THE QUADRATIC ZEEMAN EFFECT IN HYDROGEN : AN EXAMPLE OF SEMI-CLASSICAL QUANTIZATION OF A STRONGLY NON-SEPARABLE BUT ALMOST INTEGRABLE SYSTEM

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Résumé.- La quantification semi-classique de systèmes à plusieurs dimensions est discutée à l'aide de la méthode d'Einstein-Brillouin-Keller (EBK) sur les tores invariants de l'espace des phases, puis par la méthode des familles infinies de trajectoires périodiques. Les notions de séparabilité, de systèmes classiques intégrables et non-intégrables sont introduites. L'intégrabilité approchée existant dans le cas de l'effet Zeeman quadratique est utilisée pour la quantification de ce problème à l'aide de la forme normale de Birkhoff-Gustavson.

Abstract.- Semi-classical quantization of multidimensional systems is discussed both in terms of the Einstein-Brillouin-Keller quantization on invariant tori, and in terms of infinite families of periodic orbits. The notions of separability, integrability, and non-integrability of classical systems are introduced. An approximate integrability is used to quantize the quadratic Zeeman problem, via analytic calculation of the Birkhoff-Gustavson normal form.

1. Introduction.- As well illustrated in these proceedings, there is currently feverish activity in the area of the effect of external dc fields on atomic Rydberg states, and on the strong perturbations induced by both electric and magnetic fields on the ionization continuum in the neighborhood of the field free ionization threshold. At the simplest level, the complexity, and thus the novelty, of the problem stems from the fact that for any external field strength it is always possible to find a high enough Rydberg state such that the Rydberg electron feels roughly equal coupling to the Coulombic field of the atomic ion core and to the external field. Thus neither the external nor internal fields are conveniently treated as a perturbation. This is clearly possible in both the Stark and Zeeman cases. However, the Stark and Zeeman problems are essentially quite different in the sense of existence or non-existence of approximate separabilities. It is the major purpose of the present paper, which is largely pedagogical, to indicate the importance of this difference as it relates to the problem of semi-classical quantization. One's intuition for classical-quantum correspondence suggests that the high n (and sometimes even high ℓ) limit accessible in recent experiments should make semi-classical approaches essentially exact and thus make semi-classical mechanics (i.e. classical dynamics plus an appropriate quantization rule) the method of choice for calculation of individual levels (and, where appropriate, their lifetimes), densities of states, and oscillator strength densities.

However, application of semi-classical methods to multidimensional quantization involves many subtleties not present in the semi-classical quantization of one-dimensional systems. This is even the case if the multidimensional system is separable, *as* separability does not always imply that each of the separated one-dimensional problems can be treated by standard WKB techniques. As Einstein pointed out in a classic paper in 1917, multidimensional semi-classical quantization should be carried out in a canonically invariant manner.[1,2] For systems of N-degrees of freedom if there are N dynamical constants (as will always be the case if the system is separable) the system is said to be integrable and the fundamental object of semi-classical

quantization which follows from the Einstein picture (now called Einstein-Brillouin-Keller, or EBK quantization) is not a trajectory, but rather the invariant, time-independent, surface of an N-torus in phase space.[3] In Section 2, where an intro-duction to EBK theory is outlined, the contrast between quantization on <u>tori</u> and the one-dimensional WKB quantization (where tori degenerate to periodic orbits) is empha-sized, leading finally to a brief discussion of an alternative multidimensional semi-classical scheme based on orbits (not <u>an</u> orbit as in the one-dimensional case, but an infinite number of periodic orbits) which follows from the Feynman path integral and which has been developed by Gutzwiller,[4] Miller,[5] Voros,[6] Balian and Bloch.[7]

As mentioned, the EBK scheme assumes <u>integrability</u> of the classical dynamics. The class of <u>integrable</u> classical system is much broader than the class of <u>separable</u> classical systems: Most integrable systems are non-separable, although all separ-able systems are integrable. These distinctions are made more precise in Section 3. However, it is a fact of life that an arbitrary non-separable classical Hamil-tonian system will <u>not</u> be integrable. As most non-separable systems are non-inte-grable, they are not rigorously quantizable with the EBK technique. However, just as an "almost" separable system may be well approximated by approximate separable Hamiltonians, an "almost" integrable system may well be approximated via an approxi-mate integrable Hamiltonian. It is pointed out that the Stark problem, which is ex-actly separable for H-atom Rydberg states, is "almost" separable for non-hydrogenic Rydberg states allowing use of the multichannel quantum defect approach.[8] However, in Section 4, it is argued that while the quadratic Zeeman problem for hydrogen is strongly non-separable, it is "almost" integrable, thus admitting approximate con-stants of motion, and allowing, in principle, semi-classical quantization following the EBK ansatz: results are presented indicating that perturbatively determined constants of motion do exist, and give a reasonable description of the chaotic (non-integrable) classical dynamics. Preliminary semi-classical quantum results are then given. Section 5 contains a brief discussion. A fuller description of methods and results will appear elsewhere together with a more complete set of references.[9]

2. Semi-Classical Quantization.-
Restricting pedagogical discussion to calculation of discrete energy levels, the usual Bohr-Sommerfeld quantization for bound one-dimensional motion in a single potential well is easily stated as an integral along a periodic orbit:

$$\frac{1}{2\pi} \oint_C pdq = \left(n + \frac{1}{2}\right) \hbar \qquad (1)$$

where it has been assumed that the motion is a "vibration," giving rise to the " $\frac{1}{2}$ " in the "n $+ \frac{1}{2}$." The "path" in Eq. (1) is along one period of motion, p and q being the canonical conjugate momenta and position. At fixed E there is a unique such periodic orbit: Determination of the (unique) orbit which satisfies Eq. (1) for each n, thus selects a set of quantum levels E_n.

The fact that the vehicle for this B-S quantization is a single periodic orbit is apt to be highly misleading when generalization to systems of N-degrees of freedom is attempted: The direct extension of (1) might be assumed to be of the form

$$\frac{1}{2\pi} \oint_C p_i dq_i = \left(n_i + \frac{1}{2}\right) \hbar \qquad i = 1,2,\ldots,N \qquad (2)$$

where p_i, q_i (i = 1,2,...,N) are the conjugate pairs, and the n_i (i = 1,...,N) give the expected N-tuples of quantum numbers. Quantization is along the periods of the $(p_i q_i)$. The rule of Eq. (2) is not canonically invariant and must be discarded, as first realized by Einstein, who suggested a modified version of Eq. (2), for use with <u>integrable</u> N-dimensional systems.[1]

A classical Hamiltonian system of N-degrees of freedom is integrable if there are N independent global constants of the motion (a dynamical quantity $I(\bar{p},\bar{q})$ is a con-stant of motion if $\{H(\bar{p},\bar{q}),I(\bar{p},\bar{q})\} = 0$, { , } denoting the Poisson bracket). Exis-tence of constants of motion restricts motion of an individual classical trajectory

to hypersurfaces of lower dimensionality than the full 2N dimensional phase space. Thus energy conservation $\left(\{H(\bar{p},\bar{q}),H(\bar{p},\bar{q})\} = 0\right)$ implies that a trajectory moves on a 2N-1 dimensional hypersurface. Existence of N independent constants of the motion implies motion on a surface of dimension N in the 2N dimensional space. The topology of each N-surface is that of an N-torus. This is illustrated for a two-torus in Fig. 1. Einstein noted (implicitly) two important mathematical facts: (1) the multidimensional action $\bar{p}\cdot d\bar{q} = \Sigma_i\, p_i dq_i$ is, unlike the individual $p_i dq_i$, a canonical invariant; and, (2) integrals of the 1-form $\bar{p}\cdot d\bar{q}$ (the Poincaré invariant) on the surface of a torus generated by integrability of a Hamiltonian system are invariant to path distortion as long as the path remains on the surface of the torus, and as long as the path retains its topology. This is further discussed in the caption of Fig. 1. Einstein thus suggested that (2) be replaced by[1]

$$\frac{1}{2\pi} \oint_{C_i} \bar{p}\cdot d\bar{q} = \left(n_i + \tfrac{1}{2}\right)\hbar \qquad\qquad i = 1,2,\ldots,N \qquad\qquad (3)$$

where the N different quantum numbers arise from the N possible topologically distinct fundamental paths C_i on the surface of the N-torus. Equation (3) is the EBK quantization rule. Note that the paths C_i are not classical trajectories, and that there may well be no periodic orbits on a torus for which Eq. (3) is satisfied. Thus, unlike the one-dimensional case, quantization in the EBK scheme does not involve classical trajectories, and, in particular, does not involve finding periodic orbits. In one dimension the torus and the trajectory happen to coincide, which has given rise to much confusion, and to the expectation that periodic orbits have something simple to do with quantum levels, which is not the case, as discussed below. It is useful to note that while separable systems are necessarily integrable (energy in each degree of freedom is conserved giving the required N-constants), the EBK

PATH C_2

PATH C_3

PATH C_1
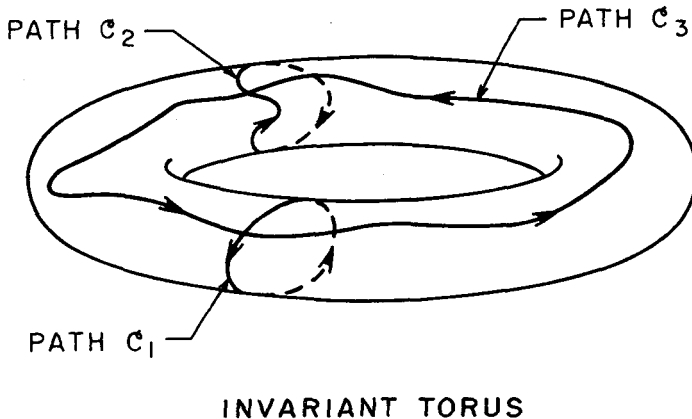
INVARIANT TORUS

Fig. 1. Invariant two-dimensional torus which would arise in the semi-classical quantization of an integrable Hamiltonian system of two degrees of freedom. This two-torus is embedded in the four-dimensional (p_x,p_y,x,y) phase space, and is a time-independent Lagrangian manifold. The two EBK quantization conditions are that

$$\int_{C_i} \bar{p}\cdot d\bar{q}/2\pi = [n_i+(\alpha/4)]\hbar$$

simultaneously for the two topologically independent paths labeled C_1 and C_3. Choice of actual path of a given topological type is immaterial as the integral of the one-form $\bar{p}\cdot d\bar{q}$ is invariant to those path distortions on the surface which can be made without breaking the path (i.e. the paths C_1 and C_2 give identical values of $\int_C \bar{p}\cdot d\bar{q}$).

condition of Eq. (3) is not generally equivalent to simply using one-dimensional WKB as applied to each degree of freedom in H, which will usually result in a non-invariant (i.e. coordinate dependent) quantization, unless the separation is performed in Jacobi variables. A case in point is H_2^+, where use of Eq. (3) gives excellent results.[10]

Do periodic orbits have any role in the semi-classical quantization of N-dimensional systems? Yes they do, but there is no 1-to-1 correspondence between a multidimensional periodic orbit and a quantum state. In fact, at each energy all possible periodic orbits must be found, and combined appropriately to determine whether a quantum state appears at that energy. This is the result of Gutzwiller's semi-classical analysis of the Feynman path integral,[4] an approach also followed by others.[5-7] This approach has the apparent advantage that integrability is not required[11] (in fact it may well be excluded!), but the even more apparent disadvantage that enumerating all of the infinitely many periodic orbits at each E is an impossible computational task. However, as beautifully explained by Berry and Tabor,[12,13] if one truncates the sum over periodic orbits, what one obtains, rather than quantum levels, is a density of states which shows oscillations. In the limit of including all orbits these oscillations become highly nonuniform and eventually coalesce to form a line spectrum. Thus low order periodic orbits, although not associated by themselves with quantum levels, are associated with spacings between oscillations in the density of states, and thus are of some utility for qualitative work. Advantage has been implicitly taken of this fact by Freeman and Economu[14] in their "periodic orbit" analysis of the Rydberg-Stark problem, and by Rau[15] whose one-dimensional model does not give an invariant quantization but can be expected to suggest level spacings.

3. Almost Separable and Almost Integrable Systems.- We begin this section with explicit definitions: A Hamiltonian system is separable if

$$H(\bar{p},\bar{q}) = \sum_{i=1}^{N} h_i(p_i,q_i) \quad , \tag{4}$$

that is if it is the sum of N sub-Hamiltonians, h_i, each of which independently generates the time evolution of the pair (p_i,q_i), even if there is implicit dependence on other variables.

A Hamiltonian system is integrable if there is a global canonical transformation to the form

$$\tilde{H}(I_1,\ldots,I_N) \tag{5}$$

$I_1 \ldots I_N$ being the constants of motion. The special case

$$\tilde{H}(I_1,\ldots,I_N) = \sum_{i=1}^{N} \tilde{h}_i(I_i) \tag{6}$$

includes all separable systems. Clearly, if $\tilde{H}(I_1,\ldots,I_N)$ is an arbitrary (say polynomial) function of the I_i's, it will not in general be separable.

A Hamiltonian system for which a global canonical transformation to form (5) does not exist is said to be non-integrable, and trajectories are not confined to N-tori. Almost all Hamiltonian systems fall into this latter class, integrability and separability being rare occurrences.

Integrable and separable systems can be quantized using the EBK prescriptions of Section 2. Additionally, if a system is separable and as long as the separation variables allow canonically invariant quantization, each sub-Hamiltonian $h_i(p_i q_i)$ may be quantized as a separate one-dimensional problem, a particularly simple and advantageous situation. However, in many cases, systems (which might be integrable or non-integrable) are almost separable: that is, an approximate separable Hamiltonian exists which quantitatively captures the essential dynamics. The atomic Stark problem for Rydberg states is an excellent case in point.

The non-relativistic hydrogenic Stark problem is exactly separable, a fact which has been widely exploited.[16-18] A more interesting case is the problem of the effects of an electric field on Rydberg states of non-hydrogenic atoms. Consider an alkali (such as Na) in a high Rydberg state. For motion of the "outer" electron near, but not inside the ion core, the dominant interaction is the monopole, and the effect of the core is described in terms of a classical quantum defect. This inner motion is separable in that ℓ and m_ℓ of the Rydberg electron are conserved. For motion far from the core the external field cannot be neglected compared to the ion monopole, but this outer problem is also exactly separable, as it is in the hydrogen problem. Frame transformation theory[19] can be used to patch together these two separable regions (where semi-classical quantization is a one-dimensional problem in each). This is essentially what has been done by Harmin, who has obtained spectacular results for the Rydberg spectrum of Na in a dc electric field.[20] In this case the motion may be thought of as almost separable in that the problem can be solved by piecing together (albeit with much cleverness) solutions to one-dimensional problems.

In strong contrast to the Stark problem, the hydrogenic Zeeman problem is a generically multidimensional problem in that it is strongly nonseparable. However, we will present evidence that it is "almost" integrable, in the sense that an approximate integrable (though not separable) Hamiltonian can be found which describes enough of the dynamics to allow EBK quantization via the approximate integrable system. A pictorial idea of how this can take place is illustrated in Fig. 2.
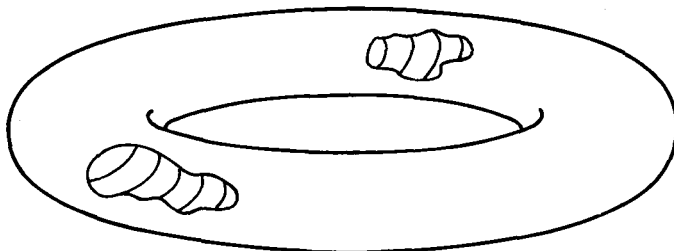
PARTIAL DESTRUCTION
OF INVARIANT TORUS

Fig. 2. Heuristic drawing indicating that chaotic classical dynamics is not incompatible with existence of "remnants" of invariant tori. What is intended by the drawing is that an approximate constant may exist in one part of chaotic phase space with strong non-integrability (indicated by the holes in the surface) in another. Application of Birkhoff-Gustavson normal form theory to a range of problems involving coupled oscillators indicates this type of strong non-uniformity of convergence of the expansion. The EBK quantization method can take advantage of such remnant structure, provided that the patches of strong non-integrability are in some sense small compared to $\hbar^N$.

4. The Quadratic Zeeman Problem.- The fact that approximate constants of motion exist for the quadratic Zeeman problem has been empirically noted by Zimmerman et al.,[21] is implicit in the classical trajectory studies of Edmonds and Pullen,[22] and has been made more explicit in the classical work of Robnik.[23] Within a fixed n (principal quantum number) manifold of hydrogenic states Hamada and Nakamura,[24] (numerically) and Herrick[25] (analytically using Lie Group theory) have found quantum constants of the motion, as has Goebel[26] using semi-classical perturbation theory.

These results give a dynamical symmetry valid in the "low" field limit. Reference 24 contains an explicit discussion of the range of validity of the "low" field results, with calculation of deviations at larger fields. Fortunately, the "low" field limit is not so low as to exclude the importance of the quadratic terms.

It is the purpose of the present work to determine and investigate the utility of approximate classical constants of motion valid beyond the low field limit of Refs. 24, 25 and 26. To the extent that these constants describe the short to middle term dynamics they then form the basis of an EBK type quantization using the integrable approximation to the full dynamics implicitly determined by the approximate constants. The technique used here is based on Gustavson's[27] modification of the Birkhoff[28] normal form, and results in an analytic power series expression for constants of the motion. As the Birkhoff-Gustavson method requires that the "unperturbed" problem be a set of uncoupled harmonic oscillators, we first transform the Zeeman Hamiltonian to a new "regularized" representation. Trajectories and Poincaré surfaces are studied in this representation and compared with the constants of motion which follow from the normal form technique. Preliminary semi-classical results are then presented. All of the results presented here are for the case m = 0, as defined below.

4.1. The classical Hamiltonian and dynamics.- In cylindrical coordinates (ρ,ϕ,z) the quadratic Zeeman-Hamiltonian for hydrogen is

$$H(\rho,\phi,z) = \frac{1}{2\mu} \left(p_\rho^2 + \frac{p_\phi^2}{\rho^2} + p_z^2 \right) + \frac{\omega^2 \mu \rho^2}{8} - \frac{e^2}{(\rho^2 + z^2)^{1/2}} \tag{7}$$

where $\rho^2 = x^2 + y^2$, and ω is the cyclotron frequency $\omega = eB/\mu c$. In the classical magnetic (CM) units used by Edmonds[22] this becomes

$$H_{CM}(\rho,\phi,z) = \frac{1}{2} \left(p_\rho^2 + \frac{p_\phi^2}{\rho^2} + p_z^2 + \rho^2 - \frac{1}{(\rho^2 + z^2)^{1/2}} \right) \quad . \tag{8}$$

As p_ϕ is a constant of motion, quantized as usual as $p_\phi = m\hbar$, m = 0,±1,±2,... a substantial simplification occurs if we restrict attention to $p_\phi = m\hbar = 0$, noting that it is the low m states which are experimentally accessible. To put the m = 0 problem in regularized form we use the Levi-Civita regularization[22] for plane motion:

$$\rho = (u')^2 - (v')^2 \tag{9a}$$

$$z = 2u'v' \tag{9b}$$

$$\frac{dt}{d\tau} = 4r = 4(\rho^2 + z^2)^{1/2} \tag{9c}$$

further, setting

$$u = u'(-8E)^{-1/4} \tag{9d}$$

$$v = v'(-8E)^{-1/4} \tag{9e}$$

gives (at last)

$$H = H^0 + H^1 = \left(-\frac{1}{2E}\right)^{1/2} \tag{10}$$

with

$$H^0 = \frac{1}{2}\left(p_u^2 + u^2\right) + \frac{1}{2}\left(p_v^2 + v^2\right) \tag{11a}$$

$$H^1 = \frac{1}{32E^2}\left(u^6 + v^6 - u^2v^4 - v^2u^4\right) \quad . \tag{11b}$$

H^0 is the $m_\ell = 0$ hydrogenic Hamiltonian, which in the new representation is a

two-dimensional isotropic oscillator. Equipotential contours of the "potential"

$$\frac{1}{2}(u^2 + v^2) + \frac{1}{32E^2}(u^6 + v^6 - u^2v^4 - v^2u^4) \qquad (12)$$

are illustrated in Figs. 3 and 4 where typical trajectories are shown, for E = -0.275 in the u,v space. Figures 5 and 6 show the corresponding phase space (p_u, p_v, u, v) structure utilizing the Poincaré surface of section defined in the caption of Fig. 5. The orbit in Fig. 4 at 45° to the u,v, axes is an orbit which at higher energies could ionize, while that of Fig. 3 is up the "potential ridge" discussed by Fano[29] and by Taylor and Clark.[30] As the surfaces of section (Figs. 5 and 6) illustrate, motion at 45° (in the potential valleys) is chaotic at this energy, while
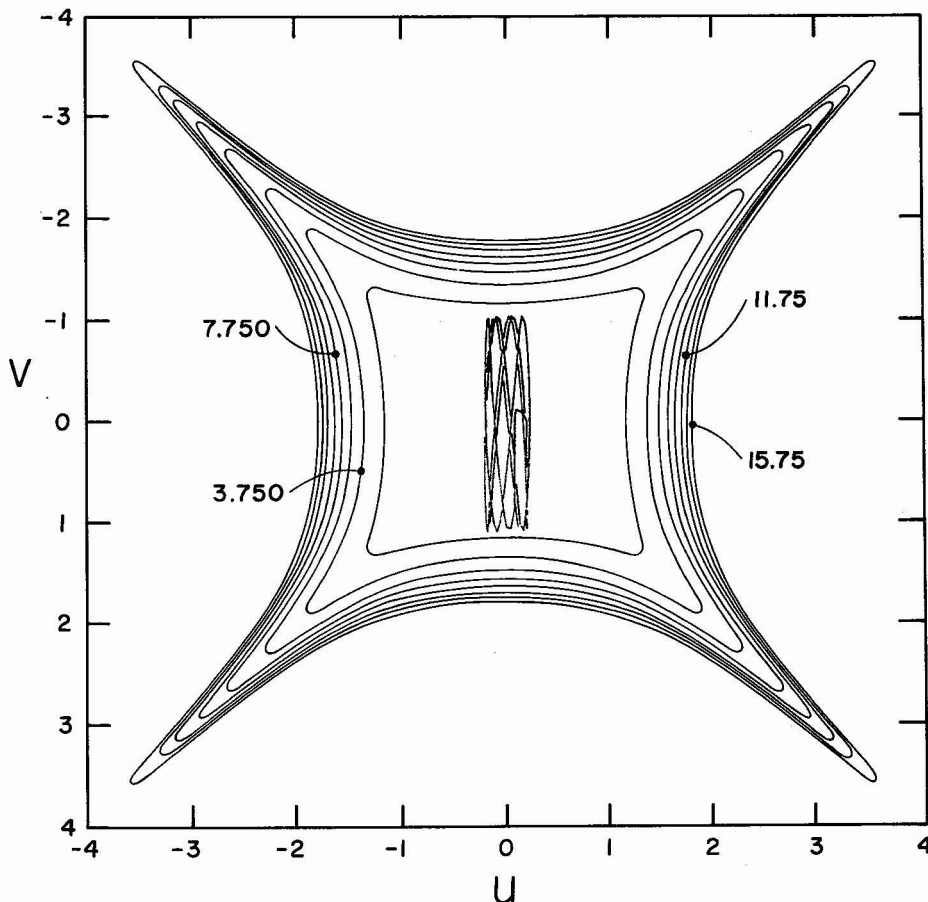

Fig. 3. Equipotentials and a quasi-periodic trajectory in the u,v plane, for E = -0.275. This trajectory, whose surface of section is shown in Fig. 5, is confined (at least to numerical accuracy) to the surface of a torus, indicating near integrability of the system in this region of the classical phase space. Note that the motion is up along a ridge on the potential surface, suggesting that the corresponding quantum wave functions will also concentrate there, see Refs. 29 and 30.
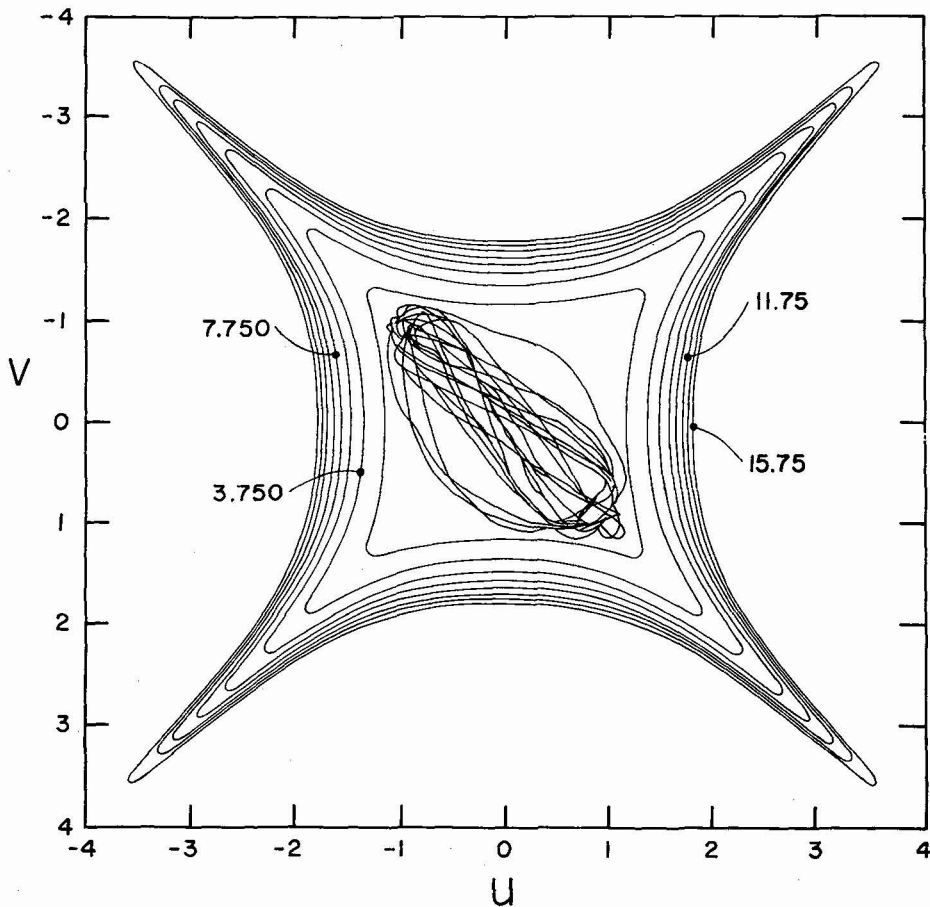
Fig. 4. Equipotentials and a chaotic classical trajectory in the u,v plane for E = -0.275. This trajectory, whose surface of section is shown in Fig. 6, oc- cupies a chaotic volume in phase space, suggesting lack of even an approxi- mate second constant of motion for the two-dimensional dynamics. However, this is misleading in that for times on the order of many classical periods good approximate constants exist, as determined by the Birkhoff-Gustavson technique. Trajectories, such as this one, which oscillate at 45° to the u,v axes are those which ionize at higher energies.

that up the ridge is highly stable. The fact that such non-separable classical mo- tion up the ridge is stable, and that this type of motion occupies a large volume of phase space immediately implies that the corresponding classical coordinate space wave functions will tend to peak in amplitude up the ridge as this is where the caus- tics are, rather than at classical turning points defined by zero kinetic energy, as would be the case in a one-dimensional system. Thus an alternate interpretation to the Fano "diffraction on a ridge" phenomenon[29] is found in the classical-quantum correspondence principle.
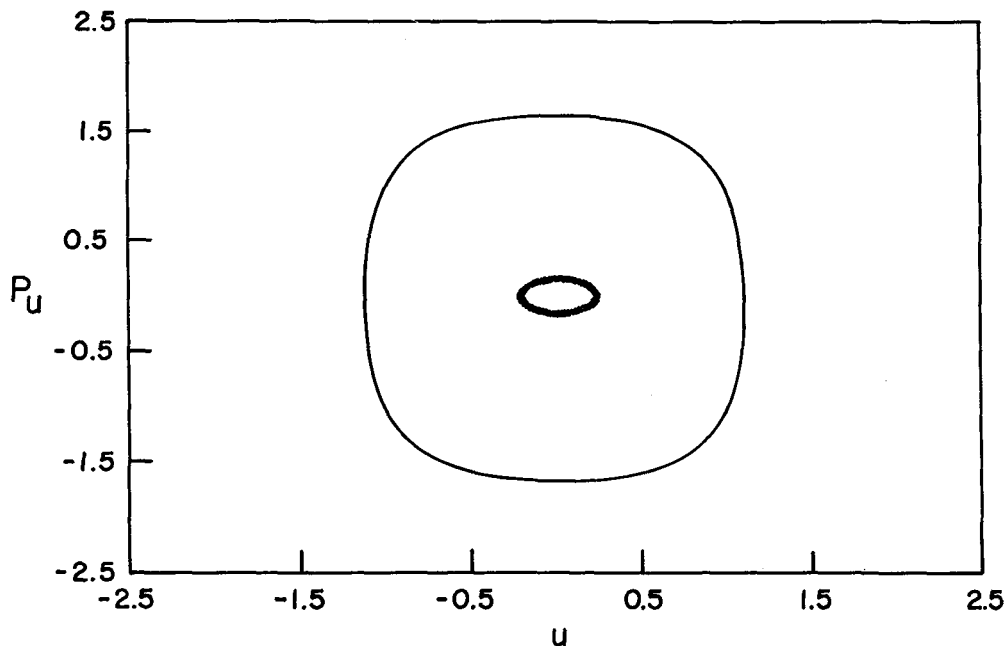
Fig. 5. Poincaré surface of section for the trajectory of Fig. 3. Shown are successive intersections of the four-dimensional phase space trajectory $(p_u(t), p_v(t), u(t), v(t))$ with the plane $v = 0$ ($p_v \geq 0$) as projected onto the (p_u, u) plane, i.e. the values $p_u(\tau), u(\tau)$ when $v(\tau) = 0$ and $p_v(\tau) \geq 0$. The collection of points is called the Poincaré surface of section. In the present case the points of intersection lie on the small ellipse near the center of the figure. The fact that the points lie on a closed curve in the (p_u, u) plane is consistent with the existence of a second constant (i.e. a constant in addition to H, itself) which confines the four-dimensional motion to the surface of a torus.

4.2. Approximate constants of motion.- For a classical Hamiltonian of the form

$$H(\bar{p}, \bar{q}) = H^0 + H^1 \tag{13}$$

where

$$H^0 = \sum \frac{\omega_i}{2} (p_i^2 + q_i^2)$$

and

$$H^1 = \sum_{j=1}^{\infty} \varepsilon^j \, h_{j+n}$$

and where h_k is a homogeneous polynomial of degree k in the phase space variables $(p_i, q_i, i = 1, \ldots, N)$, the Birkhoff-Gustavson procedure gives a systematic algorithm for transforming, through order ε^m, to a new Hamiltonian of form

$$H^{New} = \tilde{H}_m(\bar{P}, \bar{Q}) + \text{terms } O(\varepsilon^{m+1}) \text{ and higher} \tag{14}$$

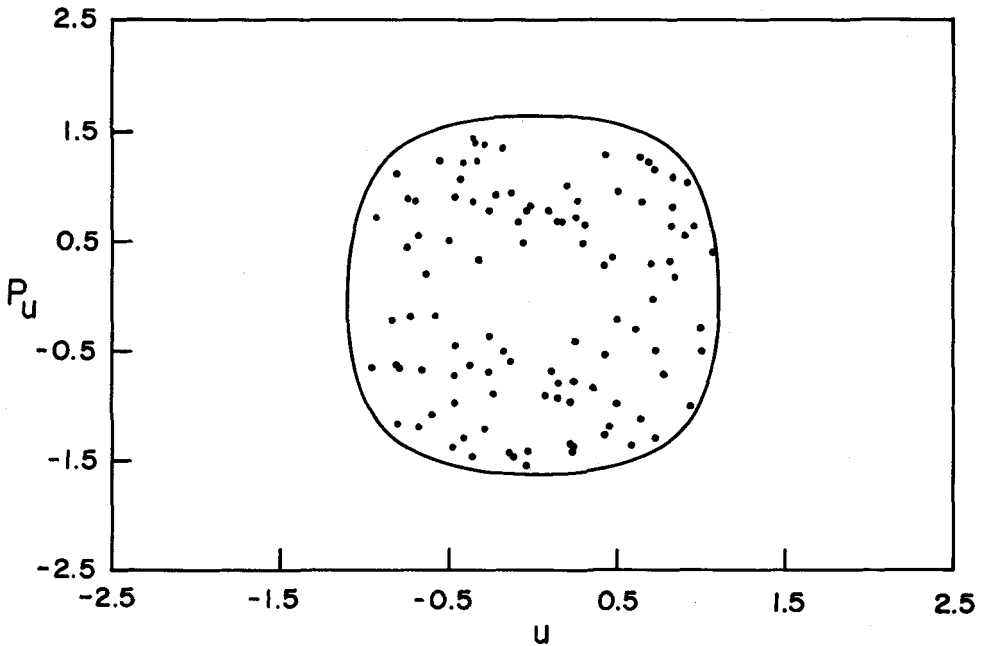where (assuming non-degeneracy of H^0)

Fig. 6. Poincaré surface of section for the chaotic trajectory of Fig. 4. Clearly
the motion is not on a torus, but this does not preclude existence of rem-
nants of structure as indicated in Fig. 2. This possibility allows EBK
quantization <u>even</u> in the chaotic regions of phase space.

$$\widetilde{H}_m(\widetilde{P},\widetilde{Q}) = f\left(P_1^2 + Q_1^2,\ P_2^2 + Q_2^2,\ P_3^2 + Q_3^2, \ldots, P_N^2 + Q_N^2 \right) \quad . \tag{15}$$

That is, the "new" Hamiltonian $\widetilde{H}$, said to be normalized through order ε^m, is a func-
tion of the "new" variables P_i and Q_i, these latter occurring only in the combina-
tions $(P_i^2 + Q_i^2)$, $i = 1, \ldots, N$. It is immediate from the canonical equations

$$\dot{P}_i = -\frac{\partial \widetilde{H}}{\partial Q_i} \tag{16a}$$

$$\dot{Q}_i = \frac{\partial \widetilde{H}}{\partial P_i} \tag{16b}$$

that $d/dt\ (P_i^2 + Q_i^2) = 0$ and then each $(P_i^2 + Q_i^2)$, $i = 1, \ldots, N$ is thus a constant
of motion of the partially normalized Hamiltonian $\widetilde{H}_m(P,Q)$, which approximates
the original Hamiltonian through ε^m. Defining $I_i = (P_i^2 + Q_i^2)/2$ we then have an
integrable approximation to $H(\bar{p},\bar{q})$ of the form (again in the non-degenerate case)

$$\widetilde{H}_m(I_1, I_2, \ldots, I_N) \quad . \tag{17}$$

EBK quantization of $\widetilde{H}_m(I_1, I_2, \ldots, I_N)$ follows by taking

$$I_i = \left(n_i + \frac{\alpha_i}{4} \right) \hbar \quad , \tag{18}$$

where α_i (the Maslov index, see Ref. 3) is a term determined by the caustic struc-
ture, giving the desired semi-classical levels. Additionally, the $I_i = \left(P_i^2 + Q_i^2 \right)/2$

can be tested for constancy, as the sequence of canonical transformations gives I_1 as an explicit polynomial function of the original phase space variables.

For the Hamiltonian of Eqs. (11a,b) level curves of a possible second constant of motion are obtained by running trajectories (Fig. 7) and compared with those obtained from the Birkhoff-Gustavson integrable approximation (Fig. 8) to the exact Hamiltonian. The comparison is excellent and indicates that at this energy (E = -1.0) the hydrogenic Zeeman problem is essentially integrable. Figure 9 shows a composite surface of section [obtained by running trajectories using Eq. (11)] indicating that classical chaos has set in. However, the motion is still "almost" integrable: Although not shown here (see Ref. 9) the second constant obtained using the Birkhoff-Gustavson technique is still remarkably accurate for many successive periods of motion, even in the chaotic regions of Fig. 9. The suggests that the chaos is not as great as might be suggested in Fig. 9. Similar conclusions for other coupled oscillator systems have been reached by Shirts and Reinhardt.[31]

4.3. _Semi-classical quantization of the normal form_.- In application of the normal form theory to the Hamiltonian of Eq. (11) some technical subtleties arise due to the fact that H^0 is an isotropic oscillator (i.e. a 1:1 resonant system), without going into detail (see Gustavson,[27] Swimm and Delos[32] and Jaffé and Reinhardt[33]) this results in a normalized Hamiltonian of the form
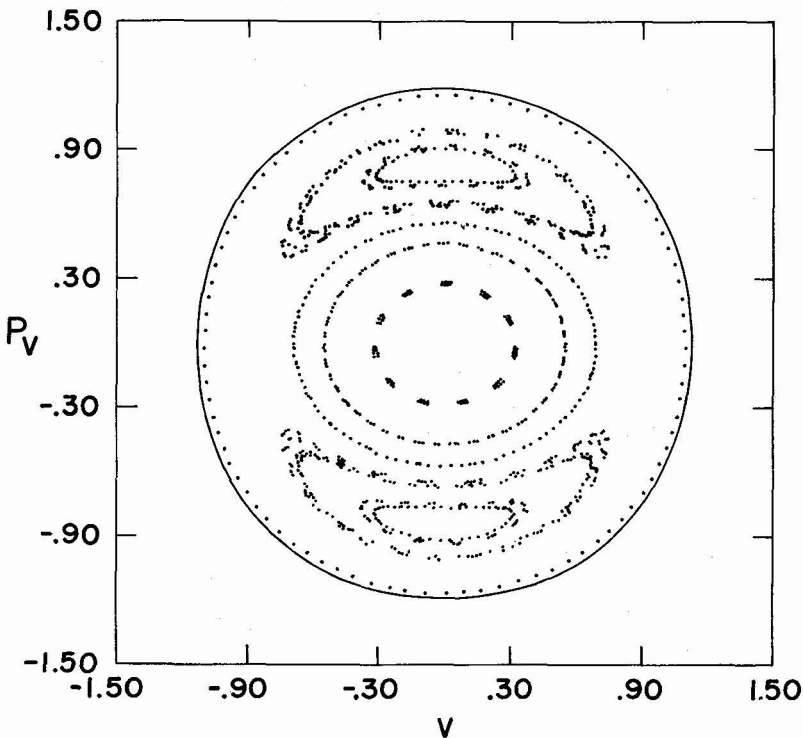
$$\tilde{H}(I_1, I_2, \theta_2) \tag{19}$$

Fig. 7. Composite Poincaré surface of section at E = -1.0; obtained by running fourteen classical trajectories chosen to give an indication of the major structures in phase space. At this energy the motion is integrable to high precision in the whole phase space.
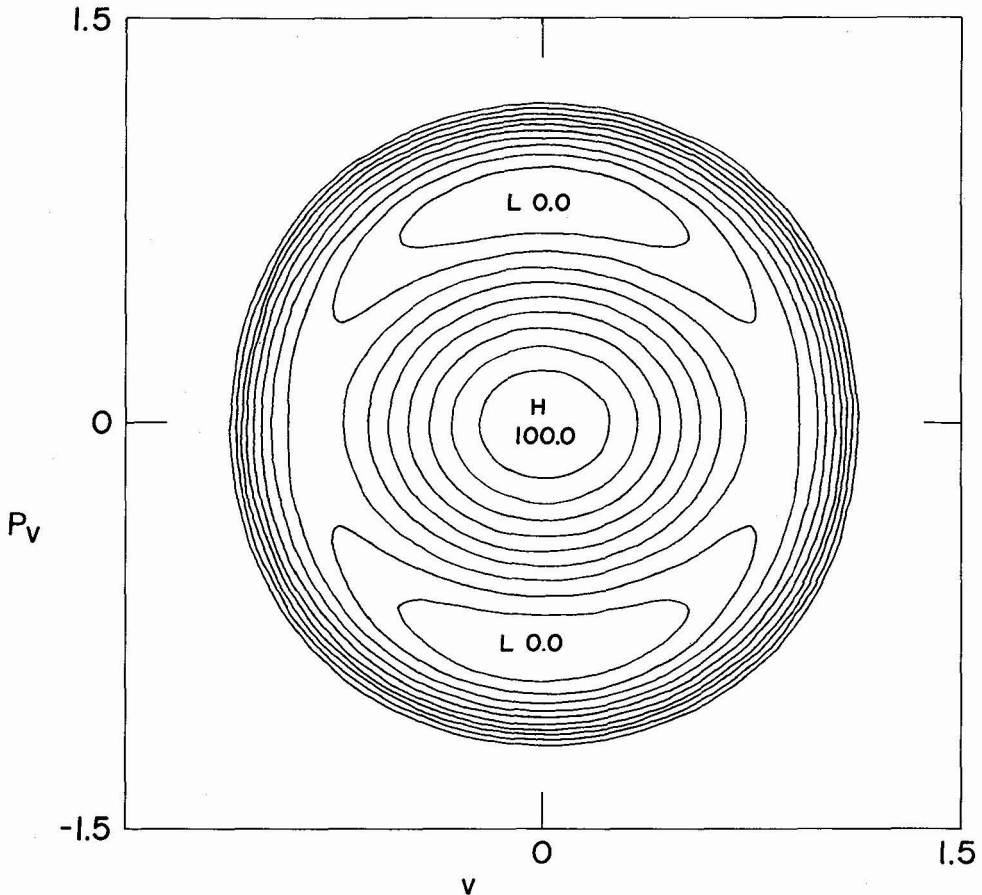
Fig. 8.   Surfaces of constant $I(\overline{p},\overline{q})$ at $E = -1.0$, obtained from the Birkhoff-
          Gustavson procedure through order ε^4. These curves are to be compared with
          those of Fig. 7 generated from the exact dynamics by running trajectories.
          Agreement is excellent, indicating that not only does a second constant
          exist (as is implicit in Fig. 7), but that the normal form procedure allows
          its analytic computation to high precision.

where θ_2 is the angle conjugate to the action I_2. Note that no angle conjugate to
I_1 appears, and thus $dI_1/dt = 0$. The result is that quantization follows by setting
$I_1 = (n_1 + (\alpha_1/2))\hbar$ for $n_1 = 0,1,2,\ldots$, followed by a uniform semi-classical quan-
tization in I_2,θ_2. Results of this procedure are shown in Fig. 10, where quantum
levels for the $m = 0$ case are shown at fields up to 200 T.

5. Discussion.- The results of Section 4 indicate that good approximate classical
constants of motion for the quadratic Zeeman problem can be explicitly obtained from
the Birkhoff-Gustavson normal form technique. In regular regions of phase space
(where trajectory studies indicate existence of tori) the constants are excellent.
In chaotic regimes the constants can describe short-to-middle term dynamics, thus
allowing their use in semi-classical calculations. The hydrogenic quadratic Zeeman
problem is thus "almost" integrable, in that large pieces of the dynamics can be
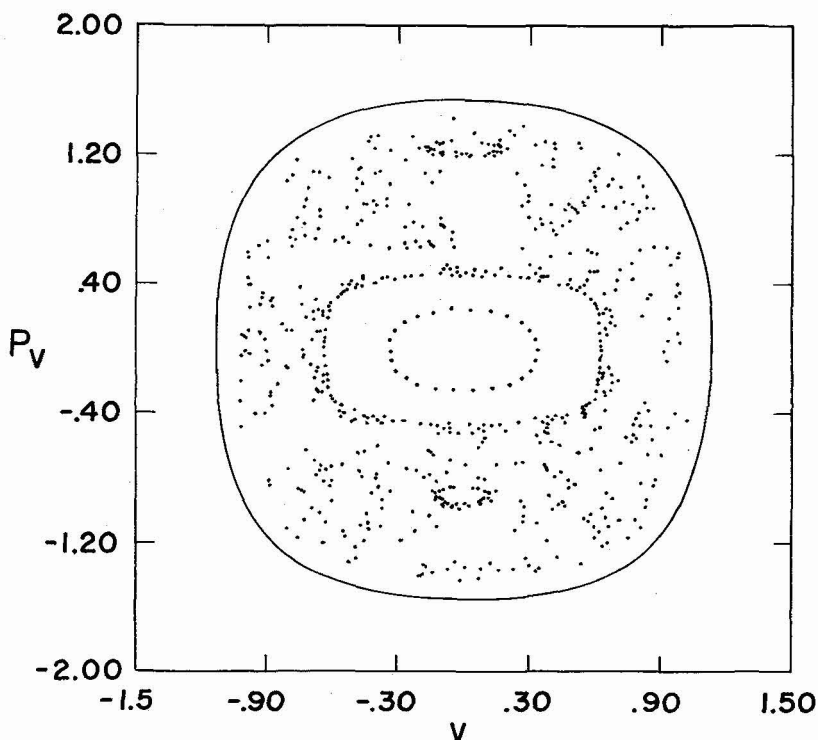well approximated by an integrable Hamiltonian, even when the trajectory studies

Fig. 9. Composite Poincaré sections at $E \approx -0.35$. At this higher energy a large volume of phase space is filled with tori, and a complementary large volume with chaotic motion. However, even in the chaotic volume EBK quantization can be performed on remnants of tori.

indicate chaos. The results of Fig. 10 are in agreement with the quantum calculations of Zimmerman et al.[21] indicating the power of the method.
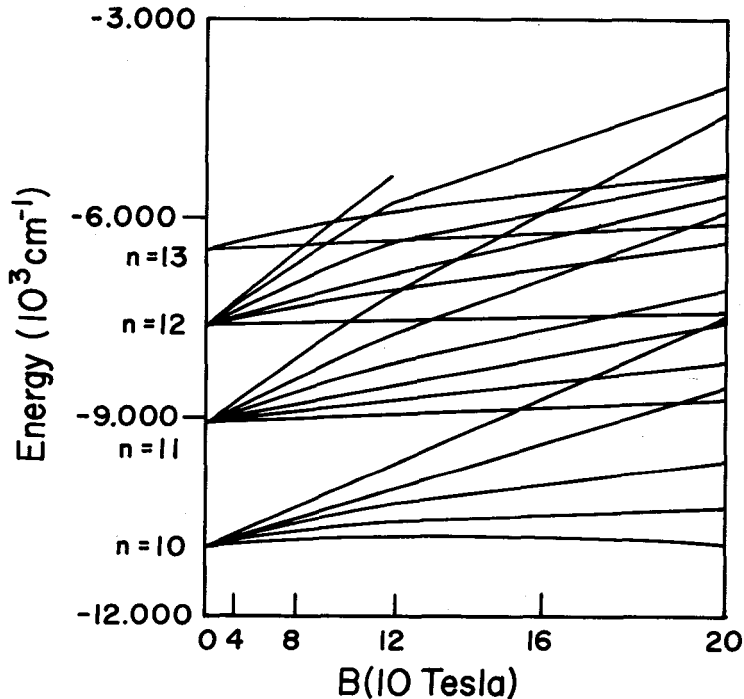
Fig. 10.   Hydrogenic Rydberg states strongly perturbed via the quadratic Zeeman effect, as calculated via EBK quantization of the Birkhoff–Gustavson normal form. The agreement with the fully quantum results of Ref. 21 is satisfactory.

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