The Journal of Chemical Physics

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Cite as: J. Chem. Phys. **67**, 4640 (1977); https://doi.org/10.1063/1.434630
Published Online: 26 August 2008

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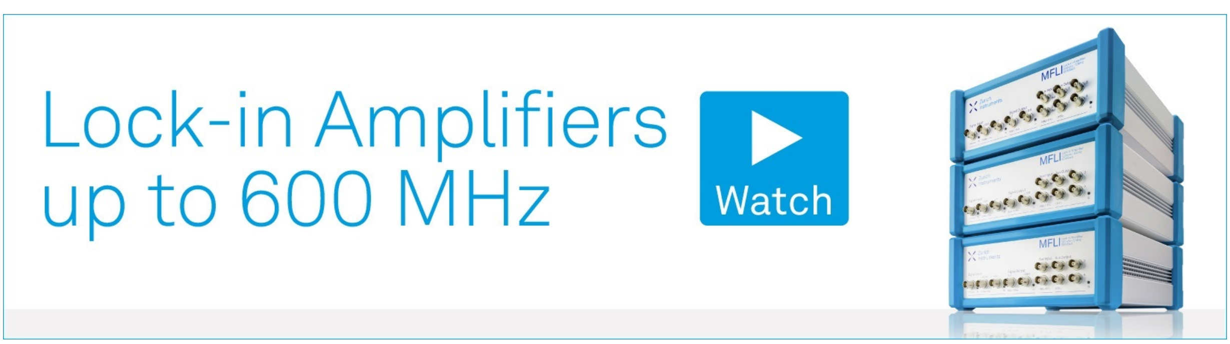

The adiabatic theorem in the complex plane and the semiclassical calculation of nonadiabatic transition amplitudes[a)]

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(Received 1 July 1977)

This paper is concerned with the problem of calculating amplitudes for nonadiabatic transitions induced by a time-dependent Hamiltonian, in the semiclassical limit $\hbar \to 0$, with emphasis on questions relevant to semiclassical theories of electronically inelastic scattering. For this problem the semiclassical limit is mathematically equivalent to the adiabatic limit, and the adiabatic theorem says that all these transition amplitudes vanish in the limit; the question is, what is the asymptotic form of the nonadiabatic amplitudes, as they go to zero? We consider Hamiltonia that are analytic matrix functions of time. *We prove a generalization of the adiabatic theorem to the complex time plane*; paradoxically, the adiabatic theorem in the complex plane gives us directly the nonadiabatic amplitudes along the real time axis. We derive Dykhne's remarkable formula for the two-state case, which says that the limiting form of the transition amplitude depends only on the energy curves of the two states, not on the nonadiabatic coupling which is responsible for transition between them. We discuss the three-state problem at length and show that the obvious generalization of the Dykhne formula is sometimes true, sometimes false. To indicate the scope of methods based on the adiabatic theorem in the complex plane, we give an elementary proof of the semiclassical formula for above-barrier reflection of a one-dimensional particle.

I. INTRODUCTION

The adiabatic theorem has to do with solutions to a time-dependent Schrödinger equation in which the Hamiltonian is itself time-dependent. Loosely stated, the theorem says that once in an eigenstate, always in an eigenstate, provided the Hamiltonian varies "infinitely slowly" with time and provided the spectrum of H is always nondegenerate. One proves this[1] by considering a family of time-dependent Hamiltonians indexed by a parameter that governs the rate of change of each Hamiltonian; one calculates the amplitudes for transition from one eigenstate of H to another—the "nonadiabatic transition amplitudes"—as a function of this parameter and finds that the amplitudes vanish in the adiabatic limit. Thus, let $H(t)$, $-\infty < t < +\infty$, be a time-dependent Hamiltonian and $H(t,\lambda)$ the family of Hamiltonians defined by $H(t,\lambda) = H(\lambda t)$. The adiabatic limit is $\lambda \to 0$ and the adiabatic theorem says that all nonadiabatic transition amplitudes vanish as $\lambda \to 0$.

There is another parameter in the time-dependent Schrödinger equation

$$i\hbar\, \partial\psi/\partial t = H(t,\lambda)\psi\,, \tag{1.1}$$

Planck's constant $\hbar$. The adiabatic limit $\lambda \to 0$ ($\hbar$ fixed) is in fact related to the semiclassical limit $\hbar \to 0$ (λ fixed), for if $\psi(t,\hbar)$ is a family of solutions to Eq. (1.1) for $\lambda = 1$ and variable $\hbar$, then $\phi(t,\lambda) = \psi(\lambda t, \lambda\hbar)$ is a family of solutions to Eq. (1.1) for fixed $\hbar$ and variable λ. From the asymptotic behavior of ϕ as $\lambda \to 0$ we can deduce the asymptotic behavior of ψ as $\hbar \to 0$, and *vice versa*; in particular, the adiabatic theorem is equivalent to the statement that nonadiabatic transition amplitudes vanish in the semiclassical limit $\hbar \to 0$ (see Sec. III for direct proof of this statement).

One can ask for the asymptotic form of these nonadiabatic amplitudes in the semiclassical limit; in particular, how does the amplitude for transition from an eigenstate of $H(-\infty)$ to an eigenstate of $H(+\infty)$ go as $\hbar \to 0$? The question is interesting in itself and also because of its importance for semiclassical theories of electronically inelastic scattering, especially the recent theory of Miller and George.[2] It was first answered by Dykhne,[3] who calculated the asymptotic form of the nonadiabatic transition amplitude for the case that $H(t)$ is a real symmetric 2×2 matrix that can be analytically continued into the complex time plane.

Dykhne's formula is very simple, and very mysterious. The amplitude is calculated solely from the potential curves $E_1(t)$ and $E_2(t)$, the eigenvalues of $H(t)$; it is independent of the nonadiabatic coupling responsible for the transition. Transition "occurs" at the nearest point in the complex time plane where the potential curves "cross," $E_1 = E_2$, and all that matters are the phase integrals of the energies to this point.

It seems absurd on the face of it that a nonadiabatic transition amplitude should be independent of the nonadiabatic coupling that causes the transition, but Dykhne's formula is correct, as Davis and Pechukas recently proved in exhaustive detail.[4] The essential point is that in the semiclassical limit the transition amplitude depends only on the leading term in the nonadiabatic coupling around the crossing point, and this leading term is in general a simple pole with residue that is the same for all 2×2 matrices. It is not that the nonadiabatic coupling does not matter, but rather that—in its leading term—it is the same for all problems.

It is important to know whether this result is peculiar to the two-state case, or whether generalizations of the Dykhne formula to problems with more than two states—proposed by Landau and Lifshitz[5] and by McLafferty and George[6]—are in fact valid. However, the two-state calculation consists of more (Davis and Pech-

[a)]This work was supported by a grant from the National Science Foundation.

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ukas) or less (Dykhne) complicated analysis in the immediate vicinity of a single crossing point and is difficult to generalize to multistate problems, where sequential transitions involving several crossing points may be important.

We report in this paper a new method of calculating nonadiabatic transition amplitudes that avoids detailed analysis around crossing points and is not restricted to the two-state case.

The method rests on a generalization of the adiabatic theorem to contours in the complex plane. Not all contours will do: the eigenvalues of $H(t)$ must satisfy certain conditions along a contour in order that the theorem hold. When these conditions are satisfied, the adiabatic theorem in the complex plane says the same thing as its real axis counterpart, that as $\hbar \to 0$ the coefficient of the initial state—in an eigenfunction expansion of ψ along the contour—approaches unity at all points on the contour.

Paradoxically, the adiabatic theorem in the complex plane then gives directly a nonadiabatic amplitude along the real axis.

The origin of the paradox lies in the multivalued nature of the eigenvalues and eigenvectors of an analytic matrix. The subject has been discussed in detail by Pechukas *et al.*[7] Briefly, the energy curves $\{E_j(t)\}$ may cross at points in the complex t plane; in general, the crossing points are isolated, and only two eigenvalues coincide at a crossing; in general, these two eigenvalues have a square-root branch point at the crossing, and as we circle the crossing we find that one eigenvector becomes the other and *vice versa*. The eigenvectors and eigenvalues of $H(t)$ are therefore multivalued functions of t. If we start at the left edge of the complex plane, in state i, and follow a contour in the complex plane on which the adiabatic theorem holds, we can calculate from the theorem the amplitude to remain in state i; but at the right edge of the complex plane the state we have been calling i, along the contour, may coincide with the state we labeled f along the real axis. It is then a simple matter to compare the coefficients in an expansion of the wavefunction in eigenstates of H along the complex contour with the corresponding expansion coefficients along the real axis, and thereby calculate the amplitude for transition $i \to f$ along the real axis.

The reader may suspect that there is fraud here—that to start in state i and end in state f, following the adiabatic theorem along a contour in the complex plane, cannot be consistent with what we know to be true from the adiabatic theorem along the real axis, which is that in the adiabatic limit a system that starts in state i stays in state i for all time. Actually, there is no inconsistency. The adiabatic theorem along the real axis yields an asymptotic bound on the $i \to f$ transition amplitude (see Sec. III), which gives us crude information on how this amplitude goes to zero as $\hbar \to 0$; the adiabatic theorem in the complex plane gives an asymptotic formula for this amplitude which is consistent with that bound (see Sec. IV). The adiabatic theorem along the real axis says that the $i \to i$ amplitude goes to unity as $\hbar \to 0$; the adiabatic theorem in the complex plane gives an asymptotic bound for this amplitude which is consistent with that limiting value (see Sec. IV). The adiabatic theorem in the complex plane is an extension, not a negation, of the adiabatic theorem along the real axis, and the information we get from it supplements what we already know from the adiabatic theorem along the real axis.

It should be mentioned here, since we do not emphasize the point in the body of the paper, that one can also use an appropriate complex contour as a contour of integration when one wants to go beyond the semiclassical limiting formula for a given nonadiabatic transition and calculate the amplitude accurately for small but nonzero $\hbar$, namely, the $\hbar$ that really is. One can either compute the asymptotic expansion, in powers of $\hbar$, of the correction to the semiclassical limiting formula—one can see how to do this by studying the calculation in Sec. III—or one can numerically integrate Eqs. (3.3) along the contour. There are definite advantages to this strategy, provided the nonadiabatic couplings can be extended accurately to the complex plane: along the complex contour one is integrating for the "adiabatic" amplitude, which is slowly varying and close to unity; along the real axis, by contrast, one is integrating directly for the final state amplitude, which is oscillatory and of order $\hbar$ for finite t, settling down to something exponentially small in $\hbar$ only as $t \to +\infty$ (see Ref. 4).

II. EQUATIONS AND NOTATION

This section is mainly to establish notation, but also to review certain elementary facts about systems of linear differential equations with analytic coefficients.

We shall be studying the time-dependent Schrödinger equation with time-dependent Hamiltonian,

$$i\hbar\psi'(t) = H(t)\psi(t)\,, \tag{2.1}$$

where the prime indicates differentiation with respect to time, $H(t)$ is a symmetric $n \times n$ matrix that is real-valued for real t, and $\psi(t)$ is an n-component vector. It will be necessary to move from the real t axis into the complex t plane, so we require that $H(t)$ be analytic throughout some strip S of the complex plane centered on the real axis; that is, each matrix element $H_{ij}(t)$ must be analytic for all t with $|\mathrm{Im}\, t| < \sigma/2$, where σ is the width of the strip S. Standard theory[8] then ensures that for any $t_0 \in S$ and any n-vector ψ_0 there exists a unique solution $\psi(t)$ to Eq. (2.1), analytic throughout S, such that $\psi(t_0) = \psi_0$.

We have in mind that Eq. (2.1) is a simple model for a collision, so in the distant past or the distant future $H(t)$ should reduce to a constant, "unperturbed," Hamiltonian. More precisely, we require that in S the limits

$$\lim_{\mathrm{Re}\, t \to \pm\infty} H(t) = H_\pm \tag{2.2}$$

exist. The Hamiltonian matrix at the left "edge" of S, H_-, may or may not equal the Hamiltonian H_+ at the right "edge" of S.

Similarly, we want to label solutions of Eq. (2.1), not by their values at some intermediate time t_0, but by their limiting behavior as $t \to \pm\infty$, where they propagate according to the unperturbed Hamiltonians $H_\pm$. To ensure that this is possible we must require that $H(t)$ go sufficiently rapidly to $H_\pm$ at the edges of S. The following condition suffices: there is an $\epsilon > 0$ such that

$$|t|^{1+\epsilon} \sum_{i,j} |H_{ij}(t) - H_{\pm ij}| \to 0 \tag{2.3}$$

as $\mathrm{Re}\, t \to \pm\infty$ in S. Under this condition it is not hard to show[9] that with any solution $\psi(t)$ there are associated two n vectors ψ_{in} and ψ_{out} such that

$$\begin{aligned} &\lim_{t\to-\infty} \exp(iH_- t/\hbar)\psi(t) = \psi_{\mathrm{in}} , \\ &\lim_{t\to+\infty} \exp(iH_+ t/\hbar)\psi(t) = \psi_{\mathrm{out}} ; \end{aligned} \tag{2.4}$$

that is, $\psi(t)$ is asymptotic to $\exp(-iH_- t/\hbar)\psi_{\mathrm{in}}$ in the indefinite past and to $\exp(-iH_+ t/\hbar)\psi_{\mathrm{out}}$ in the indefinite future. Conversely, given any n vector ψ_{in} (or ψ_{out}) there is a solution $\psi(t)$ asymptotic to $\exp(-iH_- t/\hbar)\psi_{\mathrm{in}}$ in the indefinite past [or to $\exp(-iH_+ t/\hbar)\psi_{\mathrm{out}}$ in the indefinite future].

Under the condition that $H(t)$ go sufficiently rapidly to its limits at the edges of S, then, we can designate solutions of Eq. (2.1) by boundary conditions at the left (or right) edge of S. The simplest way to specify boundary conditions is with respect to a basis of eigenvectors of the Hamiltonian $H(t)$.

We assume that for all real t the eigenvalues of $H(t)$ are nondegenerate, and that the same is true of the eigenvalues of the limiting matrices $H_\pm$. For *real t*, let $\phi_j(t), j = 1, \ldots, n$, be eigenvectors of $H(t)$, numbered in order of increasing energy: $E_1(t) < E_2(t) < \cdots < E_n(t)$. We stipulate that the $\phi_j(t)$ be real, which is possible since $H(t)$ is real; continuous in t, which is possible since H is continuous in t; and normalized,

$$(\phi_j, \phi_j) = \sum_{m=1}^{n} \phi_{jm}\phi_{jm} = 1 , \tag{2.5}$$

where ϕ_{jm} is the mth component of ϕ_j. This defines each eigenvector function $\phi_j(t)$ up to a constant multiplicative factor of ± 1; that is, up to a sign.

If $\psi(t)$ is a solution to Eq. (2.1), we can expand ψ, along the real t axis, as

$$\psi(t) = \sum_{j=1}^{n} c_j(t) \exp\left(-i \int_0^t d\tau E_j(\tau)/\hbar\right) \phi_j(t) . \tag{2.6}$$

The expansion coefficients $c_j(t)$ satisfy the following system of linear differential equations:

$$c_j'(t) = \sum_{k=1}^{n} \gamma_{jk}(t) \exp[i\Delta_{jk}(t)/\hbar] c_k(t) , \tag{2.7}$$

where

$$\gamma_{jk}(t) = (\phi_j', \phi_k) \equiv \sum_{m=1}^{n} \phi_{jm}'(t)\phi_{km}(t) , \tag{2.8a}$$

$$\Delta_{jk}(t) = \int_0^t d\tau (E_j - E_k)(\tau) . \tag{2.8b}$$

For each t the eigenvectors ϕ_j are real valued and orthonormal,

$$(\phi_j, \phi_k) = \delta_{jk} , \tag{2.9}$$

so the nonadiabatic couplings $\gamma_{jk}(t)$ are antisymmetric in j and k,

$$\gamma_{jk} = (\phi_j', \phi_k) = -(\phi_j, \phi_k') = -(\phi_k', \phi_j) = -\gamma_{kj} , \tag{2.10}$$

and, of course, $\Delta_{jk} = -\Delta_{kj}$.

Under the condition that $H(t)$ go sufficiently rapidly to $H_\pm$ as $t \to \pm\infty$, there is one and only one solution of Eq. (2.1) such that

$$c_j(t) \xrightarrow[t\to-\infty]{} \delta_{ji} , \tag{2.11}$$

and for this solution the limits

$$c_j(+\infty) = \lim_{t\to+\infty} c_j(t) \tag{2.12}$$

exist. This is the solution that "starts" in eigenstate i at $t = -\infty$, and the amplitudes $c_j(+\infty)$ are the various nonadiabatic transition amplitudes induced by the time dependence of $H(t)$.

We will study the behavior of solutions to Eq. (2.1), regarded as functions of $\hbar$ as well as of the time, in the semiclassical limit $\hbar \to 0$. Thus, let $c_j(+\infty, \hbar)$ be the nonadiabatic transition amplitudes defined in the previous paragraph, that is, the expansion coefficients as $t \to +\infty$ of the solution $\psi(t, \hbar)$ for which $c_j(t, \hbar) \to \delta_{ji}$ as $t \to -\infty$. The semiclassical limit $\hbar \to 0$ is mathematically equivalent to the adiabatic limit of an "infinitely slowly varying" Hamiltonian (see Sec. I), so from the adiabatic theorem it follows that as $\hbar \to 0$ $c_j(+\infty, \hbar) \to \delta_{ji}$: the nonadiabatic transition amplitudes go to zero with $\hbar$. What we want is the functional dependence of $c_j(+\infty, \hbar)$ on $\hbar$ in the limit $\hbar \to 0$.

As promised, the solution to this problem involves integration of Eqs. (2.7) in the complex t plane, and the only subtlety in the business is that, in general, the expansion coefficients $c_j(t, \hbar)$ are *not* analytic throughout S, for in general the eigenvector functions $\phi_j(t)$ are not analytic throughout S.

The analytic properties of eigenvalues and eigenvectors of an analytic symmetric matrix have been discussed by Pechukas *et al.*[7] All the trouble is at points where the matrix has degenerate eigenvalues. The typical case is an isolated point where two and only two eigenvalues are equal—a "crossing" of two energy "curves" $E_k(t)$ and $E_l(t)$—and one finds that, at the crossing, E_k and E_l in general have a branch point of square-root type while the associated eigenvectors ϕ_k and ϕ_l are singular.

In integrating Eqs. (2.7) along a curve in the complex plane, then, one certainly wants to choose a contour that avoids crossing points. However, there is an effect of the crossing points that cannot be avoided: the eigenvector functions $\phi_j(t)$ are not single valued throughout S, for in one circuit around a crossing point the eigenvalues involved—and therefore also the eigenvectors—switch labels. $E_k(t)$, followed around a circle about a (kl) crossing, becomes $E_l(t)$, and *vice versa*, while $\phi_k(t) \to \pm\phi_l(t)$ and *vice versa*. Thus, if one starts at $t = -\infty$, with a given set of expansion coefficients $c_j(-\infty)$, and wanders off into the complex plane, keeping track of the $c_j(t)$ by continually integrating Eqs. (2.7), the coefficients $c_j(+\infty)$ one has in hand on returning to the real axis at $t=+\infty$ may not be the expansion coefficients one wants, for what was state 1 along the contour may have become, on returning to the real axis, the state one labeled, say, number 37 along the real axis.

This is both a source of confusion and the essence of our method of calculating transition amplitudes.

Getting the coefficients straightened out is a matter of permuting the labels properly, keeping in mind that $\psi(t)$ is single valued throughout S and therefore that its value at any particular point does not depend on the contour one chooses, in integrating Eq. (2.1), to reach that point.

Thus, let C be a smooth curve in S, parametrized as $t(s)$ where the real variable s runs from $-\infty$ to $+\infty$ and such that $\mathrm{Re}\,t(s)\to\pm\infty$ as $s\to\pm\infty$. Suppose that for every t on C the matrix $H(t)$ has n distinct eigenvalues, that is, the curve C avoids all crossing points in S. Then at every point of C, $H(t)$ has n distinct eigenvectors $\tilde{\phi}_j(t)$, which we define unambiguously by the following requirements:

$$(\tilde{\phi}_j,\tilde{\phi}_k)\equiv\sum_{m=1}^{n}\tilde{\phi}_{jm}\tilde{\phi}_{km}=\delta_{jk}\,, \tag{2.13a}$$

$$\tilde{\phi}_j(t)\text{ continuous in } t \text{ for } t\in C\,, \tag{2.13b}$$

$$\tilde{\phi}_j(t)\xrightarrow[s\to-\infty]{}\phi_j(-\infty)\,, \tag{2.13c}$$

where the $\phi_j(-\infty)$ are the eigenvectors of H_-—the Hamiltonian at the left edge of S—as defined above [see the discussion surrounding Eq. (2.5)].

A few comments on requirements (2.13) may be helpful. First, since $H(t)$ is a symmetric matrix its eigenvectors are automatically orthogonal in the sense of Eqs. (2.13a), so that these equations simply specify the normalization of each eigenvector. There is one difficulty, which is that the components of a given eigenvector are in general complex numbers, and if the sum of the squares of these components is zero the eigenvector cannot be normalized according to Eqs. (2.13a); but one can show[7] that this difficulty cannot arise at points where $H(t)$ has n distinct eigenvalues. At any point on C, then, Eqs. (2.13a) define each eigenvector $\tilde{\phi}_j(t)$ up to a sign, and (2.13b)—the requirement of continuity—specifies the entire function $\tilde{\phi}_j(t)$ up to a constant factor of ± 1. Finally, Eq. (2.13c) requires that the numbering and sign of the eigenvectors $\tilde{\phi}_j$ agree, at the left edge of S, with the numbering and sign of the eigenvectors ϕ_j defined on the real t axis.

As $s\to+\infty$, at the right edge of S, each eigenvector $\tilde{\phi}_j(t)$ becomes an eigenvector of H_+, differing at most in sign from one of the eigenvectors $\phi_{j'}(+\infty)$ defined on the real t axis. Thus,

$$\tilde{\phi}_j(+\infty)\equiv\lim_{s\to+\infty}\tilde{\phi}_j(t)=\epsilon_{j'}\phi_{j'}(+\infty)\,, \tag{2.14}$$

where $\epsilon_{j'}$ is either $+1$ or -1; the rearrangement $j\to j'$ is of course just a permutation of the integers 1 through n. The corresponding eigenvalue $\tilde{E}_j(t)$ goes to $E_{j'}(+\infty)$ as $s\to+\infty$.

Let $\psi(t)$ be the solution of Eq. (2.1) with expansion

$$\psi(t)=\sum_{j=1}^{n}c_j(t)\exp\left(-i\int_0^t d\tau E_j(\tau)/\hbar\right)\phi_j(t) \tag{2.15}$$

on the real axis and expansion

$$\psi(t)=\sum_{j=1}^{n}\tilde{c}_j(t)\exp\left(-i\int_0^t d\tau\tilde{E}_j(\tau)/\hbar\right)\tilde{\phi}_j(t) \tag{2.16}$$

on the curve C. Here the integral from 0 on the real axis to t on C is taken down the real axis R, along the left edge of S, and then along C to t:

$$\int_0^t d\tau\tilde{E}_j(\tau)=\lim_{t',s'\to-\infty}\left(\int_{R0}^{t'}d\tau E_j(\tau)+E_j(-\infty)[t(s')-t']+\int_{C\,t(s')}^{t}d\tau\tilde{E}_j(\tau)\right)\,. \tag{2.17}$$

Contact between the expansions (2.15) and (2.16) is established at the edges of S. As $\mathrm{Re}\,t\to\pm\infty$ in S,

$$\psi(t)-\sum_{j=1}^{n}c_j(\pm\infty)\exp\left(-i\int_0^{\mathrm{Re}\,t}d\tau E_j(\tau)/\hbar\right)\times\exp[E_j(\pm\infty)\,\mathrm{Im}\,t/\hbar]\phi_j(\pm\infty)\to 0\,. \tag{2.18}$$

Comparing with the limiting expansions of $\psi(t)$ on C, as $s\to\pm\infty$, we find that

$$\tilde{c}_j(-\infty)\equiv\lim_{s\to-\infty}\tilde{c}_j(t)=c_j(-\infty)\,, \tag{2.19a}$$

$$\epsilon_{j'}\tilde{c}_j(+\infty)\exp\left(-i\oint d\tau\tilde{E}_j(\tau)/\hbar\right)=c_{j'}(+\infty)\,, \tag{2.19b}$$

where the integral of $\tilde{E}_j$ is around the contour consisting of the real axis R and the curve C, closed at the edges of S, in the direction from right to left on R:

$$\oint d\tau\tilde{E}_j(\tau)=\lim_{\substack{t',s'\to-\infty\\ t'',s''\to+\infty}}\left(\int_{R0}^{t'}d\tau E_j(\tau)+E_j(-\infty)[t(s')-t']+\int_{C\,t(s')}^{t(s'')}d\tau\tilde{E}_j(\tau)+E_{j'}(+\infty)[t''-t(s'')]+\int_{R\,t''}^{0}d\tau E_{j'}(\tau)\right)\,. \tag{2.20}$$

At the left end of C the expansion coefficients $\tilde{c}_j$ agree with c_j, for the corresponding eigenvectors agree; at the right end of C each $\tilde{c}_j$ is related, by Eq. (2.19b), to the $c_{j'}$ attached to the appropriate eigenvector.

The message of the adiabatic theorem we prove in the following section is that, in the adiabatic limit $\hbar\to 0$ and along properly chosen curves C in the complex t plane, a system that starts in state i—$\tilde{c}_j(-\infty,\hbar)=\delta_{ji}$—stays in state i, in the sense that $\tilde{c}_i(t,\hbar)\to 1$ as $\hbar\to 0$ for all t on C. For these curves we can calculate $\lim\tilde{c}_i(+\infty,\hbar)$ as $\hbar\to 0$—it is unity—and then use Eq. (2.19b) to deduce the *nonadiabatic* amplitude $c_{i'}(+\infty,\hbar)$ in the semiclassical limit $\hbar\to 0$.

III. THE ADIABATIC THEOREM IN THE COMPLEX PLANE

On the curve C the expansion coefficients $\tilde{c}_j(t)$ of the preceding section [Eq. (2.16)] satisfy differential equations analogous to Eqs. (2.7),

$$\tilde{c}_j'(t) = \sum_{k=1}^{n} \tilde{\gamma}_{jk}(t) \exp[i\tilde{\Delta}_{jk}(t)/\hbar]\tilde{c}_k(t) , \tag{3.1}$$

where

$$\tilde{\gamma}_{jk}(t) = (\tilde{\phi}_j', \tilde{\phi}_k) = -\tilde{\gamma}_{kj}(t) ,$$

$$\tilde{\Delta}_{jk}(t) = \int_0^t d\tau(\tilde{E}_j - \tilde{E}_k)(\tau) , \tag{3.2}$$

and the integral from 0 to t is as specified in Eq. (2.17). We shall study the solution that satisfies the boundary condition $\tilde{c}_j(-\infty) \equiv \lim_{s\to-\infty}\tilde{c}_j(t) = \delta_{ji}$, and we shall study this solution as a function of $\hbar$ as well as of time. To simplify the notation in this section, we drop the overhead squiggle that distinguishes quantities evaluated on C from quantities evaluated on the real axis, because all the integration in this section is along C; to complicate the notation, we indicate explicitly those quantities that depend on $\hbar$. Thus, we write $c_j(t,\hbar)$ instead of $\tilde{c}_j(t)$, and the problem is this:

$$c_j'(t,\hbar) = \sum_{k=1}^{n} \gamma_{jk}(t) \exp[i\Delta_{jk}(t)/\hbar]c_k(t,\hbar) , \tag{3.3a}$$

$$c_j(-\infty, \hbar) = \delta_{ji} . \tag{3.3b}$$

What we prove below is that, under two conditions on the Hamiltonian $H(t)$ and the curve C, the limiting value $c_i(+\infty,\hbar) \equiv \lim_{s\to+\infty} c_i(t,\hbar)$ goes to unity as $\hbar \to 0$.

The first condition, on the behavior of the eigenvalues of H along C, is critical and must always be checked in any application of the adiabatic theorem in the complex plane. We require that for all j $\mathrm{Im}\Delta_{ji}(t)$ be nonincreasing on C; that is, if $s < s'$, we require that $\mathrm{Im}\Delta_{ji}(t) \geq \mathrm{Im}\Delta_{ji}(t')$, where t is the point on C labeled by s and t' the point on C labeled by s'.

The purpose of this condition is to ensure that at any point on C the exponential $\exp[i\Delta_{ji}(t)/\hbar]$ is at least as large, in absolute value, as it is at any preceding point. It is the exponentials in Eqs. (3.3) that dominate as $\hbar \to 0$. We shall convert Eqs. (3.3) to integral equations, integrate by parts, and claim that the leading contribution as $\hbar \to 0$ comes from the exponential at the endpoint; this would be a difficult argument to make if there were a larger exponential lurking somewhere in the middle of the leftover integrals, ready to explode as $\hbar \to 0$.

Remember that state i is the state in which the system starts, at the left end of C [Eq. (3.3b)]; the condition is that, as we follow C from left to right, the product $\mathrm{Im}(E_j - E_i)dt$ is never greater than zero. At any point on C this imposes $n-1$ restrictions—one for each j not equal to i—on the direction dt in which the curve is going, and one suspects, correctly (see Sec. V), that the adiabatic theorem is harder to apply the larger the matrix $H(t)$, for it becomes more difficult to find an acceptable way to get from the left edge of S to the right edge. Notice, however, that the real axis is always an acceptable curve C, since on the real axis $\mathrm{Im}\Delta_{ji} = 0$ for all t and therefore is certainly nonincreasing. The argument below therefore serves equally well as a proof of the adiabatic theorem along the real axis.

The second condition on $H(t)$ and C is essential to the proof of the adiabatic theorem but in practice serves merely to rule out certain pathological cases that one would never consider anyway. It is that $H(t)$ and C not "wiggle" too much at the edges of S, and the purpose is to ensure that all the integrals that appear in the calculation below actually exist. We shall spell out more precisely what this requires of H and C in the comments that follow the calculation.

Here, then, is the adiabatic theorem in the complex plane: As $\hbar \to 0$,

i. $c_i(t,\hbar) \to 1$ for all t on C, and

ii. $c_i(+\infty, \hbar) \to 1$.

Further, for all $j \neq i$,

iii. $c_j(t,\hbar) \sim \hbar\gamma_{ji}(t) \exp[i\Delta_{ji}(t)/\hbar]\{i[E_j(t) - E_i(t)]\}^{-1}$

at any t on C where $\gamma_{ji}(t) \neq 0$, and

iv. $|c_j(+\infty,\hbar)| = o\{\hbar \exp[-\mathrm{Im}\Delta_{ji}(+\infty)/\hbar]\}$.

To prove these statements we rewrite Eqs. (3.3) in integral form and integrate once by parts,

$$c_j - \delta_{ji} = \sum_k \int^t d\tau \gamma_{jk} \exp(i\Delta_{jk}/\hbar)c_k \tag{3.4a}$$

$$= \sum_k \hbar\gamma_{jk} \exp(i\Delta_{jk}/\hbar)c_k/i(E_j - E_k) - \sum_k (\hbar/i) \int^t d\tau[\gamma_{jk}c_k/(E_j - E_k)]' \exp(i\Delta_{jk}/\hbar) \tag{3.4b}$$

$$= \sum_k \hbar\gamma_{jk} \exp(i\Delta_{jk}/\hbar)c_k/i(E_j - E_k)$$

$$- \sum_k (\hbar/i) \int^t d\tau[\gamma_{jk}/(E_j - E_k)]' \exp(i\Delta_{jk}/\hbar)c_k - \sum_k \sum_l (\hbar/i) \int^t d\tau[\gamma_{jk}\gamma_{kl}/(E_j - E_k)] \exp(i\Delta_{jl}/\hbar)c_l . \tag{3.4c}$$

We define

$$M_j(\hbar) = \operatorname*{lub}_{t\in C} |\exp[i\Delta_{ij}(t)/\hbar]c_j(t,\hbar) - \delta_{ji}| \tag{3.5}$$

and multiply Eq. (3.4c)(by $\exp[i\Delta_{ij}(t)/\hbar]$. To bound a typical term on the right-hand side we reason as follows:

$$\left|\int^t d\tau[\gamma_{jk}/(E_j-E_k)]'\exp[i\Delta_{ij}(t)/\hbar]\exp[i\Delta_{jk}(\tau)/\hbar]c_k(\tau,\hbar)\right|$$

$$=\left|\int^t d\tau[\gamma_{jk}/(E_j-E_k)]'\exp[i\Delta_{ij}(t)/\hbar]\exp[i\Delta_{ji}(\tau)/\hbar]\exp[i\Delta_{ik}(\tau)/\hbar]c_k(\tau,\hbar)\right|$$

$$\leq[\delta_{ki}+M_k(\hbar)]\int^t|d\tau|\,|[\gamma_{jk}/(E_j-E_k)]'|\leq[\delta_{ki}+M_k(\hbar)]\int|d\tau|\;|[\gamma_{jk}/(E_j-E_k)]'|\;,$$

where the last integral is over the entire curve C. We have used the fact that

$$|\exp[i\Delta_{ij}(t)/\hbar]\exp[i\Delta_{ji}(\tau)/\hbar]|$$
$$=|\exp[-i\Delta_{ji}(t)/\hbar]\exp[i\Delta_{ji}(\tau)/\hbar]|\leq 1\,, \tag{3.7}$$

since $\mathrm{Im}\Delta_{ji}$ is nonincreasing on C.

For all t on C, then, we have

$$|\exp[i\Delta_{ij}(t)/\hbar]c_j(t,\hbar)-\delta_{ji}|\leq\hbar\sum_k A_{jk}[\delta_{ki}+M_k(\hbar)]\,, \tag{3.8}$$

and therefore

$$M_j(\hbar)\leq\hbar\sum_k A_{jk}[\delta_{ki}+M_k(\hbar)]\,, \tag{3.9}$$

where the positive constants A_{jk} are independent of $\hbar$:

$$A_{jk}=\operatorname*{lub}_{t\subset C}|\gamma_{jk}|/|E_j-E_k|+\int|d\tau|\,|[\gamma_{jk}/(E_j-E_k)]'|$$
$$+\sum_l\int|d\tau|\,|\gamma_{jl}\gamma_{lk}/(E_j-E_l)|\,. \tag{3.10}$$

It is easy to go from inequality (3.9) to the assertion that $M_j(\hbar)$ is $O(\hbar)$. Let

$$M(\hbar)=\sum_j M_j(\hbar),\;\; A=\max_k\sum_j A_{jk}\,. \tag{3.11}$$

Then

$$M(\hbar)\leq\hbar A[1+M(\hbar)]\,, \tag{3.12}$$

which implies

$$M(\hbar)\leq\hbar A/(1-\hbar A)\leq 2\hbar A \tag{3.13}$$

for all sufficiently small $\hbar$ (i.e., $\hbar\leq 1/2A$). Therefore

$$M_j(\hbar)\leq M(\hbar)\leq 2\hbar A \tag{3.14}$$

for all j.

Statements (i) and (ii) follow immediately. Since

$$|c_i(t,\hbar)-1|\leq M_i(\hbar) \tag{3.15}$$

for all t on C, we have $c_i(t,\hbar)\to 1$ as $\hbar\to 0$, and since the convergence is uniform in t the same is true of the limit $c_i(+\infty,\hbar)$.

To check statements (iii) and (iv) we return to Eq. (3.4c),

$$c_j(t,\hbar)-\frac{\hbar\gamma_{ji}(t)\exp[i\Delta_{ij}(t)/\hbar]}{i[E_j(t)-E_i(t)]}$$
$$=\hbar\gamma_{ji}\exp(i\Delta_{ji}/\hbar)(c_i-1)[i(E_j-E_i)]^{-1}$$
$$+\text{various integrals.} \tag{3.16}$$

We integrate once more by parts in all integrals containing c_i; this drags out another $\hbar$ and ensures that all terms on the right hand side containing c_i are multiplied by $\hbar^2$. Using the bounds (3.14), and proceeding as in Eq. (3.16), we calculate

$$\left|c_j(t,\hbar)-\frac{\hbar\gamma_{ji}(t)\exp[i\Delta_{ij}(t)/\hbar]}{i[E_j(t)-E_i(t)]}\right|$$
$$\leq A'\hbar^2|\exp[i\Delta_{ji}(t)/\hbar]|\,, \tag{3.17}$$

where A' is independent of $\hbar$ and t. This implies (iii) directly, and gives (iv) on taking the limit $s\to\infty$, where γ_{ji} vanishes.

Several comments are necessary.

a. The proof rests on the assertion that the least upper bounds (3.5) are finite. This is true. The expansion coefficient $c_j(t,\hbar)$ is continuous in t on C, and approaches limits at the left and right ends of C, so $|c_j(t,\hbar)|$ is bounded on C. As for the exponential, $\Delta_{ij}(t)$ is continuous on C and $\mathrm{Im}\Delta_{ij}(t)$ goes to $(E_i-E_j)\,\mathrm{Im}t$ at the ends of C; since C is confined to the strip $\mathrm{Im}t<\sigma/2$ (see Sec. II), $|\exp(i\Delta_{ij})|$ is bounded on C. Therefore, $|c_j\exp(i\Delta_{ij})-\delta_{ji}|$ is bounded on C and the least upper bound is finite.

b. The constants A_{jk} [Eqs. 3.10)] must be finite. The only possible problems are at the ends of C; that is, the edges of the complex plane, for C avoids all crossing points and therefore the nonadiabatic couplings and energies are analytic at all points on C[7] while the energy differences that occur as denominators are never zero. It is necessary that γ_{jk}, γ'_{jk}, and $(E_j-E_k)'$ all go to zero sufficiently rapidly as $|t|\to\infty$ in S, in order that the integrals in Eq. (3.10) exist.

From Eq. (2.3), which says that $H(t)$ goes to a constant matrix faster than $1/|t|$, one might expect that γ_{jk} goes to zero faster than $1/|t|^2$, that $(E_j-E_k)'$ goes to zero faster than $1/|t|^2$, and so on; but it is not necessarily so. One can design matrix functions $H(t)$ that satisfy Eq. (2.3) but approach the limiting matrices $H_\pm$ in an oscillatory manner, with frequency of oscillation growing so rapidly as $|t|\to\infty$ that the nonadiabatic couplings do not go to zero rapidly, or at all. One does not expect to meet such matrices in real life, and the condition that the A_{jk} be finite amounts to ignoring such wildly oscillating Hamiltonians.

Again, someone of perverse imagination can construct a curve C that oscillates so rapidly on its way to the edges of S that the integrals in (3.10) blow up, even when the γ's go to zero faster than $1/|t|^2$. He is not allowed to use the adiabatic theorem.

c. The adiabatic theorem says what one would expect from first-order time-dependent perturbation theory, applied along the curve C: the asymptotic formula (iii) for $c_j(t,\hbar)$ is just the leading term, as $\hbar\to 0$, in the first-order approximation

$$c_j(t,\hbar)=\int^t d\tau\gamma_{ji}(\tau)\exp[i\Delta_{ji}(\tau)/\hbar] \qquad (3.18)$$

obtained by setting $c_k=\delta_{ki}$ on the right side of Eq. (3.4a). One must not be led by this to the misapprehension that what we are doing here is just first-order perturbation theory in elaborate disguise. One can calculate the nonadiabatic transition amplitudes $c_j(+\infty,\hbar)$ along the real axis by first-order perturbation theory,

$$c_j(+\infty,\hbar)=\int_{-\infty}^{+\infty} dt\,\gamma_{ji}(t)\exp[i\Delta_{ji}(t)/\hbar], \qquad (3.19)$$

and then look at the asymptotic behavior of the integral as $\hbar\to 0$,[4,10] but what one gets is wrong.

d. There is of course an adiabatic theorem for problems defined by boundary conditions at the right edge of S: if $c_j(+\infty,\hbar)=\delta_{ji}$ and $\mathrm{Im}\Delta_{ji}$ is nonincreasing as one goes from right to left on C, then $c_i(-\infty,\hbar)\to 1$ as $\hbar\to 0$. This remark will be important in Sec. V.

e. The adiabatic theorem applies to a somewhat wider class of differential equations than we considered above. In Eqs. (3.3) it is not necessary that the coupling matrix $\{\gamma_{jk}\}$ be antisymmetric. It is not even essential that the diagonal elements γ_{jj} vanish, for diagonal elements can be transformed away: if the functions $\{c_j(t,\hbar)\}$ satisfy Eqs. (3.3) with couplings $\{\gamma_{jk}(t)\}$, then the functions

$$\bar{c}_j(t,\hbar)=\exp\left(-\int^t \gamma_{jj}d\tau\right)c_j(t,\hbar) \qquad (3.20)$$

satisfy Eqs. (3.3) with couplings

$$\bar{\gamma}_{jk}(t)=\exp\left(-\int^t \gamma_{jj}d\tau\right)(\gamma_{jk}-\gamma_{jj}\delta_{jk})\exp\left(\int^t \gamma_{kk}d\tau\right). \qquad (3.21)$$

According to the adiabatic theorem, under the boundary condition $\bar{c}_j(-\infty,\hbar)=\delta_{ji}$ we have

$$\bar{c}_i(t,\hbar)\xrightarrow[\hbar\to 0]{}1,\ \text{all}\ t\in C, \qquad (3.22)$$

and therefore

$$c_i(t,\hbar)\xrightarrow[\hbar\to 0]{}\exp\left(\int^t \gamma_{ii}d\tau\right). \qquad (3.23)$$

With respect to the exponents Δ_{jk}, what we require in the proof of the adiabatic theorem is that $\Delta_{jk}+\Delta_{kl}=\Delta_{jl}$ for all j, k, and l, and the adiabatic theorem applies to any system of differential equations of the form (3.3) in which the exponents satisfy this relation; but in fact this relation implies that each Δ_{jk} can be represented as the time integral of the difference of two "energies" labeled j and k, $\Delta'_{jk}=E_j-E_k$.

The Appendix to this paper illustrates an extracurricular application of the adiabatic theorem in the complex plane: we use the theorem to derive the semiclassical formula for "above-barrier reflection" of a one-dimensional particle moving in a potential.

IV. THE TWO-STATE PROBLEM

In this section we use the adiabatic theorem in the complex plane to derive Dykhne's formula[3] for the two-state problem.

Given an analytic 2×2 matrix $H(t)$, real and symmetric for real t, with eigenvalues $E_1(t)$ and $E_2(t)$ where $E_1<E_2$ for real t, we ask for the transition amplitude from state 1, at $t=-\infty$, to state 2 at $t=+\infty$.

The important function is

$$\Delta_{21}(t)=\int_0^t d\tau(E_2-E_1)(\tau), \qquad (4.1)$$

and the important curves in the complex plane are the level lines

$$\mathrm{Im}\Delta_{21}=K, \qquad (4.2)$$

K a constant. For small K these level lines are described by the equation

$$y(x)=K/(E_2-E_1)(x), \qquad (4.3)$$

where x is the real part of t and y the imaginary part; in particular, the level lines bulge away from the real axis in the vicinity of an avoided crossing (a point on the real axis where E_2-E_1 has a local minimum). For $K>0$ the level lines lie in the upper half-plane and move up the plane, away from the real axis, as K increases. The various level lines run smoothly from the left edge of the complex plane to the right edge until K is so large that the level line encounters a crossing point, where $E_1=E_2$. This, clearly, is the crossing point at which $\mathrm{Im}\Delta_{21}$ is smallest; we label it t_c. We assume in this section that there is only one such point; that is, that no other crossing points lie on the level line $\mathrm{Im}\Delta_{21}(t)=\mathrm{Im}\Delta_{21}(t_c)$.

At t_c the energies E_1 and E_2 in general have a square-root branch point. For small $|t-t_c|$, E_2-E_1 goes as $(t-t_c)^{1/2}$ and $\Delta_{21}(t)-\Delta_{21}(t_c)$ goes as $(t-t_c)^{3/2}$. It follows that the level line "splits" at t_c (see Fig. 1 and Ref. 4).

To maintain sanity in dealing with a multivalued function it helps to cut the complex plane and consider a particular branch of the function, single valued throughout the cut plane. Here we cut along the "extra" level line that grows up from t_c; then $E_1(t)$, $E_2(t)$, and $\Delta_{21}(t)$ are single valued in the cut plane. The level lines for $K>\mathrm{Im}\Delta_{21}(t_c)$ curve up on either side of the branch cut and do not extend from the left edge of the plane to the right edge (see Fig. 1).

For application of the adiabatic theorem we need a contour C, in the *uncut* plane, that crosses from left to

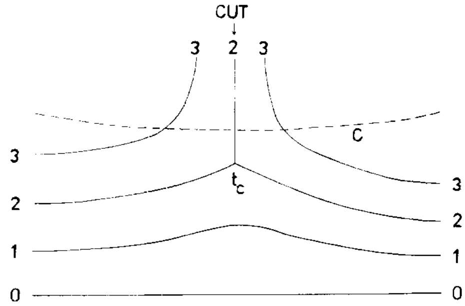

FIG. 1. Level lines of $\mathrm{Im}\Delta_{21}$ in the upper half plane (——). C (-----) is a contour for application of the adiabatic theorem in the complex plane.

right above the crossing point (Fig. 1). To distinguish between functions evaluated along the contour C, in the uncut plane, and the single-valued functions defined in the cut plane, we reinstate the overhead squiggle of Sec. II as a mark on the former. Thus $\tilde{E}_1(t)$, on curve C, is the energy of the state that goes continuously to state 1 at the left edge of the plane: $\tilde{E}_1(t) = E_1(t)$ to the left of the branch cut, $\tilde{E}_1(t) = E_2(t)$ to the right of the branch cut.

We have now to examine the behavior of $\mathrm{Im}\tilde{\Delta}_{21}(t)$ along the curve C drawn in Fig. 1. Since $\tilde{\Delta}_{21} = \Delta_{21}$ to the left of the branch cut, $\mathrm{Im}\tilde{\Delta}_{21}$ clearly decreases on C as C runs from the left edge of the plane to the left edge of the branch cut. To the right of the branch cut, using the notations t_l and t_r for the points on the left and right edges of the branch cut where C crosses it, we calculate

$$\begin{aligned}\mathrm{Im}\tilde{\Delta}_{21}(t) &= \mathrm{Im}\tilde{\Delta}_{21}(t_l) + \mathrm{Im}\int_{t_r}^{t} d\tau(\tilde{E}_2 - \tilde{E}_1)(\tau)\\ &= \mathrm{Im}\Delta_{21}(t_l) - \mathrm{Im}\int_{t_r}^{t} d\tau(E_2 - E_1)(\tau)\\ &= \mathrm{Im}\Delta_{21}(t_l) - \mathrm{Im}\Delta_{21}(t) + \mathrm{Im}\Delta_{21}(t_r)\\ &= 2\,\mathrm{Im}\Delta_{21}(t_c) - \mathrm{Im}\Delta_{21}(t)\,, \end{aligned} \tag{4.4}$$

where the last equation follows because $\mathrm{Im}\Delta_{21}(t_l) = \mathrm{Im}\Delta_{21}(t_r) = \mathrm{Im}\Delta_{21}(t_c)$ (see Fig. 1). To the right of the branch cut, then, $\mathrm{Im}\tilde{\Delta}_{21}(t)$ again decreases along C, because $\mathrm{Im}\Delta_{21}(t)$ increases. The adiabatic theorem therefore applies and on C we have $\tilde{c}_1(-\infty) = 1, \tilde{c}_1(+\infty) \to 1$ as $\hbar \to 0$.

From Eq. (2.19b), then,

$$c_2(+\infty) \underset{\hbar\to 0}{\sim} \epsilon_2 \exp\left(-i \oint d\tau \tilde{E}_1(\tau)/\hbar\right), \tag{4.5}$$

where the phase integral is defined in Eq. (2.20); the path of integration is down the real axis, up the left edge of the complex plane, from left to right along C, and down the right edge.

ϵ_2 is either $+1$ or -1, depending on whether $\tilde{\phi}_1(+\infty)$ is $+\phi_2(+\infty)$ or $-\phi_2(+\infty)$. The sign of $\phi_2(t)$ on the real axis is at our disposal, so we may assume without loss of generality that it is chosen so that $\epsilon_2 = +1$. As for the phase integral, the path of integration can be shrunk to a loop around the crossing point; going up from 0 to t_c we are integrating E_1, coming down we are integrating E_2, so that finally we have

$$\begin{aligned} c_2(+\infty) &\underset{\hbar\to 0}{\sim} \exp\left(-i\int_0^{t_c} d\tau E_1(\tau)/\hbar - i\int_{t_c}^{0} d\tau E_2(t)/\hbar\right)\\ &= \exp[i\Delta_{21}(t_c)/\hbar]\,, \end{aligned} \tag{4.6}$$

which is Dykhne's formula.[3]

Given the adiabatic theorem in the complex plane, this solution to the two-state problem is almost trivially simple, yet mathematically impeccable. There are, however, problems that cannot be analyzed in this way, notably the case of two or more crossing points lying on the same level line (see Ref. 4) and the atypical but not impossible case that the crossing t_c is a regular point or higher order branch point of the energy functions $E_1(t)$ and $E_2(t)$. The reader should sketch the level line patterns for these problems (see also Fig. 2 of Ref. 4), to see why the only interesting contour from the left edge of the complex plane to the right edge, along which $\mathrm{Im}\tilde{\Delta}_{21}(t)$ is nonincreasing, is the level line passing directly through the crossing point. For these cases one needs the more complicated analysis of Davis and Pechukas, which attacks the singularities at the crossing point head on.

It is instructive, finally, to compare what we learn from the adiabatic theorem along the contour C with what we know from the adiabatic theorem along the real axis.

From part (iv) of the adiabatic theorem (see Sec. III), applied along the real axis, we have

$$|c_2(+\infty)| = o(\hbar)\,. \tag{4.7}$$

From Eq. (4.6),

$$|c_2(+\infty)| \sim \exp[-\mathrm{Im}\Delta_{21}(t_c)/\hbar] = o(\hbar)\,, \tag{4.8}$$

since $\mathrm{Im}\Delta_{21}(t_c)$ is positive and $\exp[-\mathrm{Im}\Delta_{21}(t_c)/\hbar]$ therefore goes to zero faster than $\hbar$. The Dykhe formula for the $1 \to 2$ transition amplitude, obtained from the adiabatic theorem along C, is therefore consistent with the asymptotic bound on this amplitude given by the adiabatic theorem along the real axis.

Similarly, from part (iv) of the adiabatic theorem, applied along contour C, we have

$$\begin{aligned}|\tilde{c}_2(+\infty)| &= o\{\hbar\exp[-\mathrm{Im}\tilde{\Delta}_{21}(+\infty)/\hbar]\}\\ &= o\{\hbar\exp[\mathrm{Im}\Delta_{21}(+\infty)/\hbar - 2\,\mathrm{Im}\Delta_{21}(t_c)/\hbar]\}\,, \end{aligned} \tag{4.9}$$

using Eq. (4.4). From Eq. (2.19b) we know that

$$\begin{aligned}|c_1(+\infty)| &= \left|\tilde{c}_2(+\infty)\exp\left(-i\oint d\tau\tilde{E}_2(\tau)/\hbar\right)\right|\\ &= |\tilde{c}_2(+\infty)\exp[-i\Delta_{21}(t_c)/\hbar]|\\ &= |\tilde{c}_2(+\infty)|\exp[\mathrm{Im}\Delta_{21}(t_c)/\hbar]\,. \end{aligned} \tag{4.10}$$

Therefore the adiabatic theorem along C gives us an asymptotic bound on $|c_1(+\infty)|$; namely,

$$|c_1(+\infty)| = o\{\hbar\exp[\mathrm{Im}\Delta_{21}(+\infty)/\hbar - \mathrm{Im}\Delta_{21}(t_c)/\hbar]\}\,. \tag{4.11}$$

On the other hand, we know from the adiabatic theorem along the real axis that $c_1(+\infty) \to 1$ as $\hbar \to 0$. This is in fact consistent with the asymptotic bound (4.11): $\mathrm{Im}\Delta_{21}(+\infty)$ is greater than $\mathrm{Im}\Delta_{21}(t_c)$ (see Fig. 1), so all that Eq. (4.11) tells us is that $|c_1(+\infty)|$ does not go to infinity, as $\hbar \to 0$, as fast as $\hbar\exp[\mathrm{Im}\Delta_{21}(+\infty)/\hbar - \mathrm{Im}\Delta_{21}(t_c)/\hbar]$.

V. THE THREE-STATE PROBLEM

The three-state problem is more complicated than the two-state problem in two essential respects: first, there are three distinct types of pairwise curve crossings in the complex plane, namely, (12), (13), and (23) crossings; second, there is the possibility of sequential transitions involving more than one crossing point—for example, $1 \to 2 \to 3$. It is the second aspect of the problem that we shall focus on here; the first has been dis-

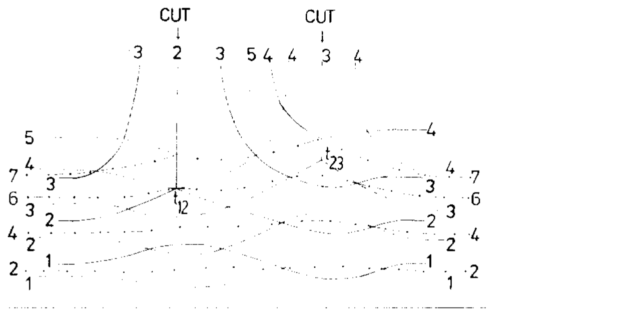

FIG. 2. Level lines of $\mathrm{Im}\Delta_{21}$ (———), $\mathrm{Im}\Delta_{32}$ (------), and $\mathrm{Im}\Delta_{31}$ (-·-·-·-·) in the upper half-plane.

cussed elsewhere in considerable detail by one of us,[11] with particular attention to the possible level line patterns for various distributions of pairwise curve crossings in the complex plane.

We assume, then, that we are given an analytic 3×3 matrix $H(t)$, real and symmetric for real t, with eigenvalues $E_1(t)$, $E_2(t)$, and $E_3(t)$ where $E_1 < E_2 < E_3$ for real t, and we shall ask for the amplitudes of transition from state 1, at $t=-\infty$, to states 2 and 3 at $t=+\infty$. We shall consider the case that the crossing points nearest the real axis are a (12) crossing and a (23) crossing, one of each; that is, we assume that (13) crossings lie farther out in the complex plane. Hwang[11] has shown that this is generally the case, and it is not hard to see why: complex crossing points are often manifestations of avoided crossings on the real axis, and a (13) avoided crossing usually indicates a (12) and/or (23), avoided crossing nearby, since $E_2(t)$ is sandwiched between $E_1(t)$ and $E_3(t)$.

It is easy to write down the generalization of Dykhne's two-state formula to this three-state problem.[5,6] Suppose the (12) crossing is at t_{12} and the (23) crossing at t_{23}, in the upper half-plane. For the amplitude of transition from state 1 to state 2 we expect the asymptotic formula $\exp[i\Delta_{21}t_{12})/\hbar]$; that is, direct transition from state 1 to state 2 at the crossing where these states connect. For the amplitude of transition from state 1 to state 3 we expect the asymptotic formula $\exp[i\Delta_{21}(t_{12})/\hbar]\exp[i\Delta_{32}(t_{23})/\hbar]$; that is, sequential transition, from state 1 to 2 at the crossing where these states connect, then from state 2 to state 3 at their crossing. Speaking anthropomorphically, we would say that the system gets from state 1 to state 3 by traveling first to t_{12}, then to t_{23}.

The main lesson of this section is that this obvious generalization of the Dykhne result is not always correct.

To proceed we have first to construct the level lines of $\mathrm{Im}\Delta_{21}$, $\mathrm{Im}\Delta_{32}$, and $\mathrm{Im}\Delta_{31}$. Figure 2 shows one possible arrangement. The figure is complicated and deserves a bit of commentary.

Near the real axis, the level lines are related to the real-time energy curves by equations like Eq. (4.3), and the level line pattern is fairly simple. What we have in Fig. 2 is evidently a (12) avoided crossing on the real axis, followed by a (23) avoided crossing, while $E_1(t)$ and $E_3(t)$ run along pretty much parallel. Notice that the level lines of $\mathrm{Im}\Delta_{31}$ can be constructed from those of $\mathrm{Im}\Delta_{32}$ and $\mathrm{Im}\Delta_{21}$, since $\Delta_{31}=\Delta_{32}+\Delta_{21}$.

We have a (12) crossing at t_{12} and a (23) crossing at t_{23}. The level line pattern of $\mathrm{Im}\Delta_{21}$ around t_{12}, and the level line pattern of $\mathrm{Im}\Delta_{32}$ around t_{23}, is as in the two-state case: at t_{12}, for instance, E_1 and E_2 are connected by a branch point of square-root type, and this is what determines the level line pattern of $\mathrm{Im}\Delta_{21}$ in the immediate vicinity of t_{12}.

As in the two-state case, we make the energies and Δ functions single valued by cutting the complex plane along the "extra" level line that grows up from each crossing point.

The other level line patterns, in the immediate vicinity of a crossing point, are not hard to unravel. Consider the (12) crossing and let E_c be the common value of E_2 and E_1 at the crossing; around t_{12} we have

$$E_2=E_c+\alpha(t-t_{12})^{1/2},\quad E_1=E_c-\alpha(t-t_{12})^{1/2}, \tag{5.1}$$

neglecting terms of order $(t-t_{12})$. $E_3(t)$ is a constant if we neglect terms of order $(t-t_{12})$: $E_3(t)\simeq E_3(t_{12})\equiv E_3$. The various Δ functions, then, are

$$\begin{aligned}
&\Delta_{21}(t)-\Delta_{21}(t_{12})\simeq(4\alpha/3)(t-t_{12})^{3/2},\\
&\Delta_{32}(t)-\Delta_{32}(t_{12})\simeq(E_3-E_c)(t-t_{12})-(2\alpha/3)(t-t_{12})^{3/2},\\
&\Delta_{31}(t)-\Delta_{31}(t_{12})\simeq(E_3-E_c)(t-t_{12})+(2\alpha/3)(t-t_{12})^{3/2},
\end{aligned}\tag{5.2}$$

the error being of order $(t-t_{12})^2$. For the case envisioned in Fig. 2, E_3-E_c lies on or near the positive real axis, so that the level lines of $\mathrm{Im}(E_3-E_c)(t-t_{12})$ run almost parallel to the real axis and $\mathrm{Im}(E_3-E_c)\times(t-t_{12})$ increases as one goes up to complex plane. One can verify from Eqs. (5.2), then, that the level lines of $\mathrm{Im}\Delta_{32}$ curve up and those of $\mathrm{Im}\Delta_{31}$ curve down as t_{12} is approached from below; the level lines of $\mathrm{Im}\Delta_{32}$ and $\mathrm{Im}\Delta_{31}$ are tangent at the crossing point t_{12}, while the curvature of each is discontinuous there; this discontinuity becomes a "kink" in the level lines as one goes up the branch cut from t_{12} (see Fig. 2).

Notice that the level lines of $\mathrm{Im}\Delta_{32}$ connect smoothly with those of $\mathrm{Im}\Delta_{31}$ across the branch cut: the slope of a (32) level line is determined by E_3-E_2 while the slope of a (31) level line is determined by E_3-E_1, and E_2 on one side of the branch cut equals E_1 on the other side. Notice also that the various functions $\mathrm{Im}\Delta_{ij}$ are continuous across the branch cut: the numerical value of, say, $\mathrm{Im}\Delta_{32}$ at a point t_l on the left edge of the branch cut equals the numerical value of $\mathrm{Im}\Delta_{32}$ at the corresponding point t_r on the right edge. This is because

$$\mathrm{Im}\Delta_{32}(t_r)=\mathrm{Im}\Delta_{32}(t_l)+\mathrm{Im}\int_{t_l}^{t_r}d\tau(E_3-E_2)(\tau), \tag{5.3}$$

where the integral from t_l to t_r is down the left edge of the branch cut, around t_{12}, and up the right edge. Since E_3 is continuous across the branch cut while E_2 connects with E_1, we have

$$\operatorname{Im}\Delta_{32}(t_r) - \operatorname{Im}\Delta_{32}(t_l) = \operatorname{Im}\int_{t_{12}}^{t_l} d\tau (E_2 - E_1)(\tau)$$
$$= \operatorname{Im}\Delta_{21}(t_l) - \operatorname{Im}\Delta_{21}(t_{12}) = 0\,. \qquad (5.4)$$

Finally, at the left and right edges of the complex plane the various level lines run parallel to the real axis and the numerical value of each function $\operatorname{Im}\Delta_{ij}$ varies linearly with $\operatorname{Im}t$, at a rate determined by the real eigenvalues of the limiting matrices $H_\pm$. For simplicity, we have illustrated in Fig. 2 a case where the eigenvalues at the left edge of the complex plane coincide with those at the right edge.

Now for a contour along which to apply the adiabatic theorem: refer to Fig. 2 and consider the contour C that follows $\operatorname{Im}\Delta_{32} = 5$ from the left edge of the complex plane up to the (12) branch cut, $\operatorname{Im}\Delta_{31} = 7$ from the (12) branch cut to the (23) branch cut, and $\operatorname{Im}\Delta_{21} = 4$ from the (23) branch cut to the right edge of the complex plane. We have to check that on C the functions $\operatorname{Im}\tilde{\Delta}_{21}(t)$ and $\operatorname{Im}\tilde{\Delta}_{31}(t)$ are nonincreasing as one goes from left to right.

Recall that these functions are defined in terms of integrals along C of the continuous functions $\tilde{E}_1(t)$, $\tilde{E}_2(t)$, and $\tilde{E}_3(t)$; to express them in terms of the functions Δ_{21}, Δ_{32}, and Δ_{31} we use the fact that

$$\tilde{E}_1 = E_1,\ \ \tilde{E}_2 = E_2,\ \ \tilde{E}_3 = E_3 \qquad (5.5)$$

to the left of the (12) branch cut,

$$\tilde{E}_1 = E_2,\ \ \tilde{E}_2 = E_1,\ \ \tilde{E}_3 = E_3 \qquad (5.6)$$

between the (12) and (23) branch cuts, and

$$\tilde{E}_1 = E_3,\ \ \tilde{E}_2 = E_1,\ \ \tilde{E}_3 = E_2 \qquad (5.7)$$

to the right of the (23) branch cut. To the left of the (12) branch cut we have

$$\operatorname{Im}\tilde{\Delta}_{21}(t) = \operatorname{Im}\Delta_{21}(t)\,, \qquad (5.8a)$$

$$\operatorname{Im}\tilde{\Delta}_{31}(t) = \operatorname{Im}\Delta_{31}(t)\,. \qquad (5.8b)$$

To calculate, say, $\operatorname{Im}\tilde{\Delta}_{31}(t)$ for t between the (12) branch cut and the (23) branch cut we write

$$\begin{aligned}\operatorname{Im}\tilde{\Delta}_{31}(t) &= \operatorname{Im}\tilde{\Delta}_{31}(t_l) + \operatorname{Im}\int_{t_r}^{t} d\tau(\tilde{E}_3 - \tilde{E}_1)(\tau)\\ &= \operatorname{Im}\Delta_{31}(t_l) + \operatorname{Im}\int_{t_r}^{t} d\tau(E_3 - E_2)(\tau)\\ &= \operatorname{Im}\Delta_{31}(t_r) + \operatorname{Im}\Delta_{32}(t) - \operatorname{Im}\Delta_{32}(t_r)\\ &= \operatorname{Im}\Delta_{21}(t_r) + \operatorname{Im}\Delta_{32}(t)\\ &= \operatorname{Im}\Delta_{21}(t_{12}) + \operatorname{Im}\Delta_{32}(t)\,, \end{aligned} \qquad (5.9a)$$

where t_l and t_r are the corresponding points on the left and right edges of the (12) branch cut where C crosses it. In similar fashion we find

$$\operatorname{Im}\tilde{\Delta}_{21}(t) = 2\operatorname{Im}\Delta_{21}(t_{12}) - \operatorname{Im}\Delta_{21}(t) \qquad (5.9b)$$

between the (12) and (23) branch cuts, and

$$\operatorname{Im}\tilde{\Delta}_{21}(t) = 2\operatorname{Im}\Delta_{21}(t_{12}) + \operatorname{Im}\Delta_{32}(t_{23}) - \operatorname{Im}\Delta_{31}(t)\,, \qquad (5.10a)$$

$$\operatorname{Im}\tilde{\Delta}_{31}(t) = \operatorname{Im}\Delta_{21}(t_{12}) + 2\operatorname{Im}\Delta_{32}(t_{23}) - \operatorname{Im}\Delta_{32}(t) \qquad (5.10b)$$

to the right of the (23) branch cut.

From Eqs. (5.8)–(5.10) it is clear that on C the functions $\operatorname{Im}\tilde{\Delta}_{21}(t)$ and $\operatorname{Im}\tilde{\Delta}_{31}(t)$ are nonincreasing as one goes from left to right. For instance, between the (12) and (23) branch cuts $\operatorname{Im}\Delta_{21}(t)$ increases along C, so from Eq. (5.9b) $\operatorname{Im}\tilde{\Delta}_{21}(t)$ decreases; since $\operatorname{Im}\Delta_{31}(t)$ is constant on C in this region, it follows that $\operatorname{Im}\Delta_{32}(t)$—and therefore, from Eq. (5.9a), $\operatorname{Im}\tilde{\Delta}_{31}(t)$—decreases on C.

Under the boundary conditions $c_1(-\infty) = \tilde{c}_1(-\infty) = 1, c_2(-\infty) = \tilde{c}_2(-\infty) = 0, c_3(-\infty) = \tilde{c}_3(-\infty) = 0$, then, the adiabatic theorem holds along C and we have $\tilde{c}_1(+\infty) \to 1$ as $\hbar \to 0$. From Eq. (5.7) we see that state 1, along C, becomes state 3 at the right edge of the complex plane; we may assume that the sign of $\phi_3(t)$, on the real axis, has been chosen so that $\tilde{\phi}_1(+\infty) = \phi_3(+\infty)$, and then the adiabatic theorem yields the asymptotic formula

$$c_3(+\infty)_{\hbar\to 0}\ \exp\left(-i\oint d\tau \tilde{E}_1(\tau)/\hbar\right)\,, \qquad (5.11)$$

where the phase integral is defined in Eq. (2.20). The path of integration is down the real axis, up the left edge of the complex plane, from left to right along C, and down the right edge; it can be shrunk to a double loop around the crossing points, from 0 up and around t_{12} and back to 0, then from 0 up and around t_{23} and back to 0. Going up to t_{12} we are integrating E_1, coming down we are integrating E_2; going up to t_{23} we are integrating E_2, coming down we are integrating E_3; therefore

$$\begin{aligned} c_3(+\infty) \underset{\hbar\to 0}{\sim} \exp\Big(&-i\int_0^{t_{12}} d\tau E_1(\tau)/\hbar - i\int_{t_{12}}^{0} d\tau E_2(\tau)/\hbar\\ &- i\int_0^{t_{23}} d\tau E_2(\tau)/\hbar - i\int_{t_{23}}^{0} d\tau E_3(\tau)/\hbar\Big)\\ = \exp&[i\Delta_{21}(t_{12})/\hbar]\exp[i\Delta_{32}(t_{23})/\hbar]\,. \end{aligned} \qquad (5.12)$$

For this case, then, the three-state generalization of Dykhne's formula is correct: the transition $1 \to 3$ is sequential, $1 \to 2 \to 3$, and the amplitude for it is the product of two-state amplitudes, each calculated from the appropriate crossing point.

We cannot calculate the transition amplitude to state 2, $c_2(+\infty)$, from this contour; the adiabatic theorem does, however, give us an asymptotic bound on the amplitude (see Sec. III), and we can ask whether the Dykhne formula $\exp[i\Delta_{21}(t_{12})/\hbar]$ is consistent with this bound. From Eq. (5.7) we see that it is state 3, on curve C, that becomes state 2 at the right edge of the complex plane. From the adiabatic theorem we know that

$$|\tilde{c}_3(+\infty)| = o\{\hbar\exp[-\operatorname{Im}\tilde{\Delta}_{31}(+\infty)/\hbar]\} \qquad (5.13)$$

and therefore—using Eq. (2.19b)—that

$$\begin{aligned}|c_2(+\infty)| = o\Big[&\hbar\exp[-\operatorname{Im}\tilde{\Delta}_{31}(+\infty)/\hbar]\\ &\times\exp\Big(\operatorname{Im}\oint d\tau\tilde{E}_3(\tau)/\hbar\Big)\Big]\,.\end{aligned} \qquad (5.14)$$

We calculate

$$\oint d\tau\tilde{E}_3(\tau) = \Delta_{32}(t_{23}) \qquad (5.15)$$

by contracting the integration path to a loop around t_{23} (there is no contribution from the crossing at t_{12} since

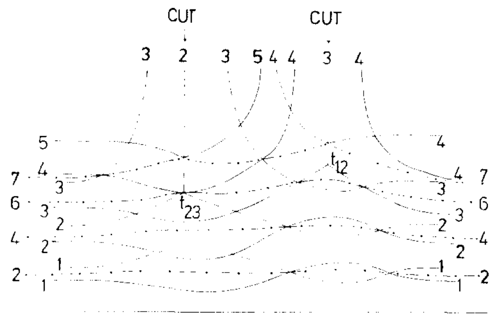

FIG. 3. Level lines of $\mathrm{Im}\Delta_{21}$ (———), $\mathrm{Im}\Delta_{32}$ (------), and $\mathrm{Im}\Delta_{31}$ (-·-·-·) in the upper half-plane.

$\tilde{E}_3 = E_3$ is analytic there). Using Eq. (5.10b), then, we have

$$|c_2(+\infty)| = o\{\hbar \exp[-\mathrm{Im}\Delta_{21}(t_{12})/\hbar] \times \exp[\mathrm{Im}\Delta_{32}(+\infty)/\hbar - \mathrm{Im}\Delta_{32}(t_{23})/\hbar]\}, \quad (5.16)$$

where $\Delta_{32}(+\infty)$ means Δ_{32} evaluated at the right end of C. $\mathrm{Im}\Delta_{32}(+\infty) - \mathrm{Im}\Delta_{32}(t_{23})$ is positive (see Fig. 2) and

$$\exp[-\mathrm{Im}\Delta_{21}(t_{12})/\hbar] = o\{\hbar \exp[-\mathrm{Im}\Delta_{21}(t_{12})/\hbar]\exp(K/\hbar)\} \quad (5.17)$$

for any positive constant K, so the Dykhne formula for the $1 \to 2$ transition amplitude is consistent with what we can deduce from the adiabatic theorem along contour C.

This does not mean, of course, that the formula is correct, but only that it might be. To calculate the $1 \to 2$ transition amplitude from the adiabatic theorem we should select a contour that passes above the (12) crossing point but below the (23) crossing point and along which the adiabatic theorem holds. The reader should try to find one; he will discover from Fig. 2 that there is no such contour, for we require—in the region to the right of the (12) branch cut—that $\mathrm{Im}\Delta_{21}(t)$ be nondecreasing and $\mathrm{Im}\Delta_{32}(t)$ be nonincreasing [see Eqs. (5.9)], and any curve along which $\mathrm{Im}\Delta_{21}(t)$ does not decrease eventually is tangent to a level line of $\mathrm{Im}\Delta_{32}$, after which point $\mathrm{Im}\Delta_{32}$ increases.

There is a way to calculate the $1 \to 2$ transition amplitude from the adiabatic theorem; it involves a slightly complicated trick which we shall explain after considering a second three-state problem, with level lines as in Fig. 3.

The reader will notice a resemblance between Figs. 2 and 3; they are in fact the same figure, with different labeling. Evidently in Fig. 3 we have, on the real axis, an avoided crossing between states 2 and 3, followed by an avoided crossing between states 1 and 2.

Consider now the contour C that follows $\mathrm{Im}\Delta_{21} = 5$ from the left edge of the complex plane up to the (23) branch cut, $\mathrm{Im}\Delta_{31} = 7$ from the (23) branch cut to the (12) branch cut, and $\mathrm{Im}\Delta_{32} = 4$ from the (12) branch cut to the right edge of the complex plane. This is in fact the same curve that we used with Fig. 2, and it is easy to verify that the functions $\mathrm{Im}\tilde{\Delta}_{21}(t)$ and $\mathrm{Im}\tilde{\Delta}_{31}(t)$ are nonincreasing as we go from left to right on C. The energies are as follows:

$$\tilde{E}_1 = E_1,\ \tilde{E}_2 = E_2,\ \tilde{E}_3 = E_3 \quad (5.18)$$

to the left of the (23) branch cut,

$$\tilde{E}_1 = E_1,\ \tilde{E}_2 = E_3,\ \tilde{E}_3 = E_2 \quad (5.19)$$

between the (23) and (12) branch cuts, and

$$\tilde{E}_1 = E_2,\ \tilde{E}_2 = E_3,\ \tilde{E}_3 = E_1 \quad (5.20)$$

from the (12) branch cut to the right edge of the complex plane. For the $\tilde{\Delta}$ functions we find

$$\mathrm{Im}\tilde{\Delta}_{21}(t) = \mathrm{Im}\Delta_{21}(t), \quad (5.21a)$$

$$\mathrm{Im}\tilde{\Delta}_{31}(t) = \mathrm{Im}\Delta_{31}(t) \quad (5.21b)$$

to the left of the (23) branch cut,

$$\mathrm{Im}\tilde{\Delta}_{21}(t) = \mathrm{Im}\Delta_{31}(t) - \mathrm{Im}\Delta_{32}(t_{23}), \quad (5.22a)$$

$$\mathrm{Im}\tilde{\Delta}_{31}(t) = \mathrm{Im}\Delta_{21}(t) + \mathrm{Im}\Delta_{32}(t_{23}) \quad (5.22b)$$

between the (23) and (12) branch cuts, and

$$\mathrm{Im}\tilde{\Delta}_{21}(t) = \mathrm{Im}\Delta_{32}(t) + \mathrm{Im}\Delta_{21}(t_{12}) - \mathrm{Im}\Delta_{32}(t_{23}), \quad (5.23a)$$

$$\mathrm{Im}\tilde{\Delta}_{31}(t) = 2\,\mathrm{Im}\Delta_{21}(t_{12}) + \mathrm{Im}\Delta_{32}(t_{23}) - \mathrm{Im}\Delta_{21}(t) \quad (5.23b)$$

from the (12) branch cut to the right edge of the complex plane. From Eqs. (5.21)–(5.23) and the level line patterns of the Δ functions in Fig. 3 it is clear that $\mathrm{Im}\tilde{\Delta}_{21}(t)$ and $\mathrm{Im}\tilde{\Delta}_{31}(t)$ are nonincreasing on C; then under the boundary condition $\tilde{c}_1(-\infty) = 1$, $\tilde{c}_2(-\infty) = \tilde{c}_3(-\infty) = 0$, the adiabatic theorem holds along C and therefore $\tilde{c}_1(+\infty) \to 1$ as $\hbar \to 0$.

From Eq. (5.20) we see that state 1, along C, becomes state 2 at the right edge of the complex plane; we may assume that the sign of $\phi_2(t)$, on the real axis, has been chosen so that $\tilde{\phi}_1(+\infty) = \phi_2(+\infty)$, and then the adiabatic theorem yields the asymptotic formula

$$c_2(+\infty) \underset{\hbar \to 0}{\sim} \exp\left(-i \oint d\tau \tilde{E}_1(\tau)/\hbar\right) = \exp[i\Delta_{21}(t_{12})/\hbar], \quad (5.24)$$

where the phase integral has been evaluated by shrinking the path of integration to a loop around t_{12} (there is no contribution from t_{23} since $\tilde{E}_1 = E_1$ is analytic there).

Equation (5.24) is of course just the Dykhne two-state formula. It is interesting to note that we got it from the adiabatic theorem along a contour that encloses *both* crossing points t_{12} and t_{23}, and interesting to note that we could not have gotten it from a contour that goes below t_{23} but above t_{12}, for there is no such contour along which the adiabatic theorem holds.

We cannot calculate the transition amplitude $1 \to 3$ from this contour, but we can get an asymptotic bound for it: since

$$|\tilde{c}_2(+\infty)| = o\{\hbar \exp[-\mathrm{Im}\tilde{\Delta}_{21}(+\infty)/\hbar]\} \quad (5.25)$$

and since state 2 along C becomes state 3 at the right edge of the complex plane (see Eq. (5.20), we have

$$|c_3(+\infty)| = o\left[\hbar \exp[-\mathrm{Im}\tilde{\Delta}_{21}(+\infty)/\hbar] \times \exp\left(\mathrm{Im} \oint d\tau \tilde{E}_2(\tau)/\hbar\right)\right], \quad (5.26)$$

by use of Eq. (2.19b). We calculate

$$\oint d\tau \tilde{E}_2(\tau) = -\Delta_{32}(t_{23}) \tag{5.27}$$

by contracting the integration path to a loop around t_{23} (there is no contribution from t_{12} since $\tilde{E}_2 = E_3$ is analytic there). Using Eq. (5.23a), we find that

$$|c_3(+\infty)| = o\{\hbar \exp[-\operatorname{Im}\Delta_{32}(+\infty)/\hbar] \times \exp[-\operatorname{Im}\Delta_{21}(t_{12})/\hbar]\}, \tag{5.28}$$

where $\Delta_{32}(+\infty)$ means Δ_{32} evaluated at the right end of C.

Equation (5.28) is the most important result in this section. It says that the Dykhne formula for the $1\to 3$ transition amplitude is wrong in this case, for $\operatorname{Im}\Delta_{32}(+\infty)$ is greater than $\operatorname{Im}\Delta_{32}(t_{23})$, and therefore as $\hbar\to 0$ $c_3(+\infty)$—whatever it may be—is negligibly small relative to the Dykhne formula $\exp[i\Delta_{32}(t_{23})/\hbar]\exp[i\Delta_{21}(t_{12})/\hbar]$.

Why does the Dykhne formula for the $1\to 3$ transition work for the case of Fig. 2 and not for that of Fig. 3? Evidently the order of the crossing points matters; apparently, to get sequential transition $1\to 2\to 3$ the (12) crossing must in some sense come earlier than the (23) crossing. This is puzzling, at first, because the complex plane is famous for not being linearly ordered—one cannot say, of two points in the complex time plane, which is the earlier—and anyone with a little imagination would think of making a $1\to 2\to 3$ transition in the case of Fig. 3 by following a contour that goes first to the (12) crossing and then backtracks to the (23) crossing. The difficulty, of course, is that the adiabatic theorem would not hold on such a contour. It is the condition that the various $\tilde{\Delta}$ functions be nonincreasing, along a contour from the left edge of the complex plane to the right edge, that imposes a natural ordering on the crossing points in the complex plane. In the case of Fig. 2 any contour that encloses both crossing points, and along which the adiabatic theorem holds, crosses the (12) branch cut first; in the case of Fig. 3, any such contour crosses the (23) branch cut first.

Remember also that complex crossing points often show up on the real time axis as avoided crossings, and it would not surprise the practical man, who refuses to leave the real axis for the complex plane, that there should be a substantial difference, in the amplitude for a $1\to 2\to 3$ transition, between the case of a (12) avoided crossing followed by a (23) avoided crossing and the case in which the (23) avoided crossing comes first.

What, then, *is* the asymptotic form of the $1\to 3$ transition amplitude, in the case of Fig. 3? Using just the adiabatic theorem and the information in Fig. 3, we cannot tell. We can improve the asymptotic bound on the $1\to 3$ amplitude by raising the contour C, until finally other crossing points are encountered. It is these crossing points higher up in the complex plane that determine the form of the $1\to 3$ amplitude: perhaps a (12) crossing to the left of the lower (23) crossing, or a (23) crossing to the right of the lower (12) crossing, or a (13) crossing, giving direct $1\to 3$ transition, between the lower (23) and (12) crossings.

We close this section by returning to the case of Fig. 2, to calculate the asymptotic form of the $1\to 2$ transition amplitude. We use the adiabatic theorem to calculate this amplitude, but indirectly.

The differential equations (2.7) for the expansion coefficients $c_j(t)$ are linear, so any solution to the three-state problem—in particular, the solution we want, defined by the boundary conditions $c_j(-\infty) = \delta_{j1}$—can be expressed as a linear combination of three linearly independent solutions. For example, we can write

$$c_j(t) = a_1\,{}^1c_j(t) + a_2\,{}^2c_j(t) + a_3\,{}^3c_j(t) \tag{5.29}$$

where the solutions ${}^ic_j$ are defined by boundary conditions at $t = +\infty$:

$${}^ic_j(+\infty) = \delta_{ij}. \tag{5.30}$$

The expansion coefficients must be chosen so that

$$\sum_i a_i\,{}^ic_j(-\infty) = \delta_{j1}. \tag{5.31}$$

From Eqs. (5.29) and (5.30) we see that these expansion coefficients give the transition amplitudes directly:

$$c_2(+\infty) = a_2, \quad c_3(+\infty) = a_3. \tag{5.32}$$

The expansion coefficients of course depend on $\hbar$; we are interested in the limit $\hbar\to 0$.

From the adiabatic theorem along the real axis, we know that as $\hbar\to 0$

$${}^ic_i(-\infty) = 1 + o(1), \tag{5.33a}$$

$${}^ic_j(-\infty) = o(1) \text{ if } i\neq j. \tag{5.33b}$$

This implies, by Eqs. (5.31), that

$$a_1 = 1 + o(1). \tag{5.34}$$

From the adiabatic theorem in the complex plane we know the $1\to 3$ transition amplitude and therefore the coefficient a_3,

$$a_3 = \exp[i\Delta_{21}(t_{12})/\hbar]\exp[i\Delta_{32}(t_{23})/\hbar][1 + o(1)] = o(1)\exp[i\Delta_{21}(t_{12})/\hbar], \tag{5.35}$$

where the second relation follows because $\operatorname{Im}\Delta_{32}(t_{23})$ is positive.

It turns out that we need only one more piece of information, namely, the value of ${}^1c_2(-\infty)$. To find it we consider the same contour used before in the analysis of Fig. 2, but now running in the opposite direction: from the right edge of the complex plane to the (23) branch cut along $\operatorname{Im}\Delta_{21} = 4$, from the (23) branch cut to the (12) branch cut along $\operatorname{Im}\Delta_{31} = 7$, and from the (12) branch cut to the left edge of the complex plane along $\operatorname{Im}\Delta_{32} = 5$. We have to check that $\operatorname{Im}\tilde{\Delta}_{21}(t)$ and $\operatorname{Im}\tilde{\Delta}_{31}(t)$ are nonincreasing as we go from right to left along this contour.

Here are the energies:

$$\tilde{E}_1 = E_1, \quad \tilde{E}_2 = E_2, \quad \tilde{E}_3 = E_3 \tag{5.36}$$

to the right of the (23) branch cut,

$$\tilde{E}_1 = E_1, \quad \tilde{E}_2 = E_3, \quad \tilde{E}_3 = E_2 \tag{5.37}$$

between the (23) and (12) branch cuts, and

$$\tilde{E}_1 = E_2,\ \tilde{E}_2 = E_3,\ \tilde{E}_3 = E_1 \tag{5.38}$$

from the (12) branch cut to the left edge of the complex plane. For the $\tilde{\Delta}$ functions we find

$$\mathrm{Im}\tilde{\Delta}_{21}(t) = \mathrm{Im}\Delta_{21}(t)\,, \tag{5.39a}$$

$$\mathrm{Im}\tilde{\Delta}_{31}(t) = \mathrm{Im}\Delta_{31}(t) \tag{5.39b}$$

to the right of the (23) branch cut,

$$\mathrm{Im}\tilde{\Delta}_{21}(t) = \mathrm{Im}\Delta_{31}(t) - \mathrm{Im}\Delta_{32}(t_{23})\,, \tag{5.40a}$$

$$\mathrm{Im}\tilde{\Delta}_{31}(t) = \mathrm{Im}\Delta_{21}(t) + \mathrm{Im}\Delta_{32}(t_{23}) \tag{5.40b}$$

between the (23) and (12) branch cuts, and

$$\mathrm{Im}\tilde{\Delta}_{21}(t) = \mathrm{Im}\Delta_{32}(t) + \mathrm{Im}\Delta_{21}(t_{12}) - \mathrm{Im}\Delta_{32}(t_{23})\,, \tag{5.41a}$$

$$\mathrm{Im}\tilde{\Delta}_{31}(t) = -\,\mathrm{Im}\Delta_{21}(t) + 2\,\mathrm{Im}\Delta_{21}(t_{12}) + \mathrm{Im}\Delta_{32}(t_{23}) \tag{5.41b}$$

between the (12) branch cut and the left edge of the complex plane. $\mathrm{Im}\tilde{\Delta}_{21}(t)$ is therefore constant along the contour, while from Fig. 2 it is evident that $\mathrm{Im}\tilde{\Delta}_{31}(t)$ decreases as we go from right to left on the contour.

The adiabatic theorem therefore applies, under the boundary conditions ${}^1c_1(+\infty) = 1,\ {}^1c_2(+\infty) = {}^1c_3(+\infty) = 0$. From Eq. (5.38) we see that state 1, along the contour, becomes state 2 at the left edge of the complex plane, and we may assume that the sign of $\phi_2(t)$, on the real time axis, is chosen so that $\tilde{\phi}_1(-\infty) = -\phi_2(-\infty)$. Then

$${}^1c_2(-\infty) \sim -\exp\left(-i \oint d\tau \tilde{E}_1(\tau)/\hbar\right)\,, \tag{5.42}$$

where the path of integration is from left to right on the real axis, up the right edge of the complex plane, from right to left on the contour, and down the left edge. We shrink the path of integration to a loop around $\tilde{t}_{12}$—there is no contribution from t_{23} since $\tilde{E}_1 = E_1$ is analytic there—and find

$$\begin{aligned} {}^1c_2(-\infty) &\sim -\exp\left(-i \int_0^{t_{12}} d\tau E_1(\tau)/\hbar - i \int_{t_{12}}^0 d\tau E_2(\tau)/\hbar\right) \\ &= -\exp[i\Delta_{21}(t_{12})/\hbar]\,. \end{aligned} \tag{5.43}$$

Now we return to Eqs. (5.31). We must have

$$a_1{}^1c_2(-\infty) + a_2{}^2c_2(-\infty) + a_3{}^3c_2(-\infty) = 0\,; \tag{5.44}$$

using Eqs. (5.33)–(5.35) and (5.43), we find

$$\begin{aligned} a_2 &= \frac{-a_1{}^1c_2(-\infty) - a_3{}^3c_2(-\infty)}{{}^2c_2(-\infty)} \\ &= \{[1 + o(1)]\exp[i\Delta_{21}(t_{12})/\hbar] \\ &\quad - o(1)\exp[i\Delta_{21}(t_{12})/\hbar]\}/[1 + o(1)] \\ &= \exp[i\Delta_{21}(t_{12})/\hbar][1 + o(1)]\,. \end{aligned} \tag{5.45}$$

Since a_2 equals $c_2(+\infty)$, Eq. (5.45) is in fact the desired asymptotic formula for the $1 \to 2$ transition amplitude:

$$c_2(+\infty) \sim \exp[i\Delta_{21}(t_{12})/\hbar]\,. \tag{5.46}$$

After some effort, then, we have recovered the Dykhne two-state formula for transition between neighboring eigenstates in the three-state case.

VI. DISCUSSION

We hope the reader is as impressed as we are by the power of the adiabatic theorem in the complex plane. Complicated problems in the dynamics of nonadiabatic transitions are reduced to structural questions: how do the energy curves look, and where do they cross? The collision theory based on curve-crossing amplitudes of the form that we derived above, that is, the theory of Miller and George,[2] does for electronically nonadiabatic problems what the Born–Oppenheimer approximation does for electronically adiabatic problems, namely, remove the electrons from the dynamics.

In a sense, then, it is a shame that we found in Sec. V a case for which the Dykhne formula fails. At first it seems absurd, that one should calculate the amplitude for a nonadiabatic transition just as for adiabatic motion, except that the phase integral of the energy must be taken around branch points where adiabatic states change into each other; later, the idea seems so marvelous that one wants it never to fail.

Much remains to be done. We would like to prove that the Miller–George theory is the correct semiclassical theory of electronically nonadiabatic collisions. The theory is so beautiful that it must be right, but one of us felt the same way about an earlier theory[12] in this field, and he was wrong, on account of a lack of mathematical rigor; so proofs are not always redundant. The original argument[2] for the Miller–George theory is suggestive: one drops the Dykhne formula into a Feynman path integral for the inelastic scattering amplitude[12] and proceeds in canonical semiclassical fashion to look for points of stationary phase; but the Dykhne formula holds only for analytic paths, while almost all the paths one integrates over in a Feynman integral are far from analytic. We believe, on the basis of some preliminary work,[11] that the adiabatic theorem in the complex plane will again prove useful in this investigation.

APPENDIX

We derive the semiclassical formula for "above-barrier reflection"[13]; that is, the reflection coefficient of a one-dimensional particle moving in a potential $V(x)$ at energies E that are greater than V for all x.

The Schrödinger equation is

$$\psi''(x) + p^2(x)\psi(x)/\hbar^2 = 0\,, \tag{A1}$$

where $p(x) = \{2m[E - V(x)]\}^{1/2}$ is the local momentum. Consider the WKB functions

$$\phi_\pm(x) = p(x)^{-1/2}\exp[\pm iS(x)/\hbar]\,, \tag{A2a}$$

$$S(x) = \int_0^{x'} dx' p(x')\,, \tag{A2b}$$

where $p(x)$ and $p(x)^{1/2}$ are positive on the real axis. We can represent an exact solution of Eq. (A1) as a linear combination of ϕ_+ and ϕ_- with variable coefficients,

$$\psi(x) = c_+(x)\phi_+(x) + c_-(x)\phi_-(x)\,. \tag{A3}$$

This representation is not unique; we make it unique by requiring that

$$\psi' = (ip/\hbar)(c_+\phi_+ - c_-\phi_-) \tag{A4}$$

for all x, which is essentially the requirement that the variable linear combination (A3) of variable-wavelength waves (A2) behave as much as possible like a fixed linear combination of plane waves. The reader may check that any function of x, not just a solution of Eq. (A1), can be represented in the form (A3) with coefficients $c_\pm$ that are uniquely determined by Eq. (A4).

If $\psi(x)$ is to satisfy the Schrödinger equation (A1), with "expansion" coefficients $c_\pm$ defined by Eq. (A4), it is necessary that these coefficients satisfy the following equations:

$$c_\pm'(x) = [p'(x)/2p(x)]\exp[\mp 2iS(x)/\hbar]c_\mp(x) . \qquad (A5)$$

Conversely, any solution of Eqs. (A5) gives, via (A3), a solution of the Schrödinger equation (A1); the Schrödinger equation and Eqs. (A5) are equivalent.[14]

To find the reflection coefficient of a particle incident on the potential from the left we must solve Eqs. (A5) under the boundary condition $c_+(+\infty)=1, c_-(+\infty)=0$; the reflection coefficient is then

$$R = c_-(-\infty)/c_+(-\infty) . \qquad (A6)$$

Equations (A5) are similar to Eqs. (2.7), for the two-state problem, except that the analogue of the two-state nonadiabatic coupling—the term $p'/2p$—occurs with the same sign in each of Eqs. (A5). This does not prevent use of the adiabatic theorem (see the discussion at the end of Sec. III). We assume, then, that $V(x)$ is analytic throughout a strip of the complex plane centered on the real axis, and we assume that $E-V$ has one zero nearest the real axis, at x_c, in the vicinity of which $E-V$ is linear in $(x-x_c)$. The momentum function $p(x)$ then has a square-root branch point at x_c, and changes sign in one circuit around x_c.

Consider the level lines of $\operatorname{Im} S(x)$ in the upper half-plane. If $E-V$ has a minimum on the real axis, at the top of the barrier, the level lines look as in Fig. 1, except that t_c of course is now x_c. We cut the plane as indicated in Fig. 1.

To apply the adiabatic theorem under the boundary condition $c_+(+\infty)=1, c_-(+\infty)=0$, we need a contour on which $\operatorname{Im}\tilde{S}(x)$ is nonincreasing as we go from right to left (the squiggle distinguishes functions evaluated on the contour from functions evaluated in the cut plane). Consider the contour C of Fig. 1. We have

$$\tilde{p}(x)=p(x), \ \operatorname{Im}\tilde{S}(x)=\operatorname{Im}S(x) , \qquad (A7)$$

to the right of the branch cut and

$$\tilde{p}(x)=-p(x), \ \operatorname{Im}\tilde{S}(x)=-\operatorname{Im}S(x)+2\operatorname{Im}S(x_c) \qquad (A8)$$

to the left. It is clear from Fig. 1 that $\operatorname{Im}\tilde{S}(x)$ is nonincreasing as we go from right to left on C, so the adiabatic theorem implies that

$$\tilde{c}_+(-\infty) \underset{\hbar\to 0}{\longrightarrow} 1 . \qquad (A9)$$

To calculate $c_-(-\infty)$ we use the fact, evident from Eq. (8), that

$$\tilde{c}_+(-\infty)\tilde{\phi}_+(x) = c_-(-\infty)\phi_-(x) \qquad (A10)$$

as x approaches the left end of C. We have

$$\tilde{\phi}_+(x) = \tilde{p}(x)^{-1/2}\exp[i\tilde{S}(x)/\hbar]$$
$$= \tilde{p}(x)^{-1/2}\exp\left(i\int_0^x dx'\tilde{p}(x')/\hbar\right) , \qquad (A11)$$

where the phase integral of $\tilde{p}$ is from 0 to $+\infty$ on the real axis, up the right edge of the complex plane, and from right to left on C. We shrink the path of integration to a loop from 0 up and around x_c and back down, then from 0 to x; using Eqs. (A7) and (A8) we find

$$\tilde{\phi}_+(x) = \tilde{p}(x)^{-1/2}\exp[-iS(x)/\hbar]\exp[2iS(x_c)/\hbar] . \qquad (A12)$$

As for the momentum, we have $\tilde{p}(x)=-p(x)$ to the left of the branch cut; to decide whether $\tilde{p}(x)^{-1/2}$ is $\pm ip(x)^{-1/2}$ we have to follow the function $\tilde{p}$ around the contour. We can see what happens from the level line diagram in Fig. 1. If dx is a displacement along a level line of $\operatorname{Im}S$, at the point where it cuts the curve C, we must have $\operatorname{Im}\tilde{p}\,dx=0$ at that point. At the right end of C, $\tilde{p}$ and $\tilde{p}^{1/2}$ are real and positive, and the level lines of $\operatorname{Im}S$ are parallel to the real axis. As we proceed to the left on C the level lines slope down to the right, so $\tilde{p}$ must slope up to the right, that is, $\tilde{p}$ and therefore $\tilde{p}^{1/2}$ move into the upper half-plane. From the pattern of level lines in Fig. 1, then, it is clear by continuity that

$$\tilde{p}(x)^{1/2} = ip(x)^{1/2} \qquad (A13)$$

at the left end of C, and we find that

$$\tilde{\phi}_+(x) = -i\exp[2iS(x_c)/\hbar]\phi(x) . \qquad (A14)$$

From Eqs. (A9) and (A10), then, we get the asymptotic form of $c_-(-\infty)$ as $\hbar\to 0$. This is the same as the reflection coefficient in the limit $\hbar\to 0$, since $c_+(-\infty)\to 1$, by the adiabatic theorem on the real axis; therefore

$$R \underset{\hbar\to 0}{\sim} -i\exp[2iS(x_c)/\hbar] . \qquad (A15)$$

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