Perturbative and nonperturbative processes in adiabatic population transfer

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Abstract. With the help of superadiabatic techniques for quantum systems depending slowly on time, we demonstrate how the total transition amplitude, tracked in time in the usual adiabatic basis, can be decomposed into a perturbative part consisting of terms proportional to powers of the adiabaticity parameter, and a nonperturbative component. The interference of both components underlies the oscillations that accompany transitions in the adiabatic basis. Whereas for traditionally considered systems the final non-adiabatic transition probability is determined by the nonperturbative part alone, this is no longer correct for models describing stimulated Raman adiabatic passage (STIRAP). We explain the recently discovered breakdown of the Dykhne-Davis-Pechukas formula on general grounds, and provide simple, but accurate approximations for transition amplitudes in STIRAP systems.

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1 Introduction

The adiabatic theorem of quantum mechanics [1–3] states that the wave function of a system governed by a slowly changing Hamiltonian follows the instantaneous eigenstates. With the advent of modern lasers capable of delivering pulses with controllable and reproducible shapes, this concept has gained enormous practical importance for the coherent manipulation of atoms or molecules. For instance, the STIRAP mechanism, which allows one to accomplish highly efficient population transfer in effective three-level systems [4–7], is based entirely on adiabatic following induced by two partially overlapping laser pulses. It is then of interest to study not only how the system behaves in the adiabatic limit, but also how this limit is approached, that is, how the system responds to parameter variations that do *not* occur "infinitely slowly".

For two-level systems with instantaneous energy eigenvalues that remain nondegenerate for all times, a classic result due to Dykhne [8] and Davis and Pechukas [9] states that deviations from the adiabatic limit are beyond any power of the adiabaticity parameter ε, namely exponentially small in $1/\varepsilon$; an extension of this treatment to N-level systems has been formulated in reference [10]. However, it has recently been discovered by Laine and Stenholm [11] and Vitanov and Stenholm [12] that this exponential dependence breaks down and gives way to a power-law dependence in the case of typical STIRAP mod-

els, where the instantaneous eigenvalues become degenerate in both the distant past and distant future. It is now a conceptually important question just how this breakdown of the Dykhne-Davis-Pechukas exponential behavior comes about, since it is *not* related to any non-smoothness of the parameter variation. Is there a possibility to compute the deviations from the adiabatic limit in a simple, yet accurate way, even for models that are not analytically solvable?

The answer to this question, which will be given in Section 6, turns out to be affirmative, and surprisingly simple, but to get to this answer in a systematic fashion requires quite some work. We start in the following section by outlining an iterative scheme [13] that yields superadiabatic bases, *i.e.*, bases which in some sense take over the role which the usual adiabatic basis plays in the limit $\varepsilon \to 0$, so that they are particularly well suited for describing the dynamics for finite ε. In Section 3 we apply this scheme to the Landau-Zener transition, and show that it behaves quite similar to another superadiabatic scheme investigated in great detail by Berry [14]: Both schemes yield an optimal basis with respect to which the transition amplitude acquires a universal, error-function-like form. In Section 4 we then collect the necessary prerequisites of STIRAP, and apply the superadiabatic techniques to a generic three-level system.

The following, more technical Section 5 then demonstrates that the total transition amplitude, tracked in time in the customary adiabatic basis, can be uniquely decomposed into a nonperturbative component — that is, a

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component beyond all powers of the adiabaticity parameter ε —, which equals just Berry's universal error function previously met in the optimal superadiabatic basis, and a perturbative component with terms proportional to powers of ε. The fast oscillations that accompany, *e.g.*, the Landau-Zener transition in the adiabatic basis can hence be understood as resulting from the interference of these two parts.

In most cases considered so far, the perturbative component dies out when merely the final transition amplitude is considered, leaving only the nonperturbative component corresponding to the Dykhne-Davis-Pechukas result. This is what is different in the case of STIRAP: As elaborated in Section 6, the behavior of the nonadiabatic coupling at infinite times effectuates the survival of the perturbative component. Evaluating this component to lowest nonvanishing order in ε and adding the nonperturbative contribution gives a total transition probability that agrees very favourably with exact numerical data.

Our work builds on the seminal papers by Davis and Pechukas [9] and by Berry [14], but we have tried to explain all the required technical details, in order to make the key ideas accessible to as wide an audience as possible.

2 Beyond the adiabatic basis

We consider a Hamiltonian $H^{(0)}$ that describes an N-level system depending slowly on time t, *i.e.*, $H^{(0)} = H^{(0)}(t/T_0)$, where T_0 is some long time scale. $H^{(0)}$ is assumed to be analytic. Transforming to the dimensionless time variable $\tau = t/T_0$, the Schrödinger equation can be written in the form

$$\left(H^{(0)}(\tau) - i\varepsilon\partial_\tau \right) |\psi^{(0)}(\tau)\rangle = 0 \,, \qquad (1)$$

where the small adiabaticity parameter ε is given by the ratio $\hbar/T_0$, scaled by a suitable characteristic energy. For ease of notation, we will often suppress the argument τ in the following.

At each moment τ there are instantaneous eigenstates $|u_j^{(0)}\rangle$ and eigenvalues $E_j^{(0)}$:

$$H^{(0)}|u_j^{(0)}\rangle = E_j^{(0)}|u_j^{(0)}\rangle \qquad (2)$$

with

$$\langle u_j^{(0)}|u_k^{(0)}\rangle = \delta_{jk} \,. \qquad (3)$$

These equations still leave the phases of the eigenstates $|u_j^{(0)}\rangle$ unspecified at each instant τ. We fix these phases by requiring parallel transport [15]

$$\langle u_j^{(0)}|\partial_\tau|u_j^{(0)}\rangle = 0 \qquad (4)$$

for each state j. Taken together, the instantaneous eigenstates now form the columns of a unitary matrix $U^{(0)}$.

Applying the unitary transformation defined by $U^{(0)}$ to the Schrödinger equation, one obtains

$$U^{(0)\dagger}\left(H^{(0)} - i\varepsilon\partial_\tau \right) U^{(0)} U^{(0)\dagger}|\psi^{(0)}\rangle$$
$$\equiv \left(H^{(1)} - i\varepsilon\partial_\tau \right) |\psi^{(1)}\rangle = 0 \,, \quad (5)$$

with the transformed wave function

$$|\psi^{(1)}\rangle = U^{(0)\dagger}|\psi^{(0)}\rangle \qquad (6)$$

and the new Hamiltonian

$$H^{(1)} = U^{(0)\dagger}H^{(0)}U^{(0)} - i\varepsilon U^{(0)\dagger}\left(\partial_\tau U^{(0)} \right) \,. \qquad (7)$$

By construction, the first term on the r.h.s. is a diagonal matrix with elements $E_j^{(0)}$, while the diagonal elements of $U^{(0)\dagger}\partial_\tau U^{(0)}$ are zero, as a consequence of the parallel transport (4). Note that the off-diagonal elements of $H^{(1)}$ carry a prefactor ε.

The usual adiabatic approximation [2,3] now consists in neglecting the off-diagonal elements of $H^{(1)}$ altogether. Assuming that the system was prepared in the j-th eigenstate of $H^{(0)}$ in the infinite past, and denoting the solution to the Schrödinger equation (1) that evolves from this initial condition as $|\psi_j^{(0)}\rangle$, one finds the familiar approximate "adiabatic" wave functions

$$|\psi_j^{(0)}(\tau)\rangle \approx U^{(0)}(\tau)|e_j\rangle \exp\left(-\frac{i}{\varepsilon}\int_0^\tau d\tau' E_j^{(0)}(\tau') \right)$$
$$= |u_j^{(0)}(\tau)\rangle \exp\left(-\frac{i}{\varepsilon}\int_0^\tau d\tau' E_j^{(0)}(\tau') \right) \,, \quad (8)$$

where $|e_j\rangle$ is the j-th unit vector.

Instead of adopting this adiabatic approximation, one can also iterate the whole scheme [13]: the new Schrödinger equation (5) has the same form as the original equation (1), with $H^{(0)}$ replaced by $H^{(1)}$, and $U^{(0)\dagger}|\psi^{(0)}\rangle$ appears instead of $|\psi^{(0)}\rangle$. We fix the phases of the orthonormal eigenstates $|u_j^{(1)}\rangle$ of $H^{(1)}$ again by parallel transport; these eigenstates yield a matrix $U^{(1)}$ that defines a further unitary transformation. Proceeding in this manner, one obtains after $(n+1)$ steps a Schrödinger equation

$$\left(H^{(n+1)} - i\varepsilon\partial_\tau \right) |\psi^{(n+1)}\rangle = 0 \,, \qquad (9)$$

where

$$|\psi^{(n+1)}\rangle = U^{(n)\dagger}\ldots U^{(0)\dagger}|\psi^{(0)}\rangle \qquad (10)$$

and

$$H^{(n+1)} = U^{(n)\dagger}H^{(n)}U^{(n)} - i\varepsilon U^{(n)\dagger}\left(\partial_\tau U^{(n)} \right) \,. \qquad (11)$$

By induction, the off-diagonal elements of $H^{(n+1)}$ are of order ε^{n+1}. Hence it is tempting to neglect these elements

and to construct, in strict analogy to equation (8), improved adiabatic approximations to the true solutions of equation (1):

$$|\psi_j^{(0)}(\tau)\rangle \approx U^{(0)}(\tau)\dots U^{(n)}(\tau)\,|e_j\rangle$$
$$\times \exp\left(-\frac{i}{\varepsilon}\int_0^\tau d\tau'\,E_j^{(n)}(\tau')\right)$$
$$\equiv |\varphi_j^{(n)}(\tau)\rangle_I\,. \tag{12}$$

It should be noted that the eigenvalues $E_j^{(n)}$ pertaining to different steps are approximately equal. In particular, they coincide in those time intervals where $H^{(0)}$ remains constant, as follows from the parallel transport (4).

The above construction tries to exploit the idea of parallel transport as consistently as possible even beyond the adiabatic limit $\varepsilon \to 0$. Hence, the approximation (12) follows the true j-th evolving state, but cannot describe transitions to other states. Because such nonadiabatic transitions do become important beyond the adiabatic limit, even if they are only of order $e^{-const./\varepsilon}$ [8,9], the procedure is bound to diverge for $n \to \infty$, and thus has an asymptotic meaning. One has to expect that the off-diagonal elements of $H^{(n)}$ first become rapidly smaller from step to step, but then start to blow up, since the decrease of ε^n is eventually overcompensated by the growth of the time-derivative that enters into $U^{(n)\dagger}\partial_\tau U^{(n)}$. When terminating the procedure at that step $n = n_c$ where the off-diagonal elements are smallest, one should obtain an optimal description of the "transition-free component" of the total wave function. In other words, we are seeking an asymptotic representation of the adiabatic part [16] of the solution to Schrödinger's equation. When expanding the full wave function with respect to the basis $\{|\varphi_j^{(n_c)}(\tau)\rangle_I\,|\,j = 1,\dots,N\}$, the characteristic features of nonadiabatic transitions will stand out most clearly.

There is a closely related concept that aims in the same direction, namely the series of superadiabatic bases introduced by Berry in his study of histories of quantum transitions in two-level systems [14]. Applying Berry's ideas to N-level systems, we write $|\psi_j^{(0)}\rangle$ as a formal power series in ε,

$$|\psi_j^{(0)}(\tau)\rangle = \exp\left(-\frac{i}{\varepsilon}\int_0^\tau d\tau'\,E_j^{(0)}(\tau')\right)\sum_{m=0}^\infty \varepsilon^m\,|v_j^{(m)}(\tau)\rangle\,, \tag{13}$$

where the vectors $|v_j^{(m)}\rangle$ defined here are expressed as linear combinations of the instantaneous eigenstates (2):

$$|v_j^{(m)}(\tau)\rangle = \sum_{k=1}^N a_{jk}^{(m)}(\tau)\,|u_k^{(0)}(\tau)\rangle\,. \tag{14}$$

Stipulating again that the system occupies the j-th state for $\tau \to -\infty$, the determination of the coefficients $a_{jk}^{(m)}$ starts from the initial conditions

$$a_{jk}^{(0)}(\tau) = \delta_{j,k} \tag{15}$$
$$a_{jk}^{(m)}(-\infty) = 0 \qquad \text{for } m > 0\,. \tag{16}$$

Inserting the formal series (13) into the Schrödinger equation (1) and comparing coefficients of equal powers of ε, we obtain the recursion relations

$$a_{jk}^{(m)} = \frac{-i}{E_j^{(0)} - E_k^{(0)}}$$
$$\times \left\{\partial_\tau a_{jk}^{(m-1)} + \sum_{l=1}^N a_{jl}^{(m-1)}\gamma_{lk}^*\right\} \quad (j \neq k) \tag{17}$$

$$\partial_\tau a_{jj}^{(m)} = -\sum_{l=1}^N a_{jl}^{(m)}\gamma_{lj}^*\,, \tag{18}$$

where the quantities γ_{lk} denote the coupling matrix elements

$$\gamma_{lk} = -\langle u_l^{(0)}|\partial_\tau|u_k^{(0)}\rangle\,. \tag{19}$$

Note that $\gamma_{jj} = 0$, by virtue of equation (4). Having computed the coefficients $a_{jk}^{(m)}$ for $j \neq k$ from the coefficients $a_{jk}^{(m-1)}$ by means of equation (17), the diagonal elements $a_{jj}^{(m)}$ can be obtained by solving the first-order differential equation (18). As shown in more detail in Appendix A, the evaluation of this recursive scheme can be reduced to the computation of the matrix elements of $\partial_\tau^n H^{(0)}$, combined with the integration required by equation (18).

Since nonadiabatic transitions are of order $e^{-(const./\varepsilon)}$, that is, beyond any power of ε, the series (13) cannot describe these transitions and therefore must diverge [14], as does the previous iterative scheme. However, by terminating the series at some finite order n one gets the superadiabatic basis states [14]

$$|\varphi_j^{(n)}(\tau)\rangle_S \equiv \exp\left(-\frac{i}{\varepsilon}\int_0^\tau d\tau'\,E_j^{(0)}(\tau')\right)$$
$$\times \sum_{m=0}^n \varepsilon^m \sum_{k=1}^N a_{jk}^{(m)}(\tau)\,|u_k^{(0)}(\tau)\rangle \tag{20}$$

that can be employed to expand the wave function $|\psi_l^{(0)}\rangle$ evolving from the initially occupied l-th eigenstate of $H^{(0)}$. As shown by Berry for the two-level case $N = 2$, there is an optimal order $n = n_c$ that provides a distinguished, "natural" basis for the description of the dynamics (see Sect. 3).

The superadiabatic scheme based on the series (13) will be labelled by "S" in the following; the previous iterative scheme by "I". In the next section we will show with the help of a typical example that both schemes are in a certain sense complementary, but lead to very similar physical results.

3 The Landau-Zener transition

For a two-level system with a Hamiltonian $H^{(0)}$ given by a traceless real symmetric matrix, the iterative scheme

produces after $n + 1$ steps a Hamiltonian matrix of the form

$$H^{(n+1)} = \begin{pmatrix} E^{(n)} & -i\varepsilon\gamma^{(n)*} \\ i\varepsilon\gamma^{(n)} & -E^{(n)} \end{pmatrix} , \qquad (21)$$

with diagonal elements given by

$$E^{(n)} = \sqrt{E^{(n-1)2} + \left(\varepsilon|\gamma^{(n-1)}|\right)^2}$$

$$= E^{(0)} \sqrt{1 + \varepsilon^2 \sum_{k=0}^{n-1} \left(\frac{|\gamma^{(k)}|}{E^{(0)}}\right)^2} \qquad (22)$$

and off-diagonal elements determined by the recursion relation

$$\gamma^{(n)} = i\varepsilon \frac{\gamma^{(n-1)}\partial_\tau E^{(n-1)} - E^{(n-1)}\partial_\tau\gamma^{(n-1)}}{2E^{(n)2}}$$

$$= -i\varepsilon \frac{1}{2} \left(\frac{E^{(n-1)}}{E^{(n)}}\right)^2 \partial_\tau\left(\frac{\gamma^{(n-1)}}{E^{(n-1)}}\right) . \qquad (23)$$

Hence, $E^{(n+1)} - E^{(n)}$ is of order ε^{2n+2}.

As an archetypal example [17], we consider in this section the Landau-Zener Hamiltonian

$$H^{(0)} = \begin{pmatrix} \tau & 1 \\ 1 & -\tau \end{pmatrix} . \qquad (24)$$

In this case one finds

$$E^{(0)} = \sqrt{\tau^2 + 1} \qquad (25)$$

$$\gamma^{(0)} = \frac{i}{4(\tau + i)} - \frac{i}{4(\tau - i)} . \qquad (26)$$

Expanding the the wave function $|\psi_1^{(0)}(\tau)\rangle$ in the n-th order superadiabatic bases, either in the bases (12) corresponding to the scheme I or in the bases (20) provided by S,

$$|\psi_1^{(0)}(\tau)\rangle = \sum_{k=1}^{2} c_{1k}^{(n)}(\tau) |\varphi_k^{(n)}(\tau)\rangle , \qquad (27)$$

the coefficients $c_{12}^{(n)}$ denote the transition amplitudes with respect to these bases. These amplitudes can approximately be obtained from first-order time-dependent perturbation theory in the nonadiabatic coupling [9]. For the iterative scheme, this yields

$$c_{12}^{(n)}(\tau) = \int_{-\infty}^{\tau} d\tau' \, \gamma^{(n)}(\tau') \exp\left(-2\frac{i}{\varepsilon}\int_0^{\tau'} d\tau'' \, E^{(n)}(\tau'')\right) . \qquad (28)$$

To elucidate the flaw of this perturbative treatment, let us first compute the final transition amplitude $c_{12}^{(0)}(+\infty)$ in the usual adiabatic basis $n = 0$. In this case it is useful to introduce the new variable [14]

$$w(\tau) = 2\int_0^{\tau} d\tau' \, E^{(0)}(\tau') \qquad (29)$$

and to close the path of integration along the real axis by a semicircle in the lower half of the complex w-plane:

$$c_{12}^{(0)}(\infty) = \frac{1}{2} \oint dw \, \frac{\gamma^{(0)}(w)}{E^{(0)}(w)} \exp\left(-\frac{iw}{\varepsilon}\right) . \qquad (30)$$

According to equation (23), a (complex) degeneracy of the two eigenvalues $E^{(n)}$ and $-E^{(n)}$ is generally accompanied by a pole of the nonadiabatic coupling $\gamma^{(n)}$. For the Landau-Zener system, the equations (25) and (26) show that there are degeneracies of $\pm E^{(0)}$ and poles of $\gamma^{(0)}$ at $\tau = \pm i$; for the computation of $c_{12}^{(0)}(\infty)$ we only need to know $\gamma^{(0)}/E^{(0)}$ close to $w_c \equiv w(\tau_c)$, with $\tau_c = -i$. From the definition (29) one readily finds

$$w \approx w_c + \frac{1}{3} E^{(0)}(\tau) \, 4(\tau + i) \qquad (31)$$

with

$$w_c = -\frac{i\pi}{2} , \qquad (32)$$

hence we have

$$\frac{\gamma^{(0)}(w)}{E^{(0)}(w)} \approx \frac{i}{3(w - w_c)} \qquad (33)$$

for w close to w_c. Contour integration then gives

$$c_{12}^{(0)}(\infty) = \frac{\pi}{3} \exp\left(-\frac{|w_c|}{\varepsilon}\right) . \qquad (34)$$

It is well known that the prefactor $\pi/3$ is wrong. The error is an artifact of first-order perturbation theory in the adiabatic basis; adding the contributions from all orders renormalizes the prefactor to unity [9]. We shall repeatedly come back to this "$\pi/3$-problem" [14]. The corrected formula $c_{12}^{(0)}(\infty) = \exp(-|w_c|/\varepsilon)$, which shows that the transition amplitude is simply determined by the value of w at the point of degeneracy, is often referred to as the Dykhne-Davis-Pechukas formula ("DDP-formula"; see Refs. [8,9]).

We now turn to the transition histories $c_{12}^{(n)}$ pertaining to the iterative scheme I. The computation runs parallel to Berry's calculation for the scheme S [14], but there is an interesting difference, since for S the iterated energies $E^{(n)}$ with $n \geq 1$ do not appear. We briefly sketch the line of reasoning: Aiming at the amplitudes $c_{12}^{(n)}(\tau)$ for finite τ, we cannot close the path of integration as before, and have to remain on the real axis. The approximation (33) is valid only in the vicinity of the pole at w_c. However, if we tentatively approximate $E^{(n)}$ by $E^{(0)}$ for all n, the recursion relation (23) becomes

$$\frac{\gamma^{(n)}(w)}{E^{(0)}(w)} = -i\varepsilon \, \partial_w\left(\frac{\gamma^{(n-1)}(w)}{E^{(0)}(w)}\right) \qquad (35)$$

and thus produces, with increasing n, poles of successively higher order at w_c. The "domain of influence" of these

higher-order poles eventually reaches the real axis for sufficiently large n [14]. Hence, we can then evaluate the transition integral (28) with the approximation

$$\frac{\gamma^{(n)}(w)}{E^{(0)}(w)} \approx \frac{i(i\varepsilon)^n n!}{3} \left(\frac{1}{(w - w_c)^{n+1}} - \frac{1}{(w + w_c)^{n+1}} \right) \tag{36}$$

that results from plugging (33) into equation (23) with all $E^{(n)}$ replaced by $E^{(0)}$, and we have also added the contribution from the pole in the upper half-plane. Expanding to second order in $w/|w_c|$ then gives

$$\frac{\gamma^{(n)}(w)}{2E^{(0)}(w)} \approx \frac{\pi}{3} \frac{\varepsilon^n n^{n+\frac{1}{2}} e^{-n}}{\sqrt{2\pi} |w_c|^{n+1}} \exp\left(-\frac{(n+1)w^2}{2|w_c|^2} \right)$$
$$\times \left[\exp\left(i\frac{(n+1)w}{|w_c|} \right) + (-1)^n \exp\left(-i\frac{(n+1)w}{|w_c|} \right) \right]. \tag{37}$$

Approximating $E^{(n)}$ by $E^{(0)}$ also in the exponential of the integrant (28), and changing to the variable w, the factor $\exp(-iw/\varepsilon)$ counteracts the oscillation of the first term in the square brackets of (37), but enhances the oscillations of the second term, which is therefore neglected. Setting [14]

$$n = n_c \equiv \text{Int} \frac{|w_c|}{\varepsilon} \tag{38}$$

eliminates even the slow oscillations and thus defines the order of the optimal superadiabatic basis. In this way, one finally arrives at

$$c_{12}^{(n_c)}(\tau) = \frac{\pi}{3} \exp\left(-\frac{|w_c|}{\varepsilon} \right)$$
$$\times \int_{-\infty}^{w(\tau)} dw' \frac{1}{\sqrt{2\pi\varepsilon|w_c|}} \exp\left(-\frac{w'^2}{2\varepsilon|w_c|} \right)$$
$$= \frac{\pi}{3} \frac{1}{2} \left[1 + \text{erf}\left(\frac{w(\tau)}{\sqrt{2\varepsilon|w_c|}} \right) \right] \exp\left(-\frac{|w_c|}{\varepsilon} \right) \tag{39}$$

This error-function transition history is universal in the sense that it does not depend on the details of the Hamiltonian [14]. Unfortunately, the replacement of all $E^{(n)}$ by $E^{(0)}$ in equation (23) causes the result (39) to be too large, since on the real axis we have $E^{(n)} \geq E^{(n-1)}$. This is the reason why the incorrect prefactor $\pi/3$ remains present here. As shown by Berry [14] and Berry and Lim [18] for the scheme S, first-order perturbation theory in the optimal basis $n = n_c$ does indeed produce the correct transition amplitude when n_c goes to infinity. In the present case I this superadiabatic renormalization is destroyed by the approximation $E^{(n)} \approx E^{(0)}$, and the recovery of the correct prefactor appears to be difficult. However, as sketched in Appendix B, already for $n = 1$ the prefactor is reduced from $\pi/3 \approx 1.047$ to $\pi \sin(1/3) \approx 1.028$.

Even though the iterative scheme appears to be more difficult to handle analytically than the scheme S it has its merits, in particular when ε is *not* small. Then S becomes problematic because the bases (20) are not properly

orthonormalized, whereas I remains sound. This allows one to use the iterative scheme even when nonadiabatic effects become sizeable. In the n-th I-basis (12) the "transition-free component" of the wave function acquires a total phase $(1/\varepsilon) \int_{-\infty}^{\infty} d\tau\, E_1^{(n)} + \Phi_1^{(n)}$, measured with respect to the parallel-transported basis state $|u_1^{(n)}\rangle$, and the magnitude of $\Phi_1^{(n)}$ characterizes the deviation from ideal parallel transport. In the adiabatic basis one meets the familiar dynamical phase $(1/\varepsilon) \int_{-\infty}^{\infty} d\tau\, E_1^{(0)}$ for $\varepsilon \to 0$, whereas for finite ε the additional piece $\Phi_1^{(0)}$ does not vanish. The optimal superadiabatic basis $n = n_c$, on the other hand, is by its very construction just that basis which describes the actual quantum evolution as closely as possible by parallel transport even for finite ε, hence $\Phi_1^{(n_c)} \approx 0$. If we now restrict ourselves to systems for which the unitary transformations $U^{(1)}$, ..., $U^{(n_c)}$ connecting the optimal and the adiabatic bases at $\tau = \pm\infty$ reduce to the identity operation, as is the case for the Landau-Zener model, then we have

$$\frac{1}{\varepsilon} \int_{-\infty}^{+\infty} d\tau\, E_1^{(n_c)}(\tau) = \frac{1}{\varepsilon} \int_{-\infty}^{+\infty} d\tau\, E_1^{(0)}(\tau) + \Phi_1^{(0)}, \tag{40}$$

so that there appears the correction

$$\Phi_1^{(0)} = \frac{1}{\varepsilon} \int_{-\infty}^{+\infty} d\tau \left[E_1^{(n_c)}(\tau) - E_1^{(0)}(\tau) \right] \tag{41}$$

to the dynamical phase of the transition-free component [19]. The argument employed here is similar to the reasoning used by Berry [13] for computing quantum phase corrections for cyclic evolution. In particular, for the Landau-Zener model itself we obtain

$$\Phi_1^{(0)} = \frac{\varepsilon}{6} + \frac{\varepsilon^3}{45} + \frac{8\,\varepsilon^5}{315} + \frac{8\,\varepsilon^7}{105} + \frac{128\,\varepsilon^9}{297} + \dots$$
$$= \sum_{k=1}^{n_c} \frac{(-1)^{k-1} B_{2k}\, (2\varepsilon)^{2k-1}}{2k(2k-1)} + O(\varepsilon^{2n_c+1}), \tag{42}$$

with B_{2k} denoting the Bernoulli numbers. For $n_c \to \infty$ this gives [20]

$$\sum_{k=1}^{\infty} \frac{(-1)^{k-1} B_{2k}\, (2\varepsilon)^{2k-1}}{2k(2k-1)} \sim \frac{\pi}{4} + \frac{1}{2\varepsilon} \ln\left(\frac{1}{2\varepsilon} \right)$$
$$- \frac{1}{2\varepsilon} + \arg(\Gamma[1 - i/(2\varepsilon)]), \tag{43}$$

which is precisely the asymptotic series for the Stueckelberg phase that accompanies the Landau-Zener transition [21]. This phase is unimportant for small ε, when the evolution is mostly adiabatic, but it has to be taken into account when the Landau-Zener transition probability becomes large. It should also be observed that approximating the exponential $\exp(-2i/\varepsilon \int_0^\tau d\tau'\, E^{(n)})$ in the transition integral (28) by $\exp(-2i/\varepsilon \int_0^\tau d\tau'\, E^{(0)})$ means neglecting a phase factor $\exp[-2i/\varepsilon \int_0^\tau d\tau'\, (E^{(n)} - E^{(0)})]$ in

the derivation of equation (39), so that, strictly speaking, the error function should be equipped with a Stueckelberg-like phase in the optimal superadiabatic basis, whereas there is no such phase for the transition amplitude in the adiabatic basis. In the following we will neglect the Stueckel-berg phase, since it is quite small in the examples considered. However, the fact that the iterative scheme yields this phase in an appealingly simple manner appears to be noteworthy.

Apart from their different performance for large ε, the schemes I and S match well. In both cases the optimal orders are given by equation (38), and both schemes provide, if properly executed, a superadiabatic basis in which the transition amplitude takes the universal form

$$c_{12}^{(np)}(\tau) = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{w(\tau)}{\sqrt{2\varepsilon|w_c|}}\right)\right]\exp\left(-\frac{|w_c|}{\varepsilon}\right) \ . \quad (44)$$

As will be shown in Section 5, this expression has a clear-cut meaning also in the adiabatic basis.

To demonstrate the range of applicability of the above concepts, we display in Figure 1 transition histories for $\varepsilon = 1$, which is clearly *not* asymptotically small. According to equation (38), the optimal superadiabatic order then is $n_c = 2$. We have plotted the probabilities $|c_{12}^{(n)}|^2$ in the adiabatic basis $n = 0$ (Fig. 1a), and in the superadiabatic bases $n = 2$ (Fig. 1b) and $n = 4$ (Fig. 1c). Full lines refer to the iterative scheme I, dashed lines to S. For $n = 0$ both schemes give the same amplitudes; the final value is approached after significant overshooting. For $n = n_c = 2$ both schemes yield a history that already resembles the ideal error function; the remaining wiggles can be traced to the neglected fast-oscillating exponential [22]. For $n = 4$, beyond the optimal order, the scheme I is more well behaved than S, which then produces rather large values. This is partly due to the fact that the bases (20) are not normalized exactly, but even normalizing the basis vectors (dotted line) does not bring the two schemes into agreement.

Figure 2 shows the histories for $\varepsilon = 1/3$ and $n = 0$ (a), $n = 2$ (b), and $n = n_c = 5$ (c). The overshooting for $n = 0$ is now even more pronounced. For $n > 0$ the two schemes behave fairly similar up to the optimal order; the histories provided by I tend, in general, to be smoother.

Figure 3 demonstrates that transition dynamics viewed in the optimal superadiabatic basis looks profoundly different from the dynamics in the adiabatic basis: the upper line (exhibiting unresolved fast oscillations at large τ) is the history $|c_{12}^{(0)}|^2$ for $\varepsilon = 1/6$; the lower line is $|c_{12}^{(n_c)}|^2$ for the same process ($n_c = 10$; computed within scheme S). The physical significance of the "optimal" transition amplitude will become obvious in Section 5, where it will reappear as part of the total amplitude in the adiabatic basis.

4 Application to three-level systems

A particularly important example for adiabatic population transfer is provided by the STIRAP mechanism (see,

e.g., Refs. [4–7]; the acronym stands for "Stimulated Raman Adiabatic Passage"): Taking a three-level Λ-system, the initially populated bare level 1 is coupled to the intermediate bare level 2 by a pump laser with Rabi frequency $\Omega_1(\tau)$, while level 2 is coupled to the final bare level 3 by a Stokes laser with Rabi frequency $\Omega_2(\tau)$. The laser frequencies are chosen such that levels 1 and 3 are on two-photon resonance, whereas the intermediate level can be off-resonant by a detuning Δ. Within the rotating wave approximation, the Hamiltonian then reads

$$H^{(0)}(\tau) = \begin{pmatrix} 0 & \Omega_1(\tau) & 0 \\ \Omega_1(\tau) & \Delta & \Omega_2(\tau) \\ 0 & \Omega_2(\tau) & 0 \end{pmatrix} . \quad (45)$$

Usually the two laser pulses are applied in counterintuitive order, so that the Stokes pulse $\Omega_2(\tau)$, coupling initially unpopulated levels, *precedes* the pump pulse $\Omega_1(\tau)$, but both pulses have to overlap sufficiently [4].

The instantaneous ("dressed") energies $E_j^{(0)}$ of $H^{(0)}$ are

$$E_1^{(0)} = \frac{1}{2}\left(\Delta + \sqrt{\Delta^2 + 4(\Omega_1^2 + \Omega_2^2)}\right)$$
$$E_2^{(0)} = 0$$
$$E_3^{(0)} = \frac{1}{2}\left(\Delta - \sqrt{\Delta^2 + 4(\Omega_1^2 + \Omega_2^2)}\right), \quad (46)$$

so that $E_2^{(0)}$ does not depend on the laser parameters. The working principle of the STIRAP mechanism relies on the fact that the corresponding instantaneous eigenstate $|u_2^{(0)}\rangle$,

$$|u_2^{(0)}\rangle = \frac{\Omega_2}{\sqrt{\Omega_1^2 + \Omega_2^2}}|1\rangle - \frac{\Omega_1}{\sqrt{\Omega_1^2 + \Omega_2^2}}|3\rangle, \quad (47)$$

is a linear combination of the bare levels 1 and 3 only, without admixture of the intermediate level 2. For $\tau = -\infty$, when Ω_1/Ω_2 vanishes, $|u_2^{(0)}\rangle$ coincides with the initially populated bare state $|1\rangle$; for $\tau = +\infty$, when Ω_2/Ω_1 becomes negligible, $|u_2^{(0)}\rangle$ coincides with the bare target state $-|3\rangle$. Hence, *in the adiabatic limit* the counterintuitive pulse sequence leads to complete population transfer from the bare level 1 to 3, irrespective of the detuning Δ.

Going beyond the adiabatic limit, *i.e.*, considering the actually relevant case of pulses that change on a finite time scale, there must be nonadiabatic corrections to the ideal population transfer [11,12] resembling the ones encountered in the Landau-Zener transition. A mathematically most appealing way of studying the emergence of these corrections is to follow the STIRAP dynamics in the superadiabatic bases. For $\Delta = 0$, when the STIRAP Hamiltonian can be reduced exactly to an effective two-level system [4], this type of superadiabatic analysis has been initiated by Elk [23], resulting in transition histories very similar to those shown in Figures 1 and 2. For $\Delta \neq 0$ an exact reduction to a two-level system is not possible, so that we resort to the N-level scheme outlined
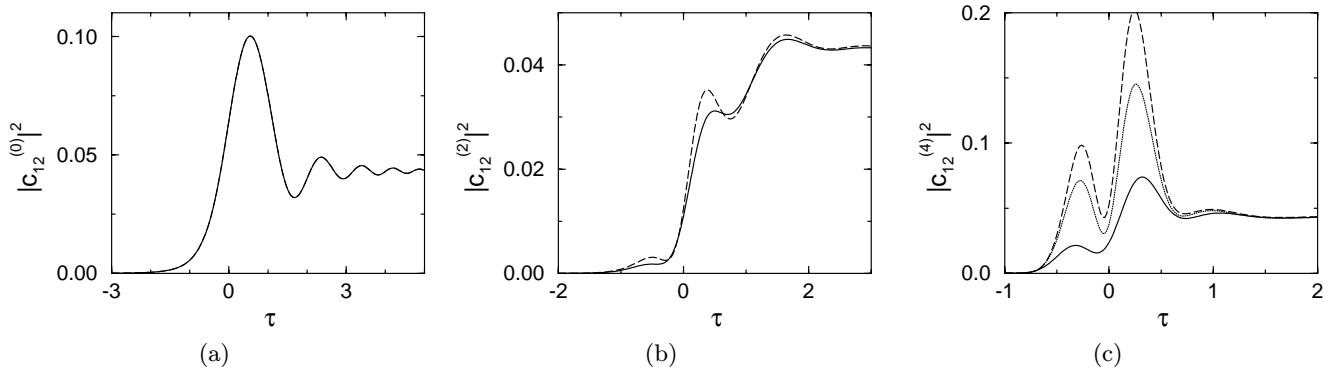
Fig. 1. Transition histories $|c_{12}^{(n)}(\tau)|^2$ in the n-th order superadiabatic basis corresponding to the iterative scheme I (full line) and to the series scheme S (dashed), for the Landau-Zener Hamiltonian (24) with $\varepsilon = 1$ and $n = 0$ (a), $n = n_c = 2$ (b), and $n = 4$ (c). The dotted line in Figure 1c has been obtained from S after normalizing the basis (20).
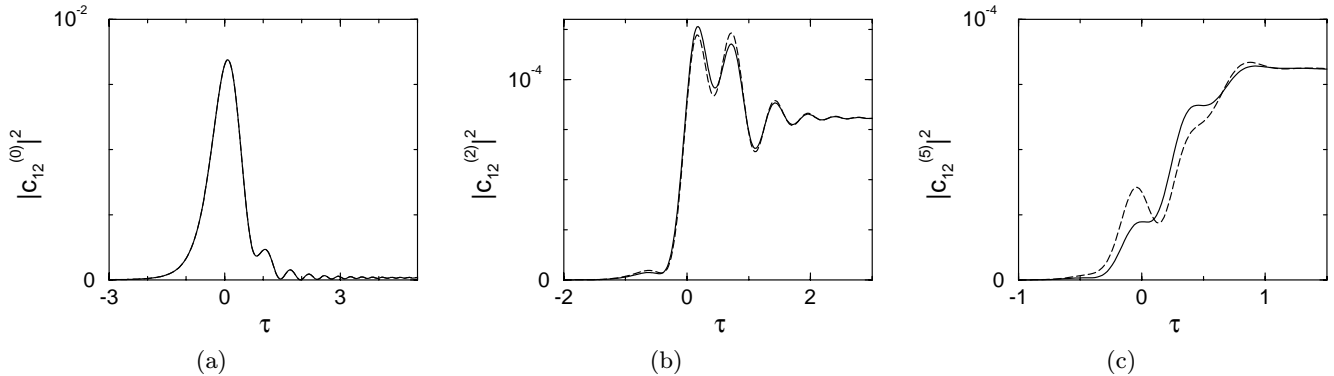

Fig. 2. As Figure 1, with $\varepsilon = 1/3$ for $n = 0$ (a), $n = 2$ (b), and $n = n_c = 5$ (c). The scales of the ordinates are linear.
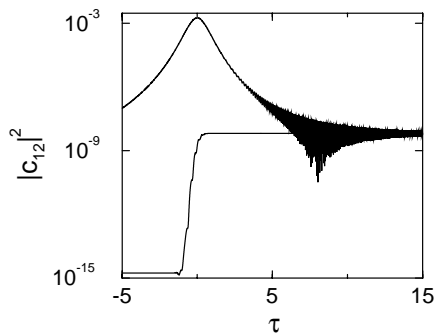
Fig. 3. Landau-Zener transition history for $\varepsilon = 1/6$ in the adiabatic basis (upper line), and in the optimal superadiabatic basis ($n_c = 10$, computed within scheme S). The black area is caused by unresolved fast oscillations.

in Appendix A. Following Elk [23], we investigate "ramp pulses" [11] and parametrize the time dependence of the Rabi frequencies as

$$\Omega_2(\tau) = \cos(\theta(\tau))$$
$$\Omega_1(\tau) = \sin(\theta(\tau)), \qquad (48)$$

with
$$\theta(\tau) = \frac{1}{2} \arctan(\tau) + \frac{\pi}{4} \qquad (49)$$

and τ varying from $-\infty$ to $+\infty$, so that Ω_2 decreases monotonically from unity to zero, while Ω_1 increases from zero to one. We set $\varepsilon = 1/6$ and plot in Figure 4 the histories $|c_{21}|^2$ and $|c_{23}|^2$ of the transitions from the initially occupied state $|u_2^{(0)}\rangle$; the detuning is $\Delta = 1/2$. The superadiabatic orders considered here are $n = 5$ (heavy full lines) and $n = 8$ (dashed); these are the optimal superadiabatic orders for the two transitions. It can be seen that (i) also in this generic multilevel case the population losses reach their final values in an erf-like manner in the optimal bases (the ideal error-function histories are indicated by the thin lines), and (ii) the order n_c of the optimal basis depends on the transition in the expected way: the smaller the nonadiabatic population loss, the larger n_c.

Figure 5 shows histories of the total population loss $|c_{21}|^2 + |c_{23}|^2$, again for $\varepsilon = 1/6$. The detuning Δ is varied between 0 to 0.5; each history refers to its respective optimal basis. Evidently, the larger Δ, the larger the population loss, so that $\Delta = 0$ is the best choice for minimizing this adiabaticity defect [24]. We stress that the transition dynamics have been reduced to their essentials in this figure, whereas the same dynamics appears much more complicated in the usual adiabatic basis. In that basis there
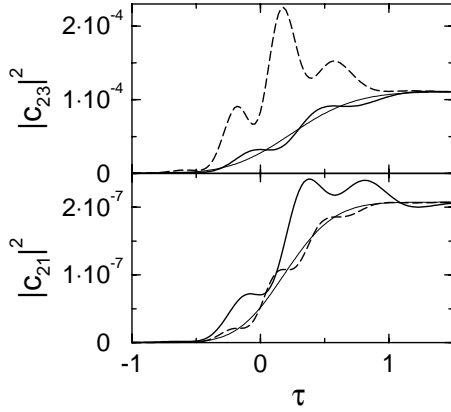
Fig. 4. Transition histories for the STIRAP Hamiltonian (45) with $\Delta = 1/2$ and Rabi frequencies (48); the adiabaticity parameter is $\varepsilon = 1/6$. These histories have been calculated in the scheme S according to Appendix A, with normalized basis functions. The superadiabatic orders are $n = 5$ (heavy full line) and $n = 8$ (dashed). The thin lines indicate the ideal error functions.
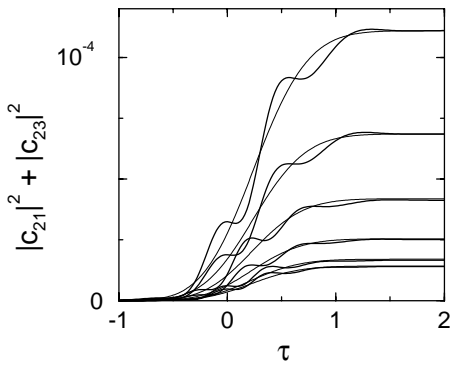

Fig. 5. Adiabaticity defect for STIRAP with $\varepsilon = 1/6$, and detunings Δ ranging from 0.0 to 0.5, in steps of 0.1 (bottom to top). The thin lines are fits to error functions. The scale of the ordinate is linear.

is strong "overshooting", similar to the one depicted in Figures 1a and 2a, and the final transition probability is attained much later, in an oscillatory manner.

5 Summing the perturbation series in the adiabatic basis

With respect to the optimal superadiabatic bases (12) and (20), the transition amplitudes acquire the simple error-function form (44). In this section we will discuss the transition dynamics exclusively in the customary adiabatic basis ($n = 0$). We will focus on the two-level case for simplicity, and omit the superscript (0).

To begin with, we consider the first-order approximation (28) to the transition amplitude,

$$c_{12}(\tau) = \frac{1}{2} \int_{-\infty}^{w(\tau)} dw' \, \frac{\gamma(w')}{E(w')} \exp\left(-\frac{i}{\varepsilon} w'\right). \quad (50)$$

Integrating n times by parts, which constitutes a standard technique for constructing asymptotic series [25], and assuming that γ/E and all its derivatives vanish for $w \to -\infty$, we find

$$c_{12}(\tau) = -\frac{1}{2} \sum_{k=1}^{n} (-i\varepsilon)^k \, \partial_w^{k-1}\left(\frac{\gamma(w)}{E(w)}\right) \exp\left(-\frac{i}{\varepsilon} w\right)$$

$$+ \frac{1}{2} \int_{-\infty}^{w(\tau)} dw' \, (-i\varepsilon)^n \, \partial_{w'}^n\left(\frac{\gamma(w')}{E(w')}\right) \exp\left(-\frac{i}{\varepsilon} w'\right). \quad (51)$$

Provided that $\partial_w^n(\gamma/E)$ is absolutely integrable, the integral goes to zero for $\varepsilon \to 0$, as a consequence of the Riemann-Lebesgue lemma [9], so that the remaining sum, which is merely a power series in ε, has to account for the main contribution to the exact transition amplitude at *finite* τ. This series, of course, does *not* contribute to the factor $\exp(-|w_c|/\varepsilon)$ that appears in the final transition amplitude; this factor is contained in the integral.

The integral, on the other hand, coincides exactly with the expression (28) for the transition amplitude *in the n-th order superadiabatic basis*, when the latter is evaluated within scheme I, making use of the approximation (35). Hence, it becomes the universal error function for $n = n_c$. This observation suggests a fairly intuitive interpretation of the superadiabatic schemes: Performing the unitary transformations to the successive superadiabatic bases amounts to removing from the total transition amplitude the terms proportional to powers of ε, the sum of which we will denote as the perturbative contribution $c_{12}^{(pt)}$. The universal error function that remains after this removal then has a well-defined meaning also in the adiabatic basis: it provides the nonperturbative contribution $c_{12}^{(np)}$.

This interpretation is based on first-order perturbation theory in the nonadiabatic coupling, and therefore still faces the $\pi/3$-problem. However, it can actually be made water-tight by adapting an argument due to Davis and Pechukas [9] that aims at summing the entire perturbation series. For later use, we first slightly generalize the pole approximation (33) to the nonadiabatic coupling of the Landau-Zener model, and consider instead

$$\frac{\gamma(w)}{E(w)} \approx \frac{ir}{w - w_c}, \quad (52)$$

from which the Landau-Zener case can be recovered by setting $r = 1/3$ [26]; w_c now indicates the pole of γ/E in the lower half of the complex w-plane that lies closest to the real axis. Then, defining

$$b_1 = c_{11}$$
$$b_2 = c_{12} \exp(iw_c/\varepsilon), \quad (53)$$

introducing the variable

$$x = \frac{w - w_c}{\varepsilon}, \quad (54)$$

utilizing the approximation (52), and keeping only the leading singularities, the integral form of the Schrödinger

equation for the two-level system becomes (see also Refs. [9,27])

$$b_2(x) = -\frac{r}{2} \int_{-\infty}^{x} dx' \frac{e^{-ix'}}{ix'} b_1(x') \tag{55}$$

$$b_1(x) = 1 + \frac{r}{2} \int_{-\infty}^{x} dx' \frac{e^{ix'}}{ix'} b_2(x')$$

$$= 1 - \frac{r^2}{4} \int_{-\infty}^{x} dx' \frac{e^{ix'}}{ix'} \int_{-\infty}^{x'} dx'' \frac{e^{-ix''}}{ix''} b_1(x''), \tag{56}$$

where the integrations for b_2 and b_1 have to pass above $x' = 0$. For computing the transition amplitude b_2, we first formally evaluate the amplitude b_1 for staying in the initially occupied state with the help of the ansatz

$$b_1(x) \sim \sum_{n=0} \alpha_n \frac{n!}{(ix)^n} \tag{57}$$

with $\alpha_0 = 1$; this ansatz features the typical "factorial by power"-terms characteristic of asymptotic series. By means of successive integration by parts one obtains

$$b_1(x) \sim 1 + \frac{r^2}{4} \sum_{n=0} \alpha_n \sum_{m=0} (-1)^m \frac{(n+m)!}{n+m+1} \frac{1}{(ix)^{n+m+1}} . \tag{58}$$

Equating this expression with the ansatz (57), comparing powers of x, and solving the resulting recursion relation then yields

$$\sum_{m=0}^{n-1} (-1)^m \alpha_m = \prod_{m=1}^{n-1} \left(1 - \frac{r^2}{4m^2}\right) \equiv g_{n-1} . \tag{59}$$

So far, this calculation follows the argument that Davis and Pechukas have designed for computing $b_2(\infty)$ [9]. Now comes the essential difference: Inserting the ansatz (57) into equation (55), we sum the resulting series only up to $n = n_c$,

$$b_2(x) \sim -\frac{r}{2} \sum_{n=0}^{n_c} \alpha_n n! \int_{-\infty}^{x} dx' \frac{e^{-ix'}}{(ix')^{n+1}}, \tag{60}$$

and integrate each term by parts until the exponent n_c+1 appears in the denominator:

$$b_2(x) \sim -\frac{ir}{2} \sum_{n=0}^{n_c} \alpha_n \sum_{m=0}^{n_c-n-1} (-1)^m (n+m)! \frac{e^{-ix}}{(ix)^{n+m+1}}$$

$$-\frac{r}{2} \sum_{n=0}^{n_c} (-1)^{n_c-n} \alpha_n n_c! \int_{-\infty}^{x} dx' \frac{e^{-ix'}}{(ix')^{n_c+1}}. \tag{61}$$

Interchanging the order of summation over n and m, and exploiting the equation (59) that embodies the knowledge about $b_1(x)$, we arrive at

$$b_2(x) \sim -\frac{ir}{2} \sum_{m=0}^{n_c-1} (-1)^m g_m m! \frac{e^{-ix}}{(ix)^{m+1}}$$

$$-\frac{r}{2} (-1)^{n_c} g_{n_c} n_c! \int_{-\infty}^{x} dx' \frac{e^{-ix'}}{(ix')^{n_c+1}}. \tag{62}$$

Upon resubstituting w for x, the sum corresponds term by term to the sum obtained in the first order-calculation (51), except for the factor g_m that now multiplies the m-th term, with $g_0 = 1$ denoting the empty product. The integral gives precisely the error function (39), with the prefactor $\pi/3$ replaced by πr, and with the additional factor g_{n_c}. Since

$$g_\infty = \prod_{m=1}^{\infty} \left(1 - \frac{r^2}{4m^2}\right) = 2 \frac{\sin(r\pi/2)}{r\pi}, \tag{63}$$

the previous formula (44) now generalizes for $\varepsilon \to 0$ (that is, for large n_c) to

$$c_{12}^{(np)}(\tau) = \sin(r\pi/2) \left[1 + \mathrm{erf}\left(\frac{w(\tau)}{\sqrt{2\varepsilon|w_c|}}\right)\right]$$

$$\times \exp\left(-\frac{|\mathrm{Im}\, w_c|}{\varepsilon}\right), \tag{64}$$

and the DDP-formula becomes

$$c_{12}(+\infty) = 2\sin(r\pi/2) \exp(-|\mathrm{Im}\, w_c|/\varepsilon), \tag{65}$$

in agreement with a result obtained first by Joye [27] with the help of a rigorous comparison-equation technique and by Berry and Lim [18] from first-order perturbation theory in the superadiabatic bases. In particular, in the Landau-Zener case one now finds the correct prefactor unity, so that the representation (62) is no longer plagued by the remnants of the $\pi/3$-problem.

The value of these deliberations lies in the fact that they reveal just how to decompose the adiabatic transition amplitude into a universal, nonperturbative part — the error function $c_{12}^{(np)}$ — and a power series in the adiabaticity parameter ε, truncated at $n = n_c$, that gives the perturbative contribution $c_{12}^{(pt)}$. The total transition probability, tracked in time, can be written as a phase-coherent superposition of both parts:

$$|c_{12}(\tau)|^2 = |c_{12}^{(pt)}(\tau) + c_{12}^{(np)}(\tau)|^2 . \tag{66}$$

Since the first contribution is universal, and the second is usually well approximated by the lowest nonvanishing order in ε, the complicated transition dynamics can be understood as resulting from the interference of two easily accessible parts.

To substantiate this claim, we return once more to the Landau-Zener transition. The lowest-order perturbative part

$$c_{12}^{(pt)}(\tau) = \frac{i\varepsilon}{2} \frac{\gamma(\tau)}{E(\tau)} \exp\left(-\frac{i}{\varepsilon} w(\tau)\right) \tag{67}$$

then becomes

$$c_{12}^{(pt)}(\tau) = \frac{i\varepsilon}{4(\tau^2+1)^{3/2}}$$

$$\times \exp\left(-\frac{i}{\varepsilon}\left[\tau\sqrt{\tau^2+1} + \mathrm{arsinh}(\tau)\right]\right). \tag{68}$$
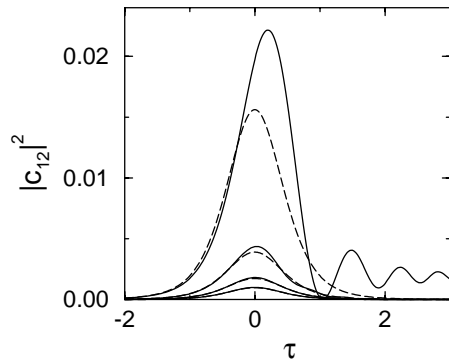
Fig. 6. Exact histories for the Landau-Zener transition in the adiabatic basis (full lines), compared with the prediction (68) of first-order perturbation theory (dashed), for $\varepsilon = 1/2$, $1/4$, $1/6$, and $1/8$ (top to bottom). The corresponding ratios of perturbative and exact peak heights are 0.69, 0.90, 0.96, and 0.98. For $\varepsilon = 1/8$ the graphs of the perturbative and the exact history cannot be distinguished.
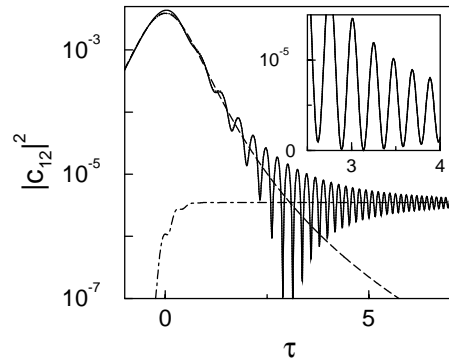

Fig. 7. Exact history for the Landau-Zener transition with $\varepsilon = 1/4$ (full line), together with the prediction of perturbation theory (dashed) and the history in the optimal superadiabatic basis (dashed-dotted). The phase-coherent superposition (66) of the two latter parts is also plotted as a dotted line, but is practically indistinguishable from the exact data (except for the vicinity of the peak). The inset shows the oscillations on a linear scale. Even here the exact results are indistinguishable from the superposition.

In Figure 6 we compare $|c_{12}^{(pt)}|^2$ with the exact transition probabilities $|c_{12}|^2$, for $\varepsilon = 1/2$, $1/4$, $1/6$, and $1/8$. Even for $\varepsilon = 1/2$ the perturbative part alone gives a good description of the actual probability for $\tau < 0$; naturally, the agreement has to break down when the nonperturbative part $c_{12}^{(np)}$ becomes significant. For the smaller values of ε the performance of the perturbation theory is impressive: for $\varepsilon = 1/4$, the first-order approximation yields 90% of the exact maximum transition probability; summing the perturbation series up to $n = n_c = 6$ gives 100.7%. For $\varepsilon = 1/8$, the first-order contribution is 98%. Of course, this trend reflects the fact that already the perturbative part alone is asymptotic to the exact amplitude, as long as τ remains finite [9].

Figure 7 demonstrates the striking accuracy with which the composition formula (66) can describe the full

dynamics even when it is evaluated approximately; the adiabaticity parameter here is $\varepsilon = 1/4$. We have plotted the numerically computed, exact probability $|c_{12}|^2$ (full line), together with the perturbative part given by equation (68) (dashed) and the nonperturbative part computed from the series scheme S (dashed-dotted; optimal superadiabatic order $n_c = 6$). The curve resulting from the addition of both parts has been plotted as a dotted line — but it is practically indistinguishable from the exact data; the only visible difference is close to the maximum at $\tau \approx 0$. Even in the inset exact and approximate data (full and dotted line) lie on top of each other. This figure nicely illustrates the essentials of nonadiabatic transitions: The final, exponentially small transition probability is already born when it is still overwhelmed by a perturbative overshooting. Lowest-order perturbation theory describes the exact amplitude well up to the point where the perturbative prediction crosses the graph of the error function. The crossover from the perturbative to the nonperturbative dynamics is accompanied by fast oscillations that stem from the interference of both components, so that their amplitude is largest right in the vicinity of the crossing point. Since the perturbative overshooting decreases merely as a power of ε, whereas the final transition amplitude decreases exponentially in $1/\varepsilon$, the relative mismatch between the maximum overshooting and the final value of $|c_{12}|^2$ *grows* substantially with decreasing ε.

6 Adiabatic perturbation theory for STIRAP

In the previous section it has been assumed that the ratio γ/E and all its w-derivatives vanish for $w \to \pm\infty$, so that, for example, the integrations by parts leading to equation (51) did not pick up contributions from $w = -\infty$, and the final transition amplitude was given entirely by the DDP-formula (65). The STIRAP mechanism, however, provides important examples where this assumption fails [11,12,24]. For discussing the consequences of this failure from the perturbative point of view, we restrict ourselves to the case $\Delta = 0$, where the three-level system (45) is exactly equivalent to a two-level system [4]. Sticking to the notation employed in equation (21), and again omitting the superscripts as we will be working in the adiabatic basis only, the effective two-level system has instantaneous energies [11]

$$E(\tau) = \frac{1}{2}\sqrt{\Omega_1^2(\tau) + \Omega_2^2(\tau)} \,. \tag{69}$$

The nonadiabatic coupling

$$\gamma(\tau) = \frac{1}{2}\partial_\tau\theta(\tau) \tag{70}$$

is given by the derivative of the "mixing angle"

$$\theta(\tau) = \arctan\left(\frac{\Omega_1(\tau)}{\Omega_2(\tau)}\right) \,, \tag{71}$$

which varies from 0 to $\pi/2$ in STIRAP systems with counterintuitive pulse sequence, as in the previous example (49).

Instead of considering "ramp pulses" [11] like those defined by equations (48) and (49), which mimic the actual pulse shapes only during the phase where both pulses overlap, we now treat models incorporating realistic pulses that vanish properly for $\tau \to -\infty$, increase smoothly and monotonically to maximum strength, then decrease and finally vanish for $\tau \to +\infty$. As a consequence, the instantaneous energies $\pm E$ of the effective two-level system become degenerate for $\tau \to \pm\infty$. However, it has to be kept in mind that it is not E but rather the ratio γ/E that matters.

As a first example of how adiabatic perturbation theory works for such STIRAP configurations, we investigate an analytically solvable model introduced by Vitanov and Stenholm [12]. It is defined by

$$E(\tau) = \frac{1}{2}\mathrm{sech}^2(\tau)$$

$$\gamma(\tau) = \frac{b}{2}\mathrm{sech}^2(\tau)\,\mathrm{sech}[\sigma\tanh(\tau)]\,, \tag{72}$$

with constants b and σ that determine the relative strength and shape of the nonadiabatic coupling, respectively. This describes a genuine STIRAP system, *i.e.*, the mixing angle (71) varies from 0 to $\pi/2$, provided these parameters obey [12]

$$\frac{b}{\sigma} = \frac{\pi}{4\arctan(\sinh\sigma)}\,. \tag{73}$$

However, the techniques discussed here are valid for an arbitrary system of the type (72), so that we need not consider this restriction (73) in the following.

Since now the ratio γ/E does not vanish for $\tau \to \pm\infty$, but rather approaches $b\,\mathrm{sech}(\sigma)$, there is a perturbative contribution to the final transition amplitude that can easily be obtained by adapting equation (67):

$$c_{12}^{(pt)}(+\infty) = \frac{i\varepsilon}{2}\left.\frac{\gamma(\tau)}{E(\tau)}\exp\left(-\frac{i}{\varepsilon}w(\tau)\right)\right|_{-\infty}^{+\infty}$$

$$= \varepsilon b\,\mathrm{sech}(\sigma)\sin(1/\varepsilon)\,. \tag{74}$$

Since, moreover,

$$\frac{\gamma(w)}{E(w)} = b\,\mathrm{sech}(\sigma w) \approx \frac{b}{\sigma}\frac{i}{w - w_c} \tag{75}$$

close to $w_c = -i\pi/(2\sigma)$, the nonperturbative contribution

$$c_{12}^{(np)}(+\infty) = 2\sin\left(\frac{\pi b}{2\sigma}\right)\exp\left(-\frac{\pi}{2\varepsilon\sigma}\right) \tag{76}$$

follows from the DDP-formula (65) by setting $r = b/\sigma$.

The exact analytical result [12], which can be calculated the by relating the model (72) to the Rosen-Zener model [17], acquires for moderately large values of σ the form [28]

$$|c_{12}(+\infty)|^2 \approx \Big|2\varepsilon b\exp(-\sigma)\sin(1/\varepsilon)$$

$$+ \sin\left(\frac{\pi b}{2\sigma}\right)\mathrm{sech}\left(\frac{\pi}{2\varepsilon\sigma}\right)\Big|^2\,, \tag{77}$$
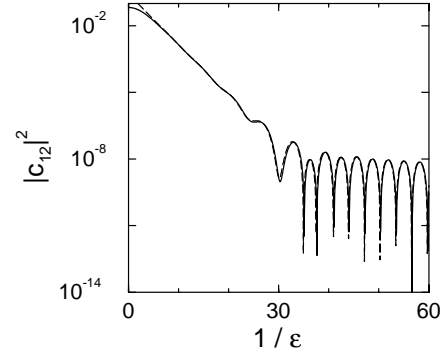

Fig. 8. Full line: Exact final transition probability for the STIRAP system (72) with $b = 1$ and $\sigma = 6$; dashed line: coherent superposition of the perturbative and the nonperturbative component, as approximated by equations (74) and (76).

in beautiful agreement with what follows by adding our approximations (74) and (76). In Figure 8 we compare the total transition probability $|c_{12}^{(pt)}(+\infty) + c_{12}^{(np)}(+\infty)|^2$, as given by equations (74) and (76) and plotted as the dashed line, to the exact data (full line), for $b = 1$ and $\sigma = 6$. The agreement is close to perfect. Thus, our analysis explains the breakdown of the Dykhne-Davis-Pechukas exponential behavior that is observed for large values of $1/\varepsilon$, without having to recourse to specific properties of the model.

The actual strength of the perturbative approach, however, stems from the fact that it lends itself, with equal accuracy and simplicity, also to models that can *not* be treated exactly, such as the following STIRAP-like model considered by Laine and Stenholm [11]:

$$E(\tau) = \frac{1}{2}\left[\mathrm{sech}^2(\tau + \delta) + \mathrm{sech}^2(\tau - \delta)\right]^{1/2}$$

$$\gamma(\tau) = \frac{b}{2}\frac{\sinh(2\delta)}{\cosh^2(\tau + \delta) + \cosh^2(\tau - \delta)}. \tag{78}$$

Again, this describes an actual STIRAP process if the parameters b and δ are chosen such that

$$\theta(\infty) = 2\int_{-\infty}^{+\infty} d\tau\,\gamma(\tau) = \frac{\pi}{2}\,, \tag{79}$$

but our results for the system (78) are valid even without this restriction. Now the perturbative part of the final transition amplitude becomes

$$c_{12}^{(pt)}(+\infty) = \frac{i\varepsilon}{2}\left.\frac{\gamma(\tau)}{E(\tau)}\exp\left(-\frac{i}{\varepsilon}w(\tau)\right)\right|_{-\infty}^{+\infty}$$

$$+ \frac{\varepsilon^2}{4E(\tau)}\left.\partial_\tau\left(\frac{\gamma(\tau)}{E(\tau)}\right)\exp\left(-\frac{i}{\varepsilon}w(\tau)\right)\right|_{-\infty}^{+\infty} + O(\varepsilon^3). \tag{80}$$

Since γ/E vanishes for $\tau \to \pm\infty$, but $(1/E)\partial_\tau(\gamma/E)$ does not, the leading term of the perturbative amplitude is proportional to ε^2:

$$c_{12}^{(pt)}(+\infty) = -\frac{\varepsilon^2}{4}\,b\,\sinh(2\delta)\,\mathrm{sech}^2(2\delta)\,\cos\left(\frac{w(+\infty)}{\varepsilon}\right). \tag{81}$$
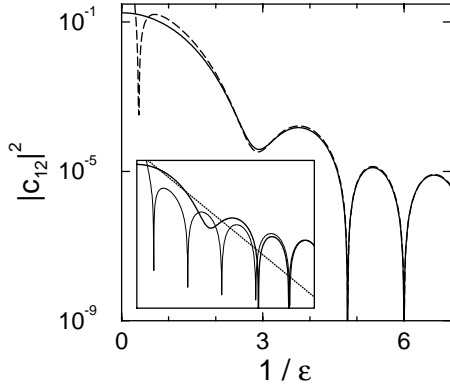
Fig. 9. Full line: Exact final transition probability for the STI-RAP system (78) with $b = 1$ and $\delta = 0.5$; dashed line: coherent superposition of the perturbative and the nonperturbative component, as approximated by equations (81) and (84). The inset shows the exact probability (full line), the nonperturbative part $|c_{12}^{(np)}|^2$ alone (dotted), and the perturbative part $|c_{12}^{(pt)}|^2$ alone (thin line).

The approximate calculation of the nonperturbative amplitude starts from the degeneracy of the eigenvalues $\pm E(\tau)$ at [11]

$$\tau_c = -i \arctan[\coth(\delta)] . \tag{82}$$

After some elementary steps, one finds

$$\frac{\gamma(w)}{E(w)} \approx \frac{b}{3} \frac{i}{w - w_c} \tag{83}$$

in the vicinity of $w_c = w(\tau_c)$, hence

$$c_{12}^{(np)}(+\infty) = 2 \sin\left(\frac{\pi b}{6}\right) \exp\left(-\frac{|w_c|}{\varepsilon}\right) . \tag{84}$$

Figure 9 confirms the accuracy of this reasoning for $b = 1$ and $\delta = 0.5$; the integrals w_c and $w(+\infty)$ have been computed numerically. In the adiabatic regime, *i.e.*, for $1/\varepsilon \gg 1$, there is perfect agreement between the exact final transition probability (full line) and the prediction derived by summing and squaring equations (81) and (84). The inset shows, on the same scale, the exact data (full line) in comparison with the DDP exponential decay alone (dotted) and the perturbative component alone (thin line). Evidently, the perturbative component dominates for large $1/\varepsilon$, while the nonperturbative DDP component alone does not suffice to give a satisfactory description of the exact result for any ε, at least not for the values of b and δ chosen here. It is only when the interference of both components is taken into account that one gets a complete understanding of the dynamics.

Quite a particular example emerges if one chooses [29]

$$E(\tau) = \frac{1}{2}\text{sech}^2(\tau)$$
$$\theta(\tau) = \frac{\pi}{4}\left(\tanh(\tau) + 1\right) , \tag{85}$$

which implies that the crucial ratio γ/E has no poles at all,

$$\frac{\gamma(\tau)}{E(\tau)} = \frac{\pi}{4} . \tag{86}$$

Hence, there is no nonperturbative contribution to the final transition amplitude, and one finds to lowest order

$$c_{12}(+\infty) = \frac{i\varepsilon}{2} \frac{\pi}{4} \exp\left(-\frac{i}{\varepsilon}\tanh(\tau)\right)\Bigg|_{-\infty}^{+\infty} = \frac{\varepsilon\pi}{4}\sin(1/\varepsilon) . \tag{87}$$

Moreover, equation (23) shows that the first superadiabatic transformation produces a diagonal Hamiltonian, so that even the exact solution to Schrödinger's equation can easily be found:

$$|c_{12}(+\infty)|^2 = \left(\frac{\varepsilon\pi}{4}\right)^2 \frac{1}{1 + \left(\frac{\varepsilon\pi}{4}\right)^2} \sin^2\left(\frac{1}{\varepsilon}\sqrt{1 + \left(\frac{\varepsilon\pi}{4}\right)^2}\right) , \tag{88}$$

which confirms that the perturbative result (87) merges into the exact one for $\varepsilon \to 0$. Thus, the exact solution to the system (85), first stated in reference [29], follows from the general framework in a remarkably transparent manner. From the viewpoint of laser-induced population transfer, it is noteworthy that one can design γ/E such that the nonperturbative losses are avoided altogether.

7 Conclusions

The superadiabatic schemes have a twofold interpretation: On the one hand, they provide a basis with respect to which the transition amplitude acquires a simple and universal form, namely Berry's error function (64); on the other, they isolate from the total transition amplitude that part which cannot be represented by terms proportional to powers of the adiabaticity parameter ε. This part has been denoted as the nonperturbative component. Figure 3 can thus be read as showing *either* the same process in two different bases, *or* the evolution of the total transition probability and of its nonperturbative component. Both schemes I and S considered in the present paper behave quite similar up to the optimal order, and the scheme S may be a bit more tractable in practice, but I is distinguished by the explicit appearance of the eigenvalues of the iterated Hamiltonian. Since quantum evolution at finite ε corresponds, as closely as possible, to parallel transport in the optimal superadiabatic basis, phase corrections that appear in the adiabatic basis can be directly related to these eigenvalues, as shown explicitly in Section 3 for the Stueckelberg phase emerging in the Landau-Zener transition.

The decomposition of the total transition amplitude into a "perturbative" and a "nonperturbative" component allows one, first of all, to get a simple physical picture for the large oscillations that characterize the transition

amplitude in the adiabatic basis: These oscillations stem from the interference of both components, and are largest in amplitude just at the point of crossover from the perturbative to the nonperturbative dynamics, see Figure 7.

Whereas in "classic" systems covered by the Dykhne-Davis-Pechukas formula only the nonperturbative component survives in the final transition amplitude, the description of the STIRAP process within the rotating wave approximation has led to models where this is no longer true [11,12]. In such cases even the final outcome is determined by the interference of the perturbative and the nonperturbative part, but already low-order approximations to the perturbative part, together with the DDP-approximation for the nonperturbative component, suffice to give a very satisfactory description of the exact transition probability. It is this combination of simplicity and accuracy that makes the present approach interesting also for the analysis of more involved systems occurring in laser-controlled population transfer.

Appendix A: Numerical implementation of scheme I

The iterative scheme for constructing the superadiabatic bases (12) for N-level systems hinges on the solution of the recursion relations (17) and (18) for the coefficients $a_{jk}^{(m)}$. Utilizing

$$\langle u_k^{(0)}|\partial_\tau|u_l^{(0)}\rangle = \frac{\langle u_k^{(0)}|\partial_\tau H^{(0)}|u_l^{(0)}\rangle}{E_l^{(0)} - E_k^{(0)}} \qquad (A.1)$$

for $k \neq l$, and abbreviating $E_l^{(0)} - E_k^{(0)} \equiv \Delta E_{lk}$, we write the first of these equations in the form

$$a_{jk}^{(m)} = \frac{-i}{\Delta E_{jk}} \left\{ \partial_\tau a_{jk}^{(m-1)} + \sum_{\substack{l=1 \\ l \neq k}}^{N} a_{jl}^{(m-1)} \frac{\langle u_k^{(0)}|\partial_\tau H^{(0)}|u_l^{(0)}\rangle}{\Delta E_{lk}} \right\}. \qquad (A.2)$$

Differentiating n times, one gets

$$\partial_\tau^n a_{jk}^{(m)} = -i \sum_{l_1=0}^{n} \binom{n}{l_1} \left(\partial_\tau^{l_1} \frac{1}{\Delta E_{jk}} \right)$$

$$\times \left[\partial_\tau^{n+1-l_1} a_{jk}^{(m-1)} + \sum_{\substack{l=1 \\ l \neq k}}^{N} \sum_{l_2=0}^{n-l_1} \binom{n-l_1}{l_2} \right.$$

$$\left. \times \left(\partial_\tau^{n-l_1-l_2} a_{jl}^{(m-1)} \right) \left(\partial_\tau^{l_2} \frac{\langle u_k^{(0)}|\partial_\tau H^{(0)}|u_l^{(0)}\rangle}{\Delta E_{lk}} \right) \right]. \qquad (A.3)$$

The further processing of this equation necessitates to compute the derivatives

$$\partial_\tau^n \frac{1}{\Delta E_{jk}} = -\frac{1}{(\Delta E_{jk})^2} \left[\partial_\tau^n \Delta E_{jk} + \sum_{l_1=1}^{n-1} \binom{n-1}{l_1} \right.$$

$$\left. \times \left(\partial_\tau^{n-l_1} \frac{1}{\Delta E_{jk}} \right) \sum_{l_2=0}^{l_1} \binom{l_1}{l_2} \left(\partial_\tau^{l_2} \Delta E_{jk} \right) \left(\partial_\tau^{l_1-l_2} \Delta E_{jk} \right) \right], \qquad (A.4)$$

which, in turn, demand the evaluation of

$$\partial_\tau^n E_j^{(0)} = \sum_{l_1=0}^{n-1} \binom{n-1}{l_1} \sum_{l_2=0}^{n-1-l_1} \binom{n-1-l_1}{l_2}$$

$$\times \langle \partial_\tau^{l_1} u_j^{(0)}|\partial_\tau^{n-l_1-l_2} H^{(0)}|\partial_\tau^{l_2} u_j^{(0)}\rangle. \qquad (A.5)$$

Employing

$$|\partial_\tau^n u_j^{(0)}\rangle = \sum_{\substack{k=1 \\ k \neq j}}^{N} \sum_{l=0}^{n-1} \binom{n-1}{l} |\partial_\tau^l u_k^{(0)}\rangle$$

$$\times \left(\partial_\tau^{n-1-l} \frac{\langle u_k^{(0)}|\partial_\tau H^{(0)}|u_j^{(0)}\rangle}{\Delta E_{jk}} \right), \qquad (A.6)$$

we are left with the derivatives

$$\partial_\tau^n \frac{\langle u_k^{(0)}|\partial_\tau H^{(0)}|u_j^{(0)}\rangle}{\Delta E_{jk}} =$$

$$\sum_{l_1=0}^{n} \binom{n}{l_1} \sum_{l_2=0}^{n-l_1} \binom{n-l_1}{l_2} \sum_{l_3=0}^{n-l_1-l_2} \binom{n-l_1-l_2}{l_3}$$

$$\times \langle \partial_\tau^{l_1} u_k^{(0)}|\partial_\tau^{l_2+1} H^{(0)}|\partial_\tau^{l_3} u_j^{(0)}\rangle \left(\partial_\tau^{n-l_1-l_2-l_3} \frac{1}{\Delta E_{jk}} \right). (A.7)$$

Combining these equations gives an algorithm that is well suited for determining the coefficients $a_{jk}^{(m)}$ recursively, starting from the initial conditions (15). It requires the instantaneous eigenvalues $E_j^{(0)}$ and eigenstates $|u_j^{(0)}\rangle$ as input, and reduces the actual calculation, apart from adding the various sums, to the computation of the matrix elements $\langle u_j^{(0)}|\partial_\tau^n H^{(0)}|u_k^{(0)}\rangle$. When employing this algorithm for stepping from the set of coefficients $a_{jk}^{(l)}$ (with $l = 1, \ldots, m-1$) to the coefficients $a_{jk}^{(m)}$, the task that remains after having solved equation (A.2) is the solution of the first-order differential equation (18) for the diagonal coefficients $a_{jj}^{(m)}$. This task is simplified by the fact that the knowledge of the higher derivatives $\partial_\tau^n a_{jj}^{(m)}$ can be exploited for the numerical integration.

Appendix B: Prefactor renormalization in the iterative scheme

In this Appendix we sketch how the incorrect prefactor $\pi/3$ obtained in the perturbative calculation of the final

Landau-Zener transition amplitude (34) is changed towards unity by the first step of the iterative scheme I. We start from the pole approximation to the nonadiabatic coupling,

$$\frac{\gamma^{(0)}(w)}{E^{(0)}(w)} = \frac{i}{3(w - w_c)} - \frac{i}{3(w + w_c)}$$
$$= \frac{2iw_c}{3(w^2 - w_c^2)} \tag{B.1}$$

with $w_c = -i\pi/2$. Inserting this into the iteration equation (23), we end up with

$$\frac{\gamma^{(1)}(w)}{E^{(0)}(w)} = \frac{12i\varepsilon w|w_c|}{9(w^2 + |w_c|^2)^2 + 4\varepsilon^2|w_c|^2} . \tag{B.2}$$

The poles of this expression are located at

$$w = \pm i|w_c|\sqrt{1 \pm \frac{2i\varepsilon}{3|w_c|}}$$
$$\approx \pm i|w_c| \pm \frac{\varepsilon}{3} . \tag{B.3}$$

We now have to evaluate the integral (28) for $\tau = \infty$ and $n = 1$, so that the argument of the exponential is $-(2i/\varepsilon)\int_0^\infty d\tau' E^{(1)}(\tau')$, rather than $-iw/\varepsilon$, with w as given by equation (29). However, according to equation (22) the iterated eigenvalue $E^{(1)}$ differs from $E^{(0)}$ merely by an amount of order ε^2, so that the difference $(E^{(1)} - E^{(0)})/\varepsilon$ still vanishes for $\varepsilon \to 0$. Hence, we may for small ε approximate $E^{(1)}$ by $E^{(0)}$ at least in the exponential, and then change to the variable w. Closing the contour of integration in the lower complex w-plane, the residue theorem gives

$$c_{12}^{(1)}(\infty) = \frac{\pi}{2i}\left[\exp\left(-\frac{|w_c|}{\varepsilon}\sqrt{1 - \frac{2i\varepsilon}{3|w_c|}}\right)\right.$$
$$\left. - \exp\left(-\frac{|w_c|}{\varepsilon}\sqrt{1 + \frac{2i\varepsilon}{3|w_c|}}\right)\right]$$
$$\approx \pi \sin(1/3)\exp\left(-\frac{|w_c|}{\varepsilon}\right) \tag{B.4}$$

Thus, the prefactor reduces from $\pi/3$ to $\pi \sin(1/3)$. We emphasize that the origin for this reduction lies in the fact that the poles (B.3) are shifted by amounts of order ε with respect to $\pm w_c$. This feature is not captured when approximating all $E^{(n)}$ by $E^{(0)}$, as done in the derivation of equation (39).

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