Lawrence Berkeley National Laboratory

Recent Work

Title

ON THE QUANTUM MECHANICAL IMPLICATIONS OF CLASSICAL ERGODICITY

Permalink

<https://escholarship.org/uc/item/512387kc>

Author

Stratt, R.M.

Publication Date

1979-05-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to the Journal of Chemical Physics

RECEIVED
LAWRENCE
BERKELEY LABORATORY

SEP 14 1979

ON THE QUANTUM MECHANICAL IMPLICATIONS OF
CLASSICAL ERGODICITY

LIBRARY AND
DOCUMENTS SECTION

Richard M. Stratt, Nicholas C. Handy and William H. Miller

May 1979

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

LBL-9197c 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ON THE QUANTUM MECHANICAL IMPLICATIONS OF
CLASSICAL ERGODICITY

By

Richard M. Stratt, Nicholas C. Handy* and William H. Miller[†]

Department of Chemistry and Materials and Molecular Research Division
of the Lawrence Berkeley Laboratory, University of California,
Berkeley, California 94720

Abstract

The concept of quantum ergodicity is examined empirically through a qualitative study of the eigenfunctions of both the Barbanis and Casati-Ford potentials. By considering the behavior of the nodes of the wave functions and by employing a combination of natural orbital and spectral analyses, many of the higher eigenstates can apparently be classified as ergodic. These particular states seem to correspond quite well not only to classical ergodic trajectories but also to (currently) unquantizable semiclassical wave functions. The relationship between this quantal ergodicity and its classical equivalent is discussed.

I. Introduction.

For some time it has been recognized that classical dynamics permits what is essentially ergodic behavior¹ in systems with just a few degrees of freedom. The most familiar example of this, the Henon-Heiles Hamiltonian,² has been shown to undergo a transition from regular classical trajectories--which occupy a limited amount of the energetically allowed phase space and have well defined Poincaré surfaces of section--to irregular (ergodic, stochastic) trajectories--which appear to fill up the allowed phase space and have effectively random Poincaré surfaces.³ As has been previously demonstrated, this transition also implies that the classical power spectrum becomes irregular.^{4,5}

The very existence of this type of stochastic behavior in what are clearly deterministic systems has some interesting consequences. Because the Henon-Heiles system models a pair of coupled oscillators, the observation of ergodicity would seem to bear directly on a variety of intramolecular vibrational energy transfer problems, including multiphoton dissociation,⁶ unimolecular reactions,⁷ and infrared spectroscopy in general. Moreover, these systems may be simple enough to provide a practical means for examining some of the fundamental axioms of statistical mechanics.⁸

Implicit in all of these potential applications, however, is the assumption that this purely classical phenomenon will occur in real, i.e., quantum mechanical, systems. In as much as the concept of ergodicity is usually couched in the language of classical phase space, it is by no means clear what form quantum ergodicity should take--if it exists at all. For example, do there exist ergodic quantum states in the same way that

there are ergodic classical trajectories, or does quantal ergodicity require an ensemble of states?

One might hope that semiclassical approaches could prove helpful in answering these questions since ergodicity is basically a high energy occurrence. Yet in spite of the fact that bound state semiclassical methods increase in accuracy as energy increases, no one (as of this writing) has yet succeeded in quantizing ergodic states semiclassically. Of course the reason for this failure does not necessarily have to lie in the quantum mechanical states--it could be the fault of the semiclassical methods. Methods which rely on trajectories closing in phase space⁹ or on regular Poincaré surfaces¹⁰ are clearly inappropriate. Similarly, those methods which implicitly equate classical action variables with quantum numbers¹¹ cannot succeed because invariant tori (and therefore action-angle variables) are not well defined in the irregular region.

An alternative approach is to examine the quantum states directly. Nordholm and Rice¹² did this for the Henon-Heiles system, and they were indeed able to characterize some of the states as ergodic by virtue of their "nonlocalization". Unfortunately their results have been criticized for being coordinate and basis set dependent.¹³ Other investigations have been undertaken by McDonald and Kaufman,¹⁴ who examined the nodal lines of eigenfunctions, and by Pomphrey,¹⁵ who verified Percival's¹⁶ predictions that ergodic states should be unstable with respect to variations in the size of a nonseparable perturbation.

This paper seeks to extend these studies by considering several different approaches for characterizing the regular/ergodic nature of individual quantum states. As with previous work, the eigenfunctions are

generated by diagonalizing the matrix representation of a model Hamiltonian. Section II examines the nodal lines of the wave functions and discusses how these are related to the regular/ergodic character of the states, while Section III shows how a natural orbital analysis can also be used to reveal this nature of the states. Section IV then looks at the power spectrum associated with various of the quantum states and shows that this also is correlated with the regular and ergodic-like behavior of the corresponding classical system.

II. Nodal Behavior of Wave Functions.

For one-dimensional systems the nodes of a wave function provide a definite prescription for assigning a quantum number to each state. In the multidimensional case these nodal points become nodal surfaces (nodal lines for two dimensions). If a two-dimensional system, say, is separable, then the nodal lines will intersect in a regular "checkerboard"-like pattern (cf. Figure 1a) which permits the assignment of definite quantum numbers for each degree of freedom by "counting nodes". As has been emphasized by Pechukas,¹⁷ however, if the two-dimensional system is non-separable, then the pattern of nodal lines need not intersect in this manner, or at all; e.g., an intersection of nodal lines can become an "avoided intersection" if the system becomes non-separable (cf. Figure 1b). In this case it is clear that one can no longer unambiguously assign a complete set of quantum numbers to the state in question by counting nodes. This is consistent with the fact that the states of a non-separable system cannot in general be assigned a complete set of quantum numbers.

Even for non-separable systems, though, some states may nevertheless have intersecting nodal lines, or at least have narrowly avoided intersections (cf. Figure 1c), so that it is possible (or approximately so) to count nodes and thus identify quantum numbers for the various degrees of freedom. One expects such states to correlate with the regular trajectories of the corresponding classical mechanical system for which a complete set of "good" action-angle variables exist. One further anticipates that quantum states which show a complete break-up of the intersecting nodal structure will correlate with irregular, or ergodic-like classical motion of the corresponding

classical system. The remainder of this section tests these notions by considering two specific model two-dimensional systems.

A. The Barbanis Hamiltonian.

The Barbanis Hamiltonian,

$$H = \frac{1}{2} p_x^2 + \frac{1}{2} p_y^2 + \frac{1}{2} \omega_x^2 x^2 + \frac{1}{2} \omega_y^2 y^2 + \alpha xy^2, \quad (2.1)$$

is a simple variant of the Henon-Heiles model, and its classical,^{9,18} semiclassical,⁹ and quantal¹² behavior has been extensively investigated. It is somewhat simpler to use for present purposes than Henon-Heiles since it does not possess C_3 symmetry and thus does not have the requisite degeneracy of eigenvalues and associated difficulties.¹⁹

Proceeding with Eq. (2.1), it is convenient to use the parameters of Sorbie and Handy⁹

$$\omega_x = (1.6)^{1/2}, \quad \omega_y = (0.9)^{1/2}, \quad \alpha = -0.08 \quad (2.2)$$

and to diagonalize the Hamiltonian in a basis of normalized, direct product harmonic oscillator states

$$\Phi_{N_x, N_y} = N H_{N_x} [(\omega_x)^{1/2} x] H_{N_y} [(\omega_y)^{1/2} y] \exp[-\frac{1}{2} (\omega_x x^2 + \omega_y y^2)] \quad (2.3)$$

that is, eigenstates of Eq. (2.1) with $\alpha = 0$. It was found that the first 135 eigenvalues were converged to five significant figures with the following basis of 420 functions, $\{\Phi_{N_x, N_y}\}$,

$$0 \leq N_x \leq 19, \quad 0 \leq N_y \leq 40 \quad (N_y \text{ even})$$

Because of the symmetry of the potential, only even values of N_y need be included to determine the states even with respect to reflection about the x-axis (which are the ones we consider).

It should also be noted that since the potential allows dissociation, there is a definite limit to the number of eigenfunctions one can calculate. Since the dissociation energy is 25.313, the 135th state ($E = 23.892$) may very well represent the highest state one can confidently describe as being confined to the potential well. An inspection of the coefficients of the basis functions for the first 135 states, however, does show small contributions from the highest basis functions, so that at least these wave functions can be considered as being confined to the well.

The desired results of these calculations, the nodal lines, can most easily be displayed by plotting the positive and negative regions of the wave functions; this is done in Figures 2, 3, and 4 for selected states. In these plots the positive regions are represented by dark areas, the negative regions by light areas, and the regions too small to ascertain by dotted areas. [This last classification is only required because of numerical noise in the calculations. Consequently the boundary of the region should not be taken too literally.]

Even a casual inspection of these plots suggests that it is reasonable to label the wave functions according to their nodal patterns. The type shown in Figure 2 are labeled regular (R) because it is possible to imagine two curved but orthogonal coordinates along which black and white alternate; giving a count of the nodes in two directions. Those in Figure 4, on the

other hand, do not permit this type of visualization of nodal patterns and should therefore be labeled ergodic (E). In fact, based on Figure 4, it appears that the ergodic states are those with competing nodal patterns. The remaining plots, Figure 3, were classified as uncertain (U) in recognition of the subjective nature of the classification.

This type of analysis was carried out for a large number of Barbanis eigenfunctions and the results are presented in Table I along with the best estimate for the quantum numbers of the states. Interestingly, these estimates match the semiclassical assignments of Sorbie and Handy (SH)⁹ extremely well. Just as significant, too, is the fact that SH were not able to semiclassically quantize states which we characterized as U or E because the classical trajectories involved were ergodic. This alone seems sufficient to suggest that the above description of irregular nodal patterns as ergodic is appropriate.

Another piece of confirming evidence is provided by the extent of the wave functions. In Table I are listed the expectation values of x^2 and y^2 for each state, numbers which one expects to be given approximately by the harmonic oscillator results

$$\langle x^2 \rangle = \frac{\hbar}{2\omega_x}(2n_x + 1) \quad , \quad \langle y^2 \rangle = \frac{\hbar}{2\omega_y}(2n_y + 1) \quad .$$

However this is found to be true only for R states. Ergodic and uncertain states seem to have disproportionately large values of $\langle y^2 \rangle$ in accordance with both the classical idea of ergodicity and the results of Nordholm and Rice.¹² Of course one should probably be cautious in ascribing any undue significance to the "size" of a wave function.

Other support for the identification of irregular nodal lines with ergodicity comes from the distribution of ergodic states among the other eigenstates being generally what one would expect. There are no ergodic or uncertain states below an energy of 18, and there are no ergodic classical trajectories below an energy of 19.⁹ Above this "critical energy" ergodic states begin to appear interspersed among regular states, in a fashion analogous to the way ergodic classical trajectories emerge interspersed with regular ones.

Still another consideration involving the distribution of ergodic states is revealed by a scattergram showing the classification of the states deemed to have enough energy to be ergodic as a function of their estimated quantum numbers (Figure 5). If one allows for the disparity in x and y frequencies and for the asymmetry of the potential, it seems clear that only those states with comparable x and y "quantum numbers" actually turn out to be ergodic. By analogy with classical mechanics one knows that it is precisely these states which are most efficient in transferring energy from one degree of freedom to another. Thus it is just these states which one would predict not to have independent degrees of freedom, i.e., ergodic states.

One must nevertheless emphasize the qualitative nature of this classification. The fact that the extreme cases of regularity and ergodicity are quite distinct does not necessarily mean that the same is true for intermediate cases. Even the most regular states seem to have the same nodal topology as ergodic states in as much as both categories have avoided crossings. Thus the distinction at this level is probably just one of the degree of "avoidedness".

One can verify this conjecture by examining the nodal crossings of an obviously regular state in detail, as is done in Figure 6. In spite of the obvious checkerboard pattern it is evident that the nodal lines do not intersect. Moreover, decreasing the amount of nonseparability (α) does not force the lines to intersect but rather simply decreases the amount of distortion in the pattern. Because this kind of state allows such easy node counting, one must therefore conclude that it is not the mere presence of avoided crossings which makes a state ergodic.

Interestingly enough, this conclusion seems to require that Pechukas' ideas on semiclassical quantization by Miller-Good transformations¹⁷ be generalized. This prescription for quantization was limited to systems with intersecting nodal lines, so it clearly omits easily quantizable states such as those discussed above.

B. The Casati-Ford Hamiltonian

By studying the Barbanis system we have been able to observe a transition in the behavior of quantum mechanical nodal lines which apparently corresponds to the classical regular/ergodic transition in the same system. However, if this correspondence is genuine one should find nothing but irregular quantum states in any system which is always classically ergodic and nothing but regular quantum states in any system which is always classically regular. Indeed, the first of these conditions has been observed to be true for the stadium problem by McDonald and Kaufman.¹⁴ In this system every classical trajectory is ergodic and, as required, every (examined) quantum state does have an irregular nodal pattern.

The purpose of this section is to investigate the second of these

suppositions, i.e., that a completely regular classical system will give rise to only regular quantal nodal lines. The example employed is the Hamiltonian proposed by Casati and Ford²⁰

$$H = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + e^{-x} + e^{x-y} + e^y - 3 \quad (2.4)$$

This system can be shown to be integrable if $m_x = m_y$ and therefore it cannot be (classically) ergodic. However if $m_x \neq m_y$, the constant of motion which makes Eq. (2.4) integrable in the equal mass case disappears and the system develops an ergodic/regular transition. One would thus predict that all the quantum states will be regular with equal masses and that the quantum states should behave in the same fashion as the Barbanis eigenstates with different masses.

The nodal lines obtained by diagonalizing the Hamiltonian matrix as in Section IIa are displayed in Figures 7, 8, 9, and 10 for two choices of parameters discussed by Casati and Ford:²⁰

$$\text{integrable case: } m_x = 1.0, m_y = 1.0 \quad (2.5a)$$

$$\text{nonintegrable case: } m_x = 1.0, m_y = 0.54 \quad (2.5b)$$

As in the Barbanis calculation the diagonalization was accomplished using a large harmonic basis (Eq. (2.3)). In particular, 400 functions

$$\{\phi_{N_x, N_y}\}$$

$$0 \leq N_x \leq 19, \quad 0 \leq N_y \leq 19$$

$$\omega_x = \omega_y = 1.0$$

were employed to converge the first twelve eigenstates to within an accuracy of 5×10^{-7} in energy (Table II). It should be noted, though, that this basis set was chosen only because it allowed an easy analytical evaluation of the Hamiltonian matrix and not because it was especially appropriate to the problem. In fact an extraordinarily large basis was required to ensure convergence of the nodal plots of even the twelve lowest states because of the highly anharmonic character of the potential.

These states, however, are sufficient to demonstrate the validity of our predictions. The integrable Hamiltonian, for example, produces a readily definable sequence of sharp nodal patterns which are distorted, though recognizably so, in the first nine states of the nonintegrable Hamiltonian. However the last three nonintegrable states seem to have no interpretable pattern whatsoever and probably should be labeled ergodic. Corroborating this assignment is the fact that the corresponding classical regular/ergodic transition for the nonintegrable system²⁰ occurs at an energy of 7.0, in reasonable agreement with the energies of eigenstates 9 and 10 ($E = 7.0$ and 7.6 , respectively).

Indeed it is somewhat encouraging that this behavior matches our expectations based on the Barbanis potential in view of the sizeable differences between the two potentials. Unlike the Barbanis system the Casati-Ford system is not x-y oriented and it is decidedly nonharmonic. Perhaps more importantly, it is also nondissociative. The only similarity between the two is the presence of a plane of symmetry in both the Barbanis system and the integrable Casati-Ford system (along the line $y=-x$), but even that is removed in the nonintegrable Casati-Ford case.

III. Natural Orbital Analysis.

Nordholm and Rice's¹² approach to analyzing the quantum mechanical wave functions involved examination of the coefficients $\{C_{N_x, N_y}\}$ in the expansion

$$\psi(x,y) = \sum_{N_x, N_y} C_{N_x, N_y} \theta_{N_x}(x) \phi_{N_y}(y) \quad , \quad (3.1)$$

where $\{\theta_{N_x}(x)\}$ and $\{\phi_{N_y}(y)\}$ are harmonic oscillator basis functions [cf. Eq. (2.3)]. A broadly distributed set of coefficients was suggestive of ergodic-like behavior, and conversely if the coefficients were "localized".

This approach has been criticized because it depends on the particular choice of the basis functions $\{\theta_{N_x}\}$ and $\{\phi_{N_y}\}$, but this defect can be overcome by introducing natural orbitals, familiar in the theory of electronic structure.^{21,22} The idea is that one looks for the "best" of all possible orbitals, i.e., one particle functions, the ones which make the expansion in Eq. (3.1) most rapidly convergent. The result of this analysis (see the Appendix) is that the wave function has a diagonal expansion in the natural orbitals,

$$\psi(x,y) = \sum_n (\lambda_n)^{1/2} \Theta_n(x) \Phi_n(y) \quad , \quad (3.2)$$

where the natural orbitals $\{\Theta_n\}$ and $\{\Phi_n\}$ are given by

$$\Theta_n(x) = \sum_{N_x} \theta_{N_x}(x) U_{N_x, n} \quad (3.3a)$$

$$\Phi_n(y) = \sum_{N_y} \phi_{N_y}(y) V_{N_y, n} \quad (3.3b)$$

The matrices $\underline{U}$ and $\underline{V}$ are the unitary matrices (i.e., the matrix of eigenvectors) which diagonalize the matrices $\underline{C} \cdot \underline{C}^\dagger$ and $\underline{C}^\dagger \cdot \underline{C}$, respectively, where $\underline{C}$ is the matrix whose elements are the coefficients C_{N_x, N_y} of Eq. (3.1). The occupation numbers $\{\lambda_n\}$ are the eigenvalues which result from these diagonalizations (the same eigenvalues result in both cases.) One can show (see the Appendix) that the natural orbitals have the property that in terms of them the expansion of the wave function [Eq. (3.2)] is most rapidly convergent. Since the occupation numbers sum to unity,

$$\sum_n \lambda_n = 1 \quad , \quad (3.4)$$

λ_n can be interpreted as the fractional occupation of the configuration $\phi_n(x) \phi_n(y)$.

It thus seems reasonable that one might be able to correlate regular or ergodic character with the distribution of occupation numbers. If only one λ is significant, then only one term contributes to the sum in Eq. (3.2), and the wave function is separable and would have a set of intersecting nodal lines. If many λ 's are of comparable size, then the state is in some sense "more non-separable", at least in the chosen coordinates (x,y), and presumably more ergodic-like.

Such calculations have been carried out for Barbanis model of Section IIa. From the coefficient matrix $\underline{C}$ for a given state, the matrix $\underline{C} \cdot \underline{C}^\dagger$ is constructed and diagonalized to obtain the occupation numbers $\{\lambda_n\}$. Table I gives the largest occupation number for all the states considered, and Table III gives the largest few occupation numbers for several selected states. A comparison of these results, Table III in particular, with Figures 2, 3 and 4 suggests that there is indeed a direct correspondence

between the nodal concept of ergodicity and the natural orbital concept. Not only does a small leading occupation number seem to imply a complex nodal pattern (and vice-versa) but there is also a correlation with the distribution of occupations. Regular states tend to have one large coefficient followed by a rapid exponential decay whereas irregular states have a much gentler falloff.

This distribution is highly suggestive in itself, for in Section II it was seen that the ergodic states were composed of conflicting nodal patterns, in contrast to the single nodal pattern characteristic of regular states. Since one can regard each configuration (in the sense of Eq. (3.2)) as a single nodal pattern, it is evident that the broad distribution of occupations for ergodic states is in accord with the nodal picture.

By way of contrast, it should be pointed out that the original expansion coefficients [the C_{N_x, N_y} of Eq. (3.1)] do not show nearly this degree of correspondence. A highly regular state may have a widely scattered set of expansion coefficients simply because of an inappropriate choice of basis set. Therefore it should be no surprise that in our case (with its intrinsically curved nodal lines), a state with a quantum number assignment (N_x, N_y) will often not have C_{N_x, N_y} as its largest coefficient.

IV. Spectral Analysis.

Vibrational states of molecules are investigated experimentally by spectroscopic methods, typically infra-red absorption spectroscopy. It is thus a pertinent question to see how the regular/ergodic character of a system is manifest in its infra-red absorption spectrum. This has been discussed for the classical case,^{4,5} and here we consider it quantum mechanically.

The autocorrelation function of the dipole moment is given by

$$\begin{aligned} C(t) &= \text{tr}[\hat{\rho}\hat{\mu}(0)\hat{\mu}(t)] \\ &= \text{tr}[\hat{\rho}\hat{\mu}e^{-i\hat{H}t/\hbar}\hat{\mu}e^{i\hat{H}t/\hbar}] \end{aligned} \quad (4.1)$$

where ρ is the density operator of the system. Expanding the trace in the eigenstates of $\hat{H}$ gives

$$C(t) = \sum_{n,n'} \rho_n |\mu_{n,n'}|^2 e^{-i(E_n - E_{n'})t/\hbar} \quad (4.2)$$

where

$$\mu_{n,n'} = \langle n | \hat{\mu} | n' \rangle \quad (4.3)$$

The absorption spectrum is then given by the Fourier transform of $C(t)$,

$$\begin{aligned} I(\omega) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t) \\ &= \sum_{n,n'} \rho_n |\mu_{n,n'}|^2 \delta[\hbar\omega - (E_n - E_{n'})] \end{aligned} \quad (4.4)$$

Since we wish to consider the spectrum associated with individual quantum states, we choose

$$\rho_n = \delta_{n,n_0} ,$$

so that

$$I(\omega) = \sum_{n'} |\mu_{n_0, n'}|^2 \delta[\hbar\omega - (E_{n'} - E_{n_0})] ,$$

and this is made more realistic by averaging over frequency $\Delta\omega$ to smooth out the delta function:

$$I(\omega) = \sum_{n'} |\mu_{n_0, n'}|^2 \chi_{n', n_0}(\omega) ,$$

where

$$\chi_{n', n_0}(\omega) = \begin{cases} \frac{1}{\Delta\omega} , & \text{if } \left| \frac{E_{n'} - E_{n_0}}{\hbar} - \omega \right| < \Delta\omega \\ 0 , & \text{otherwise} \end{cases} . \quad (4.5)$$

Eq. (4.5) has been used to generate the absorption spectrum from various specific quantum states of the Barbanis Hamiltonian of Section IIa, with the dipole moment $\hat{\mu}$ taken simply as the coordinate x .²³ The results are shown in Figure 11, with (a) $\rightarrow$ (d) being the direction of increasing ergodicity; i.e., case (a) is a highly regular state and case (d) the most ergodic-like one. All states show prominent absorption lines at the dipole allowed harmonic frequencies $\pm \omega_x$, but it is clear that the spectra for the ergodic-like states are more irregular than for the regular states.

The qualitative conclusion of these calculations is thus to reinforce the classical results, namely that regular states have regular spectra and

and vice versa. This further supports the belief that spectroscopy should be able to distinguish between regular and ergodic-like vibrational states of molecules.

V. Concluding Remarks.

This paper has considered several different ways of characterizing quantum states of multidimensional systems with regard to the regular or ergodic-like behavior of the corresponding classical motion. For these examples the three different approaches all give reasonably consistent qualitative pictures of the regular/ergodic nature of the states, and they are also in good qualitative agreement with the behavior of the corresponding classical trajectories for these systems. This suggests that regular or ergodic-like behavior of classical mechanical systems has a rather direct counterpart quantum mechanically, at least in a qualitative sense. This is consistent with the conclusions of other workers.²⁴

The nodal analysis of Section II is very appealing since it is a basis set and coordinate-independent concept. It is also illuminating in that it shows that ergodic-like classical behavior is often correlated with a competition between more than one well-ordered nodal pattern. This idea is reminiscent of the existence of "overlapping resonances" that has been suggested²⁵ as the origin of classical ergodic-like behavior.

The natural orbital analysis of Section III is essentially a modification of Nordholm and Rice's approach for characterizing wave functions, but it has the advantage of being independent of the specific basis set used to carry out the calculation. This approach, however, is not independent of the coordinates chosen to describe the system; i.e., if the system were separable in the polar coordinates (r, θ) , then the wave function would be separable in these coordinates but not in (x, y) , and a natural orbital analysis in (x, y) coordinates would thus not yield single occupation number of unity. This feature is a clear disadvantage of trying to base any fundamental concepts on this approach.

The most experimentally relevant way of characterizing states is via their spectrum. If one is able to prepare specific quantum states and then probe their absorption spectrum, this is a direct measure of the quantity $I(\omega)$. The suggestion is that different states will have qualitatively different spectra depending on whether they are regular or ergodic-like.

In concluding, one must confess that although the regular/ergodic character of individual quantum states seems to be a physically relevant concept, the approaches we have suggested for analyzing it are at best qualitative. (Of course the qualitative nature of the distinction is also true to some extent for the corresponding classical mechanical situation.) Perhaps one can do no better; i.e., it may be like the notion of "percentage ionic character" of a chemical bond--a useful qualitative concept but one that is awkward to quantify. Whether this is true or not, it seems likely that the nature of intramolecular vibrational structure and dynamics will be an increasingly interesting one as more sophisticated laser techniques are developed for probing this behavior.

Appendix: Natural Orbitals for Systems of Two Coupled Oscillators.

The results presented here are well-known for two-electron systems, i.e., two particle systems where the two particles are identical. The point of this appendix is to show that these notions carry over almost identically to the case of two non-identical degrees of freedom.

The Hamiltonian for the two oscillator system is assumed to be of Cartesian form,

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + V(x,y) \quad , \quad (A.1)$$

and the wave function for a particular eigenstate is assumed to be available as the following expansion:

$$\psi(x,y) = \sum_{n_x, n_y} C_{n_x, n_y} \theta_{n_x}(x) \phi_{n_y}(y) \quad , \quad (A.2)$$

where $\{\theta_{n_x}\}$ and $\{\phi_{n_y}\}$ are some convenient one particle basis sets (such as harmonic oscillator functions). The wave function, i.e., the set of coefficients $\{C_{n_x, n_y}\}$, is obtained, for example, by diagonalizing the matrix representation of the Hamiltonian, $H_{n'_x n'_y, n_x n_y}$, in this direct product basis.

The first order reduced density matrix ρ_x is defined by

$$\rho_x(x|x') = \int dy \quad \psi(x,y) \psi(x',y) \quad , \quad (A.3a)$$

where the wave function is assumed to be real so that complex conjugation is omitted, and the other first order reduced density matrix ρ_y is similarly defined:

$$\rho_y(y|y') = \int dx \psi(x,y) \psi(x,y') \quad (\text{A.3b})$$

With ψ given by Eq. (A.1) one readily finds that

$$\rho_x(x|x') = \sum_{n_x, n_x'} \rho_{n_x, n_x'}^x \theta_{n_x}(x) \theta_{n_x'}(x') \quad (\text{A.4a})$$

$$\rho_y(y|y') = \sum_{n_y, n_y'} \rho_{n_y, n_y'}^y \phi_{n_y}(y) \phi_{n_y'}(y') \quad (\text{A.4b})$$

where

$$\rho_{n_x, n_x'}^x = \sum_{n_y} C_{n_x, n_y} C_{n_x', n_y} \quad (\text{A.5a})$$

$$\rho_{n_y, n_y'}^y = \sum_{n_x} C_{n_x, n_y} C_{n_x, n_y'} \quad (\text{A.5b})$$

If $\underline{\rho}_x$, $\underline{\rho}_y$, and $\underline{C}$ are the matrices whose matrix elements are $\rho_{n_x, n_x'}^x$, $\rho_{n_y, n_y'}^y$, and C_{n_x, n_y} , then in matrix notation Eq. (A.5) reads

$$\underline{\rho}_x = \underline{C} \cdot \underline{C}^\dagger \quad (\text{A.6a})$$

$$\underline{\rho}_y = \underline{C}^\dagger \cdot \underline{C} \quad (\text{A.6b})$$

where $\underline{C}^\dagger$ is the transpose of $\underline{C}$.

Let $\underline{U}$ and $\underline{V}$ be the unitary matrices that diagonalize $\underline{\rho}_x$ and $\underline{\rho}_y$, respectively; i.e.,

$$\underline{\rho}_x = \underline{U} \cdot \underline{\lambda}_x \cdot \underline{U}^\dagger \quad (\text{A.7a})$$

$$\underline{\rho}_y = \underline{V} \cdot \underline{\lambda}_y \cdot \underline{V}^\dagger, \quad (\text{A.7b})$$

where $\underline{\lambda}_x$ and $\underline{\lambda}_y$ are diagonal matrices. Since

$$\text{tr}(\underline{\rho}_x) = \text{tr}(\underline{\rho}_y) = 1,$$

one notes that

$$\text{tr}(\underline{\lambda}_x) = \sum_n \lambda_n^x = 1$$

$$\text{tr}(\underline{\lambda}_y) = \sum_n \lambda_n^y = 1,$$

where $\{\lambda_n^x\}$ and $\{\lambda_n^y\}$ are the eigenvalues of $\underline{\rho}_x$ and $\underline{\rho}_y$. Because $\underline{\rho}_x$ and $\underline{\rho}_y$ are related to each other in such a simple way, Eq. (A.6), it is not hard to show that their eigenvalues are the same, i.e.,

$$\underline{\lambda}_x = \underline{\lambda}_y \equiv \underline{\lambda}, \quad (\text{A.8})$$

and their common eigenvalues $\{\lambda_n\}$ are referred to as occupation numbers.

The natural orbitals of $\underline{\rho}_x$ and $\underline{\rho}_y$ are defined, respectively, by

$$\Theta_{n_x}(x) = \sum_{n_x} \theta_{n_x}(x) U_{n_x, n_x} \quad (\text{A.9a})$$

$$\Phi_{n_y}(y) = \sum_{n_y} \phi_{n_y}(y) V_{n_y, n_y}, \quad (\text{A.9b})$$

and in terms of these natural orbitals--the eigenfunctions of the first order density matrices--the wave function $\psi(x,y)$ has the expansion

$$\psi(x,y) = \sum_{n_x, n_y} \tilde{C}_{n_x n_y} \phi_{n_x}(x) \phi_{n_y}(y), \quad (A.10)$$

where the matrix $\tilde{C}$ is given by

$$\tilde{C} = U^\dagger \cdot C \cdot V \quad (A.11)$$

A simpler expression for $\tilde{C}$ can be found by the following argument: Eqs. (A.6), (A.7), and (A.8) imply that

$$\lambda = U^\dagger \cdot C \cdot C^\dagger \cdot U,$$

and also that

$$\lambda = V^\dagger \cdot C^\dagger \cdot C \cdot V.$$

Since

$$V \cdot V^\dagger = U \cdot U^\dagger = 1,$$

these expressions for λ are equivalent to

$$\lambda = U^\dagger \cdot C \cdot V \cdot V^\dagger \cdot C^\dagger \cdot U = \tilde{C} \cdot \tilde{C}^\dagger$$

and

$$\lambda = V^\dagger \cdot C^\dagger \cdot U \cdot U^\dagger \cdot C \cdot V = \tilde{C}^\dagger \cdot \tilde{C}.$$

These two latter equations imply that

$$\tilde{C} = \lambda^{1/2} \quad ; \quad (A.12)$$

i.e., the coefficient matrix in the natural orbital representation, $\tilde{\underline{C}}$, is diagonal. Eq. (A.10) thus reads

$$\psi(x,y) = \sum_n \lambda_n^{1/2} \phi_n(x) \phi_n(y) \quad . \quad (A.10')$$

Finally, it is also possible to give a variational interpretation to this natural orbital analysis. For this discussion let U_{n_x, n_x} and V_{n_y, n_y} be arbitrary unitary transformations of the basis set, and $\tilde{\underline{C}}$ the matrix of coefficients in this new basis. Thus

$$\tilde{\underline{C}} = \underline{U}^\dagger \cdot \underline{C} \cdot \underline{V} \quad ,$$

and the square of a particular coefficient $\tilde{C}_{n_x, n_y}$ is

$$\begin{aligned} |\tilde{C}_{n_x, n_y}|^2 &= \left(\sum_{n'_x, n'_y} U_{n_x, n'_x}^\dagger C_{n'_x, n'_y} V_{n'_y, n_y} \right)^2 \\ &\equiv (\underline{a}^\dagger \cdot \underline{C} \cdot \underline{b})^2 \quad , \end{aligned}$$

where $\underline{a}$ and $\underline{b}$ are unit vectors. It is convenient to let $\underline{a}$ and $\underline{b}$ be arbitrary, unnormalized vectors, so that

$$|\tilde{C}_{n_x, n_y}|^2 = (\underline{a}^\dagger \cdot \underline{C} \cdot \underline{b})^2 / (\underline{a}^\dagger \cdot \underline{a}) (\underline{b}^\dagger \cdot \underline{b}) \quad . \quad (A.13)$$

The variational idea is then to choose the vectors $\underline{a}$ and $\underline{b}$ --i.e., the unitary transformations $\underline{U}$ and $\underline{V}$, or equivalently, the new one-particle basis sets--so that $|\tilde{C}_{n_x, n_y}|^2$ is an extremum. By making the new expansion coefficients as large or as small as possible one thus makes the expansion the most rapidly convergent.

Setting to zero the first variation of Eq. (A.13) with respect to $\underline{\tilde{a}}$ and with respect to $\underline{\tilde{b}}$ leads to the following two equations

$$(\underline{\tilde{a}}^\dagger \cdot \underline{\tilde{a}}) \underline{\tilde{C}} \cdot \underline{\tilde{b}} = (\underline{\tilde{a}}^\dagger \cdot \underline{\tilde{C}} \cdot \underline{\tilde{b}}) \underline{\tilde{a}} \quad (\text{A.14a})$$

$$(\underline{\tilde{b}}^\dagger \cdot \underline{\tilde{b}}) \underline{\tilde{C}}^\dagger \cdot \underline{\tilde{a}} = (\underline{\tilde{a}}^\dagger \cdot \underline{\tilde{C}} \cdot \underline{\tilde{b}}) \underline{\tilde{b}} \quad (\text{A.14b})$$

which determines $\underline{\tilde{a}}$ and $\underline{\tilde{b}}$. Eq. (A.14b) implies that

$$\underline{\tilde{b}} = \text{constant} \times \underline{\tilde{C}}^\dagger \cdot \underline{\tilde{a}},$$

and substituting this into Eq. (A.14a) gives

$$\underline{\tilde{C}} \cdot \underline{\tilde{C}}^\dagger \cdot \underline{\tilde{a}} = \frac{(\underline{\tilde{a}}^\dagger \cdot \underline{\tilde{C}} \cdot \underline{\tilde{C}}^\dagger \cdot \underline{\tilde{a}})}{(\underline{\tilde{a}}^\dagger \cdot \underline{\tilde{a}})} \underline{\tilde{a}},$$

implying that the $\underline{\tilde{a}}$ must be an eigenvector of the matrix $\underline{\tilde{C}} \cdot \underline{\tilde{C}}^\dagger$. One similarly concludes that $\underline{\tilde{b}}$ must be an eigenvector of $\underline{\tilde{C}}^\dagger \cdot \underline{\tilde{C}}$, i.e., the "best" one-particle basis sets in this variational sense are the natural orbitals.

Acknowledgments

We would like to thank A. N. Kaufman, S. W. McDonald, C. Cerjan, P. Pechukas, W. Reinhardt, and W. C. Swope for helpful discussions.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48. N.C.H. acknowledges a NATO award. W.H.M. acknowledges additional support from the Miller Institute of Sciences.

References

- * Permanent address: University Chemical Laboratory, Lensfield Road, Cambridge, England.
- † Camille and Henry Dreyfus Teacher-Scholar.
1. For a discussion of ergodicity in its normal statistical context see, R. Jancel, Foundations of Classical and Quantum Statistical Mechanics (Pergamon Press, Oxford, 1963).
 2. M. Henon and C. Heiles, *Astron. J.* 69, 73 (1964).
 3. J. Ford, "The Statistical Mechanics of Classical Analytical Dynamics" in Fundamental Problems in Statistical Mechanics III, ed. E. G. D. Cohen (North Holland, Amsterdam, 1975), p. 215.
 4. D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.* 67, 404 (1977).
 5. K. D. Hansel, *Chem. Phys.* 33, 35 (1978).
 6. K. D. Hansel, *Chem. Phys. Lett.* 57, 619 (1978).
 7. K. S. J. Nordholm and S. A. Rice, *J. Chem. Phys.* 62, 157 (1975).
 8. See, for example, V. I. Arnold and A. Avez, Ergodic Problems of Classical Mechanics (Benjamin, N.Y., 1968).
 9. K. S. Sorbie and N. C. Handy, *Mol. Phys.* 33, 1319 (1977) and references therein.
 10. See, for example, D. W. Noid and R. A. Marcus, *J. Chem. Phys.* 62, 2119 (1975).
 11. See, for example, S. Chapman, B. C. Garrett, and W. H. Miller, *J. Chem. Phys.* 64, 502 (1976).
 12. K. S. J. Nordholm and S. A. Rice, *J. Chem. Phys.* 61, 203 (1974); 61, 768 (1974).

13. D. W. Noid and R. A. Marcus, J. Chem. Phys. 67, 559 (1977).
14. S. W. McDonald and A. N. Kaufman, Phys. Rev. Lett. 42, 1189 (1979).
15. N. Pomphrey, J. Phys. B 7, 1909 (1974).
16. I. C. Percival, J. Phys. B 6, L229 (1973); Adv. Chem. Phys. 36, 1 (1977).
17. P. Pechukas, J. Chem. Phys. 57, 5577 (1972).
18. B. Barbanis, Astron. J. 71, 415 (1966).
19. Leaving aside the problem of uniquely defining the particular linear combination of degenerate states given by the diagonalization, degenerate states may be rigorously excluded from ergodic behavior. See E. J. Heller, Chem. Phys. Lett. 60, 338 (1979).
20. G. Casati and J. Ford, Phys. Rev. 12A, 1702 (1975).
21. R. McWeeny and B. T. Sutcliffe, Methods of Molecular Quantum Mechanics, (Academic Press, N.Y., 1969), p. 94.
22. H. F. Schaefer III, The Electronic Structure of Atoms and Molecules, (Addison Wesley, Reading, Mass., 1972), p. 41.
23. For the Barbanis system there is no absorption in the y direction because of the plane of symmetry in the x direction.
24. See, for example, D. W. Noid, M. L. Koszykowski, and R. A. Marcus, "Semiclassical Calculation of Bound States in Multidimensional Systems With Fermi Resonance," J. Chem. Phys. (in press).
25. B. V. Chirikov, E. Keil, and A. M. Sessler, J. Stat. Phys. 3, 307 (1971); D. W. Oxtoby and S. A. Rice, J. Chem. Phys. 65, 1676 (1976).

Table I. Properties of Selected Eigenstates of the Barbanis Hamiltonian

<u>No. (a)</u>	<u>Energy</u>	<u>Nodal Classification</u>	<u>Type (b)</u>	<u>$\langle \psi x^2 \psi \rangle$</u>	<u>$\langle \psi y^2 \psi \rangle$</u>	<u>Largest Natural Orbital Occupation</u>
1*	1.1058	(0,0)	R	0.40	0.53	
33	11.744	(7,2)	R	5.9	3.3	.804
34	12.196	(3,8)	R	3.1	10.0	.711
40	12.995	(8,2)	R	6.7	3.4	.882
68	17.018	(1,16)	R	6.1	11.7	.668
74	17.726	(9,6)	R	7.5	9.5	.508
75	17.997	(12,2)	R	9.7	3.8	.687
76	18.080	(5,12)	U	5.0	16.5	.386
77	18.128	(2,16)	R	3.5	18.5	.353
78	18.222	(8,8)	R	6.9	12.2	.453
79	18.472	(11,4)	R	8.9	6.9	.538
80	18.645	(4,14)	R	4.8	18.1	.406
81	18.729	(7,10)	R	6.3	14.7	.434
82	18.777	(14,0)	R	11.4	0.8	.935
83	18.780	(1,18)	R	2.9	20.0	.442
84*	18.946	(10,6)	R	8.3	9.9	.501
85	19.225	(6,12)	E	5.1	18.9	.326
86	19.247	(13,2)	R	10.5	4.0	.668
87	19.264	(3,16)	E	5.2	17.7	.353
88	19.424	(9,8)	R	7.7	12.7	.449
89*	19.484	(0,20)	R	2.1	21.1	.494

Table I continued

90	19.708	(12,4)	R	9.7	7.2	.537
91	19.782	(5,14)	U	5.5	19.3	.365
92	19.874	(2,18)	R	4.0	20.8	.373
93	19.912	(8,10)	R	7.1	15.4	.431
94	20.039	(15,0)	R	12.2	0.8	.929
95	20.166	(11,6)	R	9.0	10.3	.493
96	20.346	(4,16)	E	5.5	20.7	.351
97	20.419	(7,12)	U	7.5	17.9	.394
98	20.497	(14,2)	R	11.3	4.1	.650
99	20.541	(1,20)	R	3.4	22.1	.419
100*	20.625	(10,8)	R	8.4	13.3	.449
101	20.906	(6,14)	E	7.1	21.1	.289
102	20.944	(13,4)	R	10.4	7.5	.535
103	20.977	(3,18)	E	5.2	21.1	.320
104	21.093	(9,10)	R	7.9	16.1	.434
105	21.268	(0,22)	R	2.6	23.1	.476
106	21.301	(16,0)	R	13.0	0.8	.923
107*	21.384	(12,6)	R	9.7	10.8	.484
108	21.454	(5,16)	U	6.2	22.3	.353
109	21.575	(8,12)	R	7.2	19.1	.380
110	21.607	(2,20)	R	4.7	22.7	.372
111	21.747	(15,2)	R	12.0	4.3	.634
112	21.825	(11,8)	R	9.1	14.0	.450
113	22.007	(7,14)	E	6.5	23.5	.311

Table I continued

114	22.094	(4,18)	E	6.6	21.3	.335
115	22.179	(14,4)	R	11.2	7.8	.532
116*	22.272	(10,10)	R	8.6	16.9	.427
117	22.286	(1,22)	R	4.0	24.3	.396
118	22.548	(6,16)	E	6.9	24.3	.316
119	22.563	(17,0)	R	13.8	0.89	.918
120*	22.603	(13,6)	R	10.4	11.3	.475
121	22.673	(3,20)	U	5.8	23.7	.313
122	22.737	(9,12)	R	8.0	19.6	.387
123	22.998	(16,2)	R	12.7	4.4	.621
124	23.025	(12,8)	R	9.7	14.7	.449
125	23.040	(0,24)	R	3.3	25.1	.467
126	23.088	(5,18)?	E	7.0	25.3	.322
127	23.218	(8,14)	R	7.6	22.2	.356
128	23.321	(2,22)	R	5.2	25.1	.367
129	23.418	(15,4)	R	11.7	8.0	.528
130*	23.451	(11,10)	R	9.2	17.8	.419
131	23.626	(7,16)?	E	7.5	26.0	.276
132	23.756	(4,20)?	E	7.9	24.4	.284
133	23.827	(18,0)	R	14.3	1.1	.886
134	23.827	(14,6)	R	10.9	11.4	.452
135*	23.893	(10,12)	R	8.7	20.5	.398

^aAn asterisk denotes a state studied by Sorbie and Handy [ref. 9]. Note that the x and y quantum numbers are reversed in S.H. because of the different coordinates. Note also that the numbering of eigenstates is slightly different due to the smaller basis set of SH. In particular, our states 116, 120, 130, and 135 correspond to SH states 115, 118, 128, and 133.

^bR = Regular, U = Uncertain, E = Ergodic.

Table II. Selected Eigenstates of the Casati-Ford Hamiltonian

No.	Energy		$\langle \psi x^2 \psi \rangle$		$\langle \psi y^2 \psi \rangle$	
	Integrable	Nonint. ^(a)	Integrable	Nonint.	Integrable	Nonint.
1	1.4325	1.7062	0.365	0.367	0.365	0.482
2	2.5107	2.9244	0.820	0.977	0.820	0.829
3	3.2588	3.9417	0.731	0.717	0.731	1.238
4	3.6523	4.2283	1.157	1.388	1.157	0.978
5	4.3634	5.1980	1.277	1.392	1.277	1.738
6	4.8485	5.5934	1.448	1.819	1.448	1.110
7	5.1761	6.3034	1.066	1.085	1.066	1.931
8	5.5330	6.5552	1.645	1.713	1.645	1.873
9	6.0944	7.0135	1.709	2.237	1.709	1.216
10	6.3104	7.6002	1.683	1.781	1.683	2.546
11	6.7578	7.9735	1.955	2.130	1.955	2.050
12	7.1805	8.4839	1.375	2.646	1.375	1.311

^aIntegrable and nonintegrable refer to the use of the parameters in Eqs. (2.5a) and (2.5b) respectively.

Table III. Leading Natural Orbital Occupations for Selected Eigenstates
of the Barbanis Hamiltonian

Regular States	Largest Occupations
98	.650, .210, .071, .049
104	.434, .168, .111, .089
125	.467, .215, .147, .075
Uncertain States	
76	.386, .178, .160, .103
121	.313, .208, .116, .111
Ergodic States	
87	.353, .214, .173, .104
103	.320, .228, .147, .095
118	.316, .206, .169, .106

Figure Captions

- Figure 1. Schematic drawing of the intersection of nodal lines for a) separable and b) coupled two dimensional systems. A special case of a coupled system is shown in Figure 1c.
- Figure 2. Nodal plots of selected regular eigenstates of the Barbanis Hamiltonian. The abscissa and ordinate are the x and y axes marked in units of $(\omega_x)^{1/2}$ and $(\omega_y)^{1/2}$ respectively. Figures 2a, 2b, and 2c represent the 98th, 104th, and 125th states, respectively.
- Figure 3. Nodal plots of selected uncertain Barbanis states. Figures 3a and 3b represent the 76th and 121st states, respectively.
- Figure 4. Nodal plots of selected ergodic Barbanis states. Figures 4a, 4b, and 4c represent the 87th, 103rd, and 118th states, respectively.
- Figure 5. Scattergram of the computed Barbanis eigenstates with energy greater than 19.0.
- Figure 6. Nodal plot of the 34th eigenstate. Figure 6a uses the same scaling as that in Figures 2, 3, and 4. Figure 6b uses magnified scaling and Figure 6c uses the same scaling as 6b but displays the corresponding eigenstate of Eq. (2.1) with $\alpha = -0.04$ instead of -0.08 .
- Figure 7. Nodal plots of eigenstates 1, 2 and 3 of the Casati-Ford Hamiltonian with equal masses (classically integrable) and with unequal masses (nonintegrable). The square boundary is arbitrary.

Figure 8. Nodal plots of Casati-Ford eigenstates 4, 5, and 6.

Figure 9. Nodal plots of Casati-Ford eigenstates 7, 8, and 9.

Figure 10. Nodal plots of Casati-Ford eigenstates 10, 11, and 12.

Figure 11. The power spectra of selected eigenstates of the Barbanis Hamiltonian. Figures 11a and 11b show the regular states 98 and 104, Figure 11c shows the uncertain state 121, and Figure 11d shows the irregular state 87. The smoothing parameter, $\Delta\omega = 0.1$ unit.

	+	-	+	-	
	-	+	-	+	
	+	-	+	-	
	-	+	-	+	

(a)

(b)

(c)

XBL 794-9186

Figure 1

XBL 793-9061

Figure 2a

XBL 793-9062

Figure 2b

XBL 793-9063

Figure 2c

XBL 793-9064

Figure 3a

XBL 793-9065

Figure 3b

XBL 793-9066

Figure 4a

XBL 793-9067

Figure 4b

XBL 793-9068

Figure 4c

XBL 794-9185

Figure 5

XBL 793-9069

Figure 6a

XBL 793-9070

Figure 6b

XBL 793-9071

Figure 6c

STATE

INTEGRABLE

NONINTEGRABLE

1

2

3

XBL 795-9725

Figure 7

STATE	INTEGRABLE	NONINTEGRABLE
4
5
6

XBL 795-9726

Figure 8

STATE

INTEGRABLE

NONINTEGRABLE

7

8

9

XBL 795-9727

Figure 9

STATE	INTEGRABLE	NONINTEGRABLE
10
11
12

XBL 795-9728

Figure 10

XBL 793-9072

Figure 11

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720