ADVANCES IN CHEMICAL PHYSICS VOL. 138

Editor
STUART A. RICE

ADVANCES IN CHEMICAL PHYSICS

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VOLUME 138

Series Editor

STUART A. RICE

Department of Chemistry
and
The James Franck Institute
The University of Chicago
Chicago, Illinois

WILEY-INTERSCIENCE
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Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

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Library of Congress Catalog Number: 58-9935

ISBN: 978-0-471-68234-9

Printed in the United States of America

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VOLUME 138

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

CONTENTS

THE INFLUENCE OF THE GEOMETRIC PHASE ON REACTION DYNAMICS

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CONTENTS

Advances in Chemical Physics, Volume 138, edited by Stuart A. Rice

I. INTRODUCTION

Research over the past 15 years has established that conical intersections (CIs) are much more common than previously thought, and that they play a central role in photochemistry [1, 2]. The main role of a CI is to act as a funnel, transferring population between the upper and lower adiabatic electronic states. This effect has been studied extensively, and is well known to be caused by the derivative coupling terms between the two electronic surfaces [3], which are singular at the CI. However, an accompanying effect, which has received less attention, is the so-called geometric (or Berry) phase (GP), in which the adiabatic electronic wave function changes sign upon following a closed loop around the CI [4–9]. This effect is particularly interesting when the system is confined to the lower adiabatic surface, since it is then the only nonadiabatic effect produced by the CI.

The GP affects the nuclear dynamics by introducing a corresponding sign change in the continuity boundary condition, which cancels out the sign change in the electronic wave function (in order to keep the total wave function single valued). In a model particle-on-a-ring system, with the CI at the center of the ring, the GP boundary condition changes the allowed values of M in the nuclear wave function, $\exp(iM\phi)$, from integer to half-integer values. The GP brings about analogous changes in the quantum numbers and energy levels of more realistic systems, and some of these have been predicted and observed in a variety of Jahn–Teller molecules [10–13]. One can say with some confidence, therefore, that the effect of the GP on the nuclear wave function of a bound-state system is well understood.

Until very recently, however, the same could not be said for reactive systems, which we define to be systems in which the nuclear wave function satisfies scattering boundary conditions. It was understood that, as in a bound system, the nuclear wave function of a reactive system must *encircle* the CI if nontrivial GP effects are to appear in any observables [6]. Mead showed how to predict such effects in the special case that the encirclement is produced by the requirements of particle-exchange symmetry [14]. However, little was known about the effect of the GP when the encirclement is produced by reaction paths that loop around the CI.

Very recently, this state of affairs has changed, and there is now a good general understanding of GP effects in gas-phase reactions. This has come about mainly through detailed reactive-scattering studies, both theoretical [15–37] and experimental [30–39], on the prototype hydrogen-exchange reaction ($H + H_2 \rightarrow H_2 + H$). This is the simplest reaction to possess a CI, and at high energies ($>$ 1.8eV above the potential minimum) it is just possible for some reaction paths to encircle the CI. Reactive-scattering calculations are difficult, and the first calculations that included the GP boundary condition were reported by Kuppermann and co-workers in the early 1990s [15–19]. These calculations predicted large GP effects at high energies, but unfortunately these predictions were not reproduced by later calculations [20–29], nor, most crucially, by experiment [30–39]. Instead, the experiments found no evidence at all of GP effects in the $H + H_2$ reaction. Detailed scattering data from the experiments agreed quantitatively with theoretical predictions that omitted the GP boundary condition.

This negative result seemed to imply that $H + H_2$ could not be used to investigate the effect of the GP because the nuclear wave function does not encircle the CI. However, a series of calculations by Kendrick [20–22] yielded a surprising result, which we will refer to in this chapter as the "cancellation puzzle". This is that GP effects appear in the scattering observables at specific values of the total angular momentum quantum number J, but cancel on summing over J to give the full reactive scattering wave function (describing a rectilinear collision of the reagents). This is puzzling because the sum over J is a unitary transformation in the external, angular, degrees of freedom, which describe the scattering of the products, and there is no direct relation linking this space to the GP boundary condition (which acts on the internal degrees of freedom describing motion around the CI).

This chapter surveys the work we did [25–29] to solve the cancellation puzzle, and the general explanation of GP effects in reactive systems that came out of it [27,28]. The latter uses ideas that were introduced in the late 1960s in Feynman path-integral [40] work on the analogous Aharonov–Bohm effect [41–45]. These early papers seem to have passed unnoticed in the chemical physics community, perhaps because they are written in the language of path-integral theory and algebraic topology. However, the central result of this work is surprisingly simple, and can be derived without path-integrals [27,28]. It is that the nuclear wave function has two components, and that the sole effect of the GP is to change their relative sign. One component contains all the Feynman paths that loop an even number of times around the CI; the other contains all the paths that loop an odd number of times.

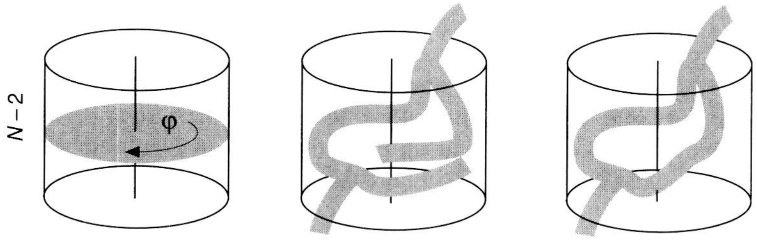
In Section II, we introduce this central result, deriving it first without path integrals, by using a diagrammatic representation of the nuclear wave function; we then give a heuristic summary of the ideas behind the early Aharonov–Bohm papers, and show how they can be combined with the diagrammatic approach. In Section III, we describe in detail the solution to the cancellation puzzle in $H + H_2$, which demonstrates how to explain GP effects in a reaction in terms of the even- and odd-looping Feynman paths. In Section IV, we discuss some further aspects of the topology, explaining the effect of particle-exchange symmetry, and the difference between GP effects in bound and reactive systems. Section V concludes the chapter.

II. UNWINDING THE NUCLEAR WAVE FUNCTION

A. Topology and Encirclement

We will consider a system with N nuclear degrees of freedom, which possesses one CI seam [1,2] of dimension $N - 2$. The topology of the nuclear space can then be represented schematically as shown in Fig. 1 [28]. The line at the center represents every CI point in the seam. Each circular cut through the cylinder represents the two degrees of freedom in the nuclear "branching space", in which the adiabatic potential energy surfaces have the familiar double-cone shape, centred about the CI point. We assume that the seam line extends throughout the entire region of energetically accessible nuclear coordinates space. We also assume that the system is confined to the lower (adiabatic) electronic state, because it has insufficient energy to approach the region of strong coupling with the upper state close to the conical intersection. The CI seam line is therefore surrounded by a tube of inaccessible coordinate space.

We then define an internal coordinate ϕ such that $\phi = 0 \rightarrow 2\pi$ denotes a a path that has described one complete loop around the CI in the nuclear branching space. Other than this, we need specify no further details about ϕ. We do not even need to specify whether the complete set of nuclear coordinates give a direct product representation of the space. It is sufficient that ϕ permits us to count how many times a closed loop has wound around the CI. Using this definition of ϕ, we can express the effect of the GP on the



(a) (b) (c)

Figure 1. (a) Diagram illustrating the topology of the N-dimensional nuclear coordinate space of a reactive system with a CI. The vertical line represents the $(N - 2)$-dimensional space occupied by the CI seam. The gray disk represents a two-dimensional (2D) branching-space cut through one point on the seam, with the angle ϕ describing internal rotation around the CI. (b) A nuclear wave function that wraps around the CI, but is not a torus, and thus exhibits only trivial GP effects. (c) A torus-shaped nuclear wave function encircling the CI. The "arms" are to be understood as extending to infinity, and are the portions of the wave function in the reagent and product channels.

adiabatic ground-state electronic wave function $\Phi(\phi)$ and the nuclear wave function $\Psi(\phi)$ as

$$\Phi(\phi + 2n\pi) = (-1)^n \Phi(\phi) \tag{1}$$

$$\Psi(\phi + 2n\pi) = (-1)^n \Psi(\phi) \tag{2}$$

The dependence on the other $N - 1$ nuclear degrees of freedom has been suppressed.

The effects of the GP are therefore the differences between the nuclear dynamics described by the wave function

$$\Psi_{\mathrm{G}}(\phi) = (-1)^n \Psi_{\mathrm{G}}(\phi + 2n\pi) \tag{3}$$

which correctly includes the GP boundary condition, and the wave function

$$\Psi_{\mathrm{N}}(\phi) = \Psi_{\mathrm{N}}(\phi + 2n\pi) \tag{4}$$

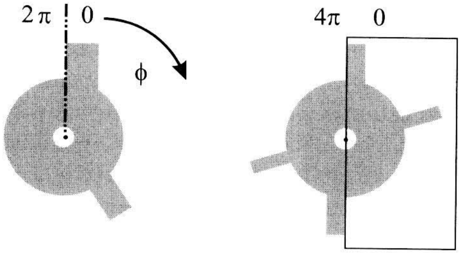
which ignores it (and is therefore physically incorrect). It is well known in the literature that the GP will only produce a nontrivial effect on the dynamics when $\Psi_{\mathrm{G}}(\phi)$ *encircles* the CI. Otherwise the effect is simply a change in the phase of $\Psi_{\mathrm{N}}(\phi)$, which has no effect on any observables. Hence, throughout this chapter, we are seeking to explain how the dynamics described by $\Psi_{\mathrm{G}}(\phi)$ differs from the dynamics described by $\Psi_{\mathrm{N}}(\phi)$, when these wave functions encircle the CI.

It is worth clarifying what is meant by encirclement. As already mentioned, the nuclear coordinates need not form a direct product, and in fact the notion of taking a cut through the nuclear coordinate space, in order to see whether $\Psi_{\mathrm{G}}(\phi)$ encircles the CI in this cut, is not useful. Figure 1(b) shows a nuclear wave function which, if a certain choice of nuclear coordinates were used, could easily be made to "encircle" the CI if a suitable 2D cut were taken. However, this particular wave function would not show nontrivial GP effects, because it does not encircle the CI: it has unconnected "ends". For nontrivial GP effects to appear, $|\Psi_{\mathrm{G}}(\phi)|^2$ must have the form of a *torus* in the nuclear coordinate space, as shown in Fig. 1(c). If one were to take a series of branching-space cuts through this wave function, none of them would encircle the CI, and hence one might get the mistaken impression that this wave function would only show a trivial phase change upon inclusion of the GP boundary condition. However, the wave function of Fig. 1(c) would definitely show strong, nontrivial GP effects. There are various ways in which one can prove this and we will mention one below. It is important to emphasise that it is $|\Psi_{\mathrm{G}}(\phi)|^2$, which has the form of a torus and not the wave function $\Psi_{\mathrm{G}}(\phi)$.

B. Symmetry Approach

To explain the effect of the GP on the nuclear dynamics [i.e., to explain the difference between the dynamics described by an encircling $\Psi_G(\phi)$ and an encircling $\Psi_N(\phi)$], we need to compare the topology of $\Psi_G(\phi)$ with the topology of $\Psi_N(\phi)$. In Section II. C, we review how this can be done using the homotopy of the Feynman paths [41–45] that make up these wave functions. But first, to demonstrate the simplicity of the problem, we use the diagrammatic approach developed in Refs. [27 and 28].

We represent the internal coordinate space occupied by the nuclear wave function as shown in Fig. 2. The gray area represents the energetically accessible region of the potential energy surface; the conical intersection is the point at the center; the arms represent the reagent entrance and product exit channels. To simplify the discussion, we place a restriction on ϕ (which will be relaxed later), stating that ϕ tends to a constant value as the system moves down the entrance or exit channel toward an asymptotic separation of the reagents or products. This places no restriction on the generality of the diagram, other than that the conical intersection should be located in the "strong-interaction region" of the potential energy surface, where all the nuclei are close together. Note that, although we have restricted the number of product channels to one, the diagram is immediately generalizable to systems with multiple product channels. We also assume that the reaction is bimolecular (leaving unimolecular reactions until Section II.D), which means that it is initiated at the asymptotic limit of the reagent channel, at the value of ϕ that is reached in this limit. We will define this to be $\phi = 0$.



(a) (b)

Figure 2. (a) Schematic picture of the potential surface of a reactive system, indicating that there is an energetically accessible (gray) "tube" through the potential surface, permitting encirclement of the CI (dot at center). The "arms" are the reagent and product channels. (b) The same surface, represented in the $0 \rightarrow 4\pi$ cover space. The rectangle represents a $0 \rightarrow 2\pi$ sector that can be cut out of the double space so as to map back onto the single space, where the $\phi = 0$ and $\phi = 2\pi$ "edges" are joined together at the cut line (chains).

Figure 2(b) represents the potential surface of the identical system, mapped onto the double-cover space [28]. The latter is obtained simply by "unwinding" the encirclement angle ϕ, from $0 \rightarrow 2\pi$ to $0 \rightarrow 4\pi$, such that two (internal) rotations around the CI are represented as one in the page. The potential is therefore symmetric under the operation $\hat{R}_{2\pi}$ defined as an internal rotation by 2π in the double space. To map back onto the single space, one cuts out a 2π-wide sector from the double space. This is taken to be the $0 \rightarrow 2\pi$ sector in Fig. 2(b), but any 2π-wide sector would be acceptable. Which particular sector has been taken is represented by a cut line in the single space, so in Fig. 2(b) the cut line passes between $\phi = 0$ and 2π. Since the single space is the physical space, any observable obtained from the total (electronic + nuclear) wave function in this space must be independent of the position of the cut line.

To construct a diagrammatic representation of the wave function, we start in the double space, as shown in Fig. 3a. The arrow at the top indicates that the incoming boundary condition is applied here, and the arrows at each of the other channels indicate outgoing boundary conditions. Note that we are treating the second appearance of the reagent channel (at $\phi = 2\pi$) as though it were a product channel, and are treating the second appearance of the product channel (in the $2\pi \rightarrow 4\pi$ sector) as though it were physically distinct from the first appearance of this channel, which is indicated by the use of wavy lines. Consequently, the wave function Ψ_e is neither symmetric nor antisymmetric under $\phi \rightarrow \phi + 2\pi$, which means it cannot be mapped back onto the physical space independently of the position of the cut line. In other words Ψ_e is the wave function of a completely artificial system.

To construct wave functions that can be mapped back onto the physical space, one needs to take symmetric and antisymmetric linear combinations of $\Psi_e(\phi)$ and $\Psi_o(\phi) = \Psi_e(\phi + 2\pi)$, and these are illustrated in Fig. 3b. It is then

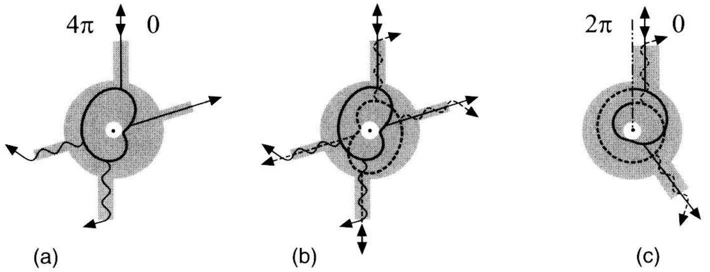


Figure 3. (a) The unsymmetrised nuclear wave function Ψ_e (solid line) in the double space. The arrows indicate the application of incoming and outgoing scattering boundary conditions, (b) The symmetrized linear combinations of Ψ_e (solid) and Ψ_o (dashed), which yield $\Psi_{N/G} = 1/\sqrt{2}[\Psi_e \pm \Psi_o]$. (c) The same functions mapped back onto the single space.

clear that these functions can mapped onto the physical space (Fig. 3c), and that they correspond to Ψ_N and Ψ_G, respectively. Thus we may write,

$$\begin{aligned}\Psi_G &= \frac{1}{\sqrt{2}}[\Psi_e + \Psi_o] \\ \Psi_N &= \frac{1}{\sqrt{2}}[\Psi_e - \Psi_o]\end{aligned} \tag{5}$$

This equation is the main result needed to explain the effect of the GP on the nuclear dynamics of a chemical reaction. Clearly, the sole effect of the GP is to change the relative sign of Ψ_e and Ψ_o. Within each of these functions the dynamics is completely unaffected by the GP. We emphasize that, despite remaining unnoticed for so long in the chemical physics community, Eq. (5) is exact.

If we can compute Ψ_G and Ψ_N numerically (as described below), it is therefore trivial to extract Ψ_e and Ψ_o by evaluating

$$\begin{aligned}\Psi_e &= \frac{1}{\sqrt{2}}[\Psi_N + \Psi_G] \\ \Psi_o &= \frac{1}{\sqrt{2}}[\Psi_N - \Psi_G]\end{aligned} \tag{6}$$

Once one has extracted Ψ_e and Ψ_o, an explanation of the GP effect on the nuclear dynamics will follow immediately. The dynamics in Ψ_e is decoupled from the dynamics in Ψ_o, and thus any observable will show GP effects only if the corresponding operator samples Ψ_e and Ψ_o in a region of space where these functions overlap. In a nonencircling nuclear wave function, Ψ_e and Ψ_o never overlap, and this gives us a diagrammatic proof (Fig. 4) of the well-known result that a nonencircling wave functions shows no nontrivial GP effects.

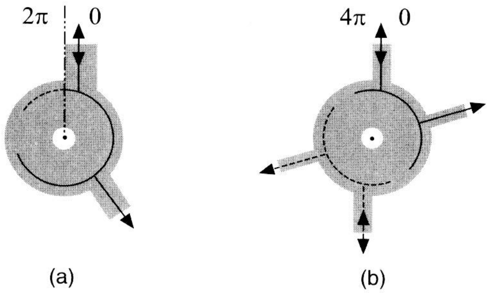


Figure 4. (a) Single- and (b) double-space representations of Ψ_e (solid) and Ψ_o (dashed) for a system that does not encircle the CI.

C. Feynman Path Integral Approach

We now explain the physical significance of the two components Ψ_e and Ψ_o in terms of the path integral theory developed in Refs. [41–45]. This theory was developed originally to treat the Aharonov–Bohm system, in which an electron encircles, but does not touch, a magnetic solenoid. The vector potential of the solenoid has an effect that is exactly equivalent to the application of the GP boundary condition, and scattering boundary conditions are applied at long range. The Aharonov–Bohm system is therefore exactly analogous to a nuclear wave function in a reactive system that encircles a CI.

To avoid discouraging the reader, we point out that only a few, basic concepts of path integrals are required. We review these here in a heuristic manner, beginning with the celebrated result of Feynman and Hibbs [40], which is that the time-evolution operator or Kernel, $K = \exp(-i\hat{H}t/\hbar)$, can be constructed using

$$K(\mathrm{x}, \mathrm{x}_0|t) = \int \mathcal{D}\mathrm{x}(t) e^{iS(\mathrm{x},\mathrm{x}_0)/\hbar} \tag{7}$$

Here, $\mathcal{D}\mathrm{x}(t)$ represents the sum over all possible paths connecting the points x and x_0 in the time interval t, and S is the classical action evaluated along each of these individual paths. It is useful to point out two properties of this expression: (1) the overall sign of the Kernel is arbitrary, because S is only defined up to an overall constant (because S is the time integral over the Lagrangian, and the latter is only defined up to a total derivative in t [46]); (2) each path has equal weight, so the relative contribution of a given path to the sum is determined by the extent to which it is canceled out by its immediate neighbors.

Any prediction expressed in the language of path integrals must have an equivalent formulation in the language of wave functions. Point (1) is equivalent to saying that a wave function is only specified up to an overall phase factor. Point (2) can be thought of as saying that, when computing $K(\mathrm{x}, \mathrm{x}_0|t)$, all possible paths between x and x_0 in time t are coupled. If we start with one particular path between x and x_0, then we need to know all of its immediate neighbors, in order to assess the extent to which this path is canceled out by them. These neighbouring paths are obtained by all possible tiny distortions that can be applied to the first path. We then need to know all of the immediate neighbors of each of the latter paths (in order to assess the extent to which each of these is canceled out), and then we need to find out the immediate neighbors of the new paths, and so on. In other words, if we start with one particular path between x and x_0, then this path is coupled (in the sense just described) to all the other paths into which it can be continuously deformed. This is equivalent to saying that one cannot accurately compute just part of a wave function; one must compute all of it, since all parts of the function are coupled by the Hamiltonian operator.