Mode specificity in unimolecular reaction dynamics: The Henon–Heiles potential energy surface

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Energies and lifetimes (with respect to tunneling) for metastable states of the Henon–Heiles potential energy surface $V(x,y) = 1/2x^2 - 1/3x^4 + 1/2y^2 + xy^2$ have been computed quantum mechanically (via the method of complex scaling). This is a potential surface for which the classical dynamics is known to change from quasiperiodic at low energies to ergodic-like at higher energies. The rate constants (i.e., inverse lifetimes) for unimolecular decay as a function of energy, however, are seen to be well described by standard statistical theory (microcanonical transition state theory, RRKM plus tunneling) over the entire energy region. This is thus another example indicating that mode specificity in unimolecular reaction dynamics is not determined solely by the quasiperiodic/ergodic character of the intramolecular mechanics.

I. INTRODUCTION

There is considerable interest nowadays in the question of mode specificity in chemical reaction dynamics. For a unimolecular reaction, for example, the question is whether the rate of reaction depends on the specific mode of the molecule which is excited or only on the total energy of excitation.

Pursuant to this question there have been a number of theoretical studies on intramolecular dynamics of model systems. One particular feature of such studies, which has received much attention, is the existence of classical motion that is quasiperiodic at low energies but which becomes ergodic-like (or stochastic, chaotic) at higher energies. This transition of the intramolecular motion from quasiperiodic at low energy to ergodic-like at high energies is related to the KAM theorem and related topics which are currently receiving much attention in the mathematics community.

Some theoretical studies have also been concerned with whether this quasiperiodic/ergodic behavior in the classical mechanics of intramolecular motion has a direct manifestation in a quantum mechanical description of the corresponding system. A variety of quantum mechanical features have been considered—the sensitivity of individual energy levels to small perturbations of the potential function, the “localized” or “extended” distribution of coefficients of basis functions used to expand the wave function, the nodal patterns of the wave functions, etc.—and they all do indeed show quantum mechanical features that correlate qualitatively with the quasiperiodic/ergodic aspects of the classical mechanics.

However, while these quantum mechanical studies have been of interest, they do not bear directly on the question of mode specificity in the reaction dynamics. In a recent paper the present authors thus undertook a series of calculations designed to investigate the extent to which mode specificity in unimolecular rate constants correlates with the quasiperiodic/ergodic character of the intramolecular classical dynamics of the system. Specifically, for a system of two coupled oscillators (i.e., a collinear triatomic molecule in its center of mass), one of which could dissociate by tunneling through a barrier, quantum mechanical calculations for the energies and lifetimes of all metastable (or quasibound) states were made. Mode-specific or statistical behavior was then interpreted by plotting the unimolecular decay rates of all such states versus their energy to see if the rates were indeed a smooth function only of their energy. The expectation was that quasiperiodic classical motion would lead to modespecific behavior of the rate constants and that ergodic-like classical motion would correlate with statistical behavior of the rates.

Quite surprisingly, however, we found very little correlation between the quasiperiodic/ergodic motion of the classical mechanics and mode specific/statistical behavior of the unimolecular rate constants. For some potential surfaces for which the classical motion was quasiperiodic, the rate constants showed strong mode specificity, and for others they did not.

To pursue further the question of how classical quasiperiodic/ergodic behavior is related to mode specificity in unimolecular rate constants, the present paper reports the results of calculations similar to our earlier ones for the Henon–Heiles potential surface. The Henon–Heiles model is a system of two coupled oscillators, and its classical quasiperiodic/ergodic behavior is perhaps the most extensively studied of all such model systems: At low energies the classical motion is quasiperiodic, but at higher energies it becomes ergodic-like. It is thus an excellent example to see if the mode-specific character of the unimolecular rate constants shows any similar transitional behavior as a function of energy.

Section II defines the Henon–Heiles model and summarizes the computational method. The results are discussed in Sec. III, and it is seen that the unimolecular decay rates are described quite well by a simple statistical model, microcanonical transition state theory (i.e., RRKM plus tunneling), over the entire range of energies. For this system, therefore, the quasiperiodic/ergodic behavior of the classical dynamics does not have a direct manifestation in the mode-specific character of...
the individual rate constants. Section IV considers a modified Henon–Heiles-like potential that does show significant mode specificity, and our conclusions are summarized in Sec. V.

II. THE MODEL AND METHOD

The quantum mechanical version of the Henon–Heiles system is that of two coupled oscillators (e.g., a collinear triatomic molecule in its center of mass) with the following quantum mechanical Hamiltonian:

\[
H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} m \omega^2 (x^2 + y^2) + \lambda (x^2 + xy^2) .
\]

(2.1)

This can be transformed to standard form by introducing the reduced quantum of action \( \hbar \)

\[
\hbar = \frac{\hbar^2}{m \omega^2} , \tag{2.2a}
\]

and measuring energy in unit \( \epsilon \),

\[
\epsilon = \frac{m \omega^2}{\hbar^2} . \tag{2.2b}
\]

In these units \( H \) becomes

\[
H = -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2}(x^2 + y^2) - \frac{1}{2} x^2 + xy^2 , \tag{2.3}
\]

and in polar coordinates \( (r, \theta) \) the potential energy has a form that more clearly depicts its \( C_3 \) symmetry,

\[
V(r, \theta) = \frac{1}{2} r^2 - \frac{1}{2} r^2 \cos(3\theta) . \tag{2.4}
\]

This potential has three equivalent saddle points at positions \( (r, \theta) = (1, 0), (1, 2\pi/3), (1, -2\pi/3) \), and the value of the potential at the saddle points is \( V_{sp} = \frac{1}{2} \approx 0.167 \). Henceforth we will denote \( \hbar \) simply as \( \hbar \) and allow it to be a variable parameter which measures the "quantumness" of the system.

As noted in the Introduction, the classical version of the Henon–Heiles model has been studied extensively; for energies below a critical value \( E_c \approx 0.11 \), all classical trajectories are quasiperiodic, but above this value an increasingly large fraction of initial conditions in phase space leads to ergodic-like trajectories. Classically, the system cannot dissociate, of course, for any energy below \( V_{sp} \).

Quantum mechanically, however, the system has no bound states, only metastable states that decay by tunneling through the barriers. Using the complex scaling method, we have calculated the complex eigenvalues of the system, i.e., the Siegert eigenvalues, which give the energy (real part of the eigenvalue) and unimolecular decay rate \(-2/\hbar \times \text{imaginary part of the eigenvalue}) of the metastable states.

The \( C_3 \) symmetry of the Henon–Heiles potential gives rise to the states of symmetry \( A_1 \), \( A_2 \), and \( E \). Using a basis set in polar coordinates,

\[
\phi_{n, m}(r, \theta) = r^n \exp\left(-\alpha r^2/2\right) e^{i m \theta} ,
\]

(2.5)

these three types of states correspond to the following grouping of the basis functions:

\[
A_1: \cos(m\theta) , \quad m=0, 3, 6, 9, \ldots , \quad m \leq n , \tag{2.6a}
\]

\[
A_2: \sin(m\theta) , \quad m=3, 6, 9, \ldots , \quad m \leq n , \tag{2.6b}
\]

\[
E: e^{i m \theta} , \quad m=\ldots , -5, -2, 1, 4, 7, \ldots , \quad |m| \leq n ,
\]

(2.6c)

where the two groups of \( m \) values for the \( E \) states give rise to the double degeneracy of these states.

With these special features due to symmetry, the method of calculation is essentially the same as that used earlier. In polar coordinates \( (r, \theta) \) the radial coordinate is scaled as \( \tau = r e^{i \omega t} \) and \( \theta \) remains real, i.e., the Hamiltonian \( H(\alpha) \),

\[
H(\alpha) = e^{-i \alpha \theta} \left( -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) \right) + e^{i \alpha \theta} (\frac{1}{2} r^2 - \frac{1}{2} r^2 \cos(3\theta)) ,
\]

is diagonalized in the basis set of Eq. (2.5) and the complex eigenvalues thus obtained.

The value of \( \hbar \) can be chosen to make the system more (larger \( \hbar \)) or less (smaller \( \hbar \)) quantum-like, and to speed up or slow down, respectively, the tunneling rates. Since the harmonic approximation to the number of quantum states less than or equal to energy \( E \) is

\[
N(E) \approx \frac{1}{2} (E/\hbar)^{3/2} , \tag{2.8}
\]

the value of \( \hbar \) is related to \( N_0 = N(V_{sp}) = N(E) \), the number of classically bound states, by

\[
N_0 \approx \frac{1}{72 \hbar^2} . \tag{2.9}
\]

A value \( \hbar = 0.04 \) thus produces about nine classically bound states, i.e., metastable states with energy \( \leq V_{sp} \); a value \( \hbar = 0.02 \) leads to \( \approx 35 \) classically bound states. Since smaller \( \hbar \) means more states, the calculation of which requires larger basis sets, there is a practical limit to how small we are able to choose \( \hbar \). For the present calculations this is about \( \hbar = 0.02 \), and for this smallest value we did not calculate the \( E \)-type complex eigenvalues since this symmetry required about twice the size of basis set of that for the \( A_1 \) and \( A_2 \) states.

III. RESULTS AND DISCUSSION

Figures 1–3 show the unimolecular decay rates versus energy for values \( \hbar = 0.04, 0.03, \) and 0.02, respectively. Decreasing the value of \( \hbar \) makes the system more classical-like and is thus the interesting limit to explore to see if features related to the classical quasiperiodic/ergodic behavior appear in the quantum rate constants.

Several observations are apparent from Figs. 1–3.

(1) The \( A_0 \) states decay more slowly than the \( A_1 \) and \( E \) states, for a given energy. This is readily understandable, however, by realizing that \( A_0 \) states have a nodal line from the origin through each saddle point; cf. the factor \( \sin(m\theta) \), \( m=3, 6, \ldots \), in the wave function of \( A_0 \) states, Eq. (2.6). In the language of transition state theory (see the Appendix), for example, this
means that the vibrational states of the "activated complex," i.e., the local vibrational modes at the saddle points of the potential energy surface, must be odd. Thus, in the tunneling region where only the lowest state of the activated complex contributes, transition state theory implies that

$$k_{\Delta}(E) \sim (\text{frequency factor}) \times P(E - \hbar \omega^t),$$  \hspace{1cm} (3.1a)

$$k_{\Delta}(E) \sim (\text{frequency factor}) \times P(E - \frac{1}{2} \hbar \omega^t),$$  \hspace{1cm} (3.1b)

where \( P \) is a one-dimensional tunneling probability; this implies that

$$k_{\Delta}(E) = k_{\Delta}(E - \hbar \omega^t),$$  \hspace{1cm} (3.2)

where \( \omega^t \) is the vibrational frequency at the saddle point. For the present potential surface,

$$\omega^t = \sqrt{3},$$

and Figs. 1–3 do indeed show that the rate constants for \( A_1 \) and \( A_2 \) states are displaced in energy by approximately \( \hbar \omega^t = \sqrt{3} \hbar \).

(2) Apart from this symmetry-induced mode specificity the rate constants show essentially no mode specificity; that is, within each symmetry class the rate constants appear to be a smooth function only of the total energy. There is certainly no hint of any transitional behavior in the vicinity of the critical energy \( E_c = 0.11 \). The most mode-specific features are in the \( E \) states of Fig. 2, and they become more significant with increasing energy.

To test the statistical character of the rate constants more quantitatively, we computed the rate via microcanonical transition state theory, i.e., the simple "RRKM plus tunneling" model\footnote{This model has been used recently for several molecular systems of physical interest (\( \text{CH}_3\text{O} \to \text{CO} + \text{H}_2 \), \( \text{HNC} \to \text{HCN} \), \( \text{H}_2\text{C}=\text{C} : - \text{HC} = \text{CH}_3 \)).} that has been used recently for several molecular systems of physical interest (\( \text{CH}_3\text{O} \to \text{CO} + \text{H}_2 \), \( \text{HNC} \to \text{HCN} \), \( \text{H}_2\text{C}=\text{C} : - \text{HC} = \text{CH}_3 \)). The Appendix describes the specifics of this calculation. The solid curves in Figs. 1–3 show the rate obtained in this way, and one sees that the decay rates of the \( A_1 \) and \( E \) states are reasonably well described by this simple statistical model. The fact that the \( A_1 \) states decay more slowly is understood from the discussion above and could be described by the statistical model by excluding the even vibrational states, \( n = 0, 2, \ldots \), from the activated complex (i.e., the sum in Eq. (A1) of the Appendix).

There is one final issue that could possibly cloud any correlation that might exist between classical quasi-periodic/ergodic behavior and mode specificity in the rate constants we have calculated, namely, the possibility that we have not allowed \( \hbar \) to become sufficiently small for any underlying classical structure to emerge in the quantum rate constants. In order to extrapolate better to \( \hbar \to 0 \), we thus take cognizance of the form the rate constant has within the statistical model described in the Appendix, namely,

$$k(E) \sim (\text{frequency factor}) \times (\text{tunneling probability}).$$  \hspace{1cm} (3.3)

The frequency factor has a classical limit independent of \( \hbar \), and the tunneling probability has the limiting form

$$\text{tunneling probability} \approx \exp[-2\theta(E)/\hbar],$$  \hspace{1cm} (3.4)

where \( \theta(E) \) is the classical action integral given for the present example by Eq. (A4) and (A6) of the Appendix.
This implies that the quantity $\hbar \log (k(E))$ should have a classical limit,

$$\lim_{\hbar \to 0} \hbar \ln k(E) = -2\theta(E),$$

or

$$\lim_{\hbar \to 0} \hbar \log_{10} k(E) = -2\theta(E) \log_{10} e \approx -0.87\theta(E).$$  \hspace{1cm} (3.5)

Figures 4 and 5 show the quantity $\hbar \log k(E)$ for $\hbar = 0.02, 0.03, 0.04$, for the $A_1$ and $A_2$ states. Also shown is the RRKM plus tunneling approximation to the $\hbar \to 0$ limit of this quantity, Eq. (3.5), and it appears that (1) the quantum rate constants are approaching the $\hbar \to 0$ limit in a smooth manner with no evidence of any new classical structure emerging, (2) the simple RRKM plus tunneling model is a reasonably good approximation to the $\hbar = 0$ limit of the quantum rate constants, and (3) both the $A_1$ and $A_2$ states converge to the same $\hbar \to 0$ limit [as is implied by the approximate relation in Eq. (3.2)].

The unavoidable conclusion, therefore, is that the Henon–Heiles system shows little mode specificity in its unimolecular rate constants (other than that imposed by symmetry) and, thus, that in this case the quasiperiodic/ergodic character of the intramolecular classical mechanics does not determine the degree of mode specificity in the reaction dynamics.

IV. A ONE-BARRIER HENON–HEILES POTENTIAL

It occurred to us that the lack of mode specificity for the Henon–Heiles potential surface might be related to the fact that there are two exit valleys, i.e., dissociation channels. One might thus reason that even if the intramolecular mechanics is quasiperiodic, i.e., quasiseparable, there is no mode (or direction in the $x$–$y$ plane) in which the energy can be trapped that does not project onto one of the dissociative reaction coordinates.

To test this idea we have carried out similar quantum mechanical calculations to determine the energies and lifetimes of the metastable states of the one-barrier Henon–Heiles–like potential,

$$V(r, \theta) = \frac{1}{2} r^2 - \frac{1}{2} r^3 \cos \theta - \frac{1}{2} x^2 - \frac{1}{2} x^3 + \frac{1}{2} y^2 - \frac{1}{2} x y^2.$$  \hspace{1cm} (4.1)

The saddle point occurs at $(r, \theta) = (1, 0)$, and the barrier height is still $V_{sb} = \frac{1}{2}$.

The states divide into two symmetry classes, even and odd with respect to reflection about the $x$ axis. Figure 6 shows the unimolecular rate constants as a function of their energy for $\hbar = 0.03$. The results are quite different from the three-barrier case of Sec. III; namely, there is substantial mode specificity even within each symmetry class.

We next generated classical Poincaré surfaces of

FIG. 4. Plot of $\hbar \log k$ versus energy for various values $\hbar$, for $A_1$ states. The $\hbar = 0$ curve is the $\hbar = 0$ limit of the statistical rate, as given by Eq. (3.5).

FIG. 5. Same as Fig. 4, except for $A_2$ states.

FIG. 6. Same as Fig. 1, except for the one-barrier Henon–Heiles–like potential of Eq. (4.1), for $\hbar = 0.03$. The solid points and circles denote even and odd states, respectively.
section\textsuperscript{5} to determine the classical quasiperiodic/ergodic features as a function of energy and found that this system is totally quasiperiodic for all energies up to the top of the barrier.

This potential surface, therefore, does show the expected correlation, i.e., the classical mechanics is quasiperiodic for all energies (below the top of the barrier), and the quantum mechanical unimolecular decay rates are highly mode specific. Since this potential surface does not have a transition from quasiperiodic to ergodic-like classical dynamics as a function of energy, however, this example does not provide a stringent test of these notions.

V. CONCLUDING REMARKS

The Henon–Heiles potential has been a benchmark for the study of quasiperiodic/ergodic behavior of classical mechanics and is thus an important example to consider with regard to mode specificity in the quantum mechanical unimolecular decay rates. The observation is that this system shows little mode specificity, and the little that does exist seems in no way related to the quasiperiodic/ergodic transition in the classical mechanics.

The conclusions from the study of this model are essentially the same as from our earlier study, namely, that there seems to be no mandatory correlation between the quasiperiodic/ergodic character of the classical mechanics of the system and the mode specificity of its unimolecular rate constants. Such a correlation may exist (cf. the example in Sec. IV), but unlike our initial intuition it appears that it is not necessary.

Furthermore, we do not think that this lack of correlation is due to a quantum-classical dichotomy, i.e., to result because the quasiperiodic/ergodic notion is one of classical mechanics while the tunneling rate constants must be determined quantum mechanically. It was noted in the Introduction that some quantum mechanical features, e.g., nodal patterns of wave functions, etc., do show rather direct correlation with quasiperiodic/ergodic character of the classical mechanics.

What features of a system, then, are relevant to determining mode specificity in its reaction dynamics? The nature of the intramolecular dynamics, quasiperiodic or ergodic, is certainly one relevant consideration, but there are at least two others that come to mind. One is the rate of randomization in phase space, as compared to the rate of the chemical process of interest. The statement that the intramolecular dynamics is ergodic (on the basis of Poincaré surfaces of section, for example) refers to an indefinitely long time period, but the molecular system does not have an infinite amount of time to decide whether or not it is going to behave ergodically. If the rate of the chemical process is faster than the rate of randomization, then one would observe mode-specific chemistry even though the intramolecular dynamics might, given sufficient time, be ergodic-like.

Another relevant factor, which is illustrated by the example in this paper, is the coupling of the intramolecular motion to the reaction product channels; mode-specific reaction dynamics requires not only mode-specific (i.e., quasiperiodic) intramolecular dynamics but also mode-specific coupling to the reaction products. Thus, even though the Henon–Heiles system has mode-specific (i.e., quasiperiodic) intramolecular dynamics at energies below $E_\text{r}$, the three exit valleys effectively provide statistical-like coupling to products since there is no mode (i.e., direction in the $x$–$y$ plane) that does not project significantly onto a reaction coordinate for at least one of the exit valleys. For the one-barrier potential of Sec. IV, however, certain modes (e.g., motion in the $y$ direction) avoid the saddle point leading to dissociation.

Further theoretical studies, some on more realistic models of chemical systems, are planned to elucidate more clearly the features related to mode-specific chemistry.

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APPENDIX: RRKM PLUS TUNNELING RATE CONSTANT

The microcanonical transition state theory rate expression is

$$k(E) = 3 \times [2\pi\hbar p(E)]^{-1} \sum_{\omega_\alpha} P(E - (n + \frac{1}{2}) \hbar \omega_\alpha),$$

(1)

where the factor of three is due to the three equivalent saddle points of the potential surface. The density of states $\rho(E)$ for the present case is

$$\rho(E) = E/\hbar^2,$$

(2)

and the one-dimensional tunneling probability $P$ is given semiclassically by

$$P(E) = (1 + e^{\pi\hbar p(E)})^{-1},$$

(3)

$$\theta(E) = \frac{\hbar}{E} \int_{x_0}^{x_\infty} dx \sqrt{2\mathcal{V}(x) - E},$$

(4)

$$\mathcal{V}(x) = \frac{1}{2} x^2 - \frac{1}{3} x^3.$$  

(5)

The barrier penetration integral $\theta$ is well approximated by

$$\theta(E) = \frac{\hbar}{E} [\frac{1}{2} (E - E_\text{r}) + \frac{1}{4} (E - E_\text{r})^2 + \frac{3}{8} (E - E_\text{r})^3].$$  

(6)

The statistical frequency factor $(2\pi\hbar p(E))^{-1}$ can be used to define an effective mechanical frequency $\omega_s$,

$$\frac{1}{2\pi\hbar p(E)} = \frac{\omega_s}{2\pi},$$

(7)

and with $p$ given by Eq. (2), this effective mechanical frequency is

$$\omega_s = \hbar/E.$$  

(8)
At the lowest eigenvalue $E \approx k_{\lambda}$, i.e., the zero-point energy of the two oscillators, one thus has

$$\omega_{s} \approx 1,$$  \hspace{1cm} (A9)

which is the actual mechanical frequency of the oscillator. The classical density of states of Eq. (A2) thus gives essentially the correct frequency factor for the lowest quantum mechanical state. (In general, we note that for a system of $s$ oscillators of frequency $\omega$ at their zero-point energy $(s/2)k_{\omega}$, Eq. (A7) gives

$$\omega_{s} = \omega(s-1)! \left( \frac{s}{e} \right)^{s-1}.$$  

For $s = 1, 2, 3, \ldots, 5, \ldots, 10$, for example, the multiplicative factor on the RHS is $1.0, 1.0, 0.89, \ldots, 0.61, \ldots, 0.19$, respectively. This indicates that for larger values of $s$, one should probably modify the classical density of states in such a way that $\omega_{s} \approx \omega$ at the zero-point energy.)


5See, for example, (a) S. A. Rice, Ref. 1d, p. 2; (b) R. A. Marcus, D. W. Noid, and M. I. Koszykowski, Ref. 1d, p. 286.


