Semiclassical quantization using classical perturbation theory: Algebraic quantization of multidimensional systems

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The method of algebraic quantization, a semiclassical analog of Van Vleck perturbation theory, is applied to multidimensional resonant, nonresonant, and nearly resonant systems. PERTURB, a special purpose program written in C, is utilized to implement classical perturbation theory efficiently to high order. States corresponding to both regular and chaotic classical regimes are quantized, and accurate eigenvalues obtained in both cases. Various quantization rules are compared, and a novel symmetry preserving rule is given which leads to good agreement with quantum mechanics. The method is able to reproduce purely quantum mechanical splittings to very good accuracy. Algebraic quantization combined with Padé resummation is used to determine energy eigenvalues for a resonant system with five degrees of freedom.

I. INTRODUCTION

Recent theoretical work on molecular vibrations has been concerned not only with accurate calculation of energy eigenvalues for coupled oscillators,1–5 but also with obtaining a deeper understanding of intramolecular dynamics.4,6 There has been intense interest in the semiclassical approach,7,8 both as a practical method for finding vibrational energies,9 and as a way to use recent fundamental advances in nonlinear classical dynamics10,11 to obtain insights into the behavior of corresponding quantum systems.6,12 Many methods for semiclassical quantization have been proposed, most based in some way on finding invariant tori whose actions satisfy the EBK quantization conditions1,13; the energy of the quantum state is then approximated by that of the quantizing torus. A fundamental problem with torus quantization, however, is that it is not strictly applicable in the chaotic regime, where tori do not exist.10 Nevertheless, chaotic trajectories for which actions are approximately conserved for times longer than several vibrational periods have been quantized, using, e.g., the method of adiabatic switching.14–16 When no such approximate actions exist these techniques are expected to be inapplicable.

Classical perturbation theory10,17 has been used extensively to calculate vibrational eigenvalues.18–30 In this approach, which does not require classical trajectories to be run, canonical transformations are found to express the Hamiltonian in terms of good action variables, to a given order.10 Semiclassical energies are then calculated by substituting quantizing action values into the Hamiltonian. (A more elaborate procedure is necessary in the case of resonant motion: see below.) The method is surprisingly successful—in the uniform semiclassical quantization of the Hénon–Heiles system by Jaffé and Reinhardt,31 accurate eigenvalues for highly excited vibrational states of a two degree of freedom system were obtained even when the underlying classical motion was chaotic. The applicability of classical perturbation theory in the chaotic regime is certainly intriguing, since the theory can by design only describe motion confined to a torus.10 Evidently, the success of the method is to some extent independent of whether the torus generated by the perturbation expansion actually exists or not; it is apparent that the use of finite order perturbation theory effectively smooths over chaotic regions of phase space,31,32 if they are sufficiently small. Further investigation into the convergence properties and summability of classical perturbation theory,33–35 as well as application to a wider range of problems, including systems with three or more degrees of freedom, is clearly called for.

Previous work along these lines has, however, been hampered by the need to keep track of the huge number of terms generated in carrying out classical perturbation theory to high order in multidimensional systems.36 Low order analysis,22,29 on the other hand, can yield accurate results for the first few vibrational states, but is unlikely to be accurate at higher energies, or for highly anharmonic systems. To implement high order classical perturbation theory for multidimensional systems efficiently, we have written a special purpose algebraic manipulation program, called PERTURB.37 Details of the program and a brief discussion of its application to the semiclassical quantization of nonresonant systems are given elsewhere.37

In the application of classical perturbation theory to multidimensional systems, the well known problem of small denominators arises.10 Low order near commensurabilities between zeroth order frequencies give rise to resonant motions, which are usually greatly distorted from the unperturbed trajectories.38 The presence of resonances leads to divergences in the perturbation theory10; without some sort of special treatment such as Padé resummation,39,40 high order terms in the perturbation expansion become meaningless. Moreover, as the dimensionality of a system increases, the number of possible near resonances rises rapidly.41 In practice, nonresonant perturbation theory applied to an arbitrary multidimensional system will therefore diverge.

In this work, we consider the quantization of nonresonant, resonant, and nearly resonant multidimensional systems. For nonresonant systems, straightforward primitive
EBK quantization is used, as well as a treatment based on the Weyl quantization rule. For resonant and nearly resonant systems, we use the method of algebraic quantization to obtain uniform semiclassical energy levels. This approach has been previously applied to resonant systems with two degrees of freedom. We discuss here the extension to resonant systems of higher dimensionality, and to nearly resonant systems. The convergence of the method as higher order corrections are included is also studied. Resonant Hamiltonians with up to five degrees of freedom are treated. Ordering issues, which have been briefly discussed by Robnik, are considered in detail. We compare the accuracy of various quantization rules for a variety of systems.

Before embarking on a detailed description of our results, we give a brief overview here. In algebraic quantization, the classical Hamiltonian is reduced by a sequence of canonical transformations to a simple form in such a way as to avoid divergence. Thus, all nonresonant couplings are eliminated, but resonant and nearly resonant terms are left in the transformed Hamiltonian. The resulting Hamiltonian then depends, in general, both on the new canonical momenta and a subset of the new angle variables, as opposed to just good action variables as in the nonresonant case. In effect, convergent results are obtained at the price of a more complicated form of the Hamiltonian. The simplification of the classical Hamiltonian, with particular emphasis on resonances and their associated constants of the motion, is given in Sec. II.

After simplifying the classical Hamiltonian, a quantization rule is used to convert the transformed classical Hamiltonian into a quantum mechanical operator. The general properties of these quantization rules are discussed in Sec. III, together with a novel rule we have used to obtain good agreement with quantum mechanics. If linear invariants exist in the classical Hamiltonian, the corresponding quantized Hamiltonian is diagonal in the quantum analog of the invariant. The correspondence between classical and quantum linear invariants is discussed in Sec. III. The resulting diagonal blocks can turn out to be finite, so that large matrix diagonalizations are unnecessary. Even in cases where the Hamiltonian is not block diagonal, the basis used in algebraic quantization is better than a zeroth order basis set, since the nonresonant couplings which break the block diagonal structure of the Hamiltonian are small.

Section IV gives results for a variety of nonresonant, resonant, and nearly resonant systems. All of the problems treated have a finite block structure after simplification of the Hamiltonian. Therefore, accurate eigenvalues are produced without the need to diagonalize large matrices. Finally, the merits of the method, as well as problems involved in applying it to systems of many degrees of freedom, are discussed in Sec. V.

It should be noted that the algebraic quantization just outlined is the semiclassical analog of Van Vleck perturbation theory, as used in the conventional contact transformation approach to calculation of rotation–vibration energy levels. Comparisons between the semiclassical method and its quantum mechanical counterpart to evaluate their relative efficiency and accuracy would clearly be of interest, and are the subject of current investigation. The relationship between the two methods could perhaps be used to gain further insight into the surprising accuracy of eigenvalues obtained by classical perturbation theory in the chaotic regime, and ultimately may provide the basis for a "quantum mechanical KAM theorem."

II. SIMPLIFYING THE CLASSICAL HAMILTONIAN
A. Operator based perturbation theory

Both simple EBK quantization via perturbation theory and the method of algebraic quantization use a Hamiltonian which has been simplified by canonical transformations. There are several perturbative schemes for effecting these transformations. In this section we briefly review operator based classical perturbation theory, with an emphasis on its application to semiclassical quantization. The operator approach discussed here is easier to implement than approaches based on traditional canonical perturbation theory, such as the Birkhoff–Gustavson method, since it requires no functional inversions to obtain explicit relations between old and new variables. It is also closely related to quantum mechanical perturbation theory. Therefore, it provides a useful basis of comparison between classical and quantum perturbation theory.

The aim of classical perturbation theory is to find (to a given order) a transformation from the original set of variables to a new set of variables, in terms of which the motion is simple. Usually, this means writing the Hamiltonian as a function of zeroth order action-angle variables \(J, \Theta\), then finding a transformation \(T\) taking the zeroth order variables into good action-angle variables \(J, \Theta\) to a given order in perturbation. When expressed in terms of these good variables, the Hamiltonian is a function of action only, so the motion is simply a uniform winding in angle, with the action constant. The resulting time evolution is topologically equivalent to uniform motion on a torus. Types of classical perturbation theory differ in the way the coordinate transformation \(T\) is produced. The traditional approach uses mixed variable generating functions \(F(J, \Theta)\):

\[
J = \frac{\partial F}{\partial \Theta}; \quad \Theta = \frac{\partial F}{\partial J}.
\]  

(1)

The principal disadvantage of using such generating functions is that relations (1) must be inverted to provide an explicit equation for one set of variables in terms of another.

More recently, methods based on Lie operators rather than generating functions have been introduced. The Lie methods avoid the need for the inversion of equations. Furthermore, these methods are closely related to quantum mechanical Van Vleck perturbation theory, making them a natural choice for semiclassical treatments. In the present work we describe one of these methods, Dragt–Finn perturbation theory. We have selected this method for discussion because it is both the simplest and the most closely related to the usual form of Van Vleck perturbation theory. It is important to note, however, that all canonical perturbation theories based on a simple expansion in a small parameter (as opposed to "superconvergent" theories) give identi-
Dratt–Finn perturbation theory is based on the central observation that the exponential of a Lie operator induces a canonical transformation. That is, let \( L_f \) be the Lie operator associated with \( f \):

\[
L_f = \{f, \cdot\},
\]

where \( \{,\} \) denotes the Poisson bracket. Then the transformation

\[
z \rightarrow \tilde{z} = \exp(L_f)z
\]

is canonical, where we have used \( z \) to denote the pair \((j, \theta)\), and similarly, \( \tilde{z} \) denotes the pair \((J, \Theta)\). Moreover, any analytic canonical transformation can be written as the product of a (possibly infinite) sequence of transformations of the form (3). Note that transformation (3) requires no inver-
sion of implicit equations. The inverse transformation is simply expressed as

\[
z = \exp(-L_f)\tilde{z},
\]

where \( f(z) \) is understood to be replaced by \( f(\tilde{z}) \), and the Poisson brackets are taken with respect to \( \tilde{z} \). The explicit invertibility of the coordinate transformation is a substantial practical improvement over mixed variable perturbation theories. The Hamiltonian in the new coordinate system can also be given in terms of Lie operators:

\[
K(\tilde{z}) = \exp(L_f)H(\tilde{z}).
\]

In order to turn these fundamental observations into a systematic perturbation theory, Dratt and Finn use a sequence of transformations, each of which brings the Hamiltonian into a simple form to one more power of an expansion parameter \( \epsilon \):

\[
K = \cdots \exp(\epsilon L_{\alpha}) \cdots \exp(\epsilon^2 L_f) \exp(\epsilon L_{\alpha}) H.
\]

Let

\[
H^0 = H,
\]

\[
H^k = \exp(\epsilon^2 L_f)H^{k-1}.
\]

Then

\[
H^{k-1} = K.
\]

Let us expand \( H^k \) in powers of \( \epsilon \):

\[
H^k = \sum_{m=0}^{\infty} \epsilon^m h^m = \exp(L_{\alpha}) H^{k-1}.
\]

Equating powers of \( \epsilon \) in Eq. (8) then yields the fundamental equation of Dratt–Finn perturbation theory:

\[
h^k = \int \cdots \int_{(-\infty, 0)^k} \frac{1}{n!} (L_{\alpha} h^{k-1})_{\alpha} \cdot
\]

where \( \int (j/k) \) is the integer part of \((j/k)\). The meaning of this equation can be made clearer by considering two special cases:

\[
h^k = h^{k-1}, \quad j < k;
\]

\[
h^k = h^{k-1} + L_f h_0, \quad j = k.
\]

Equation (12) implies that the terms of \( H^k \) which are of lower order in \( \epsilon \) than \( k \) are unchanged by subsequent transform-

B. Perturbed harmonic oscillators

Dratt–Finn perturbation theory can in principle be applied to a Hamiltonian having an arbitrary functional form which allows expansion in a perturbation parameter. In order to derive explicit equations, and relate this method to more conventional types of perturbation theory, we specialize our discussion to the case that the Hamiltonian \( H \) is a polynomial in variables \((q, p)\). An arbitrary analytic Hamiltonian can always be brought into this form to a given order by expansion about an equilibrium point. In what follows, terms of polynomial degree \( n \) are described as being of order \( \epsilon^n - 2 \). It should be noted that this ordering scheme is equivalent to the ordering used in the usual Birkhoff–Gustavson approach. For harmonic oscillators, \( H_0 \) is linear in action, with zeroth order frequencies \( \omega_0 \):

\[
H_0 = \omega_0^2 J.
\]

\( H_j \), which is a polynomial in variables \((q, p)\), can then be written as a Fourier series in zeroth order angles, multiplied by polynomials of \( (m, n) \) order:

\[
H_j = \sum_{m=-\infty}^{\infty} \left[ \sum_{m=-\infty}^{\infty} C_m(\alpha) J^m \exp(i m \theta) \right],
\]

where \( J^m \) denotes \( j_1^m \cdots j_n^m \), \( m \in \mathbb{Z}^N \).

In this type of perturbation theory, \( h^k \) in Eq. (13) is required to have a particular simple form, and Eq. (13) is then solved for \( f_k \). A general algorithm for doing so in resonant and nonresonant cases can be given if \( H \) is of the form (15). In nonresonant systems, we choose \( h^k \) to be the angle independent part of \( h^{k-1} \). Then, given that \( h^{k-1} \) has the above form (15), we find that

\[
f_k = \sum_{m=0}^{\infty} \left[ \sum_{m=-\infty}^{\infty} C_m(\alpha) q^m \right].
\]

If a resonance between the zeroth order frequencies appears, that is, if \( \omega_0^m = 0 \) for some \( m \) in the sum, an infinite term appears in Eq. (16). The offending resonant term in \( h^{k-1} \) must then be explicitly included in \( h^k \). The final transformed Hamiltonian \( K \) will therefore contain angle dependent terms.

A generalization criterion for the choice of \( h^k \) can be stated, which includes both the resonant and nonresonant cases: \( h^k \) is chosen to be in the null space of the operator \( L_{\alpha} \). This condition clearly holds only if a term is independent of \( \theta \), or if the term is resonant. A Hamiltonian can, therefore, be brought into normal form using Lie operators by ordering terms according to their polynomial degree, and applying the appropriate criterion to choose \( h^k \).

A nearly resonant term introduces additional complica-

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tions into the choice of \( h^k \), since the presence of such a term in \( f^k \) will cause the latter to be large. This will in turn lead to a divergence of the perturbation theory. Therefore, the null space criterion for the choice of \( h^k \) cannot be used without introducing severe difficulties in the treatment of nearly resonant systems. This is the problem of small denominators, and is one of the principal difficulties in the application of perturbation theory to systems with many degrees of freedom.\(^{10} \)

C. Invariants for nearly resonant systems

In the Birkhoff–Gustavson formalism,\(^{53} \) the normal form \( K \) is chosen so that it is in the null space of the operator \( L_{H_0} \), i.e., \( \{ H_0, K \} = 0 \). Therefore, \( H_0 \) is always an invariant of the transformed Hamiltonian \( K \), a simplification guaranteed by the Birkhoff–Gustavson algorithm. For a nearly resonant system, in which \( \omega_{\nu} \) is small but not identically zero, the requirement that \( K \) be in the null space of \( H_0 \) leads to an expression for \( K \) that diverges rapidly. If, however, such a nearly resonant term were to be treated as resonant, the expression for \( K \) would show no divergence, but the condition that \( \{ H_0, K \} = 0 \) would no longer be satisfied, i.e., \( H_0 \) would no longer be an invariant of the transformed Hamiltonian. Nonetheless, other invariants often exist, leading to classical constants of motion, and a block diagonal quantum mechanical matrix problem. The determination of such invariants is, therefore, an important part of the method of algebraic quantization. We give here a treatment of the problem for both resonant and nearly resonant systems.

Consider a final Hamiltonian \( K \), which is the product of a number of coordinate transformations. For these transformations to be executed without producing a divergent series, it is often necessary for angle dependent terms to be retained in \( K \). We wish to find the number of invariants possessed by \( K \). We will restrict the discussion to invariants which are linear functions of actions. More complicated invariants that are not merely functions of the linear invariants, while possible in special cases, will not exist generically. The invariant is thus written

\[
I = \mu \cdot j .
\]

The condition that \( I \) be an invariant is just

\[
\{ I, K \} = 0.
\]

In the case of a polynomial Hamiltonian, however, \( K \) will have the form (15), so the condition (18) may be formulated more explicitly. Let us consider the Poisson bracket of \( I \) with a single term of \( K \):

\[
\{ \mu \cdot j^+ e^{\mu \cdot m} \} = -i (\mu \cdot m) j^+ e^{\mu \cdot m}.
\]

(19)

\( I \) will be a linear invariant if and only if its Poisson bracket with each term of the Hamiltonian is zero. This requirement can be given a simple matrix formulation. Place all of the vectors \( m \) into an \( M \) by \( N \) matrix, where \( N \) is the number of degrees of freedom, and \( M \) is the number of angle dependent terms in \( K \). Then \( I \) is a linear invariant if and only if \( \mu \) is in the null space of this matrix, making it easy to determine such invariants using a computer program. Furthermore, the vector \( \mu \) can always be chosen to have integer components, yielding a simple and convenient form for the invariant (see the Appendix).

It is of interest to see how our criterion applies to a normal form generated by the Birkhoff–Gustavson algorithm.\(^{53} \) In this approach, nearly resonant terms are always treated as strictly nonresonant. Therefore, the angle dependent terms in \( K \) all correspond to exact resonances. This implies that \( H_0 \) itself is one of the invariants \( f \), since

\[
\omega_{m \mu} = 0
\]

for all terms in the normal form \( K \). As a result, the Birkhoff–Gustavson approach always generates at least one invariant, as is well known. The existence of at least one invariant in addition to the transformed Hamiltonian itself can in fact be used to explain the method's lack of true convergence (as opposed to apparent convergence for a finite number of terms in the series), since generic Hamiltonian systems display no global invariants.\(^{10} \)

In nearly resonant systems, it is useful to modify the Birkhoff–Gustavson algorithm, and treat all terms with denominators \( \omega_{m \mu} \) less than a certain threshold value as resonant. This approach helps avoid the problems associated with divergent series, but introduces a new difficulty. As we proceed to higher order, more and more near resonances arise, which must all be included in the new Hamiltonian \( K \). Eventually, so many linearly independent resonances have to be included in \( K \) that it no longer has any invariants. This problem becomes particularly severe in systems with many degrees of freedom.\(^{41} \) Nonetheless, even if there are no invariants, progress has still been made in reducing the Hamiltonian to simpler form, for the terms that fail to commute with the various invariants are expected to be small, since they arise from high order corrections.

III. QUANTIZING THE TRANSFORMED HAMILTONIAN

A. The quantum analog of classical invariants

Our generalization of the Birkhoff–Gustavson algorithm to nearly resonant systems will often generate Hamiltonians with linear classical invariants. It was asserted above that systems with such invariants have block diagonal matrices in the corresponding quantum problem. The method of algebraic quantization relies on this block diagonal structure to reduce the solution of the eigenvalue problem to the diagonalization of small finite matrices. Therefore, the correspondence between linear classical invariants and quantum invariants is one of the foundations of algebraic quantization. We now explore that correspondence. Consider a Hamiltonian \( K \) which is in the form (15). It can be expressed in terms of the classical analogs of creation–annihilation operators:

\[
a_\nu = j^{1/2} e^{i \nu},
\]

\[
a_\nu^\dagger = j^{-1/2} e^{-i \nu}.
\]

(21)

(22)

Since \( K \) is of the form (15), it follows that it is a polynomial in the new set of variables \((a, a^\dagger)\), which makes the quantization of the transformed Hamiltonian tractable.\(^{57} \) In order to transcribe \( K \) into a quantum mechanical Hamiltonian, it is necessary to specify the quantization rule to be used. We
shall assume that a relation of the form
\[(a^*)^{m}a^n \rightarrow \sum_{j=0}^{\min(m,n)} C(j)(a^*)^{m-j}a^{n-j}\] (23)
holds. This result is true for both the Weyl quantization rule and the symmetrization rule, and will in fact hold for any rule that simply reorders the terms of a noncommuting polynomial.

Consider a classical Hamiltonian, \(K\). If \(K\) is of the form (15), then it can be expressed in terms of the classical variables \((\alpha, \alpha^*)\) as
\[K = \sum_{\mathbf{m}, \mathbf{n}} C(\mathbf{m}, \mathbf{n})(\alpha^* \alpha)^\mathbf{m} \alpha^\mathbf{n},\] (24)
where \(\alpha^\mathbf{m}\) denotes \(\alpha_1^{m_1}\alpha_2^{m_2}\cdots\alpha_N^{m_N}\) if all the \(m_i\) are positive, and if any of the \(m_i < 0\) denotes \(\alpha_1^{m_1}\alpha_2^{m_2}\cdots(\alpha^*)^{|m_i|}\alpha_3^{m_3}\cdots\alpha_N^{m_N}\). We shall employ a similar notation for \(\hat{\mathbf{m}}\), with the operator \(\hat{a}\) taking the role of \(\alpha\), and \(\hat{a}^*\) taking the role of \(\alpha^*\). The rule (23) implies that the corresponding quantum mechanical Hamiltonian will also be of this form, with the classical variables replaced by annihilation and creation operators. Furthermore, any lattice vector \(\mathbf{m}\) appearing in the classical Hamiltonian will also be found in the quantum mechanical Hamiltonian.

Let \(\mu_1\) be a classical invariant of the Hamiltonian \(K\). Then \(\mu_\mathbf{m}\) is an invariant of the quantum mechanical system, where \(\hat{\mathbf{m}}\) is the number operator vector \((\hat{a}_1, \ldots, \hat{a}_N)\). This follows from the commutation relation
\[\{\hat{\mathbf{m}}, \mu_\mathbf{m}\} = (\mu \cdot \mathbf{m}) \hat{\mathbf{m}}\hat{\mathbf{m}}^*,\] (25)
and the fact that \(\mu \cdot \mathbf{m}\) is zero, since the vector \(\mu\) defines a classical invariant.

The existence of a quantum mechanical invariant implies that the Hamiltonian matrix will be block diagonal. Such blocks are often finite for nearly resonant systems, and are always finite for resonant systems (if the Birkhoff–Gustavson method has been used). The blocks are finite if there exists an invariant given by \(\mu\), where all the \(\mu_i\) are positive, for in that case there can be only a finite number of nonnegative integer valued solutions to
\[\mu \cdot \mathbf{n} = \alpha,\] (26)
where \(\alpha\) is the eigenvalue of \(\mu \cdot \mathbf{a}\) labeling the block. If the Birkhoff–Gustavson algorithm has been used, the zeroth order Hamiltonian is always an invariant. The \(\mu_i\) are just the zeroth order frequencies in this case, so the existence of a finite block diagonal structure is guaranteed. In nearly resonant systems, there often exists an invariant which can be identified as the zeroth order Hamiltonian of an exactly resonant system that is in some sense close to the nearly resonant system. In this case as well, there will be finite blocks.

The existence of a finite block structure is fundamental for the method of algebraic quantization. For low lying states, or for systems with few degrees of freedom, such blocks are typically quite small. Diagonalization of the quantum Hamiltonian derived from perturbation theory can then be done on a computer with relatively little effort. As \(N - Q\) increases, where \(N\) is the number of degrees of freedom, and \(Q\) is the number of invariants, the size of the blocks will increase rapidly. For instance, a 1:1 resonance in \(N\) dimensions, with no invariants other than the zeroth order

Hamiltonian, will have
\[\binom{N + m - 1}{N - 1} \text{ for the } m\text{th block},\] (27)
states in the \(m\)th block, a quantity which rapidly becomes unmanageably large as \(N\) increases. Although this example is the worst possible case, it is evident that methods other than straightforward matrix diagonalization, such as resummation, must be used to treat the highly excited states of nearly resonant systems with many degrees of freedom. An investigation of such methods is in progress.

B. Quantization rules

As shown in the previous section, a quantization rule must be chosen when implementing algebraic quantization, since the transformed Hamiltonian is a polynomial in non-commuting variables. A wide latitude in the choice of quantization rule is possible. Nevertheless, it is found that the accuracy of the energy eigenvalues depends quite strongly on the quantization rule used. Several rules are discussed in this section, including a novel method of quantization which, although empirically derived, gives accurate results.

There are several useful criteria that a quantization rule should ideally satisfy.\(^{51}\) It is desirable to have a rule \(R\) that is:
(1) linear: \(R(aK_1 + bK_2) = aR(K_1) + bR(K_2)\).
(2) Canonicity: \((-i/\hbar) [\hat{J}, \hat{\mathbf{g}}] = \{\hat{J}, \hat{\mathbf{g}}\}\). In particular, a new set of canonical coordinates has the same commutation rules as Cartesian variables:
\[\{\hat{Q}(q, p), \hat{P}(q, p')\} = \{\hat{Q}, \hat{p}\} = i\hbar.\]
(3) Reduces to EBK for diagonal Hamiltonians: \(R(K_j) = K(\hat{a} + \frac{1}{2})\).

Condition (1) is desirable, because it is a great convenience to quantize a complicated expression term by term. Nonlinear quantization rules, while possible, have been largely unexplored. Canonical invariance is also a desirable feature; results should ideally be independent of the classical representation of the problem. Finally, the EBK substitution (3) has been shown to be a reliable and accurate means of quantizing Hamiltonians which depend only on action. Whatever rule is used should be at least as good as EBK when applied to diagonal Hamiltonians. We have found that rules which do reduce to EBK give better results than those which do not, with the possible exception of very highly excited states.

Unfortunately, it can be shown that no quantization rule can satisfy even conditions (1) and (2) simultaneously.\(^{58}\) Robnik\(^{27}\) has suggested that the Weyl rule should be used, as it is the only rule which is linear and invariant under linear canonical transformations.\(^{45}\) The Weyl rule, when applied to polynomials in creation–annihilation operators, gives
\[W(a^n a^m) = \sum_{l=0}^{\min(m,n)} \frac{1}{2l!}\binom{n}{l} a^{l} a^{m-l} a^{n-l}.\] (28)

The Weyl rule, however, does not satisfy the squaring axiom. That is,
\[W(A^2) \neq W(A)^2\] (29)
for arbitrary \(A\), where \(W\) denotes the Weyl quantization. This implies that the use of the Weyl rule does not reduce to
IV. RESULTS

A. Nonresonant systems

Accurate energies for highly excited states of nonresonant systems can be found by going to sufficiently high orders of perturbation theory.\(^{60}\) However, energy eigenvalues are sensitive to the quantization rule used. To demonstrate this, we consider the 0.7:1.3 Hénon–Heiles system treated in the work of Swimm and Delos.\(^{19}\) The Hamiltonian is

\[
H = \frac{1}{2} \sum_{i=1}^{2} \left( p_i^2 + \omega_i^2 q_i^2 \right) + \lambda q_2 (q_1^2 + q_2^2 ) .
\]  

(34)

For the system treated by Swimm and Delos, the following parameter values are used:

\[
\omega_1 = 1.3 , \quad \omega_2 = 0.7 , \quad \lambda = -0.1 , \quad \eta = 0.1 .
\]  

(35)

Table I gives energy eigenvalues obtained by the quantization of a 16th order normal form. Our results were converged to all digits given for the first group of states, and to four digits for the second group of states. No near resonances were found, so the normal form had no angle dependence. Both the Weyl quantization rule and the EBK substitution \( J \rightarrow n + 1/2 \) were used to quantize the normal form. No energies for Robnik’s approximation or the SPSC rule are given, since they reduce to EBK for a normal form which is independent of angle.

The relative accuracy of the Weyl and the EBK quanti-

TABLE I. Energy eigenvalues for the 0.7:1.3 Hénon–Heiles system of Eqs. (34) and (35).

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<td>4.9794</td>
<td>4.9721</td>
<td>4.9794</td>
</tr>
</tbody>
</table>

* Semiclassical values from a 16th order normal form.
* Obtained from Weyl quantization of normal form above.
* Quantum mechanical values from Ref. 19.
zation shows an interesting dependence on energy. For low energies, the EBK quantization of the normal form is clearly superior. At energies very close to dissociation, however, the Weyl quantization becomes more accurate than the semiclassical quantization. Presumably, the Weyl rule quantizes the high order perturbation terms more accurately than does the semiclassical rule, while producing less accurate results for the low order terms. The reason for this behavior is not fully understood. Finally, we note that using a 16th order normal form yields more accurate results for highly excited states than the 6th order results reported by Swimm and Delos. 19

Results of comparable accuracy are also obtained for nonresonant systems with more than two degrees of freedom. We have, for example, quantized a realistic polynomial potential for \( \text{SO}_2 \) 61:

\[
H = \frac{3}{2} \sum_{i=1}^{3} \alpha_i (p_i^2 + q_i^2) + k_{111} q_1^4 + k_{112} q_1^2 q_2 + k_{122} q_2^2 + k_{133} q_3^2 + k_{222} q_2^2 + k_{233} q_2^2 q_3 + k_{111} q_1^4 + k_{112} q_1^2 q_2 + k_{122} q_2^2 + k_{222} q_2^2 + k_{333} q_3^3
\]

\[(36)\]

using the parameter values given in Table II.

A 12th order normal form was calculated, which produced results converged to at least 4 digits for each state. As seen in Table III, we obtain good agreement with quantum mechanical results for the low lying states. 63 Furthermore, the excellent agreement between our semiclassical results and the EBK FFT results of Martens and Ezra 5 indicates that most of the disagreement between our values and the quantum values can be attributed to approximations inherent in the semiclassical quantization condition. For all states where quantum values are available, we find that the EBK quantization is better than the Weyl quantization. This does not rule out the possibility, however, that highly excited states of \( \text{SO}_2 \) may be given more accurately by the Weyl rule, as was seen in the 0.7:1.3 Hénon–Heiles Hamiltonian treated by Jaffé and Reinhardt. 21 The parameter values for this system, in the nota-

### TABLE II. Parameters for the \( \text{SO}_2 \) Hamiltonian of Eq. (36) in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (cm(^{-1}))</th>
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</thead>
<tbody>
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<td>( k_{112} )</td>
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\( ^{a} \)Semiclassical quantization of a 12th order normal form.

\( ^{b} \)Weyl quantization of the same form as in footnote a.

\( ^{c} \)Fourier transform method of Ref. 5.

\( ^{d} \)Semiclassical self-consistent field method of Ref. 62.

\( ^{e} \)Quantum values of Ref. 63.

### TABLE III. Energy eigenvalues for the \( \text{SO}_2 \) Hamiltonian of Eq. (36).

<table>
<thead>
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<th>( N_1 )</th>
<th>( N_2 )</th>
<th>( N_3 )</th>
<th>( E_{nc} )</th>
<th>( E_{w} )</th>
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</table>

\( ^{a} \)Semiclassical quantization of a 12th order normal form.

\( ^{b} \)Weyl quantization of the same form as in footnote a.

\( ^{c} \)Fourier transform method of Ref. 5.

\( ^{d} \)Semiclassical self-consistent field method of Ref. 62.

\( ^{e} \)Quantum values of Ref. 63.

J. Chem. Phys., Vol. 86, No. 11, 1 June 1987
TABLE IV. Energy eigenvalues for the 1:1 Hénon–Heiles system of Eqs. (34) and (37).

<table>
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<th>$E_{SPSC}^*$</th>
<th>$E_{US}^*$</th>
<th>$E_{QM}^*$</th>
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**TABLE V. Energy splittings for the 1:1 Hénon–Heiles of Eqs. (34) and (37).**

<table>
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<th>n</th>
<th>l</th>
<th>$\Delta E_R^*$</th>
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<td>0.0084</td>
<td>0.0077</td>
<td>0.0077</td>
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</tbody>
</table>

* Robnik’s quantization rule.
* Weyl quantization rule.
* Uniform semiclassical quantization of a sixth order normal form (Ref. 21).
* Algebraic quantization of a fourth order normal form (Ref. 28).
* Quantum mechanical results (Ref. 64).

It should be noted that the Weyl rule gave more accurate results for the highly excited states of the 1:3:0.7 Hénon–Heiles system. Although Robnik’s rule and our symmetry preserving semiclassical rule give roughly the same results for the $A$ states, the SPSC rule reproduces exact degeneracies for states belonging to multidimensional representations (not given in Table IV), a desirable property not shared by Robnik’s rule.

The energy splittings for the interesting $A$ states are given in Table V. The Weyl rule and Robnik’s rule are found to be of comparable accuracy, and in excellent agreement with quantum mechanics. No splittings are given for the SPSC rule, since it produces the same splittings as the Weyl rule.

Both quantization rules yield splittings which are generally superior to both the sixth order uniform results of Jaffé and Reinhardt, 21 and the fourth order algebraic quantization of Uzer and Marcus. 28,60 Thus, it is seen that algebraic quantization gives a highly accurate approximation to the entire bound spectrum of the Hénon–Heiles system. Both chaotic and regular states are quantized with good accuracy. Purely quantum mechanical splittings are reproduced well, showing that the method of uniformization used accounts for the most significant quantum mechanical features.

The fact that accurate energy eigenvalues can be obtained even when the underlying classical motion is chaotic indicates that the success of quantization via perturbation theory does not require that tori actually exist, or that the perturbation expansion ultimately converge. As discussed by Reinhardt, 32 quantum mechanics is to a large extent insensitive to phase space features such as resonance zones or localized chaos that occupy regions of volume smaller than $f^p$.

Algebraic quantization is also an accurate means of quantizing resonant systems with more degrees of freedom. To illustrate this, and to demonstrate difficulties which arise in systems with many modes, we have quantized the family of related systems with three, four, and five degrees of freedom treated by Skodje, Borondo, and Reinhardt, 14 as well as...
H_N = \frac{1}{2} \sum_{i=1}^{N} (p_i^2 + \omega_i q_i^2) - 0.1 \sum_{i=1}^{N-1} q_i (q_{i+1}^2 + 0.1 q_i^2) \quad (38)

for N = 3, 4. The five-dimensional Hamiltonian is

H_5 = H_4 + \frac{1}{2} (p_5^2 + \omega_5 q_5^2) - 0.1 q_5 (q_5^2 + 0.1 q_5^2). \quad (39)

The frequencies are taken to be

\omega_1 = 0.7, \quad \omega_2 = 1.3, \quad \omega_3 = 1.0, \quad \omega_4 = 1.53, \quad \omega_5 = 0.89. \quad (40)

All of the systems show an exact 1:1:2 resonance between the first three frequencies, which first appears in second order corrections to the normal form. For the three-dimensional system, Ramaswamy, Siders, and Marcus give a nonresonant second order normal form with arbitrary zeroth order frequencies. Our second order normal form is identical to theirs, except for the addition of a resonant coupling term. Although their Hamiltonian is valid away from resonance, it is not correct for this particular choice of frequencies. The presence of the resonance is manifested by the appearance of an infinite second order generating function. No divergence is seen in the second order Hamiltonian, although higher order corrections would be infinite. The results of Ramaswamy, Siders, and Marcus are best thought of as an interpolation of a nonresonant second order normal form to a resonant case where it is not strictly valid. Nevertheless, good results may be obtained for the first few states using this procedure, since these states are not coupled by the resonant term left out of the Hamiltonian. We find that the blocks are quite small for all the states given. In fact, the largest block found in Table VI couples three states.

Results are given in Table VI for the three-dimensional system using the Weyl quantization rule, Robnik’s approximation, and the SPSC rule. Use of an eighth order normal form converges the first group of eigenvalues given to five digits, while the second group was converged to four digits. Both Robnik’s rule and the SPSC rule give excellent agreement with available quantum values. For the first few states, the Weyl rule gives poorer agreement with quantum mechanics. Although there are to our knowledge no other excited state eigenvalues with which to compare our results for the second group of states, results for the two degree of freedom system treated above together with the observed convergence of the energy values leads us to expect that the energies given by either Robnik’s quantization rule or the SPSC rule are good approximations to the actual spectrum of the system.

Second order results are also given, using both resonant and nonresonant normal forms. The resonant normal form was quantized using the SPSC rule. For the first few states, the second order results are in good agreement with quantum mechanics. In fact, for some levels the second order results give slightly better agreement with quantum mechanics than the eighth order results. Nevertheless, the eighth order energies reproduce results derived from other semiclassical methods better than the second order energies. As an illustration of this, we give semiclassical energies found by Martens and Ezra using the Fourier transform method. The close agreement between the eighth order results and those of Martens and Ezra suggest that the apparent superiority of the second order results in certain cases is at least partly fortuitous. For the group of highly excited states given, the difference between eighth order and second order results becomes somewhat more pronounced, as might be expected.

Although the second order resonant and nonresonant normal forms give identical results for the first few states, this is not always the case. For example, the difference between the resonant and nonresonant forms is apparent in the last three states given in Table VI, where resonant coupling has modified the eigenvalues by an appreciable amount. The use of nonresonant normal forms cannot be recommended as a general procedure for implementing low order perturbation theory. It is expected to work well only when the coupling introduced by using the resonant normal form is negligible, or for states which are not coupled by the resonant term.

Table VII gives energy eigenvalues for the four-dimensional system. An eighth order normal form was used, which converges the energies given for the first group of states to

| \begin{array}{cccccccc}
N_1 & N_2 & N_3 & E_R^a & E_w^b & E_{SPSC}^c & E_s^d & E_{NR}^e & E_{PT}^f & E_{QM}^g \\
0 & 0 & 0 & 1.4930 & 1.4904 & 1.4930 & 1.4931 & 1.4931 & 1.4928 & 1.494 \\
1 & 0 & 0 & 2.1844 & 2.1817 & 2.1840 & 2.1840 & 2.1841 & 2.1841 & 2.185 \\
0 & 0 & 1 & 2.4847 & 2.4822 & 2.4847 & 2.4853 & 2.4853 & 2.4848 & 2.486 \\
0 & 1 & 0 & 2.7712 & 2.7684 & 2.7712 & 2.7712 & 2.7721 & 2.7721 & 2.777 \\
2 & 0 & 0 & 2.8723 & 2.8695 & 2.8723 & 2.8735 & 2.8735 & 2.8721 & 2.873 \\
1 & 0 & 1 & 3.1758 & 3.1731 & 3.1758 & 3.1771 & 3.1771 & 3.1757 & 3.177 \\
3 & 0 & 0 & 3.5567 & 3.5537 & 3.5576 & 3.5590 & 3.5590 & 3.5590 & 3.5590 \\
0 & 1 & 1 & 3.7542 & 3.7514 & 3.7542 & 3.7563 & 3.7563 & 3.7563 & 3.7563 \\
0 & 1 & 0 & 3.7542 & 3.7514 & 3.7542 & 3.7563 & 3.7563 & 3.7563 & 3.7563 \\
\end{array} |
TABLE VII. Energy eigenvalues for the four-dimensional Hamiltonian of Eq. (38).

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<th>$N_1$ $N_2$ $N_3$ $N_4$</th>
<th>$E_b$</th>
<th>$E_w$</th>
<th>$E_{spc}$</th>
<th>$E_a$</th>
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* Eighth order normal form, using Robnik's approximation.
* Weyl quantization of normal form in footnote a.
* SPSC quantization normal form of footnote a.
* Semiclassical quantization of a second order nonresonant normal form by Saini (Ref. 29).
* Adiabatic switching (Ref. 14).
* Fourier transform method (Ref. 5).
* Quantum mechanical eigenvalues, using a finite difference technique (Ref. 67).

The algebraic quantization procedure is very straightforward for the three and four degrees of freedom problems. The five-dimensional Hamiltonian, however, poses a more difficult practical problem. This system is qualitatively different from the three- or four-dimensional systems, in that many near resonances are found as one proceeds to higher order. Thus, if all near resonances found with $|\omega_{n0}|<0.01$ are included in the transformed Hamiltonian, a linearly independent set of included resonance vectors is

$$n_1 = (1, 1, -2, 0, 0),$$
$$n_2 = (1, -1, 1, -2, 3),$$
$$n_3 = (0, 3, -3, 0, -1),$$
$$n_4 = (5, -2, 0, 0, -1).$$

This leaves a single invariant:

$$I = 14j_1 + 26j_2 + 20j_3 + 31j_4 + 18j_5.$$  

This first resonance is the same (exact) resonance found in the three and four degrees of freedom problems. The other resonances are not exact. Nonetheless, transforming them away would lead to a rapidly divergent expression for the new Hamiltonian. We have included a maximal set of near resonances consistent with a block diagonal Hamiltonian, since including another resonance linearly independent of the given set would leave no linear invariants. The size of the blocks for relatively low lying states is quite small, because of the relatively large integer coefficients found in $I$.

The proliferation of near resonances just described is a generic problem with systems having many modes. In order to quantize typical systems of many dimensions it will be necessary to deal with resonances in ways other than by algebraic quantization. We are currently investigating the application of resummation techniques to multidimensional systems. Another possible approach would be to use perturbation theory to generate in a convergent fashion Hamiltonians which do not have a block diagonal form. The resulting Hamiltonian would be expected to be nearly block diagonal, however, so that the basis set used in such a calculation would be much better than an unperturbed harmonic oscillator basis.

The inclusion of the resonance terms of Eq. (41) in the transformed Hamiltonian, however, does not completely solve the convergence problems associated with near resonances for the five degrees of freedom system. The eighth order Hamiltonian still shows a weak divergence for some of the states given in Table VIII. In order to overcome this divergence we have used the epsilon algorithm (Padé ap-
proximation), a technique which replaces the original Taylor series in the perturbation parameter with a rational function of the perturbation parameter. This procedure is successful for most of the states given, with the exceptions indicated in the table. The energies given by both Robnik’s procedure and the symmetry preserving procedure are in excellent agreement with results from adiabatic switching. The Weyl rule is less accurate for the states where comparison can be made. It is interesting to note that the classical dissociation energy of this system is quite low. In fact, we have found a dissociating trajectory with an energy of 2.34. The low dissociation energy may in part explain the poor convergence of the perturbation theory.

Finally, we give second order results for this system. Saini has also presented a nonresonant second order normal form for this system. We find this normal form to be in error. In fact, it corresponds to the system

\[ H = H_0 + \frac{1}{2} \left( p_2^2 + \omega_2^2 q_2^2 \right) - 0.1 q_4 \left( q_3^2 + 0.1 q_2^2 \right). \]  

(43)

The second order results that we present, while less accurate than the eighth order calculations, are still in good agreement with the eigenvalues obtained by adiabatic switching.

C. Nearly resonant systems

The algebraic quantization of nearly resonant systems is entirely analogous to that of resonant systems, with the exception that the frequency denominators \( \omega_0 \) are nonzero. We use a cutoff in the denominator size to determine whether a particular term is to be treated as resonant or not. If \( |\omega_0| \) is less than this cutoff, the term is considered resonant; otherwise, it is treated as nonresonant. This is the same method used to treat the nearly resonant terms arising in the resonant five degrees of freedom system treated above. To show that algebraic quantization is effective on nearly resonant systems, we have quantized a 1:1:01 Barbanis Hamiltonian previously treated by Farrelly and Uzer:

\[ H = \frac{1}{2} \sum_{i=1}^{2} \left( p_i^2 + \omega_i^2 q_i^2 \right) + \lambda q_1^2 q_2, \]  

(44)

with the parameter values

\[ \omega_1 = 1, \quad \omega_2 = 1.01, \quad \lambda = \frac{\sqrt{2}}{10}. \]  

(45)

Table IX gives energy eigenvalues this system. A 12th order normal form was used, allowing the energy of all the states to be converged within 0.002. The quantum number assignments are those of Farrelly and Uzer.

A quantum mechanical variational calculation was done using a 306 state energy ordered basis for the even parity states, and a 289 state basis for the odd parity states. Good agreement between variational and algebraically quantized eigenvalues is seen for all the levels. The Weyl rule is less accurate than either Robnik’s rule, or the SPSC rule, for all of the states given. Finally, resummed results for a 12th order normal form are given. The algebraic quantization energies are superior to the resummed results for all of the levels given. This is perhaps to be expected in a system that is so close to resonance. The nonresonant normal form for this system diverges quite strongly, making resummation difficult. More sophisticated methods of resummation than the Padé approximation used by Farrelly and Uzer are most likely required to resum very nearly resonant systems. Results for realistic nearly resonant systems in more degrees of freedom, and a further discussion of resummation, will be given elsewhere.

V. CONCLUSION

We have shown that algebraic quantization of a classical normal form is an accurate and efficient means of uniform semiclassical quantization for a wide range of systems. In particular, the method is able to calculate quantum mechanical splittings to good accuracy, and can be used to find reliable eigenvalues in the chaotic regime. Our implementation of the method, using the special purpose program PERTURB, is very efficient. For example, quantization of a five degree of freedom system takes 4 h on a minicomputer. This is a very economical procedure, considering that the method yields a global expression for the transformed Hamiltonian, which enables a large number of energy eigenvalues to be calculated. Lower order perturbation results, and results for systems with fewer degrees of freedom, can be obtained very rapidly.

Difficulties remain, however, in the application of algebraic quantization to systems with many degrees of freedom. Even with an efficient program such as PERTURB, the large number of intermediate terms generated in the quantization of multimode systems leads to a practical upper limit of about six degrees of freedom (this is, however, sufficient to treat tetratomic). Obvious solutions are the development of even more efficient computer programs, the use of computers with large memory capacity, and the exploration of more efficient algorithms for classical perturbation theory. A fundamental problem for the quantization of multidimen-

Table IX. Energy eigenvalues for the near 1:1 Barbanis Hamiltonian of Eqs. (44) and (45).

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<th>( N_1 )</th>
<th>( N_2 )</th>
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<th>( E_w^* )</th>
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*Algebraic quantization of a 12th order normal form, using Robnik’s rule.
*Algebraic quantization of the same form as above, using the Weyl rule.
*AQ of the normal form in footnote a, using the SPSC rule.
*Resummation of a 12th order nonresonant normal form using the epsilon algorithm (Ref. 25).
*Quantum mechanical variational calculation.
sional systems is the extremely rapid proliferation of near resonances with increasing number of degrees of freedom, an unavoidable manifestation of the small denominator problem. Such an explosion of near resonances leaves a choice between calculating convergently a Hamiltonian with no invariants, or finding a divergent normal form and then resuming energy eigenvalues. The best path to follow is not yet clear. More work needs to be done on the resummation properties of normal forms; sparse matrix diagonalization techniques need to be investigated in the context of almost block diagonal normal forms.

Future work and work in progress will address some of these issues, and consider the application of algebraic quantization to realistic multimode Hamiltonians.

ACKNOWLEDGMENTS

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APPENDIX

In the text it was asserted that an invariant could always be chosen to have integer components. We prove that statement here. Consider an $N$-dimensional system with $N - Q$ linearly independent integer valued resonance vectors $m_i$. Then there will be $Q$ invariants. In order to find these invariants, it is most convenient to start with a set of orthogonalized resonance vectors. This may be carried out by using Gramm–Schmidt orthogonalization on the original set of resonance vectors. The vectors resulting from the orthogonalization are still integer valued, given that a slightly modified version of the usual Gramm–Schmidt procedure is used. Namely, the transformation

$$m_i \rightarrow m_i (m_j, m_k) - m_j (m_i, m_k) \quad (A1)$$

is used to orthogonalize $m_i$ with respect to $m_j$, rather than the more usual version:

$$m_i \rightarrow m_i - m_j (m_i, m_j) (m_j, m_k) \quad (A2)$$

Once a convenient set vectors spanning the resonance subspace is produced, the invariant vectors may be found, for they span the complement of the resonance subspace. Therefore, the invariant subspace may be found by orthogonalizing, using Eq. (A1), a set of basis vectors spanning the entire $N$-dimensional space with respect to each of the new resonance vectors. This produces a set of $N$ integer valued linearly independent vectors spanning the set of invariants. $Q$ linearly independent vectors must be chosen from these, yielding the desired set of invariants.

Invariant vectors generated by the above scheme, while integer valued, are not necessarily simplified. Therefore, our program simplifies the invariants further, largely by trial and error.

2. N. C. Handy, in Semiclassical Methods in Molecular Scattering and Spec-
35. L. E. Fried and G. S. Ezra (work in progress).
42. A. M. Molchanov, Icarus 8, 203 (1968); M. Hénon, ibid. 11, 93 (1969).
49. By convergence, we mean that the corrections calculated show no sign of divergence. In more than one dimension, classical canonical perturbation theory has a zero radius of convergence, although it may yield excellent asymptotic results.
59Dragt and Finn use polynomial degree to order the perturbation, rather than a perturbation parameter. Our use of a perturbation parameter here is in our view both clearer and more general.
60The direct use of action-angle variables involves, in general, nontruncating power series in differential operators, yielding an infinite order ordinary differential equation.
62From now on, we will refer only to the symmetrized version of Robnik’s approximation.
63The asymptotic nature of classical perturbation theory, however, prevents arbitrary accuracy from being achieved.
68The splittings given for Jaffe and Reinhardt were derived by subtracting the eigenvalues given in Table I of their paper, rather than using the splittings given in Table II in their paper. The eigenvalues in Table I of their paper agree with those given in Jaffe’s Ph.D. thesis.
70J. W. Neuberger and D. W. Noid (preprint).