Perturbation theory approach to dynamical tunneling splitting of local mode vibrational states in ABA molecules

A. A. Stuchebrukhov and R. A. Marcus
Arthur Amos Noyes Laboratory of Chemical Physics,[a] 127-72, California Institute of Technology, Pasadena, California 91125

(Received 18 December 1992; accepted 24 February 1993)

We introduce a point of view for treating the dynamical tunneling splitting of symmetric local mode vibrational states in ABA molecules (A=H typically) which is the one we have employed in treating the vibrational spectroscopy of CH overtones in molecules such as $(CX_3)_3YCCH$. Namely, the vibrational coupling corresponding to the dynamical tunneling in semiclassical mechanics via many intermediate off-resonance weak transitions between initial and final states can be treated by a standard high-order perturbation theory. We apply that method to the present simpler problem of tunneling splittings in ABA molecules, and compare the results with those of exact diagonalization, the semiclassical method, and the periodic orbit quantization. Of all the approximate methods, the perturbation theory was found to provide the best approximation to the results of exact diagonalization for the system treated. The relationship between these three methods and application to the problem of vibrational relaxation in polyatomic molecules with tunneling mechanism of intramolecular vibrational relaxation is discussed.

I. INTRODUCTION

In recent experiments[1] on intramolecular vibrational relaxation (IVR) of the acetylenic CH stretch excitation in $(CH_3)_3CCCH$ and $(CH_3)_3SiCCH$ molecules, an unusually slow relaxation, on the time scale of several hundred picoseconds, has been observed. Our analysis[2] has shown that in these molecules the vibrational relaxation of the excited CH states to the appropriate quasiresonant background states occurs through a sequence of many weak intermediate off-resonance transitions. This type of relaxation in the semiclassical limit of quantum mechanics corresponds to tunneling in action space between tori, which has been called in the literature dynamical tunneling.[3,4]

In this paper we discuss the concept of dynamical tunneling in a simplier one-dimensional case and apply a conventional perturbation theory, which we employed for treating vibrational couplings in the $(CX_3)_3YCCH$ molecules, to treat the splittings of symmetric local mode vibrational states in ABA molecules, which are attributed to dynamical tunneling. For a model local mode Hamiltonian we compare the results of perturbation theory with those of the semiclassical method, the periodic orbit quantization method, and with the results of exact diagonalization and show how different approaches are related to each other. Our results provide, we believe, a deeper insight into the nature of the dynamical tunneling phenomenon.

The qualitative semiclassical concept of dynamical barriers and dynamical tunneling emerged more than a decade ago in the studies of near degenerate vibrational states in two-dimensional potentials with the symmetry of ABA molecules.[3-6] Lawton and Child[3] proposed that the small splittings of the vibrational states of H_2O corresponding to the excitation of individual OH bonds (local modes) are due to tunneling. The tunneling appeared to be unusual in that it was in momentum space rather than in coordinate space. Later, Heller and Davis[4] generalized and refined this qualitative idea and introduced a term of dynamical tunneling in order to distinguish it from the usual potential tunneling. They noted that even in the absence of any barriers of the potential function, classical integrals of motion can break the phase space into several equivalent zones (tori) such that a trajectory with initial conditions in one of the zones would remain localized in the same zone indefinitely long, thereby breaking the symmetry of the potential. The localized zones were associated with dynamical wells separated by dynamical barriers. The classical trajectories localized in the equivalent zones can be associated with the degenerate quantum states. Due to tunneling these states mix to produce correct symmetry combinations, and the degenerate states split. In this picture the resulting split components in the energy spectrum of ABA molecules, the doublets, were associated with tunneling through the dynamical barriers.

In a related study Kellman[7] developed a concept of dynamical symmetry breaking. Harter and Patterson[8,9] recently treated the problem of multiplets in rotational spectra of polyatomic molecules from a semiclassical perspective and came to the same conclusion that the clusters of eigenstates observed in the energy spectrum result from tunneling in phase space. The equivalence of the local mode problem and the rotational problem was discussed by Lehmann.[10] In a more general context the correspondence between vibrational resonant interactions and the rotational problem has been recently reviewed by Uzer.[11] Similar ideas of quantum mechanical tunneling have also been discussed in connection with a heavy atom blocking effect[12] in symmetric molecular chains such as CCMCC and for the problem of avoided crossings in nonlinear vibrational systems.[13]

A quantitative one-dimensional semiclassical treatment of a local mode problem in ABA molecules was de-

[a]Contribution No. 8753.

veloped by Sibert, Reinhardt, and Hynes.[14,15] Using Chirikov's angle-action representation of a resonant system,[16] these authors found that the local mode problem can be reduced to quantization of an effective hindered rotor. Their analysis provides a transparent distinction between local and normal mode states as those associated with two different types of motion—a hindered rotation and torsion. A similar classification of two possible types of motion in a nonlinear system with an isolated resonance was introduced earlier by Noid and Marcus,[17] who also implicitly considered dynamical barriers and developed a quantitative semiclassical method for treating the splittings of degenerate bound states. Sibert, Reinhardt, and Hynes[14,15] showed that the removal of the twofold degeneracy of free rotor states by a hindering potential corresponds to the splitting of local mode states. To find the splittings they applied semiclassical formulas developed by Miller[18] for the hindered rotor problem.

The picture of Sibert, Reinhardt, and Hynes[14,15] seemed to be in contradiction with the analysis of Lawton and Child[3] and that of Davis and Heller.[4] The latter authors associated local mode states with the motion below a dynamical barrier, a barrier in momentum (action) space, while in the picture of Sibert, Reinhardt, and Hynes[14,15] those states were associated with the rotor motion above the hindering potential barrier, but in angle space. Later Stefanski and Pollak[19] provided an explanation to this apparent paradox with their method utilizing the periodic orbit quantization.[20–22] Their method is based on the stability analysis and semiclassical quantization of stable periodic classical trajectories corresponding to the local mode wells and unstable periodic trajectories corresponding to the dynamical barriers.[4,23]

In the present paper a high-order perturbation theory approach to dynamical tunneling splitting of local modes is described. In this approach the tunneling amplitude (and the splitting) Δ is calculated as a product of appropriate matrix elements V_{ij} with corresponding energy denominators along the quantum path over virtual off-resonance states connecting two local mode states $|a\rangle$ and $|b\rangle$,

$$\Delta = V_{a1}\frac{V_{12}}{(E_1-E_b)}\frac{V_{23}}{(E_2-E_b)}\cdots\frac{V_{nb}}{(E_n-E_b)}. \tag{1.1}$$

We show how this familiar expression is related to the semiclassical tunneling formula and periodic orbit quantization method, providing a practical way of treating dynamical tunneling in multidimensional cases. Of all the approximate methods, the perturbation theory method was found to provide the best approximation to the results of exact diagonalization.

The structure of the paper is as follows. In Sec. II the rotor Hamiltonian for the local mode problem is introduced. In Secs. III and IV the semiclassical and periodic orbit methods are briefly reviewed. Our main result is presented in Sec. V, where the relationship between the perturbation theory approach to dynamical tunneling and two other approximate methods of the previous sections are discussed, and the results of various approximations are compared with those of exact diagonalization. In Sec. VI a generalization of the perturbation method to multidimensional systems and some aspects of the dynamical tunneling mechanism of IVR in polyatomic molecules are discussed.

II. ROTOR HAMILTONIAN

It is well known[16] that a system of two coupled nonlinear oscillators in the vicinity of an isolated resonance can be reduced to an effective hindered rotor, if action-angle variables are used. The case of two Morse oscillators with a bilinear coupling, which describes the vibrational Hamiltonian for the ABA molecule with a frozen bending motion, was treated with this method in Refs. 14 and 15. The bilinear coupling is sufficient to describe the 1:1 resonance between two bonds AB and BA,[24] it can be of potential or kinetic nature.[4,14,15]

After transformation to a sum P and a difference p of the action variables of the two bonds, the original vibrational Hamiltonian, consisting of two coupled identical Morse oscillators, takes the following form:[14,15]

$$H = H_M - H_R. \tag{2.1}$$

In this equation H_M is the Morse oscillator for the action variable P,

$$H_M = \Omega P - \frac{\Omega^2}{8D}P^2, \tag{2.2}$$

where Ω and D are the parameters of the bonds. H_R is the hindered rotor Hamiltonian,

$$H_R = \frac{p^2}{2I} + V_0\cos(2\psi), \tag{2.3}$$

where p and ψ are the action variable (momentum) and the conjugate angle, respectively, and V_0 and I are the effective barrier and the moment of inertia of the rotor. The higher frequency terms in Eq. (2.3), corresponding to other than the 1:1 resonances, have been neglected.[14,15]

In a quantized form $P=(m+1)$, where m is the sum of vibrational quantum numbers of the two bonds, $m=n_1+n_2$, and $p=r=n_1-n_2$ is the difference of these quantum numbers. The Hamiltonian (2.1) does not contain a coordinate conjugate to P, hence P is an integral of the motion and m is a good quantum number. Accordingly, the dynamics of (2.1) is reduced to an effective one-dimensional hindered rotor (2.3). The factor 2 in the argument of $\cos(2\psi)$ in Eq. (2.3) accounts for the fact that the variable p in a quantized form can change only by quanta ± 2, when a one quantum exchange occurs between n_1 and n_2,

$$\Delta p = \Delta(n_1-n_2) = \pm 2. \tag{2.4}$$

In the absence of interaction between the vibrational bonds, $V_0=0$, the quantum states of the whole molecule are then described by the two quantum numbers, m and r, with the energy

$$E^0(m,r) = \Omega(m+1) - \frac{\Omega^2}{8D}(m+1)^2 - \frac{r^2}{2I}. \tag{2.5}$$

The barrier height V_0 is a function of both P and p. In Refs. 14 and 15 the authors adopted an approximation in which V_0 depends only upon the zero-order energy of the system E^0. As will be seen later, this simplified assumption of independence of V_0 of the individual actions of bonds is, in fact, a critical point for applicability of the semiclassical formula, since only in this case can one easily express the action of the rotor as an explicit function of the angle. This function is explicitly used in the calculation of the semiclassical action, as in Eq. (3.2). Although such an approximation is not important for the perturbation method discussed later in the present paper, we follow the approach of Refs. 14 and 15 in order to be able to compare their results with ours. Thus, for each unperturbed state with a pair of quantum numbers (m,r), there is a corresponding rotor Hamiltonian (2.3) with a barrier

$$V_0=V_0(m,r). \tag{2.6}$$

An explicit expression for V_0 is given in Refs. 14 and 15.

There are two possible types of classical motion of the effective hindered rotor—precession and libration,[14,15,17] depending upon whether the energy of the rotor is higher than the potential barrier V_0 or not. This allows one to distinguish naturally between normal and local modes of ABA molecules.[3,14,15] The difference between classical normal and local modes is in the degree of the vibrational mixing of AB and BA bonds. For libration the momentum p oscillates with changing sign, such that the average momentum p is zero, while for precession it is not. The implication of this fact for a vibrational system is easy to understand. If one recalls that the momentum p is a difference of the action variables of the two bonds in the ABA molecule (i.e., p is proportional to the difference of vibrational energies in two bonds) then it becomes clear that in the course of libration the total vibrational energy symmetrically oscillates between AB and BA bonds, which is typical for normal modes. For precession the vibrational energy is asymmetrically distributed between AB and BA bonds all the time (because the average $p=n_1-n_2$, where n_1 and n_2 are vibrational numbers of AB and BA bonds, is nonzero), and vibrational exchange between AB and BA is restricted. The higher the asymmetry of distribution of energy the smaller the energy exchange and vibrational mixing. This occurs because the vibrational frequency of a bond depends on the degree of excitation. The higher the difference in excitation, the farther vibrational frequencies of the two bonds from the 1:1 resonance, which is a necessary condition for the classical energy exchange. Thus, vibrations of AB and BA bonds can essentially be uncorrelated, if the difference of vibrational energies (or, equivalently, of the actions) of the two bonds is large. This type of behavior is typical for local modes.[3,14,15]

In the rotor picture, a large difference in energies of two bonds for a local mode trajectory corresponds to a large value of the rotational energy $p^2/2I$, large compared with the barrier V_0. For each rotational energy there are two symmetric local mode trajectories corresponding to two opposite directions of rotation. The classical evolution of the rotational momentum for such symmetric trajectories is described as follows:

$$p(t)\approx\pm p_0+(V_0/\omega_R)\cos(2\omega_R t), \tag{2.7}$$

where p_0 is a constant and ω_R is the unperturbed rotational frequency, $\omega_R=\partial H_R(p_0)/\partial p_0=p_0/I$. As is seen from Eq. (2.7), when p_0 is large compared with V_0/ω_R, the changes of $p(t)$ are small, which is a sign of the vibrational decoupling of the two bonds. Two different signs of p_0 correspond to two opposite directions of rotation of the rotor with the same energy. In a quantum picture these two trajectories correspond to two degenerate quantum local mode states, which split when tunneling between the two trajectories is allowed. This splitting is the subject of discussion in the following sections in this paper.

III. SEMICLASSICAL DYNAMICAL TUNNELING

The semiclassical expression for the splitting of two degenerate levels in a symmetric double well has been known for a long time[25]

$$\frac{\Delta}{2}=\frac{\omega_0}{2\pi}e^{-\theta}, \tag{3.1}$$

where ω_0 is the frequency of vibrations in the well and the action integral of the system, θ, is calculated between two turning points on both sides of the double well barrier. Usually this formula is used in coordinate space. It can also be used for momentum coordinate p, which is a "tunneling coordinate" for a local mode problem.[3] The two minima of a double well problem correspond to $\pm p_0$, the opposite momenta of two degenerate classical trajectories of the hindered rotor, as discussed in the preceding section. We note that in coordinate space the local mode states lie above the barrier top V_0 of the hindering potential; however, in momentum space the same local states are separated by a dynamic barrier. The frequency ω_0 is associated with the time evolution of the momentum variable p which oscillates around $\pm p_0$ in each of the dynamic wells, as in Eq. (2.7). From the classical equations of motion for the Hamiltonian (2.3) one finds that the frequency associated with the p variable is approximately two times the rotational frequency, $\omega_0=2\omega_R=2\partial H_R/\partial p$, as is seen in Eq. (2.7). The factor of 2 comes from the fact that the perturbation $V_0\cos 2\psi$, which give rise to oscillations of p, has a double frequency. Hence, in the period of one rotation the system passes twice the point from which it can tunnel. The action integral θ is calculated as usual:

$$\theta=\int p(\psi)d\psi \tag{3.2}$$

with

$$p=[2I(E_R^0-V_0\cos(2\psi))]^{1/2}, \tag{3.3}$$

where E_R^0 is the rotational energy of the unperturbed state and the integral (3.2) is taken between two turning points, $p=0$. We note that the action integral can be explicitly calculated only when V_0 is independent of p, which is usually not the case.

TABLE I. Splittings of the local mode vibrational states for the effective rotor Hamiltonian, Eq. (2.3). Parameters for the Hamiltonian correspond to H_2O (Refs. 14 and 15): $I=4D/\Omega^2$, $D=44\,500$ cm^{-1}, $\Omega=3871$ cm^{-1}. For each of the local mode states (m,r) shown are the corresponding rotational energy E_R, the rotation barrier V_0, Eq. (2.6), the exact splitting Δ_{ex}, the perturbation theory splitting Δ_{PT}, the semiclassical splitting Δ_{SC}, and the periodic orbit splitting Δ_{PO}.

(m,r)	E_R^0	V_0	Δ_{ex}	Δ_{PT}	Δ_{SC}	Δ_{PO}
(2,2)	168.36	76.74	16.12	17.49	19.98	17.88
(3,3)	378.83	97.81	2.01	2.06	2.25	1.24
(4,4)	673.46	116.77	0.134	0.135	0.144	0.032
(5,5)	1052.0	133.72	5.7×10^{-3}	5.8×10^{-3}	6.1×10^{-3}	3.3×10^{-4}
(6,6)	1515.3	148.79	1.73×10^{-4}	1.74×10^{-4}	1.8×10^{-4}	1.5×10^{-6}
(3,2)	168.36	99.10	25.7	29.2	34.1	32.6
(5,3)	378.80	137.35	5.4	5.7	6.4	4.72

As has been argued in Sec. II, the local mode states are those lying above the barrier, $E_R^0 > V_0$. In this case the turning points, $p=0$, correspond to pure imaginary values of angle $\psi=i\eta$. For a pure imaginary argument $\cos 2\psi$ becomes an exponentially growing function, $\cosh(2\eta)$. Actual integration then takes the form

$$\theta=\int_{-\eta^*}^{\eta^*} d\eta[2I(E_R^0-V_0\cosh(2\eta))]^{1/2}, \tag{3.4}$$

where η^* is the point where the expression under the square root becomes zero,

$$\eta^*=\tfrac{1}{2}\,\mathrm{Arch}(E_R^0/V_0). \tag{3.5}$$

Thus, the semiclassical procedure of calculation of the splitting of a degenerate local mode state, within the rotor Hamiltonian model, is as follows. For a particular state (m,r), one defines $V_0(m,r)$ from Eq. (2.3), substitutes $E_R^0=r^2/2I$ in Eq. (3.4), and finally uses $\omega_0=2\omega_R=2r/I$ to calculate the splitting by Eq. (3.1). There are several approximations involved in this procedure, as, for example, in the equation for E_R^0. More detailed and accurate semiclassical theory of tunneling splittings for a hindered rotor was developed in Refs. 18 and 26. The splitting for a number of local mode states in a system with parameters given in Refs. 14 and 15 were recalculated with a procedure described above, and the results are shown in Table I.

IV. PERIODIC ORBIT QUANTIZATION METHOD. HARMONIC APPROXIMATION

Although the rotor Hamiltonian method described above gives a quantitative answer to the problem of dynamical tunneling, the qualitative picture stemmed from this method seems to be quite different from that suggested by Lawton and Child[3] and that of Davis and Heller.[4] Indeed, in the rotor picture the local mode states are those lying above the barrier V_0 and splitting of the degenerate states seems to arise due to the over-the-barrier reflection rather than due to the underbarrier tunneling, as one would expect. Stefanski and Pollak[19] proposed to use a periodic quantization method[20–22] which helps to resolve this paradox.

In this method the stability properties of the classical periodic trajectories are studied. Two stable local mode periodic orbits correspond to two symmetric wells while the unstable periodic orbit, which is a symmetric stretch of ABA, corresponds to the dynamical barrier. The complex stability frequency (the stability frequency is a frequency associated with the time evolution of small deviations from a periodic trajectory[19–22]) of the unstable periodic orbit is then associated with the frequency at the barrier maximum and the real stability frequency of the stable periodic orbit is associated with the harmonic frequencies for the wells. Energies corresponding to the barrier top and the bottoms of the wells are then calculated from the usual semiclassical quantization rules applied to corresponding periodic trajectories. Finally, the conventional semiclassical formula (3.1) for the harmonic barrier (which contains only the frequencies of the wells and the barrier and the barrier height) is used with self-evident substitutions.

The two stable local mode orbits in the rotor picture correspond to free rotation with opposite direction, i.e., to two rotor states with $\pm r$. The corresponding quantized total energy is $E_M^0(m)-E_R^0(r)$, as seen in Eq. (2.5). The unstable periodic orbit (the symmetric stretch of the ABA molecule) corresponds to the rotor at rest, $p=0$, at one of the maxima of the potential $V_0\cos(2\psi)$. The corresponding quantized total energy is $E_M^0(m)-V_0$. Hence, the dynamical barrier height is $E_R^0(r)-V_0$. One then finds the stability frequencies of the periodic orbits. Real frequency of the stable orbit corresponds to the frequency of vibrations in the well, i.e., frequency of oscillations of the momentum variable $p(t)$. In this case it is $2\omega_R$, as we discussed in the preceding section, and also after Eq. (2.7). The pure imaginary frequency of the unstable orbit corresponds to the frequency of the barrier. The latter in our case is the imaginary frequency ω_b at one of the maxima of the potential $V_0\cos 2\psi$, which is

$$\omega_b=(4V_0/I)^{1/2}. \tag{4.1}$$

The next step is to calculate the action integral under the barrier, assuming that it has a form of an inverted parabola. As Stefanski and Pollak[19] realized, the result is just the harmonic approximation of Eqs. (3.2)–(3.4),

$$\theta_h=\int_{-\eta_h^*}^{\eta_h^*} d\eta[2I(E_R^0-V_0)]^{1/2}\left(1-\frac{2V_0}{E_R^0-V_0}\eta^2\right)^{1/2}$$
$$=\pi(E_R^0-V_0)(I/4V_0)^{1/2}, \tag{4.2}$$

where the turning points now correspond to the harmonic approximation, η_h^*. Thus, the periodic quantization method provides a harmonic approximation of the semiclassical expression, and so it is not surprising that the results are less accurate than those of the original semiclassical expression, as seen in Table I. The method, however, clearly shows that the top of the dynamical barrier can be associated with the rotor quantum states with small momentum $p=r$. Further insight into the nature of dynamical tunneling can be be obtained by studying the relationship between the semiclassical approximation and the quantum perturbation theory result.

V. PERTURBATION THEORY APPROACH

In this section we show how the two semiclassical approaches, briefly reviewed in the previous sections, are related to ordinary quantum perturbation theory.

In a quantum approach one considers the potential $V_0\cos(2\psi)$ of the Hamiltonian (2.3) as a perturbation for a free rotor with energies $E_R^0(k)$ and wave functions $\langle\psi|k\rangle$,

$$E_R^0(k)=k^2/2I, \tag{5.1}$$

$$\langle\psi|k\rangle=1/\sqrt{2\pi}e^{ik\psi}. \tag{5.2}$$

The perturbation couples states which differ in two rotational quanta with the matrix element $V_0/2$. Two local mode states $(m,\pm r)$ are coupled through a sequence of intermediate virtual transitions over the states with quantum numbers $-(r-2)\leqslant k\leqslant(r-2)$.

The local mode nature of the vibrational states indicates that there is no significant mixing of the zero-order states of the two bonds with different energies. (However, the degenerate states are strongly mixed.) This means, in turn, that the coupling matrix elements, $V_0/2$, between the zeroth-order states is small, compared with the appropriate energy differences. Otherwise, the states would be strongly mixed, as in the normal mode picture. The relative smallness of V_0 provides the basis for application of the perturbation theory.

Formally, for the perturbation calculation of the splitting of two rotor states $(\pm r)$ [or two local mode states $(m,\pm r)$ as in Sec. II] to be valid, it is sufficient to require that the matrix element $V_0/2$ be small compared with the following energy denominator:

$$\frac{V_0}{2}\ll E_R(r)-E_R(r-2)\simeq 2\omega_R. \tag{5.3}$$

The splitting of the degenerate states $(\pm r)$ is two times the value of the effective coupling matrix element between these states. In the lowest nonzero order of perturbation theory the effective coupling is a product

$$\frac{\Delta}{2}=\frac{V_0}{2}\prod_{m=-(r-2)}^{(r-2)}\frac{V_0/2}{E_R^0(r)-E_R^0(m)}. \tag{5.4}$$

This expression is related in a simple way to semiclassical expression (3.1).

To show this result we first change the variable of integration in Eq. (3.2). Instead of integrating over the angle variable in Eq. (3.2) we integrate over the momentum p. After integration by parts the integral for θ can be rewritten as

$$\theta=\int_{-p_m}^{p_m}dp\eta(p), \tag{5.5}$$

where $\eta=-i\psi$ is a complex angle variable. In Eq. (5.5) p_m is the minimum classical value of the momentum of the rotor excited above the barrier V_0. The integration in Eq. (5.5) is over classically forbidden values of the momentum, $|p|\leqslant p_m$. The appropriate expression for $\eta(p)$ is found from Eq. (3.3) with $\psi=i\eta$,

$$\cosh(\eta)=\frac{e^{2\eta}+e^{-2\eta}}{2}=\frac{E_R^0(r)-E_R^0(p)}{V_0}, \tag{5.6}$$

where $E_R^0(p)=p^2/2I$. For most values of p in the interval $-p_m\leqslant p\leqslant p_m$, except for those in the vicinity of $\pm p_m$, $0\leqslant p_m-|p|\leqslant V_0/\omega_R$, one can disregard the negative exponent in the cosh and write

$$\eta(p)=\frac{1}{2}\ln\left(\frac{E_R^0(r)-E_R^0(p)}{V_0/2}\right). \tag{5.7}$$

The integral (5.5) then can be approximated by a sum over discrete points, as in Fig. 1. The discrete integration points are chosen in such a way as to correspond to the quantized values of the p variable, which are the integer points within the interval $-p_m\leqslant p\leqslant p_m$. The integration step is $\Delta p=2$, in accordance with allowed increments of the quantized values of p, as in Eq. (2.3). Then, the whole expression for $\exp(-\theta)$ can be written (as in the Appendix) as

$$e^{-\theta}=F\frac{V_0}{2}\prod_{k=-(r-2)}^{(r-2)}\frac{V_0/2}{E_R^0(r)-E_R^0(k)}, \tag{5.8}$$

$$F=\frac{f}{E_R^0(r)-E_R^0(r-2)}, \tag{5.9}$$

where $E_R^0(k)=k^2/2I$ are the energies of a free rotor. Except for the factor F, Eq. (5.8) coincides with the perturbation theory expression for the effective matrix element between two local mode states (m,r) and $(m,-r)$. This part of the expression comes from a trapezoidal approximation of the integral over the internal discrete points $-(r-2)\leqslant m\leqslant(r-2)$, as in Fig. 1. The factor F is the contribution of the end points of the interval. As is shown in the Appendix, the factor f in Eq. (5.9) is well approximated by $e^{2-\delta}$, where δ is a small, compared with unity, positive number which depends on V_0. We note that the numerical value of f is very close to 2π,

$$f\simeq e^{2-\delta}\simeq 2\pi. \tag{5.10}$$

The energy denominator of the factor F can be written as

$$E_R(r)-E_R(r-2)\simeq 2\frac{\partial E_R(r)}{\partial r}=2\omega_R. \tag{5.11}$$

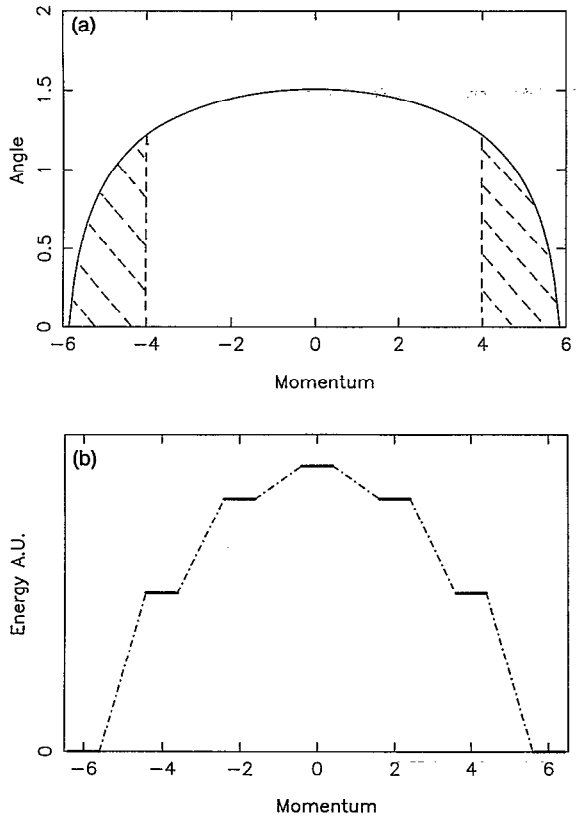

FIG. 1. (a) Complex phase angle η as a function of the momentum p (in units of $\hbar$) in Eq. (5.5) for a local mode state $(m,r)=(6,6)$. The integration in (5.5) is over the interval between the two turning points, $\pm p_m \simeq \pm(r-V_0/\omega_R)$, where $\eta=0$. Within the interval there are several discrete integration points $-(r-2)\leqslant k\leqslant(r-2)$, corresponding to the intermediate quantum states of the rotor. Contribution of the end points, dashed segments, are evaluated separately from the internal points; see the Appendix. (b) Two quantum local mode states, $(m,\pm r)=(6,\pm 6)$, are coupled through a sequence of the intermediate rotor states, $-(r-2)\leqslant k\leqslant(r-2)$, corresponding to the discrete integration points in (a). The transition amplitude between the neighboring states is $V_0/2$. The energy scale is $-E_R$, in accordance with the rotor contribution to the total energy, Eq. (2.1).

In this expression ω_R is the free rotor frequency corresponding to the local state $(m,\pm r)$, which is the same frequency ω_R as in the preceding section, discussed after Eq. (3.1).

It is seen now that the multiplication of the exponential factor $e^{-\theta}$ in Eq. (5.8) by $\omega_0/2\pi$, according to Eq. (3.1), reproduces essentially the perturbation expression for the matrix element (5.4). It is not exactly the same expression because of the approximations made.

In Table I the perturbation theory results are compared with those of numerical integration of the semiclassical expressions, and the results of exact diagonalization. As is seen in Table I, perturbation theory gives the best approximation to the exact diagonalization. From the above analysis one can conclude that the perturbation theory provides a discrete counterpart to the integrals of the semiclassical expression. It is interesting that the two methods agree as well as they do even when there are only few off-resonance states coupling them, as in the case of $(m,\pm 2)$ local states. One reason for such an agreement is that the function being integrated in Eq. (5.5) is a logarithm which is a slowly varying function at most of the points of the integration interval except those in the vicinity of the end points.

It is worthwhile mentioning the similarity of the results and ideas of this section and those of the discrete variable representation, discussed recently[27,28] in a different context.

VI. DISCUSSION

As is shown in the preceding section, in addition to two semiclassical points of view on dynamical tunneling perturbation theory provides another description of the phenomenon as a sequence of weak virtual transitions over the intermediate off-resonance states. In Ref. 29 it was argued that such a "nonclassical" mechanism of energy transfer is basically different from tunneling and resembles an activation barrier crossing, rather than tunneling. It is interesting to observe, however, that the case of the usual potential tunneling can be presented in a similar way, as a sequence of virtual transitions through the off-resonance states.

Consider tunneling between two points a and b separated by a potential barrier $V(x)$. Instead of a continuum coordinate x we introduce a discrete approximation $\{x_i\}$, as one would do for a numerical integration. The best way to choose a given number of points of integration has been discussed in the literature.[27,28] For our purpose it is sufficient to choose them equally spaced on the x axis. In the discrete representation of the x coordinate one can write an equivalent Hamiltonian of a particle hopping between the discrete sites $\{x_i\}$. In this Hamiltonian the potential energy at a point x_i can be associated with the energy of the state, $|x_i\rangle$. The discrete form of the kinetic energy operator provides the hopping amplitudes between neighboring states. In the lowest order of approximation for the discrete kinetic energy operator, there are only transitions between the nearest-neighbor states,

$$H=\sum_i V(x_i)\,|x_i\rangle\langle x_i| + \sum_i \frac{1}{2m\delta^2}\,(2|x_i\rangle\langle x_i| - |x_{i+1}\rangle \times\langle x_i| - |x_{i-1}\rangle\langle x_i|), \tag{6.1}$$

where m is the mass of a tunneling particle and δ is a distance between adjacent x points. From Eq. (6.1) one can see that the two turning points $|x=a\rangle\langle x=a|$ and $|x=b\rangle\langle x=b|$, having the same energy and separated by the barrier, are connected through a sequence of virtual transitions over the off-resonance states, $|x_i\rangle\langle x_i|$ with $a<x_i<b$. One can show, in a way similar to that of the preceding section, that the perturbation theory expression of the amplitude of the transition between $|x=a\rangle\langle x=a|$ and $|x=b\rangle\langle x=b|$, written as a product of the terms corresponding to each virtual transition, reduces to the usual exponential expression $e^{-\theta}$, where θ is the action integral calculated under the potential barrier $V(x)$ between points $x=a$ and $x=b$. Thus, the whole picture is equivalent to that of the preceding section.

It is also worthwhile mentioning quite a different situation where tunneling is revealed as a sequence of virtual transitions. Namely, in the long-distance electron transfer theory a similar mechanism of the quantum transition over off-resonance bridge states is known as superexchange[30–32] and is also associated with tunneling. For this reason the dynamical tunneling considered in the present paper and also in Ref. 2 can be termed also as a vibrational superexchange.

The discussion in the previous sections shows that the semiclassical methods contain essentially nothing new compared with the perturbation theory. This qualitative result is important for the problem of generalization of the concept of dynamical tunneling to the multidimensional cases and to polyatomic molecules. Neither the semiclassical nor the periodic orbit method have been generalized, to the best of our knowledge, to the multidimensional case, although some work has been done for systems with two and three degrees of freedom.[17,33,34] On the other hand, the generalization of the perturbation method to the multidimensional case is quite straightforward. Of course, the perturbation theory approach is possible only for the systems where the zeroth-order states (local mode basis, or local-mode–normal-mode basis) are readily recognizable. If the perturbations in a molecule are so large that one is not able to find a simple zeroth-order basis, the perturbation theory would not be appropriate. For such systems direct diagonalization or the semiclassical periodic orbit method is preferable.

In recent experiments[1] on intramolecular vibrational relaxation of the acetylenic CH excitation in $(CH_3)_3CCCH$ and $(CH_3)_3SiCCH$ extremely narrow homogeneously broadened vibrational lines have been observed, which correspond to an unusually slow relaxation on the time scale of several hundred picoseconds. Our analysis[2] shows that the vibrational relaxation in these molecules of the CH vibrational states to the appropriate quasiresonant background vibrational states occurs through a sequence of many weak intermediate off-resonance transitions.[2] This type of vibrational coupling resembles, as we have already mentioned, the superexchange in a long-distance electron transfer[30–32] and can be called a vibrational superexchange. In the semiclassical limit, as has been argued in the preceding section, such a type of quantum dynamics is associated with dynamical tunneling in action space of the molecule. This is a new type of the intramolecular irreversible vibrational relaxation where the quantum tunneling in phase space is involved.[2]

The easiest way to treat such a multidimensional tunneling is to use a discrete space of zeroth-order quantum states instead of using the continuum action-angle variables. As we have seen, using a simple one-dimensional case as an example, this procedure is almost equivalent to the semiclassical method. In a one-dimensional case there is only one path coupling two degenerate states. In the multidimensional case there are many such paths. As in the conventional semiclassical methods of continuum variables, the action associated with the discrete paths can be analyzed in order to identify the most important paths for the relaxation. Such a procedure has been implemented[2] recently for the case of $(CX_3)_3YCCH$ molecules.

Although we have described the method of calculation of tunneling relaxation rates in polyatomic molecules with ideas of perturbation theory, to complete the qualitative picture of multidimensional dynamical tunneling it would be interesting to find in action space of the molecule $I_1,...,I_n$ an explicit form of the effective dynamic potential with barriers which separate the initially prepared state from other quasiresonant states in a molecule and result in tunneling relaxation. At present this problem is not solved. However, we believe that the discrete variable representation of the dynamic barriers in action space with quantum states $|v_1,...,v_n\rangle$, where v_j are quantum numbers corresponding to continuum action variables I_j, $\hbar v_j = I_j$, in the present paper and in Ref. 2, provides a clue to this problem.

ACKNOWLEDGMENTS

The authors wish to thank Kevin Lehmann for many stimulating discussions as well as Jonathan Connor, Mark Child, and Eli Pollak for many useful comments on the subject of the present paper. We are pleased to acknowledge the financial support of NSF.

APPENDIX

The details of the discrete approximation of the action integral (5.5) are discussed here.

As is seen in Fig. 1, within the integration interval there are several discrete points, $-(r-2),...,(r-2)$. The integration step is 2. Outside the interval, in the immediate vicinity of the end points, $\pm p_m$, there are two discrete points $\pm r$ corresponding to the degenerate local mode states. The contribution of the end points of the integration interval, which represent the turning points in the complex plane for ψ, is evaluated separately from the contribution of the internal points.

For the internal points the usual trapezoidal rule is applied,

$$\int_{-(r-2)}^{(r-2)} dp\, \eta(p) = \sum_{k=-(r-2)}^{(r-4)} \ln\left(\frac{E_R^0(r)-E_R^0(k)}{V_0/2}\right), \tag{A1}$$

where for $\eta(p)$ the approximate expression (5.7) is used. The latter is a good approximation, as explained in Sec. IV.

At each end point the following approximations are made. First, for the function $\eta(p)$ its logarithmic approximation is taken. The deviation of the logarithmic function from the Arch function in the immediate vicinity of the end points $\pm p_m$ is of the order V_0/ω_R, which is assumed to be small. This deviation contributes $(V_0/\omega_R)^2$ to the integral and, hence, can be neglected. Second, the range of the integration is slightly shifted to

$$\bar{p}_m = p_m + V_0/2\omega_R, \tag{A2}$$

where $\pm\bar{p}_m$ are the turning points of the logarithmic approximation of $\eta(p)$. For the same reason as above the

contribution of this correction is also small. Finally, the rotation energy $E_R^0(p)$ in the vicinity of the turning points is written in a linear approximation as

$$E_R^0(p)=E_R^0(\pm r)-V_0/2\mp\omega_R(p-\bar{p}_m). \tag{A3}$$

For $p=\pm\bar{p}_m$ the logarithmic expression for $\eta(p)$, Eq. (5.7), vanishes.

With these approximations, the contribution of each of the end intervals can be evaluated as

$$\frac{1}{2}\int_0^2 \ln\left(1+\frac{2\omega_R x}{V_0}\right)dx=\ln\left(\frac{E_R^0(r)-E_R^0(r-2)}{V_0/2}\right)-1+\frac{\delta}{2}, \tag{A4}$$

where in the left-hand side we substituted for $2\omega_R$ its original expression in terms of energies, $E_R(r)-E_R(r-2)$. A small positive number, δ, is defined as

$$\frac{\delta}{2}=\frac{V_0}{4\omega_R}\ln\frac{4\omega_R}{V_0}. \tag{A5}$$

Summation of contributions (A1) and (A4) results in Eqs. (5.8) and (5.9).

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