Semiclassical Quantization of Intermittency in Helium

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(Received 27 March 1995)

We develop a new method to include intermittency into the periodic orbit description of a dynamical system. The technique allows removal of typical singularities in classical and semiclassical zeta functions caused by the coexistence of regular and chaotic dynamics. Approximate quantum numbers are derived from the regular dynamics, which provide a natural connection between periodic orbit theory and the semiclassical quantization of integrable systems. Interference effects and level repulsion in the quantum spectrum are resolved by including the classical chaotic dynamics in a perturbation expansion. Results are given for the Rydberg series structures in S helium.

PACS numbers: 32.30.Jc, 03.65.Sq, 05.45.+b

The increasing understanding of low dimensional chaos has led to a variety of new concepts to characterize dynamical systems through average quantities based on the principles of thermodynamics [1]. Closed expressions for the phase space averages can be given in terms of the set of all periodic orbits, which is densely embedded in the dynamical flow for generic systems [2]. Semiclassical approximations for quantum operators can be derived in the form of periodic orbit expressions [3–5] starting directly from Schrödinger's equation. The formulas of the thermodynamical formalism and the semiclassical theory have the same form and make use of the same classical information, suggesting a common theoretical basis [6]. Periodic orbit theories, however, suffer from a fundamental problem: The number of orbits increase exponentially with their period, and convergent resummation techniques could up to now only be given for systems close to uniform hyperbolicity, where exponential separation of trajectories occurs at approximately the same rate everywhere in phase space. The extension of these techniques to the generic case of Hamiltonian flows with stable islands and marginally stable fixed points has not been possible so far. Systems of this kind show the typical behavior of intermittency; a generic trajectory on the outside of stable islands alternates between regular motion near marginally stable components and chaotic motion in other regions of the phase space. The Lyapunov exponents of periodic orbits that approach the regular regime tend to zero, thus causing divergences in the periodic orbit formulas.

In this Letter, we present a method that is in principle capable of overcoming the problems mentioned above, and apply it to the semiclassical quantization of *collinear helium*. The dynamics of this system is not only interesting on its own, but it contains important features of the full three-body Coulomb problem helium. The first semiclassical calculations of parts of the helium spectrum could be carried out only recently on this model [7–9].

We start with a brief survey of the spectrum of S helium, which is defined by taking the total angular momentum $\mathbf{L} = 0$ and neglecting spin-orbit coupling. The spectrum consists of families of Rydberg series converging towards the single particle breakup thresholds $E_N = -Z^2/2N^2$, with $Z = 2$ for helium. (We use atomic units throughout.) Only the series below the $N = 1$ threshold corresponds to bound states; all other states are resonances embedded in the continuum. The number of series with a common threshold increases like N, and various approximate quantum numbers have been proposed to label this structure [10,11]. All these classification schemes break down in the large N limit ($N \geq 10$), where series towards different thresholds overlap strongly and interference effects become dominant. Modern techniques allow for a numerical calculation of the spectrum up to $N = 10$ by direct diagonalization of the Hamilton operator in a large basis set [12,13].

The classical dynamics of the three-body Coulomb system for $\mathbf{L} = 0$ is restricted to a plane, so the phase space is six dimensional. The structure of the dynamics is energy independent due to the scale invariance of the equations of motion. Appropriate coordinates are the electron-nucleus distances r_1, r_2, and the angle $\theta = \angle(\vec{r}_1, \vec{r}_2)$. The lowest Rydberg series to each N threshold is built up by eigenstates with expectation value $\langle\cos\theta\rangle \approx -1$. These states correspond to the energetically favored configuration of electrons localized on the opposite sides of the nucleus. A semiclassical description of these series follows from quantizing the corresponding near collinear dynamics, which is dominated by the four-dimensional invariant subspace $\theta = \pi$, $\dot{\theta} = 0$, a stable fixed plane of the full dynamics. In this collinear subspace the classical Hamiltonian has the form

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_1 + r_2} = E. \quad (1)$$

The dynamic is invariant under the exchange $r_1 \leftrightarrow r_2$, and we restrict ourselves to the fundamental domain $r_1 \geq r_2$. The Hamiltonian (1) is chaotic in the sense that all periodic orbits are unstable. Furthermore, a symbolic description exists that assigns a binary sequence to each trajectory based on the following rules: 0 if the trajectory does not hit the axis $r_1 = r_2$ between two consecutive events $r_1 = 0$, 1 otherwise. Perturbations perpendicular

 0031-9007/95/75(16)/2928(4)$06.00

to the collinear configuration correspond to stable bending modes in the θ coordinate. We refer to [14] for a detailed discussion of the full classical problem.

Although the motion in the collinear plane is ergodic and chaotic, nearly regular dynamics takes place when one electron is far from the nucleus compared to the other. The potential in (1) becomes separable in that limit, i.e., $V(r_1, r_2) \approx -Z/r_2 - (Z-1)/r_1$ for $r_1 \gg r_2$, and there exists a marginally stable orbit at $r_1 = \infty$, $p_1 = 0$. This orbit causes the intermittency in our system; a typical trajectory alternates between chaotic behavior in the region $r_1 \approx r_2$ and laminar motion out in the channel $r_1 \gg r_2$. The classical system is unbounded, so sooner or later almost all trajectories escape.

The starting point of our semiclassical approximation is the Gutzwiller-Voros zeta function [15], which is a semiclassical expression for the quantum spectral determinant $\det(E - \hat{H})$. This zeta function can be derived from the periodic orbit trace formula [3,4], and its leading term is for scale invariant classical Hamiltonians of the form

$$\zeta^{-1}(E) = \prod_p (1 - A_p e^{iS_p(E)/\hbar}). \tag{2}$$

The product runs over single repeats of all periodic orbits. The action $S = \oint p\, dq$ is taken along the orbit and the amplitude A_p includes both the winding number [16] and the linear stability exponents. The semiclassical approximation to the quantum eigenvalues is given by the zeros of the zeta function. The product representation (2) is, however, absolutely convergent only for $\mathrm{Im}E > h_c > 0$, so a suitable representation with larger analyticity domain as provided by the *cycle expansion* [2] is preferable. The product is expanded by multiplying out the single factors and regrouping the terms in such a way that maximal cancellations occur. The ordering procedure makes intensive use of the self-similar structure of the dynamics by exploiting a symbolic description of the flow and grouping together orbits and pseudo-orbits into contributions of increasing total symbol length [2].

The dynamics of collinear helium is strongly influenced by the regular behavior in the $r_1 \gg r_2$ regions. As a consequence, the amplitudes in (2) drop off algebraically and not exponentially with the code length for periodic orbits with a long tail of 0's. This is the typical behavior for trajectories approaching a marginally stable fixed point [17]. A straightforward application of a cycle expansion as outlined above is useless, as the symbolic description alone does not account for the laminar channel dynamics. Orbits with the same symbol length and comparable actions contribute very differently in amplitude depending on their behavior in phase space. Cancellation effects in the cycle expansion are therefore poor, and an analytic continuation of the zeta function is no longer provided.

We now present a general method to deal with this fundamental problem in periodic orbit theory. Following Ref. [2], we separate the regular and chaotic contributions by summing over the algebraic tails before regrouping terms in a cycle expansion. This is done by a summation over families of periodic orbits of the form $c\,0^n$, with a common head symbol string c and an increasing 0 tail. The cycle expansion now has the form

$$\zeta^{-1} = \prod_p (1 - t_p) = 1 - \hat{t}_1 - (\hat{t}_{11} - \hat{t}_1 t_1) - [(\hat{t}_{101} - \hat{t}_1 t_{01}) + (\hat{t}_{111} - \hat{t}_{11} t_1)] - \cdots \tag{3}$$

with $\hat{t}_c(E) = \sum_{n=n_0}^{\infty} t_{c\,0^n}(E)$. The lower index n_0 denotes the length of the shortest 0 tail possible in the family. For collinear helium, the weights t_p are given by

$$t_p = e^{2\pi i\{zS_p - [k+1/2]n_p - [m+1/2]\sigma_p\} - \lambda_p/2}. \tag{4}$$

Here, we write the action as $S_p(E) = 2\pi z(E) S_p$; the scaling factor $z = Z/\hbar\sqrt{-2E}$ contains all the energy dependence. Furthermore, λ_p denotes the stability exponent of the periodic orbit *in* the plane, whereas the stability index σ_p characterizes the stable dynamics *perpendicular* to the plane. For collinear helium, the winding number of the stable/unstable manifold in the plane equals twice the code length n_p of the periodic orbit. The integer number $m = 0, 1, \ldots$, labels quantum excitations of the stable degree of freedom in the harmonic oscillator approximation [7]. The integer number k has no effect on the weight t_p; its meaning will become clear in what follows.

Various quantities introduced in (4) can be written as smooth functions of the tail length n, with asymptotic behavior given by

$$S_c(n) = n\left[1 + \left(\frac{Z}{Z-1}n\right)^{-2/3}\right]^{3/2} + s_0^{(c)} + s_1^{(c)} n^{-1} + \cdots, \tag{5}$$

$$\sigma_c(n) = n + b_0^{(c)} + b_1^{(c)} n^{-1} + \cdots, \tag{6}$$

$$\lambda_c(n) = \tfrac{5}{3}\ln n + l_0^{(c)} + l_1^{(c)} n^{-1} + \cdots. \tag{7}$$

The leading terms in (5)–(7) are universal, i.e., independent of the head string c, and can be obtained in the separable limit $r_1 \gg r_2$ of the Hamiltonian (1) [8,18].

Making use of the identity $\sum_{n=-\infty}^{\infty} \delta(x-n) = \sum_{r=-\infty}^{\infty} \exp(2\pi i r x)$, we write the sums $\hat{t}_c$ as

$$\hat{t}_c(z) = \frac{t_c(z, n_0)}{2} + \sum_{r=-\infty}^{\infty} \int_0^{\infty} dx\, e^{2\pi i r x} t_c(z, n_0 + x), \tag{8}$$

where we introduced the notation $t_c(z, n)$ instead of $t_{c\,0^n}(z)$. Fixing $k = [\mathrm{Re}z] - m$ in (4), the $r = 0$ integral in (8) is the leading term of the expansion.

Before evaluating the full cycle expansion (3), we will study the dominant z-dependent behavior of the zeta function by approximating the leading integral $r = 0$ by the stationary phase. The stationary phase condition is

$$\frac{\partial}{\partial x}[zS_c(x) - (k + \tfrac{1}{2})x - (m + \tfrac{1}{2})\sigma_c(x)] = 0 \tag{9}$$

for z real. The solutions $x_0(z)$ of Eq. (9) tend to infinity for integer real z values, i.e., at the single ionization thresholds $E = -Z/2N^2$, with $N = k + m + 1$. Approximating the zeta function by its leading term only, i.e., $\zeta^{-1} \approx 1 - \hat{t}_c(z)$ (where $\hat{t}_c$ denotes the family sum with smallest coefficient $l_0^{(c)}$), the zeros of ζ^{-1} provide a quantization condition for the real parts of the energies,

$$zS(x_0) - (k + \tfrac{1}{2})x_0 - (m + \tfrac{1}{2})\sigma(x_0) = l + \tfrac{1}{8}, \quad (10)$$

in terms of the integer quantum numbers N, l, m.

A close look reveals an interesting connection between Eqs. (9) and (10) and the semiclassical Einstein-Brillouin-Keller (EBK) quantization [3], a generalization of the WKB approach for integrable systems with f degrees of freedom. For such systems the classical Hamiltonian can be written in the form $H = H(\vec{J})$, with conserved actions $\vec{J}$ and frequencies $\vec{\omega} = \partial H/\partial \vec{J}$. The manifold $\vec{J} = \text{const}$ has the topology of an f-torus embedded in the $2f$-dimensional phase space. The EBK quantization condition is then simply given by $E_{\vec{n}} = H[\hbar(\vec{n} + \vec{\nu}/4)]$ and the numbers ν_i are integers. The action of a trajectory moving on a 3-torus after the time $T = 2\pi/\omega_1$ is given by

$$J(\alpha, E) = J_1(\alpha, E) + \alpha J_2(\alpha, E) + \alpha_3(\alpha) J_3(\alpha, E), \quad (11)$$

with winding numbers $\alpha = \omega_2/\omega_1$ and $\alpha_3 = \omega_3/\omega_1$. We assumed here a harmonic oscillator in the third degree of freedom, i.e., α_3 is constant for fixed J_1, J_2, and arbitrary J_3. For the integrable system (11), the additional condition

$$\frac{\partial J}{\partial \alpha} = J_2 + \frac{\partial \alpha_3}{\partial \alpha} J_3 \quad (12)$$

is valid for fixed energy. Equations (11) and (12) are indeed equivalent to (10) and (9) if we set $J = zS/x$, $\alpha = 1/x$, and $\alpha_3 = \sigma/x$ and choose the quantization conditions

$$J_1 = k + 1/2, \qquad J_2 = l + 1/8, \qquad J_3 = m + 1/2. \quad (13)$$

We identify J_1, J_2 with the motion of the inner, outer electron, while J_3 represents the stable degree of freedom. This procedure establishes a direct connection of Gutzwiller's periodic orbit formula, valid only for isolated periodic orbits, with the EBK quantization of integrable systems. Furthermore, our derivation suggests a generalization of the usual EBK approach to nearly integrable dynamics. The nonintegrability enters here just through the unusual term 1/8 in (13) and the nonleading terms in the expansion of the action and winding number in (5) and (6).

Results for our simple quantization condition (which we call QEBK for quasi-EBK from now on) are listed in Table I. We compare the energy eigenvalues deduced from (9) and (10) with the real part of S helium resonances obtained from full quantum calculations using complex rotation [13]. The spectra deviate not more than 4% with respect to the mean level spacing, except for the helium ground state $(N, l) = (1, 0)$ and the energy region around $E = -0.130$, where the Rydberg series $N = 4$ is perturbed by the lowest resonance of the $N = 5$ states. The good agreement for large l quantum numbers would be completely destroyed choosing the usual harmonic oscillator term 1/2 instead of 1/8 in (10) and (13). Note that there is no free parameter; the functions $S(x)$ and $\sigma(x)$ are completely determined by (5) and (6) with nonleading coefficients fixed by the periodic orbit data.

The QEBK treatment describes the gross structure of the spectrum. Finer details such as perturbations due to overlaps of different N Rydberg series causing level repulsion are not resolved (see Table I at $E \approx -0.130$). These effects are a manifestation of the strong violation of the near integrability condition in the region close to the nucleus. To include the chaotic dynamics in a systematic way we need to evaluate the full cycle expansion

TABLE I. Quantum energies of the bound Rydberg states $N = 1$ and the resonance series $N = 4$ from [13] are compared with semiclassical QEBK and cycle expansion calculations in ${}^1S^e_{m=0}$ helium. The error ϵ is given in percentage of the mean level spacing.

l	QM	QEBK	ϵ	Cyc Exp	ϵ
$N = 1$					
0	2.903721	2.780992	5.6	2.928251	1.0
1	2.145974	2.149378	2.1	2.135623	6.9
2	2.061272	2.062035	1.8	2.059238	4.9
3	2.033587	2.033870	1.6	2.032887	4.1
4	2.021177	2.021313	1.6	2.020860	3.7
5	2.014563	2.014639	1.5	2.014394	3.4
6	2.010626	2.010672	1.5	2.010525	3.3
7	2.008094	2.008124	1.5	2.008029	3.2
8	2.006370	2.006391	1.5	2.006326	3.1
9	2.005143	2.005158	1.5	2.005112	3.0
10	2.004239	2.004251	1.5	2.004216	3.0
11	2.003555	2.003563	1.5	2.003537	2.9
12	2.003023	2.003030	1.4	2.003001	2.9
∞	2.0	2.0		2.0	
$N = 4$					
0	0.200990	0.201365	0.6	0.199970	1.7
1	0.165734	0.166631	3.8	0.165150	2.5
2	0.150824	0.151114	2.4	0.150382	3.8
3	0.142602	0.142676	1.1	0.142345	4.0
4	0.137685	0.137653	0.8	0.137616	1.7
5	0.134551	0.134464	3.3	0.134569	0.7
6	0.132452	0.132330	6.8	0.132501	2.7
7	0.130999	0.130839	12.5	0.131066	5.0
8	0.129993	0.129758	24.5	0.130042	4.8
5 0	0.129323			0.129298	4.2
9	0.128777	0.128951	25.6	0.128735	6.4
10	0.128262	0.128332	13.1	0.128237	4.8
11	0.127816	0.127848	7.7	0.127795	5.0
12	0.127446	0.127463	4.8	0.127428	5.3
∞	0.125	0.125		0.125	

in (3). The motion in the region $r_1 \approx r_2$ is resolved in ever finer detail by taking families with increasing head string length into account. Note, however, that the sums $\hat{t}_c$ and also the integral representation (8) are divergent for $\mathrm{Im} z < 0$ due to the algebraic decay of the amplitudes. This is the basic problem of periodic orbit formulas in the presence of marginally stable behavior. In the periodic orbit family picture, these divergences can now be removed step by step. An analytic continuation for the sum $\hat{t}_c$ follows from rotating the line of integration for each r integral in (8) onto the imaginary axis to obtain the compact expression

$$\hat{t}_c(z) = \frac{1}{2} t_c(z, n_0) - i \int_0^\infty dx\, t_c(z, n_0 - ix) + i \int_0^\infty dx\, \frac{e^{-2\pi x}}{1 - e^{-2\pi x}} [t_c(z, n_0 + ix) - t_c(z, n_0 - ix)]. \quad (14)$$

The sum is converted into two integrals; each integrand decreases exponentially for large x and for all complex z values with noninteger real part. This analytic continuation technique together with the cycle expansion in terms of periodic orbit families is the main result of this Letter. We are now able to calculate periodic orbit product formulas of the type (2) in the form of exponentially converging expansions also for marginally stable behavior.

The real part of the zeros of the cycle expanded function (3) including contributions up to head string length 4 are listed in Table I. Agreement remains for the regular parts of the spectrum; in addition, the perturbation of the $N = 4$ series is now clearly resolved. Results of similar quality are obtained for the $m = 1$ states. The error is expected to increase for larger off-line excitations, and the full six-dimensional phase space dynamics then has to be taken into account. The imaginary part of the resonances can at present be only qualitatively reproduced; the width of the resonances is typically orders of magnitude smaller than the level spacings and still below the resolution of the semiclassical method used here [18].

We conclude that the structure of the helium spectrum can be well understood from semiclassical arguments. The regular parts of the spectrum can be assigned to a regular limit of the dynamics, whereas interference effects are caused by strong electron-electron interactions, which give raise to chaotic motion. We claim that this correspondence is valid in general for multithreshold spectra; a semiclassical quantization of the diamagnetic Kepler problem can be worked out successfully in the same spirit [18]. The results are based on a new method to include regular parts of the classical dynamics in a convergent way within the zeta function formalism. This approach is a step towards a general treatment of intermittency in periodic orbit expressions and a detailed study of generic mathematical properties of zeta functions for dynamical systems with marginally stable behavior. Our QEBK formulas suggest a generalization of the EBK theory and have been shown here to describe threshold behavior in atomic spectra.

G. T. thanks Sara Solla for carefully reading the manuscript, and Kai Hansen, Debabrata Biswas, and Predrag Cvitanović for useful comments and discussions. The project was supported by the Deutschen Forschungsgemeinschaft and the SFB 276 at the University Freiburg.

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