

Competing tunneling trajectories in a two-dimensional potential with variable topology as a model for quantum bifurcations

V. A. Benderskii and E. V. Vetoshkin

Institute of Problems of Chemical Physics, RAS, 142432 Moscow Region, Chernogolovka, Russia

E. I. Kats

*Laue-Langevin Institute, F-38042 Grenoble, France**and L. D. Landau Institute for Theoretical Physics, RAS, Moscow, Russia*

H. P. Trommsdorff

*Laboratoire de Spectrométrie Physique, Université Joseph-Fourier de Grenoble, CNRS (UMR 5588),**Boîte Postale 87, F-38402 St. Martin d'Hères Cedex, France*

(Received 2 September 2002; published 5 February 2003)

We present a path-integral approach to treat a two-dimensional model of a quantum bifurcation. The model potential has two equivalent minima separated by one or two saddle points, depending on the value of a continuous parameter. Tunneling is, therefore, realized either along one trajectory or along two equivalent paths. The zero-point fluctuations smear out the sharp transition between these two regimes and lead to a certain crossover behavior. When the two saddle points are inequivalent one can also have a first order transition related to the fact that one of the two trajectories becomes unstable. We illustrate these results by numerical investigations. Even though a specific model is investigated here, the approach is quite general and has potential applicability for various systems in physics and chemistry exhibiting multistability and tunneling phenomena.

DOI: 10.1103/PhysRevE.67.026102

PACS number(s): 05.30.-d, 05.40.Jc, 05.45.Gg, 11.30.Qc

I. INTRODUCTION

Molecules possessing more than one stable or metastable configurations (so-called non-rigid molecules [1,2]) are interesting as many of their properties differ considerably from those of rigid molecules. In addition, such molecules have practical applications as building blocks of present and future display and sensor technologies. Theoretical modeling of nonrigid molecules is often hampered by a lack of detailed knowledge concerning their eigenstates and eigenfunctions. As a rule, vibrational spectra of the nonrigid molecules are characterized by local oscillations around the minima and tunneling splittings due to transitions between these quasilocal states. When only one “coordinate” (the reaction path) is related to a large amplitude motion while all other degrees of freedom can be approximated as small amplitude oscillations [3,4], the behavior of the system is determined completely by a single minimum action trajectory. The dynamics becomes more complex when more than one coupled large amplitude motions (i.e., more than one strongly fluctuating variables) are present. In this case, several minimum energy paths connect minima of the potential energy surface (PES). Phenomena like instabilities or bifurcations can appear in certain regions of parameters describing the PES, and the analysis of such a situation is the main issue of the present paper.

In the general case of a PES with n minima, states of the system can be described using n sets of eigenfunctions, quasilocalized near each minimum, while tunneling between different states is related to the overlap between these functions. The characteristic energy scale for tunneling, usually much smaller than the thermal energy, is determined by the chemical nature of the nonrigid molecule, or, in other words,

by the quantum chemistry of the system. Depending on the parameters describing the PES of a nonrigid molecule, one may expect different types of behavior, which can be treated in terms of quantum instabilities also called quantum phase transitions.

Quantum phase transitions (that occur in a quantum mechanical system at zero temperature as a function of some nonthermal control parameter) and related phenomena, like quantum bifurcations and instabilities have been a subject of great theoretical interest in recent years (see, e.g., monograph [5] and references herein). Unlike ordinary phase transitions, quantum transitions occur between ground states and involve negligible changes in entropy. Examples include transitions in quantum Hall systems, localization phenomena, and the superconductor-insulator transition in two-dimensional systems [5,6]. Usually these phenomena take place in many particle systems driven by competing interactions (a well-known example is the superconductor—normal metal quantum phase transition at $T=0$ arising from electron-electron correlation competing with electron-phonon interaction [7]). As a result of the competition, a quantum bifurcation may occur at a critical value of the coupling constant, leading to singularities of some properties. The most robust features of quantum bifurcations are divergences or singularities in certain characteristics of the system at the critical value of the coupling constant and drastic changes of the behavior below and above. Both classical and quantum critical points are governed by a divergent correlation length, although quantum systems possess additional properties that do not have classical counterparts. The fact that the ground state wave function undergoes a qualitative change at a quantum instability is one of these and is the subject of this paper.

Remarkably, similar features may arise in few-body systems. A well-known example is the so-called level crossing phenomenon [8] when an excited level becomes the ground state at a critical value of the interaction parameter. In this paper, we analyze another type of quantum instability taking place for a two-dimensional (2D) PES changing its topology as a function of a continuous parameter α and illustrate the results by numerical investigations. The model PES has two equivalent minima separated by one or two saddle points. The change from one to two saddle points takes place for a certain critical value of $\alpha = \alpha_c$. In addition, the PES may be symmetric or asymmetric with respect to the second coordinate, perpendicular to that relating the two minima. For the symmetric case (two equivalent saddle points) there are two regions (I and II) of the phase diagram, where tunneling is realized either along one minimum action trajectory essential for the semiclassical description of the motion (region I), or along two equivalent paths (region II). The zero-point fluctuations smear out a sharp second order transition between the two regions and lead to a certain crossover behavior. For the asymmetric case, one can have also a first order phase transition related to the fact that one of the two trajectories becomes unstable.

The competition between trajectories in this model plays the role of competing interactions in many-body systems with quantum bifurcations. Divergences in thermodynamic quantities are mapped onto a certain singular behavior in our model (critical fluctuations at finite temperatures have their equivalent in the zero-point quantum delocalization) and, in fact, reflect more fundamental phenomena. Loosely speaking, any continuous quantum bifurcation is related to specific conditions (or specific values of parameters) when the lowest excitations become gapless and a qualitative change in the nature of the frequency spectrum occurs.

In the literature [9,10], several analogies have been proposed to describe the ground state stability of a small system (such as an atom or a molecule) in terms of phase transitions, mapping a d -dimensional quantum systems onto a $(d+1)$ -dimensional classical system. This formal equivalence (first proposed long ago [11,12]) is based on the observation that the quantum action includes not only an integration over the space variables but includes also one imaginary time dimension, which, for $T=0$, is of infinite extent. The quantum-classical mapping is a very general fact. One can always reinterpret the imaginary time functional integral of a d -dimensional quantum theory as a finite-temperature Gibbs distribution function of a $(d+1)$ -dimensional classical theory.

Naively, this seems to imply that quantum bifurcations are not very interesting. However, as elsewhere in science, the devil is in the details of this mapping. For example it turns out [5] that there is no guarantee that the Gibbs weights, found by such a mapping, are positive (they can even be complex valued). This implies that one may not use the mapping blindly, i.e., for any arbitrary system. Thus a direct and explicit treatment of the quantum models is required.

Instead of the divergence of the correlation length (which is the cornerstone of traditional descriptions of criticality in determining the scaling behavior of all other quantities) any

quantity that changes its scaling behavior at $\alpha = \alpha_c$ can be used. Thus, it is not necessary to restrict analogies of phase transition to the search for the points where the correlation length diverges. As shown below, in the present model the wave functions itself manifest a characteristic critical behavior.

The remainder of this paper is organized as follows. In Sec. II we investigate a model 2D potential having two equivalent minima, and two saddle points. The shape and the topology of the potential depend on one continuous parameter, α , playing the role of a controlling parameter in a phase transition terminology. At the critical value $\alpha = \alpha_c$, two saddle points (and the maximum of the potential in between) merge into one saddle point. In this section we also present a qualitative picture of the quantum bifurcation. Section III is devoted to the numerical verification of the qualitative scenario. Minimum energy and extremal tunneling trajectories of the potential are determined. In the Sec. IV the results presented in the Sec. III are generalized to an anisotropically deformed PES, with the aim to relate predictions of the theoretical results to possible experimental verifications such as the effect of partial deuteration. Some specific examples of nonrigid molecules are also discussed in this section. Finally, in Sec. V we conclude.

II. INSTANTON APPROACH TO A MODEL 2D POTENTIAL

In order to investigate the scenario of quantum bifurcations described above, one should solve the Schrödinger equation for a 2D PES of variable shape and topology. No standard method of solution is known for a 2D PES of general shape. In the semiclassical approximation (the concern of this paper), the commonly used WKB method [8,13], is reduced to matching wave functions between classically allowed and forbidden regions. This matching is easily achieved in the 1D case with only one strongly fluctuating variable. Technically, already for two dimensions with one strongly and one weakly fluctuating variable the procedure becomes tedious and computationally demanding. However, for higher-dimensional PES and for more than one coupled large amplitude motions, fundamental difficulties are encountered of how to match many-valued semiclassical wave functions at a nontrivial set of boundaries between allowed and forbidden regions in multidimensional phase space. To the best of our knowledge this problem has not been investigated previously in any general form.

However, there is an alternative to the universal WKB semiclassical formalism, the so-called extreme tunneling trajectory or instanton method, which is not only very efficient for calculating globally uniform wave functions of the ground state (as initially formulated [14,15]) but which can also be adapted for the description of low-energy excited states [16–18] (and which can even be extended with reasonable accuracy to highly excited states [19]). The instanton method eliminates much of the tedious WKB calculations because there are no classically allowed regions in the formalism (and as a consequence there are no singularities of semiclassical wave functions). Within the instanton method, bifurcations or instabilities are simply related to the exist-

tence of multiple-valued solutions of the equations of motion, i.e., appearance of two (or more) solutions with similar values of their action. Unlike WKB wave functions, which have singularities at the boundaries between classically allowed and forbidden regions, the variations over the space of instanton wave functions can be followed continuously. The price to pay for this advantage is related to the nonexistence of classically allowed regions and the absence of natural Bohr-Sommerfeld quantization rules. In the instanton approach, these rules must be established by different methods. In addition, the instanton equations contain second order turning points whereas the WKB equations have only linear, first order, turning points.

The main steps of the instanton method, used to determine semiclassical solutions to the Schrödinger equation in the potential $V(X, Y)$, are as follows:

(i) The so-called Wick rotation in phase space, corresponding to the transformation to imaginary time ($t \rightarrow -it$), is made.

(ii) Solutions of the Schrödinger equation are represented in the form

$$\Psi = A(X, Y) \exp[-\gamma W(X, Y)], \quad (1)$$

$\gamma \gg 1$ is a large semiclassical parameter, $\gamma \equiv m\Omega_0 a_0^2 / \hbar$, where m is a mass of a particle, a_0 is a “microscopic” characteristic length of the problem, e.g., the tunneling distance, Ω_0 is a characteristic frequency, e.g., the oscillation frequency around the potential minimum, \hbar is set equal to 1, measuring energies in frequency units, and W has a meaning of action.

(iii) The terms in the Schrödinger equation, first and second order in γ^{-1} , become identically zero, if the wave function in the form of Eq. (1) satisfies the time independent Hamilton-Jacobi equation for W and the so-called transport equation for A (see below and also [16–18] for details).

Below, the instanton approach is used to determine semiclassical solutions of the Schrödinger equation in the following model 2D PES:

$$V(X, Y) = \frac{1}{2}(1 - X^2)^2 + \frac{\omega^2}{1 - \alpha} \left[\frac{1}{2}(X^2 - \alpha)Y^2 + \frac{1}{4}Y^4 \right]. \quad (2)$$

The PES given by Eq. (2) is dimensionless: coordinates X and Y are measured in units of the distance a_0 between two minima along X , the energy is measured in units of the oscillation frequency Ω_0 in one of the wells [thus for the potential (2) the characteristic frequency for oscillations in X direction is $4\Omega_0$, and in Y direction it is $\omega\Omega_0$]. The prefactor of the second term of Eq. (2) is chosen such that the oscillation frequency along Y (at $X = \pm 1$) is independent of α , and equals the parameter ω . The potential, Eq. (2), is bound for $\alpha < 1$ and has in this case the following stationary points: $\{X = \pm 1, Y = 0\}$ are two equivalent minima; $\{X = 0, Y = 0\}$ is a saddle point for $\alpha < 0$ and becomes a maximum at $0 < \alpha < 1$; $\{X = 0, Y = \pm \sqrt{\alpha}\}$ are two saddle points at $0 < \alpha < 2/(2 + \omega^2)$, becoming minima when $\alpha > 2/(2 + \omega^2)$ with the ap-

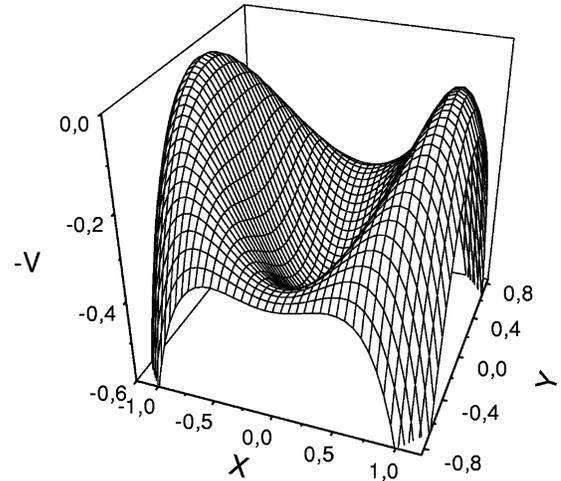


FIG. 1. 3D plot of the inverted PES (2) with $\omega = 1$, and $\alpha = 0.55$.

pearance of four additional saddle points. In the following, the discussion is restricted to the region of $0 < \alpha < 2/(2 + \omega^2)$, where additional stationary points, having no “critical” behavior, are absent. We show the 3D shape of the potential (2) in the Fig. 1 for $\omega = 1$, and $\alpha = 0.55$. The bifurcation phase diagram in the plane of the dimensionless parameters α, ω^2 is shown in Fig. 2. For a classical system, one would have a continuous bifurcation at the line $\alpha = 0$ from a behavior governed by one minimum energy trajectory (region I in the Fig. 2) to dynamics with two minimum energy paths passing through the two saddle points (region II). Representative equipotential maps of PES corresponding to the two regions are shown in Fig. 3. As discussed in the following Section, quantum zero-point fluctuations shift and de-

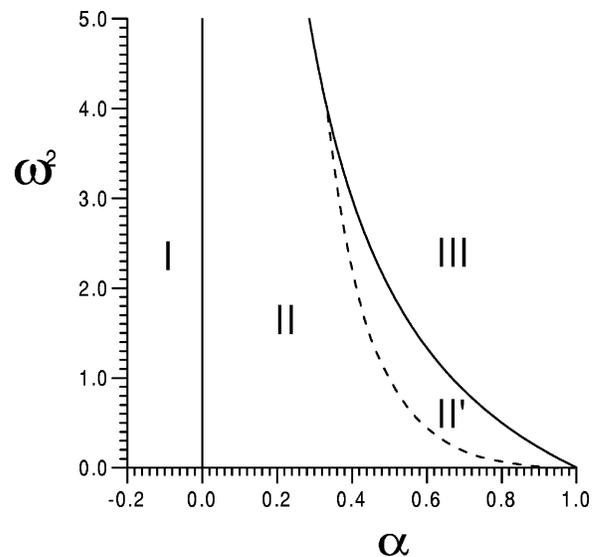


FIG. 2. $\omega^2 - \alpha$ phase diagram. In the region II the PES has two minima and two saddle points, only in the region II' two minimum action paths coexist with 1D trajectory $Y = 0$, in the region I the PES has two minima and one saddle point and in the region III more than two minima.

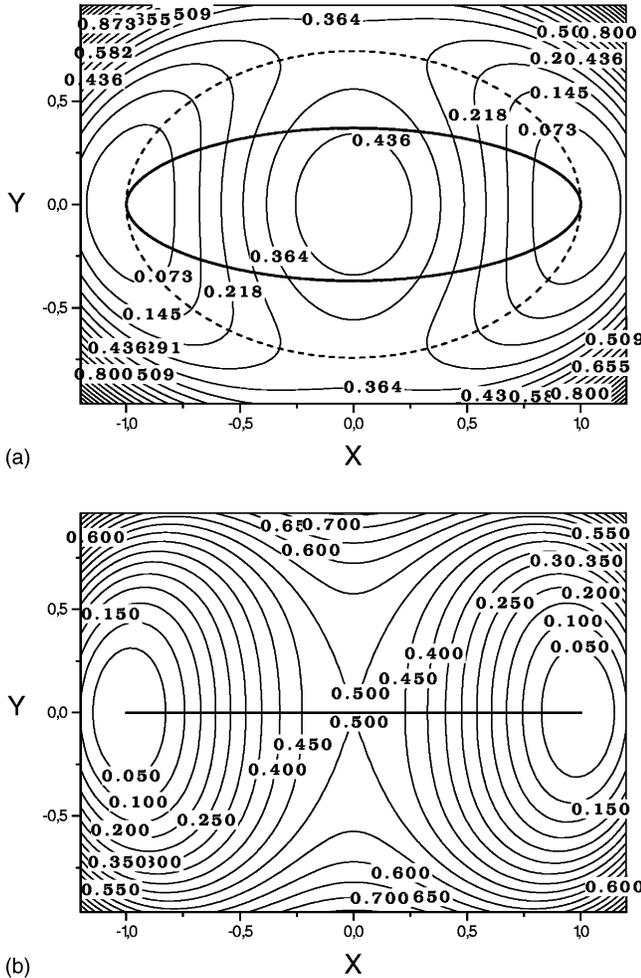


FIG. 3. Equipotential map for 2D PES Eq. (2); dashed lines designate minimum energy trajectories, and the solid lines show the minimum action (tunneling) trajectories. (a) $\omega=1, \alpha=0.55$, (b) $\omega=1, \alpha=-0.20$.

form the transition line and smear out the bifurcation line. Finally there is a certain crossover behavior between regions (I and II).

A simple physical realization of a PES such as given by Eq. (2) would be a molecule with two equivalent coupled wide amplitude coordinates x and y describing, for example, proton tunneling (in monograph [16] many such examples are discussed). When the coupling between the tunneling particles is neglected, the dimensionless PES is represented as a sum of two strongly fluctuating motions:

$$V_0(x, y) = \frac{1}{2}(1-x^2)^2 + \frac{1}{2}(1-y^2)^2. \quad (3)$$

Taking into account symmetric coupling, a term,

$$V_1(x, y) = c(x^2 + x_0^2)y^2, \quad (4)$$

must be added to Eq. (3). After a transformation to coordinates $X = (x+y)/2$ and $Y = (x-y)/2\sqrt{3}$, one obtains the PES given by Eq. (2), provided that the parameters ω and α are related as follows:

$$\omega = 3\sqrt{2(1-\alpha)},$$

$c=1$, and $x_0^2=1-\alpha$. To explore the behavior of the system with respect to variations of parameters ω and α , controlling the shape and the topology of the model PES, Eq. (2), the minimum energy and extreme tunneling trajectories should be fully analyzed. Dealing with quantum transitions between different states of the system, one must distinguish between adiabatic and nonadiabatic transitions. Adiabatic transitions take place at $\omega \gg 1$ along the minimum (maximum) energy paths (MEP), defined by the condition that the PES should have an extremum orthogonal to the MEP:

$$\frac{dY}{dX} = \frac{\partial V / \partial Y}{\partial V / \partial X} = \frac{(X^2 - \alpha)Y^2}{-2(1-X^2)(1-\alpha) + \omega^2 Y^2} \frac{X}{\omega^2 Y}. \quad (5)$$

From the symmetry of Eq. (5) is clear that Y^2 is a function of $1-X^2$, and $dY/dX=0$ on the surface $X=0$. In the region II of Fig. 2, there exist, therefore, two types of paths satisfying Eq. (5): (i) two equivalent paths I via the saddle points; (ii) a shorter path II, $Y=0$ passing through the maximum.

The extreme tunneling (i.e., instanton) zero energy trajectories are described by the equation of motions (“Newton laws”) in imaginary time and for the inverted PES (i.e., for $V \rightarrow -V$)

$$\ddot{X} = \frac{\partial V}{\partial X}, \quad \ddot{Y} = \frac{\partial V}{\partial Y}. \quad (6)$$

At $\alpha > 0$, the trajectories satisfying Eq. (6) lie between the paths I and II due to a nonadiabaticity of the transitions caused by the finite frequency of the transverse oscillations. The instanton action increases when α decreases, since the absolute value of the potential at the saddle points increases as

$$V^* \equiv V(0, \pm\sqrt{\alpha}) = \frac{1}{2} - \frac{\omega^2 \alpha^2}{4(1-\alpha)}. \quad (7)$$

III. QUANTUM BIFURCATION

In this section, the results of the preceding section are used to illustrate numerically the appearance of quantum bifurcations (already qualitatively discussed in the introduction). Standard applications of the instanton method reduce to minimizing the nonlocal action along a one-dimensional trajectory. Such an approach supposes that there is a single path connecting initial and final states. This is evidently not the case for our model. As a first step, the equations of motion, Eq. (6), are solved and the resulting minimum energy and extreme tunneling (instanton) trajectories are shown in Fig. 3 for two values of the controlling parameter α . As the instanton trajectories deviate from the minimum energy paths, the collapse of the two instanton trajectories, when α decreases, occurs at a certain finite value of $\alpha^* > 0$ which does not coincide with the point $\alpha=0$, where the PES changes its topology. The dashed line in Fig. 2 defines region II' within region II, where two minimum action trajectories exist, in the remainder of region II the minimum action tra-

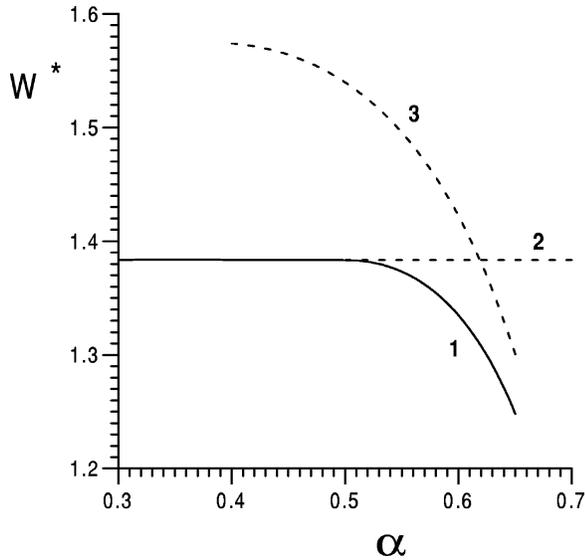


FIG. 4. The action W^* as a function of the parameter α at $\omega=1$ for: (1) the minimum action tunneling trajectory, (2) the 1D path, $Y=0$, and (3) the minimum energy trajectory.

jectory is the 1D trajectory $Y=0$. Thus, the potential Eq. (2), admits two types of instantons: a 1D instanton ($Y=0$ and $\dot{Y}=0$); and 2D instantons where the transverse displacements have a maximum at the plane $X=0$, separating initial and final states, while the transverse velocities achieve extrema at intermediate points where the trajectories deviate from the 1D instanton. The contribution of any trajectory to the transition rate is a result of the tradeoff between the length of the path and the barrier height along this path. Naively, exploiting such idea, we come to the bifurcation criterion, which determines the critical value of the controlling parameter α as the value at which the actions along the both competing trajectories become equal. We designate the value by α^* . However, by definition of instanton actions, the point α^* corresponds to the harmonic approximation of the potential, and therefore this criterion is too crude for our anharmonic model potential, Eq. (2). In Fig. 4, the minimum action as a function of α is plotted for $\omega=1$. In the same figure the action along the minimum energy paths is also represented.

A more rigorous approach is based on the observation that at the bifurcation point a new type of the trajectory (2D) appears, and the initial 1D trajectory becomes unstable. To study the stability of the trajectory it is sufficient to restrict oneself to a Gaussian (harmonic) approximation for the transverse motion, and the instanton approach is therefore adequate. The one-dimensional instanton solution becomes unstable when the lowest eigenvalue of the second functional derivative of the action over the trajectory variations becomes zero,

$$\frac{\delta^2 W}{\delta X^2} = 0.$$

This lowest eigenvalue is traditionally called the stability parameter λ . When the value of λ becomes zero (the corre-

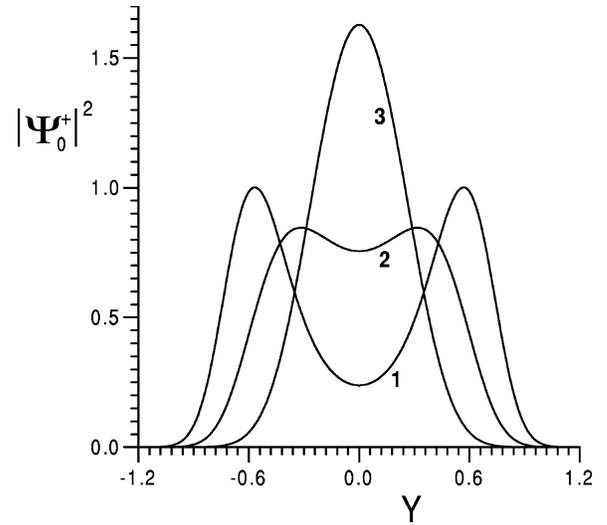


FIG. 5. Ground state wave functions ($n=0$) at $X=0$ for $\omega=1$ and $\gamma=20$: (1) $\alpha=0.625$; (2) $\alpha=0.55$; (3) $\alpha=0.3$.

sponding value of α will be called the critical value and denoted α_c .) the tunneling channel centred around an extreme 1D path becomes infinitely wide (and the transverse fluctuations are no longer Gaussian) and new types of the trajectories (2D), possessing a smaller action, appear. We believe that this criterium is physical, and it will be shown below that just around the value α_c the critical behavior of the tunneling splitting takes place (more precisely the crossover due to quantum zero-point fluctuations).

The next step is to determine the wave functions. The ground state instanton wave functions can be represented in the form of Eq. (1) as

$$\Psi_0(X, Y) = A_0(X, Y) \exp[-\gamma W(X, Y)], \quad (8)$$

where the functions $A_0(X, Y)$ and $W(X, Y)$ should satisfy the Hamilton-Jacobi and transport equations [16–18]

$$\frac{1}{2} \left(\frac{\partial W}{\partial X} \right)^2 + \frac{1}{2} \left(\frac{\partial W}{\partial Y} \right)^2 = V(X, Y), \quad (9)$$

and

$$\frac{\partial W}{\partial X} \frac{\partial A_0}{\partial X} + \frac{\partial W}{\partial Y} \frac{\partial A_0}{\partial Y} + \frac{1}{2} \left(\frac{\partial^2 W}{\partial X^2} + \frac{\partial^2 W}{\partial Y^2} - 2E_0 \right) A_0 = 0. \quad (10)$$

E_0 is the ground state energy.

In Fig. 5, the ground state wave function at the surface $X=0$ is shown for different values of the parameter α . Far away from the critical region, the wave functions are localized at the saddle points while the probability distribution is smeared out over the whole region between the potential minima in the critical region. The tunneling splitting is given by the expression

$$\Delta_0 = \int_{-\infty}^{+\infty} \Psi(0, Y) \left(\frac{\partial \Psi}{\partial Y} \right)_{X=0} dY. \quad (11)$$

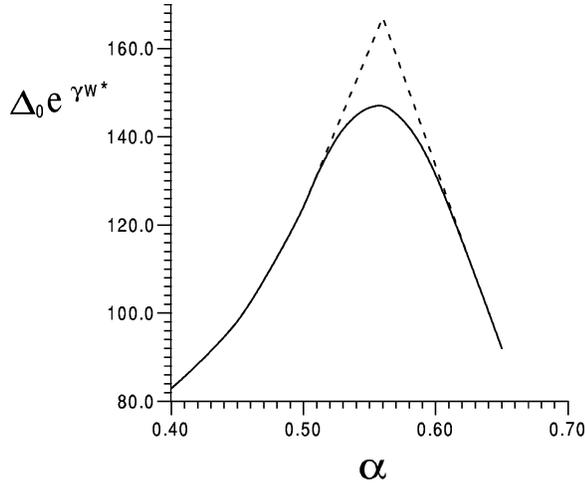


FIG. 6. Tunneling splitting as a function of α for $\omega=1$, and $\gamma=20$ in the critical region (the dashed line is a continuation to the stability region).

The value of this splitting given by the probability flow integrated over the dividing plane $X=0$ depends on the exponential factor, $\exp(-\gamma W^*)$, where W^* is Euclidean action between the minima. Apart from this leading term, Δ depends on prefactors characterizing both type of trajectories. In order to eliminate the leading term contribution and visualize the critical behavior of Δ , $\Delta_0 \exp(\gamma W^*)$ is plotted as a function of α in Fig. 6. The width of the maximum around the critical value, $\alpha = \alpha_c$, is determined by quantum (zero-point) fluctuations.

Tunneling leads to an energy splitting (tunneling splitting, Δ_0) between two otherwise degenerate states and the eigenstates are symmetric and antisymmetric combination of these states. This tunneling splitting between the two lowest eigenstates of the Hamiltonian is therefore the quantity of interest. Alternatively, the rate of oscillation between the two classically degenerate states can be measured after the system has been prepared in one of these states.

At small values of α some new phenomenon could occur due to these quantum fluctuations. In this region, at the surface $X=0$, the depth of the wells becomes so small that wave functions are effectively delocalized due to quantum fluctuations. The natural (though qualitative) criterion of the delocalization should compare amplitude of zero-point oscillations along Y in one well with the distance between wells. The same criterion as given above, could be formulated as the condition that there are no discrete energy levels in a shallow well. Both criteria compare the energy difference between the maximum and the saddle point of the PES, Eq. (2), $V(0,0) - V(0, \sqrt{\alpha})$, with the energy of zero-point oscillations in one well, $\tilde{\omega}/\gamma$, where $\tilde{\omega}$ is the frequency of oscillations around $\pm \sqrt{\alpha}$ in the potential $V(0,Y)$, renormalized by anharmonic corrections. Taking into account all numerical factors we obtain

$$\frac{\alpha_c^2 \omega^2}{4(1-\alpha_c)} \approx (1+\sqrt{2}) \frac{\omega}{\gamma} \sqrt{\frac{2\alpha_c}{1-\alpha_c}}. \quad (12)$$

Equation (12) is fulfilled for $\alpha_c = 0.56$ (at $\omega=1$) as found in our numerical computations shown in Fig. 6.

The square root divergence of the localization length at α_c corresponds to the critical behavior of the correlation length in standard classical second order phase transitions. The tunneling splitting Δ_0 , calculated above, is our main result. Δ_0 is the product of an exponential and preexponential factor, and only the prefactor demonstrates the critical behavior (more precisely—the crossover behavior) shown in the Fig. 6. It may, of course, not be easy (if possible at all) to measure directly the contribution of a small prefactor with a singular behavior as a function of α when Δ_0 is dominated by the large exponential factor with a regular behavior. Given that a measurement of a nonlinear susceptibility of the system is equivalent to the measurement of the corresponding derivative of Δ_0 over the controlling parameter α offers one possibility. For example, when a local dipole moment is associated with the tunneling particles in a system with inversion symmetry, an applied external electric field will make the two 2D paths inequivalent, while the single 1D path would be unaffected. Let us emphasize that the symmetry breaking phenomenon takes place due to tunneling processes only and is thus by its nature a dynamic phenomenon. We will discuss this issue in the following section.

The second possibility to observe this kind of critical (crossover) behavior is based on the general Herring-Lifshits formula (see Eq. (11) and [8]), which shows that the splitting Δ_0 is determined by the integral over the Y coordinate at the dividing surface $X=0$, and is thus proportional to the total width of the tunneling channels. Therefore, the effect we got, might be considerably enhanced in 3D systems due to increase of the phase volume of tunneling channels. A 3D model PES, of which our 2D model PES, Eq. 2, is a plane section, is given by $V(X,\rho)$, where $\rho = (Y^2 + Z^2)^{1/2}$.

IV. ANISOTROPY

The PES, investigated in the previous sections, is symmetric with respect to the reflection $Y \rightarrow -Y$. Both tunneling particles are therefore identical as are the two tunneling paths.

As mentioned above, breaking this symmetry may be useful, in order to expose more clearly the singular behavior of the prefactor. Indeed, the response should expose a qualitatively different behavior with respect to any factor breaking the symmetry near the critical region (i.e., close to the bifurcation point) or far from it. This idea, the so-called fluctuation-dissipation theorem relating correlation and response functions, is well known for conventional thermodynamic phase transitions. Two mechanisms of breaking this mirror symmetry, which are easily realized, will be analyzed below. First, partial deuteration will make the tunneling particles different. Second, as mentioned above, an external electric field may render inequivalent the tunneling channels for the two particles. Both mechanisms can be described in a phenomenological way by adding the following anisotropic perturbation to the bare symmetric PES, Eq. (2):

$$V_a(X,Y) = \beta(1-X^2)Y. \quad (13)$$

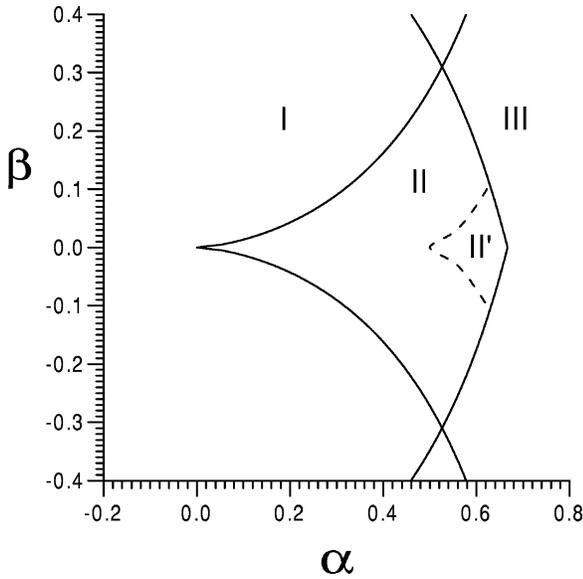


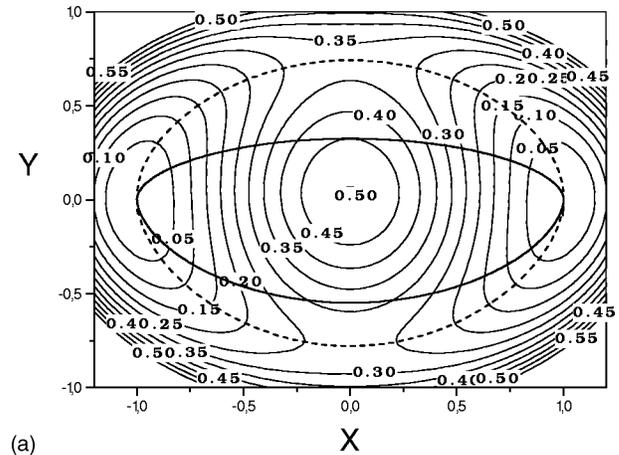
FIG. 7. The phase diagram for the anisotropic PES, Eq. (13), in the $(\alpha-\beta)$ -plane with $\omega=1$. In the region II the the PES has one maximum and two saddle points and in the region I only one saddle point. In the region III one of the saddle points from region II (more distant from the maximum) is transformed into the minimum. In the region II' there are two minimum action trajectories.

The parameter β describes the strength of the anisotropy. In the potential (13) higher order anisotropic terms, $Y^3(1-X^2)$, and so on, were neglected for the sake of simplicity. Even though, strictly speaking, this assumption is not justified, since Y is a strongly fluctuating degree of freedom, this approximation correctly identifies the characteristic scales in the problem and all qualitative features of its behavior. For hydrogen-deuterium substitution of one of the two tunneling atoms, for example, the resulting anisotropy parameter is easily evaluated as

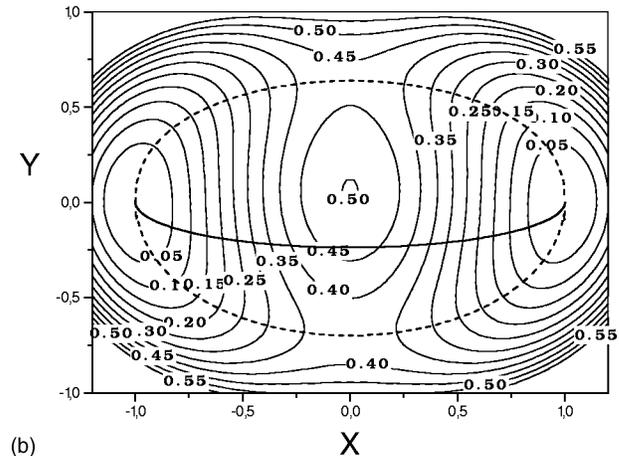
$$\beta = \frac{1}{4} \left(\sqrt{\frac{m_1}{m_0}} - 1 \right), \quad (14)$$

where m_0 and m_1 are masses of the H and D isotopes. In an applied electric field, the anisotropy parameter β will be proportional to the field strength. The precise choice of the anisotropic PES, Eq. (13), is delicate, and depends on the detailed structure of the system under consideration. Aiming at a qualitative description, we have chosen the simplest form of breaking the $Y \rightarrow -Y$ symmetry while the symmetry $X \rightarrow -X$ is preserved, so that the two potential well are still equivalent.

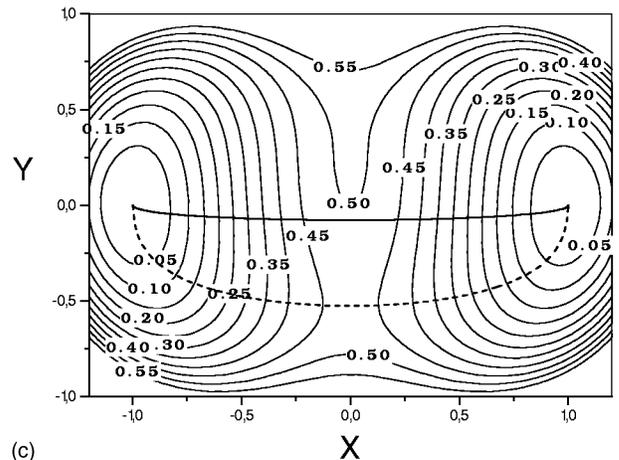
The analysis of this modified PES is analogous with that presented in the Sec. II for the symmetric PES. In the α, β parameter phase plane, we should first find all minimum energy and extreme tunneling trajectories. There are four different regions on this plane as shown in Fig. 7. In the region II one maximum and two saddle points exist, in region I there is only one saddle point. The behavior is more subtle in region III, where the saddle point that is more distant from the maximum is transformed into the minimum (i.e., the X -“oscillation” frequency changes its sign). By the dashed



(a)



(b)



(c)

FIG. 8. Equipotential map for the anisotropic PES. Instanton (solid lines) and minimum energy (dashed lines) trajectories. $\omega=1$, $\beta=0.05$: (a) $\alpha=0.58$; (b) $\alpha=0.45$; (c) $\alpha=0.20$.

lines we depicted also the subregion II', where there are two extreme tunneling trajectories. In the remaining part of the region II, corresponding to relatively small values of α , the extreme tunneling trajectory close to the maximum becomes unstable.

In Fig. 8 we show the minimum energy and extreme tunneling (instanton) trajectories for a small value of the anisot-

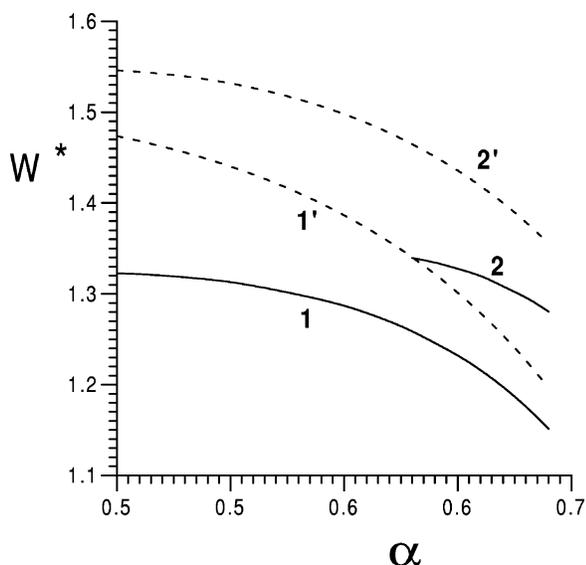


FIG. 9. The action W^* as a function of α along the instanton (solid lines) and minimum energy (dashed lines) paths. $\omega=1$, and $\beta=0.05$. The curves 1 and 1' correspond to the trajectories more distant from the maximum, whereas lines 2 and 2' correspond to the trajectories close to the maximum.

ropy parameter ($\beta=0.05$) and for different values of α . It illustrates that even a small anisotropy lifts the degeneracy of two instanton trajectories. In addition, the straight line path II, passing through the maximum $\{X=0, Y=0\}$, for the symmetric PES, Eq. (2), becomes curvilinear and deviates from $Y=0$. Hence for the anisotropic PES ($\beta \neq 0$) all regions in the phase diagram with different types of the trajectories have the same symmetry, and therefore only first order bifurcations between the regions are allowed. Finally, in Fig. 9, the actions along the instanton and the minimum energy paths are plotted. The figure shows again that the anisotropy, Eq. (13), removes the degeneracy, and that two instanton trajectories appear when α exceeds a certain threshold value. This disappearance of one instanton trajectory is a specific feature of discontinuous first order bifurcations. Concluding this section, we emphasize that it is this sensitivity to anisotropy, which can lead to a drastic change of behavior.

V. EXPERIMENTAL CONSEQUENCES

Bifurcations of minimum energy paths (due to the presence of more than one saddle point separating stable configurations of the PES) are rather common in molecules with several strongly fluctuating coordinates. In nonrigid molecules, dynamically strongly fluctuating coordinates of this sort are typically different combinations of hydrogen transfer, hindered rotation of $-XH_n$ groups, or inversions. Molecular systems with two hydrogen transfers (synchronous or stepwise) attract special attention, as these processes are thought to be relevant for many biological processes, including so-called tautomeric reactions [1–3,16].

Two proton exchange in pairs of $\text{OH} \dots \text{O}$ fragments of various carbonic acid dimers is an example of synchronous tunneling. In our model, this transfer corresponds to a one-

dimensional trajectory in region II, and the longitudinal X and transverse Y coordinates are symmetric and antisymmetric combinations of proton displacements d_1, d_2 :

$$X = \frac{1}{2}(d_1 + d_2); Y = \frac{1}{2\sqrt{3}}(d_1 - d_2). \quad (15)$$

The coefficients are chosen such that Eq. (2) is the sum of Eqs. (3) and (4), and the results of Secs. II and III can therefore be used. For the 1D path $Y=0$, with one saddle point $\{X=0, Y=0\}$, the displacements of the both tunneling protons are always (i.e., at any point of the trajectory) equal to each other ($d_1=d_2$). In the pure classical limit, the width of the tunneling channel is determined by the corresponding potential curvature:

$$\Delta_{\perp} = \left(\frac{\partial^2 V}{\partial Y^2} \right)_{0,0}^{1/2}.$$

Within the harmonic approximation, there is a mean field ($\propto \alpha^{-1/2}$) divergency. In the plane $X=0$, the anharmonic Y^4 contribution provides a cutting-off of this divergency.

Quantum, zero-point transverse fluctuations spread out this singularity, and the width of the tunneling channel depends on α even in region II of Fig. 2. The characteristic potential barrier height V^* for the synchronic two proton transfer in the carbonic acid dimers is $V^* \approx (10 - 15) \text{ Kcal mol}^{-1}$ (5000–7000 K), while the energy E_{st} corresponding to a step wise transfer (that is paths $d_1=0, d_2=1$ or $d_1=1, d_2=0$) is two or even three times larger [21,22]. On the other hand, within the frame of our model PES, the ratio E_{st}/V^* depends on the controlling parameter α as follows:

$$\frac{E_{st}}{V^*} = 1 - \frac{3}{2}\alpha, \alpha < 0. \quad (16)$$

Inserting the numerical values of the characteristic energies given above into Eq. (16), one can see that even in the systems where the strongly fluctuating motions are believed to be strongly correlated, the controlling parameter α is close to -0.5 , and quantum fluctuations must be taken into account to describe correctly the tunneling dynamics.

Many examples of intermediate (between synchronic and step wise) dynamics exist also, one example being the so-called free base porphyrin compounds [21,23]. In these compounds with molecular symmetry D_{4h} , four nitrogen atoms (numbered clockwise A, B, C, D) form a square and two mobile protons a and b occupy positions such that configurations (aA, bC) and (aB, bD) are equivalent minima, while configurations (aA, bD) and (aB, bC) are equivalent saddle points (taking into account clockwise motions only). Our model PES, Eq. (2), can be adapted to this case. According to experimental data and quantum chemistry calculations [21,23] the energy of the saddle points is of the order of 0.3–0.5 of the energy at the maximum ($X=0, Y=0$). Thus from Eq. (7) we come to the estimation $\alpha \approx 0.3 - 0.4$. For these intermediate values of α , the quantum (minimum ac-

tion) and the classical (minimum potential) trajectories are quite different. Indeed, the classical and tunneling trajectories pass through the saddle points, and the maximum, respectively. The existence of saddle points lead to a considerable broadening of the tunneling channel as it is illustrated in the Fig. 4. Similar considerations are easily applied to the hydrazine molecule with two coupled inversion motions (see Ref. [22] and references therein).

For the partially deuterated molecule, we can also evaluate the anisotropy parameter β entering the PES, Eq. (12). According to Eq. (13) $\beta=0.1$, and the H—D isotopomer remains, therefore, in the same region I of the phase diagrams as protonated porphyrin. The main conclusion of this short analysis is that our simple model gives a fairly realistic representation of nonrigid molecules.

We have shown that effects due to competition of trajectories and quantum fluctuations are relevant in a broad range of the parameters entering our model. The examples discussed above lead to the conclusion that the widely accepted classification of synchronic and stepwise motions must be used with care, since in typical cases both types of motions are involved. This implies also that the traditional [15] Gaussian approximation (small fluctuations around one extreme tunneling trajectory) is not valid in the case of strong coupling between both tunneling particles, and one must take into account both competing tunneling channels. Similar phenomena might play a role in pairing of isolated nucleic-acid bases in the absence of the DNA backbone. In Ref. [24] spectroscopic characteristics of the hydrogen bonding in isolated guanine-cytosine ($G-C$) and guanine-guanine ($G-G$) base pairs have been investigated. The results show that the gas phase $G-C$ base pair adopts a single configuration, whereas $G-G$ exists in two different configurations. We already mentioned in Sec. II that the effect, obtained here, may be considerably enhanced in 3D systems due to the increase of the phase volume of the tunneling channels (our 2D model PES can be considered as a section of the corresponding 3D space). Among systems, where a 3D generalization of our model could be applicable, are cubic alkali halide crystals doped with a light atomic or molecular ions as substitutional impurity. Due to mismatch in size, these impurities frequently occupy off-center positions in the lattice. There is a small number of equivalent off-center positions, so that the impurity ground state is degenerate, and tunneling transitions between these positions are observed. However, the vibrational frequencies of off-center impurities are usually much smaller than characteristic host lattice phonon frequencies, and therefore the coupling to the lattice vibrations is relatively small. As a first approximation, one can visualize the system as one particle in a potential where the tunneling transitions between the initial and the final state can proceed in several alternative ways. In the trajectory language it signifies the possibility of competition (and bifurcation) between extremal paths of different types. Since transitions between different off-center positions are associated to a charge displacement, the corresponding PES changes upon application of external electric field or mechanical stress. We anticipate that the bifurcations described above by our model could be observable for off-center impurities as well, and

that understanding this mechanism will be essential to predict and to describe the behavior. A more specific study of 3D systems undergoing this kind of the quantum bifurcations, might become appropriate as suitable experimental results become available.

A completely different system might also be a physical realization of our model. The tunneling of magnetic spins has recently received much attention (see, e.g., Ref. [25]) in view of its promise as one of the few realistic candidates for quantum computing. Conventional magnetic materials used in the experiments contain many domains, each possessing its own set of parameters. Besides the spins interact with the crystal matrix and complicates the physical picture with respect to our model. However, quantum tunneling of spin is also possible in a spinor condensate trapped in double-well potential [25] and this system possesses several decisive advantages compared with more conventional solid state materials and is more suitable for a description in the frame work of our model (the system is characterized by a few simple parameters amenable to experimental control).

VI. CONCLUSION

We have presented here a path-integral approach to treat a 2D model of quantum bifurcations. A PES, the shape of which is determined by a continuous parameter, offers a natural way to examine quantum instability phenomena. Candidates that realize our model for quantum bifurcations are nonrigid molecules, spin condensates, and some other systems. In any system exhibiting some kind of quantum phase transitions it is important to understand how its genuine quantum aspects evolve throughout the transition. We investigated the behavior of the ground state wave function undergoing qualitative changes at a quantum instability, but other indicators of the phase transition could be examined in the same way (in a very recent publication, for example, the authors studied wave function entanglement phenomena [26]).

A second order bifurcation takes place for a 2D model PES with mirror symmetry, which changes its topology at a certain critical value α_c of the continuous parameter α . At $|\alpha - \alpha_c| \gg \alpha_c$ only one minimum action trajectory is essential for semiclassical description of the particle motion, while in the “critical” region at $|\alpha - \alpha_c| \ll \alpha_c$ the behavior is governed by two different trajectories almost degenerate with respect to the magnitude of the action. In our model, the competition between trajectories plays the role of competing interactions in many-body systems experiencing quantum phase transitions. The divergence in correlation length is mapped onto a singular behavior of the localization length. Due to zero-point quantum fluctuations, the system manifests a smoothed crossover behavior only instead of a sharp bifurcation. When the PES becomes asymmetric, a first order phase transition is associated with the disappearance (in a certain region of the potential parameters) of one minimum action trajectory. We illustrate the results by numerically investigating this behavior. The approach is general and has potential applicability for large (many particle) systems. Furthermore, it is possible to fabricate structures which are small

enough (mesoscopic) for the electronic transport to be largely coherent, so that the wave (quantum) properties of electrons dominate. Note also that the usefulness of our results can be substantially enhanced by the advent of semiconductor heterostructures in which the potential for the electrons can be tuned and varied in space with great precision.

One more interesting line of thought for future work would be to analyze, in analogy with the approach presented here, a phase stability with respect to small fluctuations for conventional phase transitions. It is known for Landau-Ginzburg type models [20] that the corresponding Landau-Khalatnikov equations have a form analogous to the Schrödinger equation (where a coordinate plays the role of an imaginary time) [27].

Our results can in principle be tested also by investigations of low temperature properties of disordered materials, containing certain point defects that undergo atomic tunneling [28]. Recently [29,30] the low temperature dielectric properties of certain multicomponent glasses were tentatively assigned to the existence of coupled two-level tunneling systems. This means that several tunneling paths between potential minima exist, as in the model presented here.

It is important to notice that the investigation of our paper refers to a singular behavior in the ground state of the system, as, strictly speaking, quantum phase transitions occur only at $T=0$. Because all experiments are necessarily done at some nonzero temperature, care must be taken when comparing our theoretical results to experiment, and we have to keep in mind the consequences of the $T=0$, and $\alpha=\alpha_c$ singularity on physical properties at $T>0$. Technically, finite temperature effects also can be incorporated into the instanton method. To do this, one should take into account the finite period ($1/T$) of instanton trajectories (an analogous approach was developed for the WKB method [31,32]). When these contributions become comparable to zero-point quantum oscillations, the quantum phase transition is smeared out.

ACKNOWLEDGMENTS

The research described in this publication was made possible in part by RFFR grants. We thank A. Hüller and P. Nozières, and J. Lajzerowicz for thought-provoking discussions. One of us (E.K.) is indebted to INTAS Grant (No. 01-0105 for partial support).

-
- [1] V.A. Benderskii, V.I. Goldanskii, and D.E. Makarov, *Phys. Rep.* **233**, 195 (1993).
- [2] K. Liu, J.D. Gruzan, and R.S. Saykally, *Science* **271**, 929 (1996).
- [3] H.P. Trommsdorff, *Adv. Photochem.* **24**, 147 (1998).
- [4] V.A. Benderskii, S.Yu. Grebenshchikov, E.V. Vetoshkin, G.V. Milnikov, and D.E. Makarov, *J. Phys. Chem.* **98**, 3300 (1994).
- [5] S. Sachdev, *Quantum Phase Transitions* (Cambridge University Press, Cambridge, 1999).
- [6] S.I. Sondhi, S.M. Girvin, J.P. Carini, and D. Shahar, *Rev. Mod. Phys.* **69**, 8039 (1997).
- [7] P. Morel and P.W. Anderson, *Phys. Rev.* **125**, 1263 (1962).
- [8] L.D. Landau and E.M. Lifshits, *Quantum Mechanics (Non-relativistic Theory)* (Pergamon Press, New York, 1965).
- [9] S. Kais and P. Serra, *Int. Rev. Phys. Chem.* **19**, 97 (2000).
- [10] R.A. Sauerwein and S. Kais, *Phys. Rev. E* **64**, 056120 (2001).
- [11] J. Lajzerowicz and P. Pfeuty, *Phys. Rev. B* **11**, 4560 (1975).
- [12] P. Bastie, J. Lajzerowicz, and J.R. Schneider, *J. Phys. C* **11**, 1203 (1978).
- [13] J. Heading, *An Introduction to Phase-Integral Methods* (Wiley-Interscience, London, 1962).
- [14] A.M. Polyakov, *Nucl. Phys. B* **129**, 429 (1977).
- [15] S. Coleman, *Aspects of Symmetry* (Cambridge University Press, Cambridge, 1985).
- [16] V.A. Benderskii, D.E. Makarov, and C.A. Wight, *Chemical Dynamics at Low Temperatures* (Wiley-Interscience, New York, 1994).
- [17] V.A. Benderskii, E.V. Vetoshkin, and H.P. Trommsdorff, *Chem. Phys.* **244**, 273 (1999).
- [18] V.A. Benderskii and E.V. Vetoshkin, *Chem. Phys.* **257**, 203 (2000).
- [19] V.A. Benderskii, E.I. Kats, and E.V. Vetoshkin, *JETP* **95**, 645 (2002).
- [20] L.D. Landau and E.M. Lifshits, *Statistical Physics, Part 1* (Pergamon Press, Oxford, 1980).
- [21] T.J. Butenhoff and C.B. Moore, *J. Am. Chem. Soc.* **110**, 8336 (1988).
- [22] W. Lodyga, M. Kreglewski, and J. Makarewicz, *J. Mol. Spectrosc.* **183**, 374 (1997).
- [23] Z. Smedarchina, *Chem. Phys.* **136**, 289 (1989).
- [24] E. Nir, K. Kleinermanns, and M.S. de Vries, *Nature (London)* **408**, 949 (2000).
- [25] *Quantum Tunneling of Magnetization*, edited by L. Gunther and B. Barbara (Kluwer, Dordrecht, Netherlands, 1995).
- [26] A. Osterloh, L. Amico, and R. Fazio, *Nature (London)* **416**, 608 (2002).
- [27] I. Affleck, *Phys. Rev. B* **43**, 3215 (1991).
- [28] *Tunneling Systems in Amorphous and Crystalline Solids*, edited by P. Esquinazi (Springer, Berlin, 1998).
- [29] S. Kettemann, P. Fulde, and P. Strehlow, *Phys. Rev. Lett.* **83**, 4325 (1999).
- [30] A. Wurger, *Phys. Rev. Lett.* **88**, 075502 (2002).
- [31] D. Waxman and A.J. Leggett, *Phys. Rev. B* **32**, 4450 (1985).
- [32] H. Grabert, P. Olschowski, and U. Weiss, *Phys. Rev. B* **36**, 1931 (1987).