

FEATURE ARTICLE

Semiclassical Quantization of Polyatomic Molecules: Some Recent Developments

Gregory S. Ezra,*† Craig C. Martens,† and Laurence E. Fried

Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853

(Received: January 27, 1987)

Recent progress in the semiclassical quantization of multidimensional molecular potentials is reviewed. We discuss quantization of multimode and resonant systems using the Fourier transform method and operator-based Lie transform perturbation theory, quantization in the multiresonance and chaotic regime using algebraic quantization and resummation techniques, and application of unitary group methods to the description of resonant dynamics.

I. Introduction

Recent experimental advances are providing information on the properties of highly excited vibration-rotation states of polyatomic molecules in unprecedented detail, and are revealing new and poorly understood spectral regimes (see, for example, ref 1). It is now possible to probe experimentally the dynamics of unimolecular decay² of state-selected molecules. The interpretation of such experiments to elucidate the rate and extent of intramolecular energy flow and its role in dynamical processes poses many challenging problems for theory. In light of the correspondence principle,³ we expect that semiclassical approximations will be useful in characterizing highly excited states in the large quantum number regime.⁴

The traditional approach to the vibration-rotation problem is based on application of perturbation theory to a zeroth-order harmonic oscillator plus rigid rotor model appropriate for small-amplitude oscillations.⁵ Highly excited states typically involve large-amplitude nuclear excursions from equilibrium, a situation which renders low-order perturbation treatments inadequate. In addition, generalized Fermi resonances between modes signal the local failure of nondegenerate perturbation theory and require special treatment.⁵

In principle, a variational solution of Schrodinger's equation for coupled anharmonic nuclear motion (in the Born-Oppenheimer approximation⁶) will provide accurate energies and wave functions for highly excited states.⁷ In practice, it is extremely difficult, if not impossible, to obtain accurate quantum dynamics or highly excited energy levels and eigenstates for anharmonic multimode molecules, due to the extremely large number of basis functions required, which increases exponentially with the number of modes N .⁷ Moreover, if vibration-rotation levels for large values of the total angular momentum J are required, the size of the appropriate secular matrix increases linearly with J . Practical difficulties with conventional variational approaches are apparent, for example, in the case of triatomics such as H_3^+ and its isotopomers,⁸ which exhibit large-amplitude nuclear motions and strong rotation-vibration coupling for moderate vibrational excitation.^{8,9} It is therefore imperative to develop other approaches for the calculation of highly excited vibration and vibration-rotation levels in polyatomics.

As alternatives to exact quantum variational methods,⁷ dynamical approximations such as the self-consistent field approach¹⁰ or adiabatic approximation¹¹ have been investigated. In the past few years, there has also been intense interest in the application of semiclassical quantization techniques to determine bound states in nonseparable multidimensional systems.¹² These methods

utilize information from classical mechanics (e.g., trajectories, generating functions for canonical transformations) to obtain quantum mechanical quantities such as energy levels and wave functions.¹³ (We note also that semiclassical methods are useful for defining ensembles of initial trajectories and final quantum number "bins" in quasi-classical trajectory studies of inelastic and reactive collisions involving anharmonic polyatomics.) The present article describes some of our recent work in this active field.

Much of the recent activity in semiclassical quantization of multidimensional systems can be viewed as a fulfillment of the program of the Old Quantum Theory¹⁴ in the light of recent fundamental advances in classical mechanics and nonlinear dynamics.¹⁵ Historically,¹⁶ the first quantization condition appeared in Bohr's treatment of the hydrogen atom, where quantization

(1) Dai, H. L.; Korpa, C. L.; Kinsey, J. L.; Field, R. W. *J. Chem. Phys.* **1985**, *82*, 1688. Abrahamson, E.; Field, R. W.; Imre, D.; Innes, K. K.; Kinsey, J. L. *J. Chem. Phys.* **1985**, *83*, 458. Sundberg, R. L.; Abrahamson, E.; Kinsey, J. L.; Field, R. W. *J. Chem. Phys.* **1985**, *83*, 466. Garland, N. G.; Lee, E. K. C. *J. Chem. Phys.* **1986**, *84*, 28.

(2) Crim, F. F. *Annu. Rev. Phys. Chem.* **1984**, *35*, 657. Moore, C. B.; Weissbar, J. C. *Annu. Rev. Phys. Chem.* **1983**, *34*, 525. Lawrance, W. D.; Moore, C. B.; Hrvoje, P. *Science* **1985**, *227*, 895. Beulow, S.; Noble, M.; Radhakrishnan, G.; Reisler, H.; Wittig, C.; Hancock, G. *J. Phys. Chem.* **1986**, *90*, 1015. Janda, K. C. *Adv. Chem. Phys.* **1985**, *60*, 201. Miller, R. E. *J. Phys. Chem.* **1986**, *90*, 3301.

(3) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*; Pergamon: New York, 1977.

(4) Heller, E. J. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 141. Miller, W. H. *Science* **1986**, *233*, 171.

(5) Papoušek, D.; Aliev, M. R. *Molecular Vibrational-Rotational Spectra*; Elsevier: New York, 1982.

(6) Koppel, H.; Domcke, W.; Cederbaum, L. S. *Adv. Chem. Phys.* **1984**, *57*, 59. Whetten, R. L.; Ezra, G. S.; Grant, E. R. *Annu. Rev. Phys. Chem.* **1985**, *36*, 277.

(7) Carney, G. D.; Sprandel, L. L.; Kern, C. W. *Adv. Chem. Phys.* **1978**, *37*, 305.

(8) Tennyson, J.; Sutcliffe, B. T. *Mol. Phys.* **1986**, *58*, 1067.

(9) Carrington, A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1089. Tennyson, J.; Sutcliffe, B. T. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1151.

(10) Ratner, M. A.; Gerber, R. B. *J. Phys. Chem.* **1986**, *90*, 20. Bowman, J. M. *Acc. Chem. Res.* **1986**, *19*, 202.

(11) Ezra, G. S. *Chem. Phys. Lett.* **1983**, *101*, 259. Johnson, B. R.; Reinhardt, W. P. *J. Chem. Phys.* **1986**, *85*, 4538 and references therein.

(12) (a) Percival, I. C. *Adv. Chem. Phys.* **1977**, *36*, 1. (b) Noid, D. W.; Koszykowski, M. L.; Marcus, R. A. *Annu. Rev. Phys. Chem.* **1981**, *32*, 267. (c) Reinhardt, W. P., In *The Mathematical Analysis of Physical Systems*; Mickens, R., Ed.; Van Nostrand: New York, 1984.

(13) Davis, M. J.; Heller, E. J. *J. Chem. Phys.* **1980**, *75*, 3916. Knudson, S. K.; Delos, J. B.; Bloom, B. J. *J. Chem. Phys.* **1985**, *83*, 5703. Knudson, S. K.; Delos, J. B.; Noid, D. W. *J. Chem. Phys.* **1986**, *84*, 6886.

(14) ter Haar, D. *The Old Quantum Theory*; Pergamon: Oxford, U.K., 1967.

(15) Lichtenberg, A. J.; Lieberman, M. A. *Regular and Stochastic Motion*; Springer: New York, 1983.

(16) Jammer, M. *Conceptual Foundations of Quantum Mechanics*; McGraw-Hill: New York, 1966. Mehra, J.; Rechenberg, H. *The Historical Development of Quantum Mechanics*; Springer: New York, 1982; Vol. I.

† Alfred P. Sloan Foundation Fellow.

† Mathematical Sciences Institute Fellow.

of electronic angular momentum around the nucleus was invoked to derive the hydrogenic spectrum. A generalization of Bohr's prescription was sought by Ehrenfest¹⁷ who, arguing that reversible (adiabatic) transformations transformed allowed motions into allowed motions, suggested that the so-called adiabatic invariants or *actions* were appropriate quantities for quantization. Such a procedure could be straightforwardly implemented only for one-dimensional or separable multidimensional systems, leading to the well-known Bohr–Wilson–Sommerfeld quantization conditions.¹⁶ The latter quantization conditions were subsequently justified after the emergence of wave mechanics through the short-wavelength WKB approximation to solutions of the Schrodinger equation for separable systems.³ The quantization of *nonseparable* multidimensional systems (for example, multi-electron atoms), however, clearly presented fundamental difficulties for the Old Quantum Theory. Practical procedures for the determination of good action variables in multidimensional systems were proposed by Born,¹⁸ who adopted the methods of canonical perturbation theory from celestial mechanics. Nevertheless, in their highest state of development these methods were unable to effect a quantization of the helium atom,¹⁹ the well-known failure of the Old Quantum Theory (for recent work on this venerable problem, see ref 20).

In the remarkable analysis of Einstein,²¹ it was recognized that, for quasi-periodic trajectories, quantization of $\oint p \, dq$ along topologically distinct paths on the invariant trajectory manifold (invariant torus²²) constituted a properly coordinate-independent quantization procedure for multidimensional systems. Einstein also noted that the existence of non-quasi-periodic, chaotic motions (as found in the 3-body problem by Poincaré²³) rendered the canonical quantization of good action variables inapplicable. The deep problem of the nature of quantum–classical correspondence in the irregular regime remains essentially unsolved up to the present,²⁴ although there have been successful efforts to quantize ergodic²⁵ and mixing²⁶ systems. (Both classical perturbation theory^{27,28} and the method of adiabatic switching²⁹ have been used to quantize coupled oscillator potentials in the irregular regime, cf. section IV.)

The work of Keller,³⁰ in which Einstein's canonical quantization conditions for quasi-periodic motions were rederived by imposing a single-valuedness condition on the multidimensional analogue of the WKB wave function, rekindled interest in the problem (for a historical account, see ref 31). It is now customary to refer to the EBK (Einstein,²¹ Brillouin,³² Keller³⁰) quantization conditions for good action variables. Implementation of EBK quantization for multidimensional systems became feasible with the availability of computers to provide exact numerical solutions to the classical equations of motion, and Marcus and co-workers were the first to apply the method to potentials of chemical in-

terest³³ (for historical comments, see ref 34). There has subsequently been an enormous amount of work in this area.³⁵

The modern mathematical formulation of semiclassical theory for multidimensional systems is due to Maslov,³⁶ and accessible accounts are available in the reviews of Percival^{12a} and Delos.³⁷ (See also the work of Littlejohn³⁸ on symplectically invariant wavepacket methods.)

While it is apparent that semiclassical methods hold great promise for the calculation of properties of excited states of polyatomic molecules, there are formidable technical difficulties to be overcome, which are intimately associated with the need for a deeper understanding of the phase space structure of classical nonlinear systems. The focus of the present article is on some recent developments in the semiclassical quantization of multidimensional systems of chemical interest. We discuss quantization of multimode and resonant systems using the Fourier transform method^{39–42} and operator-based perturbation theory,^{43–45} quantization in the multiresonant and chaotic regimes using algebraic quantization^{44,46} and resummation methods,^{47,48} and application of unitary group techniques to the description of resonant dynamics.⁴⁹ In keeping with the spirit of these feature articles, we make no attempt to be comprehensive (extensive references to earlier work are provided in ref 35, 39, and 40) but focus instead on the contributions of our own research group. In particular, we shall not discuss the many recent applications of the method of adiabatic switching,²⁹ which is the practical realization of Ehrenfest's idea¹⁷ described above, or associated fundamental studies of the validity of the principle of adiabatic invariance.⁵⁰ This topic has recently been reviewed by Reinhardt.⁵¹ We note, however, that a comprehensive review of semiclassical methods for calculation of molecular properties is in preparation.³⁵

To provide some background and motivation, we briefly discuss the significance of classical *resonances* for molecular spectra and dynamics in section II, together with the problems resonant motion poses for semiclassical quantization. In section III we review the Fourier transform quantization approach and its application to multimode and resonant systems. Section IV discusses the use of operator-based classical perturbation theory as an efficient quantization method in the multimode case. Combining perturbation theory with algebraic quantization and/or resummation techniques, it is possible to quantize systems in the multiply resonant and/or chaotic regimes. In section V, we consider recent progress in the application of unitary group methods to coupled oscillator problems. Concluding remarks are given in section VI.

(17) Ehrenfest, P. *Philos. Mag.* **1917**, *33*, 500.

(18) Born, M. *Mechanics of the Atom*; Ungar: New York, 1960.

(19) Kramers, H. A. *Z. Phys.* **1923**, *13*, 312.

(20) Leopold, J. G.; Percival, I. C.; Tworowski, A. S. *J. Phys. B* **1980**, *13*, 1028. Leopold, J. G.; Percival, I. C. *J. Phys. B* **1980**, *13*, 1037. Coveney, P. V.; Child, M. S. *J. Phys. B* **1984**, *17*, 319. Solovov, E. A. *Sov. Phys.* **1985**, *62*, 1148. Wiesenberger, G. E.; Noid, D. W.; Delos, J. B. *Chem. Phys. Lett.* **1985**, *118*, 72.

(21) Einstein, A. *Verh. Dtsch. Ges.* **1917**, *19*, 82. An English translation by C. Jaffe is available as JILA Report No. 116, University of Colorado, Boulder, CO.

(22) Arnold, V. I. *Mathematical Methods of Classical Mechanics*; Springer: New York, 1978.

(23) Poincaré, H. *Les Methodes Nouvelles de la Mechanique Celeste*; Dover: New York, 1957; Vol. I–III.

(24) Berry, M. V. In *Chaotic Behavior of Deterministic Systems*; Gerard, I., Helleman, R. H. G., Stora, R., Eds.; North-Holland: New York, 1983.

(25) Gutzwiller, M. C. *Physica D* **1982**, *5*, 183.

(26) Berry, M. V. *Ann. Phys.* **1980**, *131*, 163.

(27) Swimm, R. T.; Delos, J. J. *Chem. Phys.* **1979**, *71*, 1706.

(28) Jaffe, C.; Reinhardt, W. P. *J. Chem. Phys.* **1979**, *71*, 1862.

(29) (a) Solovov, E. A. *Sov. Phys. JETP* **1978**, *48*, 635. (b) Skodje, R. T.; Borondo, F.; Reinhardt, W. P. *J. Chem. Phys.* **1985**, *82*, 4611. (c) Johnson, B. R. *J. Chem. Phys.* **1985**, *83*, 1204.

(30) Keller, J. B. *Ann. Phys.* **1958**, *4*, 180.

(31) Keller, J. B. *SIAM Rev.* **1985**, *27*, 485.

(32) Brillouin, M. L. *J. Phys.* **1926**, *7*, 353.

(33) Marcus, R. A. *Discuss. Faraday Soc.* **1973**, *55*, 34. Eastes, W.; Marcus, R. A. *J. Chem. Phys.* **1974**, *61*, 4301. Noid, D. W.; Marcus, R. A. *J. Chem. Phys.* **1975**, *62*, 2119. See also: Chapman, S.; Garrett, B. C.; Miller, W. H. *J. Chem. Phys.* **1976**, *64*, 502.

(34) Marcus, R. A. *J. Phys. Chem.* **1986**, *90*, 3460.

(35) Ezra, G. S.; Martens, C. C.; Fried, L. E. *Chem. Rev.*, manuscript in preparation.

(36) Maslov, V. P.; Fedoriuk, M. V. *Semiclassical Approximation in Quantum Mechanics*; Reidel: Dordrecht, 1981.

(37) Delos, J. B. *Adv. Chem. Phys.* **1986**, *65*, 161.

(38) Littlejohn, R. *Phys. Rep.* **1986**, *138*, 193.

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

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

(41) Eaker, C. W.; Schatz, G. C.; DeLeon, N.; Heller, E. J. *J. Chem. Phys.* **1984**, *81*, 5913.

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

(43) Fried, L. E.; Ezra, G. S. *J. Comput. Chem.*, in press.

(44) Fried, L. E.; Ezra, G. S. *J. Chem. Phys.*, in press.

(45) Sibert III, E. L. *Chem. Phys. Lett.* **1986**, *128*, 287.

(46) Robnik, M. *J. Phys. A* **1984**, *17*, 109.

(47) Fried, L. E.; Ezra, G. S., manuscript in preparation.

(48) Farrelly, D.; Uzer, T. *J. Chem. Phys.* **1986**, *85*, 308. See also: Shirts, R. B.; Reinhardt, W. P. *J. Chem. Phys.* **1982**, *77*, 5204.

(49) Martens, C. C.; Ezra, G. S. *J. Chem. Phys.*, in press.

(50) Dana, I.; Reinhardt, W. P. preprint. Tennyson, J. L.; Cary, J. R.; Escande, D. F. *Phys. Rev. Lett.* **1986**, *56*, 2117. Hannay, J. H. *J. Phys. A* **1986**, *A19*, L1067.

(51) Reinhardt, W. P. *Adv. Chem. Phys.*, in press.

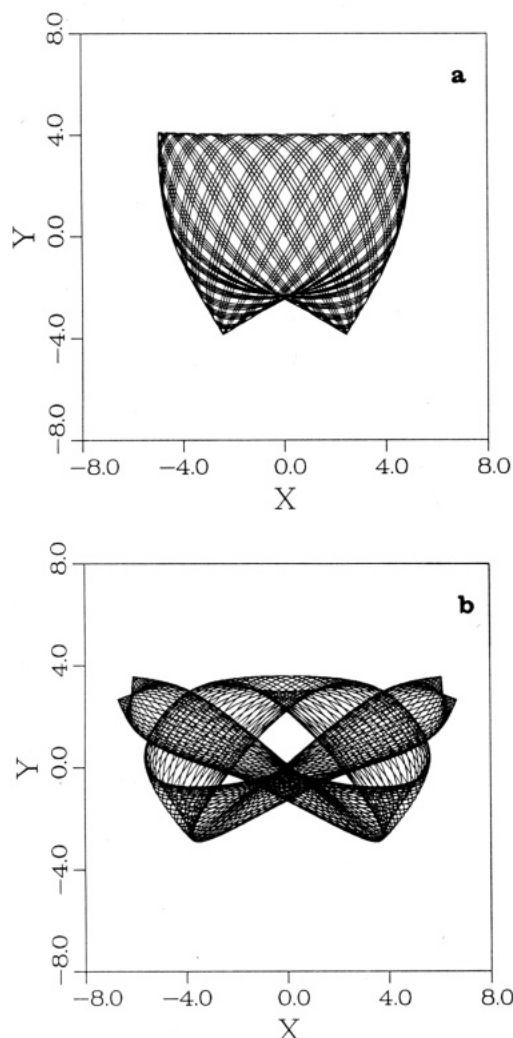


Figure 1. Quasi-periodic trajectories for the 2-mode Barbanis potential treated in ref 40, 53, and 54: (a) nonresonant trajectory at energy $E = 16.504$; (b) 3:4 resonant trajectory at $E = 16.343$.

II. On the Importance of Resonances

In the present context, the term "resonance" refers to a local frequency commensurability condition of the form $\mathbf{m} \cdot \boldsymbol{\omega} = 0$ (a generalized classical Fermi resonance⁵²), where, for a system of N degrees of freedom, $\boldsymbol{\omega}^0(\mathbf{I}) = \partial H_0(\mathbf{I})/\partial \mathbf{I}$ is the vector of N zeroth-order fundamental frequencies, \mathbf{I} is a vector of N zeroth-order action variables, H_0 is the unperturbed reference Hamiltonian (e.g., for the case of molecular vibrations, usually a set of uncoupled normal mode harmonic oscillators), and \mathbf{m} is a vector of N integers. It has long been known that resonances have a profound effect on the phase space structure of nonseparable systems, rendering resonant zeroth-order invariant tori unstable with respect to small perturbations.¹⁵ At the most fundamental level, the ubiquity of resonances in phase space is responsible for the divergence of canonical classical perturbation theory (the small-denominator problem¹⁵). Qualitatively, resonances lead to gross changes in the appearance ("topology") of configuration space projections of invariant tori (if they exist¹⁵), as illustrated in Figure 1. Figure 1a shows a trajectory for the 2-mode model Hamiltonian treated in ref 40, 53, and 54; it is continuously deformable into a rectangular boxlike³³ trajectory characteristic of an uncoupled harmonic oscillator and is therefore nonresonant. The trajectory of Figure 1b, on the other hand, clearly *cannot* be deformed into a boxlike trajectory and is thus recognized as the

configuration space projection of a resonant torus. From Figure 1b, it can be seen that a point on the resonant trajectory makes (approximately) three oscillations in the x direction for every four in the y direction, implying an underlying frequency commensurability $4\omega_x = 3\omega_y$. We therefore refer in this case to a 3:4 resonance and in general to $m:n$ resonances for 2 degree of freedom systems. Note that both trajectories shown in Figure 1 are quasi-periodic.

Why are low-order, i.e., small m and n , resonances such as that shown in Figure 1b of importance for the semiclassical study of molecular spectra and dynamics? From the point of view of nonlinear mechanics, isolated classical resonances lead to the appearance of localized stochastic motions associated with the existence of homoclinic oscillations,¹⁵ while the criterion of overlapping primary resonances has been used to give a rough estimate of the onset of global classical chaos.⁵⁵ For resonant tori, zeroth-order (e.g., normal mode) actions are no longer even approximately conserved along the trajectory,¹⁵ even when the latter is quasi-periodic. Resonant tori therefore correspond to stable patterns of motion for which there is extensive energy flow between the zeroth-order modes. Important examples abound (see ref 40 and references therein). For instance, the transition between normal- and local-mode behavior in ABA triatomics,⁵⁶ dihalomethanes,⁵⁷ and formaldehyde⁵⁸ has been studied as the result of an isolated nonlinear resonance: when viewed from a local-mode perspective, normal-mode motions correspond to pronounced energy flow between the zeroth-order bond modes. A 2:1 bend/stretch (Fermi⁵²) resonance between the CH bond stretch and the CH wag has been identified as the primary mechanism for rapid energy flow out of excited CH bonds in benzene and is an essential first step in the explanation of apparent homogeneous experimental overtone line widths⁵⁹ proposed by Sibert et al.⁶⁰ (Recent studies have shown that initial rapid CH energy decay rates are sensitive to the form of potential coupling included in the Hamiltonian⁶¹). 2:1 bend-rotation resonances have been shown to lead to extensive vibration-rotation energy flow in classical trajectory studies on rigid bender models⁶² and realistic triatomics.⁶³ So-called sequential nonlinear resonances provide a mechanism for irreversible energy decay in multimode systems.⁶⁴ Cantori,⁶⁵ which are invariant sets characterized by highly irrational or *antiresonant* frequency ratios,⁶⁶ are the vestiges of the most robust invariant tori of the uncoupled system and have been found to be bottlenecks to intramolecular energy flow in 2-mode models of collinear OCS⁶⁷ and HeI₂.⁶⁸

Resonant regions of phase space can be large enough to support quantum states (see Figure 2a), and the underlying classical resonances can dominate the morphology of the associated quantum wave functions.⁵⁴ The correspondence can be seen particularly clearly by using a quantum mechanical phase space representation, such as the Husimi transform⁶⁹ (cf. Figure 2b,c).

(55) Chirikov, B. V. *Phys. Rep.* **1979**, 52, 263.

(56) Sibert III, E. L.; Hynes, J. T.; Reinhardt, W. P. *J. Chem. Phys.* **1982**, 77, 3583, 3585. Kellman, M. E. *Chem. Phys. Lett.* **1985**, 113, 489; *J. Chem. Phys.* **1985**, 83, 3843.

(57) Jaffe, C.; Brumer, P. *J. Chem. Phys.* **1980**, 73, 5646.

(58) Gray, S. K.; Child, M. S. *Mol. Phys.* **1984**, 53, 961.

(59) Reddy, K. V.; Heller, D. F.; Berry, M. J. *J. Chem. Phys.* **1982**, 76, 2814.

(60) Sibert, E. L.; Reinhardt, W. P.; Hynes, J. T. *J. Chem. Phys.* **1984**, 81, 1115. Sibert, E. L.; Hynes, J. T.; Reinhardt, W. P. *J. Chem. Phys.* **1984**, 81, 1135.

(61) (a) Lu, D.-H.; Hase, W. L.; Wolf, R. J. *J. Chem. Phys.* **1986**, 85, 4422. (b) Garcia-Ayllon, A.; Santamaria, J.; Ezra, G. S., work in progress.

(62) (a) Frederick, J.; McClelland, G. M. *J. Chem. Phys.* **1986**, 84, 4347. (b) Ezra, G. S. *Chem. Phys. Lett.* **1986**, 127, 492.

(63) Frederick, J.; McClelland, G. M.; Brumer, P. *J. Chem. Phys.* **1985**, 83, 190.

(64) Hutchinson, J. S.; Reinhardt, W. P.; Hynes, J. T. *J. Chem. Phys.* **1983**, 79, 4247.

(65) (a) MacKay, R. S.; Meiss, J. D.; Percival, I. C. *Physica D (Amsterdam)* **1984**, 13D, 55. (b) Bensimon, D.; Kadanoff, L. P. *Physica D (Amsterdam)* **1984**, 13D, 82.

(66) Greene, J. M. *J. Math. Phys.* **1979**, 20, 1183.

(67) Davis, M. J. *J. Chem. Phys.* **1985**, 83, 1016.

(68) Davis, M. J.; Gray, S. K. *J. Chem. Phys.* **1986**, 84, 5389. Gray, S. K.; Rice, S. A.; Davis, M. J. *J. Phys. Chem.* **1986**, 90, 3470.

(52) Herzberg, G. *Molecular Spectra and Structure*; Van Nostrand: New York, 1945; Vol. II.

(53) Sorbie, K.; Handy, N. *Mol. Phys.* **1976**, 32, 1327; **1977**, 33, 1319.

(54) DeLeon, N.; Davis, M. J.; Heller, E. J. *J. Chem. Phys.* **1984**, 80, 794.

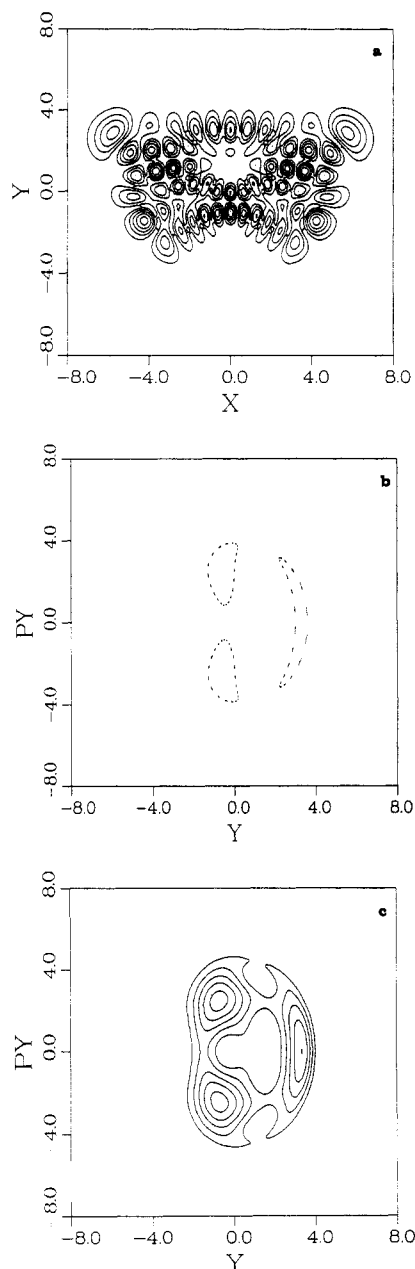


Figure 2. (a) Quantum mechanical wave function for state number 62 of the 2-mode Barbanis potential treated in ref 40, 53, and 54. The eigenstate has energy $E = 16.351$ and corresponds to the resonant quantizing trajectory of Figure 1b. (b) Surface of section for the resonant quantizing trajectory of Figure 1b. (c) Section through the quantum phase space density (Husimi transform) of the eigenstate shown in Figure 2a. This plot should be compared with Figure 2b.

Resonant quantum states of the type shown in Figure 2a can act as bottlenecks to multiphoton pumping up a vibrational ladder:⁷⁰ transition moments between nonresonant and resonant states having different nodal structures are in general smaller than those between nonresonant states, and zeroth-order selection rules are violated.

Nonresonant classical systems with a small number of degrees of freedom can be semiclassically quantized by using any of the several methods developed during the past decade.¹² In contrast, the complicated topology of resonant as compared to boxlike trajectories poses some severe practical difficulties for the imposition of the EBK quantization conditions. Methods recently developed in our laboratory, which are described below, enable resonant motion of arbitrary topology to be quantized. For

discussion of the many other approaches to quantization of resonances, we refer to ref 35 and 40.

III. Fourier Method for EBK Quantization

The major practical difficulty in implementing semiclassical quantization for multidimensional systems involves the calculation (and possible nonexistence¹⁵) of good action variables and imposition of the appropriate quantization conditions.¹² In this section we describe recent progress on this problem using the Fourier approach.³⁹⁻⁴² This method has proved to be a general and efficient technique for quantizing both nonresonant and resonant states of multimode Hamiltonians and has provided considerable insight into the phase space structure of such systems. The Fourier transform approach to EBK quantization is based on the fact that, for motion in quasi-periodic (regular) regions of phase space, coordinates and momenta can be expanded as convergent Fourier series in the angle variables θ

$$q(\theta, J) = \sum_k q_k(J) e^{ik \cdot \theta} \quad (1a)$$

$$p(\theta, J) = \sum_k p_k(J) e^{ik \cdot \theta} \quad (1b)$$

where the angle variables evolve with time as follows

$$\theta_\alpha = \omega_\alpha t + \theta_\alpha^0 \quad \alpha = 1, \dots, N \quad (2)$$

with ω_α the α th fundamental frequency

$$\omega_\alpha = \partial H(J) / \partial J_\alpha \quad (3)$$

Note that the J are good action variables for the full Hamiltonian H and are assumed to exist, so that $H = H(J)$ (at least locally). The ω are then the *actual* (as opposed to zeroth order) fundamental frequencies of the motion: for an N -mode system, there are N fundamentals ω_α , $\alpha = 1, \dots, N$, but these are *not* necessarily in direct correspondence with the zeroth-order fundamentals ω^0 . This is the case for resonant trajectories, as will be seen below.

By virtue of the expansion of eq 1, the action integrals

$$J_\alpha = 1/(2\pi) \int_0^{2\pi} d\theta_\alpha p \cdot (\partial q / \partial \theta_\alpha) \quad (4)$$

can be expressed directly in terms of the Fourier coefficients $\{q_k, p_k\}$

$$J_\alpha = \sum_k i k_\alpha p_k^* \cdot q_k \quad (5)$$

This result simplifies in the case that the Hamiltonian H is of the form

$$H = \sum_j \frac{1}{2} p_j^2 + V(q) \quad (6)$$

(for example, harmonic oscillators coupled by an anharmonic perturbation) to

$$J_\alpha = \sum_{\alpha'} G_{\alpha\alpha'} \omega_{\alpha'} \quad (7a)$$

with

$$G_{\alpha\alpha'} = \sum_k k_\alpha |q_k|^2 k_{\alpha'} \quad (7b)$$

A 1-dimensional version of this remarkable formula was given by Heisenberg.⁷¹ The multidimensional case was derived by Percival⁷² in the context of a variational theory of invariant tori and has since been rederived several times.^{41,73} Percival proposed an iterative scheme for determination of the Fourier coefficients $\{q_k, p_k\}$.⁷⁴ However, the result takes on its full significance when it is realized^{39,41} that the required Fourier coefficients can be determined directly by Fourier transformation of trajectories.

(71) Heisenberg, W. *Z. Phys.* **1925**, 33, 879.

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

(73) (a) Binney, J.; Spergel, D. *Astrophys. J.* **1982**, 252, 308; *Mon. Not. R. Astron. Soc.* **1984**, 206, 159. (b) Klein, A.; Li, C.-t. *J. Math. Phys.* **1979**, 20, 572.

(74) Percival, I. C.; Pomphrey, N. *Mol. Phys.* **1976**, 31, 97; *J. Phys. B* **1976**, 9, 3131.

(69) Martens, C. C.; Davis, M. J.; Ezra, G. S., manuscript in preparation.
(70) Brown, R. C.; Wyatt, R. E. *J. Chem. Phys.* **1985**, 82, 4777.

TABLE I: Energy Eigenvalues for the Four-Dimensional Hamiltonian of ref 29a

N_1	N_2	N_3	N_4	E_R^a	E_W^b	E_{SPSC}^c	E_S^d	E_{AS}^e	E_{FT}^f	E_{QM}^g
0	0	0	0	2.2565	2.2533	2.2565	2.2566	2.2567	2.2562	2.2558
1	0	0	0	2.9479	2.9445	2.9479	2.9484	2.9479	2.9492	2.9471
0	0	1	0	3.2455	3.2422	3.2455	3.2463	3.2465	3.2465	3.2439
0	1	0	0	3.5347	3.5313	3.5347	3.5356	3.5350	3.5359	3.5208
2	0	0	0	3.6358	3.6323	3.6358				
0	0	0	1	3.7805	3.7773	3.7805	3.7808	3.7809	3.7808	3.6371
1	0	1	0	3.9365	3.9331	3.9365				
1	1	0	0	4.2141	4.2105	4.2140				
0	0	2	0	4.2298	4.2263	4.2299				
⋮	⋮	⋮	⋮	⋮	⋮	⋮				
0	1	1	1	6.0353	6.0316	6.0353				
0	3	0	0	6.0511	6.0470	6.0511				
2	2	0	0	6.1299	6.1257	6.1297				
2	0	1	1	6.1440	6.1403	6.1440				
1	1	2	0	6.1658	6.1618	6.1658				
0	0	4	0	6.1826	6.1787	6.1827				
4	1	0	0	6.2301	6.2258	6.2299				
0	0	1	2	6.2807	6.2773	6.2807				
3	0	2	0	6.2905	6.2865	6.2906				
0	2	0	1	6.3244	6.3206	6.3244				

^a Eighth-order normal form, using Robnik's approximation (ref 44). ^b Weyl quantization of normal form in (a) (ref 44). ^c Symmetry preserving semiclassical (SPSC) quantization normal form of (a) (ref 44). ^d Semiclassical quantization of a second-order nonresonant normal form by Saini (ref 93). ^e Adiabatic switching (ref 29b). ^f Fourier transform method (ref 39). ^g Quantum mechanical eigenvalues, using a finite difference technique (ref 77).

Equation 7 therefore suggests the following quantization scheme (we consider Hamiltonians of the form eq 6, although it is straightforward to implement the general result (5) for systems with nontrivial G -matrices⁷⁵):

- Run a trajectory to obtain coordinate time series $\{q(t)\}$.
- Using efficient fast Fourier transform routines, obtain the Fourier coefficients $\{q_k\}$. This involves (i) identification of the fundamental frequencies $\{\omega_\alpha\}$, and (ii) accurate determination of the amplitudes $|q_k^i|$.
- Calculate N actions $\{J_\alpha\}$.
- Either, (i) update the initial conditions until the EBK quantization conditions

$$J_\alpha^Q = (n_\alpha + 1/4\mu_\alpha)\hbar \quad (8)$$

are satisfied (\mathbf{n} is a vector of integer quantum numbers, μ is a vector of Maslov indices³⁶), or (ii) linearly extrapolate to obtain the energy of the quantum state⁷⁶

$$E(J^Q) \sim E_{\text{traj}} + \omega \cdot (J^Q - J) \quad (9)$$

This scheme works.^{39,40} The key step needed to make it a practical method is a stable and accurate means of calculating frequencies and Fourier amplitudes using fast Fourier transforms: this numerical problem⁴¹ has been solved by using a special windowing technique.³⁹

An important point concerning the Fourier quantization method is that the result (7) giving the good actions in terms of coordinate Fourier components holds regardless of trajectory topology and so can be applied to both nonresonant³⁹ and resonant⁴⁰ motions. The relation is also invariant with respect to canonical transformations of coordinates $\{q, p\}$ (to $\{Q, P\}$, say), provided that the new coordinates and momenta $\{Q, P\}$ are periodic functions of the good angles.

For nonresonant trajectories, there are by definition no commensurabilities between normal-mode frequencies, and assignment of the classical power spectrum is straightforward. In Figure 3a, we show coordinate power spectra obtained for the 2-dimensional nonresonant trajectory of Figure 1a. The largest peaks in the individual coordinate spectra are each assigned to nonresonant fundamentals, $\omega_1^{\text{nr}} = 0.865$ and $\omega_2^{\text{nr}} = 1.221$, whose values are close to the zeroth-order frequencies $\omega_x^0 = 0.949$ and $\omega_y^0 = 1.265$, respectively. Since the x and y modes are coupled by a perturbation, combination and overtone peaks appear in the spectrum

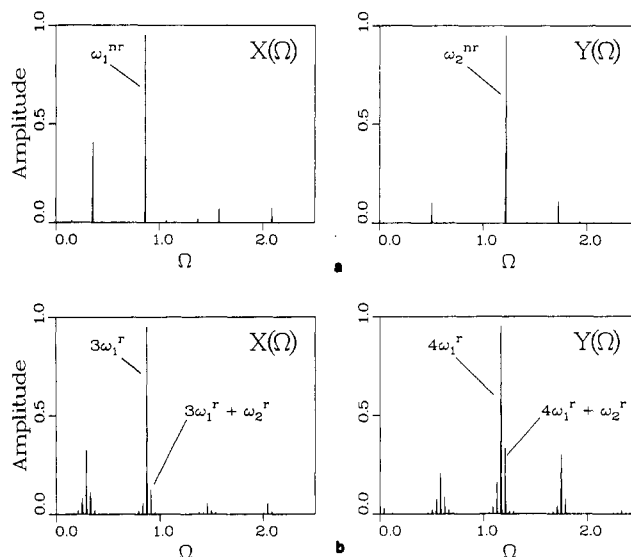


Figure 3. Coordinate power spectra for the trajectories shown in Figure 1: (a) nonresonant; the nonresonant assignment of fundamental frequencies is shown; (b) resonant; the resonant assignment of fundamental frequencies is shown.

at frequencies $\Omega = \mathbf{k} \cdot \omega$, where \mathbf{k} is a vector of integers.

The Fourier method has been applied to quantize a variety of nonresonant systems with up to 4 degrees of freedom.³⁹ In Table I, we give a representative set of energy eigenvalues for the 4-mode system treated in ref 29b; quantal, adiabatic switching, and perturbation theory (see below) results are given for comparison. The FFT EBK energies are very accurate. (In fact, this system is resonant:³⁹ in order to apply the Fourier quantization method, it is necessary to resort to an interpolation or "resonance avoidance" procedure, cf. ref 29b.) The quantum eigenvalues of Neuberger and Noid,⁷⁷ obtained by using a grid method, are apparently not converged with respect to grid size.

For resonant motions, the normal-mode frequencies are "locked" into a fixed integer ratio, as can be seen in the coordinate spectra shown in Figure 3b for the 3:4 resonant trajectory of Figure 1b. A detailed analysis of coordinate power spectra for resonances in 2 degrees of freedom has been given.⁴⁰ In essence, for an $m:n$ resonance two new fundamental frequencies ω_1^r and ω_2^r appear

(75) Garcia-Ayllon, A.; Martens, C. C.; Santamaria, J.; Ezra, G. S., submitted for publication.

(76) DeLeon, N.; Heller, E. J. *J. Chem. Phys.* **1983**, *78*, 4005.

(77) Neuberger, J. W.; Noid, D. W., preprint.

in place of the nonresonant fundamentals, so that $\omega_1^r \sim \omega_x^0/m \sim \omega_y^0/n$ is the frequency of the $m:n$ periodic orbit at the center of the resonance, while ω_2^r is the frequency characteristic of the slow rotation of the trajectory around the resonant torus, and at the center of the resonance is just the stability frequency⁷⁸ of the periodic orbit. For the trajectory of Figure 1b, $\omega_1^r = 0.292$ and $\omega_2^r = 0.040$. The assignment of spectral peaks using the resonant fundamentals is given in Figure 3b. It can be seen that the peaks fall into characteristic clumps centered around multiples of the fundamental ω_1^r , reflecting a time scale separation of motion "along" and "around" the resonant torus. The Fourier method has been used to quantize systems with 1:1, 2:1, and 3:4 resonances; details are given in ref 40.

At present very little is known concerning the phase space structure of resonances in $N \geq 3$ mode Hamiltonians.^{79,84} The Fourier approach promises to be of great utility in studying and quantizing such systems.

Since it provides a direct route from trajectories to actions via the Fourier components, the Fourier method has great potential for obtaining highly excited vibrational states of small polyatomic molecules described by realistic potential surfaces.⁸⁰ Work on this problem is in progress. (Eaker and Schatz have combined the Fourier quantization scheme with the Sorbie-Handy dynamical approximation to obtain energy levels for several triatomic molecules.⁴²)

One caveat should be borne in mind, however: the Fourier approach for calculating good action variables will not work if the trajectory is chaotic. In that case, the Fourier transforms of long (several hundred periods) trajectories are "grassy",^{81a} and it is not possible to assign individual lines as combinations of a set of N fundamental frequencies. However, examination of coordinate power spectra of shorter segments (approximately 50 periods) of chaotic trajectories can provide valuable insight into the long-time dynamics (cf. ref 82). Typically, a variety of behavior is found. Such spectra can be grassy with many peaks (Figure 4a), reflecting a lack of regularity in the motion over the segment, or relatively clean and almost quasi-periodic in appearance (Figure 4b), corresponding to correlated or trapped motion (inside a resonance zone, for example). In this way, an intrinsic characterization of the phase space regions visited by a non-quasi-periodic trajectory can be obtained and long-time correlations in the dynamics elucidated.^{83,84}

The Fourier method is also being applied to the semiclassical quantization of rotation-vibration states.⁸⁵ Frederick and McClelland have considered the EBK and uniform quantization of rotation-bending states for a rigid bender model of H_2O ,⁸⁶ but no treatment of a full rotating-vibrating triatomic has been given. Such calculations for highly excited rotational states would be very helpful in interpreting spectra in systems such as H_3^+ ,⁹ for which quantum variational calculations are currently unable to obtain accurate rotation-vibration levels in the energy regime of interest.⁸ Insights gained from classical trajectory studies of vibration-rotation interactions of model systems⁶² are essential for successful quantization of vibration-rotation states. Use of the Augustin-Miller⁸⁷ representation of rotational motion leads to the full vibration-rotation problem having only one degree of

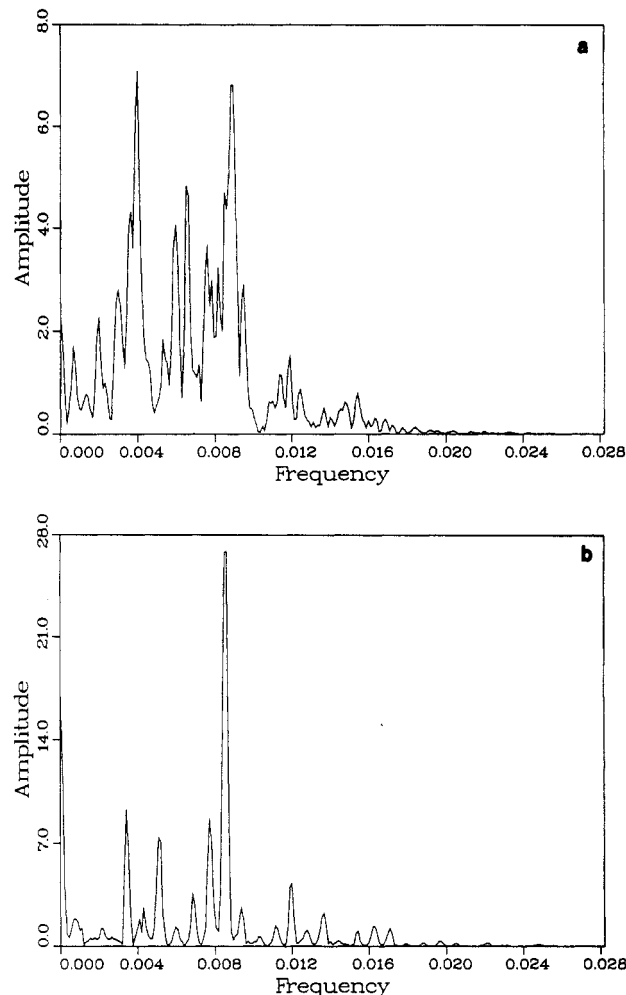


Figure 4. Coordinate power spectra for segments (1.38 ps) of a trajectory of the 3-dimensional OCS model of ref 83 with $E = 20000 \text{ cm}^{-1}$. (a) A segment with a "grassy" appearance, indicating a lack of correlated motion. (b) A segment with a relatively clean, almost quasi-periodic appearance, indicating trapping.

freedom more than the rotationless case. For example, a triatomic can be treated as a 4 degree of freedom system whose quantization is quite feasible.

In addition to providing an efficient route to calculation of actions, determination of the Fourier components of trajectories provides, via (1), the numerical transformation to good action and angle variables, the so-called "topological paths" on tori (cf. ref 40). Using the numerical transformation to good angle variables, it is possible to define an ensemble of points (initial conditions) uniformly distributed on a quantizing torus, as required, for example, for quasi-classical trajectory studies of molecular collisions.⁸⁸ Moreover, the transformation to angle variables is a direct parametrization of the "Lagrangian manifold" (torus) required to construct semiclassical wave functions in the theory of Maslov (ref 36, cf. also ref 37).

Thus far we have only considered the calculation of *primitive* semiclassical eigenvalues using the EBK quantization condition (8). A *uniform* quantization of the Henon-Heiles system has been carried out using the Fourier method to determine an effective resonance Hamiltonian; for details, see ref 89.

It should be noted that the work of Marcus and co-workers^{81a} initiated the use of coordinate power spectra as a diagnostic for quasi-periodic and chaotic motions, while approximate determination of transition frequencies and intensities^{81b,c} has also been made using Fourier transforms of the dipole moment autocorrelation function for trajectories run at *mean* actions. However,

(78) Whittaker, E. *A Treatise on the Analytical Dynamics of Particles and Rigid Bodies*; Dover: New York, 1944.

(79) Neshyba, S.; DeLeon, N., preprint.

(80) Murrell, J. N.; Carter, S.; Farantos, S.; Huxley, P.; Varandas, A. J. C. *Molecular Potential Energy Functions*; Wiley: New York, 1984.

(81) (a) Noid, D. W.; Koszykowski, M. L.; Marcus, R. A. *J. Chem. Phys.* **1977**, *67*, 404. (b) Koszykowski, M. L.; Noid, D. W.; Marcus, R. A. *J. Phys. Chem.* **1982**, *86*, 2113. (c) Wardlaw, D. M.; Noid, D. W.; Marcus, R. A. *J. Phys. Chem.* **1984**, *88*, 536.

(82) McDonald, J. D.; Marcus, R. A. *J. Chem. Phys.* **1976**, *65*, 2180.

(83) Carter, D.; Brumer, P. *J. Chem. Phys.* **1982**, *77*, 4208. Davis, M. J.; Wagner, A. *ACS Symp. Ser.* **1984**, *263*, 337.

(84) Martens, C. C.; Davis, M. J.; Ezra, G. S., work in progress.

(85) Sumpter, B. G.; Ezra, G. S., work in progress.

(86) Frederick, J.; McClelland, G. M. *J. Chem. Phys.* **1986**, *84*, 976. Frederick, J. *Chem. Phys. Lett.* **1986**, *131*, 60.

(87) Augustin, S. D.; Miller, W. H. *J. Chem. Phys.* **1974**, *61*, 3155.

(88) Schatz, G. C. In *Molecular Collision Dynamics*; Bowman, J. M., Ed.; Springer: New York, 1983.

(89) Martens, C. C.; Ezra, G. S. In *Tunneling*; Jortner, J., Pullman, B., Eds.; Reidel: Dordrecht, 1986.

the idea of using Fourier transforms to calculate actions directly was not discussed in these papers.

IV. Operator-Based Perturbation Theory

In this section we discuss a second, trajectory-independent, approach that has been developed as a practical tool for semiclassical quantization of multidimensional systems based on the use of high-order operator-based classical perturbation theory.^{43-45,47,48} The basic aim of the method is to find a canonical transformation to new variables in terms of which the full Hamiltonian H , considered to be perturbed with respect to the reference Hamiltonian H_0 , is (to given order in the perturbation strength) in as simple a form as possible. The problem of transforming a Hamiltonian into normal form, i.e., eliminating the effect of a perturbation, is of course the fundamental problem of mechanics.²³ In the absence of resonances, the normal form depends only on good actions, so that the equations of motion are trivially solved. The normalization algorithm of Birkhoff,^{90a} as modified by Gustavson^{90b} to treat the resonant case, has been applied to semiclassical quantization of molecules following the work of Swimm and Delos.²⁷ Once the transformation to good actions has been found, semiclassical energy levels can be calculated in a straightforward fashion by substituting quantizing values of the good actions (eq 8) into the Hamiltonian. For systems having exact or near resonances between zeroth-order frequencies, the transformed Hamiltonian will be a function of a minimal set of angle variables in addition to the good actions. A more elaborate uniform quantization procedure or matrix diagonalization is then necessary (see below).

Quantization via classical perturbation theory is in many respects complementary to the Fourier approach discussed in the previous section. One virtue of perturbation theory is that it yields global, analytical results for the transformed Hamiltonian as a function of the new actions. The method has achieved some unforeseen successes: in the uniform quantization of the Henon-Heiles system by Jaffe and Reinhardt²⁸ using the Birkhoff-Gustavson normal form,⁹⁰ it was found that accurate eigenvalues for highly excited vibrational states of a 2-mode system could be obtained *even when the underlying classical motion is chaotic*. The applicability of classical perturbation theory to obtain accurate semiclassical eigenvalues in the irregular regime is of both fundamental and practical significance, since it overcomes the restriction to the regular regime of many trajectory-based methods such as the Fourier quantization approach. As discussed by Reinhardt,⁹¹ use of finite-order perturbation theory effectively "smooths over" chaotic regions of phase space, if they are sufficiently small.

From a practical point of view, it is clear that application of the perturbation theory quantization method to realistic systems with 3 or more degrees of freedom would be desirable. Further study of the performance of the method in the presence of chaos would also be of interest. However, the need to keep track of the huge number of terms generated when carrying out classical perturbation theory to high order in multidimensional systems has hampered previous work along these lines.⁹² Low-order results,⁹³ on the other hand, are unlikely to be accurate at high energies or for very anharmonic systems.

To implement high-order classical perturbation theory for multidimensional systems efficiently, a special purpose numerical/algebraic manipulation program called PERTURB⁴³ has been developed. Details of the program have been given elsewhere.⁴³ Here we note only that it is written in C, has a very flexible modular structure, and makes extremely efficient use of CPU time and memory by dynamical allocation of storage and reuse of memory (dumping of intermediate expressions).

The program PERTURB is capable of implementing a variety of Lie-operator-based perturbation algorithms⁹⁴ to very high order.

These methods avoid the mixed variables (one old set, one new set) of conventional canonical perturbation theory¹⁸ and the associated functional inversion required to express new variables in terms of the old (cf. ref 28). Lie transform methods are currently being applied to a variety of physical problems.⁹⁵

One very powerful algorithm we have applied in our studies is due to Dragt and Finn.⁹⁶ This version of classical perturbation theory uses the exponential of a *Lie operator* (hence the term "operator-based" perturbation theory) to generate canonical coordinate transformations

$$Z(z) = e^F z \quad (10)$$

where z denotes the pair of old variables (I, ϕ) , Z denotes the pair of new variables (J, θ) , and F is the Lie operator associated with the function $f(z)$, defined by

$$F(\cdot) = \{f, \cdot\} \quad (11)$$

where $\{, \}$ is the Poisson bracket. It is most important to note that the *inverse* relationship is also given directly in terms of Lie operators:

$$z(Z) = e^{-F} Z \quad (12)$$

A key result is that a transformation of the form (12) leaves the Poisson bracket invariant⁹⁶ and is therefore canonical. Moreover, any canonical transformation continuously connected to the identity can be written as a (possibly infinite) sequence of transformations of the form (12).⁹⁶ The Hamiltonian in the new coordinate system, K , is given directly in terms of Lie operators as follows:

$$K(\theta, J) = e^F H(\phi, I) \quad (13)$$

In order to solve the problem of normalizing the Hamiltonian perturbatively, H must be written as a power series in a small parameter ϵ

$$H = \sum H_n \epsilon^n \quad (14)$$

where the reference Hamiltonian H_0 depends only on I . A series of canonical transformations is then introduced, each of which eliminates the dependence of the new Hamiltonian K on θ to one higher order in ϵ :

$$K = \dots \exp(\epsilon^3 F_3) \exp(\epsilon^2 F_2) \exp(\epsilon F_1) H \quad (15)$$

Defining H^k by

$$H^k \equiv \exp(\epsilon^k F_k) \dots \exp(\epsilon F_1) H \quad (16)$$

and expanding in powers of ϵ

$$H^k = \sum H_n^k \epsilon^n \quad (17)$$

enables explicit equations for the H_n^k to be obtained in terms of the generators f_k .^{94,96} The generators are chosen to simplify the transformed Hamiltonian to the maximum possible extent; in the absence of exact resonances, H_n^k can be chosen to be the angle-independent part of H^{k-1}_k .

The above procedure can be implemented to provide an efficient route to the calculation of semiclassical eigenvalues for 2- and 3-mode systems for which the frequencies ω^0 are sufficiently far from resonance.^{43,44} Attempting to make the transformed Hamiltonian completely independent of the angles results in the presence of denominators of the form $k \cdot \omega^0$ in the expressions for the generators f_k . This is the famous "small denominator problem", which is responsible for the eventual failure of the classical perturbation scheme. Resonances or near-resonances between zeroth-order frequencies cause the perturbation expansion ultimately to diverge;¹⁵ it is found that high-order terms oscillate wildly while increasing in magnitude (Figure 5) and are of little

(90) (a) Birkhoff, G. D. *Dynamical Systems*; A.M.S. Colloquium: New York, 1927; Vol. IX. (b) Gustavson, F. G. *Astron. J.* **1966**, 71, 670.

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

(92) Williams, R. D.; Koonin, S. E. *Nucl. Phys.* **1982**, A391, 72.

(93) Saini, S. *Chem. Phys. Lett.* **1986**, 125, 194.

(94) Cary, J. *Phys. Rep.* **1981**, 79, 129.

(95) Steinberg, S. *Lect. Notes Phys.* **1986**, 251, 45.

(96) Dragt, A. J.; Finn, J. M. *J. Math. Phys.* **1976**, 17, 2215; **1979**, 20, 2649.

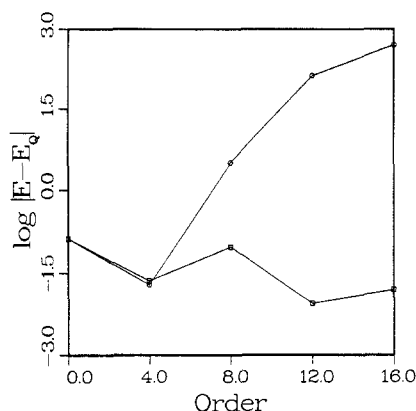


Figure 5. This plot illustrates the utility of resummation procedures for semiclassical quantization of nearly resonant systems. Plotted are unresummed (circles) and resummed (squares) values of the difference between the semiclassical and quantal eigenvalues for the (2,2) state of the near 1:1 resonant system of ref 48. Note the logarithmic scale. The rapid divergence of the unresummed eigenvalues is clearly seen, as is the relatively slow convergence of the resummed energy.

apparent significance or use. Moreover, the severity of the problem increases with the number of degrees of freedom, since the number of possible near-resonances rises rapidly with dimension.

It turns out, however, that there is useful information contained in the divergent perturbation expressions.^{44,47,48} By applying resummation procedures to the perturbation series, it is possible to extract accurate semiclassical eigenvalues for nearly resonant coupled oscillator systems.^{44,47,48} Such resummation procedures replace the divergent perturbation theory power series expansion by a better behaved function of the perturbation parameter. Pade,⁹⁷ Pade-Borel,⁹⁸ and a generalized Euler transform⁹⁹ methods have been tested so far,^{47,48} all with some success. (Note that an efficient program such as PERTURB is needed to carry out the perturbation expansion to high enough order to make resummation methods feasible for multimode systems.) In Table II, we present semiclassical eigenvalues for a near 1:1 resonant 2-mode system, obtained by using perturbation theory⁴⁴ together with Pade resummation.⁴⁸ Although the unresummed perturbation eigenvalues are clearly strongly divergent (see Figure 5), good agreement is obtained between the resummed energies and quantum mechanical results.⁴⁸

We may conclude from these studies that divergences arising from near-resonances can be tamed by use of resummation methods, rendering accurate calculations on realistic multimode systems feasible. Further work is in progress.

In the case that the reference Hamiltonian has an *exact* resonance, even resummed perturbation theory is not directly applicable. A different approach is then required: the transformed Hamiltonian K must be taken to be a function not only of a set of new actions but also of all angle combinations $\mathbf{k} \cdot \phi$ for which $\mathbf{k} \cdot \omega^0$ is either zero or less than some small threshold value (in the multiresonance case).⁴⁴ It is then necessary to perform a uniform quantization of the resulting angle-dependent Hamiltonian. Several approaches to this uniform quantization have been given. We have used the method of *algebraic quantization*,⁴⁶ in which the classical transformed Hamiltonian, expressed as a function of classical creation and annihilation operators, is mapped via a quantization rule (for example, the Weyl¹⁰⁰ rule) into a quantum mechanical operator. The resulting operator is then diagonalized in a suitable basis set. (Note that algebraic quantization is nonetheless a semiclassical method, since classical, rather than quantum, perturbation theory is used to derive the transformed Hamiltonian.) A key point is that the transformed Hamiltonian

TABLE II: Energy Eigenvalues for the Near 1:1 Resonant Hamiltonian of ref 48

N_1	N_2	E_R^a	E_W^b	E_{SPSC}^c	E_{Res}^d	E_{QM}^e
0	0	0.9996	0.9973	0.9996		1.0008
0	1	1.9852	1.9827	1.9853	1.99131	1.9868
1	0	1.9927	1.9900	1.9926	1.99881	1.9938
0	2	2.9415	2.9386	2.9417	3.13407	2.9435
1	1	2.9623	2.9592	2.9622	2.96664	2.9638
2	0	2.9964	2.9933	2.9964	3.00892	2.9973
0	3	3.8743	3.8708	3.8745	3.88497	3.8768
1	2	3.8927	3.8889	3.8926	3.94187	3.8946
2	1	3.9645	3.9607	3.9644	3.92306	3.9657
3	0	3.9955	3.9917	3.9954	4.01459	3.9959
0	4	4.7750	4.7705	4.7752	4.85963	4.7781
1	3	4.7905	4.7856	4.7903	4.90260	4.7931
2	2	4.8908	4.8862	4.8909	4.88360	4.8924
3	1	4.9563	4.9513	4.9560	4.90159	4.9568
4	0	4.9982	4.9937	4.9984	5.01108	4.9981

^a Algebraic quantization of a 12th-order normal form, using Robnik's rule (ref 44). ^b Algebraic quantization the same form as above, using the Weyl rule (ref 44). ^c AQ of the normal form in (a), using the SPSC rule (ref 44). ^d Resummation of a 12th-order nonresonant normal form using the epsilon algorithm (ref 48). ^e Quantum mechanical variational calculation (ref 44).

may possess a number of *invariants*, i.e., mutually commuting operators that commute with it. For example, in the case of a single exact resonance, there are $N - 1$ invariants linear in the actions (number operators). Since the basis functions must be simultaneous eigenfunctions of these invariants, the resulting Hamiltonian matrix will be block diagonal with finite blocks. This procedure has been discussed in some detail for the case of an exact resonance in a 2-dimensional system by Robnik⁴⁶ (using the Birkhoff-Gustavson normalization⁹⁰), who has also introduced an approximate version of the Weyl quantization rule to simplify calculations. We have generalized the method to treat nearly resonant terms and systems with more than two modes and have given a prescription for determining the linear invariants that label eigenstates resulting from the diagonalization.⁴⁴ We have also introduced a hybrid quantization rule that gives accurate values for quantum mechanical splittings while reducing to the EBK expression for nonresonant systems.⁴⁴

As the number of resonant or nearly resonant terms in the Hamiltonian increases, the number of invariants decreases until finally none remain. In that case, we are left with the problem of diagonalizing the transformed Hamiltonian in an infinite basis. Nevertheless, progress toward simplifying the Hamiltonian has been made even in this limit, as the transformed Hamiltonian is an effective operator in which all nonresonant interactions are eliminated to given order.

In Table III we give semiclassical eigenvalues for a 5-mode model system.^{29b} One exact and three near-resonances were included explicitly in the transformed Hamiltonian;⁴⁴ there was therefore a single invariant, resulting in a block diagonal Hamiltonian matrix. Even after inclusion of nearly resonant couplings, eighth-order perturbation theory results still exhibit a slight divergence. The eigenvalues were therefore Pade resummed by using the epsilon algorithm.⁹⁷ The resulting energies for the lowest few states are in good agreement with the adiabatic switching results,^{29b} while there are no other excited-state eigenvalues available for comparison.

The PERTURB package in combination with algebraic quantization and resummation methods is clearly a powerful tool for study of the semiclassical mechanics of multimode anharmonic potentials. Although PERTURB is at present limited to treating perturbed harmonic oscillator or Morse oscillator systems, vibration-rotation interactions could be included by using a mapping of the asymmetric rotor Hamiltonian onto a 2-mode harmonic oscillator.¹⁰¹

It has been noted previously that Dragt-Finn perturbation theory is the classical limit of Van Vleck quantum perturbation

(97) Baker, G. A. *Essentials of Pade Approximants*; Academic: New York, 1975.

(98) Zinn-Justin, J. *Phys. Rep.* **1981**, 70, 109.

(99) Silverman, J. N. *Phys. Rev. A* **1983**, 28, 498.

(100) deGroot, S. R.; Sutorp, L. G. *Foundations of Electrodynamics*; North Holland: Amsterdam, 1972.

(101) Martens, C. C., unpublished work.

TABLE III: Energy Eigenvalues for the Five-Dimensional System of Ref 29a

N_1	N_2	N_3	N_4	N_5	E_R^a	E_W^b	E_{SPSC}^c	E_2^d	E_{AS}^e
0	0	0	0	0	2.6897	2.6800	2.6897	2.6909	2.6896
1	0	0	0	0	3.3330	3.2815	3.3330	3.3489	3.3305
0	0	0	0	1	3.5586	3.5473	3.5586	3.5630	3.5600
0	0	1	0	0	3.6787	3.6689	3.6787	3.6807	3.6785
2	0	0	0	0	3.9167	1.3813	3.9167	3.9867	
0	1	0	0	0	3.9670	3.9530	3.9670	3.9700	3.9669
1	0	0	0	1	4.1580	4.1576	4.1580	4.1873	
0	0	0	1	0	4.2138	4.2041	4.2138	4.2152	4.2139
3	0	0	0	0	4.2764	4.8898	4.2764	4.6043	
1	0	1	0	0	4.3216	4.2734	4.3216	4.3386	
0	0	0	0	2	4.4253	4.4016	4.4253	4.4338	
0	0	1	0	1	4.5477	4.5361	4.5477	4.5527	

^aResummed eighth order energies, using Robnik's quantization rule (ref 44). ^bAs in (a), except with the Weyl quantization rule (ref 44). ^cAs in (c), except with the SPSC quantization rule (ref 44). ^dQuantization of a resonant second order normal form, using the SPSC quantization rule (ref 44). ^eAdiabatic switching energies with minimum energy dispersion (ref 14) (ref 29b). ^fResummed results showed poor convergence.

theory.^{44,45} Why not, then, simply apply high-order quantum perturbation theory to obtain eigenvalues for multimode vibrational Hamiltonians? Low-order Van Vleck perturbation theory is of course used in the traditional contact transformation approach to vibration-rotation spectra,⁵ as mentioned in the Introduction. The modular structure of PERTURB is such that replacement of the Poisson bracket operation by a commutator enables Van Vleck perturbation theory to be carried out with the same degree of efficiency as Dragt-Finn. For the same problem treated to the same order the classical perturbation theory generates fewer terms, however, and is therefore simpler, since there are no difficulties with operator ordering. Using the Moyal bracket¹⁰² (the Weyl symbol³⁸ of the commutator), we have derived convergent corrections to semiclassical perturbation theory in powers of \hbar .¹⁰³ It is thereby possible to compare the relative accuracy vs. efficiency of the two approaches and to examine the passage from semiclassical to fully quantal eigenvalues. Study of the convergence properties of both types of perturbation theory might also throw some much needed light on the fundamental problem of quantum vs. classical integrability,¹⁰⁴ and could point the way to a rigorous "quantum KAM theorem".¹⁰⁵

V. Unitary Group Approach to Multimode Resonant Dynamics

In this section we discuss unitary group approaches to the study of resonant dynamics in multimode systems. We briefly describe some recent work on 2 degree of freedom $m:n$ resonant systems,⁴⁹ indicate some applications of these results currently under investigation, and discuss their possible extension to $N \geq 3$ mode systems.

It is well-known that the Hamiltonian of the N degree of freedom isotropic oscillator has the symmetry group $SU(N)$, the unitary group in N dimensions, both in classical and quantum mechanics.¹⁰⁶ The unitary group includes transformations that mix positions and momenta and so represents a higher degree of symmetry than that of the potential energy alone, $SO(N)$. In 2 degrees of freedom, for example, the symmetry group is $SU(2)$, which is homomorphic onto the rotation group $SO(3)$.¹⁰⁶ One consequence is that the degeneracy pattern of the quantum levels of the 2-mode isotropic oscillator corresponds to the degeneracies of the irreducible representations of $SU(2)$: 1,2,3,4 Underlying the global symmetry group $SU(N)$ is the Lie algebra $\mathfrak{su}(N)$, defined by the commutator (or Poisson bracket) relations satisfied by a set of generators, which are quantities bilinear in coordinates and momenta that commute with the oscillator Hamiltonian.¹⁰⁶ Each generator is therefore a constant of the motion; since, however, the generators do not mutually commute (have vanishing Poisson bracket), they cannot all be simultaneously diagonal (in

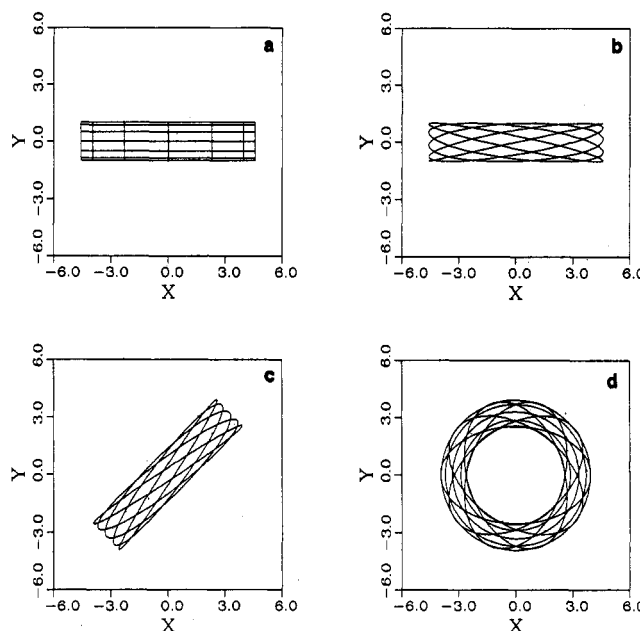


Figure 6. Angle parametrizations of invariant tori for the isotropic oscillator (see ref 49). (a) Angle paths for normal-mode action-angle variables. (b) Angle paths for the Δ (normal mode) representation. (c) Angle paths for the K (local mode) representation. (d) Angle paths for the L (angular momentum) representation.

involution²²). In $\mathfrak{su}(2)$, for example, the classical generators are ($\omega = 1$)

$$\Delta = \frac{1}{2}(p_x^2 + x^2 - p_y^2 - y^2) \quad (18a)$$

$$K = xy + p_x p_y \quad (18b)$$

$$L = x p_y - y p_x \quad (18c)$$

Each generator corresponds to a particular representation or choice of basis: normal mode (Δ), local mode (K), and precessing normal mode (L) (see Figure 6). The work of Kellman¹⁰⁷ has shown that the $SU(2)$ symmetry analysis provides powerful global insights into the interrelations between the local- and normal-mode motions in 1:1 resonant oscillator systems. Thus, transformation coefficients relating normal- and local-mode quantum states can be written directly in terms of Wigner d -matrices.¹⁰⁷ The classical $\mathfrak{su}(2)$ algebra of the isotropic oscillator also turns out to be useful in the problem of semiclassical quantization via perturbation theory: in the Henon-Heiles problem, for example, a choice of diagonal generator L rather than Δ renders the Hamiltonian diagonal to higher order in the perturbation strength than in the Cartesian representation.^{28,108} Farrelly has recently extended these

(102) Moyal, J. E. *Proc. Camb. Philos. Soc.* **1949**, *45*, 99.

(103) Fried, L. E.; Ezra, G. S., submitted for publication.

(104) Robnik, M. *J. Phys. A* **1986**, *19*, L841. Hietarinta, J. *J. Math. Phys.* **1984**, *25*, 1833.

(105) Hose, G.; Taylor, H. S. *Phys. Rev. Lett.* **1983**, *51*, 947.

(106) Wybourne, B. *Classical Groups for Physicists*; Wiley: New York, 1974.

(107) Kellman, M. E. *J. Chem. Phys.* **1982**, *76*, 4528; *Chem. Phys. Lett.* **1983**, *99*, 437; *J. Chem. Phys.* **1985**, *83*, 3843.

(108) Uzer, T.; Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 5013.

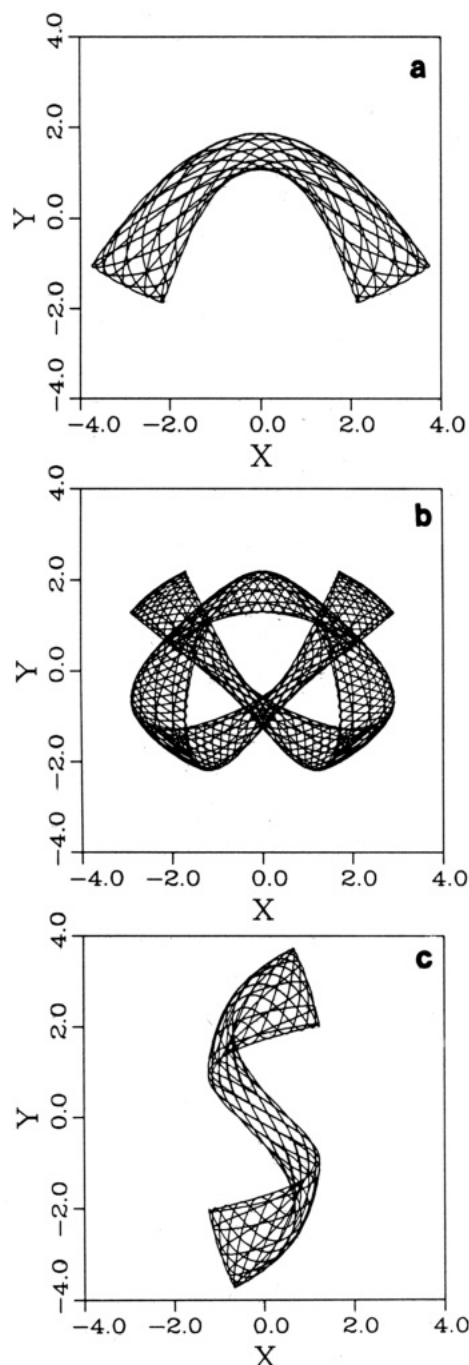


Figure 7. Angle parametrization of $m:n$ resonant tori, as determined analytically in ref 49: (a) 2:1; (b) 3:4; (c) 3:1.

considerations to the case of a 2:1 resonance¹⁰⁹ and has outlined how to proceed in the general $m:n$ resonant case.

In recent work on the $SU(2)$ symmetry of 2 degree of freedom systems inspired by the work of Kellman¹⁰⁷ and Farrelly¹⁰⁹ mentioned above, we have obtained explicit expressions for the canonical transformations from normal mode (Δ) to K and L tori and have verified that these correspond to the classical limit of the analogous quantum mechanical transformations.⁴⁹ As an important extension, it has been shown that these results can be used to generate tori of appropriate topology for *general* $m:n$ resonant systems. Thus, by mapping the (anisotropic) $m:n$ resonant 2-mode oscillator onto an isotropic oscillator,¹¹⁰ an explicit

transformation from normal-mode variables to resonant action-angle variables has been obtained. Analytically generated $m:n$ resonant tori are shown in Figure 7 (2:1, Figure 7a; 3:4, Figure 7b; 3:1, Figure 7c). This work provides a solution to a problem in the implementation of the adiabatic switching approach to semiclassical quantization of multidimensional systems, namely, how to define an ensemble of initial conditions lying on a resonant torus of the correct topology. The quantal version of the classical transformation defines a resonant basis set that can be used in studies of quantum localization.¹⁰⁵

Of great interest is the possibility of extending the analysis of classical Lie algebras for isotropic and resonant anisotropic oscillators to the $N \geq 3$ mode case. For $N = 3$ degrees of freedom, for example, the Lie algebra $su(3)$ ¹⁰⁶ defines an appropriate set of actions and associated tori for describing resonant motion. If canonical transformations analogous to those obtained for $SU(2)$ could be found, we would have an analytical tool for study of dynamics in 3 degrees of freedom. The complexity of the classical mechanics of the $N \geq 3$ mode case is such that any insights obtained by using unitary group methods would be of considerable value.

VI. Summary and Prospect

In this article we have surveyed some recent developments in the semiclassical theory of multimode molecular bound states. Powerful methods are now available for EBK and uniform algebraic quantization of excited vibrational and vibration-rotation levels of small polyatomics described by realistic anharmonic potential surfaces. We conclude by indicating briefly some prospects for future developments and applications.

A recent major advance in the classical theory of intramolecular dynamics⁶⁷ and unimolecular decay⁶⁸ has been the application of ideas from the nonlinear dynamics literature^{65,111} concerning the origin of long-time correlations in the chaotic regime. Such long-time correlations are associated with the existence of phase space bottlenecks, which may be cantori⁶⁵ (i.e., invariant cantor sets which are remnants of invariant tori that have broken up under a perturbation) or broken separatrices.¹¹¹ Cantori act as leaky barriers to mode-mode energy flow in 2-mode systems, the least permeable barriers being associated with the most irrational (antiresonant) frequency ratios.⁶⁷

As discussed in section III, trajectory Fourier analysis can be extended to non-quasi-periodic trajectories.^{82,84} The power spectra of short segments reveal directly the existence of trapped or correlated motion extending over several periods and can be used to chart the passage of a trajectory from one trapping region to another as it wanders in phase space. This approach is currently being applied to investigate the nature of phase space bottlenecks in $N = 3$ mode systems.⁸⁴

We note finally that a *fixed frequency* version (as opposed to the usual fixed action constraint of canonical perturbation theory¹⁵) of classical perturbation theory would be very useful for finding analytical approximations to phase space dividing surfaces (see also ref 112). An efficient high-order implementation such as PERTURB is required, as previous attempts to define approximate intramolecular bottlenecks have been unsuccessful.⁶⁸ We are currently investigating adaptation of PERTURB to the fixed frequency case.

Acknowledgment. We thank the participants of the Telluride Summer Research Institute for many helpful conversations. Particular thanks are due to M. J. Davis for invaluable discussions and stimulating collaboration. This work was supported by NSF Grant CHE-8410685. G.S.E. acknowledges the partial support of the Alfred P. Sloan Foundation. C.C.M. acknowledges support of the U.S. Army Research Office, through the Mathematical Sciences Institute of Cornell University.

(109) Farrelly, D. J. *Chem. Phys.* **1986**, *85*, 2119.

(110) Stehle, P.; Han, M. Y. *Phys. Rev.* **1967**, *159*, 1076.

(111) Channon, S. R.; Lebowitz, J. *Ann. N.Y. Acad. Sci.* **1980**, *357*, 108.

(112) Jaffe, C., work in progress.