabolic time dependencies of the diabatic energies have been applied, e.g., in studies of laser-induced molecular dynamics [15,16] and the parabolic level-glancing model was also recently used to study the tunneling between different energy bands in the case of merging Dirac cones [26]. The level-glancing phenomenon can also be seen as a counterpart to the case where the energy matches exactly the crossing-point energy in the time-independent models, a notoriously hard problem to

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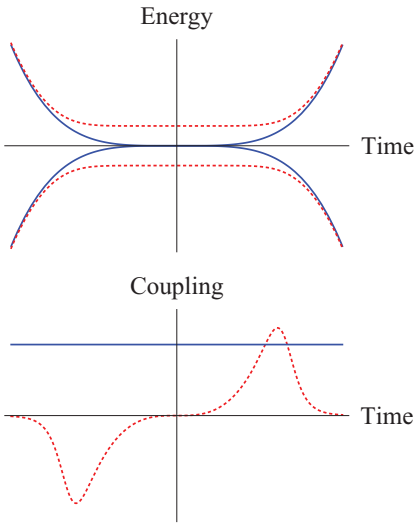


FIG. 1. (Color online) Schematics of the time dependence of the energy levels and coupling for the superparabolic models. The diabatic levels and the corresponding coupling are drawn with solid blue lines while the adiabatic ones are drawn with dashed lines in red.

approximate [1,25]. This particular parameter value remains then also as an important special case in the ZNT, being the dividing parameter value between the two approximative formulas in the theory. While both of the formulas should be applicable to this case in principle, their connection is not entirely smooth (see, for example, Fig. 1 in Ref. [27]) and seems to be even less studied.

We apply ZNT to superparabolic models and discuss particular aspects of the theory in this case. We also compare it to the other well-established approximative theory in the field of nonadiabatic transitions, namely, to the Dykhne-Davis-Pechukas (DDP) theory [28,29] studied in detail recently in [24]. The structure of this paper is as follows. In Sec. II we introduce the basic formalism for both the time-dependent and time-independent level-crossing problems and introduce the superparabolic level-glancing models. In Sec. III, the DDP theory and its application to superparabolic models is discussed shortly; more details can be found in [24]. In Sec. IV we give a very condensed overview of the ZNT and the final recommended approximate formulas in the form given in the basic reference [1]. In Sec. V we present and analyze the results that were obtained by numerical calculations and compare these to the approximative expressions. Finally, the discussion in Sec. VI ends the presentation.

## II. BASIC MODELS AND FORMALISM

### A. Time-independent two-state processes

Although our main focus in this paper is on time-dependent models, it is important to present some of the main aspects of the time-independent LZ model in order to understand ZNT better. The model describes a quantum system consisting of two states which both experience a potential that is linear in the coordinate $R$ and that have a constant coupling between them. The system is governed by the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi_1}{dR^2}+[-F_1(R-R_X)-(E-E_X)]\varphi_1=V_{12}\varphi_2, \quad (1)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi_2}{dR^2}+[-F_2(R-R_X)-(E-E_X)]\varphi_2=V_{12}\varphi_1, \quad (2)$$

with $F_1>0$, $V_{12}>0$, and $F_1>F_2$. $F_i$'s are the slopes of the potentials, $V_{12}$ the diabatic coupling, and $R_X$ and $E_X$ are the crossing point and the energy at the crossing point, respectively. Although the relative signs of the slopes can be arbitrary in the ZNT, we consider here only the case $F_1F_2>0$ only because it has a direct counterpart in the time-dependent theory.

By transforming the coupled Eqs. (1) and (2) into a momentum representation and redefining the variables suitably [1,2] we can reduce these coupled first-order equations to a second-order differential equation for, say, the state corresponding to $\varphi_1$, to an equation of the form

$$y''(z)+q(z)y(z)=0, \quad (3)$$

where

$$q(z)=\tfrac{1}{4}-ia^2z+\tfrac{1}{4}(a^2z^2-b^2)^2. \quad (4)$$

This differential equation belongs to the class of triconfluent Heun equation [21]. Instead of the explicit relationship between the reduced parameters $a$ and $b$ and the original ones, the important point here is only the physical meaning of these parameters. The parameter $a^2$ represents the effective coupling strength and $b^2$ is the effective collision energy. The parameter $a^2$ is always non-negative but that $b^2$ can be either positive or negative, depending on whether the energy $E$ is higher or lower than the crossing-point energy $E_X$, respectively. In these variables, the celebrated LZ formula for the transition probability reads [4]

$$p_{LZ}=\exp\left[-\frac{\pi}{4a|b|}\right]. \quad (5)$$

As is well known, this formula works only for large positive $b$. The physical reason is, that in a collision process the transition point is usually traversed twice and when the energy approaches the crossing-point energy, the two transitions start to overlap.

### B. Time-dependent two-state processes

Zener obtained the formula (5) by reducing the time-independent problem described in the previous section to a purely time-dependent one by assigning classical trajectories to colliding particles [4]. More generally, the time-dependent problems arise in the context of quantum systems in time-dependent external fields. In any case, the coherent dynamics of a two-state system is then given by the time-dependent Schrödinger equation of the form

$$i\hbar\frac{d}{dt}\varphi(t)=\begin{pmatrix}\varepsilon(t) & V(t)\\ V(t) & -\varepsilon(t)\end{pmatrix}\varphi(t), \quad (6)$$

with $\varphi(t)=[c_1(t),c_2(t)]^T$, where $c_1(t)$ and $c_2(t)$ are the probability amplitudes of the diabatic basis states $\tilde{\varphi}_1$ and $\tilde{\varphi}_2$, respectively. The functions $\varepsilon(t)$ and $V(t)$ are called the

diabatic energy levels and the diabatic coupling also in this time-dependent setting. The crossings happen at points of time $t_*$, where $\varepsilon(t_*) = 0$ and $\dot{\varepsilon}(t_*) \neq 0$. The overhead dot stands for time derivative.

The Schrödinger equation can be also given on the basis of the instantaneous eigenstates of the Hamiltonian matrix in (6). In this adiabatic basis the energy levels are given as

$$\mathcal{E}_{\pm}(t) = \pm\sqrt{\varepsilon(t)^2 + V^2(t)}, \tag{7}$$

and the adiabatic coupling reads

$$\gamma(t) = \pm\frac{V(t)\dot{\varepsilon}(t) - \varepsilon(t)\dot{V}(t)}{2[\varepsilon(t)^2 + V(t)^2]}, \tag{8}$$

where one can fix the sign by fixing the relative sign of the basis vectors. In general, the functions $\varepsilon(t)$ and $V(t)$ do not have the same zeros, so the level crossing usually appears only as an avoided crossing in the adiabatic basis. Moreover, when we have

$$|V(t)| \ll |\varepsilon(t)|, \quad |t| \to \pm\infty, \tag{9}$$

the basis vectors of the two bases coincide, apart from the possible swap between the labels, and the initial and final probability distributions can be obtained from the same expression. In the superparabolic models such a swapping of labels does not occur and in the rest of this paper we take the initial conditions to be $|c_2(-\infty)|^2 = 1$ so that both the diabatic and the adiabatic transition probability are given by $P \equiv |c_1(+\infty)|^2$.

### C. Superparabolic level-glancing models

The simplest time-dependent model that can take into account the double-crossing character of the process in the time-independent LZ model is the so-called parabolic model for which

$$\varepsilon(t) = \frac{At^2 - B}{2}, \quad V(t) = V_0. \tag{10}$$

The parameters $A$, $V_0$ are positive, while $B$ can also be negative. When this happens, the diabatic energy levels do not cross and the transitions are possible only by tunneling, while for positive $B$ the energy levels cross twice. In the limiting case between the two, namely when $B = 0$, the levels only touch each other at $t = 0$ and we call this a level-glancing case.

Obviously, each of these cases are in a direct correspondence with the different cases in the time-independent LZ model. In fact, by making the following identification between the variables and the parameters of these time-dependent and time-independent models,

$$t = z, \quad A = a^2, \quad \text{and} \quad B = b^2, \tag{11}$$

and choosing the units in a such way that $\hbar = 1$ and $V_0 = 1/2$, we see that differential equation for the probability amplitude $c_2$ obtained from Eq. (6) with (10) is reduced to an equation that is completely equivalent to (3) and (4). Indeed, this observation was also the starting point for ZNT [17].

Here we concentrate on the phenomenon of a level glancing and consider a direct generalization of the parabolic model, namely, the superparabolic models, where the diabatic energies are proportional to some even power of time. We can also reduce the number of free parameters to one and choose to work in units where $\hbar = 1$. The superparabolic level-glancing models are defined as [24]

$$\varepsilon(t) = t^N, \quad V(t) = \alpha = \text{const}, \tag{12}$$

where $N = 2,4,6, \ldots$ and $\alpha$ is positive. Now, the limit $\alpha \to 0$ is the sudden or diabatic limit while for large $\alpha$ the process is adiabatic. As explained at the end of Sec. II B, in both these cases we have $P \approx 0$.

It should be noted that the definition of $\alpha$ is here different from the one used in [1] or [17] for the parabolic model. We denote their parameter as $\alpha_{ZN}$ ($\alpha_{ZN} \equiv a^2$) and the connection between the two parameters is given by the relation

$$\alpha^3 = 1/(4\alpha_{ZN}). \tag{13}$$

This difference in notation is, of course, unfortunate, but we believe it is better to use the same notation as in [24] for better exposition of the new results and for comparison between the existing ones. Furthermore, this should not give rise to additional confusion as the approximate formulas of ZNT for the time-dependent case have to be transformed from the expressions for the time-independent results by replacement of parameters anyway.

## III. DYKHNE-DAVIS-PECHUKAS THEORY

One of the most important results concerning nonadiabatic transitions, and existing prior to ZNT, is given by a formula first proposed by Dykhne [29], which connects the structure of the zeros $t_c$ of the adiabatic energies in the complex plane and the way the adiabatic limit is approached by the adiabatic transition probability. This was later proved more rigorously for a class of two-level Hamiltonians by Davis and Pechukas [28]. The resulting formula, nowadays known as the DDP formula, is given by

$$P = e^{-2\mathrm{Im}D(t_c)}, \tag{14}$$

where

$$D(t) = \int_0^t [\mathcal{E}_+(s) - \mathcal{E}_-(s)]ds. \tag{15}$$

The method of Davis and Pechukas was to integrate the Schrödinger equation in the adiabatic basis along the level line of $D(t)$, defined by the condition $\mathrm{Im}[D(t)] = \mathrm{Im}[D(t_c)]$. The main assumptions allowing this approach were that there is no crossings for real $t$, that $t_c$ is well separated from other zero points or possible singularities, and that the Hamiltonian is analytic and single-valued at least in a region of complex $t$ plane bounded by the real axis and the level line mentioned above.

If there are many zero points $t_c$, Eq. (14) has to be complemented accordingly. Although there exists some rigorous results on the matter [30,31], it was discussed already in the seminal paper of Davis and Pechukas [28] and later studied by Suominen and co-workers [3,24,32], that including the contribution of all the zero points on the half plane can be very useful in order to obtain a good approximation for $P$ when the system is outside the adiabatic region. Therefore, we

define the generalization of the DDP formula as

$$P_{DDP} = \left| \sum_{k=1}^{N} \Gamma_k e^{iD\left(t_c^k\right)} \right|^2, \tag{16}$$

where

$$\Gamma_k = 4i \lim_{t \to t_c^k} \left(t - t_c^k\right) \gamma(t), \tag{17}$$

and $\gamma(t)$ is the nonadiabatic coupling defined in Eq. (8). In particular, it was found in [24] that this definition is needed in order to approximate the behavior of the superparabolic level-glancing models well. The explicit formulas are simply given below.

*Application to superparabolic models*. The zero points of the eigenvalues of the Hamiltonian defined by Eq. (12) are

$$t_c^k = \alpha^{1/N} e^{i\pi(2k-1)/2N}, \quad k = 1,2,\ldots,N, \tag{18}$$

so the zero points lie on a circle of radius $\alpha^{1/N}$ in the complex t plane. The integrals over the adiabatic energies are given by

$$D\left(t_c^k\right) = \eta e^{i\pi(2k-1)/2N}, \tag{19}$$

where

$$\eta = 2\nu_N \alpha^{(N+1)/N} \tag{20}$$

and

$$\nu_N = \int_0^1 \sqrt{1-y^{2N}}\, dy = \frac{1}{2N} B\left(\frac{1}{2N}, \frac{3}{2}\right), \tag{21}$$

where $B(x,y)$ is the $\beta$ function [33]. These explicit expressions are also used when discussing ZNT as they form the time-dependent version of the phase integrals in that context. The factors of Eq. (17) are given by $\Gamma_k = (-1)^k$ and the points $t_c^k$ are grouped into pairs with the same imaginary part to give the generalized DDP formula in the form

$$P_{DDP} = 4\left| \Sigma_{k=1}^{N/2} (-1)^k e^{-\eta \sin\left[\frac{\pi}{2N}(2k-1)\right]} \sin\left[\eta \cos\frac{\pi}{2N}(2k-1)\right] \right|^2. \tag{22}$$

## IV. ZHU-NAKAMURA THEORY

### A. Background and exact results

Determining the probability of nonadiabatic transitions can be reduced to calculating the Stokes constants as mentioned in the Introduction. This way, one obtains the connection between the different fundamental asymptotic solutions of the differential equation governing the process that are valid in different regions of the complex plane [34]. From these constants, one can construct the scattering matrix for the process, and the transition probability is then given in terms of the reduced scattering matrix elements $(S^R)_{mn}$ as $P_{12} := |(S^R)_{12}|^2$. In practice, the Stokes constants are known only for very restricted class of equations.

In Ref. [13], Zhu and Nakamura calculated the Stokes constants for four different classes of second-order differential equations. Among them was the important special cases of Eq. (3) with $q(z)$ either a quartic polynomial or a polynomial where the degree of the highest term is $2n$ and the next-highest term is of degree $n-1$, where $n$ is a positive integer. This means that, in principle, they solved both the time-independent LZ model and the time-dependent parabolic model as well as the superparabolic level-glancing models.

The important general results of this work were that the Stokes constants $U_i, \quad i = 1,\ldots,2(n+1)$ could be expressed in terms of only one of them, say $U_1$, and that this $U_1$ could be expressed as a converging infinite series depending on the constants of the polynomial $q(z)$. Unfortunately, the expression for $U_1$ is too cumbersome and so the results of [13] are not very transparent to analytical analysis and are therefore of only limited practical value (see, e.g., the discussions of their method in [35] and [36]). However, from the exact results one could also obtain the general form of the scattering matrix elements in terms of the Stokes constant $U_1$ as

$$\left(S_{LZ}^R\right)_{12} = -\frac{2i\,\mathrm{Im}(U_1)}{1+|U_1|^2}. \tag{23}$$

Furthermore, when the transition probability for one passage of the crossing point is denoted as

$$p = \frac{1}{1+|U_1|^2}, \tag{24}$$

we get the exact result concerning the functional form of the overall transition probability as

$$P_{12} = 4p(1-p)\sin^2(\psi), \tag{25}$$

where $\psi = \arg(U_1)$. This form is, of course, similar to the equation for double-passage transition probability derived by Stückelberg in the study of atomic collisions [6].

### B. The final recommended formulas of ZNT

In order to overcome the fact that the formulas for the Stokes constants are too difficult to be practical, Zhu and Nakamura have considered semiclassical approximations together with *ad hoc* modifications to obtain final formulas for the probability of nonadiabatic transitions applicable to general situations [27]. Thus, the content of ZNT is, in a way, reduced to a set of relatively simple and compact approximate formulas that are obtained by first taking the exact functional form [such as Eq. (25)] as the starting point and then making any modification to its constitutive parts in order to obtain a good approximation. These formulas have appeared in different forms over the years, but the definitive ones are given in the appendixes of Ref. [1].

We consider here first the parabolic level-glancing case and then discuss applicability of the general formulas for the superparabolic models. The parabolic model was also studied explicitly by Nakamura and co-workers but their viewpoint at the time was slightly different. They considered time-independent processes and transition probabilities for a variable collision energy and fixed values of the coupling strength. On the contrary, we have effectively fixed $b^2$ ($b = 0$) and $a^2$ is related through Eq. (13) to the variable parameter in our case. Also, using that relation, it is seen that the parameter range covered here is much larger. The superparabolic models are very similar in character to the parabolic ones

but need to be dealt the ZNT formulas meant for general models.

The final formulas for the time-independent LZ case are given for two parameter values separately, when energy is higher than the crossing energy ($E \geqslant E_X$) or lower than the crossing energy ($E \leqslant E_X$). As this corresponds to either nonnegative or nonpositive $b^2$ (i.e., the cases include equality), we could, in principle, use either one of the final formulas. The formulas for $b^2 \geqslant 0$ are more compact and considered here explicitly. Also obtaining the corresponding formulas for $b^2 \leqslant 0$ is straightforward, simply by applying the formulas (13) and (19) to the formulas (A.14)–(A.20) in Ref. [1]. However, it turns out that these formulas do not generalize well for the superparabolic models and even the resulting parameter dependence for parabolic model, for example, is not easily comprehended.

#### 1. *Double-crossing formulas for the parabolic level-glancing model*

The overall probability of nonadiabatic transition is now still given by (25) but the different terms are given by the following expressions. First, the modification of the Landau-Zener formula (5) is given by

$$p = \exp\left[-\frac{\pi}{4a}\left(\frac{2}{b^2+\sqrt{b^4+0.4a^2+0.7}}\right)^{1/2}\right], \quad (26)$$

which indicates that this form could, in principle, work also when $b = 0$. Second, the phase is given by

$$\psi = \sigma + \phi_s = \sigma - \frac{\delta}{\pi} + \frac{\delta}{\pi}\ln\left(\frac{\delta}{\pi}\right) - \arg\Gamma\left(i\frac{\delta}{\pi}\right) - \frac{\pi}{4}, \quad (27)$$

which contains the real and imaginary parts of the phase integral,

$$D\left(t_c^1\right) = \sigma + i\delta. \quad (28)$$

Furthermore, it is advantageous to replace this imaginary part $\delta$ in (27) with the modification

$$\delta_\psi = \left(1 + \frac{5\sqrt{a}}{\sqrt{a}+0.8}10^{-\sigma}\right)\delta. \quad (29)$$

This modifies the phase (27) for intermediate and large values of $a$ or, equivalently, for small and intermediate values of $\alpha$. It should be noted that the form of Eqs. (26) and (29) are obtained completely heuristically; i.e., it is not derived from anywhere (see, e.g., Ref. [27]). Actually, ZNT offers also further approximations in order to avoid the complex integration in (28). However, because the phase integral (28) appears also in the DDP formulas and can be given exactly for any superparabolic level-glancing model by Eq. (19), we do not need those approximations here but discuss them below along with other modifications when considering the superparabolic models.

The transition probability for one passage for the parabolic model in the level-glancing case is now given by

$$p = \exp\left[-\frac{\pi\alpha^{3/2}}{\sqrt{2}}\left(\frac{1}{(0.1\alpha^{-3}+0.7)^{1/4}}\right)\right]. \quad (30)$$

The real and imaginary parts of the phase integral are equal as can be seen from Eq. (19) and we simply have

$$\sigma = \delta = c\alpha^{3/2}, \quad (31)$$

where we have defined the constant

$$c = \frac{\sqrt{\pi}\Gamma(1/4)}{3\sqrt{2}\Gamma(3/4)}. \quad (32)$$

The final transition probability can now be explicitly stated:

$$P_{12} = 4e^{-\frac{\pi\alpha^{3/2}}{\sqrt{2}}(0.1\alpha^{-3}+0.7)^{-1/4}}\left(1 - e^{-\frac{\pi\alpha^{3/2}}{\sqrt{2}}(0.1\alpha^{-3}+0.7)^{-1/4}}\right) \times \sin^2\left[c\alpha^{3/2} - \frac{c\alpha^{3/2}}{\pi} + \frac{c\alpha^{3/2}}{\pi}\ln\left(\frac{c\alpha^{3/2}}{\pi}\right) - \arg\Gamma\left(i\frac{c\alpha^{3/2}}{\pi}\right) - \frac{\pi}{4}\right]. \quad (33)$$

This can be compared to the DDP result for the parabolic glancing model, which now explicitly reads

$$P_{DDP} = 4e^{-2c\alpha^{3/2}}\sin^2[c\alpha^{3/2}]. \quad (34)$$

We can compare the forms of Eqs. (34) and (33) and one could think that the argument in the sine function of the DDP result is just the first term of the corresponding term in the ZNT result. Furthermore, considering that the exact total probability is of the form of Eq. (25), one could guess that the exponential in DDP result could be interpreted as $p$. However, although its behavior is similar to the exponential in ZNT result, modifying the DDP result this way does not offer an improvement to the approximation.

#### 2. *Application to superparabolic models*

The above expressions dealt only with quadratic time dependencies. However, ZNT can be applied to models with general time dependencies by using the same formulas but with replacing the phase integral terms $\sigma$ and $\delta$ with the phase integral of each model [17]. Also, the diabatic parameters (in our case, only the diabatic coupling $\alpha$) should be modified, either by fitting the potential to a parabolic one or by using directly the final formulas given in [1],

$$a^2 = \frac{\sqrt{d^2-1}\hbar^2}{2V_0^2\left(t_t^2 - t_b^2\right)}, \quad b^2 = \sqrt{d^2-1}\frac{t_t^2 + t_b^2}{t_t^2 - t_b^2}, \quad (35)$$

and the quantities in the formulas are given as

$$V_0 = [E_2(t_0) - E_1(t_0)]/2, \quad (36)$$

and

$$d^2 = \frac{[E_2(t_b) - E_1(t_b)][E_2(t_t) - E_1(t_t)]}{[E_2(t_0) - E_1(t_0)]^2}, \quad (37)$$

where $E_2(t) > E_1(t)$ are the adiabatic potentials, $t_b$ is the moment when $E_2$ reaches minimum, $t_t$ when $E_1$ reaches maximum, and $t_0$ when the difference between the adiabatic energies is minimum. The philosophy behind this in the ZNT is that the formulas (35) and (36) only refer to adiabatic quantities

so one could take the experimentally measured adiabatic energies $E_i$ and fit them. We can, of course, use the adiabatic model parameters given by Eqs. (7) and (12).

In the case of superparabolic level-glancing models, $t_{b,t,0} = 0$, so these several points actually coincide and $d^2$ becomes unity. It is then clear from the above relations that the direct application of the final formulas of ZNT is not possible because of the several ambiguous "0/0" type relations. The diabatic coupling (36), however, gives $V_0 = \alpha$ as it should.

The phase integral for the superparabolic models was calculated in (19). However, ZNT also offers an approximate expression for its calculation in its collection of final recommended formulas in [1] as

$$\sigma + i\delta = \frac{1}{\hbar}\left[\int_0^{t_b} E_2(t)dt - \int_0^{t_t} E_1(t)dt + \sqrt{\frac{b^2}{a^2}} + \Delta\right], \quad (38)$$

where

$$\Delta = \frac{t_0 - (t_b + t_t)/2}{\sqrt{a^2(b^4 + i)}(t_b - t_t)}\sqrt{\frac{d^2}{d^2 - 1}} + \frac{1}{2\sqrt{a^2}}\int_0^i \left(\frac{1 + t^2}{t + b^2}\right)^{1/2} dt, \quad (39)$$

and it is obvious that the ambiguities arise also here.

On the other hand, also the first strategy, namely fitting the superparabolic diabatic energy level to a parabolic one, is doomed to fail (for a similar reason that the model cannot be linearized at the glancing and dealt with by the time-dependent LZ model [19]). It was also noted in [17] that once $\sigma$ and $\delta$ are obtained the final results are not so sensitive to other dependencies of the parameters. Motivated by this, we take the basic ZNT formulas (26) and (27) along with the phase integral of Eq. (19) to study how well ZNT generalizes to the superparabolic models. These are plotted in Figs. 2 and 3.

## V. RESULTS

We have seen in the previous section that the expressions of ZNT, when taken at face value, do not give well-defined equations for the final transition probability $P$ between the states of the superparabolic level-glancing models. However, our particular model problem allows us to compute the phase integral exactly and therefore to obtain the ZNT result without using these problematic terms.

The results of the DDP theory and the ZNT are compared to the results of the numerical simulations in Figs. 2 and 3. We take the example cases to be the parabolic level-glancing model and the superparabolic level-glancing models with $N = 6$ and $N = 10$. The results for other values of $N$ are similar, and thus the general behavior of the approximations can be deduced. The final transition probability itself oscillates as a function of the coupling $\alpha$. The oscillations are present already in the parabolic model as can be seen from Fig. 3 but become more enhanced when $N$ increases. This oscillatory character of the final transition probability is modulated by an exponential term which suppresses the oscillations as the adiabatic limit is approached. This can be also easily seen from the approximative analytic formulas.

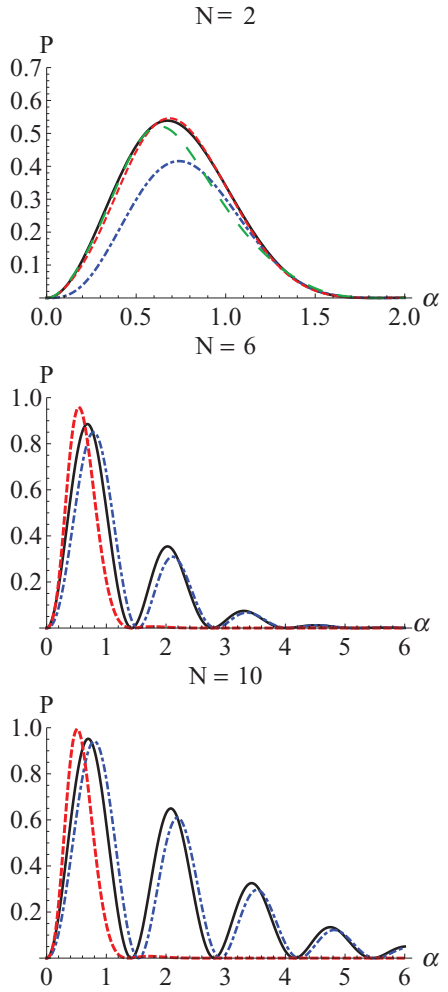


FIG. 2. (Color online) The DDP approximation is the blue dot-dashded line, ZNT (diabatic crossing case) is the red dashed line, and the numerical result is the black solid line. The sparsely dashed green line in the first plot is the ZNT formula for the tunneling case. It does not generalize well at all for higher values of $N$ and is omitted.

As expected, the parabolic model is well approximated by the ZNT theory, particularly by the approximative expression derived from the double-crossing formulas, namely, Eq. (33). This almost overlaps with the numerical result in the whole parameter region. The approximate formulas given for the tunneling transitions in ZNT were also discussed above, although they were not written explicitly out. However, it can be seen from the plots for $N = 2$ in Figs. 2 and 3 that they, along with the DDP formula, give the right qualitative behavior of the transition probability but deviate slightly from the correct numerical value in the intermediate values of the coupling. It is also interesting to note that the two approximate formulas of the ZNT do not coincide.

When going to the higher values of $N$, it is seen that the ZNT does not give a good approximation. The tunneling formulas are omitted altogether from the middle and bottom plots in Figs. 2 and 3 as they give nonsensical behavior. For the double-crossing formulas, the exponentially decaying part dies of too quickly and there is only one peak visible in the linear transition probability plot in Fig. 2. Interestingly, however, it is

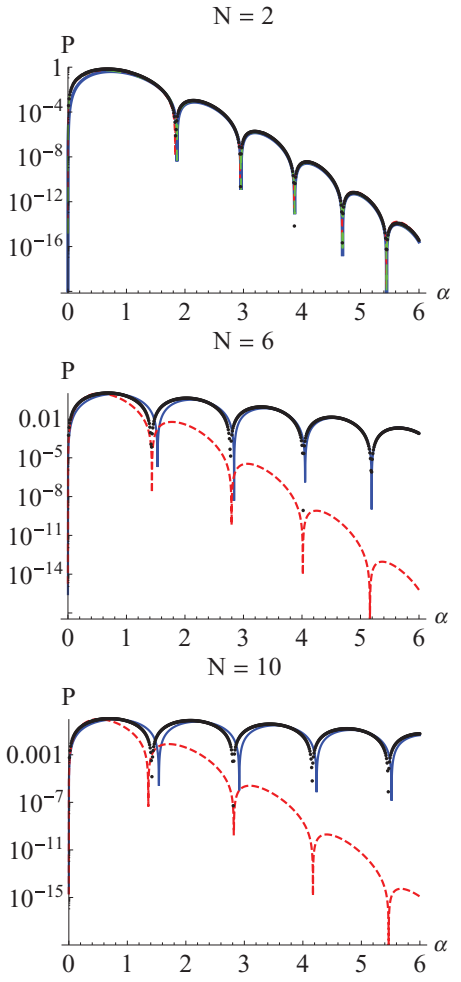


FIG. 3. (Color online) The plots in this figure correspond to the ones in the previous figure but with logarithmic ordinate in order to highlight the behavior of the oscillating and exponentially decreasing parts of the transition probability. The numerical results are depicted as black dots, the DDP result as solid blue line, and the ZNT results as a dashed red line (diabatic crossing case) and a sparsely dashed green line (tunneling case).

seen from the logarithmic plot in Fig. 3 that the oscillations of the transition probability seem to have the right frequency, so the Stokes phase of the LZ model with the modifications of the ZNT seems to work well and the problem is in the expression for the probability of one transition, i.e., in Eq. (26).

The generalization of the DDP formula for superparabolic models, on the other hand, is straightforward and it forms an increasingly good approximation as $N$ increases [24]. Apart from a small phase shift, it is a very good approximation in the whole parameter region, not just in the adiabatic limit. Also its parameter dependence is somewhat easier to understand as there is simple oscillating and exponentially decaying parts in each of the terms of the sum (22).

## VI. CONCLUSIONS

We have reviewed the basic aspects of ZNT and studied their application to the superparabolic models. Although ZNT has been studied in the context of the parabolic model before, we considered this case from a different viewpoint than done in the original works of Nakamura, Zhu, and co-workers. Our treatment was explicitly time dependent and we studied the transition probability as a function of the diabatic coupling, instead of the usual treatment of the equivalent collisional model where the independent variable is the collision energy and the coupling is held fixed. Of course, these are just two opposite viewpoints, so in effect we also studied the whole zero-energy parameter region for a wider range of values for the coupling. Obtaining approximative expressions for this region was, of course, one of the major motivating factors behind the whole Zhu-Nakamura approach, as it was not properly dealt with by the previously existing theories.

The level-glancing case resembles in many ways the double-crossing one, as there are similar oscillations in the final populations and the adiabatic coupling has two distinct peaks, for example. Indeed, the ZNT approximation derived for the double-crossing case is very accurate when applied to the parabolic level-glancing model. As the above-mentioned behavior is common to all superparabolic models, it is somewhat surprising that the ZNT at present does not work well for the models with higher values of $N$ but that at least the expression for $p$ [Eq. (26)] should be modified further. It also seems clear that the compact formulation of the ZNT for general models, namely, the parameter-fitting formulas (35)–(37), do not seem to be straightforwardly applicable to adiabatic energies that are symmetric in time, i.e., when $t_0$, $t_b$, and $t_t$ coincide.

At the same time one can see that the generalization of the DDP theory, namely, the full summation formula (16), can be directly applied in a systematic fashion and it does not lead to difficulties in the conceptual level. Of course, it also lacks of a sufficient general mathematical proof that would include superparabolic models and more work remains to be done in this direction. On the other hand, it may also be more difficult to handle multilevel problems within DDP theory [37]. Furthermore, DDP theory is not as directly related to quantities measured in experiments as ZNT due to the fact that it relies on analytic continuation of the adiabatic energies. Therefore, it has been our point to show the usefulness of both of these approaches and especially to highlight the need for more general formulation of the ZNT and also the need for more careful instructions to its application.

## ACKNOWLEDGMENTS

This research was supported by the Finnish Academy of Science and Letters and the Academy of Finland, Grant No. 133682. The author would like to thank K.-A. Suominen for discussions.

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