

Semiclassical and Quantum Vibrational Intensities

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The semiclassical theory of infrared vibrational intensities is extended and applied to multidimensional systems. The validity and utility of the semiclassical approach is assessed by comparison with perturbative and exact quantum results for one nonresonant and two resonant model Hamiltonian systems. Approximate mean trajectories are found to provide intensities accurate to within ~20% and frequencies accurate to within ~1% for almost all transitions studied. More accurate semiclassical results can be obtained by using exact mean trajectories and, for intensities in the nonresonant system, trajectories determined by an improved correspondence rule. The advantages and limitations of the semiclassical method are summarized.

I. Introduction

Vibrational intensities provide a sensitive probe of the finer structural features of a molecule. Until the 1970's the interpretation of intensity data (i.e., the relationship of dipole moment changes to atomic displacements) was severely limited by uncertainties in normal coordinates as well as the sign ambiguities of the normal-mode dipole-moment derivatives¹ (experiments measure the square of the derivative). A steady advancement in intramolecular dynamics and, in particular, vibration-rotation analysis in the 1960's and 1970's led to more reliable force con-

stants and normal coordinates, including the use of interactions, such as Coriolis coupling, to aid in the sign determination of dipole derivatives.¹ In addition, beginning in the 1960's, quantum structure calculations proved capable of independently and accurately providing the signs of the dipole derivatives, thereby removing a major obstacle to the interpretation of vibrational intensities. These breakthroughs, coupled with modern experimental methods which are capable of measuring band intensities to an estimated accuracy of 1-2%,² have led to what Crawford¹ describes as a "renaissance" in vibrational spectroscopy.

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(1) Crawford, B. In "Vibrational Intensities in Infrared and Raman Spectroscopy"; Person, W. B.; Zerbi, G., Ed.; Elsevier: Amsterdam, 1982; Volume 20 of Studies in Physical and Theoretical Chemistry, Chapter 1.
(2) Riley, G.; Suzuki, S.; Orville-Thomas, W. J.; Chapter 8 of ref 1.

TABLE I: Potential Parameters

system	ω_x	ω_y	α	β
incommensurate	0.7	1.3	-0.1	+0.1
Fermi resonance	1.4	0.7	-0.04	-0.04
Henon-Heiles	1.0	1.0	0.0125 ^{1/2}	-1/3

With the availability of accurate infrared intensity data and the possibility of its reliable interpretation, it becomes desirable to develop reliable and straightforward methods of calculating vibrational intensities for a given molecular potential energy surface and set of dipole moment derivatives. The purpose of this paper is to apply and extend the semiclassical theory of the calculation of vibrational intensities for isolated molecular systems via the power spectral method.³ The semiclassical approach to spectroscopy is of interest because it provides certain computational advantages, which are discussed later below, over purely quantum methods. We study both semiclassically and quantum mechanically the intensities of transitions induced by several arbitrary dipole moment functions in resonant and nonresonant model Hamiltonian systems. Since vibrational frequencies are a natural by-product of intensity calculations and provide an additional check on approximate methods, we include them in our study. In addition, we compare, for the nonresonant system, the semiclassical and quantum evaluations of the vibrational state dependence of the dipole moment average and its mean square deviation. The former is useful in the determination of the signs of dipole moment derivatives and the latter is related to a transition-intensity sum rule.

The paper is organized as follows. In section II we describe the model systems and dipole-moment functions to be studied. In section III a semiclassical theory of vibrational transitions is discussed; the variational and perturbative quantum calculations are outlined in section IV. Detailed results are presented in section V and discussed in section VI. Conclusions follow in section VII.

II. Model Systems and Dipole Functions

To extend semiclassical intensity calculations to multidimensional systems and to test approximations therein it is convenient to consider first a set of two-coordinate systems, since the detailed quantum mechanics is most easily handled for such cases. The semiclassical spectral method itself is readily extended to higher dimensional systems^{3,4} and has been used in dynamical studies on a variety of molecular systems.⁵ Our model systems consist of two coupled vibrational degrees of freedom and are described by the Hamiltonian

$$H = H_0 + V \quad (\text{II.1})$$

$$H_0 = \frac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) \quad (\text{II.2})$$

$$V = \alpha(xy^2 + \beta x^3) \quad (\text{II.3})$$

Here p_x and p_y are the momenta conjugate to the mass scaled coordinates x and y , $\hbar = 1$ throughout, the quantities ω_x and ω_y are unperturbed (angular) frequencies, and the constants α and β are coupling coefficients. Three sets of the parameters (ω_x , ω_y , α , β) were chosen to yield systems with qualitatively different energy eigenvalue patterns and absorption spectra, and to establish a correspondence with systems which have been fully characterized semiclassically. The most extensively studied system is nonresonant and is obtained by choosing incommensurate fundamental frequencies.⁶ Two resonant systems are also considered: the Henon-Heiles system⁷ with $\omega_x = \omega_y$ and a Fermi resonance system⁸ with $\omega_x = 2\omega_y$. The parameters for all three systems are

(3) Noid, D. W.; Koszykowski, M. L.; Marcus, R. A. *J. Chem. Phys.* 1977, 67, 404.

(4) Koszykowski, M. L.; Noid, D. W.; Marcus, R. A. *J. Phys. Chem.* 1982, 86, 2113.

(5) McDonald, J. D.; Marcus, R. A. *J. Chem. Phys.* 1976, 65, 2180. Hansel, K. D. *Chem. Phys.* 1978, 33, 35. Powell, G. E.; Percival, I. C. *J. Phys. A* 1979, 12, 2053. Poppe, D. *Chem. Phys.* 1980, 45, 371. Farantos, S. C.; Murrell, J. N. *Ibid.* 1981, 55, 205. Carter, D.; Brumer, P. *J. Chem. Phys.* 1982, 77, 4208.

(6) Noid, D. W.; Marcus, R. A. *J. Chem. Phys.* 1975, 62, 2119.

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

listed in Table I. For our model systems we consider the "intensity"

$$I_{i \rightarrow f} = |\langle \Psi_f | \hat{\mu} | \Psi_i \rangle|^2 = |\mu_{if}|^2 \quad (\text{II.4})$$

where Ψ_f and Ψ_i are final and initial vibrational wave functions, and μ is a (here unspecified) component of the dipole moment operator $\hat{\mu}^{\text{op}}$. The relationship of eq II.4 to experimentally observable quantities is discussed, among other places, in ref 9-11. Since the systems to be studied are best considered as models of coupled normal modes, the dipole functions described below are chosen to be Taylor expansions in the normal coordinates (i.e., x and y) about equilibrium values.

The dipole moment functions used to induce vibrational transitions in each system, apart from any constant term which does not contribute to transition intensities, are described below; explicit dipole expressions appear in the tables accompanying sections V and VI. For all systems we first considered the linear approximation to the dipole function, $\mu = x + y$, and arbitrarily set the coefficients $(\partial\mu/\partial x)_0$ and $(\partial\mu/\partial y)_0$ equal to unity. In addition, for the incommensurate and Fermi resonance systems we examined dipole functions with higher order terms in order to determine if the accuracy of the semiclassical results is more or less independent of the form of the dipole function. The nonlinear dipole used for the incommensurate system has the form of the component of μ parallel to the molecular axis in OCS (ref 12) without the bending coordinate; the coefficients are arbitrary. The nonlinear dipole used for the Fermi resonance system has the form of the component of μ perpendicular to the molecular axis of CO₂ (ref 13); the coefficients are approximately those for CO₂, scaled so that the coefficient of y is -1. The coefficients in our polynomial expansions of the dipole function are frequently referred to as the dipole-moment derivatives.

III. Semiclassical Theory

In the 1970's the accurate semiclassical evaluation of energy eigenvalues for bound two and three degree-of-freedom Hamiltonian systems demonstrated the validity and utility of semiclassical methods in the description of molecules. The first of these involved trajectory quantization^{6-8,14-16} and was followed by the use of classical perturbation,¹⁷⁻¹⁹ and iteration-variation²⁰ methods. The first method readily yields a Fourier series representation of any dynamical variable³ and is thereby capable of providing a quick semiclassical evaluation of dipole matrix elements. Before discussing our methodology for semiclassical spectral calculations via trajectories, we briefly outline some pertinent historical background.

The idea of spectral intensities being related to Fourier coefficients is an old one, dating back to the pre-1925 era of old quantum theory.²¹⁻²⁶ At that time, the connection between the

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classical mechanical frequencies of motion in a particular stationary state and the quantum spectral frequencies was understood only in the limit of *large* quantum numbers and was a reflection of the correspondence principle for frequencies.^{19,21-23} The associated correspondence between classical Fourier coefficients of the mechanical motion and quantum spectral intensities in this limit was regarded as an additional hypothesis.^{19,21-23} In the *small* quantum number limit, it was realized that there was also an intimate, yet unspecified, connection between the classical motion and quantum line spectra. It was considered likely that the observed transition probabilities (and frequencies) could be obtained by averaging, in some manner, the appropriate classical quantities over the "continuous succession of 'disallowed' orbits (i.e., trajectories) in between the initial and final states".²³ Many specific, ad hoc forms for this averaging were proposed²⁵ and, although some were found to qualitatively describe X-ray transitions in atoms, the limited experimental data were too crude to establish the accuracy of any one particular intensity expression.^{25,26} Although correspondence principle discussions and calculations focused on separable systems, the extension of these ideas to weakly coupled, nonseparable systems was anticipated.^{19,21}

In the modern era, renewed interest in the semiclassical calculation of spectral intensities has stemmed from (1) the success of semiclassical quantization for eigenvalues (and hence transition frequencies) of nonseparable systems, (2) the feasibility of numerically obtaining Fourier coefficients³ by integrating classical trajectories, (3) some advantages over purely quantum methods, and (4) the emergence of correspondence rules (discussed below) for selecting a *particular* intermediate orbit, thereby eliminating the impractical averaging, supposed in the old quantum theory, over a family of intermediate orbits. In a different context, Wilson and co-workers²⁷ have derived methods for obtaining purely *classical* ro-vibrational bandshapes for species in the dilute-gas and solvated phases. In this approach classical power spectra for specific trajectories are ensemble averaged over a Boltzmann distribution and then approximately corrected for quantum effects. Heller et al.²⁸ have used a wavepacket propagation technique which employs classical trajectories to obtain electronic absorption spectra for molecular photodissociation. As noted earlier⁴ their method is complementary to the present one, which deals with purely vibrational (or ro-vibrational) spectra.

Recent analytical and numerical work, relevant to this study and aimed at identifying the correspondence rules mentioned above, is summarized below. Noid, Koszykowski, and Marcus³ (NKM) compared quantum and semiclassical results in limited studies on 2D and 3D incommensurate systems. Semiclassical frequencies, obtained as averages of those associated with trajectories corresponding (approximately) to the initial and final states, were found to agree well with the quantum frequencies for fundamental transitions from the first few states of these systems; intensities were not included in this study. Subsequently, intensive studies on diatomics have confirmed the accuracy and utility of semiclassical mechanics in predicting vibrational frequencies and intensities in 1D systems. First, NKM⁴ demonstrated, for a Morse oscillator with linear dipole ($\mu = r$), that selecting a trajectory with mean action $J = (J + J')/2$ (throughout primes denote final state quantities and unprimed quantities are those of the initial state) yields, in addition to a Hermitian dipole operator,²⁹ analytic agreement between the quantum and semiclassical frequency, and approximate agreement between the intensities in the limit $\Delta/n \ll 1$ where $\Delta = n' - n$ is the difference between the final and initial quantum numbers.³⁰ Second, in a related study, Stine and Noid³²

obtained, for many of the transitions considered, excellent numerical agreement with quantum results by using trajectories with $J = (J + J')/2$ to determine frequencies and intensities of vibrational transitions in CO, NO, and HF; accurate RKR potential energy functions and ab initio dipole-moment functions were used in these calculations.

Exact analytical results for the quantum-classical intensity correspondence for both large and small quantum numbers appear thus far to be confined to the harmonic oscillator,³³ approximate analytical results are available for the Morse oscillator^{4,33} and for the Coulomb potential.³³ Our study involves other potentials and is based on numerical results. We seek accurate semiclassical results from a single trajectory for each transition and therefore test the conjecture that it will be a good approximation to use a trajectory whose actions, $J_i(n_i^c)$ [$i = 1, 2$], are the averages of the initial and final state actions, i.e., $n_i^c = (n_i + n'_i)/2 = n_i + \Delta_i/2 = \bar{n}_i$. The frequencies and intensities so determined are here termed ω_{SC} and I_{SC} , respectively. We also test the idea that more accurate semiclassical intensities, for transitions with $\Delta_i/n_i \sim 1$ in the incommensurate system, will be obtained from a correspondence rule which is based on Naccache's analytic results for the harmonic oscillator³³ and prescribes $n_i^c \leq \bar{n}_i$.

Slightly less accurate values for the transition intensities are found, in the present paper, to be

$$I_{SC} = (I + I')/2 \quad (\text{III.1a})$$

with associated frequency³

$$\omega_{SC} = (\omega + \omega')/2 \quad (\text{III.1b})$$

where (I, ω) and (I', ω') are the classical intensities and frequencies obtained from trajectories corresponding to the initial and final states, respectively. Equation III.1a is of possible interest if eigentrajectories for the states involved in the transitions under study happen to be available. In the case of exact eigentrajectories, the transition frequencies are simply given by eigenvalue differences and will agree closely with the quantum frequencies.^{6-8,14} In addition, it is desirable to ascertain the accuracy of spectral data obtained from approximately quantized trajectories rather than the exactly quantized trajectories implicit in the above discussion, i.e., from trajectories chosen to approximate those with "quantized" actions $J_i(n_i^c)$, $i = 1, 2$. These various ideas are tested in detail in section VI. We conclude the present section with an outline of the spectral analysis method.

For both quasiperiodic and ergodic motion it has been shown³ that the classical power spectrum $I_\mu(\omega)$ is related to the Fourier transform of the classical dynamical variable $\mu(t)$

$$I_\mu(\omega) = \frac{1}{2\pi} \lim_{T \rightarrow \infty} \frac{1}{T} \left| \int_0^T dt \mu(t) \exp(-i\omega t) \right|^2 \quad (\text{III.2})$$

where the time dependence of μ is obtained by integrating, in the case of a nondegenerate system, a single trajectory. (A degenerate system requires an ensemble of trajectories, chosen so as to average over the phases corresponding to the zero frequency modes.³) However, for a *transition* the connection between the classical and quantum spectra is clear, at present, only for classically quasiperiodic motion, to which we restrict our study. The evaluation of eq III.2 and the method by which intensities are obtained for finite time T are described in the Appendix.

The relation between eq III.2 and the quantum matrix element has been described elsewhere^{4,32} for 1D systems and an analogous derivation is readily given for a multidimensional system. Consider the matrix element for μ for the $|\bar{n}\rangle \rightarrow |\bar{n}'\rangle$ transition:

(30) For multidimensional systems it has been shown, via the introduction of semiclassical wave functions in the quantum matrix element⁴ or, equivalently, via the classical limit of the Wigner formulation of quantum mechanics,³¹ that arithmetic mean quantum numbers provide the correct semiclassical correspondence with quantum matrix elements in the large quantum number limit.

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(28) Heller, E. J. *Acc. Chem. Res.* 1981, 14, 368. Kulander, K.; Heller, E. J. *J. Chem. Phys.* 1978, 69, 2439. Heller, E. J. *Ibid.* 1978, 68, 3891.

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$$\begin{aligned}
 \langle \bar{n} | \mu | \bar{n} \rangle &= \int_0^1 \langle \bar{n} | \bar{\omega} \rangle \langle \bar{\omega} | \mu | \bar{n} \rangle d\bar{\omega} \\
 &\approx \int_0^1 e^{-2\pi i \bar{n} \cdot \bar{\omega}} \mu(\bar{\omega}) e^{2\pi i \bar{n} \cdot \bar{\omega}} d\bar{\omega} \\
 &\approx \int_0^1 \mu(\bar{\omega}) e^{-2\pi i \bar{\Delta} \cdot \bar{\omega}} d\bar{\omega} \quad (\text{III.3})
 \end{aligned}$$

Here $\bar{\omega} = (\omega_1, \omega_2, \dots, \omega_r)$ are the angle variables conjugate to the actions $\bar{J} = (J_1, \dots, J_r)$; the primitive semiclassical wave function $\langle \bar{\omega} | \bar{n} \rangle = \exp(2\pi i \bar{n} \cdot \bar{\omega})$ and the semiclassical action and angle operators, $\bar{J}^{\text{sc}}$ and $\bar{\omega}^{\text{sc}}$, have been introduced; and $\bar{\Delta} = \bar{n}' - \bar{n}$. Since a rigorous way of proceeding from the second to third line of eq III.3 is not known at present, we have followed previous work^{4,29,33} and obtained the classical form of the integrand by introducing the (unspecified) correspondence $\bar{J}^{\text{sc}} = \bar{J}(\bar{n}')$, with $\bar{n}' = f(\bar{n}, \bar{n}')$. Implicit in eq III.3 is the use of the same angle variables $\bar{\omega}$ for both the initial and final states. That is, it is assumed that both wave functions correspond, classically, to trajectories with the same type of motion and we therefore do not expect this semiclassical approach to describe transitions between states characterized by trajectories separated by a separatrix in resonant systems. In addition, it is not known if transitions involving initial and/or final states which require a uniform semiclassical approximation can be described by eq III.3.

The details of the relationship between eq III.3 and eq III.2 are as follows. Since the motion is assumed quasiperiodic μ can be written as a Fourier series with coefficients which only depend on $\bar{J}^{\text{sc}}$:

$$\mu(\bar{J}^{\text{sc}}, \bar{\omega}) = \sum_{\bar{m}} \mu_{\bar{m}}(\bar{J}^{\text{sc}}) e^{2\pi i \bar{m} \cdot \bar{\omega}} \quad (\text{III.4})$$

Introducing eq III.4 into eq III.3 yields

$$\begin{aligned}
 \langle \bar{n} | \mu | \bar{n} \rangle &\approx \sum_{\bar{m}} \int_0^1 \mu_{\bar{m}}(\bar{J}^{\text{sc}}) e^{2\pi i (\bar{m} - \bar{\Delta}) \cdot \bar{\omega}} d\bar{\omega} \\
 &= \sum_{\bar{m}} \mu_{\bar{m}}(\bar{J}^{\text{sc}}) \delta_{\bar{m}, \bar{\Delta}} \\
 &= \mu_{\bar{\Delta}}(\bar{J}^{\text{sc}}) \quad (\text{III.5})
 \end{aligned}$$

Thus the semiclassical intensity is $|\mu_{\bar{\Delta}}(\bar{J}^{\text{sc}})|^2$ with associated frequency $\bar{\Delta} \cdot \bar{\omega}$ where $\bar{\omega} = (\omega_1, \dots, \omega_r)$ are the fundamental frequencies of a trajectory on the torus specified by $\bar{J}^{\text{sc}}$. As has been demonstrated in ref 3, the Fourier amplitude $\mu_{\bar{\Delta}}(\bar{J}^{\text{sc}})$ can be obtained from any one trajectory with actions $\bar{J}^{\text{sc}}$. Clearly this intensity is obtained from eq III.2 by choosing $\omega = \bar{\Delta} \cdot \bar{\omega}$.

IV. Quantum Calculations

(a) *Variational Calculation.* The eigenvalues and eigenvectors were calculated by using EISPAK³⁴ with a harmonic oscillator basis set for the incommensurate and Fermi resonance systems. The largest basis set had $N_x \times N_y = 25 \times 25$ elements where $N_x - 1$ and $N_y - 1$ are the maximum number of quanta permitted in the x and y degrees of freedom, respectively. In the case of the Henon-Heiles system a basis set of polar wave functions (n, l) of the 2D isotropic harmonic oscillator Hamiltonian was used. The largest basis set had $(N + 1)(N + 2)/2 = 630$ elements, where N is the maximum value for n , and l varies in units of 2 from $-n$ to $+n$.

(b) *Perturbation Theory.* For the incommensurate system we used nondegenerate Rayleigh-Schrodinger perturbation theory³⁵ to obtain second-order eigenfunctions and third-order eigenvalues. The corresponding degenerate theory³⁵ was used for the Henon-Heiles system, with the following modification. The zeroth-order polar basis set was chosen to be

$$\begin{aligned}
 |\Psi^0\rangle &= \Psi_{n,l}^0 \quad \text{if } l = \pm 1, \pm 2, \pm 4, \pm 5, \dots \\
 &= \Psi_{n,l\pm 1}^0 = 1/2^{1/2} [\Psi_{n,l}^0 \pm \Psi_{n,l-1}^0] \\
 &\quad \text{if } l = \pm 3k, k = 1, 2, \dots \quad (\text{IV.1})
 \end{aligned}$$

(34) EISPAK is a package developed by National Activity to Test Software. See, for example, "Lecture Notes in Computer Science", Goos, G.; Hartmanis, J., Ed., Springer: Berlin, 1976; Vol. 6.

(35) Messiah, A. "Quantum Mechanics"; Wiley: New York; Vol. II. Alonso, M.; Volk, H. "Quantum Mechanics: Principles and Applications"; Addison-Wesley: Reading, MA, 1973.

rather than $|\Psi_{n,l}^0\rangle$. The third-order correction to the eigenvalues does not lift the degeneracy of the $l = \pm 3k$ pairs of states and therefore does not predict the correct zeroth order wave functions. The nature of the perturbation⁷ indicates, however, that the degeneracy of these states should be lifted by some higher order theory, and indeed the variational calculation described in part (a) displays this feature. Perturbation intensities obtained via eq IV.1 were found to be in qualitative agreement with the exact quantum results whereas those obtained by using $|\Psi_{n,l}^0\rangle$ were not. Since primitive semiclassical theory also does not predict any splitting of $l = \pm 3k$ states, we propose that semiclassical intensities for transitions involving these states be obtained from trajectories as follows. Let us consider a transition from an $l \neq \pm 3k$ initial state $\Psi_{n,l}$ to a final state $\Psi_{n',l'}$ with $l' = \pm 3k$. The semiclassical intensity is taken to be

$$\begin{aligned}
 I_{\text{SC}} &= |\langle \Psi_{n',l'} | \mu | \Psi_{n,l} \rangle|^2 \\
 &= 1/2 [A^2 + B^2 + AB^2 + A^2B] \quad (\text{IV.2})
 \end{aligned}$$

where $A = \langle \Psi_{n',l'} | \mu | \Psi_{n,l} \rangle$ and $B = \langle \Psi_{n',l'} | \mu | \Psi_{n,l} \rangle$ are obtained semiclassically from the appropriate mean action trajectories, as described in section III. This formula is tested in section VI.

In the Fermi resonance case a perturbative treatment given by Sanders³⁶ was used. In a footnote³⁷ we point out several errata for the Fermi resonance paper of NKM⁸ and the implications for Sanders' comparison to their results.

V. Results

The results for the semiclassical frequencies are reported, in Tables II-IX, to three decimal places and the intensities to two significant figures (cf. the Appendix). For the purpose of comparison the quantum results are reported to the same accuracy although the variational calculations readily yielded frequencies converged to four decimal places and intensities to three significant figures.

Table II lists exact (Q) and semiclassical (SC) frequencies and intensities for fundamental, first overtone, and binary combination transitions of the incommensurate system with $\mu = x + y$. The most highly excited initial state is (3,3) whose eigenvalue is $\sim 60\%$ of the dissociation energy. The initial state is labeled by (n_1, n_2) and the final state by (n'_1, n'_2) . The quantities labeled SC were obtained from approximate mean trajectories, i.e., from trajectories with Cartesian initial conditions determined³⁸ by the zeroth order (unperturbed) Hamiltonian H_0 and the mean "quantum numbers" $\bar{n}_i = (n_i + n'_i)/2$, $i = 1, 2$. The accuracy of spectral data obtained via such trajectories is assessed in section VI. With the resolution employed in this study (see Appendix) classical spectral peaks with intensity $\geq 10^{-6}$ were discernable above the "background" noise. Smaller intensities (e.g., higher overtones) can be obtained by increasing the spectral resolution via longer trajectories.

In Table III are given results of first-, second-, and third-order transitions in the incommensurate system, using a nonlinear dipole

(36) Sanders, J. A. *J. Chem. Phys.* 1981, 74, 5733.

(37) In the NKM⁸ paper there is a sign error in eq 1.1, the last term of which should be $\lambda x(y^2 + \alpha x^2)$ rather than $\lambda x(y^2 - \alpha x^2)$. In addition, under E_q (3rd column) in Table II, for the state (2,1) the entry should be 2.422 rather than 2.442 and for state (4,-1) it should be 3.908 rather than 3.906. In both cases the agreement with the semiclassical eigenvalue, E in column 4, improves. Furthermore, Sanders³⁶ used the NKM⁸ Hamiltonian and hence the wrong sign for α in a comparison of his perturbation theory to the NKM results. We therefore performed his calculation with the correct sign for α and found better agreement between his eigenvalues E_{α} and the quantum eigenvalues E_q than demonstrated in Table II of ref 36; no such corrections were attempted for his Table I. Finally, in Table II of ref 8 (and hence Table II of ref 36) the labels of the $n_i = 6$ states should be interchanged as follows: (6,2) $\leftrightarrow$ (6,1) and (6,-2) $\leftrightarrow$ (6,-1).

(38) For the incommensurate system the initial conditions were taken to be

$$x^0 = y^0 = 0 \quad p_x^0 = (2E_x)^{1/2} \quad p_y^0 = (2E_y)^{1/2}$$

where $E_i = (n_i^2 + 1/2)\omega_i$, $i = 1, 2$, and $H_0 = E = E_x + E_y$. Such trajectories are found to have actions, $J_1 = \oint p_x dx$ and $J_2 = \oint p_y dy$, which are approximately equal to the actions $J_i^{\text{sc}} = 2\pi(n_i^2 + 1/2)$ of the exact mean trajectory. Approximate trajectories defined in this way can be regarded as perturbations of the associated exact trajectories.

TABLE II: Frequencies and Intensities for the Incommensurate System with $\mu = x + y$

n_1, n_2	n'_1, n'_2 ^a	ω_{SC}	ω_Q	I_{SC} ^b	I_Q ^b
0,0	1,0	0.692	0.691	7.1 (1)	7.2 (1)
	0,1	1.283	1.283	3.8 (1)	3.9 (1)
	2,0	1.379	1.379	6.0 (4)	4.7 (4)
	1,1	1.963	1.963	2.3 (3)	2.3 (3)
1,0	0,2	2.552	2.552	8.6 (5)	8.0 (5)
	0,1	0.591	0.591	7.9 (3)	6.9 (3)
	2,0	0.688	0.688	1.5	1.4
	1,1	1.271	1.271	3.8 (1)	3.8 (1)
0,1	3,0	1.373	1.373	1.5 (3)	1.5 (3)
	2,1	1.947	1.948	4.7 (3)	4.7 (3)
	1,2	2.528	2.529	8.3 (5)	7.8 (5)
	1,1	0.680	0.680	7.6 (1)	7.3 (1)
1,1	0,2	1.269	1.270	7.8 (1)	7.8 (1)
	2,1	1.356	1.356	7.3 (4)	5.4 (4)
	1,2	1.937	1.938	5.2 (3)	4.9 (3)
	0,3	2.525	2.526	2.6 (4)	2.6 (4)
1,2	0,2	0.589	0.590	1.8 (2)	1.5 (2)
	2,1	0.676	0.676	1.5	1.5
	1,2	1.256	1.258	7.4 (1)	7.7 (1)
	3,1	1.348	1.349	1.6 (3)	1.7 (3)
4,1	2,2	1.920	1.922	1.1 (2)	1.0 (2)
	1,3	2.498	2.501	2.4 (4)	2.5 (4)
	0,3	0.587	0.588	2.8 (2)	2.4 (2)
	2,2	0.663	0.664	1.6	1.5
0,4	1,3	1.241	1.243	1.1	1.2
	3,2	1.321	1.323	2.5 (3)	2.0 (3)
	2,3	1.891	1.894	1.8 (2)	1.7 (2)
	1,4	2.466	2.472	5.2 (4)	5.2 (4)
3,3	3,2	0.561	0.564	7.1 (2)	6.7 (2)
	5,1	0.663	0.664	4.0	3.7
	4,2	1.214	1.218	7.0 (1)	7.4 (1)
	6,1	1.321	1.322	1.1 (2)	9.6 (3)
0,5	5,2	1.862	1.867	3.0 (2)	2.9 (2)
	4,3	2.407	2.418	1.8 (4)	2.1 (4)
	1,4	0.640	0.642	1.0	7.7 (1)
	0,5	1.222	1.227	1.9	2.0
3,5	2,4	1.274	1.277	1.2 (3)	9.0 (4)
	1,5	1.846	1.853	2.3 (2)	1.6 (2)
	0,6	2.427	2.437	1.5 (3)	1.6 (3)
	2,4	0.563	0.569	1.4 (1)	1.1 (1)
4,4	4,3	0.637	0.639	3.6	3.1
	3,4	1.189	1.198	1.4	1.5
	5,3	1.267	1.271	1.2 (2)	9.1 (3)
	4,4	1.806	1.820	6.4 (2)	5.5 (2)
3,5	3,5	2.353	2.376	6.7 (4)	8.2 (4)

^a Primes denote the final quantum state. ^b The number in parentheses is the negative of the power of ten, e.g., 7.1 (1) = 7.1×10^{-1} .

function and, for the semiclassical calculations, approximate mean trajectories. A comparison between the semiclassical ω 's and I 's obtained as above and labeled ω_{SC} and I_{SC} with those obtained from exact mean trajectories (i.e., trajectories of the perturbed system with "quantized" actions³⁹ $J_i = 2\pi(\bar{n}_i + 1/2)$, $i = 1, 2$) and labeled ω_{SC}^* and I_{SC}^* is given in Table IV for both dipole functions. In Table V we compare, for selected transitions from Tables II and III, the quantities ω_{SC} and I_{SC} , as obtained from a different correspondence rule and with approximate initial conditions,³⁸ to ω_{SC} , I_{SC} , ω_Q , and I_Q . The correspondence rule used is an extension of one derived by Naccache³³ for a harmonic oscillator and is discussed in section VI.

Only limited data for the Henon-Heiles system were calculated and are presented in Table VI whose format is that of Table II. For states labeled (n_1, n_2) , n_1 is the principal quantum number and n_2 corresponds, in zeroth order, to the angular momentum l ; states labeled $(n_1, n_2 \pm)$ with $n_2 = 3k$ ($k = 1, 2, 3, \dots$) correspond, in zeroth order, to $\Psi_{n_1, n_2 \pm}$ in eq IV.1 and have $\langle l \rangle_Q = 0$ but $\langle l^2 \rangle_Q \neq 0$. In Table VI transitions from four selected initial states to all higher energy states for which n_1 increases by ≤ 2 are considered. The semiclassical results were obtained from approximate mean tra-

TABLE III: Frequencies and Intensities for the Incommensurate System with $\mu = x - 0.75y + 0.1(x^2 + y^2) - 0.20xy$

n_1, n_2	n'_1, n'_2	ω_{SC}	ω_Q	I_{SC}	I_Q
0,0	1,0	0.692	0.691	7.6 (1)	7.7 (1)
	0,1	1.283	1.283	2.4 (1)	2.4 (1)
	2,0	1.379	1.379	7.3 (3)	6.4 (3)
	1,1	1.963	1.963	4.5 (3)	4.6 (3)
3,0	3,0	2.064	2.064	5.0 (5)	3.4 (5)
	0,2	2.552	2.552	2.2 (3)	2.0 (3)
	2,1	2.639	2.639	1.8 (4)	1.5 (4)
	1,2	3.220	3.221	9.6 (5)	8.2 (5)
4,1	0,3	3.808	3.809	4.1 (6)	3.2 (6)
	2,1	0.574	0.575	9.9 (1)	9.9 (1)
	4,0	0.681	0.681	3.5	3.4
	3,1	1.246	1.247	2.8 (1)	2.9 (1)
5,0	5,0	1.358	1.358	6.6 (2)	6.2 (2)
	2,2	1.818	1.820	1.6 (4)	1.2 (4)
	4,1	1.914	1.915	1.5 (2)	1.5 (2)
	6,0	2.031	2.031	8.6 (4)	7.5 (4)
3,2	3,2	2.476	2.479	1.4 (3)	1.4 (3)
	5,1	2.577	2.579	1.7 (3)	1.6 (3)
	4,2	3.129	3.133	3.7 (4)	3.2 (4)
	3,3	a	3.695	a	1.6 (6)
6,0	6,0	0.118	0.116	1.7 (2)	1.6 (2)
	3,2	0.561	0.564	3.1 (1)	3.0 (1)
	5,1	0.663	0.664	5.2	4.9
	4,2	1.214	1.218	6.6 (1)	6.8 (1)
6,1	6,1	1.321	1.322	1.1 (1)	9.1 (2)
	3,3	1.771	1.780	3.0 (4)	3.5 (4)
	5,2	1.862	1.867	3.1 (2)	3.1 (2)
	7,1	1.975	1.977	2.0 (3)	1.6 (3)
4,3	4,3	2.407	2.418	2.8 (3)	3.3 (3)
	6,2	2.504	2.510	5.9 (3)	5.4 (3)
	5,3	3.037	3.051	1.3 (3)	1.3 (3)
	4,4	a	3.544	a	1.2 (6)

^a Intensity too weak to yield position; $I_{SC} \leq 10^{-6}$.

jectories with Cartesian initial conditions determined⁴⁰ by the full Hamiltonian H and the mean quantum numbers $(\bar{n}_1, \bar{n}_2)$. Semiclassical intensities for transitions involving $(n_1, n_2 \pm)$ states were determined via eq IV.2. The initial conditions used here are such that trajectories with $n_2 = \pm l$, being related by time reversal, yield identical Fourier transforms of μ ; therefore only trajectories with $n_2 \geq 0$ need be considered. Furthermore, the evaluation of the average value of l , $\langle l \rangle_{traj}$, for the trajectories used in the spectral analysis provides a convenient way of detecting different types of classical motion, knowledge of which is essential in the application of the semiclassical method. Trajectories for which $\langle l \rangle_{traj} \sim n_2$ are always of the precessing⁷ type while those with $\langle l \rangle_{traj} \sim 0$ are always of the librating⁷ type.

Data for the Fermi resonance system are presented in Tables VII-IX which are analogous to Tables II-IV, respectively. The

(40) In polar coordinates the effective potential at $\Theta = 0$ for the Henon-Heiles Hamiltonian is

$$V(r, l) = \frac{1}{2}(l^2/r^2 + \omega^2 r^2) - \alpha r^3/3$$

The obvious choice for the initial value of r (i.e., at the minimum of V) failed to yield trajectories sufficiently similar to the corresponding exact trajectories. Therefore, beginning at the inner turning point r_c where $V(r_c, l = \bar{n}_2) = E = (\bar{n}_1 + 1)\omega$, we used a linear interpolation to find the value $r = r^0$ such that the difference between $\bar{n}_2$ and $\langle l \rangle_{traj}$ is minimized; $\langle l \rangle_{traj}$ is the average of l as obtained from a relatively short trajectory. The corresponding Cartesian initial conditions are (for $\Theta = 0$, $\bar{n}_2 \neq 0$).

$$x^0 = r^0 \quad y^0 = 0$$

$$p_x = p_r^0 = [2(E - \frac{1}{2}\omega^2 r^{02} - \frac{1}{2}(\bar{n}_2/r^0)^2 + \alpha r^{03}/3)]^{1/2}$$

$$p_y^0 = (\bar{n}_2 + y^0 p_x^0)/x^0 = \bar{n}_2/r^0$$

Initial conditions for $\bar{n}_2 = 0$ states (librating trajectories) were chosen (for $\Theta = 0$) to be

$$x^0 = y^0 = 0 \quad p_x^0 = [2E f_x]^{1/2} \quad p_y^0 = [2E(1 - f_x)]^{1/2}$$

where $f_x = 0.99$ in order to avoid periodic trajectories along the x axis.⁷

(39) The exact mean trajectories were obtained by the method described in ref 6.

TABLE IV: Comparison of Frequencies and Intensities from Approximate and Exact Trajectories of the Incommensurate System

n_1, n_2	n', n'_2	ω_{SC}	ω_{SC}^{ex}	ω_Q	I_{SC}	I_{SC}^{ex}	I_Q
(a) $\mu = x + y$							
4,1	3,2	0.561	0.564	0.564	7.1 (2)	6.9 (2)	6.7 (2)
	5,1	0.663	0.663	0.664	4.0	3.7	3.7
	4,2	1.214	1.218	1.218	7.0 (1)	7.2 (1)	7.4 (1)
	6,1	1.321	1.323	1.322	1.1 (2)	9.3 (3)	9.6 (3)
	5,2	1.862	1.868	1.867	3.0 (3)	2.8 (2)	2.9 (2)
3,3	4,3	2.404	2.420	2.418	1.8 (4)	2.3 (4)	2.1 (4)
	2,4	0.563	0.569	0.569	1.4 (1)	1.2 (1)	1.1 (1)
	4,3	0.637	0.639	0.639	3.6	3.1	3.1
	3,4	1.189	1.198	1.198	1.4	1.5	1.5
	5,3	1.267	1.271	1.271	1.5 (2)	8.8 (3)	9.1 (3)
	4,4	1.806	1.820	1.820	6.7 (2)	5.3 (2)	5.5 (2)
	3,5	2.353	2.377	2.376	6.7 (4)	8.0 (4)	8.2 (4)
(b) $\mu = x - 0.75y + 0.1(x^2 + y^2) - 0.2xy$							
4,1	6,0	0.118	0.115	0.116	1.7 (2)	1.5 (2)	1.6 (2)
	3,2	0.561	0.564	0.564	3.1 (1)	2.9 (1)	3.0 (1)
	5,1	0.663	0.663	0.664	5.2	4.9	4.9
	4,2	1.214	1.218	1.218	6.6 (1)	6.6 (1)	6.8 (1)
	6,1	1.321	1.323	1.322	1.1 (1)	8.9 (2)	9.1 (2)
	3,3	1.771	1.780	1.780	3.1 (4)	3.2 (4)	3.5 (4)
	5,2	1.862	1.868	1.867	3.1 (2)	3.1 (2)	3.1 (2)
	7,1	1.975	1.977	1.977	2.0 (3)	1.7 (3)	1.6 (3)
	4,3	2.407	2.420	2.418	2.8 (3)	3.4 (3)	3.3 (3)
	6,2	2.504	2.511	2.510	5.9 (3)	5.3 (3)	5.4 (3)
	5,3	3.037	3.053	3.051	1.3 (3)	1.3 (3)	1.3 (3)

quantum number labeling scheme is that of NKM.⁸ Transitions for which the principal quantum number n_1 increases by ≤ 3 for a linear dipole (Table VII) and a nonlinear dipole (Table VIII) are considered. The semiclassical results were obtained from approximate mean trajectories with Cartesian initial conditions determined⁴¹ by the zeroth order Hamiltonian H_0 and the mean quantum numbers ($\bar{n}_1, \bar{n}_2$). A comparison between semiclassical results obtained as above with those obtained from exact mean trajectories⁴² is given in Table IX for both dipole functions.

In Table X is presented a small sample of the perturbation theory (QP) results: the superscripts (1) and (2) on I_{QP} denote first- and second-order intensities. The QP results are compared to exact (Q) results for transitions from the ground state and one higher energy state for each of the incommensurate and Fermi resonance systems with a nonlinear dipole function.

(41) Initial conditions for the Fermi resonance system were chosen in terms of the parabolic coordinates (ξ, η) and momenta (p_ξ, p_η) introduced in ref 8. The initial values of the coordinates were taken to be the positions of the minima of the effective potentials in ξ and η [eq 2.7 and 2.8 of ref 8]:

$$\xi^0 = \eta^0 = (2E/3\omega)^{1/2}$$

where $E = (\bar{n}_1 + 3/2)\omega = H_0$ is the total energy. For an $\bar{n}_2 > 0$ case the initial momenta are

$$p_\xi^0 = [K^0 - \omega^2 \xi^0 + 2\xi^0 E]^{1/2}$$

$$p_\eta^0 = [-K^0 - \omega^2 \eta^0 + 2\eta^0 E]^{1/2}$$

where the value K^0 of the separation constant K [eq 2.7 and 2.8 of ref 8] is determined numerically by requiring⁸

$$\oint p_\xi(\xi, K^0) d\xi = J_\xi = 2\pi(n_1 + 1/2)$$

with $n_1 = \bar{n}_1 - 2n_2$ and $n_2 = |\bar{n}_2| - 1$. Transforming ($\xi^0, \eta^0, p_\xi^0, p_\eta^0$) to the Cartesian system yields (x^0, y^0, p_x^0, p_y^0). For $\bar{n}_2 < 0$ cases the roles of ξ and η are interchanged in the above procedure; $\bar{n}_2 = 0$ cases are not considered for reasons discussed in the text.

(42) The exact mean trajectories were obtained by quantizing the $x - p_x$ surface of section and the total action of one cycle of the motion. For details of this procedure see ref 6-8. The exact eigentrajectories corresponding to the (3,-1) and (6,-2) states were also obtained in this way: the associated semiclassical eigenvalues are $E_{SC} = 3.185$ and 5.262 , respectively, which agree well with the quantum values $E_Q = 3.185$ and 5.268 . This method, which requires only one surface of section, is simpler than, and just as accurate as, the two-surface-of-section method used previously⁴ for a slightly different Fermi resonance system.

TABLE V: Comparison of Semiclassical Results Obtained from Different Correspondence Rules for the Incommensurate System

n_1, n_2	n'_1, n'_2	ω_{sc}^a	$\omega'_{sc}{}^b$	ω_Q	I_{sc}^a	$I'_{sc}{}^b$	I_Q
(a) $\mu = x + y$							
0,0	2,0	1.379	1.380	1.379	6.0 (4)	4.8 (4)	4.7 (4)
	0,2	2.552	2.554	2.552	8.6 (5)	7.8 (5)	8.0 (5)
1,0	3,0	1.373	1.373	1.373	1.5 (3)	1.4 (3)	1.5 (3)
	1,2	2.528	2.530	2.529	8.3 (5)	7.3 (5)	7.8 (5)
0,1	2,1	1.356	1.357	1.356	7.3 (4)	5.7 (4)	5.4 (4)
	0,3	2.525	2.526	2.526	2.6 (4)	2.4 (4)	2.6 (4)
1,1	3,1	1.348	1.348	1.349	1.6 (3)	1.7 (3)	1.7 (3)
	1,3	2.498	2.500	2.501	2.4 (4)	2.4 (4)	2.5 (4)
(b) $\mu = x - 0.75y + 0.1(x^2 + y^2) - 0.2xy$							
0,0	2,0	1.379	1.380	1.379	7.3 (3)	6.5 (3)	6.4 (3)
	3,0	2.064	2.066	2.064	5.0 (5)	3.7 (5)	3.4 (5)
	0,2	2.552	2.554	2.552	2.2 (3)	2.0 (3)	2.0 (3)
	2,1	2.639	2.641	2.639	1.8 (4)	1.6 (4)	1.5 (4)
	1,2	3.220	3.224	3.221	9.6 (5)	8.1 (5)	8.2 (5)
3,0	0,3	3.808	3.816	3.809	4.1 (6)	3.3 (6)	3.2 (6)
	5,0	1.358	1.358	1.358	6.6 (2)	6.5 (2)	6.2 (2)
	2,2	1.818	1.819	1.820	1.6 (4)	1.3 (4)	1.2 (4)
	6,0	2.031	2.031	2.031	8.6 (4)	7.9 (4)	7.5 (4)
	3,2	2.476	2.479	2.479	1.4 (3)	1.2 (3)	1.4 (3)
	5,1	2.577	2.577	2.579	1.7 (3)	1.6 (3)	1.6 (3)
	4,2	3.129	3.133	3.133	3.7 (4)	3.2 (4)	3.2 (4)

^a Obtained from trajectories with mean actions. ^b Obtained from trajectories with actions determined via eq VI.1.

In Table XI we compare exact and approximate values of the $\langle \mu \rangle$'s for ten selected states of the incommensurate system, ranging from the ground state (0,0) to a highly vibrationally excited state (3,4). For both dipole functions the following notation is used to indicate the different methods of evaluating the averages. The quantities SC^{ex} and SC denote the dipole average obtained from exact and approximate eigentrajectories, respectively, corresponding to the states listed in column 1. The quantities $QP^{(1)}$ and $QP^{(2)}$ denote the average obtained from perturbation theory via the first- and second-order wave functions. The exact value, denoted Q , is provided by the quantum variational calculation. For the same ten states various evaluations of the mean square deviation of μ , $\langle \mu^2 \rangle - \langle \mu \rangle^2$, are compared, in Table XII, for the linear dipole function, using the labels SC^{ex} , SC , and Q defined above; the label MC denotes the microcanonical ensemble average of this quantity as obtained by a Monte Carlo method.

VI. Discussion

In this section we compare in (a) the semiclassical and exact quantum results for the frequencies and intensities for all three systems, discuss in (b) the quantum perturbation theory results for all three systems, evaluate in (c) methods of calculating dipole moment averages and the associated mean square deviation for the incommensurate system, and compare in (d) ω_{SC} and I_{SC} (eq III.1) to ω_{SC} and I_{SC} .

(a) *Semiclassical. (i) Incommensurate System.* The results in Tables II and III show excellent agreement (to three decimal places) between the semiclassical and exact quantum frequencies for the lower-order transitions from the lower-energy states. With increase in the transition frequency and/or initial state energy ω_{SC} consistently underestimates ω_Q , but the upper bound on this discrepancy is $\sim 1\%$ for the transitions considered here. The intensities I_{SC} are found to agree with I_Q to $\sim 20\%$ or better in all but three of the transitions listed in Tables II and III.

We compare, in Table IV, ω_{SC}^{ex} and I_{SC}^{ex} to ω_Q and I_Q for transitions out of higher-energy states. These transitions are specifically considered since deviations between approximate and exact trajectories are found to increase with increasing energy. For all but the (4,1) $\rightarrow$ (5,3) transition in (b), ω_{SC}^{ex} agrees with ω_Q to within ± 0.001 , an improvement over ω_{SC} . The intensities I_{SC}^{ex} agree with I_Q to $\sim 5\%$ or better for all but two transitions [(3,3) $\rightarrow$ (3,5) in (a) and (4,1) $\rightarrow$ (3,3) in (b)] for which the discrepancies are $\sim 10\%$. Again, this is some improvement over I_{SC} which is typically in error by $\lesssim 20\%$.

TABLE VI: Frequencies and Intensities for the Henon-Heiles System with $\mu = x + y$

n_1, n_2	n'_1, n'_2	ω_{SC}	ω_Q	I_{SC}	I_Q
0,0 ^d	1,±1	0.991	0.991	4.9 (1)	5.0 (1)
	2,0	1.956	1.957	1.5 (3)	c
	2,±2	1.987	1.987	1.6 (3)	1.4 (3)
1,1	2,0 ^e	0.970	0.966	5.2 (1)	5.1 (1)
	2,2	0.995	0.995	9.9 (1)	9.9 (1)
	2,-2	a	0.995	a	c
3,1	3,1	a	1.936	a	c
	3,-1	b	1.936	b	1.7 (3)
	3,3-f	1.995, a	1.992	2.1 (3), a	2.0 (3)
3,3-f	3,3 ^f	1.995, a	1.996	2.1 (3), a	2.1 (3)
	3,3	a, b	0.003	a, b	c
	4,0 ^e	a, a	0.888	a, a	c
4,2	4,2	0.913, a	0.916	2.7 (1), a	3.2 (1)
	4,-2	0.913, a	0.916	2.7 (1), a	3.2 (1)
	4,4	1.004, a	1.004	9.5 (1), a	9.3 (1)
5,1	4,-4	1.004, a	1.004	9.5 (1), a	9.3 (1)
	5,1	1.830, a	1.835	1.5 (3), a	1.4 (3)
	5,-1	1.830, a	1.835	1.5 (3), a	1.4 (3)
5,3-	5,3-	a, b, f	1.885	a, b, f	c
	5,3	a, b, f	1.889	a, b, f	c
	5,5	2.012, a	2.009	6.5 (3), a	6.3 (3)
5,-5	5,-5	2.021, a	2.009	6.5 (3), a	6.3 (3)
	4,4	0.091	0.088	1.1 (1)	1.1 (1)
	4,-4	a	0.088	a	c
5,1	5,1	0.917	0.918	1.1	1.1
	5,-1	b	0.918	b	c
	5,3-f	0.976, a	0.968	1.0 ^b	1.0
5,3 ^f	5,3 ^f	0.976, a	0.983	1.0 ^b	9.4 (1)
	5,5	a	1.093	a	c
	5,-5	1.103	1.093	6.2 (4)	7.9 (4)
6,0 ^e	6,0 ^e	1.835	1.839	7.4 (3)	7.6 (3)
	6,2	a	1.886	a	c
	6,-2	b	1.886	b	2.6 (4)
6,4	6,4	1.958	1.955	1.7 (2)	1.5 (2)
	6,-4	a	1.995	a	c
	6,6-f	2.104, a	2.100	5.5 (6), a	4.4 (6)
6,6 ^f	6,6 ^f	2.104, a	2.101	5.5 (6), a	6.0 (6)

^a Intensity too weak to yield position; $I_{SC} \leq 10^{-6}$. ^b Mean trajectory is of the librating type. ^c $I_Q < 10^{-6}$. ^d Initial state corresponds to a librating trajectory. ^e Final state corresponds to a librating trajectory. ^f I_{SC} to be determined from eq IV.2; the two I_{SC} entries correspond to $|A|^2$ and $|B|^2$ in that equation and the two ω_{SC} entries to the corresponding frequencies.

TABLE VII: Frequencies and Intensities for the Fermi Resonance System with $\mu = x + y$

n_1, n_2	n'_1, n'_2	ω_{SC}	ω_Q	I_{SC}	I_Q
2,1	3,1	0.672	0.678	1.7	1.5
	4,1	1.339	1.347	2.3 (1)	2.3 (1)
	5,1	2.000	2.013	3.2 (4)	2.1 (4)
2,-1	3,-1	0.714	0.714	8.4 (1)	1.2
	4,-1	1.432	1.437	2.9 (1)	3.0 (1)
	5,-1	2.154	2.161	1.4 (4)	1.6 (5)
3,1	4,1	0.667	0.669	2.3	2.0
	5,1	1.329	1.335	2.9 (1)	2.8 (1)
	6,1	1.985	1.996	4.8 (4)	3.7 (4)
6,2	6,2	2.106	2.105	1.0 (4)	6.8 (5)

TABLE VIII: Frequencies and Intensities for the Fermi Resonance System with $\mu = -y + 0.04xy + 0.004y^3$

n_1, n_2	n'_1, n'_2	ω_{SC}	ω_Q	I_{SC}	I_Q
3,1	4,1	0.667	0.669	2.1	1.8
	5,1	a	1.335	a	c
	6,1	1.985	1.996	5.8 (3)	4.5 (3)
3,-1	6,2	2.106	2.105	2.7 (4)	1.8 (4)
	4,-1	0.718	0.723	1.2	1.5
	5,-1	a	1.447	a	c
6,-2	6,-2	b	2.084	b	1.9 (4)
	6,-1	2.162	2.174	1.0 (3)	1.3 (3)

^a Intensity too weak to yield position; $I_{SC} \leq 10^{-6}$. ^b Approximate trajectory is inverted with respect to exact trajectory. ^c $I_Q < 10^{-6}$.

TABLE IX: Comparison of Frequencies and Intensities from Approximate and Exact Trajectories of the Fermi Resonance System

n_1, n_2	n'_1, n'_2	ω_{SC}	ω_{SC}^{ex}	ω_Q	I_{SC}	I_{SC}^{ex}	I_Q
(a) $\mu = x + y$							
3,1	4,1	0.667	0.670	0.669	2.3	1.9	2.0
	5,1	1.329	1.336	1.335	2.9 (1)	2.7 (1)	2.8 (1)
	6,1	1.985	1.996	1.996	4.8 (4)	3.6 (4)	3.7 (4)
3,-1	6,2	2.106	2.108	2.105	1.0 (4)	8.2 (5)	6.8 (5)
	4,-1	0.718	0.722	0.723	1.2	1.6	1.5
	5,-1	1.439	1.447	1.447	3.4 (1)	3.5 (1)	3.5 (1)
6,-2	6,-2	b	2.077	2.084	b	1.9 (5)	2.2 (6)
	6,-1	2.162	2.174	2.174	2.2 (4)	2.8 (4)	2.6 (4)
(b) $\mu = -y + 0.04xy + 0.004y^3$							
3,1	4,1	0.667	0.670	0.669	2.1	1.8	1.8
	5,1	a	a	1.335	a	a	c
	6,1	1.985	1.996	1.996	5.8 (3)	4.4 (3)	4.5 (3)
3,-1	6,2	2.106	2.108	2.105	2.7 (4)	2.8 (4)	1.8 (4)
	4,-1	0.718	0.722	0.723	1.2	1.6	1.5
	5,-1	a	a	1.447	a	a	c
6,-2	6,-2	b	2.077	2.084	b	4.6 (4)	1.9 (4)
	6,-1	2.162	2.174	2.174	1.0 (3)	1.4 (3)	1.3 (3)

^a Intensity too weak to yield position; $I_{SC} \leq 10^{-6}$. ^b Approximate trajectory is inverted with respect to exact trajectory.

^c $I_Q < 10^{-6}$.

TABLE X: Comparison of Quantum Perturbation and Exact Results

n_1, n_2	n'_1, n'_2	ω_{QP}	ω_Q	$I_{QP}^{(1)}$	$I_{QP}^{(2)}$	I_Q
(a) Incommensurate System ^a						
0,0	1,0	0.692	0.691	7.8 (1)	7.7 (1)	7.7 (1)
	0,1	1.283	1.283	2.4 (1)	2.3 (1)	2.4 (1)
	2,0	1.380	1.379	6.7 (3)	7.0 (3)	6.4 (3)
1,1	1,1	1.965	1.963	5.2 (3)	5.3 (3)	4.6 (3)
	3,0	2.066	2.064	2.5 (7)	2.7 (4)	3.4 (5)
	0,2	2.555	2.552	2.2 (3)	2.2 (3)	2.0 (3)
2,1	2,1	2.643	2.639	2.8 (4)	2.7 (5)	1.5 (4)
	1,2	3.226	3.221	8.2 (5)	1.0 (4)	8.2 (5)
	0,3	3.815	3.809	2.2 (5)	7.4 (6)	3.2 (6)
4,1	6,0	0.113	0.116	2.4 (3)	1.1 (2)	1.6 (2)
	3,2	0.569	0.564	3.5 (1)	4.2 (1)	3.0 (1)
	5,1	0.669	0.664	9.0	6.3	4.9
4,2	4,2	1.231	1.218	1.8	1.1	6.8 (1)
	6,1	1.335	1.322	1.0 (1)	5.2 (2)	9.1 (2)
	3,3	1.798	1.780	5.0 (2)	3.4 (2)	3.5 (4)
5,2	5,2	1.890	1.867	1.1 (1)	4.4 (2)	3.1 (2)
	7,1	1.998	1.977	8.3 (1)	1.4 (1)	1.6 (3)
	4,3	2.450	2.418	2.2 (2)	4.5 (4)	3.3 (3)
6,2	6,2	2.545	2.510	8.3 (2)	1.4 (2)	5.4 (3)
	5,3	3.098	3.051	3.2 (2)	1.5 (2)	1.3 (3)
	4,4	3.657	3.544	1.5 (7)	7.2 (7)	1.2 (6)
(b) Fermi Resonance System ^b						
0,0	1,0	0.698	0.698		7.1 (1)	7.0 (1)
	2,1	1.372	1.372		0.0	c
	2,-1	1.421	1.421		0.0	c
3,1	3,1	2.050	2.050		0.0	6.0 (4)
	3,-1	2.135	2.135		0.0	3.2 (4)
5,1	5,0	0.101	0.102		0.0	c
	5,-1	0.195	0.197		0.0	c
	6,1	0.661	0.661		3.0	2.8
6,2	6,2	0.769	0.770		2.2 (1)	1.9 (1)
	6,-2	0.832	0.833		6.8 (3)	5.0 (3)
	6,-1	0.921	0.924		1.2 (4)	4.6 (5)
7,1	7,1	1.319	1.318		0.0	c
	7,2	1.441	1.442		0.0	c
	7,-2	1.541	1.542		0.0	c
8,1	8,1	1.650	1.653		0.0	c
	8,2	1.972	1.971		0.0	9.8 (3)
	8,-2	2.105	2.105		0.0	4.3 (4)
8,0	8,0	2.198	2.199		0.0	1.8 (4)
	8,-2	2.267	2.268		0.0	1.5 (5)
	8,-1	2.380	2.384		0.0	c

^a $\mu = x - 0.75y + 0.1(x^2 + y^2) - 0.2xy$. ^b $\mu = -y + 0.04xy + 0.004y^3$. ^c $I_Q < 10^{-6}$. ^d $I_{QP}^{(1)}$ not evaluated for Fermi resonance system.

TABLE XI: Dipole Moment Averages for Selected States of Incommensurate System

n_1, n_2	$\langle \mu \rangle^a$					$\langle \mu \rangle^b$				
	SC ^{ex}	SC	QP ⁽¹⁾	QP ⁽²⁾	Q	SC ^{ex}	SC	QP ⁽¹⁾	QP ⁽²⁾	Q
0,0	c	0.126	0.122	0.123	0.124	c	0.240	0.234	0.236	0.237
1,0	c	0.220	0.210	0.216	0.216	c	0.484	0.470	0.477	0.478
0,1	c	0.295	0.279	0.287	0.290	c	0.499	0.477	0.486	0.490
1,1	c	0.397	0.367	0.399	0.389	c	0.764	0.731	0.754	0.744
1,2	c	0.584	0.524	0.616	0.569	c	1.06	1.02	1.08	1.03
4,1	c	0.720	0.629	0.962	0.699	c	1.61	1.71	1.87	1.55
5,1	0.812	0.841	0.717	1.28	0.809	1.82	1.92	2.16	2.45	1.83
4,2	0.910	0.948	0.786	1.51	0.907	1.89	2.01	2.28	2.72	1.89
4,3	1.13	1.20	0.943	2.26	1.13	2.29	2.47	3.03	4.08	2.26
3,4	1.23	1.32	1.01	2.38	1.23	2.32	2.57	3.07	4.24	2.32

^a $\mu = x + y$. ^b $\mu = x - 0.75y + 0.1(x^2 + y^2) - 0.2xy$. ^c No attempt made to determine exact eigentrajjectory.

The quantities ω'_{SC} and I'_{SC} in Table V were obtained from trajectories with "quantum numbers"

$$n_i^c = m_i \equiv [(n_i + \Delta_i)/(n_i)]^{1/\Delta_i} - 1/2 \quad i = 1, 2 \quad (\text{VI.1})$$

This correspondence identity has been shown³³ to yield exact agreement between semiclassical and quantum matrix elements of up to, and including, the fourth power of the position or momentum operators for a 1D harmonic oscillator. In the classical limit $\Delta_i/n_i \ll 1$, m_i approaches the mean $\bar{n}_i$ from below. Since the largest differences between m_i and $\bar{n}_i$ occur for small n_i and large Δ_i , we therefore consider in Table V transitions with $\Delta_i \geq 2$ from states with low vibrational excitation. (Transitions with $\Delta_i = 1$ are not considered since $m_i = \bar{n}_i$ if $\Delta_i = 1$.) It is in this energy regime that the incommensurate system is closest to two uncoupled harmonic oscillators for which eq VI.1 is exact. Furthermore, the approximate trajectories used to obtain ω_{SC} , I_{SC} , ω'_{SC} , and I'_{SC} are most accurate at these low energies. The agreement between I'_{SC} and I_Q is good in all cases. For 15 of the 20 transitions considered, I'_{SC} is an improvement over I_{SC} . Of the remaining five transitions, two have values of I'_{SC} which display the same accuracy as I_{SC} and three have values of I'_{SC} which are only slightly less accurate than I_{SC} . For transitions with $\Delta_i = 2$ ($i = 1, 2$) the accuracy of ω'_{SC} and ω_{SC} is comparable. For the only transition with $\Delta_i = 3$, i.e., the (0,0) $\rightarrow$ (0,3) transition in part (b) of Table V, ω'_{SC} overestimates ω_Q by 0.007 and ω_{SC} is clearly more accurate. We note that ω_{SC} is exact for a Morse oscillator.⁴

Equation VI.1 has also been applied to two Morse oscillator systems^{33,43} and, based on numerical agreement with quantum results, is found to provide more accurate semiclassical intensities than the use of mean quantum numbers. The analytical basis for this improvement is established in ref 43.

Results for the Morse oscillator^{4,43} and the incommensurate system studied here suggest the use of a mean value correspondence rule for frequencies and the above Naccache one for intensities of $\bar{n} \rightarrow \bar{n}'$ transitions with small $\bar{n}$ in coupled, nonresonant oscillator systems. Since the lower energy vibrational levels of anharmonic oscillator systems are usually well described by quadratic functions of the quantum numbers, energy level differences will be approximately linear functions of the quantum numbers in this energy regime. Therefore a trajectory with mean quantum numbers should accurately predict the transition frequencies. On the other hand, eq VI.1 could be used to obtain the corresponding and somewhat more accurate semiclassical intensities than those given by the mean value rule. Note that for larger $\bar{n}$ and $\bar{n}'$ the value of m_i (eq VI.1) approaches $\bar{n}_i$ and hence the frequency and intensity correspondence rules coalesce.

(ii) *Henon-Heiles System.* In Table VI the semiclassical frequencies ω_{SC} agree with the exact frequencies ω_Q to $\sim 1\%$ or better for all transitions considered. For transitions from non-degenerate states to $(n_1, n_2 \pm)$ pairs with $n_2 = 3k$, ω_{SC} is to be compared to the average of the two associated ω_Q 's for reasons mentioned earlier in section IV. No reliable semiclassical fre-

quencies (or intensities) could be obtained for transitions between two "precessing" states whose mean trajectory was of the librating type, in agreement with the discussion (in section III) concerning the applicability of the present semiclassical method via eq III.3. Otherwise the semiclassical intensities I_{SC} are found to agree with I_Q to $\sim 20\%$ or better. When both the initial and final states are described by librating trajectories, I_{SC} is incorrect, e.g., (0,0) $\rightarrow$ (2,0). This feature, which is displayed by other $(n_1, n_2 = 0) \rightarrow (n'_1, n'_2 = 0)$ transitions not reported here, is explained by the nature of the correct semiclassical "librating" states (see below). Noteworthy is the success of eq IV.2 for transitions involving $(n_1, n_2 \pm)$ states, as well as the fact that reliable semiclassical results are obtained for transitions from a precessing (librating) state to a librating (precessing) state for which the mean trajectory is of the precessing type. This latter feature is probably explained by noting that the correct semiclassical "librating" states are obtained from three equivalent librating trajectories (related by successive rotations of 120°) via a uniform approximation¹⁷ and, as such, span the same region of configuration space as precessing trajectories.

(iii) *Fermi Resonance System.* The semiclassical frequency ω_{SC} usually underestimates ω_Q by $\lesssim 1\%$ for the transitions considered in Tables VII and VIII. The extent of agreement between I_{SC} and I_Q is found to vary more strongly with the transition under consideration than in the incommensurate and Henon-Heiles systems. For example, in Table VII, I_{SC} and I_Q agree to two figures for the (2,1) $\rightarrow$ (4,1) transition yet differ by $\sim 30\%$ for the (2,-1) $\rightarrow$ (3,-1) transition. In general, although we find that the approximate mean trajectories chosen for this system do not provide as accurate semiclassical frequencies and intensities as do those of the other two systems, they nevertheless provide reasonable estimates of the exact results. However, semiclassical results are only available for a limited number of transitions, those in which the sign of n_2 remains unchanged. In order to understand this limitation within the context of the present semiclassical theory, we first note that the Fermi resonance system admits three distinctly different shapes of xy trajectory plots, all of which are depicted in the figures of ref 8. C-shaped trajectory plots correspond to states with $n_2 > 0$, inverted C-shaped to $n_2 < 0$ states, and the third shape to separatrix trajectories. Implicit in eq III.3 is the idea that the angle variables of one (initial state) wave function can be used to describe the other (final state) wave function, an assumption not expected to hold for transitions between states described classically by trajectories of different shapes. Attempts to obtain reliable values of ω_{SC} and I_{SC} for such transitions were unsuccessful. Furthermore, since the correct semiclassical characterization of the $n_2 = 0$ states via trajectories and their relation, if any, to the separatrix trajectories are not known at present,⁴⁴ transitions involving n_2 and/or $n'_2 = 0$ states are not considered in the present paper.

We compare, in Table IX, ω_{SC}^c and I_{SC}^c to ω_Q and I_Q for selected transitions. For all but the (3,1) $\rightarrow$ (6,2) transition in both (a) and (b) ω_{SC}^c is closer to ω_Q than is ω_{SC} and in all cases I_{SC}^c is an improvement over I_{SC} . Several features of the (3,-1) $\rightarrow$ (6,-2)

(43) Wardlaw, D. M.; Noid, D. W.; Koszykowski, M. L.; Marcus, R. A., manuscript in preparation.

(44) Noid, D. W.; Marcus, R. A., unpublished results.

TABLE XII: Transition-Intensity Sums for Selected States of Incommensurate System

n_1, n_2	energy	$I_{\text{SUM}} = \langle \mu^2 \rangle - \langle \mu \rangle^2$ ^a			
		SC ^{ex}	SC	Q	MC ^c
0,0	0.995	b	1.12	1.11	1.33
1,0	1.687	b	2.60	2.56	2.27
0,1	2.278	b	1.96	1.92	3.09
1,1	2.958	b	3.51	3.40	4.04
1,2	4.216	b	4.50	4.27	5.85
4,1	4.975	b	8.39	7.98	7.02
5,1	5.639	9.54	10.1	9.55	8.05
4,2	6.193	8.99	9.80	8.99	8.99
4,3	7.393	10.0	11.4	10.0	10.9
3,4	7.952	9.49	10.9	9.39	11.9

^a $\mu = x + y$. ^b No attempt made to determine exact eigentrajctory. ^c The error in each MC entry is $\sim 1\%$.

transition in Table IX are noteworthy. (1) $\omega_{\text{SC}}^{\text{ex}}$ and $I_{\text{SC}}^{\text{ex}}$, as obtained from an exact mean trajectory⁴⁵ with $(n_1, n_2) = (4.5, -1.5)$, differ significantly from the exact results ω_Q and I_Q . (2) An attempt to obtain reliable intensity results from the exact eigentrajctories with $(n_1, n_2) = (3, -1)$ and $(6, -2)$ via eq III.1 was also unsuccessful. (3) To understand this anomalous case we examined xy plots of the $(4.5, -1.5)$ and $(6, -2)$ exact trajectories and found them to have shapes approaching those of separatrix trajectories. (4) The discrepancy between the semiclassical and exact eigenvalues⁴² is much larger for the $(6, -2)$ state than any other state with $n_1 \leq 6$, a feature shared by the related Fermi resonance system studied elsewhere.⁸ Since it has been noted⁴⁴ that a uniform approximation is required for semiclassical states near the separatrix in this type of system, the above results indicate that the primitive semiclassical calculation for this transition is inadequate.

(b) *Perturbation Theory.* Many of the conclusions described below are illustrated by the limited data presented in Table X. We first summarize our findings for the low-order quantum perturbation treatment of the incommensurate and Henon-Heiles system. Using standard third-order perturbation theory (section IV) we found good agreement (i.e., ± 0.001) between ω_{SC} and ω_Q only for transitions of order ≤ 2 from the lowest energy states for both systems. As the energy of the initial or final state increases ω_{QP} consistently overestimates ω_Q by as much as 3% for some of the transitions studied. For example, third-order transitions from the ground state of the incommensurate system display deviations, $\omega_{\text{QP}} - \omega_Q$, of up to +0.006, whereas $\omega_{\text{SC}} - \omega_Q \leq -0.001$. Like the primitive semiclassical method, the third-order perturbation treatment does not predict a splitting of the $(n_1, n_2 \pm)$ states. The first- and second-order perturbation theory intensities $I_Q^{(1)}$ and $I_Q^{(2)}$ differ from each other by $\leq 5\%$ or less and agree consistently with I_Q only for transitions of order ≤ 2 from the lowest energy states. For low-order transitions (i.e., ≤ 1) from higher energy states $I_Q^{(2)}$ is more accurate than $I_Q^{(1)}$ but less accurate than I_{SC} . As the energy of either the initial or final state increases, $I_Q^{(1)}$ and $I_Q^{(2)}$ begin to differ substantially from each other (in some cases by more than an order of magnitude) and to provide, in general, unreliable estimates of I_Q . Nevertheless for $(n_1, 0) \rightarrow (n'_1, 0)$ transitions in the Henon-Heiles system quantum perturbation theory gives better intensity results than the semiclassical method, although deteriorating as the energy of either state becomes large. For the incommensurate system, a semiclassical treatment with approximate mean trajectories is superior to the perturbation theory used here.

When Sanders' second-order perturbation theory for the Fermi resonance system is used, the frequencies ω_{QP} agreed with ω_Q to $\sim 1\%$ or better for all transitions studied; in many cases the error was only +0.001. For transitions from each of the first six states the perturbation intensities I_{QP} agreed with I_Q to $\sim 10\%$ or better. For higher energy states this error increased and for some tran-

sitions I_{QP} differed substantially from I_Q , e.g., for the $(5, 1) \rightarrow (6, n_2)$ transitions in Table Xb the differences ranged from 8% to 260%. For certain transitions, as determined by the particular dipole function under study, Sanders' perturbation theory predicted a matrix element of zero although the exact results indicated a small but finite intensity. The semiclassical method, when applicable, predicted a finite intensity for these transitions.

(c) *Dipole Moment Averages.* In general, the measurement of vibrational intensities provides only the magnitude of the dipole derivatives and their signs must be determined by independent means (section I). One such means relies on the dependence of the average value of the dipole moment function, $\langle \mu \rangle = \langle \Psi_f | \mu | \Psi_i \rangle$, on the vibrational state.⁴⁶ That is, by comparing experimental values of $\langle \mu \rangle$, as obtained by measuring the Stark effect for lines in a vibration-rotation spectrum using ultrahigh-resolution infrared nonlinear laser spectroscopy,⁴⁷ to calculated values for various sign choices of the dipole derivatives, it is possible, in principle, to make the correct sign assignment. Approximate values of $\langle \mu \rangle$, as obtained by several different methods, are compared to the exact (Q) values in Table XI for the incommensurate system. It can be seen that the perturbation results are superior to the semiclassical results only for the lowest energy states for both dipole functions. However, as the energy increases $\text{QP}^{(1)}$ and $\text{QP}^{(2)}$ begin to diverge from each other and to provide unreliable estimates of Q. On the other hand, SC continues to provide reliable estimates of Q as the energy increases; in the worst case presented here, SC overestimates Q by 11%. Such errors at high energy could be reduced by the use of exact, rather than approximate, eigentrajctories as is indicated by the excellent agreement between SC^{ex} and Q for the states $(5, 1)$, $(4, 2)$, $(4, 3)$, and $(3, 4)$.

We next examine the quantity $\langle \mu^2 \rangle - \langle \mu \rangle^2$ which, by completeness, is equal to the sum of the intensities for transitions to all final states from a given initial state, i.e.

$$I_{\text{sum}} = \langle \mu^2 \rangle - \langle \mu \rangle^2 = \sum_{f \neq i} |\langle \Psi_f | \mu | \Psi_i \rangle|^2 \quad (\text{VI.2})$$

From Table XII it can be seen that the accuracy of the SC^{ex} and SC evaluations of I_{sum} are comparable to those for $\langle \mu \rangle$ in Table XI. We compare, in Table XII, the microcanonical (MC) values of I_{sum} to the semiclassical and quantum results. One sees that for states with $n_1 > n_2$ the MC values are $\leq$ the Q and SC values and that for all other states this relationship is reversed.

(d) *Averaged Semiclassical Intensities.* We also tested the utility of eq III.1 by comparing, for all transitions in Tables II-IV and VI-IX to which the semiclassical method applied, ω_{SC} and I_{SC} to $\bar{\omega}_{\text{SC}}$ and $\bar{I}_{\text{SC}}$, where all quantities were obtained from approximate trajectories. No data are presented here. In the majority of cases considered ω_{SC} and $\bar{\omega}_{\text{SC}}$ agreed to within ± 0.001 ; in the worst case there was a discrepancy of $\omega_{\text{SC}} - \bar{\omega}_{\text{SC}} = 0.006$ or $\sim 0.25\%$. In most cases I_{SC} and $\bar{I}_{\text{SC}}$ agreed to within $\sim 20\%$, with the best agreement (to within $\sim 5\%$) found for the first-order transitions in all three systems. Exceptions are some of the second- and third-order transitions from states of low energy. In such cases, because of the low vibrational excitation, the initial state intensity I_i corresponding to the overtone is usually poorly resolved, leading to inaccurate values of I_{SC} . Although improved spectral resolution, via longer trajectories, is possible for these cases, no attempt was made to do so here. For almost all transitions considered I_{SC} was found to be closer to I_Q than was $\bar{I}_{\text{SC}}$.

The above analysis indicates that, for the systems and transitions studied, there is an almost linear variation of the semiclassical frequencies and intensities between the initial and final states. For several transitions in the incommensurate system this observation was confirmed by obtaining frequencies and intensities from trajectories with "quantum numbers" (m_1, m_2) determined by the requirement that

$$(m_1(\lambda) - n_1):(m_2(\lambda) - n_2) = (n'_1 - n_1):(n'_2 - n_2) \quad (\text{VI.3})$$

(45) No reliable results for ω_{SC} and I_{SC} are available for this transition since the approximate mean trajectory is "inverted" with respect to the family of $n_2 < 0$ trajectories, i.e., it has the shape of an $n_2 > 0$ trajectory, probably because it lies near the separatrix.

(46) LaBoda, M. L.; Overend, J. *Spectrochim. Acta, Part A* 1976, 32, 1033.

(47) Luntz, A. C.; Swalen, J. D.; Brewer, R. G. *Chem. Phys. Lett.* 1972, 14, 512.

for ten equally spaced values of λ between 0 and 1. Here (n'_1, n'_2) and (n_1, n_2) are the quantum numbers of the final and initial states, respectively; $\lambda = 1$ corresponds to the final state and $\lambda = 0$ to the initial state; $\lambda = 1/2$ corresponds to the mean trajectory used in this study to obtain the semiclassical results.

VII. Conclusions

For the two-dimensional model systems and dipole moment functions studied here, the semiclassical method provides a good description of the frequencies and intensities of those transitions to which it is applicable, as well as accurate values of dipole-moment averages in vibrationally excited states. We summarize our findings by listing the advantages and limitations of the semiclassical approach to vibrational spectra. Types of transitions to which the method is inapplicable are discussed under the heading of limitations.

(i) *Advantages and Other Features.* 1. A single trajectory is found to be sufficient to describe transitions up to and including third order. The trajectory to be used is determined by a correspondence rule which, for nonseparable systems, is only approximate and is of necessity based on analytic results for 1D systems. For all three 2D systems, a trajectory with mean quantum numbers was found to provide reliable semiclassical frequencies and intensities, the detailed accuracy of these results depending on the system, the transition, and the use of approximate vs. exact mean trajectories. For transitions from states of low vibrational excitation in the incommensurate system more accurate intensities were obtained with Naccache's correspondence rule (eq VI.1). This rule is also found to provide improved intensity results for the Morse oscillator^{33,43} and a forced harmonic oscillator⁴⁸ but has not been tested for resonant systems.

2. Given a potential energy surface and dipole moment function, selected individual transitions can be studied by integrating the appropriate classical trajectories. In contrast, quantum methods require either diagonalization of the entire Hamiltonian matrix (variational calculation) or knowledge of a good zeroth order basis set or some suitably modified form of the Hamiltonian (perturbation theory). The usefulness of this feature has been reported by Koszykowski et al.⁴⁹ in a study of the arrangement of water molecules on a ruthenium surface. By comparing semiclassical frequencies (obtained from single trajectories) for a particular vibrational transition in each of two possible water molecule arrangements to experimental frequencies, they reported the resolution of an uncertainty in the orientation of one of the water molecules in the adsorbed cluster.

3. The approximate trajectories^{38,40,41} are found to provide estimates of frequencies, intensities, and dipole-moment averages which may be sufficiently accurate for certain applications, and are most accurate at lower energies. More accurate but more expensive results can be obtained by using exact trajectories. The advantage of the approximate trajectories lies in the easy determination of the initial conditions for given quantum numbers. However, the choice of such approximate trajectories depends strongly on the system under study. Furthermore, the suitability of these trajectories should be established by any or all of the following means: (a) configuration-space trajectory plots to determine the trajectory shape, (b) evaluation of either the exact classical actions via surfaces of section or the average and mean square values of state-dependent dynamical quantities (e.g., the zeroth order actions, J_0^1 and J_0^2 , in the incommensurate system and I in the Henon-Heiles system) to determine the proximity of the approximate trajectory to the associated exact trajectory, and (c) back-integration to establish the accuracy of the Fourier transform data.

4. For transitions involving higher energy initial and/or final states, standard perturbation theory (incommensurate and Henon-Heiles systems) provides reasonable estimates for the third-order frequencies but is unreliable for second-order intensities which are known to be much more sensitive to the wave functions.

Although Sanders' second-order perturbation theory (Fermi resonance system) is applicable over a wider energy range than the standard theory and provides accurate frequency results, it too becomes unreliable for intensities as the initial state energy increases. The semiclassical method, with exact mean eigentrajectories if necessary, was found to provide far more accurate results for such transitions, in agreement with the findings of a study⁴⁸ which compared semiclassical, perturbation, and exact transition probabilities for a forced harmonic oscillator.

5. The convergence of quantum variational calculations, which require copious quantities of computer time, falls off at high energy whereas the only restriction on the semiclassical method is that the motion be quasiperiodic. This advantage of the semiclassical method has recently been exploited by Knudson et al.⁵⁰ in order to obtain directional absorption spectra for highly excited states of the hydrogen atom in a strong magnetic field. Furthermore, the quantum situation worsens dramatically as the number of degrees of freedom increases. On the other hand, the semiclassical approach is readily extended to three or four dimensions, e.g., to the vibrational degrees of freedom of a triatomic molecule or some subset of vibrational modes for a larger polyatomic. Recently developed methods^{51,52} for plotting three-dimensional trajectories make it possible to establish the shape of a multidimensional trajectory and hence determine those transitions to which the semiclassical method can be applied. Since many triatomics are incommensurate systems, except in isolated nonlinear resonance regions, the limitations imposed by resonant systems [see (ii) below] should not be considered a major practical restriction on the utility of the semiclassical method.

6. The utility of the semiclassical method is independent of the functional form of the dipole moment function. In contrast, nonanalytic matrix elements in quantum calculations significantly increase computation times.

7. The semiclassical method could be extended to vibrational nonresonant Raman spectroscopy, namely, when the matrix element $\langle \vec{n} | \mu_{\text{ind}} | \vec{n} \rangle$ of the induced dipole moment μ_{ind} for the $|\vec{n}\rangle \rightarrow |\vec{n}'\rangle$ transition can be replaced by $\langle \vec{n} | \alpha_{AB} | \vec{n} \rangle$; $A, B = X, Y, Z$, and α_{AB} is an element of the polarizability tensor expressed in a molecule-fixed coordinate system. The conditions for this replacement are¹⁰ (1) the frequency shifts $\omega_{\vec{n}, \vec{n}'} \ll \omega_0$ where ω_0 is the frequency of the incident radiation, (2) $\omega_{\vec{n}, \vec{n}'} \ll \omega_E - \omega_0$ where ω_E is the frequency of the nearest electronic transition, and (3) the lowest electronic level is nondegenerate. The semiclassical calculation of Raman intensities would then be analogous to the evaluation of the dipole matrix elements studied here. An expression for α_{AB} in terms of the nuclear coordinates would be needed.

(ii) *Limitations.* 1. The application of the present semiclassical method is limited, in general, to transitions between (a) states having the same type of classical motion (i.e., states lying on the same side of a separatrix in resonant systems) or (b) states for which a uniform semiclassical approximation is not required. The severity of this limitation depends on the system: for example, it is worse for the Fermi resonance system studied here than for the Henon-Heiles system. (In the latter system the semiclassical method was found to describe some of the transitions involving states for which a uniform approximation is required.) For transitions not described by the semiclassical approach one might use perturbation theory, being aware of its limitations: in the Henon-Heiles system, standard perturbation theory provided unreliable second-order intensities when higher energy states were involved in transitions, and, in the Fermi resonance system, Sanders' low-order perturbation theory predicted zero intensity for certain low intensity transitions. For resonant systems the semiclassical and perturbative methods are thus complementary.

2. In order to apply the semiclassical method it is necessary to identify the relevant peaks in the power spectrum of the dipole

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TABLE XIII: Convergence of Semiclassical Results for Transitions from the (4,1) State of the Incommensurate System^a

n_1, n_2	$\omega_{SC}(1/2)$	ω_{SC}	$\omega_{SC}(2)$	$I_{SC}(1/2)$	I_{SC}	$I_{SC}(2)$
3,2	0.561	0.561	0.561	6.9 (2)	7.1 (2)	7.1 (2)
5,1	0.663	0.663	0.663	4.0	4.0	3.9
4,2	1.214	1.214	1.214	6.9 (1)	7.0 (1)	7.0 (1)
6,1	1.322	1.321	1.321	1.2 (2)	1.1 (2)	1.1 (2)
5,2	1.861	1.862	1.861	3.1 (2)	3.0 (2)	2.9 (2)
4,3	2.408	2.407	2.407	2.1 (4)	1.8 (4)	1.9 (4)

^a $\mu = x + y$.

function. Methods of making this identification without explicit knowledge of the quantum or semiclassical eigenvalue spectrum will be considered in future work. For resonant systems, it is also necessary to know the shapes of the trajectories associated with the quantum states.

3. At present, the semiclassical assignment and prediction of vibrational spectra is only understood for transitions occurring in the classical "regular" regime.

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Appendix

An approximate evaluation of eq III.2 is achieved by writing $\mu(t)$ as a finite, real Fourier series on the time interval $(0, T)$:

$$\mu(t) \simeq a_0/2 + \sum_{k=1}^{N-1} [a_k \cos(2\pi kt/T) + b_k \sin(2\pi kt/T)] \quad (\text{A1})$$

where N is an integer whose value is defined below. For $1 \leq k \leq N-1$ the coefficients are given by

$$a_k = \frac{2}{T} \int_0^T dt \mu(t) \cos(2\pi kt/T) \\ b_k = \frac{2}{T} \int_0^T dt \mu(t) \sin(2\pi kt/T) \quad (\text{A2})$$

and for $k=0$

$$a_0/2 = \frac{1}{T} \int_0^T dt \mu(t) = \langle \mu \rangle \\ b_0 = 0 \quad (\text{A3})$$

These coefficients are readily obtained from a fast Fourier transform procedure by providing $2N$ values of $\mu(t)$ on $(0, T)$ at equally spaced time increments $\delta = T/(2N-1)$, where $N = 2^M$ and M is an integer. A useful relationship between the coefficients (eq A2) and the first two moments of μ is Parseval's equality:

$$\frac{1}{2} \sum_{k=1}^{N-1} (a_k^2 + b_k^2) = \langle \mu^2 \rangle - \langle \mu \rangle^2 \quad (\text{A4})$$

where $\langle \mu^2 \rangle = (1/T) \int_0^T dt \mu^2(t)$. Equations A3 and A4 were exploited as checks on the accuracy of the Fourier transformation. For all spectra used in this study, agreement to four significant figures between the right-hand sides of eq A3 and A4, as obtained directly from the trajectories, and the corresponding left-hand sides, as obtained from the fast Fourier transform routine, is found.

Inserting eq A1 into eq III.2, considering only terms describing absorption (i.e., $\omega > 0$) and noting that all cross terms vanish in the limit of large T yields³

$$I_\mu(\omega) = \frac{1}{4} \lim_{T \rightarrow \infty} \frac{1}{\pi k=1} \sum_{k=1}^{N-1} (a_k^2 + b_k^2) \frac{\sin^2[(\omega_k - \omega)T/2]}{(\omega_k - \omega)^2 T/2} \quad (\text{A5})$$

where $\omega_k = 2\pi k/T$. The resolution of $I_\mu(\omega)$ is $\omega_\delta = 2\pi/T$ and

the maximum frequency is $\omega_{\max} = \omega_{N-1} \simeq \pi/\delta$: for an accurate spectrum the conditions $\omega_\delta \ll \omega \ll \omega_{\max}$ must be satisfied. In the $T \rightarrow \infty$ limit eq A5 reduces to the well-known line spectrum $I_\mu(\omega) = 1/4 \sum (a_k^2 + b_k^2) \delta(\omega_k - \omega)$. In practice the limit $T \rightarrow \infty$ is unattainable and $I_\mu(\omega)$ is given by eq A5. That is, each spectral feature has a finite width, as determined by the superposition of contributing terms, and the intensity (square modulus of matrix element) of a transition is the area under the associated peak. As an aside, we point out that an arbitrary trajectory displays all the spectral features characteristic of the classical motion. However, in this application of the spectral analysis method, only a single spectral feature, as determined by the particular transition under consideration, is relevant for any one trajectory involved in the semiclassical description of that transition.

The area $A(\omega_0)$ under a peak centered on frequency ω_0 is

$$A(\omega_0) = \int_{\omega_0-B/2}^{\omega_0+B/2} d\omega I_\mu(\omega) \\ \simeq \frac{1}{4} \int_{-\infty}^{+\infty} d\omega \sum_k' (a_k^2 + b_k^2) \frac{1}{\pi} \frac{\sin^2[(\omega_k - \omega)T/2]}{(\omega_k - \omega)^2 T/2} \\ \simeq \frac{1}{4} \sum_k' (a_k^2 + b_k^2) \quad (\text{A6})$$

The quantity B is the baseline width of the peak; in the second line the integration limits have been extended to infinity; the prime on the sum restricts the summation to terms in the neighborhood of ω_0 . The frequency ω_0 of the transition is taken to be the location of the peak maximum as determined by an interpolation, between the two largest terms in the last line of eq A6, based on the relative values of these two terms. An intensity is deemed to be converged when additional contributions from the "wings" of a peak do not alter the sum in the last line of eq A6. With the resolutions ω_δ (defined below) used in this study, intensities readily converged to two significant figures; however, if two peaks overlap extensively, the sum does not converge and a spectrum of greater resolution is required. This method of obtaining intensities from $I_\mu(\omega)$ is an improvement on one used previously^{3,53} which requires longer trajectories (i.e., greater resolution) to accurately determine peak heights and hence, via a suitable test function, areas under peaks.

The frequencies ω_{SC} and intensities I_{SC} in Tables II-IX were obtained, as outlined above, from Fourier analysis of trajectories with $\delta = 0.2 \simeq 0.03\tau_{av}$ and $T = 3276.6 \simeq 520\tau_{av}$ corresponding to $\omega_\delta = 0.0019$ and $\omega_{\max} = 15.7$. Here $\tau_{av} = 2\pi/\omega_{av}$ and we have taken $\omega_{av} = 1/2(\omega_x + \omega_y) \simeq 1$ for all three systems studied. To test for convergence with respect to the resolution ω_δ we used the first half of a trajectory, i.e., $T = 1638.3$, to obtain another set of frequencies $\omega_{SC}(1/2)$ and intensities $I_{SC}(1/2)$ with $\omega_\delta = 0.0038$ and $\omega_{\max} = 15.7$. In addition, a limited number of trajectories were executed with both the total time and step size doubled, i.e., $T = 6553.2$ and $\delta = 0.4$, to obtain $\omega_{SC}(2)$ and $I_{SC}(2)$ with $\omega_\delta = 0.0096$ and $\omega_{\max} = 7.85$. In Table XIII we first compare ω_{SC} to $\omega_{SC}(1/2)$ and I_{SC} to $I_{SC}(1/2)$ for transitions from state (4,1) of the incommensurate system with $\mu = x + y$. These results, which are typical of those obtained for all transitions studied, indicate the good agreement between the two sets of data. That is, frequencies agree to ± 0.001 in all cases and intensities to within ± 2 in the second significant figure in all but the following cases. Poorer convergence of $I_{SC}(1/2)$ and I_{SC} was noted for low-intensity higher-order transitions, e.g., the $2\omega_y$ transition in Table XIII, and for overlapping adjacent peaks. Although in such cases these difficulties can be eliminated by increasing the spectral resolution, this was not done here and we simply took the results obtained with $\omega_\delta = 0.0019$ as being more accurate. In addition, varying the number of Fourier transform points at fixed T by doubling and halving δ (and hence halving and doubling $\omega_{\max}$) was found to have no effect on the frequencies (to three decimal places) or the intensities (to two significant figures) for either value of T .

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We note that the sensitivity of intensities obtained in the manner described here, to ω_j and $\omega_{\max}$, is superior to the 20–30% variation reported in ref 4. The excellent agreement, in Table XIII, between I_{sc} and $I_{sc}(2)$ as well as between ω_{sc} and $\omega_{sc}(2)$ indicates that there is little to be gained, apart from the possible detection of a few very low-intensity transitions, by increasing the spectral resolution for the transitions studied in this paper.

Back-integration to at least three figures in the coordinates and

momenta, of trajectories selected at random from all of those used in the study, established the accuracy of the trajectory data for $\mu(t)$. Trajectories were integrated by using the program ODE⁵⁴ with an absolute error parameter of 10^{-8} .

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