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# Quantum Tunneling in Complex Systems

The Semiclassical Approach

With 62 Figures



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To E. and K. and E.

## Preface

Tunneling is a genuine quantum effect, a direct consequence of the matter wave structure of quantum mechanics. Recent progress in engineering and manufacturing aggregates on the nanoscopic and mesoscopic scale have led to fascinating developments in directly influencing and controlling quantum properties in general, and tunneling in particular. In parallel, an exciting exchange of experimental techniques and theoretical concepts from fields such as atomic, molecular, and condensed matter physics has emerged. The aim of this book is to provide a survey of one of the most powerful theoretical tools to describe tunneling, namely, the semiclassical approximation, and to show that tunneling phenomena are central issues in this fast rising interdisciplinary field.

The literature about quantum tunneling is enormous, and that about semiclassics as well. The intention here is to discuss tunneling from a semiclassical perspective, which in turn means that this book does not address tunneling in general nor the general methodology of the semiclassical approximation. Tunneling probabilities for one dimensional anharmonic systems can be evaluated by means of semiclassical expansions whenever energy scales, on which the barrier penetration occurs, are large compared to some intrinsic quantum mechanical energy scales of the systems. This concept has been generalized to tunneling events in presence of dissipative environments, where rate constants characterize the time scale for transmission. For multi-dimensional systems, particularly for those with non-regular phase space structures, or for time dependent approaches to capture tunneling, however, general conditions are hard to formulate and may depend on specific features of the problem under consideration. In fact, in practical applications semiclassical calculations are often more accurate than expected from general estimates, which may be one reason for their widespread and successful use in physics and chemistry. In situations such as dissipative tunneling through high barriers, numerically exact treatments are either prohibitive or so demanding that semiclassical methods are basically the only tools for a proper description. In other cases, where exact results are available, semiclassical considerations often provide a better understanding for our physical intuition and serve as starting points for elegant approximate developments.

Complex quantum systems which allow for manipulations are inevitably embedded in some sort of surrounding. This can be either an external control field, static or time dependent, a small number of additional degrees of freedom generating non-regular dynamics, or a dissipative background leading to energy exchange and fluctuations. The tunneling degree of freedom itself can be even a collective degree of freedom consisting of a macroscopically large number of microscopic entities, which has led to fundamental questions like e.g. if and if yes, to what extent quantum mechanical properties could be realized on a macroscopic level. Phenomenologically, tunneling in these complex systems displays a rich variety of facets depending on macroscopic parameters such as temperature, spectral bath densities, driving amplitudes and frequencies, magnetic and electric fields.

In this book theoretical results are applied to and illustrated by explicit realizations ranging in length from the subatomic scale of a few fermi (fm) to the mesoscopic scale of a few microns ( $\mu$ m), thus covering systems over nine orders of magnitude and objects as diverse as nuclei, ensembles of atoms, molecular structures, and superconducting circuits. Owing to my own scientific background in condensed phase systems, these examples must reflect a personal viewpoint and only in this sense can be understood as representative. The same is true for the semiclassical approaches and formulations: I did not attempt to give a comprehensive account so that some of them may deserve a deeper presentation, others are addressed only briefly.

Science is a social event and so this book would not have been possible without intensive collaborations and discussions with many colleagues from different fields in physics and chemistry. Particularly, I benefited from and enjoyed to work with H. Grabert, F. Grossmann, P. Hänggi, G.-L. Ingold, P. Pechukas, E. Pollak, C. Rummel, D. Tannor, M. Thoss, and U. Weiss. I am indebted to the Quantronics group at the CEA Saclay, particularly D. Esteve, H. Pothier, C. Urbina, D. Vion, for wonderful collaborations and thank G. Buntkowsky, D. Haviland, A. Lupascu, J. Pekola, and W. Wernsdorfer for their help in understanding experimental details and providing some of the figures. I am grateful as well to my students M. Saltzer and M. Duckheim for their important contributions, critical questions, and ideas.

Some results discussed in this book have been obtained during extended stays and short time visits at other places: as a fellow of the Alexander von Humboldt Foundation at the Columbia University, New York; as a Heisenberg fellow of the German Science Foundation at the CEA Saclay, the Weizmann Institute of Science, the Technical University of Helsinki, and the University of Geneva. I have always enjoyed the warm hospitality of my host institutions.

Most importantly, I deeply thank my wife Evangelia and our children Katerina and Elias for their never ending patience and embracing love.

Freiburg, October 2006 Joachim Ankerhold

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## Introduction

A semiclassical description of tunneling in systems with complex dynamics requires an arsenal of theoretical techniques adapted to the problem under investigation. Conceptually, two types of processes are usually distinguished, namely, coherent and incoherent tunneling. The former one appears in biand multistable potentials and, more precisely, should be termed quantum coherence. It originates from the coherent overlap of wave functions located in individual domains, which are separated by energy or phase-space barriers. The latter one describes the situation, where in the language of scattering theory asymptotic states in the distant past do not overlap in the distant future with those that have penetrated a barrier. Accordingly, incoherent tunneling is seen in scattering processes between two reservoirs and in the decay of metastable states into a continuum. However, in presence of interaction with environmental degrees of freedom coherent tunneling dynamics can be destroyed leading to relaxation via incoherent decay as well.

#### 1.1 Theoretical Concepts

The earliest approach to determine tunneling amplitudes is based on an approximate solution of the stationary Schrödinger equation in terms of an expansion in  $\hbar$  for the energy dependent wave function. Technically, this WKB treatment necessitates a matching of semiclassical wave functions, which in general is quite a cumbersome task. Hence, modern semiclassical expansions are dominantly based on the path integral representation of quantum mechanics, in particular, of the time evolution operator, of the statistical operator for the thermal equilibrium, and, as a combination of both, of the nonequilibrium density matrix. The path integral naturally operates with trajectories which in a semiclassical approximation correspond to orbits minimizing the action. A further advantage is that this formulation allows for the inclusion of additional degrees of freedom, most importantly, of a thermal heat bath. We will not explain details of the path integral formulation here, especially

their mathematical subtleties, and refer the reader to excellent books such as [1, 2, 3, 4, 5, 6]. The same is true for the semiclassical expansion, which has grown into a sub-field of theoretical physics, but is used in the sequel only with respect to tunneling. More information is provided by the extensive literature, e.g. in [7, 8, 9].

Tunneling, as quantum mechanics in general, has two perspectives: a time independent one in the energy domain and a dynamical one in the time domain (cf. also Fig. 1.1). For all conservative systems a description in the energy domain is feasible independent of whether they are pure or mixed according to an energy dependent distribution. Hence, approaches to calculate transmission probabilities (WKB) and energy averaged tunneling rates (thermodynamic methods) have been developed starting from microcanonical or canonical formulations. However, in case of external time dependent driving or dissipation a time dependent approach is necessary. Indeed, even in cases of wave packets penetrating barriers at fixed energies reveals a dynamical semiclassical picture aspects of the tunneling event that cannot be gained merely from transmission probabilities. In the last decade, intensive research to develop proper semiclassical propagation schemes has provided deeper insight into the failure of standard Gaussian semiclassics to capture deep tunneling. Eventually, the time evolution for systems out of equilibrium



Fig. 1.1. Structure of this book.

in terms of reduced density matrices, described in the context of dissipative quantum systems, has turned out to be extremely challenging. A proper semiclassical approximation is highly desired since the formally exact path integral expressions can in general not be evaluated analytically and in the long time domain, where tunneling happens to occur, not even numerically.

For systems coupled to a heat bath, quantum mechanical tunneling dominates only at sufficiently low temperatures, while at high temperatures energy barriers are surmounted via classical thermal activation. Theories for tunneling thus merge with rate theories developed originally for chemical systems and indeed, many semiclassical concepts for tunneling have been derived in the 1970s in the community of physical chemistry. Physics joined these efforts essentially in the early 1980s, partially triggered by the experimental progress to fabricate electrical devices on the mesoscopic scale. The latter ones allowed for the first time to study tunneling processes under well controlled conditions and gave rise to the most accurate verifications of theoretical rate expressions. In this century experimentalists have been extending their technology to actually design, tailor and manipulate quantum matter on ever larger scales. Ensembles of atoms reach the size of mesoscopic devices and mesoscopic devices are used to implement artificial atoms. Theory is again the complementary part in this exciting adventure.

However, the semiclassical methodology for tunneling processes is not completely developed yet, there still exist more or less "white patches". Examples include tunneling in systems with mixed phase space and tunneling through multi-dimensional barriers, where substantial progress has not been achieved so far. Some of the fundamental subtleties which one encounters are addressed in this book. For a further reading on concepts for quantum tunneling we refer to the literature, for instance: Tunneling in general is reviewed in [10]; dissipative quantum systems and applications to tunneling are presented in [11, 12] and approaches for calculations of rate constants are outlined in [13].

#### 1.2 Physical Systems

In this book we are primarily interested in complex systems, a notion which certainly needs some clarification. Roughly speaking, we call a tunneling system complex when its phenomenology exhibits qualitatively different aspects of tunneling while sweeping through the space of external and/or internal parameters. Typically, there is some relation to the underlying physical realization, which then is built up of more than one degree of freedom or influenced by additional external and/or intrinsic forces. A prominent example is the tunneling of the superconducting phase difference in Josephson junctions, where this phase is actually a collective coordinate of the superconducting condensates and as such its dynamics affects a physical system with macroscopically many degrees of freedom. Other examples of collective processes have been discovered in fission events of nuclear matter, collapse of Bose-Einstein condensates, or tunneling of magnetization in molecular nanomagnets. As a direct consequence, the interaction with residual degrees of freedom, e.g. electromagnetic modes in a circuit, vibronic degrees of freedom in molecules, phonons in condensed phase, is inevitable. Barrier penetration in presence of dissipative environments includes changeovers from coherent to incoherent dynamics, from thermal activation to deep tunneling, and even to localization. Another facet of tunneling appears in two- or higher dimensional systems when the corresponding classical dynamics is non-regular with chaotic phase space structures leading to distributions of tunneling probabilities which may strongly oscillate as functions of energy. Complexity also arises due to the application of external time dependent fields during the barrier penetration. The absorption of photons typically influences transmission rates substantially leading e.g. in case of decay from a metastable well to intrawell excitations and resonant tunneling. A similar situation can be found for atoms in strong external laser fields, which drives valence electrons out of the Coulomb-well and re-scatters them when the phase of the field changes.

To illustrate this rich phenomenology, examples on length scales from nuclei to mesoscopic devices are discussed in this book. Specifically, we will discuss fission of nuclear matter, collapse of cold atomic gases with attractive interaction, nanomagnets in form of molecular complexes, rotational tunneling in dihydride-metal compounds, and macroscopic quantum phenomena in Josephson junction devices including tunneling of quantum bits. To concentrate on the essential features and not to overload this presentation a deeper analysis of the respective systems had to be excluded. More details are contained in e.g. [14] for systems on the molecular level, in [15] for Macroscopic Quantum Tunneling and in [16] for spin tunneling in nanomagnets; for the semiclassical approximation of transport phenomena in mesoscopic physics [17] provides a thorough overview.

#### 1.3 Structure of the Book

The structure of the book closely follows the discussion of the theoretical concepts above and is sketched in Fig. 1.1. In the next Chap. 2 some basic results from the semiclassical theory are collected and the relevant notation is introduced. The remaining Sections deal with tunneling of individual wave packets on the one hand and with tunneling of ensembles described by density matrices on the other hand. The wave packet aspect is discussed in Chap. 3 in the energy domain, while in Chap. 4 dynamical approaches are outlined, particularly, for externally driven tunneling. In addition in Chap. 3 two powerful thermodynamic approaches for rate calculations are introduced, the bounce and the instanton method, however, without taking into account dissipation so that they can be regarded as effective means to perform thermal averages over tunneling rates of individual (quasi-)eigenstates. The basic structure of the corresponding semiclassical procedures becomes thus very transparent. The

generalization of these thermodynamic formulations to dissipative systems is then given in Chap. 5. The nonequilibrium dynamics of density matrices is the subject of Chaps. 6 and 7, where in the former one the temperature range above the so-called crossover temperature is addressed, while in the latter one a dynamical approach particularly for the low temperature range and covering coherent as well as incoherent tunneling processes is presented. This in turn allows to derive detailed conditions for the applicability of the thermodynamic methods and reveals the intimate relation between dynamics, dissipation, and tunneling. The book closes with some remarks about central issues, for which the semiclassical theory of tunneling needs further developments in the future.

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### Semiclassical Approximation

In the early days of quantum mechanics – before the concept of matter waves had been introduced – the understanding of atomic spectra was based on classical mechanics combined with conditions for discreteness. The latter ones related the action of a classical orbit to multiples of  $\hbar$ . This seed grew, shortly after wave mechanics was cast into Schrödinger's equation, into a semiclassical scheme known today as WKB approximation [1, 2, 3], which allowed to obtain the wave function in terms of classical trajectories. It was in the late 1960 only that semiclassics turned into the focus of intensive scientific activities. Since then semiclassical approximations, mathematically embedded in the context of asymptotic series, have been derived for the time evolution operator, its Fourier transform, the resolvent, and the statistical operator and successfully applied in basically all fields of physics and physical chemistry. Semiclassics offers a way to quantize also classically nonintegrable systems based on periodic orbits and in the last years has provided powerful tools to capture the quantum dynamics of even high dimensional systems. One appealing feature of a semiclassical description is that it suggests an understanding of quantum phenomena in terms of classical entities. However, one has to be cautious: While such an interpretation may indeed be helpful in specific cases, in general and particularly for tunneling processes, it makes no sense to speak about the real existence of individual trajectories.

In this Chapter we collect some main results of semiclassical quantum mechanics, which will then be used in the remainder of this book. For transparency we restrict ourselves in many cases to one-dimensional systems, while generalizations to higher dimensions are mostly straightforward and welldescribed in the literature.

#### 2.1 At the Very Beginning: The WKB Approach

Let us consider a quantum particle of mass M moving in one dimension under the influence of a potential field V(q). The corresponding Hamiltonian reads 8 2 Semiclassical Approximation

$$\hat{H} = \frac{\hat{p}^2}{2M} + V(\hat{q})$$
(2.1)

and its eigenbasis follows from the eigenstates of the time independent Schrödinger equation  $\hat{H}|\psi\rangle = E|\psi\rangle$ . In position representation we try for the solutions of

$$\frac{d^2\psi(q)}{dq^2} + \frac{2M}{\hbar^2} \left[ E - V(q) \right] \psi(q) = 0$$
(2.2)

an ansatz of the form

$$\psi(q) = \exp\left[\frac{\mathrm{i}}{\hbar}W(q)\right]$$
(2.3)

with an exponent determined by

$$W'(q)^{2} - i\hbar W''(q) - p(q)^{2} = 0.$$
(2.4)

Here and in the sequel we use the abbreviation W' = dW/dq and further introduced the classical momentum  $p(q) = \sqrt{2M[E - V(q)]}$ . The idea is to solve (2.4) by assuming that the momentum p(q) shows only small variations over length scales of the order of the de Broglie wave length  $\lambda_{\rm B}(q) = 2\pi\hbar/p(q)$ . One then expands in a power series of  $\hbar$  [4, 5, 6]

$$W = W_0 - i\hbar W_1 - \hbar^2 W_2 - \dots$$
(2.5)

and upon insertion into (2.4) and putting terms of equal powers in  $\hbar$  to zero separately, one arrives at a set of iteratively coupled equations for the  $W_k, k = 1, 2, 3, \ldots$  In lowest order  $(\hbar^0)$  one has  $W'_0(q)^2 - p(q)^2 = 0$ , which is immediately solved by the classical short action

$$W_0(q,q_0) = \int_{q_0}^{q} \mathrm{d}q' \, p(q') \,, \qquad (2.6)$$

where  $q_0$  defines an arbitrary, but fixed reference point. Now, for  $W_0$  to be the leading contribution of a perturbative expansion one has to impose  $\hbar |W_0''(q)| \ll |W_0'(q)^2|$  or equivalently

$$\hbar \left| \frac{p'(q)}{p(q)^2} \right| \ll 1.$$
(2.7)

This is the so-called WKB condition (Wentzel-Kramers-Brillouin) for matter waves and the analog to the eikonal condition in geometrical optics [7]. Apparently, the condition is violated at all points in the vicinity of p(q) = 0, i.e. near all turning points of the corresponding classical orbit. These give rise to caustics, a coalescence of classical orbits starting from the same initial position but with different momenta. Before we address this phenomenon in detail, we first proceed with the next order term in the expansion (2.5). From  $W'_1 = -W''_0/(2W'_0)$  one has  $W_1(q) = -\ln[p(q)]/2$  so that by neglecting higher order contributions the WKB wave function takes the form



**Fig. 2.1.** Barrier potential with ranges I, II, and III for different semiclassical approximations, which must be matched according to the connection rules (2.9) and (2.10) at the turning points  $q_1$  and  $q_r$  defined by E = V(q).

$$\psi_{\rm WKB}(q) = \frac{C_+}{\sqrt{p(q)}} e^{iW_0(q,q_0)/\hbar} + \frac{C_-}{\sqrt{p(q)}} e^{-iW_0(q,q_0)/\hbar}$$
(2.8)

with appropriate integration constants  $C_{\pm}$ . Of course, this result can be systematically improved by taking into account even higher order terms in the  $\hbar$ -expansion (2.5).

The regions around caustics require special care. There is no reason why the above expansion should not also hold in the range E < V(q), i.e. in a range not accessible by a classical orbit, but sufficiently away from a turning point E = V(q) (see e.g. Fig. 2.1). Accordingly, one puts  $p(q) \rightarrow i|p(q)|$  so that the oscillating wave function (2.8) develops exponentially decreasing and increasing contributions, thus reflecting the appearance of quantum tunneling. The matching between the WKB solutions in the classically allowed and the classically forbidden ranges is done e.g. by circumventing the turning point in the complex coordinate plane along a contour which ensures the validity of the WKB condition [4]. The result are connection rules which read for a transition from a classically accessible to a forbidden domain at a (left) turning point  $q_1$ 

$$\frac{C_{+}}{\sqrt{p(q)}} e^{\mathrm{i}W_{0}(q,q_{1})/\hbar - \mathrm{i}\pi/4} + \frac{C_{-}}{\sqrt{p(q)}} e^{-\mathrm{i}W_{0}(q,q_{1})/\hbar + \mathrm{i}\pi/4} \longrightarrow \frac{C_{+}}{\sqrt{p(q)}} e^{-|W_{0}(q,q_{1})|/\hbar},$$
(2.9)

where in the first line  $q < q_{\rm l}$  and in the second one  $q > q_{\rm l}$ . In case of an outgoing matter wave to the right of a (right) turning point  $q_{\rm r}$ , the transition from the range under the barrier is determined by

10 2 Semiclassical Approximation

$$\frac{C_{+}}{\sqrt{|p(q)|}} e^{|W_{0}(q,q_{r})|/\hbar} \rightarrow \frac{C_{+}}{\sqrt{p(q)}} e^{iW_{0}(q,q_{r})/\hbar + i\pi/4}$$
(2.10)

with  $q < q_r$  on the right and  $q > q_r$  one the left hand side.

These rules allow for the evaluation of energy dependent transmission probabilities T(E) through one-dimensional barrier potentials. As a first example, we consider a scattering barrier with asymptotically free states [4] as depicted in Fig. 2.1. Then, one has an incoming and a reflected WKB-wave on one side of the barrier (range I) and an outgoing WKB-wave on the other side (range III). The amplitude t(E) of the latter is determined by connecting these partial waves via a proper WKB solution in the classical forbidden range (range II). This way one finds

$$T(E) \equiv |t(E)|^2 = \exp\left[-\frac{2}{\hbar} \left| \int_{q_1(E)}^{q_r(E)} \mathrm{d}q p(q) \right| \right], \qquad (2.11)$$

where the exponent contains twice the absolute of the short action  $W(q_l, q_r)$  between the turning points. It is thus identical to the short action of a *periodic* orbit at energy E in the *inverted* barrier potential.

In case of bounded one dimensional potentials with a single minimum, the above connection rules give rise to a quantization scheme known as the WKB or Bohr-Sommerfeld quantization, i.e.,

$$\frac{1}{2\pi\hbar}\oint \mathrm{d}qp = n + \frac{1}{2}\,.\tag{2.12}$$

Here the integral covers a full period of a classical orbit and n is a positive integer. The additional term 1/2 on the right hand side accounts for the zero point fluctuations. This term, a direct consequence of the breakdown of the semiclassical approximation close to a turning point and associated with the appearance of additional phases in (2.9) and (2.10), was absent in the older version of this scheme. A multi-dimensional generalization of the WKB rule was first found by Einstein, later discovered independently again by Keller, and named EBK quantization (Einstein–Brillouin–Keller) [8, 9] in the literature [10]. It reads for a *d*-dimensional system

$$\frac{1}{2\pi\hbar}\oint_{C_i} \mathrm{d}\boldsymbol{p} = n_i + \frac{\nu_i}{4} \ , \ i = 1, \dots, d \,, \tag{2.13}$$

where the  $C_i$  are *d* independent closed loops on a torus in *d* dimensions and  $\nu_i$  are the corresponding Maslov indices counting the number of conjugate points along  $C_i$ .

From the above rules one derives quantized energy levels separated by a gap of order  $\hbar$ . However, in systems with classically degenerate ground states, e.g. double well potentials, an exact diagonalization of the corresponding Hamilton operator reveals that each such level consists actually of sublevels, the energies of which differ by terms exponentially small in  $\hbar$ . This fine structure due to quantum coherence between wells linked by barriers cannot be gained within the WKB/EBK schemes.

#### **Uniform Approximation**

There is an alternative way to glue together respective asymptotic WKB wave functions in the vicinity of a turning point. The idea is to linearize the barrier potential in a range around the turning point and to solve the corresponding Schrödinger equation exactly [4, 5]. Suppose the turning point is located at  $q = q_0$ , one then writes  $V(q) \approx V(q_0) - F(q - q_0)$ . The corresponding energy eigenfunctions are Airy-functions and by matching their asymptotics onto semiclassical solutions (2.8) one determines the free coefficients and obtains a uniform solution.

A similar strategy, namely to solve the Schrödinger equation for a reference potential exactly, is also used to remove the failure of the WKB-transmission probability (2.11) for energies close to the top of a smooth barrier potential [4, 5]. In this situation, left and right turning points,  $q_{\rm l}$  and  $q_{\rm r}$ , are not sufficiently separated from each other (of order  $\lambda_{\rm B}$  or less) so that the above procedure based on the connection rules (2.9) and (2.10) does not apply. However, a smooth barrier potential can be approximated around its top by an inverted harmonic oscillator. The corresponding Schrödinger equation is again exactly solvable in terms of Weber functions. The asymptotic form of these functions is matched onto the asymptotic WKB wave functions, which eventually leads to the uniform semiclassical transmission probability

$$T_{\rm uni}(E) = \frac{1}{1 + \exp[2W(E)/\hbar]}$$
(2.14)

with  $E = E(q_{\rm l}, q_{\rm r})$ . For energies sufficiently below the barrier top this expression reduces to (2.11), while it reproduces the exact result for a purely parabolic barrier  $V_{\rm pb}(q) = -M\omega^2 q^2/2$  for energies near the top, where  $W_{\rm pb}(E) = \pi E/\omega$ .

#### 2.2 Real-time Propagator

The time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$
 (2.15)

can be formally integrated over a time period t - t' to yield  $|\psi(t)\rangle = \hat{G}(t - t') |\psi(t')\rangle$ , where

$$\hat{G}(t) = \exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}t\right)$$
 (2.16)

denotes the quantum mechanical real-time propagator. Its knowledge is completely equivalent to solving the Schrödinger equation itself and leads to an alternative formulation of quantum mechanics in terms of path integrals. First