Semiclassical ergodic properties of the Henon–Heiles system

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This paper investigates the applicability of the concepts of classical ergodicity and the results of semiclassical ergodic theory to quantum mechanical systems that are away from the classical limit and that do not necessarily become ergodic as $\hbar \to 0$. To carry out this study, a new quantity, called the "constancy" F_A of classical property A, is introduced. This constancy is defined in terms of the autocorrelation function of A and its statistical equilibrium value. It measures, on an absolute scale, the extent to which the dynamics of A behave statistically. The F_A for a set of quadratically integrable properties A can be used to define the "degree of ergodicity" of a classical system with respect to this set. This analysis motivates introduction of the quantum analog of F_A as a means of judging the applicability of classical ergodicity concepts to quantum mechanical systems. To illustrate these ideas, calculations for the Henon–Heiles system are carried out which compare the quantum and classical analogs of the constancies and of the "almost microcanonical" autocorrelation functions from which they are formed. The results indicate that the quantum and classical systems exhibit similar forms of partial ergodicity at high energy. This conclusion supports the approach introduced here for identifying the quantum implications of classical ergodicity. As a consequence of the good quantum-classical agreement, the partially ergodic nature of the classical behavior is reflected in the distribution of certain quantum-mechanical matrix elements. At lower energy, the applicability of classical ergodicity concepts to this system is more limited due to differences in the quantum and classical dynamics. The kinds of quantum-classical discrepancies that limit the implications of classical ergodicity for quantum systems are identified.

I. INTRODUCTION

Ergodic theory[1] provides a mathematical framework for classifying and studying the statistical behavior of systems governed by the laws of classical mechanics. Although only a few classical systems with more than one degree of freedom can be proven to satisfy the strict conditions for ergodic behavior as specified by this theory, numerical calculations[2,3] show that a much wider variety of classical systems exhibit some of the symptoms associated with ergodicity and can thus be said to be "partially ergodic" in a certain sense. The explanation for such partial ergodicity can be traced to the phenomenon of classical chaos[4] which is responsible for the statistical behavior in the strictly ergodic systems and which is present, to varying degrees, in all nonintegrable systems.

To a large extent, recent interest [5–8] among chemical physicists in the subject of classical ergodicity is due to its potential for shedding light on the dynamics of intramolecular vibrational energy transfer and the mechanism for energy randomization in excited molecules. However, the applicability of ergodic theory to molecular systems has been the subject of much controversy. Questions that have provoked debate include: To what extent can the concepts of ergodic theory be applied to molecular systems which, of course, obey the laws of quantum mechanics? When, if ever, can one say that a quantum system is ergodic in the same sense used in classical mechanics? And what are the manifestations in a quantum system of the ergodic behavior found in the corresponding classical system?

In order to resolve some of the issues associated with this subject, a semiclassical ergodic theory[5] which systematically explores the consequences of classical ergodic behavior for quantum systems has recently been developed. That work identifies semiclassical analogs of the various forms of classical ergodic behavior, namely ergodicity, weak mixing, mixing, and absolutely continuous spectrum and, furthermore, derives the implications of such forms of behavior for quantum matrix elements and frequency distributions.

Although the semiclassical ergodic theory yields interesting new results, they are of a rather formal nature and it may not be clear how they relate to actual systems of physical interest. The difficulty is that the theory is concerned only with the limiting behavior of quantum systems as $\hbar$ approaches zero and considers only systems that become rigorously ergodic in the classical limit. Thus the theory does not attempt to describe the behavior of truly quantum systems that have a fixed, nonzero $\hbar$, and the theory does not apply to systems, such as real molecules that are, at best, only partially ergodic. The purpose of this paper is to explore numerically the extent to which the ideas of classical ergodic theory can be carried over to such classically nonergodic, quantum systems and to investigate the degree to which the results of the semiclassical theory apply to these cases.

Rather than examine the entire range of ergodic properties of our systems, we focus attention on the most elementary form of ergodic behavior, namely, simple ergodicity. Although our systems do not even fulfill the strict requirements for simple ergodicity as $\hbar \to 0$, we are able to define the degree of ergodicity of our classical systems in a manner that is relevant for our work. This degree is determined by certain quantities, F_A, called constancies, which are extracted from microcanonical autocorrelation functions of parti-

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cular properties. The quantum analogs of the F_A are defined in such a manner that they become identical to the classical constancies as $\hbar \to 0$. Then our criterion for the applicability of ergodicity concepts to quantum systems is that the quantum and classical constancies be similar, in certain respects, even for the nonzero values of $\hbar$ characterizing the quantum system.

To apply this analysis in a physical case, we perform dynamical calculations for the Henon–Heiles[9] system. Our comparison of quantum and classical correlation functions and constancies allows us to study how various differences in the two forms of dynamics affect the ability to apply the classical concept of ergodicity to the quantum system.

It turns out that the quantum analogs of the constancies are directly related to the statistical distribution of certain matrix elements. Semiclassical ergodic theory[5] shows that strict classical ergodicity has implications for such distributions as $\hbar \to 0$. The present work extends this theory and shows that even partial classical ergodicity should have certain consequences for such distributions, provided that $\hbar$ is sufficiently small. Our calculation of the quantum constancies gives us an opportunity to test the applicability of this prediction to an actual system.

Our choice of the Henon–Heiles system for these studies is especially appropriate for two reasons. First, existing evidence suggests that the degree of classical ergodicity of this system varies over a broad range. At low energies, the system is known to be highly nonergodic, with most trajectories confined to two-dimensional KAM tori on the three-dimensional energy surface.[9] At high energies, in contrast, this system seems to become more nearly ergodic in the sense that several correlation functions appear to approach their statistical equilibrium values at long times.[2,3] This large range of behavior makes the Henon–Heiles system a good candidate for testing the implications of varying degrees of classical ergodicity for quantum dynamics. The second advantage of the Henon–Heiles system for our calculations is that some of its energy levels are degenerate, enabling us to investigate certain deductions of the semiclassical ergodic theory concerning degeneracies.

It should be noted that many investigations have been carried out to explore the quantum-classical correspondence of partially ergodic systems. The Henon–Heiles system has been an especially popular subject for such studies.[10] Our work differs from previous contributions to this field in that it is based on the semiclassical ergodic theory of Ref. 5. We believe that the analysis provided by that theory, concerning the approach of quantum behavior to classical ergodicity as $\hbar \to 0$, serves as an appropriate foundation for investigating the implications of partial ergodic behavior in quantum systems.

The remainder of the paper is based on the following plan. In Sec. II we review the relevant parts of the semiclassical ergodic theory and show how they lead to the introduction of the classical and quantum constancies. Also, in that section, we discuss the expected consequences of partial ergodic behavior for quantum systems and present our tests for the relevance of classical ergodicity concepts for such systems. In Sec. III we describe details of our classical and quantum calculations on the Henon–Heiles system. In Sec. IV we present and discuss the results of these calculations. Finally, in Sec. V we summarize our work and make concluding remarks.

II. CLASSICAL ERGODICITY AND ITS SEMICLASSICAL ANALOG

A. Classical aspects

Let us consider a function $A(\mathbf{p},\mathbf{q})$ of momenta $\mathbf{p}$ and coordinates $\mathbf{q}$, describing a classical property of a system. This property evolves in time as the momenta and coordinates of the system change from their initial values of $\mathbf{p}(0)$ and $\mathbf{q}(0)$ at time zero to $\mathbf{p}(t)$ and $\mathbf{q}(t)$ at time t. The microcanonical autocorrelation function of A is defined as

$$C_A(t) = \langle A(t)|A\rangle / \langle A|A\rangle, \tag{1}$$

where $A(t) = A[\mathbf{p}(t),\mathbf{q}(t)]$, $A(0) = A(\mathbf{p},\mathbf{q})$, and the brackets denote integrals over phase space:

$$\langle A|B\rangle = \int d\mathbf{p} \int d\mathbf{q}\, \delta(E-H) A(\mathbf{p},\mathbf{q})^* B(\mathbf{p},\mathbf{q}),$$

$$\langle A(t)|B\rangle = \int d\mathbf{p} \int d\mathbf{q}\, \delta(E-H) A(\mathbf{p},\mathbf{q},t)^* B(\mathbf{p},\mathbf{q}). \tag{2}$$

The factor $\delta(E-H)$ restricts the integral to the energy surface $E = H(\mathbf{p},\mathbf{q})$. Although we use the notation of ordinary Riemann integrals in Eq. (2) to facilitate the quantum mechanical analogy presented below, we note that these phase space integrals are more properly expressed as Lebesgue integrals over the energy surface. To ensure that these integrals exist under all relevant conditions, we assume that A is quadratically integrable (i.e., $A \in L^2$) in the sense that $\langle A|A\rangle < \infty$. For simplicity, we will henceforth also assume that A is real.

The condition for ergodicity[1] is defined as the requirement that

$$\lim_{T\to\infty} (1/T) \int_0^T dt\, C_A(t) = C_{A,\mathrm{eq}} \tag{3}$$

for all quadratically integrable A, where

$$C_{A,\mathrm{eq}} = |\langle 1|A\rangle|^2 / [\langle A|A\rangle \langle 1|1\rangle]. \tag{4}$$

An alternative form[5] of this condition is

$$\overline{C_A}(\infty) - C_{A,\mathrm{eq}} = 0 \tag{5}$$

for all quadratically integrable A, where

$$\overline{C_A}(T) = (1/T) \int_0^T dt \exp(-t/T) C_A(t) \tag{6}$$

and

$$\overline{C_A}(\infty) = \lim_{T\to\infty} \overline{C_A}(T). \tag{7}$$

These equations imply that, for an ergodic system, the infinite time average of the autocorrelation function $\overline{C_A}(\infty)$ is equal to its statistical average or equilibrium value, i.e., $C_{A,\mathrm{eq}}$.

The normalization that we have adopted for the autocorrelation functions ensures that $C_A(0) = 1$ and $\overline{C_A}(0) = 1$. If the system is nonergodic, and A is a constant of motion, then $C_A(t)$ is constant for all t so that $C_A(t)$ and

$\overline{C_A}(T)$ remain equal to unity for t and $T>0$. On the other hand, if the system if rigorously ergodic, and A is any quadratically integrable function, then Eq. (5) implies that $\overline{C_A}(\infty)$ takes on its equlibrium value $C_{A,\mathrm{eq}}$ which can be shown to lie between 0 and 1.

To measure how closely the autocorrelation function of A approaches its equilibrium value for a system that may or may not be ergodic, we introduce the function

$$F_A(T)=\left[\,\overline{C_A}(T)-C_{A,\mathrm{eq}}\,\right]/(1-C_{A,\mathrm{eq}}) \tag{8}$$

which compares the difference between $\overline{C_A}(T)$ and $C_{A,\mathrm{eq}}$ at time T to the difference at time 0. Appendix A shows that $F_A(T)$ is a monotonically nonincreasing function of T and obeys the inequalities

$$0\leqslant F_A(T)\leqslant 1 \tag{9}$$

for all T. Thus, $F_A(T)$, which has the value of 1 at $T=0$, either remains constant or decreases as T increases. As $T\rightarrow\infty$, $F_A(T)$ approaches the asymptotic value

$$F_A=F_A(\infty)=\lim_{T\rightarrow\infty}F_A(T), \tag{10}$$

which lies between 0 and 1.

The condition for ergodicity can be expressed in terms of F_A as

$$F_A=0. \tag{11}$$

This condition applies to all quadratically integrable A except functions depending solely on H, since these yield indeterminate values of $F_A(T)$.

We call the quantity F_A the constancy of property A because it measures, on the absolute scale of 0 to 1, the extent to which A is invariant under time evolution. If the system is nonergodic and A is invariant [i.e., $A(t)=A(0)$] then $F_A=1$. If the system is ergodic and A is any quadratically integrable property, then $F_A=0$. For a general nonergodic system and an arbitrary quadratically integrable A, the value of F_A lies between 1 and 0, depending on how closely the infinite-time averaged correlation function of A remains equal to its initial value or how closely it approaches its statistical value.

We now use the F_A to define the degree of ergodicity of a classical system that may be only partially ergodic. The most straightforward definition for this degree would appear to be the minimum value assumed by $(1-F_A)$ as A is varied over all quadratically integrable functions. However, this approach fails because, given any nonergodic system, there always exist quadratically integrable (but, generally, very complicated and poorly behaved) functions A that yield $F_A=1$. Thus, the proposed definition yields degrees of ergodicity of 0 for all nonergodic systems and 1 for all ergodic systems. Since it never yields intermediate values for the degree of ergodicity, it does not recognize the existence of partial ergodicity.

To overcome this difficulty, we restrict the set of properties A that are used to test the degree of ergodicity. We require that these properties obey certain additional conditions beyond quadratic integrability. Then we define a system's degree of ergodicity (with respect to the restricted set of properties) as the minimum value of $(1-F_A)$ as A is varied over this set. Since this set does not include all quadratically integrable functions, the degree of ergodicity can now take on intermediate values between zero and one, as is necessary to characterize partially ergodic systems.

Our practice of testing the statistical behavior of a system by examining only a limited set of properties can be justified in a number of ways. First, only a few properties in physical systems are monitored in actual experiments and only those properties are of practical interest in judging the degree of statistical behavior in real systems. For example, although molecules are nonergodic, the existence of very complicated invariant properties does not always prevent them from displaying statistical reaction dynamics. By restricting the set of properties in our theory to those that can be observed, we can prevent "irrelevant" properties from unduly influencing our measure of ergodic behavior. Second, there are theoretical reasons for restricting the class of properties to be examined. We will see that the quantum version of ergodic theory that we will introduce is, as a matter of principle, concerned with the quantum analogs of only certain classical properties. To develop a classical theory that is analogous to the quantum treatment, we must restrict the properties considered classically to those of interest in the quantum theory. Finally, we note that, purely as a practical matter, it is not possible to examine the evolution of all quadratically integrable functions in numerical calculations such as the ones we wish to perform. Judgements of statistical behavior must necessarily be based on the study of a limited number of properties A.

In the present work, we are not especially concerned with the actual calculation of the degree of ergodicity. We are, however, interested in the F_A because they contain information about this degree. Comparison of the F_A's to their quantum analogs tests how well the idea of partial classical ergodicity applies to quantum systems. If the quantum analogs of the F_A's are very close to the corresponding classical constancies for a variety of properties A in a system that is judged to be classically "almost ergodic", then the quantum system displays a form of partial ergodicity that is similar to that of the classical system. This similarity suggests that the classical concepts and mechanisms of ergodicity apply, to a significant extent, to the quantum system as well as the classical system.

B. Semiclassical analogs

The semiclassical analogs[5] of the classical quantities defined in the previous subsection are obtained by replacing the classical phase-space integrals $\langle A\,|B\rangle$ with quantum mechanical traces:

$$\langle A\,|B\rangle^q=\mathrm{Tr}[\rho^\sigma(E-H)\hat{A}^\dagger\hat{B}\,],$$
$$\langle A(t)|B\rangle^q=\mathrm{Tr}[\rho^\sigma(E-H)\hat{A}^\dagger(t)\hat{B}\,], \tag{12}$$

where ρ^σ is a "broadened" delta function (e.g., an appropriately normalized Gaussian or generalized Lorentzian[5]) which projects out eigenstates in the energy shell of width σ about the energy E. $\hat{A}$ is the operator corresponding to the classical property $A(\mathbf{p},\mathbf{q})$ and $\hat{A}(t)$ is $\hat{A}$ propagated for time t in the Heisenberg picture.

The semiclassical analogs of the autocorrelation function and its statistical equilibrium value are now obtained by

replacing the $\langle A|B\rangle$'s in Eqs. (1) and (4) with the corresponding $\langle A|B\rangle^q$'s:

$$C_A^q(t) = \langle A(t)|A\rangle^q / \langle A|A\rangle^q, \tag{1'}$$

$$C_{A,\mathrm{eq}}^q = |\langle 1|A\rangle^q|^2 / \langle 1|1\rangle^q, \tag{4'}$$

while the semiclassical analogs of the classical quantities $\overline{C_A}(T)$ and $F_A(T)$ are obtained by placing superscripts q on all quantities in Eqs. (6) and (8):

$$\overline{C}_A^q(T) = (1/T)\int_0^T dt \exp(-t/T) C_A^q(t) \tag{6'}$$

and

$$F_A^q(T) = [\,\overline{C}_A^q(T) - C_{A,\mathrm{eq}}^q\,]/(1 - C_{A,\mathrm{eq}}^q). \tag{8'}$$

Reference 5 defines a class of operators called acceptable. Such operators are the quantum analogs of the quadratically integrable functions $A(\mathbf{p},\mathbf{q})$ appearing in the definition of ergodicity. For these operators, the quantum and classical autocorrelation functions are related by

$$\lim_{\sigma\to 0}\lim_{\hbar\to 0} C_{A,\mathrm{eq}}^q = C_{A,\mathrm{eq}} \tag{13}$$

and

$$\lim_{\sigma\to 0}\lim_{\hbar\to 0} C_A^q(t) = C_A(t). \tag{14}$$

Thus,

$$\lim_{\sigma\to 0}\lim_{\hbar\to 0} \overline{C}_A^q(T) = \overline{C}_A(T) \tag{15}$$

and

$$\lim_{\sigma\to 0}\lim_{\hbar\to 0} F_A^q(T) = F_A(T). \tag{16}$$

The limits are not interchangable in the above relations.

In direct analogy with the classical condition for ergodicity given in Eq. (5), Ref. 5 identifies the semiclassical condition for ergodicity to be

$$\lim_{\substack{\sigma\to 0\\ T\to\infty}}\lim_{\hbar\to 0} [\,C_A^q(T) - C_{A,\mathrm{eq}}^q\,] = 0 \tag{17}$$

for all acceptable A. An equivalent form is

$$\lim_{\substack{\sigma\to 0\\ T\to\infty}}\lim_{\hbar\to 0} F_A^q(T) = 0 \tag{18}$$

for all acceptable A (except functions of H).

As in Eqs. (13)–(16), the order of the limits in Eqs. (17) and (18) is important: one cannot reverse the ($\sigma\to 0$, $T\to\infty$) limits. The reason for this restriction is that, when $\hbar$ is nonzero, the quantum and classical $\overline{C}_A(T)$ resemble each other only when σ is chosen to be sufficiently large [$\sigma > \sigma_{\min}(\hbar)$] and, even then, only for a limited time period [$T < T_{\max}(\hbar)$, where $\sigma_{\min}$ and $T_{\max}$ are discussed below]. If σ and T are allowed to approach their limiting values before $\hbar$, $\overline{C}_A^q(T)$ does not generally tend to the classical value $\overline{C}_A(\infty)$. One symptom of the problems that arise when σ is chosen to be too small is that the quantum $\overline{C}_A^q(T)$ becomes complex even when the classical correlation function is real. Reference 5 determines the minimum energy shell width $\sigma_{\min}$ needed to avoid this difficulty as well as other problems: the interval $\sigma_{\min}$ must be chosen to include many levels around energy E and to be larger than the energy range $|E_m - E_n|$ for which quantum matrix elements $\langle m|A|n\rangle$ between energy eigenstates is large. For times $T > T_{\max}$ the quantum function $\overline{C}_A^q(T)$ will generally also deviate from the classical $\overline{C}_A(T)$ due to dynamical effects of purely quantum origin, such as tunneling, nonclassical recurrences, etc. To ensure that the quantum functions approach their classical values as $\hbar\to 0$, and to ensure that the semiclassical definition of ergodicity is consistent with the classical definition, it is necessary to apply the $\hbar\to 0$ limit before taking the other two limits.

Since the quantum functions do not approach their classical counterparts unless the various limits are applied in the proper order we *cannot*, in general, identify the quantity

$$F_A^q(\infty) = \lim_{T\to\infty} F_A^q(T) \tag{19}$$

as the quantum analog of the classical constancy, F_A when $\hbar$ is nonzero. In fact, for nonzero $\hbar$, there is no unique and precise *purely quantum* analog of F_A. The problem is that a quantum analog of F_A for nonzero $\hbar$ which has the correct limiting behavior as $\hbar\to 0$ must be of the form $F_A^q(T)$ with certain specific values for $\sigma(\hbar)$ (>0) and $T(\hbar)$ ($<\infty$), but there is no unique prescription for choosing these parameters. This difficulty frustrates attempts to develop a purely quantum mechanical definition of ergodicity that has the correct semiclassical limit.

However, when $\hbar$ is sufficiently small, there does exist a procedure for choosing σ and T that is meaningful and uniquely consistent with the semiclassical ergodic theory. This procedure is to select these parameters so as to make $F_A^q(T)$ and $F_A(T)$ as alike as possible for as long as possible. Clearly, to the extent that this attempt is successful, there will be no difference between the classical and quantum $F_A(T)$'s. It will no longer be meaningful to ask whether the quantum system displays a purely quantum mechanical form of ergodicity. The only question that can be asked is whether the $F_A^q(T)$'s are indeed close enough to the classical $F_A(T)$'s for a long enough period of time to allow the quantum functions $F_A^q(T)$, at some sufficiently late time T, to be identified as the analogs of the classical constancies. If the answer is yes for all relevant properties A, then we are able to draw the important conclusion that the quantum system exhibits a form of behavior that is close to the partially ergodic behavior of the classical system.

These considerations lead us to identify the quantity $F_A^q(T_{\max})$ as the quantum mechanical analog the classical constancy F_A if

$$F_A^q(T) \approx F_A(T) \quad \text{for} \quad 0 \leqslant T \leqslant T_{\max}, \tag{20}$$

where $T_{\max}$, the time interval during which the quantum and classical functions agree, is long enough that

$$F_A(T_{\max}) \approx F_A. \tag{21}$$

The σ used to calculate $F_A^q(T)$ in Eq. (20) must be greater than $\sigma_{\min}$, as defined above, and yet small enough that the appearance of different density functions $\rho^\sigma(E-H)$ and $\delta(E-H)$ in the definitions of $F_A^q(T)$ and $F_A(T)$ does not, in itself, cause significant differences in the quantum and classical quantities. This condition will be obeyed if the classical

quantity $F_A(T)$ does not change appreciably when the microcanonical density function $\delta(E-H)$ appearing in its definition is replaced by $\rho^\sigma(E-H)$.

When conditions (20) and (21) are obeyed, the quantum and classical $F_A(T)$ curves will be close together until the classical $F_A(T)$ has essentially reached its asymptotic value. Deviations between the two curves for times greater than $T_{\max}$ are irrelevant for a semiclassically based analysis of ergodicity. However, substantial discrepancies between these curves for shorter times imply that the quantum system is not characterized by the same form of partial ergodic behavior that applies to the classical system.

There is one further subtlety concerning the application of Eqs. (20) and (21) that needs to be discussed. For reasons similar to those leading to the introduction of parameters $\sigma_{\min}$ and $T_{\max}$, we must specify some restrictions on the properties A whose quantum and classical dynamics we compare. We have already mentioned that only acceptable properties should be considered when determining the quantum ergodic nature of a system. Among other things, acceptability of A guarantees that the behavior of the quantum autocorrelation function will tend to that of the classical function as $\hbar \to 0$. However, acceptability does not, by itself, ensure that the quantum autocorrelation function has even a fair chance of resembling the classical function away from the classical limit. Indeed, given an arbitrary, nonzero $\hbar$, it is possible to identify a class of properties which, although acceptable, are expected to yield very different classical and quantum behavior and to lead to violation of conditions (20) and (21). Such properties correspond to classical functions that are localized in phase space regions of volume $\lesssim \hbar^s$ (where s is the number of degrees of freedom) or to quantum operators that have only a few eigenstates in the energy shell.[11] If we insist on including such properties in our study of quantum ergodicity, we will always find that the quantum system fails to exhibit the form of ergodic behavior found in the corresponding classical system. To avoid the unconstructive conclusion that a quantum multidimensional system can never display behavior analogous to classical ergodicity, we deliberately exclude from our comparisons of quantum and classical dynamics those properties that predictably lead to disagreements. Thus, for purposes of judging whether classical ergodic concepts apply to quantum systems, we limit our examination to those properties A that are not strongly localized in phase space, in the sense described above.

We mention that the criterion used here to select $T_{\max}$ differs from that discussed in Ref. 5. In the earlier work, this parameter was chosen so that the instantaneous correlation functions $C_A^q(t)$ and $C_A(t)$ agree for all $t < T_{\max}$ while, in the present work, it is chosen esentially so that the time-averaged correlation functions $\overline{C}_A^q(T)$ and $\overline{C}_A(T)$ agree for $T < T_{\max}$. Actually, both criteria are defensible for treating ergodicity but only the criterion used earlier may be used for treating the stronger ergodic properties such as mixing. We select the present criterion here because it is easier to apply. The other choice would modify the quantitative results of our work somewhat but would not change the qualitative conclusions.

It is worth pointing out that the function $F_A^q(T)$ shares many of the mathematical properties of the corresponding classical function. Thus, it is easy to prove (see Appendix A) that, like $F_A(T)$, $F_A^q(T)$ is a nonincreasing function of T and obeys the inequalities

$$0 \leqslant F_A^q(T) \leqslant 1 \tag{22}$$

for all T.

To evaluate $C_A^q(t)$, $C_A^q(T)$, $C_{A,\mathrm{eq}}^q$, and $F_A^q(T)$, we substitute complete sets of energy eigenvectors $|n\rangle$ (obeying $H|n\rangle = E_n|n\rangle$) into the definitions of these quantities. The resulting formulas that are needed for our work are

$$C_A^q(t) = \sum_n \rho^\sigma(E-E_n) \sum_m |\langle m|\hat{A}|n\rangle|^2 \exp(i\omega_{nm}t)/D_A, \tag{23}$$

$$C_{A,\mathrm{eq}}^q = \left| \sum_n \rho^\sigma(E-E_n)\langle n|\hat{A}|n\rangle \right|^2 \Big/ D_A \sum_n \rho^\sigma(E-E_n), \tag{24}$$

and

$$F_A^q(T) = F_A^{(1)} + F_A^{(2)} + F_A^{(3)}(T), \tag{25}$$

where

$$F_A^{(1)} = B_A^{-1} \sum_n \rho^\sigma(E-E_n) \Big\{ \langle n|\hat{A}|n\rangle - \sum_m \rho^\sigma(E-E_m)\langle m|\hat{A}|m\rangle / \sum_m \rho^\sigma(E-E_m) \Big\}^2, \tag{26}$$

$$F_A^{(2)} = B_A^{-1} \sum_n \rho^\sigma(E-E_n) \sum_{\substack{m \\ m\neq n \\ E_m = E_n}} |\langle m|\hat{A}|n\rangle|^2, \tag{27}$$

$$F_A^{(3)}(T) = B_A^{-1} \sum_n \rho^\sigma(E-E_n) \times \sum_{\substack{m \\ m\neq n \\ E_m \neq E_n}} |\langle m|\hat{A}|n\rangle|^2/(1-i\omega_{nm}T), \tag{28}$$

$$D_A = \sum_n \rho^\sigma(E-E_n)\langle n|\hat{A}^2|n\rangle, \tag{29}$$

$$B_A = D_A(1-C_{A,\mathrm{eq}}^q), \tag{30}$$

and

$$\omega_{nm} = (E_n - E_m)/\hbar. \tag{31}$$

Since the condition $\sigma > \sigma_{\min}$, as described above, causes $C_A^q(t)$ and F_A to be purely real, $F_A^{(3)}(T)$ can be expressed as

$$F_A^{(3)}(T) = B_A^{-1} \sum_n \rho^\sigma(E-E_n) \times \sum_{\substack{m \\ m\neq n \\ E_m \neq E_n}} |\langle m|\hat{A}|n\rangle|^2/\{1+(\omega_{nm}T)^2\}. \tag{32}$$

Note that $F_A^{(3)}$, the only term that depends on T, vanishes as $T \to \infty$. Thus,

$$F_A^q(T) = F_A^q(\infty) + F_A^{(3)}(T), \tag{33}$$

where

$$F_A^q(\infty) = F_A^{(1)} + F_A^{(2)}. \tag{34}$$

If the $F_A^q(T)$ resemble the classical F_A, as specified by

Eqs. (20) and (21), then Eqs. (26), (27), and (28) relate the partially ergodic nature of the classical system to the statistical properties of matrix elements for operators $\hat{A}$. $F_A^{(1)}$ is the variance in the scaled diagonal matrix elements $N_A(E)\langle n|\hat{A}|n\rangle$, where the scaling factor is given by

$$N_A(E) = \left[\sum_n \rho^{\sigma}(E - E_n)/B_A\right]^{1/2}, \tag{35}$$

while $F_A^{(2)}$ and $F_A^{(3)}$ are the averages of the squares of scaled off-diagonal matrix elements $N_A(E)\langle m|\hat{A}|n\rangle$ for states with $E_m = E_n$ and $E_m \neq E_n$, respectively.

The implications of Eqs. (26), (27), and (28) for the quantum matrix elements in the case of a system that is rigorously ergodic have been described in Ref. 5. For such a system $F_A^q(T)$ approaches zero as $\hbar$, σ, and T tend to their limiting values in the manner specified by Eq. (18). Since each of the $F_A^{(i)}$'s is nonnegative, each $F_A^{(i)}$ must individually approach zero. Thus, Eqs. (26), (27), and (28) lead to the following three conditions for the matrix elements of an arbitrary acceptable operator $\hat{A}$[5]:

$$\langle m|\hat{A}|m\rangle = \text{constant, independent of } m,^{12}$$
$$\langle m|\hat{A}|n\rangle = 0, \quad \text{for } m \neq n, \text{ but } E_m = E_n,$$
$$\langle m|\hat{A}|n\rangle = 0, \quad \text{for } E_m \neq E_n \text{ but } |E_m - E_n| < \hbar/T, \tag{36}$$

where T can take on any value between the "relaxation time" of the $F_A(T)$ and $T_{\max}$.

These conditions are obeyed strictly only in the classical limit and only by systems that are classically ergodic. *The importance of the $F_A^{(1)}$, $F_A^{(2)}$, and $F_A^{(3)}$ is that they measure, on an absolute scale, the degree to which conditions (36) are still satisfied by a general, quantum mechanical system.* If the quantum and classical systems exhibit a similar form of partial ergodicity throughout an energy range, and if the classical constancies decrease in this range (perhaps indicating an increased degree of ergodicity), then the sum of the three $F_A^{(i)}$'s must also decrease in this range. This implies that at least one of these terms decreases and that the distribution of at least certain matrix elements approaches the semiclassical ergodic ideal.

III. CALCULATIONS

In this section we describe the calculations we perform on the Henon–Heiles system to investigate: (a) whether conditions (20) and (21) for the applicability of classical ergodicity concepts to quantum systems are satisfied and (b) whether the semiclassical predictions for the changing distribution of quantum matrix elements with increasing classical ergodicity are obeyed. To study these matters we need to calculate classical and quantum mechanical autocorrelation functions [$C_A(t)$ and $C_A^q(t)$], equilibrium statistical values ($C_{A,\text{eq}}$ and $C_{A,\text{eq}}^q$), the quantities describing the extent of equilibration as a function of time [$F_A(T)$ and $F_A^q(T)$], and classical constancies F_A.

A. The system and properties

The Henon–Heiles[9] system is described by the Hamiltonian

$$H = \tfrac{1}{2}(p_x^2 + x^2) + \tfrac{1}{2}(p_y^2 + y^2) + \lambda(xy^2 - x^3/3) \tag{37}$$

which can be reexpressed in terms of polar coordinates as

$$H = \tfrac{1}{2}(p_r^2 + r^2 + p_\theta^2/r^2) - (1/3)\lambda r^2 \cos 3\theta. \tag{38}$$

We choose the parameter λ to have the value 0.1118 for all of our calculations. As a result, the classical dissociation energy, $D_e = 1/6\lambda^2$, has the value 13.333.

Quantum and classical versions of $C_A(t)$ and $F_A(T)$ are calculated for the properties A listed in Table I. These properties are quadratically integrable and the corresponding quantum operators are apparently acceptable. Furthermore, as required for a valid investigation of quantum ergodicity, these properties are not strongly localized in particular regions of phase space. In the limit $\lambda \to 0$, all of these properties are classical constants of motion and the corresponding quantum mechanical operators commute with the Hamiltonian. We recall that the classical behavior of the Henon–Heiles system is predominantly quasiperiodic and, in many ways, similar to that of an integrable system at low energies ($E < 0.68D_e$), while it is predominantly chaotic and presumably, more nearly ergodic, at higher energies ($E > 0.68D_e$). We therefore expect the characteristics of correlation functions and matrix elements to vary with energy from those of a highly nonergodic system to those of a nearly ergodic one. More specifically, we anticipate the F_A to be close to 1 at low energies and close to 0 at high energies. No such trend would be anticipated for properties which fail to become constants of motion as $\lambda \to 0$.

B. Quantum mechanical calculations

We perform quantum mechanical calculations for the system described by Eq. (37) with Planck's constant $\hbar$ set equal to 1. The diagonalization of the Hamiltonian is performed using standard EISPAC[13] routines. For the values of $\hbar$ and λ used, there are 99 energy eigenstates with energies below D_e. The basis set used here consists of 903 isotropic harmonic oscillator eigenfunctions $|V, l\rangle = f_{V,l}(r)\exp(il\theta)$ satisfying

$$[\hat{H}_0 - (V + 1)]\,|V, l\rangle = 0, \tag{39}$$

where H_0 is defined in Table I. This set is found to yield satisfactory convergence of our results.

Equations (23)–(32) are used to evaluate the autocorrelation functions $C_A^q(t)$ and the $F_A^q(T)$. These calculations require, in addition to energy eigenvalues E_m, matrix elements $\langle m|\hat{A}|n\rangle$ over energy eigenstates $|m\rangle$, $|n\rangle$. These are calcu-

TABLE I. Properties $A(p,q)$ that are investigated in this study.

Property	Definition	Symmetry[a]	Remarks
H_0	$\frac{1}{2}(p_x^2 + x^2 + p_y^2 + y^2)$	A_1	Total zero-order energy
L	$xp_y - yp_x$	A_2	Angular momentum
L^2	$(xp_y - yp_x)^2$	A_1	Square of property L
D	$\frac{1}{2}(p_x^2 + x^2 - p_y^2 - y^2)$	E	Difference between energies in two modes
H_x	$\frac{1}{2}(p_x^2 + x^2)$	$A_1 + E$	Energy in x mode
D^2	$\frac{1}{4}(p_x^2 + x^2 - p_y^2 - y^2)^2$	$A_1 + E$	Square of property D

[a] Irreducible representation of C_{3v}.

lated by using the matrix of eigenvectors to transform matrix elements $\langle Vl|\hat{A}|V'l'\rangle$ over basis functions to the exact eigenstate representation. The $\langle Vl|\hat{A}|V'l'\rangle$ are evaluated using expressions derived by Louck and Shaffer.[14]

Since the Henon–Heiles potential has C_{3v} symmetry, each energy eigenstate is labeled by symmetry species A_1, A_2, or E. Only eigenstates of E symmetry are associated with degenerate energy levels and contribute to the term $F_A^{(2)}$. Due to our specific choice of the $|V, l\rangle$ as the basis functions for the E-symmetry block of the Hamiltonian, pairs of eigenstates $|n(E)\rangle$ and $|n'(E)\rangle$, associated with the same energy, turn out to be complex conjugates of each other: $|n'(E)\rangle = |n(E)^*\rangle \equiv |n(E)\rangle^*$. We thus calculate $F_A^{(2)}$ by the formula

$$F_A^{(2)} = 2B_A^{-1} \sum_n \rho^{\sigma}_{(E)}(E - E_{n(E)})|\langle n(E)^*|A|n(E)\rangle|^2. \tag{40}$$

Note that our choice of E eigenstates is not unique; unitary transformations of $|n(E)\rangle$ and $|n(E)^*\rangle$ yield different energy eigenstates and alter the values of $F_A^{(1)}$ and of $F_A^{(2)}$. However, the combination $F_A^{(1)} + F_A^{(2)}$ is invariant to such transformations. Although it is only this combination that is physically meaningful, it is nevertheless interesting to calculate $F_A^{(1)}$ and $F_A^{(2)}$ separately for our choice of the eigenstates and examine the behavior of the diagonal and off-diagonal matrix elements which, respectively, contribute to these two terms.

The "broadened delta functions" $\rho^{\sigma}(E - E_n)$ appearing in our formulas for $C_A^q(t)$ and $F_A^q(T)$ are expressed as Gaussians of the form $\exp[-(E - E_n)^2/2\sigma^2]$, where the width parameter σ is itself a function of E given by

$$\sigma = 1.06 - 0.045E. \tag{41}$$

Although there is nothing unique about this particular choice of σ, it does yield values that appear to satisfy the inequalities for this parameter described in Sec. II. Thus, the classical autocorrelation functions $C_A(t)$ and the statistical averages $C_{A,\mathrm{eq}}$ are found to change only to a small extent when the $\delta(E - H)$ in their definitions are replaced by $\rho^{\sigma}(E - H)$ and the imaginary parts of the quantum autocorrelation functions are calculated to be very small. Moreover, it is observed that the computed quantum autocorrelation functions are insensitive to moderate variations in σ about the values obtained from this equation. Thus, for our system, there is no great difficulty in choosing values of σ which allow comparison of our quantum correlation functions to the microcanonical functions $C_A(t)$.

C. Classical calculations

The classical $C_A(t)$ and $C_{A,\mathrm{eq}}$ are calculated using the expressions given in Eqs. (1) and (4). To enhance the analogy with the quantum calculations, the Dirac delta functions $\delta(E - H)$ appearing in these equations is replaced by the Gaussian function $\exp[-(E - H)^2/2\sigma^2]$ with σ given by Eq. (41). As discussed above, this substitution of broadened delta functions for the microcanonical density functions does not alter the calculated classical correlation functions significantly. The classical calculations are performed at two energies $E = 5.70$ and 12.67 to examine behavior typical of the quasiperiodic and chaotic regimes, respectively.

The $C_{A,\mathrm{eq}}$ are calculated by Monte Carlo evaluation of the phase integrals in Eq. (4), using about 10^5 points at each of the two energies. The correlation functions $C_A(t)$ are also calculated by the Monte Carlo procedure, which effectively specifies initial ($t = 0$) values for x, p_x, y, p_y, and the various properties A. Integration of Hamilton's equations then yields values for these coordinates, momenta and properties A at future times t and allows final evaluation of Eq. (1). 6000 trajectories are run at each of the two energies selected for study. The maximum integration times are 400 units (about 64 vibrational periods) at $E = 5.70$ and 120 units (about 20 periods) at $E = 12.67$. The integration step sizes are chosen to ensure accurate backintegration of the trajectories.

For the case $E = 12.67$, some trajectories have energies greater than D_e and a few such trajectories lead to "dissociations" of the Henon–Heiles system (characterized by $x^2 + y^2 > \lambda^{-2}$) on the time scale investigated. Such trajectories are removed from the ensemble averages after dissociation occurs.

The $\bar{C}_A(\infty)$, required for evaluation of the F_A, are approximated by averaging correlation functions $C_A(t)$ over the finite time intervals $80 < t < 400$ in the low energy case and $60 < t < 120$ in the high energy case. The reason for excluding early times from the averages is that the $C_A(t)$ are uncharacteristically large for small t [recall that $C_A(0) = 1$]. Restricting the time averages to late times appears to sample values of $C_A(t)$ that are more typical of the infinite-time behavior. This procedure for estimating the $\bar{C}_A(\infty)$ is, of course, dictated by practical considerations which prevent us from integrating trajectories for infinite time periods. Although one can never completely rule out the possibility that increasing the integration times will noticeably affect the calculated results, the behavior we observe for our computed $\bar{C}_A(T)$ at large T (see Sec. IV below) suggests that the time averaged correlation functions have essentially converged to their limiting values at the maximum integration times used in our calculations.

IV. NUMERICAL RESULTS

A. Autocorrelation functions

Figure 1 shows, as dashed curves, the classical autocorrelation functions $C_A(t)$ for various properties A at the two energies selected for investigation. The correlation functions for H_0 and H_x closely resemble the microcanonical correlation functions for these properties previously computed by Koszykowski, Noid, Tabor, and Marcus.[2]

Figure 1 also displays, as solid curves, the quantum autocorrelation functions $C_A^q(t)$ for the same A and the same energies examined in the classical calculations. At the higher energy, there is generally good qualitative agreement between the quantum and classical curves, especially at short times. At the lower energy, however, there are important discrepancies between these two curves. We now attempt to identify the sources of some of these disagreements.

1. Property D

The most obvious case of classical-quantum disagreement occurs for property D at low energy. The two curves begin to deviate from each other almost immediately, with the quantum curve lying below the classical curve for all $t > 0$. The difference between the curves becomes quite large for $t > 40$.

To understand why this discrepancy occurs we note that, in a rough sense, C_D measures how much of the classical energy shell is occupied by KAM tori on which D is approximately conserved. The consistently small values for

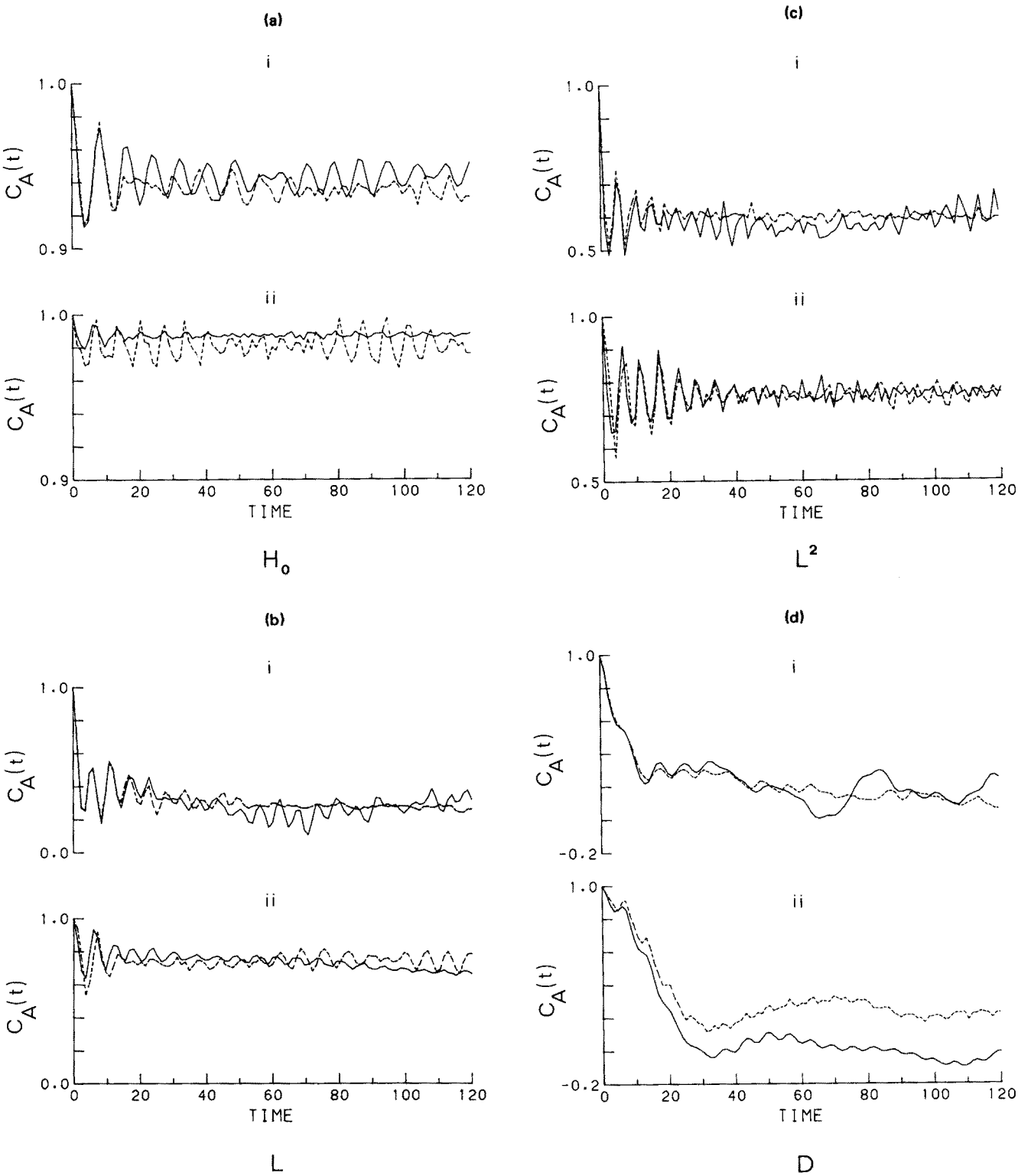

FIG. 1. Quantum autocorrelation functions $C_A^q(t)$ (solid curves) and classical autocorrelation functions $C_A(t)$ (broken curves) for the following properties A: (a) H_0, (b) L, (c) L^2, (d) D, (e) H_x, and (f) D^2. The top panel of each subfigure, labeled (i) shows results for $E = 12.67$, while the lower panel, labeled (ii) shows results for $E = 5.70$.

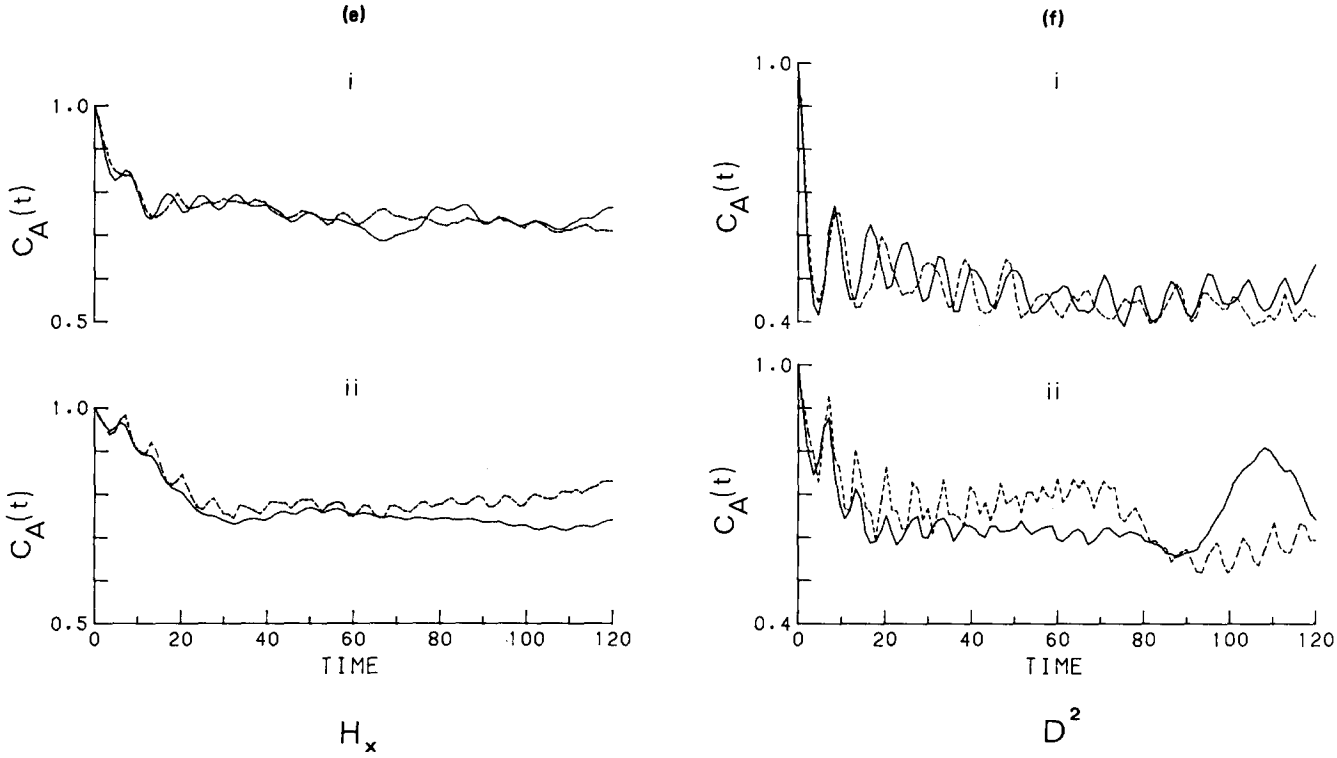

FIG. 1. (*continued*).

the quantum autocorrelation function imply that a smaller portion of the quantum energy shell is occupied by the quantum analog of such tori than is true of the classical case.

For the Henon–Heiles system in the regular region, classical tori on which D is approximately constant are indeed known to exist.[15] These tori are associated with librating (or pendular) trajectories that are mostly confined to the region around the x axis. Due to the symmetry of the Henon–Heiles potential, such tori actually occur in sets of three: for each torus associated with motion along the x axis there are two others that are obtained by rotating the trajectories through angles of 120 and 240 deg, respectively. D is not accurately conserved on the latter two tori. The quantum analogs of these three tori are states localized near the same portions of configuration space as the trajectories. However, since the energy eigenstates transform as C_{3v} symmetry species, they are not well localized on individual librating tori. Instead, quantization of these tori generates sets of eigenstates of A_1 and E symmetry with nearly equal energy, each such eigenstate being delocalized over all three tori. Thus, the analogs of the individual librating tori are not energy eigenstates, but specific linear combinations of the E and A_1 eigenstates that are obtained by quantization of these tori. The formation of these localized states from states of definite symmetry parallels the formation of the three equivalent sp^2 hybrid orbitals from p and s orbitals.

If we examine the eigenstates of the Henon–Heiles system, we find that there are only two states lying in the energy shell about $E = 5.70$ that are obtained by quantization of librating tori.[15] These are a pair of states of E symmetry associated with the doubly degenerate level at the energy 5.8170. The state of A_1 symmetry closest in energy is obtained by semiclassical quantization of a *precessing* torus. We cannot form states for which $\langle D \rangle$ remains constant, even for short time periods, from linear combinations of such states.

The difference between the quantum and classical behavior for $C_D(t)$ is thus explained by the small number of quantum states that correspond to librating tori in the energy range considered. There are too few such states to form the analog of a torus on which D is constant. The number of librating tori in a particular energy range depends, however, on the value of $\hbar$. If we decrease $\hbar$, we expect to find a larger number of states associated with librating tori in the energy shell and the quantum autocorrelation function should agree with the classical function for longer periods of time. Nevertheless, we expect significant differences to develop between the two functions at sufficiently long times even when $\hbar$ is small. These will arise because the quantum system can tunnel between distinct equivalent librating tori. The time scale for this process will be the inverse separation between energies of E and A_1 states that are formed from the same set of librating tori.

2. Property L

Figure 1 gives the impression that the classical and quantum autocorrelation functions of L are in good agreement for $E = 5.70$. Actually, as shown in Fig. 2, the agreement breaks down at late times. The quantum function eventually develops oscillations that do not occur in the classical case and, on the average, drops well below the classical long-time values.

The differences in the two autocorrelation functions can

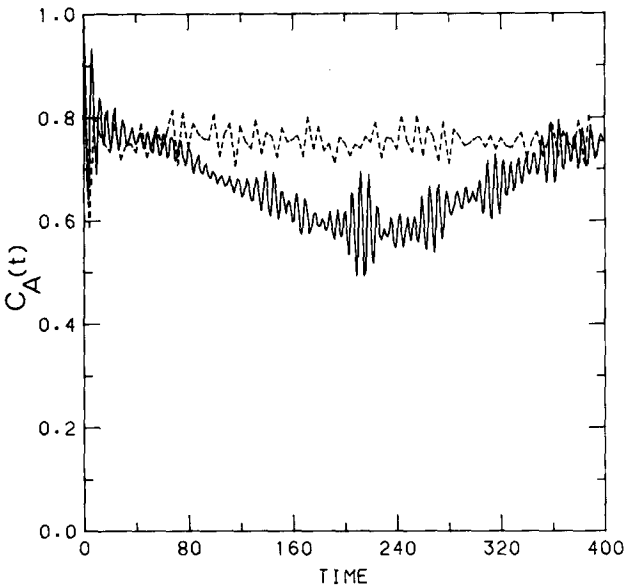

FIG. 2. The quantum autocorrelation function $C_A^q(t)$ (solid curve) and the classical autocorrelation function $C_A(t)$ (broken curve) for property L for times up to 400 units at $E = 5.70$. The resolution used to display the classical function is not as high as that used for the quantum function. For times greater than 400 units, the slow oscillation that appears in the quantum function here is superimposed with additional oscillations of even longer period.

be traced to tunneling between clockwise and counterclockwise motions in the quantum system. This statement is supported by the observation that the frequencies of the quantum oscillations are accurately given by $\Delta E(A_2, A_1)/2\pi$, where ΔE are the differences in the energy levels of certain pairs of nearby A_2 and A_1 states. As can be deduced from the perturbative treatment of Ramaswamy and Marcus,[16] one member of each such pair is, to zero order, given by the (unnormalized) linear combination $[|V, l\rangle + |V, -l\rangle]$ while the other is given by $[|V, l\rangle - |V, -l\rangle]$ with the same V and l. Although primitive semiclassical methods[15] yield a single energy level for these two states, a uniform semiclassical treatment[17] is able to reproduce the small observed, energy difference between such pairs and identifies the sourse of the energy splitting at tunneling. Roughly speaking, then, oscillations with the frequencies $\Delta E/2\pi$ represent tunneling transitions between states with positive and negative angular momentum quantum numbers 1. Similar tunneling phenomena have been described for other systems.[18]

There is evidence that some tunneling between circulating motion persists, albeit to a lesser extent, even at high energy. A plot of the quantum autocorrelation function of L at $E = 12.67$ on a time scale of 0–400 (not shown) also exhibits strong late-time oscillations. Although these oscillations are more irregular than those found at low energy, some of the prominent recurrence frequencies can be identified with the same types of A_1–A_2 state pairs discussed above. These oscillations again cause the quantum correlation function to lie below the extrapolated classical function at long times, but not to such a dramatic extent as at low energy.

We observe oscillations of this sort, causing a large discrepancy between the long-time average of the classical and quantum correlation function, only for property L. We note that L is the only operator we treat that couples states of A_1 and A_2 symmetry, such as those involved in the tunneling process.

Tunneling implies the existence of motion that is classically forbidden but quantum mechanically allowed. In multidimensional systems having no obvious barriers in the potential energy surface, forbidden classical motion indicates the presence of dynamical barriers. Such barriers are often associated with the presence of tori—real or "vague."[19] Thus, it is possible that, just as in the case of property D, the discrepancies between the quantum and classical behavior for property L can be associated with the existence of tori. If this is true, then the improved quantum-classical agreement at higher energy for both D and L may be understood to be a consequence of the scarcity of tori near the dissociation limit of the Henon–Heiles system. The persistence of some tunneling at high energy may be due to the continued presence of some tori or vague tori in this region.

B. Quantum and classical $F_A(T)$

We now compare the functions $F_A^q(T)$ and $F_A(T)$ to determine whether conditions (20) and (21) are obeyed. Recall that, if these conditions are satisfied for all A, the quantum system can be described by the same constancies F_A as the classical system and classical ergodicity concepts apply equally to both systems.

Figure 3 shows the quantum and classical $F_A(T)$. In the high energy case, the quantum and classical functions are in good agreement for all properties A treated and for the full range of T examined. Thus, conditions (20) and (21) are obeyed, and the behavior of the quantum system can be characterized by the same constancies F_A that apply to the classical system. Since this result holds for all of the properties we have examined, it appears that the quantum system displays a form of partial ergodicity similar to that of the classical system. Thus, when the energy is high, our evidence indicates that classical ergodicity concepts may be applied to the quantum system.

As is apparent from Fig. 3, however, the situation at low energy is different. For $E = 5.70$, there are instances of substantial disagreement between the quantum and classical curves and we now discuss these discrepancies.

1. Property L

The low-energy quantum and classical curves for $F_L(T)$ are in reasonably good agreement up to about $T = 30$. At later times, the quantum curve dips substantially below the classical curve as the tunneling described in Sec. III A takes effect. The disagreement between the functions grows with T and, in the limit as T becomes infinite, the function $F_L^q(T)$ approaches the value $F_L^q(\infty) = 0.54$ which differs greatly from the apparent classical limiting value of $F_L = 0.76$ (see Table II). Despite this long-time disagreement, however, conditions (20) and (21) are obeyed in this case since the classical function essentially reaches its infinite time limit before the differences set in. We can identify the time $T_{\max}$ in Eqs.

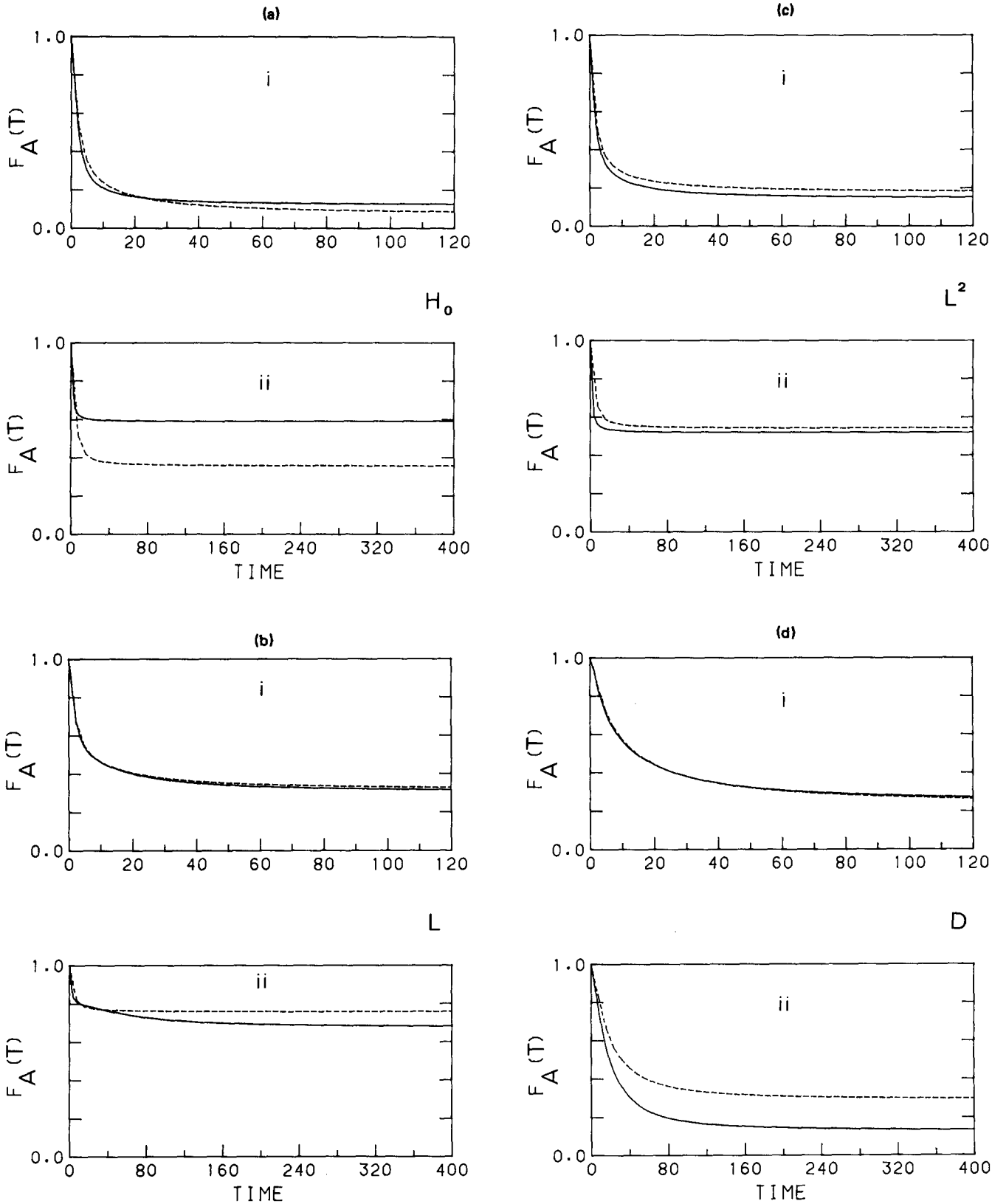

FIG. 3. Quantum functions $F_A^q(T)$ (solid curves) and classical functions $F_A(T)$ (broken curves) for the following properties A: (a) H_0, (b) L, (c) L^2, (d) D, (e) H_x, and (f) D^2. The top panel of each subfigure, labeled (i) shows results for $E = 12.67$, while the lower panel, labeled (ii) shows results for $E = 5.70$. Note that different time scales are used for the two different values of E.

(20) and (21) with approximately 30 time units and, since $F_L^q(30) \approx F_L(30) \approx F_L(\infty) = 0.76$, we conclude that classical value 0.76 can be used to describe the constancy of the quantum system.

It is appropriate to review the reasoning that leads to the interpretation presented above. By restricting the time period for comparison of the quantum and classical $F_A(T)$ to 30 units we deliberately exclude the effects of quantum me-

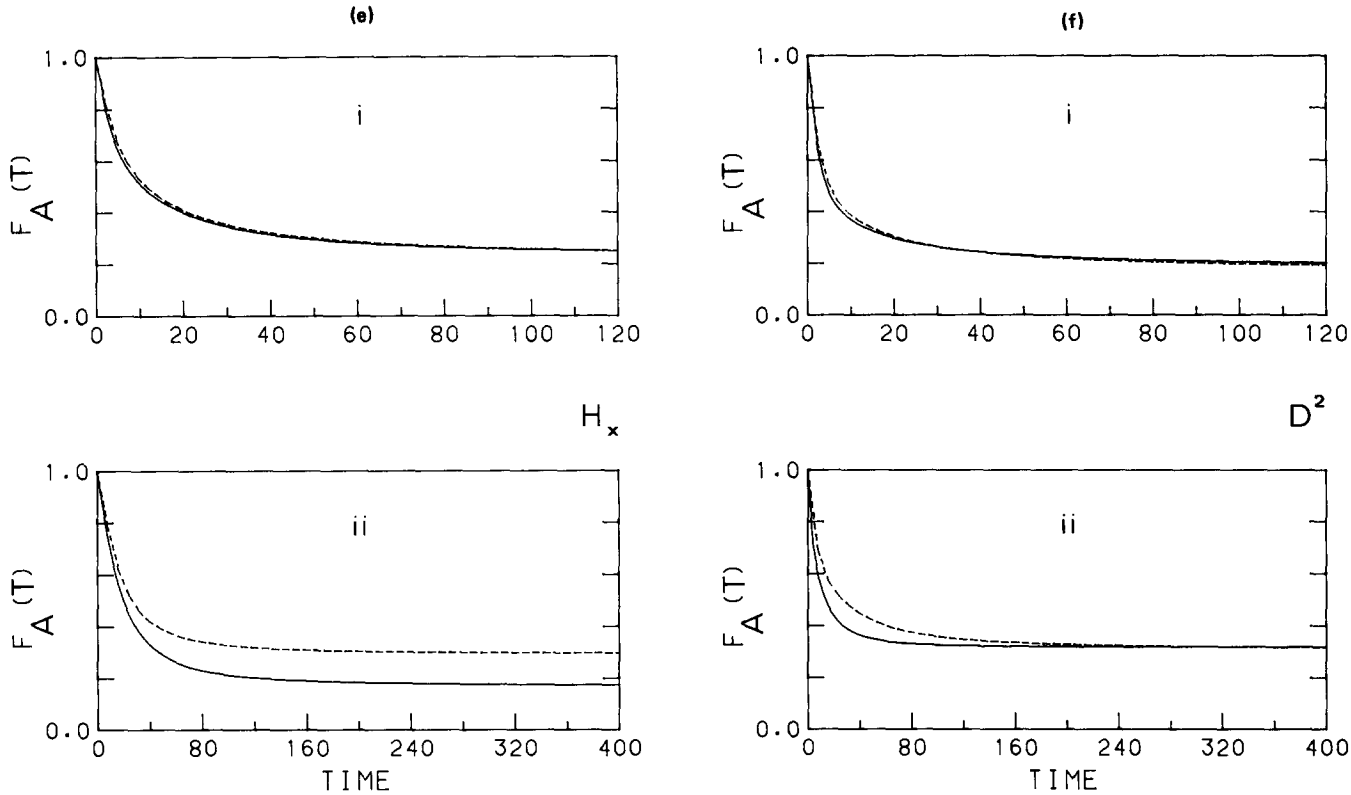

FIG. 3. (*continued*).

chanical tunneling from our identification of the semiclassical analog of the constancy. This restriction is essential since the differences between $F_A^q(\infty)$ and $F_A(\infty)$ caused by the tunneling do not tend to zero in the classical limit. As we will support with further analysis in Appendix B and Sec. IV C below, the effect of tunneling on the *infinite*-time average of the quantum correlation function does not vanish as $\hbar \to 0$ even though the time scale for the onset of tunneling tends to infinity in that case. We cannot, therefore, obtain a quantum analog F_L that tends to the classical constancy as $\hbar \to 0$ unless we restrict the observation time as we have done. Furthermore, unless the quantum version of F_L has the proper classical limiting behavior, it will not reliably reflect the consequences of partial classical ergodicity for the quantum system, as we require.

2. Property D

The low energy curves for $F_D^q(T)$ and $F(T)$ begin to diverge from one another at very early times and the disagreement between the two functions becomes very large before the classical function $F_D(T)$ reaches its apparent asymptotic value at $T \approx 80$. The source of this discrepancy is the same as that causing the disagreement between the low energy curves for C_D and C_D^q in Fig. 1, namely, the small number of librating tori in the energy range considered. Inspection of Fig. 3 for property D in the low energy case shows that there is no value of $T_{\max}$ that satisfies both conditions (20) and (21). Thus, we are unable to identify a semiclassical analog of the constancy F_D when the energy is low.

3. Remaining properties

The low energy discrepancies between classical and quantum functions for properties H_x and D^2 may be, in part, due to the same phenomenon causing the deviations for property D. As for property D, conditions (20) and (21) are not obeyed at low energy for H_x and D^2 and a semiclassical analog of the constancies cannot be identified.

For the sake of completeness, Fig. 3 presents the $F_A^q(T)$ and $F_A(T)$ in the case $A = H_0$ for both values of E, although the reliability of the classical results is uncertain, especially in the low energy case. We note, from Table II, that the classical quantities $C_A(\infty)$ and $C_{A,\mathrm{eq}}$ for $A = H_0$ have very similar values and that $C_{A,\mathrm{eq}}$ is close to 1 when $E = 5.70$. As is clear from Eq. (8), small statistical errors in the Monte Carlo evaluation of the classical phase space integrals can lead to large inaccuracies in the computed values of $F_A(T)$ in such cases. Thus, the large apparent disagreement between the classical and quantum mechanical curves for low energy may be an artifact of small ($\lesssim 0.005$) numerical uncertainties in $C_{A,\mathrm{eq}}$ and $\overline{C}_A(T)$. The relative statistical error in $F_A(T)$ at high energy is even greater than at low energy. Nevertheless, due to the larger value of $1 - C_{A,\mathrm{eq}}$ at $E = 12.67$, the absolute uncertainty is too small to affect the qualitative similarity between the classical and quantum curves in this case. Thus, the high energy results may be regarded as qualitatively reliable.

We conclude from our examination of Fig. 3 that, in contrast to the situation at high energy, it is not always possible to assign semiclassical constancies to the quantum behavior at low energy. Although we are able to characterize

the evolution of the property L (and, perhaps, some others) by such a constancy, we are not able to do so for all of the properties we have considered. Our results thus indicate a strong qualitative change in the ability to apply the language and concepts of classical ergodicity to the quantum system as the energy is lowered.

C. Classical constancies and quantum matrix elements

The circles in Fig. 4 show how the classical constancies F_A vary with energy for the properties we have examined. The quantities $\overline{C}_A(\infty)$ and $C_{A,\mathrm{eq}}$ that are used to calculate these constancies are listed in Table II. In all cases, the F_A decrease with energy, indicating that the classical system becomes more nearly ergodic as the energy is raised. These results are in qualitative agreement with those of Koszykowski, Noid, Tabor, and Marcus[3] and of Hamilton and Brumer[4] who showed that certain classical correlation functions of the Henon–Heiles system relax to values close to those expected statistically, when the energy is high. However, we note that some of the F_A (especially F_L) are rather far from zero even at high energy. This shows that the classi-

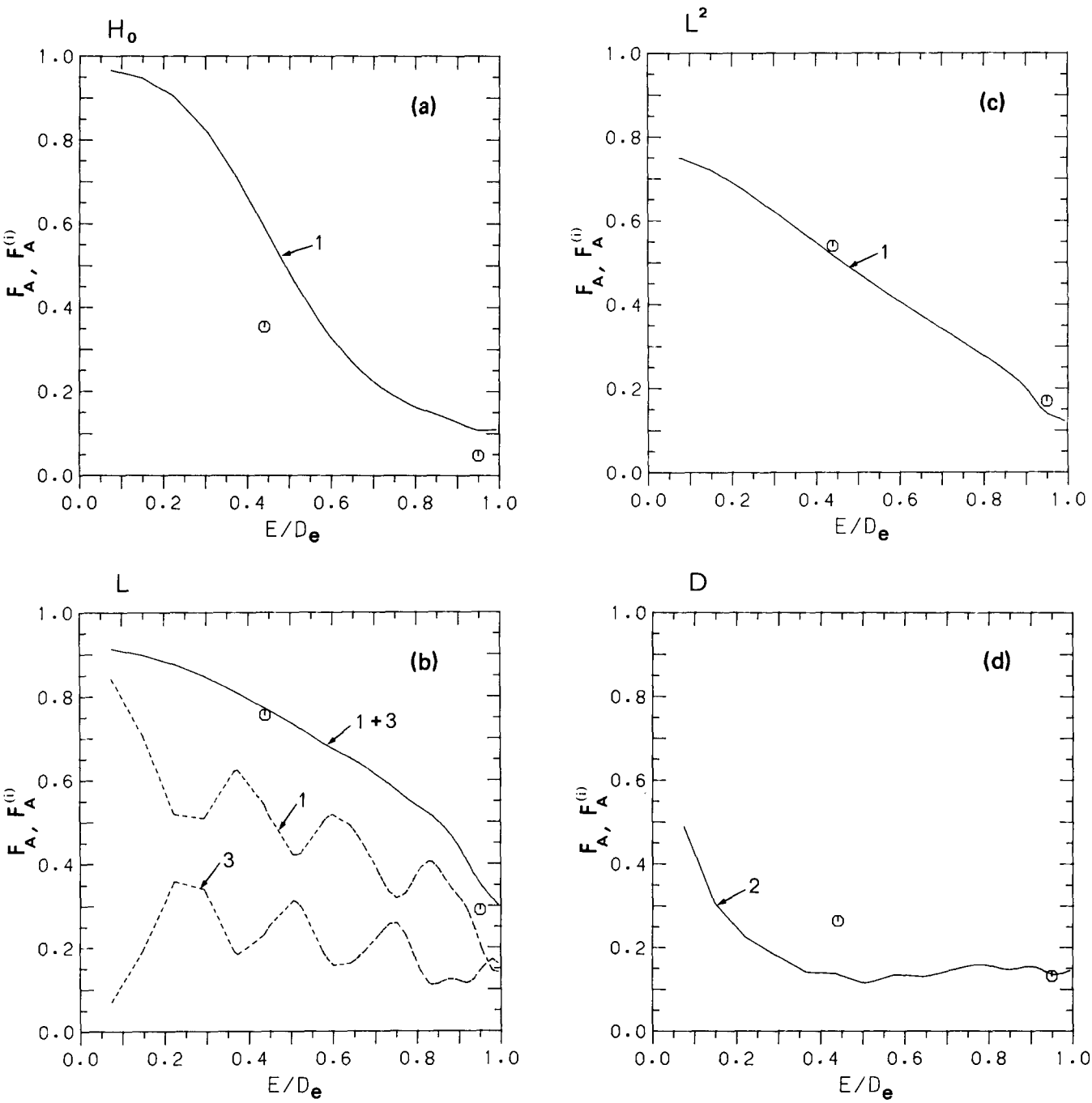

FIG. 4. Classical constancies F_A (circles) and quantum $F_A^{(i)}$ (curves) for the following properties A: (a) H_0, (b) L, (c) L^2, (d) D, (e) H_x, and (f) D^2. The numbers which label the individual quantum curves are the (i) superscripts of the $F_A^{(i)}$. Curves labeled by "1 + 2" or "1 + 3" show the sums $F_A^{(1)} + F_A^{(2)} = F_A^q(\infty)$ or $F_A^{(1)} + F_A^{(3)}(T_{\max})$. For property D, $F_A^{(1)}$ vanishes by symmetry so that the curve labeled "2" represents $F_A^q(\infty)$. For properties H_0, L, and L^2, $F_A^{(2)}$ vanishes by symmetry so that the curves labeled "1" represent $F_A^q(\infty)$ and the curve labeled "1 + 3" for property L represents $F_A^q(T_{\max})$.

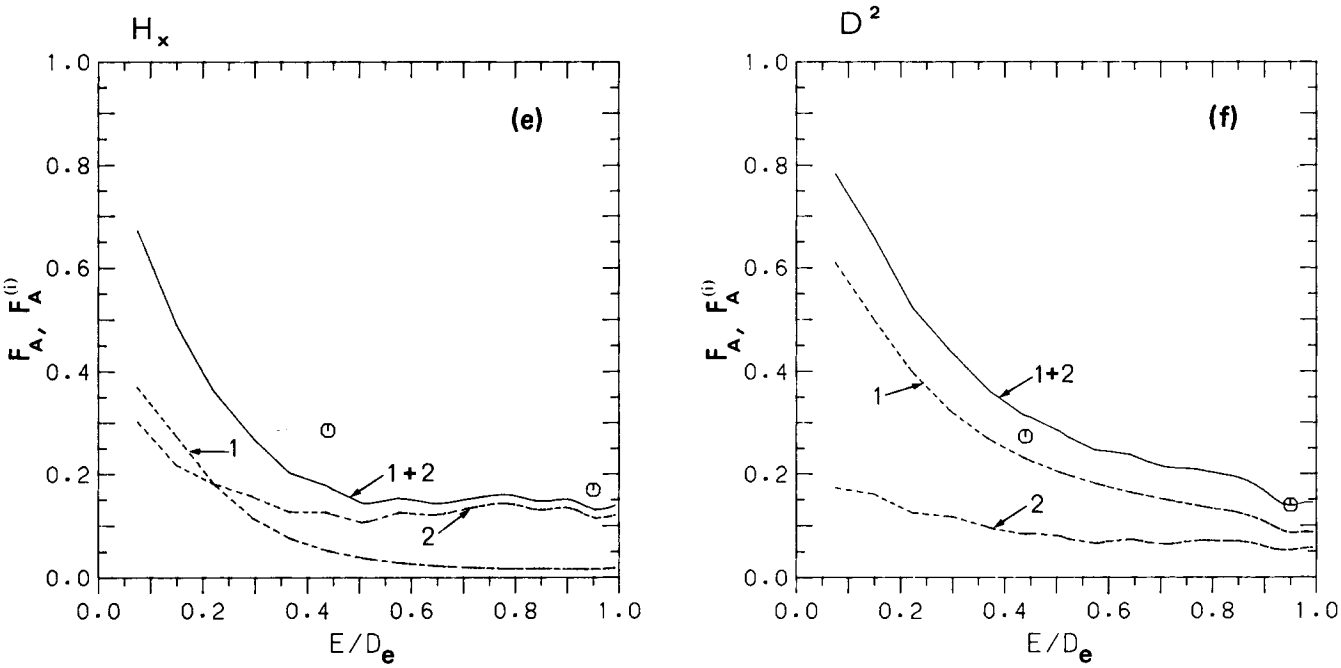

FIG. 4. (*continued*).

cal system never really comes very close to attaining complete ergodicity. It is likely that, to a large extent, the nonergodic behavior at high energy is associated with residual tori and vague tori.

Since it is not possible to identify a quantum analog of F_A for all properties at all energies, Fig. 4 compares the classical constancies to the quantum mechanical $F_A^{(1)}$, $F_A^{(2)}$, and $F_A^q(\infty) = F_A^{(1)} + F_A^{(2)}$. Note that $F_A^q(\infty)$ omits the contribution of $F_A^{(3)}(T_{\max})$, which should be included for a proper comparison of the classical and quantum results, but which is undefined when it is impossible to find a $T_{\max}$ satisfying conditions (20) and (21). Table II lists values for the quantities $\overline{C}_A^q(\infty)$ and $C_{A,\mathrm{eq}}^q$ required for the evaluation of $F_A^q(\infty)$ at $E = 5.70$ and $E = 12.67$.

TABLE II. Comparison of quantum and classical long-time behavior.

Property	Energy[a] range	$\overline{C}_A^q(\infty)$[b]	$\overline{C}_A(\infty)$[c]	$C_{A,\mathrm{eq}}^q$[d]	$C_{A,\mathrm{eq}}$	$F_A^q(\infty)$[e]	F_A[f]
H_0	Low	0.987	0.981	0.969	0.970	0.592	0.354
	High	0.943	0.935	0.936	0.932	0.107	0.047
L	Low	0.535	0.756	0	0	0.535	0.756
	High	0.211	0.290	0	0	0.211	0.290
L^2	Low	0.763	0.722	0.507	0.505	0.534	0.540
	High	0.592	0.603	0.515	0.522	0.159	0.169
D	Low	0.136	0.264	0	0	0.136	0.264
	High	0.136	0.131	0	0	0.136	0.131
H_x	Low	0.775	0.802	0.728	0.722	0.173	0.285
	High	0.727	0.741	0.686	0.688	0.131	0.169
D^2	Low	0.648	0.617	0.488	0.473	0.313	0.273
	High	0.460	0.453	0.373	0.364	0.138	0.139

[a] Low energy: $E = 5.70$. High energy: $E = 12.67$.

[b] $\lim_{T\to\infty} \overline{C}_A^q(T)$.

[c] Calculated as described in Sec. III C.

[d] Evaluated using Eq. (24).

[e] Calculated from $\overline{C}_A^q(\infty)$ and $C_{A,\mathrm{eq}}^q$ using Eq. (8′) with $T\to\infty$. Also see Eq. (34).

[f] Calculated using Eq. (8).

As might be expected from Fig. 3, the agreement between the $F_A^q(\infty)$ and F_A usually improves as the energy increases. The sources of the especially large low-energy discrepancies for properties H_0, D, and L have been discussed in Sec. III B. The pronounced oscillations in $F_L^q(\infty) = F_L^{(1)}$ will be discussed below. An interesting point to emerge from Fig. 4 is that, even with the omission of the $F_A^{(3)}$ contribution, the $F_A^q(\infty)$ are in fairly good agreement with the F_A at $E = 12.67$. This implies that the $F_A^{(3)}(T_{\max})$, which are well defined for all A in the high energy case, are relatively small at such high energies. However, as Table II makes clear, these quantities still make significant contributions to certain of the $F_A^q(T_{\max})$, even at the highest energies considered, and should not be neglected.

We recall that the energy dependences of $F_A^{(1)}$ and $F_A^{(2)}$ reveal how the distributions of matrix elements of $\hat{A}$ change as the system becomes more classically ergodic. The quantity $F_A^{(1)}$ measures the dispersion of the individual scaled diagonal matrix elements $N_A(E)\langle n|\hat{A}|n\rangle$ about their mean, while the quantity $F_A^{(2)}$ measures the magnitude of the scaled off-diagonal matrix elements $N_A(E)\langle m|\hat{A}|n\rangle$ between states n and m of equal energy. For ergodic systems in the classical limit, these deviations and these off-diagonal matrix elements should be vanishingly small.[5]

Figure 4 shows to what extent this behavior is achieved for our partially ergodic quantum system. The $F_A^{(1)}$ for H_0, L^2, H_x, and D^2 decrease monotonically as the energy is

raised, while the oscillatory $F_A^{(1)}$ for L decreases on the average as the energy is increased. These results indicate a tendency for the scaled diagonal matrix elements of these properties to become more uniform as the classical system becomes more ergodic. $F_A^{(2)}$ for D^2 also decreases monotonically as the energy is increased. This implies that the scaled off-diagonal matrix elments of D^2 between states of equal energy tend to become smaller as the system becomes more classically ergodic. However, we note that the $F_A^{(2)}$ for properties D and H_x do not show a similar, uniform tendency to decrease with energy in the range of $0.4\,D_e < E < D_e$. Thus, the scaled off-diagonal matrix elements of these operators do not monotonically decrease in this range.

The results just described for D and H_x are contrary to the naive predictions based on the classical limit for ergodic systems. However, they are not inconsistent with the theory presented in Sec. II. Recall that the treatment of Sec. II predicts only that the *sum* $F_A^q(T_{\max}) = F_A^{(1)} + F_A^{(2)} + F_A^{(3)}(T_{\max})$ should decrease as the energy is varied over a range in which the classical F_A decreases, and that this prediction is subject to the requirement that $F_A^q(T_{\max})$ exists at all energies in this range. First, note that there is actually no reason to expect the individual $F_A^{(i)}$ to decrease or the distribution of each type of matrix element to behave more "ergodically" as the energy of the system is raised. It is only necessary that one of the three $F_A^{(i)}$ decrease and that the distribution of only one kind of matrix element come closer to the ergodic ideal as the energy increases. Failure of $F_A^{(2)}$ to decrease with energy for properties D and H_x is, therefore, not inconsistent with these predictions. Second, note that the matrix elements are predicted to behave more ergodically as the energy is increased only if the quantum analog of the constancy, $F_A^q(T_{\max})$, exists for all energies in the relevant range. This requirement is strongly violated by properties D and H_x for which quantum analogs of the constancies certainly do not exist at low energy. Thus, the behavior observed for these two properties should not occasion any surprise. It may, in fact, be somewhat more surprising that the terms $F_A^{(1)}$ and $F_A^{(2)}$ do, so often, individually decrease with energy, even when $F_A^{(3)}(T_{\max})$ is not very well defined at low energy. We could not completely anticipate such behavior on the basis of the theory presented in Sec. II.

While the distributions of the scaled matrix elements are generally found to come closer to the statistical ideal as the system becomes more classically ergodic, the unscaled matrix elements do not necessarily follow this trend. The energy dependence of $N_A(E)$ is important in causing the matrix element distributions to change in the expected manner. Although it is true that even the unscaled matrix elements will obey the predictions of semiclassical ergodic theory [Eqs. (36)] for the case of an ergodic system in the classical limit, only the scaled matrix elements can be expected to show the effects of an increased degree of classical ergodicity under the more general circumstances that apply here.

We now discuss the oscillatory energy dependence of the function $F_L^q(\infty)$ exhibited in Fig. 4. The oscillations in this function can be traced to a purely quantum mechanical source: the selective omission from $F_A^q(\infty)$ of contributions from particular states. We note that there are certain energy eigenstates of the Henon–Heiles system that can be accurately approximated by those zero-order states $|V, l\rangle$ that have extreme values ($l = \pm V$) for the quantum number l.[20] Since such states lead to large diagonal matrix elements of L, they can make especially large contributions to $F_L^q(\infty)$. However, only states of E (and not A_1 or A_2) symmetry can contribute to this function. Thus states with $|l| = V = 2,4,5,7,\ldots$, which have E symmetry, indeed make large contributions to $F_L^q(\infty)$ and are mainly responsible for the local maxima observed in this function in Fig. 4. However, states with $|l| = V = 3,6,$ and 9, which have A_1 and A_2 symmetry, do not contribute to $F_L^q(\infty)$. This omission causes the minima that are observed in this function near the zero-order energies of these states at $E = 4,7,$ and 10. By demonstrating that the oscillatory behavior of the function is associated with a certain set of periodically occurring V (i.e., values divisible by 3), we prove that these oscillations have a nonclassical origin.

Since states of all symmetries contribute to $F_L^{(3)}(T_{\max})$, we may anticipate that the nonclassical oscillations can be removed by properly including this term. Fortunately, for the case of property L, $T_{\max}$ can be defined at both low and high energies so that we can indeed evaluate $F_L^{(3)}(T_{\max})$ as a function of energy. Figure 4 displays $F_L^{(3)}(T_{\max})$ [calculated using Eq. (32)] and $F_L^q(T_{\max})$ vs E. For the sake of simplicity, $T_{\max}$ is chosen to be 30 for all energies. It is seen that $F_L^{(3)}(T_{\max})$ contain maxima and minima that complement those of $F_A^q(\infty)$ so that the sum of these terms, $F_L^q(T_{\max})$, is a nonoscillatory function, as expected classically.

Including the term $F_L^{(3)}(T_{\max})$ greatly improves the agreement between the quantum and classical constancies at low energy. The agreement between $F_L^q(T_{\max})$ and F_L at high energy is only fair, but can be substantially improved by choosing a larger value of T_{max} for that case. Although the oscillatory contribution $F_L^{(3)}(T_{\max})$ does not show a generally decreasing trend for all energies $< D_e$, the total function $F_L^q(T_{\max})$ does decrease monotonically with energy, as required by the semiclassical theory.

As could be anticipated by our discussion, the dominant contribution to $F_L^{(3)}(T_{\max})$ is found to come from the pairs of states of A_1 and A_2 states of nearly equal energy that are involved in the tunneling process previously described. Thus, denoting these pairs of states by $|n(A_1)\rangle$ and $|n(A_2)\rangle$, and recognizing that the spacing between the corresponding levels is smaller than $1/T_{\max}$, we can write

$$F_L^{(3)}(T_{\max}) \simeq B_A^{-1}\Big\{\sum_{n(A_1)} \rho^{\sigma}(E - E_{n(A_1)})|\langle n(A_2)|A\,|n(A_1)\rangle|^2 + \sum_{n(A_2)} \rho^{\sigma}(E - E_{n(A_2)})|\langle n(A_1)|A\,|n(A_2)\rangle|^2\Big\}. \tag{42}$$

The similarity to Eq. (40) for $F_L^{(2)}$ should be noted. In essence, by including the term $F_L^{(3)}(T_{\max})$ in our calculation, we treat the "almost degenerate" levels associated with states of A_1 and A_2 symmetry on the same footing as the truly degenerate levels associated with states of E symmetry. This procedure is appropriate for our semiclassically based theory since, as

in the case of E states, both members of an A_1–A_2 pair arise from a single torus.[17]

The case of property L illustrates the general rule that it is important to include the term $F_A^{(3)}(T_{\max})$ in calculations of the quantum constancies. The analysis of $F_L^{(3)}(T_{\max})$ presented in Appendix B demonstrates that this term does not always vanish in the classical limit and Fig. 4 illustrates that, in practice, this term is sometimes quite large. Thus, the function $F_A^q(\infty)$, obtained by omitting this term, need not bear any relationship to the classical constancy, even as $\hbar \to 0$. Only by incorporating this contribution in the proper manner does one obtain the correct analog to F_A.

V. SUMMARY AND CONCLUSIONS

The goal of our work has been to determine how, and to what extent, classical partial ergodicity is reflected in the dynamics of quantum mechanical systems. To achieve this objective, we have identified quantum analogs of quantities that determine the ergodic nature of classical systems. Based on an analysis of these quantities, we have developed criteria for judging whether quantum systems behave in a classically ergodic manner. We have illustrated our theoretical treatment by numerical calculations on the Henon–Heiles system.

To clarify the physical basis of our work, we briefly review our approach and the principles that underlie it.

Our procedure for identifying (partially) ergodic dynamics in a quantum system ($\hbar > 0$) can be summarized as follows. We examine the features of quantum dynamics [i.e., those described by $F_A^q(t)$] that signal the presence of ergodic behavior as $\hbar \to 0$. If, to the extent possible for quantum mechanics, these dynamical features are already identifiably close to their classical limits under conditions that these limits imply ergodicity, then we identify the quantum dynamics as ergodic.

We specifically examine the features of quantum dynamics that correspond to ergodicity as $\hbar \to 0$ because we wish to study the form of quantum behavior that is a consequence of classical ergodic behavior. The relevant quantum dynamical features are identified by the semiclassical ergodic theory of Ref. 5, which describes how quantum mechanical time evolution becomes classical ergodic dynamics in the classical limit. We base our treatment on this theory because this practice appears to be the only consistent way of ensuring that the behavior we identify as ergodic in quantum systems is directly related to classical ergodic behavior.

We determine the presence of ergodicity in quantum systems by comparing the quantum behavior to the classically limiting behavior because this procedure is the only one that is really compatible with the semiclassical ergodic theory. Although adopting this approach means abandoning all attempts toward identifying purely quantum forms of ergodic behavior, there appear to be no logically consistent alternatives. As discussed in Sec. II, there are no guidelines for detecting the analog of classical ergodic behavior in a quantum system that is too far away from the classical limit. The only guideline for identifying ergodic behavior in a system that is near the classical limit is the similarity of the relevant quantum and classical dynamics.

We have formulated our definition of partial classical ergodicity in such a way that it provides a useful measure of what is normally called "statistical" behavior in systems that are not truly ergodic. We therefore define partial ergodicity by reference to the dynamics on the full energy surface, as is customary in the usual statistical theories of chemical kinetics. Our definition is appropriate in typical physical situations where the evolution of a limited number of properties is monitored.

The physical basis of our work is, thus, straightforward. The essence of our resulting procedure for examining the ergodic nature of quantum systems is also simple and direct: it is to compare quantum dynamics, as reflected in the functions $F_A^q(T)$, to classical dynamics, as reflected in the functions $F_A(T)$. The interpretation of the resulting form of statistical behavior is physically clear because it is as close as possible to the statistical behavior of classical systems. Consequently, our work treats the quantum implications of classical ergodicity in a physically oriented manner.

Let us now consider the results of the numerical studies of the Henon–Heiles system.

The most important numerical result of our work is the observation of close agreement between the $F_A^q(T)$ and $F_A(T)$ at high energy. This agreement supports our identification of the function $F_A^q(T)$ as the quantum analog of $F_A(T)$. It thus confirms our analysis of how classical ergodicity influences quantum dynamics and suggests that the theory of Sec. II has been formulated in an appropriate and meaningful way. It, furthermore, provides evidence for the validity of the semiclassical ergodic theory of Ref. 5 which underlies the present work.

The close quantum-classical agreement found at high energy implies that the quantum Henon–Heiles system exhibits a form of partial ergodicity that is similar to that of the classical system. This shows that this quantum system (which is sometimes taken as a model for a vibrating molecule) can exhibit statistical behavior as a result of the classical evolution. The statistical behavior which the quantum system obeys is explicitly defined in Sec. II. Apart from its relationship to ergodicity, as opposed to mixing, this behavior is of a form that is directly relevant for the usual statistical formulations of chemical kinetics.

Another interesting consequence of the high-energy agreement is that the partially ergodic nature of the classical system is reflected in the matrix element distribution for the quantum mechanical system. The implications of the classical behavior for the quantum matrix elements, in this case, follow immediately from the definition of $F_A^q(T)$, as presented and discussed in Sec. II.

We have seen, however, that the applicability of the classical concept of ergodicity for quantum systems is subject to limitations. At low energy, the quantum and classical dynamics of the Henon–Heiles system are generally so different that it is difficult to use even the language of classical ergodicity to characterize the quantum system. In such cases, the quantum analog of ergodic (or nonergodic) behavior becomes a very imprecise notion and there is no longer

any practical way to identify such behavior. Under these circumstances, the ergodic nature of the classical system is not necessarily reflected in the distribution of the quantum mechanical matrix elements.

These limitations of the classical ergodicity concept arise as a result of differences between the classical and quantum time evolution. However, not all forms of disagreement between classical and quantum dynamics affect the classical concept of ergodicity. The theory presented in Sec. II identifies the quantum-classical discrepancies that do and do not limit our ability to apply the classical ergodicity analysis to quantum systems. The numerical results reported in Sec. IV provide examples of both kinds of discrepancies.

The dynamical tunneling we have found in the Henon–Heiles system is an example of an effect which, though it leads to classical-quantum disagreements, does not prevent application of classical ergodicity concepts, because the deviations appear only after relaxation of the time-averaged dynamics is essentially complete. We have emphasized the importance of treating effects of this sort correctly. We have shown that their presence has implications for the proper calculation of the quantum constancy and [via $F_A^{(3)}(T)$] the distribution of quantum mechanical matrix elements. We have illustrated these points for the Henon–Heiles system.

The quantum-classical disagreement in the low-energy Henon–Heiles system, observed in the autocorrelation function for property D, is an example of an effect that does limit our ability to detect the influence of classical ergodicity in quantum systems, because the deviations set in well before the relaxation of the time-averaged dynamics is complete. The source of the disagreement between the two forms of dynamics in this case is interesting: it is the small size of the phase space region that is occupied by classical, pendular tori. Similar effects, leading to large quantum-classical discrepancies, are expected to occur in other systems with degenerate frequencies.[21] The present work, together with previous investigations,[11,22] suggests that classical ergodicity is frequently rendered irrelevant for quantum systems by effects that cause the quantum and classical behavior to disagree after short imes.

As a final remark, we mention that the expressions we have derived for $F_A^q(T_{\max})$ [Eqs. (25)–(28)] describe the quantum analog of the constancy as a sum of contributions from individual energy eigenstates. It is possible to use these expressions to identify the quantum mechanical states that are primarily responsible for the nonergodic behavior of the Henon–Heiles system. It would be interesting to compare such states to those classified as "regular" and "irregular" on the basis of various criteria. Work along these directions is in progress.

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APPENDIX A: MATHEMATICAL PROPERTIES OF THE FUNCTIONS $F_A(T)$

To begin our analysis of the $F_A(T)$, we orthogonalize A to 1 to obtain the new function A', defined by

$$A' = A - 1\langle 1|A\rangle/\langle 1|1\rangle. \tag{A1}$$

It is easy to verify by direct substitution that

$$C_{A'}(t) = \langle A'(t)|A'\rangle/\langle A'|A'\rangle = [C_A(t) - C_{A,\mathrm{eq}}]/(1 - C_{A,\mathrm{eq}}) \tag{A2}$$

so that [see Eqs. (6) and (8)]

$$F_A(T) = \overline{C}_{A'}(T) = (1/T)\int_0^\infty C_{A'}(t)\exp(-t/T)dt. \tag{A3}$$

Applying Schwarz's inequality to $\langle A'(t)|A'\rangle$, in the first line of Eq. (A2), yields

$$|C_{A'}(t)| \le [\langle A'(t)|A'(t)\rangle\langle A'|A'\rangle]^{1/2}/\langle A|A\rangle. \tag{A4}$$

Using the unitarity of the time evolution operator $U(t)$, however, we can show that $\langle A'(t)|A'(t)\rangle = \langle U(t)A'|U(t)A'\rangle = \langle A'|A'\rangle$. We therefore obtain the following bounds for $C_{A'}(t)$:

$$|C_{A'}(t)| \le 1. \tag{A5}$$

It is then a straightforward matter to combine this result with Eq. (A3) and standard integral inequalities to obtain

$$F_A(T)| \le 1. \tag{A6}$$

We now use the spectral theorem for unitary operators to express the autocorrelation function $C_{A'}(t)$ as[23]

$$C_{A'}(t) = \int \exp(i\omega t)d\mu_A(\omega), \tag{A7}$$

where $\mu_A(\omega)$ is a unique, nonnegative, Borel measure. Substituting this expression in Eq. (A3), and applying the observation that F_A is real, we obtain

$$F_A(T) = \int [1 - i\omega T]^{-1}d\mu_A(\omega) = \int [1 + (\omega T)^2]^{-1}d\mu_A(\omega). \tag{A8}$$

Equation (A8) establishes that $F_A(T)$ is a monotone nonincreasing function of T and that

$$F_A(T) > 0. \tag{A9}$$

We thus prove the inequalities stated in Eq. (9).

Inequalities (22) for the analogous quantum mechanical function $F_A^q(T)$ are also easy to prove. The result $|F_A^q(T)| \le 1$ follows from application of Schwarz's inequality which establishes, as in Eqs. (A5) and (A6), that $|C_A^q(t)|$ and $|\overline{C}_A^q(T)|$ are ≤ 1. The inequality $F_A^q(T) \ge 0$ and the conclusion that this function is monotone nonincreasing follow by inspection of Eqs. (25)–(27) and (32).

APPENDIX B: CLASSICAL LIMIT OF $F_L^{(3)}(T_{\max})$

Here we demonstrate that the contribution $F_L^{(3)}(T_{\max})$ to the classical constancy F_L does not vanish in the classical limit, when λ is small.

Let λ be small enough that the classical constancy F_L is close to 1. Then, recognizing that $F_L^{(2)}$ vanishes by symmetry, we obtain

$$F_L^{(1)} + F_L^{(3)}(T_{\max}) \simeq 1 \tag{B1}$$

in the limit as $\hbar \to 0$. Substituting the definitions for these terms [see Eqs. (28)–(30) and (40)] into this equation, recognizing that L transforms according to the A_2 representation, using $C_{L,\mathrm{eq}} = 0$ (see Table II), and rearranging the resulting expression, we obtain

$$\begin{aligned}
&2\sum_{n(E)} \rho^{\sigma}(E - E_{n(E)}) |\langle n(E)|\hat{L}\,|n(E)\rangle|^2 \\
&\quad + \sum_{n(A_1)} \rho^{\sigma}(E - E_{n(A_1)}) \sum_{m(A_2)} |\langle m(A_2)|\hat{L}\,|n(A_1)\rangle|^2 \Big/ \\
&\quad \{1 + (\omega_{nm} T_{\max})^2\} \\
&\quad + \sum_{n(A_2)} \rho^{\sigma}(E - E_{n(A_2)}) \sum_{m(A_1)} |\langle m(A_1)|\hat{L}\,|n(A_2)\rangle|^2 \Big/ \\
&\quad \{1 + (\omega_{nm} T_{\max})^2\} \\
&\simeq 2\sum_{n(E)} \rho^{\sigma}(E - E_{n(E)}) \sum_{m(E)} |\langle m(E)|\hat{L}\,|n(E)\rangle|^2 \\
&\quad + \sum_{n(A_1)} \rho^{\sigma}(E - E_{n(A_1)}) \sum_{m(A_2)} |\langle m(A_2)|\hat{L}\,|n(A_1)\rangle|^2 \\
&\quad + \sum_{n(A_2)} \rho^{\sigma}(E - E_{n(A_2)}) \sum_{m(A_1)} |\langle m(A_1)|\hat{L}\,|n(A_2)\rangle|^2 .
\end{aligned} \tag{B2}$$

The second and third terms on the left-hand side arise from the function $F_L^{(3)}(T_{\max})$. If this function really is zero in the classical limit, then Eq. (B2) implies that the last two terms on the right-hand side of this equation must also vanish. This, however, leads to a contradiction since it implies that

$$\hat{L}\,|n\rangle = 0, \tag{B3}$$

where $|n\rangle$ is any state in the energy shell having A_1 or A_2 symmetry. To show that this result cannot be correct, we consider the action of $\hat{L}$ on the eigenstate $|V, l\rangle$. The result must be equal to $l\,|V, l\rangle$. However, if l is evidently divisible by 3, then $|V, l\rangle$ projects only onto states of A_1 and A_2 symmetry. Expansion of $|V, l\rangle$ in terms of states $|n\rangle$ followed by substitution of Eq. (B3) yields incorrect results for all values of l except zero. As a result, we conclude that $F_L^{(3)}(T_{\max})$ cannot vanish in the classical limit when λ is small. Note that we have avoided using ordinary quantum perturbation theory in deriving this result, even though λ has been assumed to be small, since ordinary low order perturbation theory breaks down when $\hbar \to 0$.

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