Faculty Publications

1994-11-01

Semiclassical quantization of a nonintegrable system: Pushing the Fourier method into the chaotic regime

Karl Sohlberg

Randall B. Shirts
randy_shirts@byu.edu

Follow this and additional works at: <https://scholarsarchive.byu.edu/facpub>

Part of the [Biochemistry Commons](#), and the [Chemistry Commons](#)

Original Publication Citation

Sohlberg, Karl and Randall B. Shirts. "Semiclassical quantization of a nonintegrable system: Pushing the Fourier method into the chaotic regime." *The Journal of Chemical Physics* 11 (1994): 7763-7778.

BYU ScholarsArchive Citation

Sohlberg, Karl and Shirts, Randall B., "Semiclassical quantization of a nonintegrable system: Pushing the Fourier method into the chaotic regime" (1994). *Faculty Publications*. 693.
<https://scholarsarchive.byu.edu/facpub/693>

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact ellen_amatangelo@byu.edu.

Semiclassical quantization of a nonintegrable system: Pushing the Fourier method into the chaotic regime

Karl Sohlberg and Randall B. Shirts

Department of Chemistry, Brigham Young University, Provo, Utah 84602

(Received 13 June 1994; accepted 26 July 1994)

Semiclassical Einstein–Brillouin–Keller (EBK) quantization of the nonintegrable Hénon–Heiles Hamiltonian succeeds using the Fourier transform method of Martens and Ezra. Two innovations are required for this success: (1) the use of tunneling corrected quantizing actions obtained from an approximate, one-dimensional Hamiltonian and (2) exploitation of intermediate-time approximate quasiperiodicity or “vague tori” wherein the Fourier transform of chaotic motion over 10–100 vibrational periods allows the determination of frequencies and amplitudes which approximate motion during the time interval. Approximate tori, actions, and EBK energy levels are then straightforward. We use an interpolation method to smooth over small resonance zones that are not expected to be important quantum mechanically.

I. INTRODUCTION

For molecules of three or more atoms in which the large number of vibrational states makes standard variational calculations intractable, semiclassical techniques for determining quantum eigenvalues are useful.¹ The correspondence between quantum eigenstates and classical invariant tori provides a method for finding approximate quantum states from classical dynamics.² Invariant tori can only be constructed provided proper classical actions exist since the actions *define* the torus. Such actions can be constructed from the coefficients of a Fourier series representation of the classical coordinates and momenta.³ Indeed, semiclassical energy levels have been found for several model systems by quantizing on classical actions constructed from the Fourier coefficients of the classical coordinates and momenta.^{4–8} Schatz has developed a computer program for computing actions and primitive semiclassical eigenvalues with this method.⁹ The Fourier method has also been used to compute classical actions for purposes other than semiclassical quantization.^{10,11} While this method has seen considerable success, its application is formally limited to regions of phase space in which the classical trajectories are periodic or quasiperiodic. If the classical trajectory is not quasiperiodic, i.e., chaotic, it is not possible to represent it with a sum of components of definite frequency. Such a chaotic trajectory is not confined to an invariant torus imbedded in phase space, but samples a volume of larger dimension. With no invariant torus, no proper classical action variables exist, and it is not surprising that no proper Fourier coefficients can be found, since actions can be constructed from such coefficients. In spite of the apparent limitation of the Fourier approach (for computing classical actions and subsequently semiclassical energy levels) to only those energies where the classical trajectories are quasiperiodic in character, in this paper we will demonstrate how the Fourier approach can be applied to locate semiclassical energy levels in chaotic regions of phase space by taking advantage of regions of phase space with some residual quasiperiodic nature, and numerically exploiting the concept of a vague torus developed previously.^{12–14}

The most common method used for semiclassical quantization of chaotic systems is Gutzwiller's periodic orbit method.¹⁵ Methods based on EBK quantization have enormous computational advantage compared to periodic orbit methods, so extensions of the EBK method into the chaotic regions leave much to be desired. The adiabatic switching method has also been used to find semiclassical energy levels of nonintegrable Hamiltonian systems.^{16–18} Skodje has used the adiabatic switching method to find semiclassical energy levels of the Hénon–Heiles system in the chaotic regime,¹⁹ and his results will be compared to those produced by the Fourier method. We will also compare the present method with methods based on Gutzwiller's periodic orbit quantization.

II. QUANTUM RESULTS

The well-known Hénon–Heiles system was chosen for this work.²⁰ The classical Hamiltonian is

$$H = \left(\frac{p_x^2}{2} + \frac{x^2}{2} \right) + \left(\frac{p_y^2}{2} + \frac{y^2}{2} \right) + \epsilon \left(x^2 y - \frac{y^3}{3} \right). \quad (1)$$

We chose $\epsilon = (80)^{-1/2}$ as did previous authors. With this choice of ϵ , the dissociation energy is $D = 13\frac{1}{3}$. The Hénon–Heiles system is a prototype for nonintegrable coupled oscillator systems.^{21–26} Classical trajectories which are periodic, quasiperiodic, and chaotic are all present in this system. At low energies, quasiperiodic trajectories dominate, but as the system energy increases, chaotic trajectories become increasingly prevalent. The presence of both types of motion makes this system ideal for testing techniques for semiclassical quantization. In addition, there exists a considerable body of previous work on this system for comparison.^{13,23,24,27–31}

In order to determine the accuracy of the semiclassical methods developed below, it is necessary to know the exact quantum energy levels of the Hénon–Heiles system. We have computed the energy levels of the Hénon–Heiles system by performing a variational calculation using a basis set of Cartesian eigenfunctions of the unperturbed Hamiltonian. The necessary matrix elements were computed with the formula given by Nordholm and Rice.²⁷ Basis sets of up to 1275

TABLE I. Eigenenergies of the Hénon–Heiles system for the first 13 polyads of J_1 . The exact quantum state energies (E_{QM}) were obtained with a variational calculation. The semiclassical approximations to the energies (E_{SC}) were obtained with the Fourier method by fitting the energy using Eq. (28) and 183 points in action space to interpolate tunneling corrected actions (Table II). The zero-order actions are J_1 and J_2 . The relative error (error) in the semiclassical results is given.

J_1	J_2	Esc.	Eqm.	Error	J_1	J_2	Esc.	Eqm.	Error
1.0	-0.5	0.991 73	0.998 59	0.006 87	10.0	-0.5	10.030 20	10.035 59	0.000 54
2.0	-0.5	1.984 60	1.990 08	0.002 75	10.0	-0.5	10.030 18	10.035 41	0.000 52
2.0	-0.5	1.984 60	1.990 08	0.002 75	10.0	-1.5	9.795 22	9.794 12	0.000 11
3.0	-0.5	2.981 44	2.985 33	0.001 30	10.0	-1.5	9.795 22	9.794 12	0.000 11
3.0	-0.5	2.981 44	2.985 33	0.001 30	10.0	-2.5	9.627 73	9.629 39	0.000 17
3.0	-1.5	2.953 99	2.956 24	0.000 76	10.0	-2.5	9.627 73	9.629 39	0.000 17
4.0	-0.5	3.982 27	3.985 76	0.000 88	10.0	-3.5	9.539 82	9.552 38	0.001 32
4.0	-0.5	3.979 18	3.982 42	0.000 81	10.0	-3.5	9.517 08	9.466 77	0.005 31
4.0	-1.5	3.923 67	3.925 96	0.000 58	10.0	0.5	9.444 83	9.444 05	0.000 08
4.0	-1.5	3.923 67	3.925 96	0.000 58	10.0	0.5	9.444 83	9.444 05	0.000 08
5.0	-0.5	4.982 72	4.986 25	0.000 71	11.0	-0.5	11.047 27	11.049 67	0.000 22
5.0	-0.5	4.982 72	4.986 25	0.000 71	11.0	-0.5	11.047 27	11.049 67	0.000 22
5.0	-1.5	4.895 94	4.898 64	0.000 55	11.0	-1.5	10.782 67	10.773 98	0.000 81
5.0	-1.5	4.895 94	4.898 64	0.000 55	11.0	-1.5	10.782 67	10.773 98	0.000 81
5.0	0.5	4.872 06	4.870 14	0.000 39	11.0	-2.5	10.588 78	10.590 47	0.000 16
6.0	-0.5	5.987 16	5.991 33	0.000 70	11.0	-2.5	10.581 97	10.572 48	0.000 90
6.0	-0.5	5.987 16	5.991 33	0.000 70	11.0	-3.5	10.455 87	10.463 46	0.000 73
6.0	-1.5	5.875 46	5.881 45	0.001 02	11.0	-3.5	10.455 87	10.463 46	0.000 73
6.0	-1.5	5.864 55	5.867 01	0.000 42	11.0	0.5	10.345 02	10.318 34	0.002 59
6.0	0.5	5.818 38	5.817 02	0.000 23	11.0	0.5	10.345 02	10.318 34	0.002 59
6.0	0.5	5.818 38	5.817 02	0.000 23	11.0	0.5	10.300 65	10.305 14	0.000 44
7.0	-0.5	6.994 26	6.999 39	0.000 73	12.0	-0.5	12.066 88	12.065 04	0.000 15
7.0	-0.5	6.993 98	6.998 93	0.000 71	12.0	-0.5	12.066 88	12.065 04	0.000 15
7.0	-1.5	6.848 06	6.853 43	0.000 78	12.0	-1.5	11.772 52	11.752 30	0.001 72
7.0	-1.5	6.848 06	6.853 43	0.000 78	12.0	-1.5	11.773 12	11.749 52	0.002 01
7.0	-2.5	6.769 47	6.764 87	0.000 68	12.0	-2.5	11.545 88	11.533 51	0.001 07
7.0	-2.5	6.769 47	6.764 87	0.000 68	12.0	-2.5	11.545 88	11.533 51	0.001 07
7.0	0.5	6.741 00	6.737 92	0.000 46	12.0	-3.5	11.386 57	11.383 01	0.000 31
8.0	-0.5	8.003 61	8.009 42	0.000 73	12.0	-3.5	11.386 57	11.383 01	0.000 31
8.0	-0.5	8.003 61	8.009 42	0.000 73	12.0	-4.5	11.305 66	11.325 23	0.001 73
8.0	-1.5	7.827 92	7.832 73	0.000 61	12.0	0.5	11.221 38	11.160 26	0.005 48
8.0	-1.5	7.827 92	7.832 73	0.000 61	12.0	0.5	11.163 33	11.151 64	0.001 05
8.0	-2.5	7.728 15	7.736 88	0.001 13	12.0	0.5	11.163 33	11.151 64	0.001 05
8.0	-2.5	7.708 97	7.697 72	0.001 46	13.0	-0.5	13.089 02	13.081 20	0.000 60
8.0	0.5	7.663 36	7.659 49	0.000 51	13.0	-0.5	13.089 02	13.081 20	0.000 60
8.0	0.5	7.663 36	7.659 49	0.000 51	13.0	-1.5	12.765 15	12.711 66	0.004 21
9.0	-0.5	9.015 64	9.021 72	0.000 67	13.0	-1.5	12.765 15	12.711 66	0.004 21
9.0	-0.5	9.015 64	9.021 72	0.000 67	13.0	-2.5	12.508 74	12.480 20	0.002 29
9.0	-1.5	8.811 21	8.815 19	0.000 45	13.0	-2.5	12.508 74	12.480 20	0.002 29
9.0	-1.5	8.809 37	8.811 33	0.000 22	13.0	-3.5	12.327 98	12.333 78	0.000 47
9.0	-2.5	8.672 45	8.677 93	0.000 63	13.0	-3.5	12.310 12	12.277 19	0.002 68
9.0	-2.5	8.672 45	8.677 93	0.000 63	13.0	-4.5	12.215 37	12.205 70	0.000 79
9.0	-3.5	8.602 05	8.576 35	0.003 00	13.0	-4.5	12.190 54	12.205 70	0.001 24
9.0	0.5	8.592 02	8.576 35	0.001 83	13.0	0.5	12.025 62	11.968 08	0.004 81
9.0	0.5	8.592 02	8.576 35	0.001 83	13.0	0.5	12.025 62	11.968 08	0.004 81
9.0	0.5	8.550 82	8.554 02	0.000 37	13.0	0.5	11.988 66	11.966 08	0.001 89

functions were employed. The lowest 99 eigenvalues (there are 99 quasibound states of the Hénon–Heiles system) show convergence with basis set size to 5×10^{-6} . These results agree to all reported places with the earlier quantum calculations.²⁴ The results are included in Table I.

III. PRIMITIVE SEMICLASSICAL QUANTIZATION

The Fourier method for producing semiclassical energy levels when the classical motion is regular (quasiperiodic) is well-established and will only be reviewed here. The inter-

ested reader is referred to the previous papers which developed this method.^{4,5} The problem reduces to locating classical trajectories whose actions J_i satisfy the EBK quantization condition²

$$J_i = \hbar \left(\nu_i + \frac{\alpha_i}{4} \right), \quad (2)$$

where ν_i is the quantum number and α_i is the Maslov index. The Maslov index can be thought of as a term accounting for

the phase accumulation of the wave function in the classically forbidden region outside a classical turning point.² The Maslov index is determined by the topology of the trajectory, in particular, the number of caustics. The caustic structure can be deduced from approximate Hamiltonians or by a method developed by Littlejohn and Robbins.³² Both methods were employed in this work.

The classical actions J_i of a given trajectory were constructed from the coefficients of a Fourier series decomposition of the coordinates and momenta obtained from the trajectory. Points on the classical trajectory were found by numerically integrating the Hamiltonian equations of motion using the Adams–Pece method.³³ The Fourier series representations of the coordinates and momenta are then computed by discrete Fourier transform³⁴ and interpolated on the line shape derived from a window function.^{35,36} The Fourier representations are given by

$$\mathbf{q}(t) = \sum_{\mathbf{k}} \mathbf{q}_{\mathbf{k}} e^{i\mathbf{k} \cdot \boldsymbol{\theta}} \quad (3)$$

and

$$\mathbf{p}(t) = \sum_{\mathbf{k}} \mathbf{p}_{\mathbf{k}} e^{i\mathbf{k} \cdot \boldsymbol{\theta}}, \quad (4)$$

where $\boldsymbol{\theta}$ is a vector whose components θ_i are the angle variables conjugate to the actions J_i and have the temporal dependence $\theta_i = \omega_i t + \delta_i$; $\mathbf{k}$ is a vector of integers, and the summation is over all $\mathbf{k}$ for which a peak with frequency,

$$\mathbf{k} \cdot \boldsymbol{\omega} = k_1 \omega_1 + k_2 \omega_2 + \cdots + k_n \omega_n, \quad (5)$$

can be found in the fast Fourier transform (FFT). If the fundamental frequencies $\boldsymbol{\omega}$ are such that $\mathbf{k} \cdot \boldsymbol{\omega} = 0$ for some vector of integers $\mathbf{k}$, the system is *resonant*. Resonances are discussed in Sec. IV B. It is conventional, for a discrete Fourier transform, to choose the number of sampled points to be a power of 2, and 2^{16} was found empirically to be the optimum tradeoff between computational speed and accuracy. The trajectory was usually integrated for 10 000 units of time in the reduced units of the system (about 1500 vibrational periods), but in some cases much shorter trajectories were used. This will be elaborated upon in a later section.

The n classical actions J_i can be found by integrating the quantity $\mathbf{p} \cdot d\mathbf{q}$ along each of n topologically unique paths on the surface of the invariant torus. We base our method on Martens and Ezra who showed that when Fourier expansions for $\mathbf{p}$ and $\mathbf{q}$ are used in the above integral, the classical actions are given by^{4,5,28}

$$J_n = i \sum_{\mathbf{k}} k_n \mathbf{p}_{\mathbf{k}}^* \cdot \mathbf{q}_{\mathbf{k}}. \quad (6)$$

The work of Martens and Ezra is clearly based on the work of Percival,³ and Percival and Pomphrey,³⁷ whose method does not require trajectories. Percival iteratively solves for the Fourier expansion of the coordinates based on an initial,

zero-order, harmonic oscillator model. This method implicitly assumes the Hamiltonian is separable into a coordinate independent kinetic energy and a potential energy. One of the disadvantages of Percival's method is that it requires a detailed knowledge of the Hamiltonian to select a zero-order model. In addition, the convergence properties of the iterative procedure are unknown. On the other hand, Percival's method does produce approximations to a torus with prescribed actions and its corresponding energy.

Other previous work is closely related to that of Martens and Ezra.^{7–11} These researchers, as well as Martens and Ezra,^{4,5} employed Fourier components from numerical classical trajectories and showed how to obtain actions for a Hamiltonian like Eq. (1) using Fourier transforms of only the coordinate.^{7,8} Child³⁸ has recently reviewed these methods.

The advantage of Eq. (6) is that it is applicable to Hamiltonians with coordinate dependent kinetic energy expressions such as those which occur in molecular vibration–rotation problems. We have used Eq. (6) because of this generality. In addition, Eq. (6) does not require a zero-order Hamiltonian, or even that the structure of the Hamiltonian be known. This feature would be useful when following trajectories using *ab initio* SCF calculations.

The present Fourier transform method should be distinguished from that of Noid *et al.*³⁹ in that Noid based his analysis on autocorrelation functions. The more recent Fourier transform techniques transform the coordinates directly and thus can extract phase information not present in the autocorrelation function and with less numerical computation.

The most complicated step in computing the sum in Eq. (6) is assigning the peaks in the Fourier spectrum. The method used was essentially that of Pickett and Shirts.⁶ A table was generated of all possible vectors composed of k_1, k_2 with each index running from -20 to 20 . The vectors were then ordered by Euclidean length. For vectors of the same length, ordering was done by absolute value of the sum of the components. The Fourier spectrum was then searched for frequencies $\omega = k_1 \omega_1 + k_2 \omega_2$ corresponding to the different $\mathbf{k}$ vectors. If the difference between the test frequency given by the $\mathbf{k}$ vector and the frequency from the Fourier spectrum was less than 0.1 bins in magnitude, the $\mathbf{k}$ vector was assigned to that peak. (This accuracy is three parts in 10^4 for a low-frequency peak and improves with increasing frequency.) A table was kept to ensure that no Fourier peak was multiply assigned. For quasiperiodic spectra, it is usually not difficult to assign all peaks using this method.

The complete procedure for semiclassical quantization is as follows: First, numerically integrate the Hamilton equations of motion for the system at hand, saving a discrete representation of the coordinates and momenta. Next, compute (by FFT) the Fourier spectrum of each coordinate and momenta and determine which n peaks represent the fundamental frequencies. Third, assign each peak in the Fourier spectrum in terms of a linear combination of the n fundamental frequencies of the classical motion. Fourth, compute the classical actions with Eq. (6). Fifth, iterate the initial conditions to locate classical trajectories which have actions

FIG. 1. Typical convergence of the two classical actions as a function of the number of Fourier coefficients used in their construction. Shown here is the absolute value of the contribution of the first 15 peaks in the Fourier spectrum to each of the two classical actions for a quasiperiodic trajectory at $E=6$. The sum of the contributions may exceed the total action because of cancellation. Note that just three peaks are required to compute actions to better than 1% accuracy.

satisfying the quantization condition (e.g., by Newton search).

The convergence properties of the Fourier method are shown in Fig. 1. In this figure the contribution to the classical actions of the 15 most important peaks in the Fourier spectrum is shown. The classical trajectory was a quasiperiodic one at an energy of $E=6$. The convergence is very rapid. In nearly all cases, the inclusion of only a few peaks is sufficient to determine the classical actions to better than 1%. It should also be noted that the “total action” (the one on which the energy is principally dependent) converges more rapidly than the second action. This rapid convergence of the actions is a manifestation of the fact that just a few peaks are sufficient to determine an invariant torus. Shown in Fig. 2 are several two-dimensional representations of an invariant torus constructed from only a few Fourier coefficients. Note that the visual change in the torus due to all peaks after the fourth is quite small. This result has important implications for semiclassical quantization in the chaotic regime in that only a few major peaks are necessary to define a good representation of the torus.

It is impossible to depict the invariant torus in its full

FIG. 2. Shown here are the coordinate projections of an invariant torus as constructed from the Fourier coefficients of the coordinates of a classical trajectory. The solid, closed curves are projections of curves encircling the invariant torus. Each curve represents one angle variable incrementing through a cycle while the other is held constant. [See Eq. (3)]. The dashed line is the classical trajectory. Note that the contributions to the invariant torus made by all peaks after the fourth, are quite small. (a)=3 peaks, (b)=4 peaks, (c)=5 peaks, (d)=all assignable peaks (about 39).

FIG. 3. This representation of an invariant torus at $E=6$ was obtained by computing points on the surface of the torus in its full four dimensions. The 4D data points were projected into a three-dimensional space. Finally, the 3D data points were projected into a plane using perspective to produce this figure. The shading is a function of the third dimension. Note the torus intersects itself when projected into 3 space. No intersections are allowed in 4 space.

dimensionality since it is a two-dimensional manifold imbedded in a four-dimensional space. Figure 3, however, shows a representation of an invariant torus at $E=6$, where the four-dimensional figure has been projected into three-dimensional space and plotted in a plane using perspective. The shading in the figure is scaled to the third dimension.

IV. COMPLICATIONS

As long as phase space is dense with quasiperiodic trajectories of identical topology, there is little problem in locating trajectories whose actions fulfill the quantization condition. Unfortunately, several complications arise in computing the primitive EBK eigenenergies which diminish the usefulness of this method. First, this primitive method sometimes fails to locate some states found in the quantum calculation because of tunneling. Two (or more) neighboring potential wells can interact by tunneling through the intervening potential barrier. While any one of these wells may not contain sufficient action to bind a quantum state, the splitting of the levels arising from tunneling among these adjacent potential wells may lower the energy of one or more of the states below the intervening barrier. Similarly, some states may be "pushed" over the barrier by splitting caused by this tunneling interaction and thus, while no primitive state can be located over the barrier, one or more states exist there. In order to locate these states, the tunneling interaction

must be accounted for. We note, however, that these barriers may be dynamical in nature due to effects of resonance or symmetry.

The presence of resonance zones in phase space produces a second complication because the interpretation of the fundamental frequencies changes as one moves in phase space through a resonance zone. This change is a result of a change in the topology of phase space, because the actions are representative of a different kind of motion. Careful attention must be given to these resonance zones.^{5,6,40}

The third and most important problem arises from the fact that not all of phase space is filled with quasiperiodic trajectories. The interaction of many resonances⁴¹ gives rise to regions of space, increasing in dominance with increasing energy, containing chaotic trajectories. Since the classical motion is not quasiperiodic in these regions, it is not rigorously possible to represent the trajectory by a Fourier expansion. As a consequence, no proper Fourier coefficients exist nor do rigorous actions. Heretofore, the presence of chaotic regions of phase space has limited the applicability of EBK quantization.

In this section, methods are discussed to deal with each of these three problems. As a result of these efforts, the usefulness of the EBK method has been extended to locate semiclassical eigenstates not only in the quasiperiodic regime, but in a considerable fraction of the chaotic region as well.

A. Tunneling

For many purposes and in some systems, primitive semiclassical eigenvalues are sufficiently accurate that the techniques discussed in the previous section are adequate. In some systems, e.g., those with important resonances, it is necessary to go beyond primitive quantization and include finer details of the dynamics. For these systems one must develop a picture of the phase space structure in order to assign meaning to quantum numbers and/or to take tunneling into account. The Henon–Heiles system illustrates perhaps a worst case in that the 1:1 frequency resonance between the two zero-order harmonic oscillators dominates the dynamics even at low energy. Thus the simple assignment of states with quantum numbers (n_x, n_y) is never appropriate. States are better assigned using circulating or librating quantum numbers as determined by the nature of the quantizing classical orbit in phase space. Much can be learned about the phase space structure of the Hénon–Heiles system by developing a one-dimensional Hamiltonian which approximates the full Hamiltonian. This is done by constructing an approximate isolating integral. Gustavson²² has treated the problem of constructing such an integral numerically. More recent analytical work has been done by Delos and Swimm,^{23,31} and Shirts and Reinhardt.^{12,21} A slightly different symmetry based approach has been taken by Finkler *et al.*^{42,43} A detailed analytical treatment has been given by Jaffé and his results are employed here.^{29,30} The full Hamiltonian can be separated into two parts, a zero-order integrable part, and a perturbation which contains the noninte-

grability. Construction of the approximate Hamiltonian is accomplished with a set of functions which commute with the unperturbed Hamiltonian. These are

$$\Pi_0 = \left(\frac{p_x^2}{2} + \frac{x^2}{2} \right) + \left(\frac{p_y^2}{2} + \frac{y^2}{2} \right), \quad (7)$$

$$\Pi_1 = \left(\frac{p_x^2}{2} + \frac{x^2}{2} \right) - \left(\frac{p_y^2}{2} + \frac{y^2}{2} \right), \quad (8)$$

$$\Pi_2 = p_{xy} - p_y x, \quad (9)$$

and

$$\Pi_3 = p_x p_y + xy. \quad (10)$$

When expressed through sixth order in the perturbation parameter ϵ , the approximate integrable Hamiltonian after three successive Birkhoff–Gustavson normal form transformations is²⁹

$$\begin{aligned} H = & \Pi_0 + \frac{\epsilon^2}{12} (7\Pi_2^2 - 5\Pi_0^2) + \frac{\epsilon^4}{9} \left[\frac{7}{2} \Pi_1 (\Pi_1^2 - 3\Pi_3^2) \right. \\ & - \frac{2}{9} \Pi_0 (\Pi_0^2 + 5\Pi_1^2) \left. \right] + \frac{\epsilon^6}{729} \left[\frac{1}{16} (18\,887\Pi_2^4 \right. \\ & - 30\,246\Pi_2^2\Pi_0^2 + 11\,671\Pi_0^4) \\ & \left. - 134\Pi_0\Pi_1(\Pi_1^2 - 3\Pi_3^2) \right]. \quad (11) \end{aligned}$$

Since the Π_i commute with the zero-order Hamiltonian, they are constants of motion of the zero-order Hamiltonian, i.e., classical actions. It follows that these Π_i variables behave *like* actions for the approximate Hamiltonian. These “action-like variables” are isomorphic to $SU(2)$ generators and are related by $\Pi_0^2 = \Pi_1^2 + \Pi_2^2 + \Pi_3^2$ such that any two of Π_1, Π_2, Π_3 can be represented in terms of Π_0 , the third, and its conjugate angle. This picture has been developed for the transition from normal to local modes by Kellman and co-workers.⁴⁴ As demonstrated below, Π_0 is a rigorous constant of motion and defines a sphere of radius Π_0 , the polyad phase sphere, on which the remainder of the dynamics evolves. There may be several quantized values of a second action on the sphere for each quantized value of Π_0 . There are several possible choices for the two unique action-like variables. Jaffé has chosen Π_0 and Π_2 . He refers to these as the “total action” and the “angular momentum,” respectively. Another possible choice for the two unique action-like variables is Π_0 and Π_3 . While other possible choices exist,²³ the pairs (Π_0, Π_2) and (Π_0, Π_3) are useful because each can be used to study one of the two fundamental types of motion, circulating and pendular (librating) exhibited by the full Hamiltonian.

Consider the unperturbed Hamiltonian

$$H = \left(\frac{p_x^2}{2} + \frac{x^2}{2} \right) + \left(\frac{p_y^2}{2} + \frac{y^2}{2} \right) = H_x + H_y, \quad (12)$$

which can be thought of as two uncoupled simple harmonic oscillators whose motion is orthogonal. There are two fundamental types of periodic motions in this system. If there is much energy in one of the oscillators and none in the other, the system undergoes a pendular type of motion. Pendular motions which fall along a line not coincident with one of the coordinate axes can be brought into such a configuration with a simple coordinate rotation. If the two oscillators contain equal amounts of energy, and the motions are out of phase by $\pi/2$, the system will follow a circulating motion. The motions of the full Hénon–Heiles system can be likewise described qualitatively with the pendular and circulating nomenclature. In the neighborhood of the periodic motions of the pendular type, are pendular-type quasiperiodic motions. Likewise, in the neighborhood of the periodic motions of the circulating type, are circulating-type quasiperiodic motions. These two types of motion are separated in phase space by a separatrix.

1. Circulating motion

There are two periodic orbits of period 1 of the full Hamiltonian which are of circulating character. The two orbits correspond to different senses of circulation. Surrounding these periodic orbits are quasiperiodic orbits of the same topology. For the periodic orbit, there is only one fundamental frequency and one action. For orbits near the periodic orbit, there is a second period corresponding to precession around the periodic orbit, and a second action for this motion. This second action vanishes as the trajectory tends toward the periodic orbit and physically corresponds to the area subtended by the invariant torus in a Poincaré surface of section.⁴⁵ Since Π_3 tends to zero when Π_2 is maximum, the circulating-type motions are best investigated with the Hamiltonian which results when Π_0 and Π_3 are chosen as the unique action-like variables. We make the assignments

$$\Pi_0 = J_1, \quad (13)$$

$$\Pi_3 = J_2, \quad (14)$$

and the remaining action-like variables are given by

$$\Pi_1 = (J_1^2 - J_2^2)^{1/2} \cos \theta, \quad (15)$$

$$\Pi_2 = (J_1^2 - J_2^2)^{1/2} \sin \theta. \quad (16)$$

The resulting approximate Hamiltonian to order ϵ^6 is

$$\begin{aligned}
H \approx J_1 + \frac{\epsilon^2}{12} [-5J_1^2 + 7(J_1^2 - J_2^2) \sin^2 \theta] + \frac{\epsilon^4}{162} [-4J_1^3 - 189J_2^2(J_1^2 - J_2^2)^{1/2} \cos \theta - 20J_1(J_1^2 - J_2^2) \cos^2 \theta \\
+ 63(J_1^2 - J_2^2)^{3/2} \cos^3 \theta] + \frac{\epsilon^6}{11\,664} [11\,671J_1^4 + 6432J_1J_2^2(J_1^2 - J_2^2)^{1/2} \cos \theta \\
- 2144J_1(J_1^2 - J_2^2)^{3/2} \cos^3 \theta - 30\,246J_1^2(J_1^2 - J_2^2) \sin^2 \theta + 18\,887(J_1^2 - J_2^2)^2 \sin^4 \theta].
\end{aligned}
\quad (17)$$

Here θ is the angle conjugate to J_2 . The above approximate Hamiltonian is independent of the angle conjugate to J_1 . Therefore, J_1 is a constant of the motion of the approximate Hamiltonian. J_1 can be chosen to fulfill the EBK quantization condition $J_1 = \hbar(n+1)$, $n=0,1,2,\dots$. With J_1 fixed, all that remains is a one-dimensional Hamiltonian. In this choice of action-like variables, the second action is the area enclosed by the J_2 , θ curve and is negative for the circulating-type trajectories, because the “mass,” as defined by

$$m = \left(\frac{\partial^2 H}{\partial J_2^2} \right)^{-1}, \quad (18)$$

is less than zero. In other words, the motion in the J_2 , θ plane is in the counterclockwise sense. See Fig. 4.

Figure 4 shows a plot of the phase space structure of the approximate Hamiltonian (17) for $J_1=6$. The two fundamental types of motion can be clearly seen. Curves which encircle the point $(J_2=0, \theta=\pi/2)$ or the point $(J_2=0, \theta=-\pi/2)$ correspond to trajectories of the circulating type in the full Hamiltonian. Those encircling the point at $(J_2=0, \theta=\pi/2)$ correspond to circulating in the opposite sense from those which encircle $(J_2=0, \theta=-\pi/2)$. There are three equivalent pendular-type modes of the full Hamiltonian. These are seen in the phase space plot of the approximate Hamiltonian as curves encircling the points: $(J_2 \approx 5, \theta=0)$, $(J_2 \approx -5, \theta=0)$, $(J_2=0, \theta=\pi)$ and correspond to pendular orbits along each of the three symmetry planes of the Hénon–Heiles system.

FIG. 4. Phase space structure of the approximate Hamiltonian resulting from the choice of action-like variables, $J_1=\Pi_0$, $J_2=\Pi_3$, with $J_1=6$. This approximate Hamiltonian is suitable for investigating circulating-type motions of the full Hamiltonian.

In this picture, the line $J_2=0$ corresponds to the equator of the polyad phase sphere where the Π_3 axis is chosen as the axis. The top of Fig. 4 where J_2 is a maximum all maps to the north pole of the sphere; likewise the bottom of Fig. 4 maps to the south pole of the sphere.

The area inside one of the circulating-type closed curves in phase space has units of action and is the classical action associated with J_2 for that trajectory. It follows that primitive semiclassical quantization can be effected by locating trajectories which enclose an area of phase space which satisfies the EBK quantization condition. Energies obtained by this technique are in reasonable agreement with quantum results, with some exceptions. In the quantum picture, however, motion of the circulating-type associated with the region of phase space near the point $(J_2=0, \theta=-\pi/2)$ can interact with motions of the circulating-type associated with the region of phase space about $(J_2=0, \theta=\pi/2)$ by tunneling through the barrier at $\theta=0$. This is equivalent to the problem of the interaction of two adjacent potential wells by tunneling through the intervening potential barrier. This one-dimensional Hamiltonian, however, does not decompose into a kinetic energy term (one quadratic in the action) and a potential energy term (one dependent only on the angle). As a consequence of this complication, one cannot simply substitute the usual quantum operators in place of the classical variables and arrive at a Schrödinger-like wave equation as done by Uzer *et al.*^{46,47} It is, however, possible to apply WKB methods to the problem because all that is required for their application is knowledge of the action as a function of the angle. Miller^{48,49} has given the WKB quantization condition for the problem of a one-dimensional symmetric “double well.” The equation is

$$\tan^2 \alpha = [e^\beta + (1 + e^{2\beta})^{1/2}]^2. \quad (19)$$

Here α is the phase integral across one of the wells and β is the phase integral through the intervening barrier. For a given value of J_1 , the value of J_2 can be found numerically for a fixed value of θ from the approximate Hamiltonian by the method of bisection. Once a sufficient number of points on the curve $J_2(\theta)$ are found, the α and β phase integrals can be computed numerically. This calculation, however, results in either tunneling splittings which are much too small, or states which are split but which should not be. The reason for this is that the tunneling path used is only one of three symmetrically equivalent paths on the surface of the polyad phase sphere. If the circulating states are expressed in the variables Π_0 and Π_2 (rather than Π_0 and Π_3) the circulating states circle the north or south poles of the polyad phase sphere. In zero-order, the semiclassical wave function for

TABLE II. Tunneling corrected actions and WKB eigenenergies for the circulating-type states. The zero-order actions are J_1 and J_2 . The tunneling corrected J_2 action is $J_2(\text{WKB})$. Note that the tunneling corrected actions are *close* to the zero-order actions. WKB eigenenergies for Hamiltonian (17) were determined graphically using Eq. (19)

J_1	J_2	J_2 (WKB)	Energy (WKB)	J_1	J_2	J_2 (WKB)	Energy (WKB)
1.0	-0.5	-0.319 813	0.995 72	9.0	-3.5	-3.500 000	8.627 60*
2.0	-0.5	-0.500 000	1.986 39	10.0	-0.5	-0.499 957	10.063 38
2.0	-0.5	-0.500 000	1.986 39	10.0	-0.5	-0.500 034	10.063 36
3.0	-0.5	-0.500 000	2.982 05	10.0	-1.5	-1.500 000	9.830 64
3.0	-0.5	-0.500 000	2.982 05	10.0	-1.5	-1.500 000	9.830 64
3.0	-1.5	-1.306 250	2.954 70	10.0	-2.5	-2.500 000	9.662 45
4.0	-0.5	-0.484 145	3.983 19	10.0	-2.5	-2.500 000	9.662 45
4.0	-0.5	-0.518 184	3.980 19	10.0	-3.5	-3.331 531	9.569 35
4.0	-1.5	-1.500 000	3.923 85	10.0	-3.5	-3.675 846	9.551 89
4.0	-1.5	-1.500 000	3.923 85	11.0	-0.5	-0.500 000	11.090 27
5.0	-0.5	-0.500 000	4.985 54	11.0	-0.5	-0.500 000	11.090 27
5.0	-0.5	-0.500 000	4.985 54	11.0	-1.5	-1.500 000	10.828 63
5.0	-1.5	-1.500 000	4.898 50	11.0	-1.5	-1.500 000	10.828 63
5.0	-1.5	-1.500 000	4.898 50	11.0	-2.5	-2.480 258	10.635 78
6.0	-0.5	-0.500 000	5.993 12	11.0	-2.5	-2.521 919	10.628 79
6.0	-0.5	-0.500 000	5.993 12	11.0	-3.5	-3.500 000	10.501 17
6.0	-1.5	-1.444 193	5.882 08	11.0	-3.5	-3.500 000	10.501 17
6.0	-1.5	-1.577 260	5.870 72	12.0	-0.5	-0.500 000	12.121 05
7.0	-0.5	-0.499 235	7.005 07	12.0	-0.5	-0.500 000	12.121 05
7.0	-0.5	-0.500 772	7.004 79	12.0	-1.5	-1.500 493	11.829 87
7.0	-1.5	-1.500 000	6.859 76	12.0	-1.5	-1.498 188	11.830 50
7.0	-1.5	-1.500 000	6.859 76	12.0	-2.5	-2.500 000	11.605 36
7.0	-2.5	-2.500 000	6.776 25	12.0	-2.5	-2.500 000	11.605 36
7.0	-2.5	-2.500 000	6.776 25	12.0	-3.5	-3.500 000	11.445 40
8.0	-0.5	-0.500 000	8.020 53	12.0	-3.5	-3.500 000	11.445 40
8.0	-0.5	-0.500 000	8.020 53	12.0	-4.5	-4.328 953	11.378 64
8.0	-1.5	-1.500 000	7.846 37	13.0	-0.5	-0.499 996	13.155 962
8.0	-1.5	-1.500 000	7.846 37	13.0	-0.5	-0.500 005	13.155 959
8.0	-2.5	-2.391 739	7.743 29	13.0	-1.5	-1.500 000	12.834 59
8.0	-2.5	-2.654 881	7.722 53	13.0	-1.5	-1.500 000	12.834 59
9.0	-0.5	-0.500 000	9.039 88	13.0	-2.5	-2.500 000	12.583 21
9.0	-0.5	-0.500 000	9.039 88	13.0	-2.5	-2.500 000	12.583 21
9.0	-1.5	-1.494 731	8.837 69	13.0	-3.5	-3.447 895	12.405 00
9.0	-1.5	-1.505 469	8.835 81	13.0	-3.5	-3.563 263	12.386 08
9.0	-2.5	-2.500 000	8.695 92	13.0	-4.5	-4.500 000	12.291 87
9.0	-2.5	-2.500 000	8.695 92	13.0	-4.5	-4.500 000	12.291 87
9.0	-3.5	-3.500 000	8.627 60*				

these states is proportional to $e^{im\phi}$ where ϕ is the azimuthal angle. The exact wave functions will mix terms which differ in m by multiples of 3. The tunneling path along $J_2=0$ in Fig. 4, corresponds to $\phi=0$ with the polar angle changing. The other tunneling paths correspond to $\phi=2\pi/3$ and $\phi=-2\pi/3$ in this picture. If m is an integer multiple of 3, then the phase of the wave function will be the same at each value of ϕ where tunneling can occur. Although no rigorous WKB theory of tunneling in two or more dimensions is available, we have found that reasonable results can be obtained by the following *ad hoc* procedure. When the phase of the wave function is the same at each tunneling path, we replace every occurrence of the tunneling factor $e^{-\beta}$ by $3e^{-\beta}$ in Eq. (19). When m is not a multiple of 3, the phases of the wave function add to zero, so the tunneling integrals will be assumed to cancel in these cases and the states will not be split. We emphasize that while this procedure is somewhat *ad hoc*, it does justify, on plausible physical grounds, the neglect of

splitting. We have no rigorous justification for using Eq. (19) with e^β replaced with $\frac{1}{3}e^\beta$, however, this formula is probably accurate at least to first order in e^β .

The energy is varied until the quantization condition (19) with e^β replaced with $\frac{1}{3}e^\beta$ is satisfied by the resulting numerically determined values of α and β . A graphical technique was employed to find quantizing energies. The resulting energies are better approximations to the energy levels of the full Hénon–Heiles Hamiltonian than those found using primitive actions. These uniform WKB results which correspond to circulating-type classical motion are shown in Table II.

The results of the WKB treatment for the double-well approximate Hamiltonian can be used to improve the calculation of the energies for the full Hamiltonian. Instead of seeking actions that satisfy integer or half-integer rules, we can use the phase integral across the well in the approximate 1D Hamiltonian as a “tunneling corrected” action to be located in the full Hamiltonian. These tunneling corrected ac-

tions are *close* to the primitive quantizing actions as shown in Table II. The FFT technique and Eq. (6) are used to calculate the actions of a classical trajectory, and the energy of such a trajectory is a tunneling corrected semiclassical approximation to the quantum eigenstate. Energies for circulating states found this way are shown in Table II. These energies generally are in better agreement with the exact results than are the energies of trajectories with the same actions in the approximate Hamiltonian.

2. Pendular motion

Pendular-type motions are best studied with the approximate Hamiltonian which results from Jaffé's choice of action-like variables:

$$\Pi_0 = J_1, \quad (20)$$

$$\Pi_1 = (J_1^2 - J_2^2)^{1/2} \cos(2\theta), \quad (21)$$

$$\Pi_2 = J_2, \quad (22)$$

$$\Pi_3 = (J_1^2 - J_2^2)^{1/2} \sin(2\theta). \quad (23)$$

The resulting approximate Hamiltonian to order ϵ^6 is²⁹

$$\begin{aligned} H \sim & J_1 - \frac{5\epsilon^2}{12} J_1^2 + \frac{7\epsilon^2}{12} J_2^2 - \frac{67\epsilon^4}{432} J_1^3 - \frac{7\epsilon^4}{144} J_1 J_2^2 \\ & + \frac{7\epsilon^4}{18} (J_1^2 - J_2^2)^{3/2} \cos(6\theta) - \frac{42 \ 229 \ \epsilon^6}{155 \ 520} J_1^4 \\ & - \frac{\epsilon^6}{155 \ 520} J_2^2 (458 \ 682 J_1^2 - 575 \ 855 J_2^2) \\ & - \frac{35 \ \epsilon^6}{648} J_1 J_2^2 (J_1^2 - J_2^2)^{1/2} \cos(2\theta) - \frac{35 \ \epsilon^6}{1458} J_2^2 (J_1^2 - J_2^2) \\ & \times \cos(4\theta) - \frac{2093 \ \epsilon^6}{2160} J_1 (J_1^2 - J_2^2)^{3/2} \cos(6\theta). \end{aligned} \quad (24)$$

As before, θ is the angle conjugate to J_2 . The above approximate Hamiltonian is independent of the angle conjugate to J_1 . This means that J_1 is again a constant of the motion of the approximate Hamiltonian. J_1 can be chosen to fulfill the EBK quantization condition $J_1 = \hbar(n+1)$, $n=0,1,2,\dots$. With J_1 fixed, again all that remains is a one-dimensional Hamiltonian. In this case, however, the J_2 action is positive for the pendular-type trajectories.

Figure 5 shows a plot of the phase space structure of Jaffé's approximate Hamiltonian. The two fundamental types of motion can be identified. Motions which correspond to pendular-type trajectories along the three symmetry axes in the full Hamiltonian are manifest as curves which encircle one of the three points: $(J_2=0, \theta=\pi/6)$, $(J_2=0, \theta=3\pi/6)$, $(J_2=0, \theta=5\pi/6)$. Near these three periodic orbits the second action tends to zero, and Π_2 is the action-like variable which has this property. This representation is suitable for studying the pendular-type motions. Motions related to trajectories of the circulating type in the full Hamiltonian result in curves for which the value of θ increases (or decreases) without bound. For this choice of variables, the circulating orbits

FIG. 5. Phase space structure of the approximate Hamiltonian resulting from Jaffé's choice of action-like variables, $J_1 = \Pi_0$, $J_2 = \Pi_2$, with $J_1 = 6$. This approximate Hamiltonian is well-suited for investigating pendular-type motions of the full Hamiltonian.

encircle the north or south poles of the polyad phase sphere and the librating orbits evolve in one of three basins distributed symmetrically around the equator.

Primitive semiclassical eigenvalues could be found by requiring the area in phase space enclosed by the classical trajectory of the approximate Hamiltonian to satisfy the EBK quantization condition. A motion in one of these regions of phase space, however, can be interpreted as a librating-type motion below the barrier in a threefold hindered rotor. In the quantum picture, the motions in each of the three equivalent areas can interact through tunneling. As in the case where the circulating motion was treated as a double-well problem, we can apply the WKB method to this problem to obtain tunneling corrected actions. The quantization condition for a threefold hindered rotor as given previously^{28,50} is

$$(1 + e^{2\alpha})^{1/2} \cos \beta = \cos \left(\frac{2n\pi}{3} \right). \quad (25)$$

In this expression, β is the phase integral across the well, and α is the barrier penetration integral. The number $2n$ is equal to l , the angular momentum quantum number in the zero-order limit. The integer l must be even in the event that J_1 is odd and must be odd when J_1 is even, since $J_1 = n+1$. [See Ref. 24, Eq. (3.4).]

The function $J_2(\theta)$ was found by bisection from the approximate Hamiltonian at a fixed value of J_1 . Values of α and β for which the quantization condition is satisfied were found by graphical techniques. As in the circulating case, a tunneling corrected semiclassical approximation to the quantum eigenvalue can be found by taking the energy of a classical trajectory of the full Hénon–Heiles Hamiltonian for which the action determined by the FFT technique (6) is equal to the phase integral β of a quantum state of the approximate Hamiltonian. The tunneling corrected actions and WKB eigenenergies for the pendular states are given in Table III.

TABLE III. Tunneling corrected actions and WKB eigenenergies for the pendular-type states. The zero-order actions are J_1 and J_2 . The tunneling corrected J_2 action is J_2 (WKB). Note that the tunneling corrected actions are close to the zero-order actions. WKB eigenenergies for Hamiltonian (24) were determined graphically using Eq. (25).

J_1	J_2	J_2 (WKB)	Energy (WKB)
5.00	0.50	0.256 044	4.872 15
6.00	0.50	0.359 714	5.817 10
6.00	0.50	0.359 714	5.817 10
7.00	0.50	0.298 310	6.743 17
8.00	0.50	0.401 863	7.666 74
8.00	0.50	0.401 863	7.666 74
9.00	0.50	0.612 925	8.587 42
9.00	0.50	0.612 925	8.587 42
9.00	0.50	0.346 631	8.565 31
10.00	0.50	0.426 986	9.463 60
10.00	0.50	0.426 986	9.463 60
11.00	0.50	0.582 934	10.359 30
11.00	0.50	0.582 934	10.359 30
11.00	0.50	0.391 786	10.335 60
12.00	0.50	0.670 665	11.235 79
12.00	0.50	0.451 101	11.206 00
12.00	0.50	0.451 101	11.206 00
13.00	0.50	0.549 414	12.069 79
13.00	0.50	0.549 414	12.069 79
13.00	0.50	0.430 220	12.051 13

B. Resonances

As mentioned briefly in Sec. I, motion is said to be resonant if the two fundamental frequencies ω_1 and ω_2 are such that $k_1\omega_1 + k_2\omega_2 = 0$, where k_1 and k_2 are integers. The motion of a resonant trajectory undergoes $|k_2|$ cycles of the first fundamental motion in the same time it takes to complete $|k_1|$ of the second fundamental motion. The region of phase space which is sampled by the resonant trajectory is very much different from that sampled by a nonresonant trajectory whose initial conditions differ by only a small amount. This difference is illustrated by a Poincaré surface of section constructed by plotting y and p_y wherever $x=0$ and $p_x \geq 0$. Figure 6 shows a composite surface of section from three trajectories in which one of the contributing trajectories is

FIG. 6. Composite surface of section at $E=8$ ($E=0.6 D$). Note the island chain associated with a fivefold resonance.

resonant and exhibits a fivefold island chain. Inside a resonance zone, both frequencies which are fundamental outside the resonance can be assigned as multiples of the lowest frequency or a subharmonic of both, forming one new fundamental. A low-frequency precession around the resonance island becomes the new second fundamental.⁵ With this new definition of the fundamental frequencies comes new actions. Actions, then, do not vary continuously as one continuously varies the initial conditions through a resonance zone.

The discontinuity in the actions as the initial conditions are varied causes trouble when searching initial condition space for a trajectory which has specific actions. Figure 6 illustrates this problem. One of the trajectories is resonant and produces the readily identifiable fivefold island chain. The two other trajectories give a surface of section just inside and just outside the island chain, respectively. The curve just inside the island chain encloses an area of action $A_{\text{inside}}=0.56$, and the curve just outside the island chain encloses an area of action $A_{\text{outside}}=0.74$. If one were looking for a trajectory with the action 0.70, it could not be located as the variation in action jumps discontinuously from 0.56 to 0.74 as the island chain, whose area is approximately 0.18, is crossed. An analytic solution to this dilemma, which involves transforming to new resonance variables, has been given by Pickett and Shirts.⁶ This method, however, requires additional information about the strength and form of the resonance zone. In the present paper, it will be shown that these resonances can be "smoothed" over in the spirit of the discussion of Reinhardt and Jaffé.¹³ This smoothing procedure is based on two observations. (1) If the classical resonance zone occupies a region of phase space which is small in relation to $\hbar$, the resonance structure should not affect the quantum wave functions.¹³ (2) Only a few of the most prominent peaks in the Fourier spectrum of the classical trajectory need to be assigned in order to compute classical actions with reasonable accuracy. We assume that a quantizing invariant torus can be interpolated between two other tori of identical topology even if the phase space between the outer two tori contains a resonance structure and no such torus exists.

Actions which are good outside the resonance zone can be related to those inside the resonance zone. A related correspondence must exist between the old and new frequencies. If we assume that there exists a matrix C relating the new fundamental frequencies ω' to the old fundamental frequencies ω , such that $\omega' = C\omega$, then the matrix $D = (C^{-1})^t$ relates the k vectors which assign peaks in terms of the fundamental frequencies: $k' = Dk$. Consider a 5:1 resonance where the old fundamental frequencies are $\omega_1=1600$ and $\omega_2=320$. $\omega=(1600,320)$ and $\omega'=(320,\delta)$, where δ is the new, low-frequency, second fundamental which cannot be defined in terms of the old frequencies. Table IV gives a set of frequencies for this hypothetical system and the old and new k vectors. A matrix D which converts all k to k' is $(5,1,0,0)$. Since this matrix is singular and cannot be inverted, we use $(5,1,x,x)$ to get $C=(1/4,-1/4,-1/4x,5/4x)$. This C matrix projects that the new ω' vector is $[320, (-400/x + 400/x)]$ which becomes $(320,0)$ as x is allowed to go to zero. The new second frequency δ is of course small

TABLE IV. Example of frequencies ω which can be expressed as a linear combination of the "old" fundamental frequencies ($\omega_1=1600$, $\omega_2=320$), or the "new" fundamental frequencies associated with the resonance zone ($\omega'_1=320$, $\omega'_2=\text{unk.}$). Note that for each frequency, $\omega = k_1\omega_1 + k_2\omega_2 = k'_1\omega'_1 + k'_2\omega'_2$. The new second fundamental frequency ω'_2 is a low frequency associated with the motion about the resonance zone. Its value is not required for assigning peaks which appear both inside and outside the resonance zone.

ω	k_1	k_2	k'_1	k'_2
320	0	1	1	0
1600	1	0	5	0
1280	1	-1	4	0
1920	1	1	6	0
3200	2	0	10	0
2880	2	-1	9	0

and cannot be defined in terms of the old frequencies. The relationship of the new actions ($\mathbf{I}'$) to the old ($\mathbf{I}$) is⁶

$$\mathbf{I}' = (\mathbf{C}')^{-1} \mathbf{I}. \quad (26)$$

The corresponding old actions are then given by

$$\mathbf{I} = (\mathbf{C}') \mathbf{I}'. \quad (27)$$

This method of transformation is very useful in treating resonances. Ideally one should find the actions of a resonant trajectory based on the new resonant fundamental frequencies and then transform back to the nonresonant form using Eq. (27). Experience, however, has shown that this procedure is not necessary.

If we ignore the resonance zone and assign the fundamental frequencies as is appropriate just outside the resonance zone, the computed actions will be similar to those just outside the resonance zone. The value of J_1 is not seriously affected by the presence of the resonance. J_2 , however, is discontinuous as expected. This is exhibited in Fig. 7. Inside the resonance zone, a new low-frequency fundamental appears and as a consequence there are some new peaks which cannot be assigned in terms of the two old fundamental frequencies. These new peaks appear as side bands on the dominant peaks in the Fourier spectrum. These side bands are unassignable in terms of the nonresonant frequencies. Because these side bands make a relatively minor contribution to the actions, the actions computed with the old frequencies are similar to those outside the resonance zone, the minor discontinuity being due to the contribution of the unassigned side bands to the actions. In light of the above discussion, it is clear that the error introduced by using the old assignment of the fundamental frequencies within a resonance zone is small. The error is minimized by the fact that the energy of states in the Hénon–Heiles Hamiltonian is mainly dependent on J_1 . We minimize the effect of the minor discontinuities in J_2 by abandoning the attempt to converge to the actions corresponding to individual states. Instead, the actions are determined for a large number of trajectories. The energy surface as a function of J_1 and J_2 is fit to a low order polynomial in each of the two regions (circulating and librating). This fitting smooths out the effects of resonances which would be magnified if individual states were sought. This procedure is explained in detail in Sec. VI below.

FIG. 7. This figure shows J_2 as a function of the initial conditions of the trajectory from which it was computed. The initial conditions were slowly varied so that they passed across one of the hyperbolic (a), the elliptic (b), fixed points along the fivefold resonance island chain shown in Fig. 6. Within the resonance zone in (b), the action was computed by assigning the peaks in the Fourier spectrum ignoring the resonance's presence.

Resonance zones grow in size with increasing energy. When two neighboring resonance zones start to overlap, chaos appears.^{41,51}

V. CHAOS

While the Fourier transform method has been shown to produce semiclassical energy levels which are excellent approximations to the exact quantum eigenstates, the method requires that the classical trajectory be quasiperiodic so that the Fourier representation has assignable peaks. Such quasiperiodic classical trajectories fall on the surface of an invariant torus in phase space.⁵² At low energies, the phase space of the Hénon–Heiles Hamiltonian is filled with such tori. As the energy increases some trajectories are no longer quasiperiodic, but chaotic in nature. Chaos increases in importance with increasing energy. A composite surface of section is shown in Fig. 8. It is clear that at this energy ($E=0.75$ D) some of phase space is filled with tori and some is chaotic. The chaotic points which do not fall on simple closed curves in Fig. 8 come from a single trajectory.

FIG. 8. Composite surface of section at an energy of $E=10.0$ ($E=0.75$ D). Regions of quasiperiodic and chaotic structure can be seen.

A careful observation of a surface of section in the chaotic regime reveals that while the corresponding classical trajectory may not lie on the surface of an invariant torus, there is considerable structure remaining over intermediate times (10–100 vibrational periods). Shirts and Reinhardt¹² referred to this structure as a vague torus, the connotation being that the trajectory evolves *near* a torus-like manifold in phase space. Chaotic trajectories appear more-or-less regular for a short time and then make a transition to a different vague torus. Kosloff *et al.*⁵³ and Jaffé and Reinhardt³⁰ have suggested that the source of the irregularity in these chaotic trajectories may be highly localized in configuration space, although they disagree over the exact location of these origins of stochasticity. Gomez *et al.*⁵⁴ have also noted that chaotic trajectories occasionally sample regions of phase space near resonance zones and during these encounters have nearly regular behavior. They termed these encounters “inserts of regularity.” The term resonant trapping is also in usage. In earlier work Contopolous⁵⁵ also discussed the behavior of chaotic trajectories near periodic orbits. Davis⁵⁶ also investigated the almost quasiperiodic motion of trajectories due to remnants of tori (cantori) which serve as bottlenecks to phase space mixing. We believe that the short-term regularity of chaotic motion commonly seen in coupled oscillator motion will allow a description by approximate tori as described below, regardless of the nature and source of that regularity. Regularity over the short term is best seen in the surface of section.¹² The open circles in Fig. 9 show a surface of section constructed from a chaotic trajectory $\frac{1}{20}$ as long as those used in Fig. 8. Clearly, over the short term, the chaotic trajectory has approximately quasiperiodic behavior. The solid circles in Fig. 9 show intersections of an approximating torus, constructed from the coefficients of a Fourier representation of the short-time trajectory as described in the next paragraph. The agreement is excellent. Short-time trajectory analysis has been used previously to compute semiclassical transition frequencies,⁵⁷ but not for quantization. Note also that our approximating torus is more satisfactory and smoother than those developed by Ramachandran and Kay using adiabatic switching.⁵⁸

FIG. 9. Shown here is a surface of section from a short-time trajectory at $E=10$ (open circles) and its corresponding approximating torus (solid dots).

Just as the surface of section for a short-time chaotic trajectory is much like that of a quasiperiodic trajectory, the Fourier spectrum of a short-time chaotic trajectory shows prominent peaks as does that of a quasiperiodic trajectory. This characteristic is exhibited in Fig. 10. Figure 10(a) shows the Fourier spectrum of the chaotic trajectory shown in Fig. 8. Figure 10(b) shows the Fourier spectrum of the first $\frac{1}{20}$ of the same trajectory. It is clear that while the FFT of the full trajectory is unassignable, that of the short-time trajectory has definite peaks which are sufficiently resolved to assign and be used to compute the classical actions using Eq. (6). As shown in Sec. III, only the most prominent peaks in the Fourier spectrum need to be assigned in order to compute a reasonable approximation to the invariant torus and its associated actions. This is very helpful because the low resolution of the Fourier spectrum of a short-time trajectory limits the number of peaks that can be resolved. Fortunately, in many cases, the residual quasiperiodic structure of a chaotic trajectory remains for enough time that an assignable Fourier spectrum can be computed. Therefore, the Fourier transform of a short-time chaotic trajectory can have its major peaks assigned and actions computed. The peaks are then easily used to reconstruct the approximating torus. This technique was used in Fig. 9.

Miller⁵⁹ and de Leon⁶⁰ have developed methods of obtaining semiclassical eigenvalues from arbitrary, single classical trajectories. In light of these developments it was initially hoped that semiclassical eigenvalues could be extrapolated from the closest remaining invariant tori. Unfortunately, the success of such a method relies on the actions of the “arbitrary” classical trajectory being sufficiently close to the quantizing actions. At some energies, a large fraction of phase space is chaotic and no such quasiperiodic trajectories can be located.

We have employed a two pronged attack to apply the Fourier approach to semiclassical quantization in the stochastic regime. First, we took advantage of the remaining quasiperiodic trajectories at energies where chaotic trajectories are present by interpolating across chaotic regions (see Fig. 8). Second, in the chaotic regime, we employed short-

FIG. 10. (a) gives the Fourier spectrum of the chaotic trajectory used in the construction of the composite surface of section shown in Fig. 8. (b) shows the Fourier spectrum of the first $\frac{1}{20}$ of that trajectory. (See the corresponding surface of section in Fig. 9.) Note that the short-time trajectory has a Fourier representation with assignable peaks. The frequency is given in multiples of the fundamental frequency of the uncoupled ($\epsilon=0$) system.

time dynamics to capitalize on the residual quasiperiodic nature of chaotic trajectories.

VI. RESULTS

The techniques described above were used to find semiclassical approximations to the vibrational energy levels of the Hénon–Heiles Hamiltonian. At low energies where phase space is quasiperiodic, a quasi-Newton method⁶ was used to converge upon initial conditions which produce a classical trajectory with primitive or tunneling corrected quantizing actions. First, a trajectory was integrated from initial conditions thought to produce a trajectory with actions reasonably close to the desired values. A composite surface of section at the correct zero-order energy is very helpful in choosing these initial conditions. Next, partial derivatives of the actions with respect to the initial conditions were computed numerically by incrementing each initial condition in turn by a small step (10^{-4} was used here). These partial derivatives were then used to compute new initial conditions, and the process was iterated until the actions agreed with the desired

TABLE V. Optimized c_i coefficients for the interpolating function given by Eq. (26). The circulating (circ.)- and pendular (pend.)-type states were treated separately.

	Circ.	Pend.
c_1	0.296×10^{-2}	-0.394×10^{-1}
c_2	0.351×10^{-1}	-0.152
c_3	0.100×10^1	0.102×10^1
c_4	0.535×10^{-1}	-0.465×10^{-1}
c_5	0.142×10^{-2}	-0.832×10^{-2}
c_6	-0.297×10^{-1}	0.391×10^{-1}

values to within some tolerance (10^{-5}). When a resonance zone was encountered, this search procedure usually failed to converge. Equally problematic were chaotic regions. In spite of our success in computing classical actions for chaotic trajectories with the Fourier method using short-time trajectories, not all chaotic trajectories were successfully treated with the short-time approach. In other words, we could compute actions for *some* trajectories in the chaotic regime, but we could not find trajectories which gave any prescribed action. In order to achieve semiclassical quantization in the chaotic regime, we therefore utilized those trajectories for which we could compute actions to interpolate the energy of a trajectory with quantizing actions.

In order to interpolate, we assumed that the energy surface as a function of the two actions can be approximated by the following quadratic function:

$$E = c_1 + c_2 J_2 + c_3 J_1 + c_4 J_2^2 + c_5 J_1^2 + c_6 J_1 J_2 \quad (28)$$

Actions were then computed for a large number of trajectories. In most cases the actions could be computed easily with the Fourier method. Chaotic trajectories had to be treated with the short-time approach however. Some trial and error was required to locate trajectories in the chaotic regime for which actions could be computed. After a large number (183) of points on the energy surface $E(J_1, J_2)$ were computed, the c_i coefficients in the interpolating function were found by fitting the interpolating function to the computed points by the method of least absolute error. Those points on the energy surface arising from trajectories whose motion was of the circulating type were used to compute one set of c_i coefficients, and points on the energy surface arising from trajectories whose motion was of the pendular type were used to compute a second set. The resulting values of the c_i coefficients are given in Table V. Note that c_3 is approximately 1 for both sets. This is expected from Eqs. (17) and (24). The coefficient c_0 might be expected to be 0 based on the approximate Hamiltonians. In fact, setting $c_0=0$ for circulating motions gives better agreement for low-energy states. The values in Table V represent the best *global* fit to the functional form chosen. Sumpter and Noid⁶¹ and Ramaswamy⁶² have applied similar interpolation methods to compute semiclassical eigenvalues for systems of two or three nonresonant, weakly coupled oscillators.

With the c_i coefficients calculated, semiclassical eigenvalues for the system were obtained by inserting the appropriate (quantizing) actions into the interpolating function. In this case, the tunneling corrected quantizing actions pro-

FIG. 11. Histogram of the absolute values of the relative errors in computing the energy levels of the Hénon–Heiles system with four different semiclassical methods. WKB represents results of this paper using tunneling-corrected, graphically determined actions in the approximate Hamiltonian. SS represents results of this paper using tunneling-corrected, FFT determined actions of the full Hamiltonian. AS represents results from Ref. 19. US represents results from Ref. 30. The average error for each method is SS 0.122%, US 0.098%, WKB 0.331%, and AS 0.195%.

duced with the WKB treatment of the approximate Hamiltonians were used. Table I summarizes the results. It can be seen that the semiclassical energies are very good approximations to the exact quantum energies with the average relative error being less than 0.13%. Figure 11 gives a histogram of the absolute values of the relative error for this and previous methods. It is clear that employing the Fourier method to find semiclassical energy levels of the full Hamiltonian gives notably improved results over the WKB eigenenergies of the approximate Hamiltonians. Note also that this method is comparable in accuracy to the adiabatic switching method of Skodje,¹⁹ and the uniform semiclassical method of Jaffé.²⁹

It should be noted that the same method was tried without using the $E(J_1, J_2)$ points in the chaotic regime obtained with the short-time trajectory technique. While the semiclassical energies which resulted were of good accuracy in the quasiperiodic regime, upon extrapolation into the chaotic, the

results were quite poor with relative errors as high as several percent. It follows that in order to obtain good results, the results must be interpolated. Extrapolating does not produce accurate semiclassical approximations to the quantum energy levels. This fact necessitates finding sufficiently many points on the $E(J_1, J_2)$ surface in the chaotic regime.

In addition to enabling one to compute semiclassical approximations to the energy levels in the chaotic regime, a second feature of this global fitting technique is that small resonances can be ignored. As long as the (J_1, J_2) points have been calculated taking careful account of resonance structures, (as described in Sec. IV B), the interpolating function can be used for all quantizing actions, even those which correspond to “tori” which would lie within a resonance zone.

Unlike the adiabatic switching method, our global fitting method gives information about the splitting of energy levels which are degenerate in the zero-order limit. Such splittings are also given by the uniform semiclassical method of Jaffé.²⁹ Splittings calculated by the two methods are compared to the exact quantum values, and those computed with the WKB method applied to the approximate Hamiltonian in Table VI. It can be seen that the splittings given by our method are systematically too small. This is not a failure of the global fitting step, but of the WKB eigenvalue expression for the energy levels of a double-well potential which was used to find the tunneling corrected J_2 actions. It may be possible to improve the accuracy of the splittings by using a quantum corrected WKB eigenvalue expression for the double-well problem to find tunneling corrected actions.^{49,63} The difficulty of such an approach is exacerbated by the fact that the approximate Hamiltonians do not separate into a kinetic energy term and a potential energy one. Nevertheless, the possibility of employing a quantum correction is under investigation.

One inaccuracy appearing in the approximate Hamiltonians is not yet understood. The threefold symmetry of the pendulum states is broken by the terms containing $\cos(2\theta)$ and $\cos(4\theta)$ in the ϵ^6 part of Eq. (24). One possibility is that the flexibility of the Birkhoff–Gustavson normal form could

TABLE VI. Shown here are the splittings of states which are degenerate in the zero-order limit. The zero-order classical actions are given by J_1 and J_2 . Our results are given under SS. The exact quantum results are given under QM. US are the uniform semiclassical results of Jaffé (Ref. 29). WKB are the results of our WKB calculations [see Eqs. (19) and (25)]. Martens and Ezra (Ref. 28) have also used a phase integral method and their result is given under ME. All of the states are of the circulating type except the one indicated with the †, which is near the separatrix between the circulating and pendular.

J_1	J_2	SS	QM	US	WKB	ME
4	−0.5	0.003 09	0.003 34	0.005 50	0.003 00	...
6	−1.5	0.010 91	0.014 43	0.017 00	0.011 36	0.198
7	−0.5	0.000 28	0.000 46	0.000 05	0.000 28	...
8	−2.5	0.019 19	0.039 16	0.037 60	0.020 76	...
9	−1.5	0.001 84	0.003 86	0.004 40	0.001 88	...
10	−0.5	0.000 02	0.000 18	0.000 10	0.000 02	...
10	−3.5	0.022 74	0.085 61	0.063 60	0.017 46	...
11	−2.5	0.006 80	0.017 99	0.019 00	0.006 99	...
12	−1.5	0.000 60	0.002 78	0.000 20	0.000 63	...
12†	−4.5	0.084 28	0.164 95	0.139 00	0.142 85	...
13	−3.5	0.017 86	0.056 68	0.058 00	0.018 92	...

be used to preserve the symmetry of the Hamiltonian.^{12,43}

It is important to note that calculating the actions of a classical system using the Fourier method (6) does not tell you what the actions mean. For example, when the fundamental frequencies are chosen to be the harmonic frequency and the frequency for precession around the central circulating orbit, the actions calculated using Eq. (6) are actions which are, to zero-order, J_1 and $1/2\pi\int J_2 d\theta$ [where J_1 and J_2 are defined by Eqs. (13)–(16)]. This fact was not obvious to us when the calculations reported here were commenced. Likewise, choosing the fundamental frequencies to be the harmonic frequency and the frequency for precession around the central pendulum orbit results in actions which are J_1 and $1/2\pi\int J_2 d\theta$ [where J_1 and J_2 are defined by Eqs. (20)–(23)]. In either case, one has to know enough about the structure of phase space to apply these quantization rules and seek tunneling corrected actions.

VII. CONCLUSIONS

We have demonstrated the extension of the Fourier method of EBK quantization to chaotic motion. Results for the Hénon–Heiles system are comparable to those using Birkhoff–Gustavson normal form quantization or adiabatic switching methods. With this development, the many advantages of the Fourier method (see, e.g., Ref. 6) can be utilized in the energy regime where the classical motion is chaotic. This is particularly important because most molecular systems are chaotic at high levels of excitation.

Our method is the numerical analog of the uniform semiclassical quantization of Jaffé.²⁹ Jaffé quantized an integrable approximate Hamiltonian, effectively truncating any nonintegrability including chaos. Our method uses the most dominant terms of a Fourier expansion which describes short-time motion to give a numerically truncated approximate torus. An approximate torus provides approximate classical actions for quantization as well as phase space information about the nature of the motion (see Fig. 9).

The application of the techniques discussed here to systems of physical interest is, in principle, straightforward. Any vibrational or vibrational–rotational system can be studied by trajectory methods and analyzed using discrete Fourier transforms. As the number of degrees of freedom increases, the number of fundamental frequencies increases linearly, but the number of possible overtones and combinations increases much more rapidly. It will be important to test whether sufficient accuracy can be achieved to allow useful information to be extracted in systems of molecular interest.

The Heisenberg correspondence principle connects matrix elements of spectroscopic importance to particular Fourier components of the time development of classical functions like the dipole moment.^{39,64–67} The combination of this principle and the methods developed here to assign peaks and actions, may have considerable potential for understanding the spectra of small molecules using classical methods. We are investigating the application of this idea to realistic molecular spectra.

The most common method used to semiclassically quantize chaotic systems is Gutzwiller's periodic orbit method.¹⁵ In this method, the density of states is found using a semi-

classical approximation to the Green's function. The quantum energies are delta functions in the density of states. Berry and Tabor⁶⁸ showed how the periodic orbit method could be used in quasiperiodic systems to obtain results equivalent to those of the EBK technique. The Gutzwiller technique is not limited to quasiperiodic systems but, unfortunately, requires an exhaustive search for all of the periodic classical orbits which have a period less than Planck's constant divided by the required energy accuracy. The period of each orbit must be parametrized as a function of energy as well as the action integral along the trajectory and the stability parameters describing linearized motion in the neighborhood of the orbit. As yet, no one has accomplished this feat for a system requiring numerical trajectories. Success has been limited to model problems which can be simplified analytically (by scaling or coding schemes, for example) or questions requiring only a small number of low period orbits.⁶⁹ In order to achieve, using periodic orbit techniques, the same energy resolution as the typical accuracy we have obtained in the Henon–Heiles system, one would need to analyze all of the periodic orbits with periods less than about 25 vibrations, and no systematic method exists for finding such orbits. (See Ref. 69 for examples where a relatively small number of periodic orbits were used.) In any case, the prevailing opinion is that EBK quantization is more accurate as well as more efficient when it is applicable. In addition, the periodic orbit technique yields only energies, not tori, the semiclassical analog of wave functions. The method we have presented attempts to expand the scope of applicability of EBK techniques. Future work will need to clarify just how far the method can be extended into the chaotic part of phase space.

¹G. S. Ezra, C. C. Martens, and L. E. Fried, *J. Phys. Chem.* **91**, 3721 (1987).

²I. C. Percival, *Adv. Chem. Phys.* **36**, 1 (1977).

³I. C. Percival, *J. Phys. A* **7**, 794 (1974).

⁴C. C. Martens and G. S. Ezra, *J. Chem. Phys.* **83**, 2990 (1985).

⁵C. C. Martens and G. S. Ezra, *J. Chem. Phys.* **86**, 279 (1987).

⁶T. J. Pickett and R. B. Shirts, *J. Chem. Phys.* **94**, 6036 (1991).

⁷C. W. Eaker and G. C. Schatz, *J. Chem. Phys.* **81**, 2394 (1984).

⁸C. W. Eaker, G. C. Schatz, N. De Leon, and E. J. Heller, *J. Chem. Phys.* **81**, 5913 (1984).

⁹G. C. Schatz, *Comput. Phys. Commun.* **51**, 135 (1988).

¹⁰J. Binney and D. Spergel, *Astrophys. J.* **252**, 308 (1982).

¹¹J. Binney and D. Spergel, *Mon. Not. R. Astron. Soc.* **200**, 159 (1984).

¹²R. B. Shirts and W. P. Reinhardt, *J. Chem. Phys.* **77**, 5204 (1982).

¹³W. P. Reinhardt and C. Jaffé, *Quantum Mechanics in Mathematics, Chemistry, and Physics*, edited by K. E. Gustafson and W. P. Reinhardt (Plenum, New York, 1981), p. 167.

¹⁴W. P. Reinhardt, *J. Phys. Chem.* **86**, 2158 (1982).

¹⁵M. C. Gutzwiller, *J. Math. Phys.* **12**, 343 (1971); *J. Phys. Chem.* **92**, 3154 (1988).

¹⁶C. W. Patterson, *J. Chem. Phys.* **83**, 4618 (1985).

¹⁷C. W. Patterson, R. S. Smith, and R. B. Shirts, *J. Chem. Phys.* **85**, 7241 (1986).

¹⁸R. S. Smith, R. B. Shirts, and C. W. Patterson, *J. Chem. Phys.* **86**, 4452 (1987).

¹⁹R. T. Skodje and J. R. Cary, *Comput. Phys. Rep.* **8**, 223 (1988).

²⁰M. Hénon and C. Heiles, *Astron. J.* **69**, 73 (1964).

²¹R. B. Shirts and W. P. Reinhardt, *Quantum Mechanics in Mathematics, Chemistry, and Physics*, edited by K. E. Gustafson and W. P. Reinhardt (Plenum, New York, 1981), p. 277.

²²F. G. Gustavson, *Astron. J.* **71**, 670 (1966).

²³J. B. Delos and R. T. Swimm, *Chem. Phys. Lett.* **47**, 76 (1977).

²⁴D. W. Noid and R. A. Marcus, *J. Chem. Phys.* **67**, 559 (1977).

- ²⁵ C. Cerjan and W. P. Reinhardt, *J. Chem. Phys.* **71**, 1819 (1979).
- ²⁶ P. Brumer and J. W. Duff, *J. Chem. Phys.* **65**, 3566 (1976).
- ²⁷ K. S. J. Nordholm and S. A. Rice, *J. Chem. Phys.* **61**, 203 (1974).
- ²⁸ C. C. Martens and G. S. Ezra, *Proceedings of the 19th Jerusalem Symposium on Quantum Chemistry, "Tunneling,"* edited by J. Jortner and B. Pullman (D. Reidel, Dordrecht, 1986), Vol. 9.
- ²⁹ C. Jaffé, Ph.D. thesis, University of Colorado (1979).
- ³⁰ C. Jaffé and W. P. Reinhardt, *J. Chem. Phys.* **77**, 5191 (1982).
- ³¹ R. T. Swimm and J. B. Delos, *J. Chem. Phys.* **71**, 1706 (1979).
- ³² R. G. Littlejohn and J. M. Robbins, *Phys. Rev. A* **36**, 2953 (1987).
- ³³ L. F. Shampine and M. K. Gordon, *Computer Solution of Ordinary Differential Equations: The Initial Value Problem* (Freeman, San Francisco, 1975).
- ³⁴ W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University, Cambridge, 1986).
- ³⁵ C. W. Eaker, *J. Chem. Phys.* **90**, 105 (1989).
- ³⁶ R. B. Shirts (to be published).
- ³⁷ I. C. Percival and N. Pomphrey, *J. Phys. B* **9**, 3131 (1976); I. C. Percival and N. Pomphrey, *Mol. Phys.* **31**, 97 (1976).
- ³⁸ M. S. Child, *Semiclassical Mechanics with Molecular Applications* (Clarendon, Oxford, 1991).
- ³⁹ D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.* **67**, 404 (1977).
- ⁴⁰ S. Sinha and R. Ramaswamy, *Mol. Phys.* **67**, 335 (1989).
- ⁴¹ B. V. Chirikov, *Phys. Rep.* **52**, 263 (1979).
- ⁴² P. Finkler, C. E. Jones, and G. A. Sowell, *Phys. Rev. A* **42**, 1931 (1990).
- ⁴³ P. Finkler, C. E. Jones, and G. A. Sowell, *Phys. Rev. A* **44**, 925 (1991); *Phys. Rev. E* **48**, 2288 (1993).
- ⁴⁴ M. E. Kellman and L. Xiao, *Chem. Phys. Lett.* **162**, 486 (1989); L. Xiao and M. E. Kellman, *J. Chem. Phys.* **90**, 6086 (1989); Z. Li, L. Xiao, and M. E. Kellman, *ibid.* **92**, 2251 (1990); M. E. Kellman and L. Xiao, *ibid.* **93**, 5821 (1990); L. Xiao and M. E. Kellman, *ibid.* **93**, 5805 (1990).
- ⁴⁵ D. W. Noid and R. A. Marcus, *J. Chem. Phys.* **62**, 2119 (1985).
- ⁴⁶ T. Uzer, D. W. Noid, and R. A. Marcus, *J. Chem. Phys.* **79**, 4412 (1983).
- ⁴⁷ T. Uzer and R. A. Marcus, *J. Chem. Phys.* **81**, 5013 (1984).
- ⁴⁸ W. H. Miller, *Science* **233**, 171 (1986).
- ⁴⁹ J. N. L. Conner, *Chem. Phys. Lett.* **4**, 419 (1969).
- ⁵⁰ W. H. Miller, *J. Chem. Phys.* **48**, 1651 (1968).
- ⁵¹ G. H. Waller and J. Ford, *Phys. Rev.* **188**, 416 (1969).
- ⁵² M. V. Berry, in *Topics in Nonlinear Dynamics*, edited by S. Jorna, AIP Conf. Proc. No. 46 (AIP, New York, 1978), p. 16.
- ⁵³ R. Kosloff and S. A. Rice, *J. Chem. Phys.* **74**, 1947 (1981).
- ⁵⁴ J. M. Gomez Llorente, J. Zakrzewski, H. S. Taylor, and K. C. Kulander, *J. Chem. Phys.* **90**, 1505 (1989).
- ⁵⁵ G. Contopoulos, *Astronom. J.* **76**, 147 (1971).
- ⁵⁶ M. J. Davis, *J. Chem. Phys.* **83**, 1016 (1985); M. J. Davis and S. K. Gray, *ibid.* **84**, 5389 (1986); M. J. Davis, *J. Phys. Chem.* **92**, 3124 (1988).
- ⁵⁷ D. W. Noid and S. K. Gray, *Chem. Phys. Lett.* **145**, 9 (1988).
- ⁵⁸ B. Ramachandran and K. G. Kay, *Phys. Rev. A* **41**, 1757 (1990).
- ⁵⁹ W. H. Miller, *J. Chem. Phys.* **81**, 3573 (1984).
- ⁶⁰ N. DeLeon and E. J. Heller, *J. Chem. Phys.* **78**, 4005 (1983); N. DeLeon, *ibid.* **87**, 4722 (1987).
- ⁶¹ B. G. Sumpter and D. W. Noid, *Chem. Phys. Lett.* **126**, 181 (1986).
- ⁶² R. Ramaswamy, *J. Chem. Phys.* **82**, 747 (1985).
- ⁶³ D. Farrelly and A. D. Smith, *J. Phys. Chem.* **90**, 1599 (1986).
- ⁶⁴ W. Heisenberg, *The Principles of Quantum Theory* (Dover, New York, 1930).
- ⁶⁵ R. B. Shirts, *J. Phys. Chem.* **91**, 2258 (1987).
- ⁶⁶ M. L. Koszykowski, D. W. Noid, and R. A. Marcus, *J. Phys. Chem.* **86**, 2113 (1982).
- ⁶⁷ J. A. C. Gallas, *Phys. Rev. A* **21**, 1829 (1980).
- ⁶⁸ M. V. Berry and M. Tabor, *Proc. R. Soc. London Ser. A* **349**, 101 (1976).
- ⁶⁹ M. L. Du and J. B. Delos, *Phys. Rev. A* **38**, 1896 (1988); B. Eckhardt, G. Hose, and E. Pollak, *ibid.* **39**, 3776 (1989); M. Brack, R. K. Bhaduri, K. Law, and M. V. N. Murthy, *Phys. Rev. Lett.* **70**, 568 (1993); P. Gaspard and S. A. Rice, *Phys. Rev. A* **48**, 54 (1993).