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Robert Leonard Waterland
William & Mary

John B. Delos
William & Mary, jbdelo@wm.edu

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Construction of a multidimensional potential energy surface from an energy spectrum

R. L. Waterland and J. B. Delos

Department of Physics, The College of William and Mary, Williamsburg, Virginia 23185

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A method for the systematic construction of a multidimensional potential energy surface from an energy spectrum is presented. We show that if the Hamiltonian and the energy spectrum satisfy certain conditions then there is an inversion technique which gives a potential energy function from the spectrum. The method proceeds via a sequence of canonical transformations and leads to a potential energy which is symmetric in all its variables. We test the procedure for one- and two-dimensional examples and show that it gives reasonable results. However, the method does not give a unique result and we discuss two types of nonuniqueness exhibited by the procedure.

Given a Hamiltonian in quantum mechanics, there are many ways to calculate the spectrum of allowed discrete energy levels. We consider in this paper the inverse problem: Given a spectrum of energy levels, can we reconstruct the Hamiltonian? A general answer to this question is not presently available, but partial answers can be obtained if the problem is suitably restricted.

In particular, one-dimensional systems for which the semiclassical approximation is valid have been studied extensively and are now well understood. In the early years of quantum mechanics, shortly after the WKB method for calculating energy eigenvalues was developed, corresponding semiclassical inversion techniques were found for calculating a potential energy curve from the observed spectrum.¹ These techniques are simple and reliable and they have had great success. Also for one-dimensional systems, there is a large literature on fully quantum mechanical inversion techniques, which do not rely upon the semiclassical approximation.²

However, very little is known about inversion procedures in more than one dimension. There is a substantial spectroscopic literature based on trial and error,³ and a classic mathematical paper by Kac⁴ ("Can One Hear the Shape of a Drum?"), but we know of only two other papers that deal with the systematic construction of an N -dimensional potential energy surface from a spectrum.

Gerber, Roth, and Ratner⁵ proposed an inversion method based upon a semiclassical self-consistent-field approximation. The SCF method involves the best separable approximation to the wave function and the semiclassical approximation then gives formulas for the energy levels that are sufficiently similar to one-dimensional formulas that an approximate type of RKR inversion can be used.

Clary^{6a} developed an iterative scheme for finding the potential energy based upon Percival and Pomphrey's method⁷ for finding vibrational eigenvalues. Simplifying somewhat, the essence of his idea is the following. Expressing the potential energy as a power series containing M terms, one first has to guess the values of the coefficients in this series. Then invariant tori with quantized actions (eigentrajectories) are constructed. Each torus implies a relationship between the set of momenta p and the set of coordinates q ,

and

$$T[p(q)] + V(q) = E,$$

where E is the energy of the corresponding eigentrajectory.^{6b} Now for each torus, let us select a particular point q_0 and let us denote \hat{E} as the *observed* energy for the corresponding quantum state. Then the expression

$$V(q_0) = \hat{E} - T[p(q_0)]$$

can be used with M distinct energies and their corresponding tori to determine M coefficients in V . A new set of quantized tori is constructed, the new relationship $p(q)$ is again used in the above equation to obtain a new set of coefficients in V , and one iterates until convergence is (or is not) achieved.

In this paper, we develop a new approach to the inversion problem, using techniques involved in the Birkhoff Normal Form. We show that under certain conditions, the systematic procedures used to construct a spectrum from a Hamiltonian by the Birkhoff method can be done backwards, to obtain a Hamiltonian from a spectrum. We test this inversion method by carrying it out for one- and two-dimensional systems, and we show that it gives reasonable results for the cases studied.

I. REVIEW OF ONE-DIMENSIONAL INVERSION METHODS

Our results will be clearer if we first briefly review the well-known one-dimensional semiclassical inversion techniques as used in molecular physics. In the Rydberg-Klein-Rees (RKR) method, a potential energy curve for a diatomic molecule is constructed pointwise from an energy spectrum. If vibrational and rotational energy levels are both known, then the RKR method is unambiguous; however, if the rotational levels are unknown and only the vibrational levels for a fixed rotational state are known, then only the differences between turning points can be recovered. In that case the potential energy function could be determined uniquely only if it were known to be symmetric.⁸

A very clear derivation is given by Landau and Lifshitz,⁹ and we state their result in a slightly different way. Given $m > 0$ and given a finite function $\pi(E) > 0$ on an interval $0 < E < \hat{E}$, we define (for $V < \hat{E}$)

$$q(V) = \frac{1}{2\pi\sqrt{2m}} \int_0^V \frac{\tau(E)}{(V-E)^{1/2}} dE. \quad (1)$$

Obviously $q(V) > 0$. One can show that $q(V)$ is a monotonically increasing function of V if $\tau(E)$ is continuous and satisfies the integral inequality

$$\tau(E) > \frac{1}{2(\sqrt{2}-1)} \lim_{\epsilon \rightarrow 0} \left[\sqrt{\epsilon} \int_0^{E-\epsilon} \frac{\tau(x) dx}{(E-x)^{3/2}} \right]. \quad (2)$$

If $q(V)$ is a monotonic function of V , then the inverse function $V(q)$ exists for $q > 0$, and we define for $q < 0$,

$$V(q) = V(-q).$$

Then (theorem)

$$\tau(E) = \sqrt{2m} \int_{-q(E)}^{q(E)} [E - V(q)]^{-1/2} dq. \quad (3)$$

This theorem has the following meaning: If we have a particle of known mass m moving periodically in one dimension, and its period τ is known as a function of a parameter E associated with its motion [and if $\tau(E)$ satisfies Eq. (2)], then there exists a Hamiltonian of the usual form,

$$h(p, q) = \frac{p^2}{2m} + V(q),$$

with $V(q)$ a unique symmetric function, such that the period of motion under this Hamiltonian as a function of energy is precisely $\tau(E)$.

In quantum mechanics, the period of motion has no meaning, but in semiclassical mechanics, the period is interpolated from the discrete energy spectrum as

$$\tau = \frac{dI}{dh} \approx \frac{2\pi\hbar}{\Delta E},$$

I being an action variable and ΔE being the energy gap between adjacent levels.

Our results in N dimensions are somewhat similar to the above. We also need an interpolation of the energy spectrum, and we also obtain a symmetric potential energy by a systematic process. On the other hand, the actual method of constructing the potential energy is quite different, and the result, unfortunately, is not unique.

II. INVERSION OF THE BIRKHOFF PROCEDURE

Earlier work¹⁰ has shown that a procedure invented by Birkhoff¹¹ (for incommensurable systems) and modified by Gustavson¹² (for commensurable systems) is a very good way to calculate an energy spectrum from a Hamiltonian. If the Hamiltonian is given in the form (we call it the "standard form")

$$h = \sum_{i=1}^N \omega_i (p_i^2 + q_i^2) + V(q_1, \dots, q_N), \quad (4)$$

where the frequencies are incommensurable, and $V(q_1, \dots, q_N)$ is a power series containing cubic terms and higher, then Birkhoff showed that there exists a sequence of canonical transformations to new variables $\{P_i, Q_i\}$ such that the new Hamiltonian H is a polynomial depending upon P 's and Q 's only in the combination $\omega_i J_i$, with

$$J_i = P_i^2 + Q_i^2, \quad (5)$$

i.e.,

$$H = H(\omega_1 J_1, \dots, \omega_N J_N). \quad (6)$$

Equation (6) is called the Birkhoff Normal Form. This Normal Form directly gives the energy spectrum by quantization in the new variables

$$J_i = P_i^2 + Q_i^2 \leftrightarrow n_i + \frac{1}{2}, \quad (7)$$

$$E_{n_1, \dots, n_N} = H[\omega_1(n_1 + \frac{1}{2}), \dots, \omega_N(n_N + \frac{1}{2})]. \quad (8)$$

Our fundamental result is that the "dual" of this process can be carried out: from an interpolation of the energy spectrum in the form (8), there is a sequence of transformations that leads to a Hamiltonian in the "standard form" (4) with a symmetric potential energy.

More precisely, suppose we are given a set of energy levels of an N -dimensional system and that these levels form a regular pattern characterized by N quantum numbers n_1, \dots, n_N .¹³ Suppose the pattern is such that the energy levels are given to good approximation by a polynomial expression in the quantum numbers [Eq. (8)] and suppose that the frequencies ω_i are incommensurable. We may then interpret the function H as a Birkhoff Normal Form (6) which was quantized by the prescription (7). Then (theorem): there exists, and one can construct, a formal sequence of real canonical transformations which convert the polynomial H into the standard form (4), in which the potential energy V is a symmetric function of each of its variables

$$V(q_1, \dots, q_i, \dots, q_N) = V(q_1, \dots, -q_i, \dots, q_N), \quad i = 1, \dots, N. \quad (9)$$

The sequence begins by transforming terms of lowest degree and proceeds upwards through terms of higher degree. (There also exist other sequences of canonical transformations that construct unsymmetric potential energy functions, but coefficients of unsymmetric terms are not determined by this procedure.)

These results are proven below by methods similar to these used by Birkhoff.

(1) Given:

$$H = \sum_{\text{even } l} H^{(l)}(\omega J), \quad (9a)$$

$$J_i = P_i^2 + Q_i^2, \quad (9b)$$

$$H^{(0)} = 0, \quad (9c)$$

$$H^{(2)} = \sum_i \omega_i J_i, \quad (9d)$$

where $H^{(l)}$ is a homogeneous polynomial of degree l in P 's and Q 's, and ω_i are incommensurable.¹⁴ Obviously terms of degree 2 and lower are already in standard form. We show that if all terms of degree less than s are in standard form then the terms of degree s can be put in standard form.

To prove this, define¹⁴

$$F(P, q) = \sum_{i=1}^N P_i q_i + W^{(s)}(P, q), \quad (10)$$

where $W^{(s)}$ is a homogeneous polynomial of degree s in P and q . The transformation equations generated by F are

$$Q = q + \frac{\partial W^{(s)}}{\partial P}, \quad (11a)$$

$$p = P + \frac{\partial W^{(s)}}{\partial q}, \quad (11b)$$

$$h(p, q) = H(P, Q). \quad (11c)$$

Substitution of Eqs. (11a), and (11b) into Eq. (11c) gives

$$h\left(P + \frac{\partial W^{(s)}}{\partial q}, q\right) = H\left(P, q + \frac{\partial W^{(s)}}{\partial P}\right). \quad (12)$$

If Taylor expansions of H and h about P and q are performed and terms of equal degree in these expansions equated, the following set of equations is obtained:

$$h^{(i)}(P, q) = H^{(i)}(P, q), \quad i < s, \quad (13a)$$

$$DW^{(s)}(P, q) = H^{(s)}(P, q) - h^{(s)}(P, q), \quad i = s, \quad (13b)$$

$$h^{(i)}(P, q) = H^{(i)}(P, q) \quad i > s \quad (13c)$$

$$+ \sum_{j,l} \frac{1}{j!} \left[\frac{\partial^{[j]} H^{(l)}}{\partial q^{[j]}} \left(\frac{\partial W^{(s)}}{\partial P} \right)^j - \frac{\partial^{[j]} h^{(l)}}{\partial P^{[j]}} \left(\frac{\partial W^{(s)}}{\partial q} \right)^j \right],$$

$$j! = \prod_{i=1}^N j_i!, \quad |j| = \sum_{i=1}^N j_i,$$

$$l - |j| + |j|(s-1) = i, \quad 1 \leq |j| \leq l < i, \\ l \geq 2, \quad s \geq 3,$$

where

$$D = \sum_{i=1}^N \omega_i \left(P_i \frac{\partial}{\partial q_i} - q_i \frac{\partial}{\partial P_i} \right).$$

Equation (13a) shows that the order s transformation leaves lower orders unaffected; Eq. (13b) must be solved for $W^{(s)}(P, q)$, and when this is done, Eq. (13c) gives the higher degree terms in the new Hamiltonian.

The solution to Eq. (13b) is

$$W^{(s)} = D^{-1}(H^{(s)} - h^{(s)}). \quad (14)$$

It is most easily constructed by transforming to variables η_j, ξ_j such that

$$P_j = \frac{1}{\sqrt{2}}(\eta_j + i\xi_j), \\ q_j = \frac{i}{\sqrt{2}}(\eta_j - i\xi_j). \quad (15)$$

In these variables D has the form

$$D \rightarrow \tilde{D} = i \sum_j \omega_j \left(\xi_j \frac{\partial}{\partial \xi_j} - \eta_j \frac{\partial}{\partial \eta_j} \right) \quad (16)$$

and its eigenfunctions are

$$\Phi_{l_1 \dots l_N, m_1 \dots m_N} = \eta_1^{l_1} \eta_2^{l_2} \dots \eta_N^{l_N} \xi_1^{m_1} \xi_2^{m_2} \dots \xi_N^{m_N} \quad (17)$$

with eigenvalues

$$i \sum_j \omega_j (m_j - l_j). \quad (18)$$

We require that

$$h^{(s)} = \sum_{s \geq 3} V_{a_1 \dots a_N}^{(s)} q_1^{a_1} q_2^{a_2} \dots q_N^{a_N}, \\ \left(\sum_{j=1}^N a_j = s \right) \quad (19)$$

where $V_{a_1 \dots a_N}^{(s)}$ are coefficients which are to be determined. When $H^{(s)}$ and $h^{(s)}$ are expressed as functions of (η, ξ) it is found that they contain both range-space and null-space terms.¹⁵ For a solution to Eq. (14) to exist, it is necessary and sufficient to make the null-space terms in h cancel those in H . Write

$$\tilde{H}^{(s)} = \tilde{N}_H^{(s)} + \tilde{R}_H^{(s)}, \quad \tilde{h}^{(s)} = \tilde{N}_h^{(s)} + \tilde{R}_h^{(s)}, \quad (20)$$

where N and R denote "the set of null-space terms" and "the set of range-space terms," respectively; then

$$\tilde{N}_h^{(s)} = \tilde{N}_H^{(s)}, \quad (21)$$

$$\tilde{R}_h^{(s)} = \tilde{D}^{-1} [\tilde{R}_H^{(s)} - \tilde{R}_h^{(s)}]. \quad (22)$$

Equation (21) gives

$$\frac{(N+s-1)!}{N!(s-1)!}$$

relations for the undetermined $\{V^{(s)}\}$ of Eq. (19) in terms of known coefficients in H and the $\{V^{(k)}\}$ from previous iterations. Equation (22) gives $\tilde{R}_h^{(s)}(\eta, \xi)$, which can be used to generate higher order terms in the new Hamiltonian from Eq. (13c). This defines the iterative procedure, and completes the proof of the assertion made above Eq. (10).

(2) If s is odd, all coefficients $V_{a_1 \dots a_N}^{(s)}$ are undetermined. For odd s , H and h are odd in at least one of the P_k, q_k . Hence, when they are reexpressed in terms of η_k, ξ_k they must remain of odd degree. But the only null space terms are powers of η_k, ξ_k i.e., they are of even degree. Hence Eqs. (21) and (22) put no restriction on odd degree terms and coefficients $V^{(s)}$ with s odd are undetermined by this procedure.

(3) If s is even, those coefficients $V_{a_1 \dots a_N}^{(s)}$ for which any of the a 's are odd are undetermined. (Proof is the same as above).

(4) If s is even, then those coefficients $V_{a_1 \dots a_N}^{(s)}$ for which all a 's are even are determined from $H^{(s)}$. Since

$$q_k^m = \left[\frac{i}{\sqrt{2}} (\eta_k - i\xi_k) \right]^m$$

if m is even, the binomial expansion of q_k^m contains a term proportional to

$$(\eta_k \xi_k)^{m/2}$$

and this is in the null-space. From Eq. (21), its coefficient must be equal to that of the corresponding null-space term in H .

Since $V_{a_1 \dots a_N}^{(s)}$ are undetermined if any of the a_k are odd, we may take them to be zero. Then the remaining $V_{a_1 \dots a_N}^{(s)}$ are uniquely specified by the iterative procedure.

The convergence properties of this inversion method¹⁶ have not been established; it is useful, therefore, to examine results when the procedure is carried to various levels.

III. ONE DIMENSIONAL SYSTEMS

As discussed earlier, there already exist successful one-dimensional inversion methods. We discuss this case to illus-

trate the new technique and to show that it leads to sensible results.

A. General inversion in one dimension

For all one dimensional problems the Birkhoff Normal Form is

$$H(P, Q) = \frac{1}{2}\omega(P^2 + Q^2) + H^{(2)}[\frac{1}{2}\omega(P^2 + Q^2)]^2 + H^{(3)}[\frac{1}{2}\omega(P^2 + Q^2)]^3 + H^{(4)}[\frac{1}{2}\omega(P^2 + Q^2)]^4 + \dots, \quad (22)$$

where ω is the frequency of the unperturbed oscillator and $H^{(s)}$ are numerical coefficients. They could be found, e.g., by fitting parameters to the energy spectrum

$$E_n = (n + \frac{1}{2})\hbar\omega + H^{(2)}(n + \frac{1}{2})^2\hbar^2\omega^2 + H^{(3)}(n + \frac{1}{2})^3\hbar^3\omega^3 + H^{(4)}(n + \frac{1}{2})^4\hbar^4\omega^4.$$

The generated Hamiltonian is required to be

$$h(p, q) = \frac{1}{2}\omega(p^2 + q^2) + V^{(3)}q^3 + V^{(4)}q^4 + V^{(5)}q^5 + V^{(6)}q^6 + V^{(7)}q^7 + V^{(8)}q^8 + \dots \quad (23)$$

Equations (13) were implemented using MACSYMA,¹⁷ a LISP-based language that permits analytical calculations.

Null-space terms appeared for even order transformations. According to theorem (2), $V^{(3)}$, $V^{(5)}$, and $V^{(7)}$ are undetermined, and they were arbitrarily set to zero. Resulting null-space terms were:

(i) Fourth degree terms

$$\tilde{N}_h^{(4)} = -\frac{1}{2}V^{(4)}\eta^2\xi^2, \quad (24a)$$

$$\tilde{N}_H^{(4)} = -\omega^2H^{(2)}\eta^2\xi^2. \quad (24b)$$

(ii) Sixth degree terms

$$\tilde{N}_h^{(6)} = -\frac{1}{2}V^{(6)}i\eta^3\xi^3, \quad (25a)$$

$$\tilde{N}_H^{(6)} = \left(-\omega^3H^{(3)} - 3\omega V^{(4)}H^{(2)} + \frac{V^{(4)^2}}{4\omega}\right)i\eta^3\xi^3. \quad (25b)$$

(iii) Eighth degree terms

$$\tilde{N}_h^{(8)} = \frac{35}{8}V^{(8)}\eta^4\xi^4, \quad (26a)$$

$$\tilde{N}_H^{(8)} = \left(\omega^4H^{(4)} - \frac{245}{16}V^{(4)^2}H^{(2)} + \frac{165}{8\omega}V^{(4)}V^{(6)} - \frac{15V^{(4)^4}}{32\omega^2}\right) \times \eta^4\xi^4. \quad (26b)$$

From Eq. (21)

$$\tilde{N}_h^{(s)} = \tilde{N}_H^{(s)}.$$

The resulting equations are easily solved, giving

$$V^{(4)} = \frac{2\omega^2H^{(2)}}{3}, \quad (27)$$

$$V^{(6)} = \frac{2\omega^3}{5}\left(H^{(3)} + \frac{17H^{(2)^2}}{9}\right), \quad (28)$$

$$V^{(8)} = \frac{4\omega^4}{35}\left(2H^{(4)} + 11H^{(2)}H^{(3)} + \frac{124}{18}H^{(2)^3}\right). \quad (29)$$

Hence the required Hamiltonian is (to the eighth degree)

$$h(p, q) = \frac{1}{2}\omega(p^2 + q^2) + \frac{2\omega^2H^{(2)}}{3}q^4 + \frac{2\omega^3}{5}\left(H^{(3)} + \frac{17H^{(2)^2}}{9}\right)q^6 + \frac{4\omega^4}{35}\left(2H^{(4)} + 11H^{(2)}H^{(3)} + \frac{124H^{(2)^3}}{18}\right)q^8. \quad (30)$$

B. Comparison of results of inversion by two methods

Let us compare the results obtained above with those obtained through the more standard inversion technique. Our method of making this comparison is the following: We start from a certain zero-order potential energy

$$V_0(q) = \frac{q^2}{2} - \frac{q^3}{20}$$

which does not happen to be symmetric. From $V_0(q)$ we can compute $\tau(E)$, and from $\tau(E)$ we can compute a symmetric potential energy $V_L(q)$ using the method given by Landau and Lifschitz (L²), as described in Sec. I of this article. Also from $V_0(q)$ we can calculate a Birkhoff normal form, and then invert it to obtain another symmetric potential energy $V_B(q)$.

1. L² method

$$\tau(E) = \oint_a^b \frac{dq}{p(q)}, \quad (31)$$

where $p(q)$ is the classical momentum at position q and a, b are the classical turning points of the motion.

A particle moving in the potential

$$V_0(q) = \frac{q^2}{2} - \frac{q^3}{20} \quad (32)$$

is bound provided that the particle energy E is less than 200/27. For such a particle

$$\tau(E) = \sqrt{2} \int_a^b \frac{dq}{\sqrt{(E - \frac{q^2}{2} + \frac{q^3}{20})}}, \quad (m = 1). \quad (33)$$

Let the roots of the cubic equation in the denominator of the integrand be α, β , and γ where $\alpha > \beta > \gamma$. Substitution of

$$q = \gamma + (\beta - \gamma)\sin^2 \varphi \quad (34)$$

reduces the integral to a complete elliptic integral of the first kind, i.e.,

$$\tau(E) = \frac{2\sqrt{2}\sqrt{3}}{\{\cos(\chi(E) - \pi/6)\}^{1/3}} \int_0^{\pi/2} \frac{d\varphi}{\sqrt{1 - k^2 \sin^2 \varphi}}, \quad (35)$$

where

$$\chi(E) = \frac{1}{3} \cos^{-1} \left(1 - \frac{27E}{100}\right) \quad (36)$$

and

$$k^2 = \frac{\sin \chi(E)}{\cos(\chi(E) - \pi/6)}. \quad (37)$$

In the L² method, $\tau(E)$ determines only the difference between the two turning points. That difference can be found by direct solution of the cubic equation in the denominator of Eq. (32) and the result is

$$q_1(E) - q_2(E) = \frac{20}{\sqrt{3}} \sin \chi(E) \quad (38)$$

so therefore the L^2 method gives

$$q(V_L) = \frac{10}{\sqrt{3}} \sin \chi(V_L) \quad (39)$$

or, by use of Eq. (36),

$$V_L(q) = \frac{100}{27} \left\{ 1 - \cos \left[3 \sin^{-1} \frac{\sqrt{3}q}{10} \right] \right\}. \quad (40)$$

2. Inverse Birkhoff method

To apply the Birkhoff inversion, we require the Birkhoff-Gustavson normal form for the given Hamiltonian, i.e.,

$$h_0 = \frac{1}{2} (p^2 + q^2) - q^3/20, \quad (\omega = 1). \quad (41)$$

Using the method of Swimm and Delos¹⁰ one readily obtains

$$H = 0.5(P^2 + Q^2) - 2.34375 \times 10^{-3}(P^2 + Q^2)^2 - 8.25195 \times 10^{-6}(P^2 + Q^2)^3 - 3.70102 \times 10^{-8}(P^2 + Q^2)^4 \quad (42)$$

(to eighth degree). Comparison with Eq. (22) gives

$$H^{(2)} = -9.37500 \times 10^{-3}, \quad (43a)$$

$$H^{(3)} = -6.60156 \times 10^{-5}, \quad (43b)$$

$$H^{(4)} = -5.92163 \times 10^{-7}, \quad (43c)$$

and, using Eq. (30),

$$h = 0.5(p^2 + q^2) - 6.25000 \times 10^{-3} q^4 + 4.00000 \times 10^{-5} q^6 - 5.08259 \times 10^{-7} q^8 \quad (\text{to eighth degree}). \quad (44)$$

3. Comparison of methods

In Fig. 1 we plot the result of the Landau technique [Eq. (40)] and that for the inverse Birkhoff technique [Eq. (44)]. Agreement is excellent for $q \leq 3.5$; the maximum error in this range is 3.2%. As q increases, the inaccuracy of the inverse Birkhoff curve increases and for $4.5 \leq q \leq 5.0$ it is a poor approximation to the exact L^2 result. However the inverse Birkhoff result is everywhere a much more accurate curve

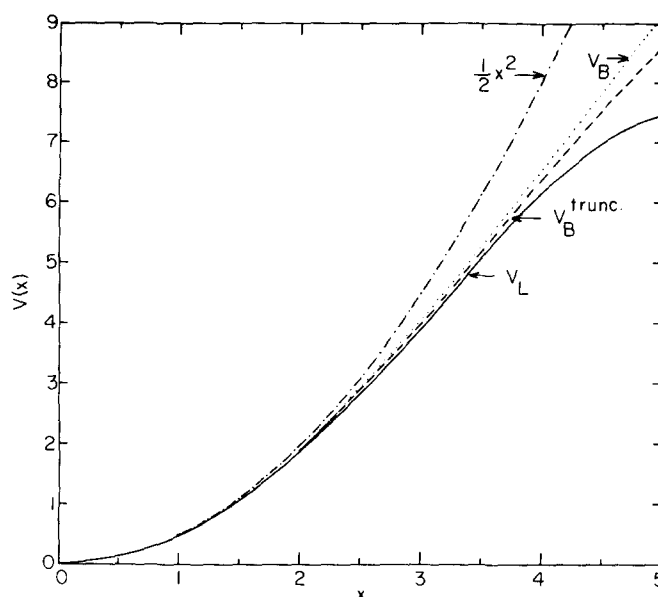


FIG. 1. Comparison of one dimensional inversion procedures: V_L is the Landau result [Eq. (40)]; V_B is the inverse Birkhoff result [Eq. (44)]; V_B^{trunc} is the inverse Birkhoff result truncated to a quartic form.

than the pure harmonic oscillator curve which is plotted for reference.

(Somewhat surprisingly, the best fit is obtained by taking terms through q^4 . Addition of the q^6 term reduces accuracy in the whole region $0 < q \leq 5$; then addition of the q^8 term increases accuracy slightly. We have also plotted the inverse Birkhoff result truncated to a quartic form; for $q \leq 3.5$ the maximum error is 1.9%).

IV. TWO DIMENSIONAL SYSTEMS

In this section we apply the inverse Birkhoff method to the general two dimensional, incommensurable frequencies problem. To illustrate the technique we examine a particular example and demonstrate the consistency of the Birkhoff inversion method.

A. General two dimensional incommensurable frequencies problem

For all two dimensional incommensurable frequencies problems, we write the normal form using simpler notation:

$$\begin{aligned} H(P_1, P_2, Q_1, Q_2) &= \frac{1}{2}\omega_1(P_1^2 + Q_1^2) + \frac{1}{2}\omega_2(P_2^2 + Q_2^2) + \beta_1[\frac{1}{2}\omega_1(P_1^2 + Q_1^2)]^2 + \beta_2[\frac{1}{2}\omega_1(P_1^2 + Q_1^2)\frac{1}{2}\omega_2(P_2^2 + Q_2^2)] + \beta_3[\frac{1}{2}\omega_2(P_2^2 + Q_2^2)]^2 \\ &+ \gamma_1[\frac{1}{2}\omega_1(P_1^2 + Q_1^2)]^3 + \gamma_2\{\frac{1}{2}\omega_1(P_1^2 + Q_1^2)\}^2\frac{1}{2}\omega_2(P_2^2 + Q_2^2) + \gamma_3\{\frac{1}{2}\omega_1(P_1^2 + Q_1^2)\}[\frac{1}{2}\omega_2(P_2^2 + Q_2^2)]^2 \\ &+ \gamma_4[\frac{1}{2}\omega_2(P_2^2 + Q_2^2)]^3 + \dots \end{aligned} \quad (45)$$

The quantized energy spectrum would satisfy a corresponding formula, and the coefficients β_i, γ_i, \dots are assumed to be obtained from the spectrum.

The generated Hamiltonian is required to be

$$h(p, q) = \frac{1}{2}\omega_1(p_1^2 + q_1^2) + \frac{1}{2}\omega_2(p_2^2 + q_2^2) + V_{4,0}^{(4)}q_1^4 + V_{3,1}^{(4)}q_1^3q_2 + V_{2,2}^{(4)}q_1^2q_2^2 + V_{1,3}^{(4)}q_1q_2^3 + V_{0,4}^{(4)}q_2^4 \\ + V_{6,0}^{(6)}q_1^6 + V_{5,1}^{(6)}q_1^5q_2 + V_{4,2}^{(6)}q_1^4q_2^2 + V_{3,3}^{(6)}q_1^3q_2^3 + V_{2,4}^{(6)}q_1^2q_2^4 + V_{1,5}^{(6)}q_1q_2^5 + V_{0,6}^{(6)}q_2^6. \quad (46)$$

Equations (13) were implemented using MACSYMA. Null-space terms appeared for even order transformations. Using theorem (2), $V_{3,1}^{(4)}$, $V_{1,3}^{(4)}$, $V_{5,1}^{(6)}$, $V_{3,3}^{(6)}$, and $V_{1,5}^{(6)}$ were set to zero. Resulting null-space terms were:

(i) Fourth degree terms

$$\tilde{N}_h^{(4)} = -\frac{3}{2}V_{4,0}^{(4)}\eta_1^2\xi_1^2 + V_{2,2}^{(4)}\eta_1\xi_1\eta_2\xi_2 - \frac{3}{2}V_{0,4}^{(4)}\eta_2^2\xi_2^2, \quad (47a)$$

$$\tilde{N}_H^{(4)} = -\omega_1^2\beta_1\eta_1^2\xi_1^2 + \omega_1\omega_2\beta_2\eta_1\xi_1\eta_2\xi_2 - \omega_2^2\beta_3\eta_2^2\xi_2^2. \quad (47b)$$

(ii) Sixth degree terms

$$\tilde{N}_h^{(6)} = \left\{ -3\omega_1 V_{4,0}^{(4)}\beta_1 + \frac{V_{4,0}^{(4)2}}{4\omega_1} + \frac{5}{2}V_{6,0}^{(6)} \right\} i\eta_1^3\xi_1^3 + \left\{ -\frac{3}{2}\beta_2\omega_2 V_{4,0}^{(4)} - \frac{\beta_1\omega_1^2\omega_2^3 V_{2,2}^{(4)}}{\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} + \frac{\beta_1\omega_1^4\omega_2 V_{2,2}^{(4)}}{\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} \right. \\ - \frac{\beta_2\omega_1^2\omega_2^3 V_{2,2}^{(4)}}{\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} + \frac{\beta_2\omega_1^4\omega_2 V_{2,2}^{(4)}}{2\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} + \frac{\omega_1^4\omega_2^3 V_{2,2}^{(4)2}}{4[\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)]^2} \\ - \frac{\omega_1^2\omega_2^5 V_{2,2}^{(4)2}}{4[\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)]^2} + \frac{3}{2}V_{4,2}^{(6)} \left. \right\} \eta_1^2\xi_1^2\eta_2\xi_2 + \left\{ \frac{\beta_2\omega_1^3\omega_2^2 V_{2,2}^{(4)}}{2\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} \right. \\ - \frac{\beta_2\omega_1\omega_2^4 V_{2,2}^{(4)}}{2\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} - \frac{\beta_3\omega_1\omega_2^4 V_{2,2}^{(4)}}{\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} + \frac{\beta_3\omega_1^3\omega_2^2 V_{2,2}^{(4)}}{\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)} \\ + \frac{\omega_1^3\omega_2^4 V_{2,2}^{(4)2}}{4[\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)]^2} \\ - \frac{\omega_1^5\omega_2^2 V_{2,2}^{(4)2}}{4[\omega_1\omega_2(\omega_2 - \omega_1)(\omega_2 + \omega_1)]^2} - \frac{3}{2}\beta_2\omega_1 V_{0,4}^{(4)} + \frac{3}{2}V_{2,4}^{(6)} \left. \right\} \eta_1\xi_1\eta_2^2\xi_2^2 \\ + \left\{ \frac{5}{2}V_{0,6}^{(6)} - 3\omega_2 V_{0,4}^{(4)}\beta_3 + \frac{V_{0,4}^{(4)2}}{4\omega_2} \right\} i\eta_2^3\xi_2^3, \quad (48a)$$

$$\tilde{N}_H^{(6)} = \omega_1^3\gamma_1 i\eta_1^3\xi_1^3 + \omega_1^2\omega_2\gamma_2\eta_1^2\xi_1^2\eta_2\xi_2 + \omega_1\omega_2^3\gamma_3\eta_1\xi_1\eta_2^2\xi_2^2 + \omega_2^3\gamma_4 i\eta_2^3\xi_2^3. \quad (48b)$$

From Eq. (21)

$$\tilde{N}_h^{(s)} = \tilde{N}_H^{(s)}.$$

The resulting equations are easily solved giving:

$$V_{4,0}^{(4)} = \frac{2\beta_1\omega_1^2}{3}, \quad (49)$$

$$V_{2,2}^{(4)} = \omega_1\omega_2\beta_2, \quad (50)$$

$$V_{0,4}^{(4)} = \frac{2\beta_3\omega_2^2}{3}, \quad (51)$$

$$V_{6,0}^{(6)} = \frac{2\omega_1^3}{5} \left\{ \frac{17\beta_1^2}{9} + \gamma_1 \right\}, \quad (52)$$

$$V_{4,2}^{(6)} = \frac{2\omega_1^2\omega_2}{3} \left\{ 2\beta_1\beta_2 + \gamma_2 + \frac{(3\omega_2^2 - 2\omega_1^2)\beta_2^2}{4(\omega_2^2 - \omega_1^2)} \right\}, \quad (53)$$

$$V_{2,4}^{(6)} = \frac{2\omega_1\omega_2^2}{3} \left\{ 2\beta_2\beta_3 + \gamma_3 + \frac{(2\omega_2^2 - 3\omega_1^2)\beta_2^2}{4(\omega_2^2 - \omega_1^2)} \right\}, \quad (54)$$

$$V_{0,6}^{(6)} = \frac{2\omega_2^3}{5} \left\{ \frac{17\beta_3^2}{9} + \gamma_4 \right\}. \quad (55)$$

Hence the required Hamiltonian is (to eighth degree)

$$h(p, q) = \frac{1}{2}\omega_1(p_1^2 + q_1^2) + \frac{1}{2}\omega_2(p_2^2 + q_2^2) + \frac{2\beta_1\omega_1^2}{3}q_1^4 + \omega_1\omega_2\beta_2q_1^2q_2^2 + \frac{2\beta_3\omega_2^2}{3}q_2^4 + \frac{2\omega_1^3}{5} \\ \times \left\{ \frac{17\beta_1^2}{9} + \gamma_1 \right\} q_1^6 + \frac{2\omega_1^2\omega_2}{3} \left\{ 2\beta_1\beta_2 + \gamma_2 + \frac{(3\omega_2^2 - 2\omega_1^2)\beta_2^2}{4(\omega_2^2 - \omega_1^2)} \right\} q_1^4q_2^2 + \frac{2\omega_1\omega_2^2}{3} \left\{ 2\beta_2\beta_3 + \gamma_3 \right. \\ \left. + \frac{(2\omega_2^2 - 3\omega_1^2)\beta_2^2}{4(\omega_2^2 - \omega_1^2)} \right\} q_1^2q_2^4 + \frac{2\omega_2^3}{5} \left\{ \frac{17\beta_3^2}{9} + \gamma_4 \right\} q_2^6. \quad (56)$$

B. An example: Birkhoff inversion for the Hénon–Heiles Hamiltonian

Swimm and Delos¹⁰ have calculated the Birkhoff normal form for the Hénon–Heiles¹⁸ Hamiltonian,

$$h_0 = \frac{1}{2}\omega_1(p_1^2 + q_1^2) + \frac{1}{2}\omega_2(p_2^2 + q_2^2) + \frac{\lambda}{\omega_1\omega_2^{1/2}}q_1^2q_2 + \frac{\lambda\eta}{\omega_2^{3/2}}q_2^3 \quad (57)$$

with

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

They obtained

$$H = \frac{1.3}{2}(P_1^2 + Q_1^2) + \frac{0.7}{2}(P_2^2 + Q_2^2) - 1.56185 \times 10^{-3}[\frac{1}{2}(P_2^2 + Q_2^2)]^2 - 1.023323 \times 10^{-2}[\frac{1}{4}(P_1^2 + Q_1^2)(P_2^2 + Q_2^2)] \\ - 5.80199 \times 10^{-3}[\frac{1}{8}(P_1^2 + Q_1^2)]^2 - 1.092 \times 10^{-5}[\frac{1}{8}(P_2^2 + Q_2^2)]^3 - 1.7719 \times 10^{-4}[\frac{1}{8}(P_2^2 + Q_2^2)^2(P_1^2 + Q_1^2)] \\ - 2.7327 \times 10^{-4}[\frac{1}{8}(P_2^2 + Q_2^2)(P_1^2 + Q_1^2)^2] - 8.625 \times 10^{-5}[\frac{1}{2}(P_1^2 + Q_1^2)]^3 \quad (\text{to eighth degree}). \quad (58)$$

Comparison of Eq. (58) with Eq. (45) gives

$$\beta_1 = -3.43313 \times 10^{-3}, \quad (59a)$$

$$\beta_2 = -1.12453 \times 10^{-2}, \quad (59b)$$

$$\beta_3 = -3.18745 \times 10^{-3}, \quad (59c)$$

$$\gamma_1 = -3.92581 \times 10^{-5}, \quad (59d)$$

$$\gamma_2 = -2.30997 \times 10^{-4}, \quad (59e)$$

$$\gamma_3 = -2.78163 \times 10^{-4}, \quad (59f)$$

$$\gamma_4 = -3.18367 \times 10^{-5}, \quad (59g)$$

and, using Eq. (56),

$$h = \frac{1.3}{2}(p_1^2 + q_1^2) + \frac{0.7}{2}(p_2^2 + q_2^2) - 3.86799 \times 10^{-3}q_1^4 - 1.02332 \times 10^{-2}q_1^2q_2^2 \\ - 1.04123 \times 10^{-3}q_2^4 - 1.494 \times 10^{-5}q_1^6 - 8.160 \times 10^{-5}q_1^4q_2^2 - 4.192 \times 10^{-5}q_1^2q_2^4 - 1.74 \times 10^{-6}q_2^6. \quad (60)$$

To within the accuracy of the Birkhoff and inverse Birkhoff procedures, this Hamiltonian (60) should give the same spectrum as does the Hénon–Heiles Hamiltonian¹⁹ (57).

V. UNIQUENESS

As noted earlier, the present method does not uniquely determine the potential energy surface. There are two distinct types of nonuniqueness in the inverse Birkhoff technique.

The inverse Birkhoff method does not determine asymmetric terms in the potential energy function. In this regard it is similar to other inversion methods. The one dimensional RKR^{1,20} method requires both rotational and vibrational data for uniqueness; if the rotational spectrum is unknown the RKR method can only give a symmetric potential energy curve. Likewise Clary^{6a} notes that his inversion “does not appear to be appropriate for determining potentials containing odd powers of the coordinates,” since it does not incorporate rotational data. However, Gerber *et al.*⁵ did include the rotational part of the spectrum, so they were able to obtain a unique result.

A second type of nonuniqueness arises from the observation that the generating function \tilde{W} is not uniquely deter-

mined. Referring to Eq. (22) it is apparent that arbitrary null-space terms could be added to \tilde{W} . In all previous work using the BGNF,^{10,12} such terms have been omitted. By direct calculation we have found that addition of arbitrary null-space terms to the generating function results in changes in the symmetric part of the potential function. Such problems also exist in the calculation of a normal form, but nevertheless the work of Gustavson, of Swimm and Delos, and of Jaffé and Reinhardt indicates that the omission of the arbitrary null-space terms leads to good results. Perhaps these extra terms are, in some sense, insignificant. At present, this type of nonuniqueness is not understood.

VI. CONCLUSION

We have presented a method for constructing a multidimensional potential energy surface from an energy spectrum. In this method, the energy spectrum is fitted to a truncated Birkhoff Gustavson Normal Form, and then a sequence of canonical transformations is applied to the truncated normal form which transform it into a Hamiltonian of standard form (4). Symmetric potential energy terms are de-

terminated by this procedure; asymmetric terms are not, and they are set to zero.

The method has been applied to the general cases in one and two dimensions, and analytic formulas relating the coefficients of the normal form to those of the generated symmetric potential have been derived. We have applied the technique to two examples and it has been found to give reasonable results.

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