Adiabatic Effective Lagrangians

John Moody

Department of Computer Science
Yale University
New Haven, CT 06520

Alfred Shapere and Frank Wilczek

School of Natural Sciences
Institute for Advanced Study
Princeton, NJ 08540

ABSTRACT

We discuss the general theory of effective Lagrangians and Hamiltonians in molecular physics. The Born–Oppenheimer effective Lagrangian for the nuclei involves a gauge potential, which may be nonabelian if the electronic energy levels are degenerate. We develop a systematic procedure for finding corrections to the adiabatic approximation, both perturbative and non-perturbative. The former may be incorporated directly into the effective nuclear Lagrangian.

1. The Adiabatic Approximation: General Considerations

Berry's original paper on geometric phases emphasized quantum systems influenced by external parameters [1]. He showed that when these parameters are slowly taken around a closed circuit, the wavefunction of the system may acquire a geometric phase. Although the external parameters were implicitly taken to be classical variables, many interesting applications of the same basic ideas occur in a fully quantum mechanical setting. One can form an effective Born–Oppenheimer Hamiltonian or Lagrangian for the external parameters, that incorporates the effect Berry's phase through a gauge–potential–like term [2] [3] [4]. Upon quantization, the presence of this extra term may lead to significant observable effects, such as shifted quantum numbers and level splittings.

Berry's phase is only the leading correction to the traditional Born–Oppenheimer approximation. Higher–order corrections may also be directly incorporated by adding further terms to the effective Lagrangian [5] [6].

In this paper, we hope to give a relatively unified account of the "modern" Born–Oppenheimer method. We shall discuss both the Hamiltonian and Lagrangian approaches, their relationship, and their apparent inequivalence. Our discussion must necessarily include a description of the procedure for incorporating corrections to the adiabatic approximation, and at the moment, this subject is far from closed. Accordingly, a significant portion of the paper is devoted to a discussion of the adiabatic approximation itself. It covers the Dykhne and Landau–Zener formulas, corrections to them, and geometric phases in the complex plane.

The Born–Oppenheimer approximation first arose in the context of molecular physics [7], but more generally applies whenever a system exhibits two widely separated energy scales. This approximation is often described as a separation of "slow" and "fast" variables; these are just the variables associated with the different energy scales. Quantum mechanically, the separation is made possible by the existence of a large energy gap.

In the original application to molecular physics, the gap involved is the spacing between the electronic energy levels. This gap is typically much larger than the separation between levels associated with vibrations and rotations of the nuclear degrees of freedom that do not involve re-arrangement of electronic orbitals.* Now if we want to describe the spectrum of low-energy excitations of the molecule, *i.e.*, the excitations with energy much less than the electronic energy gap, then we should be able to form a description that involves only the nuclear degrees of freedom. Indeed, at such low energies the electrons have no independent dynamics—they are "enslaved" to

---

* Often a small finite number of electronic states are actually or approximately degenerate. The formalism appropriate to this case is discussed further below. For now, we assume no degeneracy.

the nuclear degrees of freedom—because only one state is available to them. Therefore, it is possible to describe the low-energy excitations by an effective Lagrangian involving the nuclear degrees of freedom alone, with no explicit reference to the electrons. Of course the value of the numerical parameters appearing in this Lagrangian will depend implicitly upon the electrons.

We find this way of formulating the Born-Oppenheimer idea much more appropriate, and easier to generalize, than the usual formulation in terms of "fast" and "slow" variables. The connection between the two is as follows. Transitions to states separated by a large energy gap require large changes in frequency, and are therefore associated with "fast" variables. Rapid oscillations in time accompany such transitions, and lead to cancellations in processes whose characteristic time scale is much longer—that is, in processes associated with motion of the "slow" variables. Towards the end of this article we shall discuss the relationship between these two approaches more precisely. It is appropriate to mention one conclusion from that discussion now, however: we shall find that quantum variables can only be slow in a very weak sense. For example, in a path integral description the important space-time paths are not differentiable, and the typical velocity is strictly speaking infinite even for so-called "slow" variables. Nevertheless, not being fussy, we shall freely refer to "fast" and "slow" variables throughout this paper.

In quantum field theories containing heavy particles, there is a large gap between the ground state of these heavy particles—e.g., the filled Dirac sea for heavy fermions—and the energy of any excited state. Indeed, to reach an excited state with the same quantum numbers we must in general supply at least the energy to produce a particle-antiparticle pair. Suppose now that the theory contains in addition other fields, describing lighter particles. Then we should be able to describe slow space-time variations of these other fields by an effective Lagrangian that makes no explicit reference to the heavy particles. The usual jargon is to say that we can "integrate out" the heavy particle degrees of freedom. Clearly, the formation of effective Lagrangians in quantum field theory is fully analogous to the corresponding procedure in molecular physics [8]. (But notice that in field theory the heavy particles are the "fast" degrees of freedom!)

In the derivation of effective Lagrangians, we should expect—and will find—that geometric phases occur. This is particularly clear if we think in terms of path integrals. Then along any particular path the slow degrees of freedom can be considered as external parameters governing the state of the fast ones. Therefore, the amplitude for such a path can contain a geometric phase factor of the classic type. Geometric phases of this sort are connected with some of the most subtle and interesting phenomena in quantum field theory, including the occurrence of fractional quantum numbers

and anomalies [9] [10].

2. The Born-Oppenheimer Hamiltonian

We now return to the historical context of the Born–Oppenheimer approximation, to discuss the derivation of effective Hamiltonians and Lagrangians. In molecular physics, it is useful to treat the electronic and nuclear degrees of freedom as fast and slow variables, respectively. This is because the gap between electronic energy levels is typically much larger than the gap between nuclear levels, by a factor of order $(M/m)^{\frac{1}{4}}$ [7]. In the Born-Oppenheimer approximation, one solves for the electronic states in a fixed nuclear background. By the adiabatic theorem, one expects these electronic states to be approximately stationary with respect to the relatively slow motions of the nuclei. We can thus obtain an effective description for the nuclear motion, relative to a fixed electronic orbital, by integrating over electronic coordinates. We shall find that the effective nuclear Lagrangian obtained in this way involves both an ordinary potential term due to the electronic energy levels and a background gauge potential which couples to the nuclear current [2]. This gauge potential takes into account the Berry phase accumulated by the electronic wavefunctions when the nuclear coordinates change adiabatically [3].

The Born-Oppenheimer approximation begins with the full Schrödinger equation

$$(T_{\text{nuc}} + T_{\text{el}} + V)\Psi = E\Psi \tag{2.1}$$

where T_{el} and T_{nuc} are the electronic and nuclear kinetic energy terms, $V(r, R)$ contains the potential and interaction energies of the electrons and nucleons, and r and R are the electronic and nuclear coordinates. The wave function Ψ is separated into nuclear and electronic components Φ_n and ϕ_n as

$$\Psi(r, R) = \sum_n \Phi_n(R)\phi_n(r, R) \tag{2.2}$$

where the subscript n labels the electronic energy eigenstates in a fixed nuclear background. That is, $\phi_n(r, R)$ satisfies the electronic Schrödinger equation at a fixed value of R

$$[T_{\text{el}} + V(r, R)]\phi_n(r, R) = \epsilon_n(R)\phi_n(r, R) \tag{2.3}$$

In terms of the electronic eigenfunctions, the full Schrodinger equation may now be rewritten as

$$\sum_n [T_{\text{nuc}} + \epsilon_n(R)]\Phi_n(R)\phi_n(r, R) = E\sum_n \Phi_n(R)\phi_n(r, R) \tag{2.4}$$

We may now integrate out the electronic degrees of freedom to leave a system of equations for the nuclear wavefunction Ψ alone. Using bracket notation for the normalized electronic eigenstates, we get

$$\sum_n \langle \phi_m | T_{\text{nuc}} \Phi_n | \phi_n \rangle + \epsilon_m(R) \Phi_m = E \Phi_m \tag{2.5}$$

The nuclear kinetic energy operator $T_{\text{nuc}} = -\frac{1}{2M} \nabla^2$ (with $\hbar = 1$) operates on both the nuclear and electronic wavefunctions, $\Phi_n(R)$ and $|\phi_n(r, R)\rangle$. Thus the kinetic energy terms in (2.5) are proportional to

$$\langle \phi_m | \nabla_R^2 \Phi_n | \phi_n \rangle = \sum_k \left(\delta_{mk} \nabla_R + \langle \phi_m | \nabla_R \phi_k \rangle \right) \left(\delta_{kn} \nabla_R + \langle \phi_k | \nabla_R \phi_n \rangle \right) \Phi_n \tag{2.6}$$

The Born-Oppenheimer approximation applies when the mixing between different electronic levels is small, so that the off-diagonal matrix elements in Eq.(2.6) can be neglected. If, furthermore, the electronic states can be chosen to be real for each R, then $\langle \phi_n | \nabla_R \phi_n \rangle = 0$ and Eq.(2.6) reduces to

$$\left(-\frac{1}{2M} \nabla^2 + \sum_{k \neq n} \frac{1}{2M} \langle \phi_n | \nabla \phi_k \rangle \langle \phi_k | \nabla \phi_n \rangle + \epsilon_n(R) \right) \Phi_n = E \Phi_n \tag{2.7}$$

In this approximation, the nuclei propagate in a background potential

$$\tilde{\epsilon}_n(R) = \epsilon_n(R) + \sum_{k \neq n} \frac{1}{2M} \langle \phi_n | \nabla \phi_k \rangle \langle \phi_k | \nabla \phi_n \rangle$$

The peculiar extra term may be rewritten as follows:

$$\frac{1}{2M} \sum_{k \neq n} \left| \frac{\langle \phi_n | (\nabla H) | \phi_k \rangle}{\epsilon_n - \epsilon_k} \right|^2 \tag{2.8}$$

Hence, when the energy splittings between level n and the other levels are large, this term may be neglected. Berry has pointed out that it is proportional to the trace of the "natural metric" on projective Hilbert space [11].

However, it is not always possible to form a basis of electronic wavefunctions that are everywhere real. Furthermore, corrections to adiabatic evolution will involve mixings of electronic levels. We introduce the "gauge potential" notation

$$A_{mn} \equiv i \langle \phi_m | \nabla_R \phi_n \rangle \tag{2.9}$$

to account for both of these possibilities. Putting together Eqs.(2.4), (2.5), and (2.9), we can write a complete matrix-valued Schrödinger operator for the nuclear wave functions

$$H_{mn}^{\text{eff}} = -\frac{1}{2M} \sum_k \left(\delta_{mk}\nabla_R - iA_{mk}(R)\right) \cdot \left(\delta_{kn}\nabla_R - iA_{kn}(R)\right) + \delta_{mn}\epsilon_n(R)$$

(2.10)

which acts on the vector Φ_n

$$H_{mn}^{\text{eff}}\Phi_n = E\Phi_m$$

(2.11)

(The Schrödinger operator is, of course, associated with an effective Hamiltonian after the replacement $-i\nabla_R = p_R$.)

In the Born–Oppenheimer approximation, the effect of the off–diagonal matrix elements A_{mn} which mix different energy levels is ignored. Sections 4 and 5 will be devoted to a justification of this procedure; for now we simply state the result that corrections are indeed suppressed, by a factor depending on the ratio of the typical nuclear and electronic energy splittings. Then for a nondegenerate electronic level, the effective nuclear Schrödinger operator in the Born-Oppenheimer approximation is then simply

$$H_n^{\text{BO}} = -\frac{1}{2M}(\nabla_R - iA_n(R))^2 + \tilde{\epsilon}_n(R)$$

(2.12)

where $A_n \equiv A_{nn}$.

Eq. (2.12) looks like the Schrödinger operator of a charged particle in the presence of a background magnetic potential. To further strengthen this analogy, the vector field A_n even transforms like a $U(1)$ gauge potential, as we shall now explain. The phase each of the wavefunctions $|\phi_n(R)\rangle$ is arbitrary, and our description of the dynamics of the nuclei must always respect this arbitrariness. The effect of a redefinition of phases of the electronic wavefunctions $|\phi_n(R)\rangle \rightarrow e^{i\lambda_n(R)}|\phi_n(R)\rangle$, is to rotate the nuclear wavefunctions oppositely

$$\Phi_n(R) \rightarrow e^{-i\lambda_n(R)}\Phi_n(R),$$

(2.13)

so that the full wavefunction $\Psi(r, R)$ is preserved. From Eq. (2.9), we see that the gauge potential transforms just as it should:

$$A_n(R) \rightarrow A_n(R) + \nabla_R\lambda_n(R)$$

(2.14)

and it is easy to see that the overall effect of the phase redefinition is to leave the nuclear Schrödinger equation invariant (including the term (2.8)).

We conclude that the nuclei behave like charged particles in a magnetic field $B = \nabla \times A_n$. Semiclassically speaking, when the nuclei go around a closed path, the wavefunction will accumulate a geometrical phase proportional to the enclosed magnetic flux. (We will be able to see this more

clearly from the Lagrangian point of view discussed in the following section.) This phase is nothing but Berry's phase in quantum mechanical clothing—the phase that the evolving electron wavefunctions accumulate when their external parameters R are slowly varied has just been passed down to the nuclear wavefunctions.

The degenerate case is slightly more complicated; the evolution will generally involve $U(N)$ rotations among the N degenerate states [12] (provided there are no selection rules forbidding such rotations). In the adiabatic approximation, again restricting attention to a single energy level, we obtain an effective matrix Hamiltonian as in (2.10) with a $U(N)$ gauge potential A_{mn}. The N electronic eigenfunctions may now be regarded as an N–component vector; its "phase" is a $U(N)$ matrix.

For example, the effective nuclear Hamiltonian operator for a molecule with doubly degenerate electronic energy levels (labeled by $\uparrow$ and $\downarrow$) contains a $U(2)$ gauge potential:

$$H^{\mathrm{BO}} = -\frac{1}{2M}\left\{ \nabla_R - i \begin{pmatrix} A_{\uparrow\uparrow} & A_{\uparrow\downarrow} \\ A_{\downarrow\uparrow} & A_{\downarrow\downarrow} \end{pmatrix} \right\}^2 + \epsilon(R) \qquad (2.15)$$

Such a Hamiltonian arises in considering the degenerate Λ–levels of a diatomic molecule [3]. For $\Lambda = \frac{1}{2}$, there is no choice of electronic basis states for which the $U(2)$ gauge potential becomes everywhere diagonal.

To close this section, we remark that there is a much bigger symmetry group that is always present, which mixes states of different energies. The group in question is the unitary symmetry $U(\infty)$ of the electronic Hilbert space $\mathcal{H}_R$. It is difficult to see where all this symmetry has gone in the nuclear Schrödinger equation Eq. (2.7), because in choosing a decomposition of the total wavefunction in terms of electronic energy eigenfunctions, we have "fixed the gauge" down to a product of $U(N)$ factors (one factor for each N–fold degenerate level). However, there is an alternative formulation in which the full symmetry is manifest, involving a different effective Hamiltonian. We sandwich the time–dependent Schrödinger equation

$$(T_{\mathrm{nuc}} + T_{\mathrm{el}} + V)\Psi = E\Psi \qquad (2.16)$$

between a complete set of electronic states (not necessarily energy eigenstates) to obtain a matrix Schrödinger equation analogous to Eq. (2.5)*

$$i(\partial_t - iA_0)\Phi = -\frac{1}{2M}(\nabla_{R_i} - iA_i)^2\Phi + \delta_{mn}\epsilon_n(R) \qquad (2.17)$$

where $A_0 \equiv i\langle\phi_m|\dot{\phi}_n\rangle$, with the time derivative referring to the implicit time dependence of $|\phi_n(R(t))\rangle$ (but not on the "dynamical" phase factor

---

* A similar but not identical nuclear Hamiltonian has been obtained by Zygelman [13].

$\exp i \int \epsilon_n$). Under arbitrary R-dependent (and possibly time–dependent) unitary rotations that preserve (2.2),

$$\phi_n(r, R) \rightarrow \phi_m(r, R) U^\dagger_{mn}(R)$$
$$\Phi_n(R) \rightarrow U_{nm}(R) \Phi_m(R) \tag{2.18}$$

(where $U^\dagger = U^{-1}$), A_0 behaves like the time–component of a gauge field and Eq. (2.17) is fully $U(\infty)$-covariant. $A_\mu \equiv (A_0, A_i)$ is thus a 4-component $U(\infty)$ gauge potential.

3. Lagrangian Formulation

Often it is more convenient to work with a path-integral description. Phenomenological models are typically easier to formulate in terms of a Lagrangian, where symmetries are manifest. Non-equilibrium and non-perturbative problems, such as calculating tunneling amplitudes, may be easier to solve in the language of path integrals. In addition, as we shall see, it is much easier to incorporate corrections to the adiabatic approximation (which are higher–order in time derivatives) in an effective Lagrangian.

In models of the type we have been considering, effective Lagrangians (typically matrix-valued) for slow degrees of freedom arise naturally when one functional integrates over the fast variables. Generally, functional integration of a matrix-valued integrand requires extra care, to order the operators correctly [14]. But in the adiabatic approximation, if the fast variables are locked into a non-degenerate state, the effective Lagrangian is a scalar, and there is no time ordering to worry about.

As in the previous section, it is convenient to split the Lagrangian into slow and fast parts as follows

$$L = L_{\text{nuc}} + L_{\text{el}} \tag{3.1}$$

with

$$L_{\text{nuc}}(R) = \tfrac{1}{2} M \dot{R}^2 \tag{3.2}$$
$$L_{\text{el}}(r, R) = \tfrac{1}{2} m \dot{r}^2 - V(r, R). \tag{3.3}$$

The full time-evolution kernel which connects states at time t_0 to states at time t can be written as a Feynman sum over all paths from configuration (r_0, R_0) to configuration (r, R):

$$K(r_1, R_1, t_1; r_0, R_0, t_0) = \int_{R_0}^{R_1} \int_{r_0}^{r_1} \mathcal{D}[R] \mathcal{D}[r] \exp i \int_{t_0}^{t_1} dt \, (L_{\text{nuc}} + L_{\text{el}}(R, r)) \tag{3.4}$$

To form an effective Lagrangian for the nuclei, we now want to integrate (3.4) over the electron coordinates. The first step is to perform a Born-Oppenheimer separation on the molecular wavefunction, as we did in the last section:

$$\Psi(r, R) \equiv \sum_n \Phi_n(R)\phi_n(r, R) \tag{3.5}$$

As before, the electronic eigenstates $\phi_n(r, R)$ are solutions of the electronic Hamiltonian at nuclear configuration R, and the vector-valued nuclear states Φ_n are solutions of the matrix-valued nuclear Schrodinger equation (2.10).

In order to isolate the evolution of the nuclear wavefunctions, we now reorder the general path integral, separating the nuclear and electronic integrations:

$$K = \int_{R_0}^{R_1} \mathcal{D}[R]\, e^{i \int_{t_0}^{t_1} L_{nuc}(R)dt} \int_{r_0}^{r_1} \mathcal{D}[r]\, e^{i \int_{t_0}^{t_1} L_{el}(r,R)dt} \tag{3.6}$$

With respect to the decompostion of Eq.(3.5), we can express the result of the electronic path integral for a given nuclear path $R(t)$ in terms of an electronic time evolution kernel:

$$\int_{r_0}^{r_1} \mathcal{D}[r]\, e^{i \int_{t_0}^{t_1} L_{el}(r,R)dt} \equiv \sum_{mn} \phi_m(r_1, R_1, t_1)\, K_{mn}^{el}\, \phi_n(r_0, R_0, t_0) \tag{3.7}$$

where

$$K_{mn}^{el} = \mathrm{T} \exp\left(-i \int_{t_0}^{t_1} dt\, \left[\epsilon_m \delta_{mn} + i\langle\phi_m|\dot\phi_n\rangle\right]\right)$$
$$= \mathrm{T} \exp\left(-i \int_{t_0}^{t_1} dt\, \left[\epsilon_m \delta_{mn} + A_{mn}(R(t)) \cdot \dot R(t)\right]\right) \tag{3.8}$$

is the evolution kernel for the electronic eigenstates. (The notation conveys that we are to take the time ordered exponential of the operator whose mn matrix element is displayed in brackets.) This expression for the kernel comes from integrating the electronic Schrodinger equation for $|\phi_n(R(t))\rangle$

$$i\frac{d}{dt}|\phi_n\rangle = i\frac{\partial}{\partial t}|\phi_n\rangle + i|\dot\phi_n\rangle = \epsilon_n|\phi_n\rangle + i\dot R(t) \cdot \nabla_R|\phi_n\rangle$$
$$= \sum_m \left[\epsilon_n \delta_{mn} + i\langle\phi_m|\nabla_R\phi_n\rangle \cdot \dot R\right]|\phi_m\rangle \tag{3.9}$$

with respect to t. K^{el} just gives the usual dynamical evolution of the electronic energy eigenfunctions with an additional piece coming from the time-dependence of the eigenfunctions through $R(t)$. In the adiabatic limit, the

kernel effectively diagonalizes, and the nth electronic eigenstate obeys the evolution equation

$$|\phi_n(t_1)\rangle = K_{nn}^{\text{el}}(t_1, t_0) |\phi_n(t_0)\rangle = \exp\left(-i \int_{t_0}^{t_1} dt \left[(\epsilon_n + i\langle\phi_n|\dot\phi_n\rangle)\right]\right) |\phi_n(t_0)\rangle \tag{3.10}$$

The second term in the exponent is immediately recognized as Berry's phase.

With the electronic motion solved for, the nuclear kernel can now be extracted from the path integral:

$$\Phi_m(R_1) = \left\{ \int_{R_0}^{R_1} \mathcal{D}[R] \, \mathrm{T} \exp i \, S[R] \right\}_{mn} \Phi_n(R_0) \tag{3.11}$$

where the exact effective nuclear action is

$$S_{mn}^{\text{eff}}[R] = \int_{t_0}^{t_1} \left\{ \tfrac{1}{2} M \dot R^2 \delta_{mn} - i A_{mn}(R(t)) \cdot \dot R(t) - \epsilon_m(R)\delta_{mn} \right\} dt$$

$$\equiv \int_{t_0}^{t_1} L_{mn}^{\text{eff}} \, dt \tag{3.12}$$

As with the exact effective nuclear Hamiltonian (2.10), the electronic energies $\epsilon_m(R)$ contribute an effective potential for the nuclei, and the velocity-dependent potential term containing A_{mn} modifies the nuclear kinetic energy. In fact, L_{mn}^{eff} can be obtained directly from H_{mn}^{eff} by a Legendre transformation, provided one orders the matrix–valued canonical momenta correctly.

When the electronic levels are nondegenerate, the effective action (3.12) diagonalizes in the Born–Oppenheimer approximation and the time ordering in Eq. (3.11) is unnecessary. For electrons in the nth energy level, the approximate effective action is

$$S_n^{\text{BO}}[R] = \int_{t_0}^{t_1} \left\{ \tfrac{1}{2} M \dot R^2 - i A_n(R(t')) \cdot \dot R(t') - \epsilon_n(R) \right\} dt' \tag{3.13}$$

(see also [4]). Curiously, this is *not* the effective action we would have obtained after a Legendre transformation of (2.12), because it does not include the term (2.8). Order by order, the Hamiltonian and Lagrangian formulations of the Born–Oppenheimer approximations are not equivalent.

There are at least two ways one might directly try to incorporate super-adiabatic corrections in an effective Lagrangian framework. (The prefix "super-" indicates that we are looking for corrections to the adiabatic approximation; we are still concerned with the adiabatic regime.) The first is to take, in place of the scalar effective action (3.13), a matrix effective action including a small number of electronic levels, presumably those which are closest in energy to the particular level of interest. The problem with this

scheme is that one still must deal with path–ordered exponentials of matrices, and operator ordering makes the quantization of the nuclear degrees of freedom quite tricky. Another approach is to expand the full time–ordered exponential (3.11) out to some finite degree, and to incorporate this expansion directly into an effective Lagrangian for the nth level, by adding extra terms to (3.13). We shall see how to do this to the lowest super-adiabatic order in the next section.

4. Classical Corrections to Adiabatic Evolution

We now embark on a detailed study of corrections to adiabatic the adiabatic approximation. In this section, our focus will be on corrections to the evolution of electronic wavefunctions with respect to smooth, classical nuclear motions. In Section 5, from the vantage point of the electronic path integral, we briefly discuss why the quantization of the nuclei fundamentally alters the nature and size of these corrections.

The total evolution of a wavefunction which begins in an energy eigenstate is best split into two parts—the amplitude to remain in that eigenstate, and the amplitude to have a transition to another eigenstate. The first part of the problem has been beautifully treated by Berry [15] by means of an iterative procedure. The essential idea is, for a given Hamiltonian $H(t)$, to perform an iterative sequence of time–dependent unitary transformations. At each step, the transformations

$$\phi^{(i)}(t) = U_i(t)\,\phi^{(i-1)}(t)$$
$$H_i = U_i H_{i-1} U_i^\dagger - i U_i \dot{U}_i^\dagger \qquad (4.1)$$

(with $H = H_0$) are supposed to be chosen in such a way that the evolution of the transformed wavefunction with respect to the new Hamiltonian is more adiabatic than the last. The phase evolution of the original energy eigenstate ϕ_n is obtained by evolving

$$\phi^{(i)} = U_i U_{i-1} \cdots U_0 \phi_n \qquad (4.2)$$

with respect to H_i in the adiabatic approximation, and then transforming back to the original basis. This scheme is expected to converge rapidly, at least until the ith successive correction becomes comparable in magnitude to the typical amplitude for a transition to another level. At this point, the sequence of iterations begins to diverge—the expansion is asymptotic. (A similar scenario occurs in quantum field theory, where the perturbation expansion is an asymptotic series, which begins to diverge when tunneling processes become important.) Berry's procedure only gives the evolution of the *phase* of ϕ_n; changes in the magnitude of ϕ_n come from transitions to other levels, which are willfully ignored in this approximation.

In what follows, we shall consider two very different methods for calculating super-adiabatic transition amplitudes. The more straightforward approach is a version of time–dependent perturbation theory (TDPT), that explicitly separates adiabatic from super-adiabatic evolution. The other is essentially non-perturbative and involves analytic continuation into the complex time plane. The perturbative approach will enable us to give a proof of the adiabatic theorem and to find corrections. However, it is not very useful as a calculational tool, and indeed, not always very reliable. On the other hand, the non-perturbative method, embodied in Dykhne's formula and its generalizations, turns out to be quite powerful and accurate. (If some of the following material seems too abstract or technical, the reader may wish to refer to the example beginning with Eq.(4.21) for orientation.)

Adiabatic Perturbation Theory. Our discussion of time–dependent perturbation theory begins with the exact equation for evolution of the electronic wavefunction according to a time–dependent Hamiltonian. From Eqs.(3.8) and (3.9), we have

$$| \psi(t)\rangle = \sum_{mn} |\phi_m(R(t))\rangle \, U_{mn}(t, -\infty) \, \langle \phi_n(R(-\infty)) \mid \psi(R(-\infty))\rangle$$

$$U(t, -\infty) \equiv \mathrm{T}\exp\, - \, i \int_{-\infty}^{t} dt' \, [\epsilon_a \delta_{ab} + i\langle \phi_a \mid \dot{\phi}_b\rangle] \tag{4.3}$$

where for convenience we have taken $t_1 = -\infty$. In the nondegenerate case, the adiabatic approximation to it is

$$| \psi(t)\rangle_{\mathrm{ad}} = \sum_{n} | \phi_n(R(t))\rangle \left\{ \exp\, - \, i \int_{-\infty}^{t} dt' \, [\epsilon_n + i\langle \phi_n \mid \dot{\phi}_n\rangle] \right\}$$
$$\cdot \, \langle \phi_n(R(-\infty)) \mid \psi(R(-\infty))\rangle \tag{4.4}$$

We expect this adiabatic wavefunction to be a better and better approximation to the exact wavefunction, as the time dependence of the parameters $R(t)$ becomes slower and slower. To quantify this, we write

$$R(t, \tau) \equiv R(t/\tau)$$

and let $\psi_\tau(R(t))$ be the solution of the Schrodinger equation when the internal parameters vary as $R(t, \tau)$. Thus, the larger τ is, the more slowly the parameters R are changing. Note that replacing $R(t) \rightarrow R(t/\tau)$ in Eq.(4.3) is equivalent to rescaling time $t \rightarrow \tau t$ everywhere except inside of $R(t)$.

To compare the exact evolution to the adiabatic approximation, it is convenient to use the following general formula for untangling the time–ordered exponential integral of the sum of two operators:

$$\mathrm{T}\exp \int (M + N) = \mathrm{T}\exp \int M \cdot \mathrm{T}\exp \int N'$$
$$N' = \left(\mathrm{T}\exp \int M\right)^{-1} \cdot N \cdot \mathrm{T}\exp \int M \tag{4.5}$$

which is easily proved by differentiating both sides. In our example, we wish to take

$$M_{ab} = -i\epsilon_a \delta_{ab} + \langle \phi_a | \dot{\phi}_a \rangle \delta_{ab}$$
$$N_{ab} = \langle \phi_a | \dot{\phi}_b \rangle (1 - \delta_{ab}) \tag{4.6}$$

so that the true evolution is governed by $M + N$, and the adiabatic evolution by M. By means of these manipulations, the corrections to the adiabatic evolution operator in Eq.(4.3) are isolated into a compact formal expression, that is:

$$\mathrm{T} \exp \int_{-\infty}^{t} dt' \, N'(t') = \mathrm{T} \exp \int_{-\infty}^{t} dt' \left\{ \langle \phi_p | \dot{\phi}_q \rangle (1 - \delta_{pq}) \right.$$
$$\left. \cdot \exp \int_{-\infty}^{t'} dt'' \left[i(\epsilon_p - \epsilon_q) - \langle \phi_p | \dot{\phi}_p \rangle + \langle \phi_q | \dot{\phi}_q \rangle \right] \right\} \tag{4.7}$$

where we have used the fact that M is diagonal to get rid of some of the time ordering.

Our task is now to see how this expression approaches the identity operator as $\tau \to \infty$. Note first that rescaling the time variable does nothing to the integrals over $\langle \phi_p | \dot{\phi}_p \rangle$ and $\langle \phi_q | \dot{\phi}_q \rangle$, since the scale factors coming from the dt'' in the measure and from the time derivative in the integrand cancel. As we have seen in other contexts, these integrals have a purely geometric character. So, if we rescale the time, the only modification to Eq. (4.7) is to replace $(\epsilon_p - \epsilon_q)$ by $\tau(\epsilon_p - \epsilon_q)$. In other words, the slowness parameter appears only in an oscillatory exponential factor, which we expect will make the total integral very small as $\tau \to \infty$, *à la* the Riemann–Lebesgue lemma [16]. To get an idea of just how small, we expand the time–ordered exponential to first order:

$$T_{pq} = \mathrm{T} \exp \int_{-\infty}^{\infty} dt' \, N'(t')$$
$$= \delta_{pq} + \int_{-\infty}^{\infty} dt' \left\{ \langle \phi_p | \dot{\phi}_q \rangle (1 - \delta_{pq}) \right.$$
$$\left. \cdot \exp \int_{-\infty}^{t'} dt'' \left[i(\epsilon_p - \epsilon_q) - \langle \phi_p | \dot{\phi}_p \rangle + \langle \phi_q | \dot{\phi}_q \rangle \right] \right\} + \cdots$$
$$\equiv \delta_{pq} + \int_{-\infty}^{\infty} dt' \gamma_{pq}(t') \exp i\Delta_{pq}(t') + \cdots \tag{4.8}$$

To simplify this, let us redefine the phases of the wavefunctions $|\phi_n(R(t))\rangle$ for each t so that the wavefunctions are always real along the contour of integration; then $\langle \phi_n | \dot{\phi}_n \rangle = 0$. We now make three crucial assumptions,

that $\epsilon_p \neq \epsilon_q$ for all times, that γ_{pq} and $\epsilon_p - \epsilon_q$ are infinitely differentiable, and that as $t \to \pm\infty$, all derivatives of γ_{pq} and $\epsilon_p - \epsilon_q$ approach zero with sufficient rapidity. (If $R(t)$ is cyclic, the last assumption is not necessary.) Then integrating by parts, we may ignore all surface terms, and we find for the first–order term in (4.8)

$$T_{pq}^{(1)} = i \int_{-\infty}^{\infty} dt' \frac{\partial}{\partial t} \left(\frac{\gamma_{pq}}{\epsilon_p - \epsilon_q} \right) \exp i \int^{t'} dt'' (\epsilon_p - \epsilon_q) \qquad (4.9)$$

from which it follows that

$$|T_{pq}^{(1)}| \leq \left| \int_{-\infty}^{\infty} dt' \frac{\partial}{\partial t} \left(\frac{\gamma_{pq}}{\epsilon_p - \epsilon_q} \right) \right| \qquad (4.10)$$

The right–hand side scales like τ^{-1} when we scale $t \to \tau t$, so $T_{pq}^{(1)}$ goes to zero at least as fast as τ^{-1}. After n repeated integrations by parts, we obtain an expression that vanishes like τ^{-n}. In other words, $T_{pq}^{(1)}$ goes to zero faster than any power of τ. By a similar procedure, one may also show that the same is true for all *off–diagonal* higher–order terms in the expansion (4.8). This completes the proof of the adiabatic theorem.

The diagonal terms in (4.8) need not vanish so fast; indeed, they only vanish like powers of τ. For example, the pp component of the second–order term contains the non-oscillating piece

$$i \sum_{q \neq p} \int_{-\infty}^{\infty} dt' \frac{\gamma_{pq}(t') \, \gamma_{qp}(t')}{\epsilon_p - \epsilon_q} \qquad (4.11)$$

which vanishes only like τ^{-1}. This first–order correction to purely adiabatic evolution may be incorporated directly into the effective Lagrangian (3.13) as a counterterm

$$S_n^{(1)}[R] = \int_{t_0}^{t_1} dt' \left(\sum_{q \neq n} \frac{A_{nq}^i A_{qn}^j}{\epsilon_n - \epsilon_q} \right) \dot{R}_i \dot{R}_j \, \delta_{mn}. \qquad (4.12)$$

It modifies the metric on parameter space—which we have taken to be δ_{ij}—to

$$g_{ij} = \delta_{ij} + \frac{2}{M} \sum_{q \neq n} \frac{A_{nq}^i A_{qn}^j}{\epsilon_n - \epsilon_q}. \qquad (4.13)$$

Not surprisingly, Eq.(4.11) is the same expression we would have obtained by expanding the first–order phase approximant from Berry's iteration scheme in powers of τ. When Berry's nth–order phase approximant is rearranged as an expansion in τ, it must agree with the TDPT expansion

through the nth order in τ^{-1}. Both schemes diverge asymptotically. The difference with TDPT is that in principle, we might hope, it may give us information about super-adiabatic transitions.

Unfortunately, the expansion we have presented above is not very useful for actually computing off-diagonal corrections to adiabatic evolution, due to the presence of rapidly oscillating phases and the multiple integrations required to go beyond first order. And even when, say, the first order term in Eq.(4.8) can be evaluated, there may be no guarantee that the second-order term will be smaller—indeed, we shall discuss a specific example below where the higher-order corrections are larger. The moral of the story is that, in the adiabatic regime, transitions between levels are by nature non-perturbative, and attempting to treat them perturbatively is misguided.

Super-adiabatic transitions: Dykhne's formula. Much of what is known about transitions in the adiabatic limit is summarized by an elegant non-perturbative result known as Dykhne's formula [17], relating the amplitude for a transtion between two nondegenerate energy levels to the location of their common crossing point in the complex time plane. Suppose that $H(t)$ is a nondegenerate 2×2 Hamiltonian matrix, $E_1(t)$ and $E_2(t)$ are its two instantaneous energy levels, and $E_2 > E_1$ for all real times. If $E_1(t)$ and $E_2(t)$ are extendable into the complex time plane, there will typically be a point t_c where they cross. Dykhne's formula states that the transition probability to go from E_1 to E_2 as t runs from $-\infty$ to $+\infty$ is approximately

$$P_{12} \sim \exp - 2 \operatorname{Im} \int_0^{t_c} (E_2 - E_1)\, dt \qquad (4.14)$$

In general, Dykhne's formula is a good approximation when the crossing points are located far away from the real time axis. This will be true if the energy splittings and/or the typical time scale τ over which $H(t)$ changes are large. The relevant dimensionless expansion parameter is

$$\epsilon \sim \frac{\hbar}{\tau \Delta E} \qquad (4.15)$$

and Dykhne's formula states that super-adiabatic transition amplitudes are of order $\mathcal{O}(\exp - \lambda/\epsilon)$ for some positive constant λ. This is the canonical form for non-perturbative corrections to an asymptotic expansion.

It is somewhat ironic that Dykhne's formula for super-adiabatic transitions may be proved by using a version of the adiabatic theorem in the complex time plane [18]. Like the real-time adiabatic theorem, this theorem describes the approximate evolution of the projection of a wavefunction onto an energy eigenstate, along a contour in the complex plane. The idea behind the proof of Dykhne's formula (which we shall only sketch here) is to find an appropriate contour in complex time such that continuation along

the contour connects the two energy levels. For a non-degenerate two-level system, the crossing point will typically be a branch point of square root type for the function $(E_2 - E_1)(t)$. (If $E_2 > E_1$ on the real axis, we will take the branch point in the upper-half plane.) So if a wavefunction is initially in the eigenstate $\phi_1(-\infty)$ with energy $E_1(\infty)$, and if it is evolved along a contour C_{21} which goes over the branch point and across the cut, then one may compute its component in the direction $\phi_2(+\infty)$ (see Fig. 1). This will be related directly to the transition amplitude.
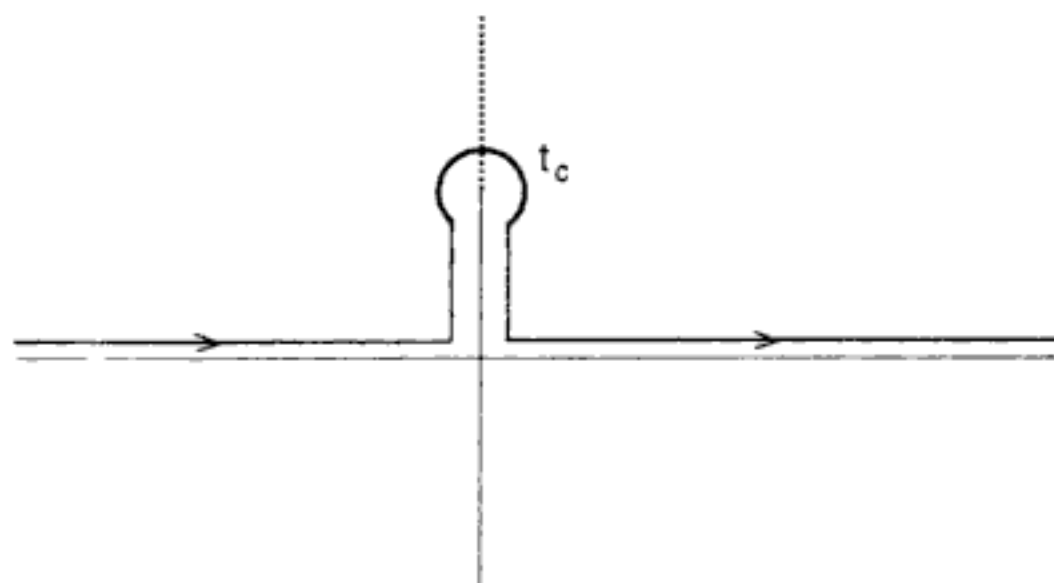
Figure 1. A contour C_{21} that connects two electronic eigenstates with energies E_1 at $t = -\infty$ and E_2 at $t = +\infty$. The function $E_1(t) - E_2(t)$ typically has a square-root branch point in the complex time plane. When the contour passes over the cut, the electron wavefunction crosses over from the E_1 to the E_2 level surface.

To be more explicit, let us choose a smooth basis of eigenstates $\phi_{1,2}(t)$ along the real time axis, and analytically continue our choice into the complex plane. Along the contour C_{21}, we also must have a smooth basis of eigenstates $|\tilde\phi_{1,2}\rangle$. Since ϕ_1 and ϕ_2 get interchanged in crossing the cut, it will generally not be possible to take $|\tilde\phi_{1,2}\rangle = |\phi_{1,2}\rangle$ everywhere. Instead, our choice along C_{21} will be as follows: to the left of the cut, we take $|\tilde\phi_{1,2}(t)\rangle = |\phi_{1,2}(t)\rangle$, but to the right, we take $|\tilde\phi_{1,2}(t)\rangle = e^{i\alpha_{2,1}}|\phi_{2,1}(t)\rangle$, where $e^{i\alpha}$ is a phase needed to make the choice of basis continuous across the cut. We shall likewise denote the energy levels along the real time axis by $E_{1,2}(t)$, and along C_{21} by $\tilde E_{1,2}(t)$; again because of the cut, $\tilde E_{1,2}(+\infty) = E_{2,1}(+\infty)$.

Finally, let $\psi(t)$ be a wavefunction evolving according to $H(t)$, initially in an eigenstate $\psi(-\infty) = \phi_1(-\infty)$. If $H(t)$ is analytic in a strip S, then

$\psi(t)$ will also be analytic and single-valued in S [19]. We may now state the result of the adiabatic theorem for evolution along C_{21}:

$$\langle \tilde{\phi}_1(+\infty)|\psi(+\infty)\rangle \simeq \exp -i \int_{C_{21}} \left[\tilde{E}_1(t) + i\langle \tilde{\phi}_1|\dot{\tilde{\phi}}_1\rangle \right] dt \qquad (4.16)$$

This is precisely of the same form as Eq.(4.4), sandwiched on the left by $\langle\phi_n|$. Just as Eq.(4.4) said nothing about the "transition" components of ψ, so Eq.(4.16) is silent about the $\tilde{\phi}_2(+\infty) = e^{i\alpha}\phi_1(+\infty)$ component (which in fact is quite large). The big difference here is that the "energies" $\tilde{E}$ need no longer be real. Hence, the norm of (4.16) need not be equal to 1; in fact, in the adiabatic limit, it will be exponentially small.

We now wish to evaluate the transition probability

$$P_{21} \equiv |\langle\phi_2(+\infty)|\psi(+\infty)\rangle|^2 \qquad (4.17)$$

The only part of (4.16) contributing to P_{21} comes from the imaginary part of the energy integral. We can put this into a convenient form by deforming the contour so that it follows along the real axis up to $t = 0$, then heads upward to the branch point, then returns to zero and continues along the real axis to infinity. The result is

$$P_{21} = \exp -2 \operatorname{Im} \int_0^{t_c} (E_2 - E_1)\, dt \qquad (4.18)$$

The transition probability is only part of the story; the phase of the transition amplitude is also of interest. From Eq.(4.16), the phase of the total amplitude is

$$\begin{aligned}
\operatorname{phase}\left(\langle\phi_2(+\infty)|\psi(+\infty)\rangle\right) \\
= e^{i\alpha} \exp -i \int_{-\infty}^0 \left[E_1 + i\langle\phi_1|\dot{\phi}_1\rangle \right] dt \\
\cdot \exp -i \int_0^{t_c} \left[\operatorname{Re}(E_1 - E_2) + i\langle\phi_1|\dot{\phi}_1\rangle - i\langle\phi_2|\dot{\phi}_2\rangle \right] dt \\
\cdot \exp -i \int_0^{+\infty} \left[E_2 + i\langle\phi_2|\dot{\phi}_2\rangle \right] dt
\end{aligned} \qquad (4.19)$$

The total phase contains, as usual, both a dynamical and a geometric component. The geometric phase itself splits into two pieces, an adiabatic phase and a *super-adiabatic* phase associated specifically with the tunneling process

$$\exp i\gamma_{1\to2} = \exp \int_0^{t_c} \left(\langle\phi_1|\dot{\phi}_1\rangle - \langle\phi_2|\dot{\phi}_2\rangle \right) dt \qquad (4.20)$$

We shall compute this phase below in the particular case of a Hamiltonian linear in t—the answer will turn out to be independent of any of the parameters appearing in $H(t)$.

The Landau-Zener formula. As an example, we now consider a Hamiltonian $H(t)$ in the vicinity of an avoided crossing, as originally studied by Landau and Zener [20] [21]. We focus upon the two levels whose energies cross, and study the equation governing their mixing in time:

$$i\frac{d\psi}{dt} = H\psi \tag{4.21}$$

$$H(t) = \begin{pmatrix} at & b \\ b & -at \end{pmatrix} = at\sigma_3 + b\sigma_1 \tag{4.22}$$

Here H is the Schrödinger operator in the two-level subspace. We have located the crossing at $t = 0$ and linearized around it, thrown away a possible constant term in the energy, and assumed $b \equiv \langle \psi_p | \dot{\psi}_q \rangle$ is real; none of these simplifications entails a loss of generality.

The eigenvalues of $H(t)$ are

$$E_{1,2}(t) = \pm\sqrt{b^2 + a^2 t^2} \tag{4.23}$$

and the crossing (a square–root branch point) is located in the upper-half t-plane at $t_c = ib/a$. Hence, according to Eq.(4.18),

$$P_{21} \simeq \exp - 2\operatorname{Im} \int_0^{t_c} 2\sqrt{b^2 + a^2 t^2}\, dt$$

$$= \exp - \pi\frac{b^2}{a} \tag{4.24}$$

Dykhne's formula works amazingly well here; in fact, this is the *exact* result obtained by Zener after a much more involved analysis. Incidentally, TDPT is worse than useless here: the first–order term in Eq.(4.8) differs from the correct amplitude by a factor of π.

To find the phase of the transition amplitude requires a little more work. First we need an explicit basis of eigenfunctions: with eigenvalue $-\sqrt{b^2 + a^2 t^2}$ we have

$$\phi_1 = \mathcal{N}_1 \begin{pmatrix} 1 \\ -\frac{at}{b} - \sqrt{1 + \left(\frac{at}{b}\right)^2} \end{pmatrix} \tag{4.25}$$

and with eigenvalue $+\sqrt{b^2 + a^2 t^2}$,

$$\phi_2 = \mathcal{N}_2 \begin{pmatrix} \frac{at}{b} + \sqrt{1 + \left(\frac{at}{b}\right)^2} \\ 1 \end{pmatrix} \tag{4.26}$$
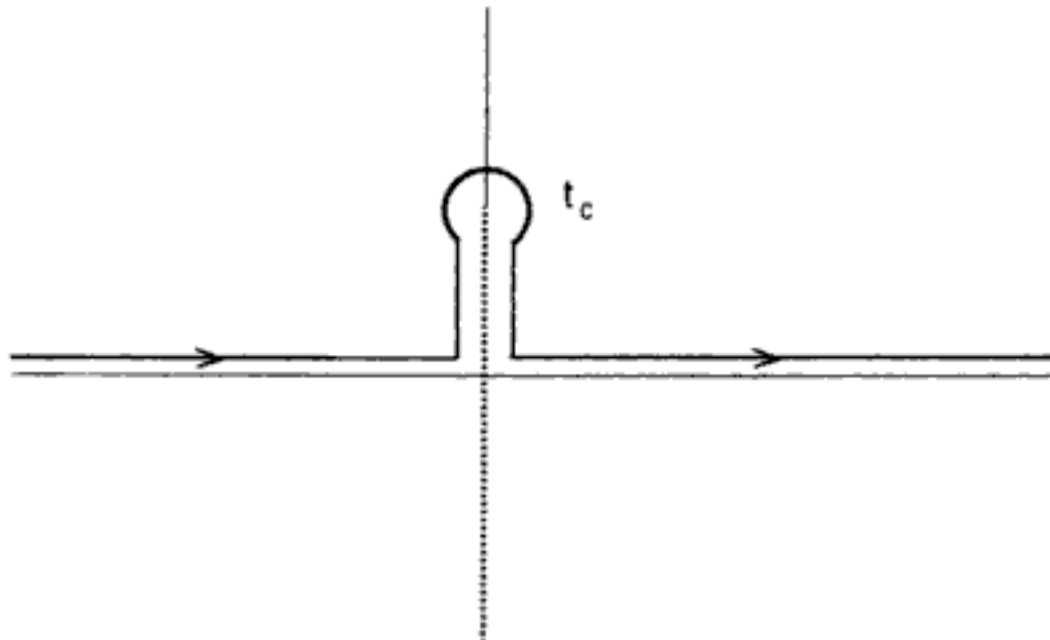
Figure 2. The same contour, from a different vantage point. This figure emphasizes that there is no discontinuity in the evolution of the electron wavefunction along the contour.

For real t, the eigenfunctions may be taken to be real, and the geometric phase receives no contribution from the integration along the real axis. For complex t, we choose the normalization $\mathcal{N}_1 = 1/\sqrt{2}$. We want to evaluate the integral

$$\int_0^{t_c} \left(\langle \phi_1|\dot{\phi}_1\rangle - \langle \phi_2|\dot{\phi}_2\rangle \right) dt = \int_C \langle \tilde{\phi}_1|\dot{\tilde{\phi}}_1\rangle \, dt \qquad (4.27)$$

along the contour shown in Fig. 2. It is important to be sure that the eigenfunctions ϕ_1 and ϕ_2 match up precisely at t_c; for this to occur, it is necessary to take $\mathcal{N}_2$ to be $i/\sqrt{2}$. Extending this choice of phase downwards, we find that ϕ_2 is imaginary along the real t-axis. The actual computation of the geometric phase (4.20) is straightforward; the result is

$$\gamma_{1\to 2} = -i\frac{\pi}{2} \qquad (4.28)$$

for a total phase of $-i$. This phase is precisely what is needed to cancel the i picked up in matching the wavefunctions at the branch point; it makes the non-dynamical part of the wavefunction real for all real times.

It is curious that the geometric phase we just computed is completely independent of a and b. In fact, we can argue that this sort of phase will arise quite generally, for Hamiltonians that are real on the real time axis. Whenever the energies cross at t_c, they will also cross at the conjugate point t_c^*. Let us join these two branch points by a cut draw contours above and below the cut, in such away that the images of the two contours are complex

conjugate (see Fig. 3). It is easy to see that the total phases obtained by integrating along either contour must also be conjugate, and since the wavefunction must be single–valued, the two phases must be equal to ± 1. Furthermore, if the contour is chosen so that the total dynamical phase vanishes, then the geometric part of the wavefunction must be real, as we found in our example above. (This argument of course does not apply to complex Hamiltonians, and in general we can obtain complex geometric phases for such processes.)
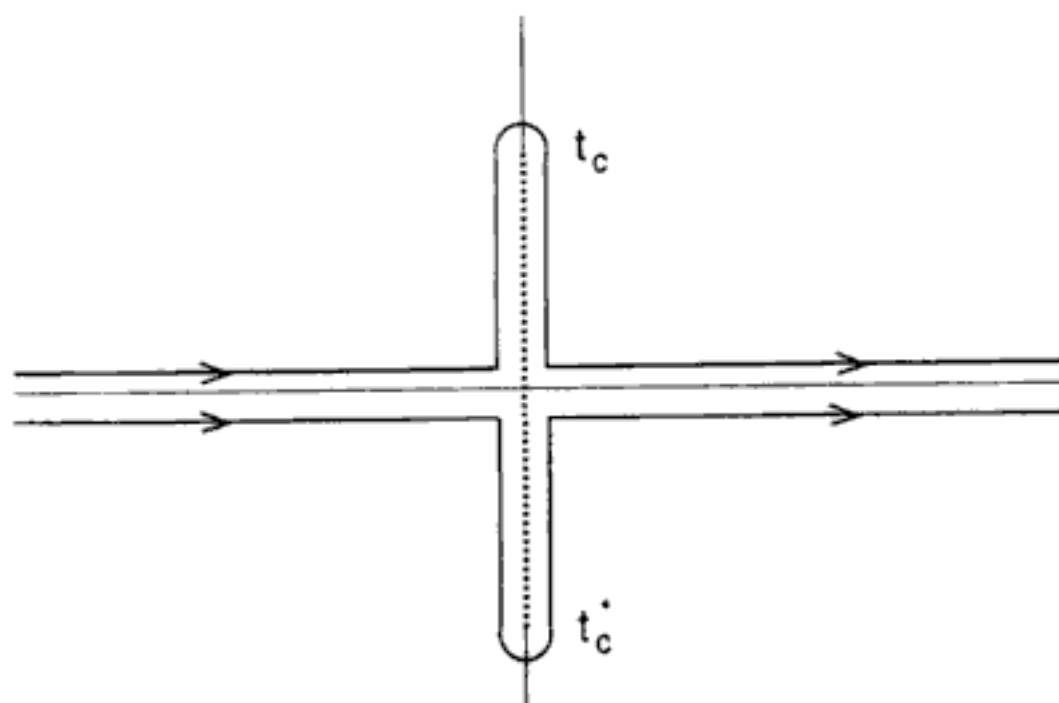
Figure 3. Real Hamiltonians will have crossings at conjugate points. The results of evolution along the lower and upper contours are conjugate, and equal.

Corrections to tunneling. We would briefly like to discuss corrections to Eqs.(4.18) and (4.19). The simplest types of corrections will come from crossing points farther from the real time axis. These will be of the same form as before, with a sum over all of the other crossing points.

Less straightforward are corrections to adiabatic evolution along a contour, modifying a super-adiabatic tunneling amplitude. To handle these, one may follow a similar prescription to the above perturbative expansion for diagonal corrections to adiabatic evolution. As in Eq.(4.7), one may separate off the adiabatic part and expand the residual path-ordered exponential; the result will be a series expansion in powers of τ. The zeroth-order term, as we have seen, is a pure geometric phase, but higher-order terms will correct both the phase and norm of the transition amplitude.

5. Quantum Corrections

In the preceding section, we discussed perturbative and non-perturbative corrections to classical adiabatic evolution. We found that corrections to the phase evolution of an energy eigenstate could be put into the form of an asymptotic expansion in powers of τ^{-1}, and that transitions could be calculated by analytically continuing a smooth nuclear path into the complex time plane.

Now we would like to understand how these conclusions are affected when the nuclear degrees of freedom are quantized. In the previous section, we assumed that the nuclear motions were infinitely differentiable, in order to derive our expansion (which involved performing successive integrations by parts) and to prove that tunneling corrections to adiabatic evolution vanish faster than any power of τ^{-1}. The delicate argument breaks down when we try to integrate over nuclear paths in quantum mechanics, because a typical path in the measure is generically *nowhere* differentiable [22]. Needless to say, for such a path, our analytic continuation method for calculating tunneling amplitudes does not apply. Furthermore, in a quantum mechanical context, there is no reason to expect the individual terms in our perturbation series to converge. Indeed, each successive term added to the effective Lagrangian, being higher-order in time derivatives than any of the preceding terms, represents a singular perturbation and diverges for a typical path. How is all this consistent with the successful use of the Born-Oppenheimer approximation in quantum mechanics? Two questions need to be asked: Do we still have a useful perturbative expansion in powers of $\dot{R}$ (and higher time derivatives) for the evolution of an eigenstate? Are tunneling processes still exponentially suppressed?

In general, this will only be true if we take matrix elements between particularly nice states. The point is the following. In passing from our effective Lagrangian to a Hamiltonian, the powers of $\dot{R}$ are converted into powers of the momentum p. (The procedure here is to treat the higher-derivative terms as perturbations, ignoring their effect on the canonical momenta, and to re-express them in terms of $p = M\dot{R}$.) Now p is an *unbounded* operator, and so our expansion "typically" diverges. However, for suitable initial and final states, p may have small matrix elements, and in that case our adiabatic expansion is useful. Similar remarks apply to semiclassical expansions around *smooth* tunneling paths.

To conclude, the validity of the adiabatic approximation in situations where the external parameters are themselves quantized is far from obvious, and should be studied on a case-by-case basis. Nevertheless, in many useful cases, the corrections are expected to be small.

References

[1] M.V. Berry, "Quantal phase factors accompanying adiabatic changes," *Proc. R. Soc. Lond. A.* **392** (1984) 45–57.

[2] C.A. Mead and D.G. Truhlar, "On the determination of Born–Oppenheimer nuclear motion wave functions including complications due to conical intersections and identical nuclei," *J.Chem.Phys.* **70**, (1979) 2284–96.

[3] J. Moody, A. Shapere, and F. Wilczek, "Realizations of magnetic–monopole gauge fields: Diatoms and spin precession," *Phys. Rev. Lett.* **56**, (1986) 893.

[4] H. Kuratsuji and S. Iida, "Effective action for adiabatic processes," *Prog.Th.Phys.* **74**(1985) 439–445

A. Bulgac, "Effective action for nonadiabatic processes," *Phys.Rev.A* **37**, (1988) 4084.

[5] R. Jackiw, "Three Elaborations on Berry's Connection, Curvature and Phase." *Int. J. Mod. Phys.* **A3** (1988) 285–297.

[6] Ph. de Sousa Gerbert, "A systematic expansion of the adiabatic phase," MIT preprint no. CTP-1537, submitted to Nuclear Physics B.

[7] A. Messiah, *Quantum Mechanics*, vol.2 (Amsterdam: North–Holland).

[8] F. Wilczek, lectures delivered at the Theoretical Advanced Study Institute in High-Energy Physics, Univ. of Michigan, 1984.

[9] Chapters 5 and 7, this volume.

[10] M. Stone, "Born–Oppenheimer approximation and the origin of Wess-Zumino terms: Some quantum mechanical examples," *Phys.Rev.D* **33** (1986) 1191;

P. Nelson and L. Alvarez-Gaume, "Hamiltonian interpretation of anomalies," *Commun.Math.Phys.* **99**, (1985) 103-114.

[11] M.V. Berry, "The quantum phase, five years later," Chapter 1, this volume.

[12] F. Wilczek and A. Zee, "Appearance of gauge structure in simple dynamical systems," *Phys. Rev. Lett.* **52** (1984) 2111.

[13] B. Zygelman, "Appearance of gauge potentials in atomic collision physics," *Phys. Lett.* **125A**, (1987) 476.

[14] L. Schulman, *Techniques and Applications of Path Integration* (New York: Wiley, 1981).

[15] M.V. Berry, "Quantum phase corrections from adiabatic iteration," *Proc. R. Soc. Lond.* A **414** (1987) 31–46.

[16] M. Reed and B. Simon, *Functional Analysis* (New York: Academic Press, 1972).

[17] A.M. Dykhne, "Adiabatic perturbation of discrete spectrum states," *JETP* **14** (1962) 941.

[18] J-T. Hwang and P. Pechukas, "The adiabatic theorem in the complex plane and the semiclassical calculation af nonadiabatic transition amplitudes," *J.Chem.Phys.* **67** (1977) 4640-4653.

[19] E.A. Coddington and N. Levinson, *Theory of Ordinary Differential Equations* (New York: McGraw–Hill, 1955).

[20] A. Zener, "Non-adiabatic crossing of energy levels," *Proc.Roy.Soc.A* **137**, (1932) 696.

[21] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics* (Oxford: Pergamon, 1977) section 52.

[22] L.F. Abbott and M.B. Wise, "Dimension of a quantum–mechanical path," *Am.J.Phys.* **49(1)** (1981) 37-39.