Semiclassical Quantization of the Diamagnetic Hydrogen Atom at the Field-free Ionization Threshold

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Semiclassical quantization methods have been successfully applied to the hydrogen atom in a magnetic field at low excitation energies where the classical dynamics is near integrable or weakly chaotic, and at high energies far above the field-free ionization threshold where the classical dynamics is completely hyperbolic. However, the energy region around $E = 0$ has so far resisted any attempts for semiclassical quantization. We present an efficient multi-shooting algorithm for the periodic orbit search and a novel quantization technique based on harmonic inversion with constraints which allow, for the first time, the semiclassical quantization of the diamagnetic hydrogen atom in the very challenging energy region.

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1. Introduction

Gutzwiller's periodic orbit theory [1] relates the classical dynamics of a chaotic system to the corresponding quantum spectrum. The semiclassical level density is given as the superposition of a smooth background and oscillatory terms which depend on parameters of the classical periodic orbits. In chaotic systems the number of periodic orbits usually proliferates exponentially with increasing orbital length and thus the periodic orbit sum does not converge. Various techniques have been developed to overcome the convergence problems of Gutzwiller's trace formula, e.g., the cycle expansion method [2], pseudo orbit expansions [3], the surface of section method [4], or harmonic inversion [5, 6]. The methods complement each other in the way that most of them are efficient only for a certain class of physical systems with special properties. As a whole, they allow for the semiclassical quantization of a quite large variety of physical systems. However, challenges still remain.

The hydrogen atom in a uniform magnetic field has served for several decades as a prototype example of a real physical quantum system with an underlying chaotic classical dynamics [7, 8]. With increasing energy, the diamagnetic hydrogen atom undergoes a transition from near-integrable phase space over mixed regular-chaotic dynamics to completely chaotic behavior. Semiclassical quantization methods have been successfully applied at rather low excitation energies where the classical motion is near-integrable or mixed regular-chaotic [9–11], and at high energies far above the field-free ionization threshold where the dynamics is completely hyperbolic, and the periodic orbits can be described by a complete symbolic code [12]. The energy region around the field-free ionization threshold, $E = 0$, has so far resisted any attempts for semiclassical quantization.

What makes that energy regime hardly accessible to semiclassical methods? The classical dynamics at $E = 0$ is chaotic but not completely hyperbolic, i.e., the symbolic code describing the periodic orbits is incomplete. Orbits are pruned in a similar way as for the closed three-disk or four-disk billiards [13, 14]. Furthermore, there exist sequences of marginally stable orbits whose actions and stability eigenvalues grow very slowly with increasing symbol length. Pruning and marginal stability of orbits prevent any rapid or decent convergence of cycle expansions. Semiclassical quantization by harmonic inversion can be applied to systems with pruning but, unfor-

tunately, in the case of the diamagnetic hydrogen atom requires extremely many period orbits for convergence similar as for the closed three-disk billiard [15]. Note that the numerical effort for the periodic orbit search in systems with smooth potentials such as the diamagnetic hydrogen atom is much higher than in billiards with hard walls.

In this paper we will present a very efficient multi-shooting algorithm for the periodic orbit search and a new method for periodic orbit quantization based on harmonic inversion with constraints. The constraints will allow us to significantly reduce the required amount of periodic orbits, and to obtain, for the first time, semiclassical eigenvalues of the diamagnetic hydrogen atom at the field-free ionization threshold. In Sec. 2 the mathematical foundation of the method is derived. In Sec. 3 we establish the multi-shooting algorithm for the periodic orbit search. The semiclassical spectra and comparisons with exact quantum spectra are presented and discussed in Sec. 4. Concluding remarks are given in Sec. 5.

2. Harmonic inversion with constraints

The density of states of a quantum system can be written as

$$\varrho(E) = \varrho_0(E) - \frac{1}{\pi} \operatorname{Im} g(E) \,, \tag{1}$$

where $\varrho_0(E)$ is a smooth background term and $g(E)$ is the oscillatory part of the trace of the retarded Green's function. In periodic orbit theory [1] a semiclassical approximation to $g(E)$ is given as a superposition of all periodic orbit (po) contributions

$$g^{\rm sc}(E) = \sum_{\rm po} \mathcal{A}_{\rm po}(E)\, {\rm e}^{{\rm i}S_{\rm po}(E)} \,, \tag{2}$$

where $S_{\rm po}$ is the classical action, and the amplitudes

$$\mathcal{A}_{\rm po} = \frac{T_{\rm ppo}}{\sqrt{|\det(\mathbf{M}_{\rm po} - \mathbf{1})|}}\, {\rm e}^{-{\rm i}\frac{\pi}{2}\mu_{\rm po}} \tag{3}$$

depend on the time period $T_{\rm ppo}$ of the primitive periodic orbit (ppo), the monodromy matrix $\mathbf{M}_{\rm po}$, and the Maslov index $\mu_{\rm po}$ of the periodic orbit. The periodic orbit sum in (2) does usually not converge. In quantum mechanics the trace of the retarded Green's function reads

$$g^{\rm qm}(E) = \sum_k \frac{d_k}{E - E_k + {\rm i}\epsilon} \,, \tag{4}$$

with E_k the energy eigenvalues, and d_k weights which in general can be, e.g., diagonal or transition matrix elements. For density of states spectra with non-degenerate states all weights are $d_k = 1$.

Harmonic inversion has been introduced as a general tool for periodic orbit quantization in Refs. [5, 6, 16]. Briefly, the idea is to adjust the semiclassical Green's function (2) to its quantum analogue (4) with the $\{E_k, d_k\}$ being free adjustable parameters. By applying a windowed Fourier transform in the energy range $[E_0 - \Delta E, E_0 + \Delta E]$ to the semiclassical and quantum version of the Green's function $g(E)$ this problem can be recast to the signal processing of the band-limited time signal

$$C^{\rm sc}_{\rm bl}(t) = \frac{\rm i}{2\pi} \int_{E_0-\Delta E}^{E_0+\Delta E} g^{\rm sc}(E)\, {\rm e}^{-{\rm i}(E-E_0)t} {\rm d}E \tag{5}$$

$$\stackrel{!}{=} C^{\rm qm}_{\rm bl}(t) = \sum_{k=1}^{K} d_k\, {\rm e}^{-{\rm i}(E_k-E_0)t} \,. \tag{6}$$

The sum in Eq. (6) is over the K eigenvalues within the chosen energy interval. Using an equidistant time grid, $t = n\tau$, with step width τ and $n = 0, 1, 2, \ldots, 2K-1$ the $2K$ parameters for the semiclassical energy eigenvalues and amplitudes $\{E_k, d_k\}$ are obtained from the set of $2K$ nonlinear equations for the signal $C^{\rm sc}_{\rm bl}(n\tau)$. Details of the numerical procedure are given in [6, 16]. Note that the usage of a filter and the construction of a band-limited signal is essential for the numerical stability of the harmonic inversion procedure.

The required signal length to achieve convergence of the results is $T_{\max} \gtrsim 4\pi\varrho_0(E)$ with $\varrho_0(E)$ the mean level density [6], i.e., all periodic orbits

with time periods $T_{\rm po} \leq T_{\rm max}$ must be known. In chaotic systems the number of periodic orbits proliferates exponentially with increasing period, and thus the value of $T_{\rm max}$ is often crucial for the successful application of harmonic inversion. In particular, for the diamagnetic hydrogen atom at energy $E \approx 0$ the required amount of periodic orbit data is too high to obtain reasonable results with the established methods.

We will now introduce harmonic inversion with constraints as a new method for periodic orbit quantization. The method is also based on the signal processing of the semiclassical time signal (5) but the implementation of the constraints allows us to reduce the required signal length by about a factor of two, i.e., $T_{\rm max} \gtrsim 2\pi\varrho_0(E)$. As mentioned above the amplitudes d_k in Eq. (6) are all $d_k = 1$ for density of state spectra with non-degenerate eigenvalues. Instead of handling the d_k as free adjustable parameters we use their known values as constraints for the signal processing. Thereby Eqs. (5) and (6) are simplified to

$$C_{\rm bl}^{\rm sc}(t) = \sum_{k=1}^{K} {\rm e}^{-{\rm i}(E_k - E_0)t} \; . \tag{7}$$

Evaluating the signal $C_{\rm bl}^{\rm sc}(t)$ at equidistant time steps $t = n\tau$ with $n = 0, 1, 2, \ldots, K-1$ again yields a set of N nonlinear equations for the K unknown energies E_k. However, with the amplitudes fixed Eq. (7) does no longer have the generic form for harmonic inversion, i.e., the numerical methods of Ref. [16] cannot be applied. For the numerical solution of Eq. (7) we therefore must follow a different approach. The substitution of

$$\lambda_k = {\rm e}^{-{\rm i}(E_k - E_0)\tau} \tag{8}$$

in (7) yields (with $t = n\tau$)

$$C_{\rm bl}^{\rm sc}(n\tau) = \sum_{k=1}^{K} \lambda_k^n \quad ; \; n = 0, 1, 2, \ldots, K-1 \; . \tag{9}$$

Assuming that the λ_k are the eigenvalues of some (unknown) linear operator $\hat{\mathbf{U}}$, Eq. (9) can be written in terms of traces of powers of this operator,

$$C_{\rm bl}^{\rm sc}(n\tau) = \sum_{k=1}^{K} \lambda_k^n = {\rm Tr}\, \hat{\mathbf{U}}^n \; . \tag{10}$$

Eq. (10) can be solved with the help of Newton's identities which relate sums of powers of roots of a polynomial with the coefficients of the polynomial. For more details and a matrix proof of Newton's identities see [17].

The procedure for periodic orbit quantization now is as follows. All periodic orbits with time period $T_{\rm po} \leq T_{\rm max}$ must be calculated. With the help of the periodic orbit parameters and Eq. (5) the semiclassical band-limited time signal $C_{\rm bl}^{\rm sc}(t)$ is constructed. Using Eq. (10) the signal at time steps $t = n\tau$ are interpreted as traces of powers of an operator $\hat{\mathbf{U}}$. The coefficients of the characteristic polynomial and thus the eigenvalues λ_k of $\hat{\mathbf{U}}$ are obtained with the help of Newton's identities. Finally, the λ_k are transformed to the energy eigenvalues E_k via Eq. (8).

As explained above the advantage of using the constraint $d_k = 1$ for the weights of the eigenvalues is that the required signal length is reduced by about a factor of two. However, the identification of additional spurious eigenvalues becomes more difficult. Without the constraint spurious eigenvalues are characterized by low weights $|d_k| \ll 1$. When the weights are fixed, in bound systems the semiclassical approximations of the true physical eigenvalues are located close to the real energy axis while spurious eigenvalues are typically shifted downwards in the complex energy plane.

3. Multi-shooting algorithm for the periodic orbit search

The numerical computation of periodic orbits is a prerequisite for the semiclassical quantization of chaotic systems. In chaotic billiards with an existing symbolic dynamics like, e.g., the three-disk scatterer or the hyperbola billiard, a periodic orbit with given symbolic code can

be computed efficiently by moving the reflection points until the orbit length becomes a minimum. For systems with smooth potentials the periodic orbit search is less easy. Using a simple shooting algorithm trajectories with varying starting points are integrated numerically until the initial and final point match. When applying this method for a systematic periodic orbit search some orbits are typically found many times while others may be overlooked. In particular, long and very unstable orbits are difficult to find.

For the computation of the periodic orbits of the diamagnetic hydrogen atom we developed a multi-shooting algorithm which is adapted to the symbolic dynamics of the system. With this algorithm we can find selectively any orbit for a given symbolic code, even when the orbit is very long and unstable [18].

Using a regularization technique for the Coulomb singularity [7, 8] the Hamiltonian of the diamagnetic hydrogen atom with the magnetic field along the z-axis and vanishing angular momentum $L_z = 0$ reads (in atomic units, $\gamma = B/(2.35 \times 10^5 \text{ T})$)

$$H = \frac{1}{2}\left(p_\mu^2 + p_\nu^2\right) + V(\mu,\nu) = 2 \,, \qquad (11)$$

where $\mu = \sqrt{r+z}$ and $\nu = \sqrt{r-z}$ are semiparabolic coordinates and the potential $V(\mu,\nu)$ is given by

$$V(\mu,\nu) = -E(\mu^2+\nu^2) + \frac{\gamma^2}{8}(\mu^4\nu^2 + \mu^2\nu^4) \,. \quad (12)$$

The shape of classical orbits does not depend separately on the energy and magnetic field strength but, using scaling properties of the Hamiltonian (11), only on the scaled energy $\tilde{E} = E\gamma^{-2/3}$.

Allowing the semiparabolic coordinates (μ,ν) to be positive or negative, the potential (12) has a C_{4v}-symmetry. Periodic orbits can be described by a ternary symbolic code [19] in a similar way as for the hyperbola or four-disk billiard with the same symmetry. At high energies $\tilde{E} > \tilde{E}_c = 0.329$ there is a one-to-one correspondence between orbits and the symbolic code, whereas below the critical energy orbits undergo bifurcations and the symbolic dynamics is pruned [20, 21].

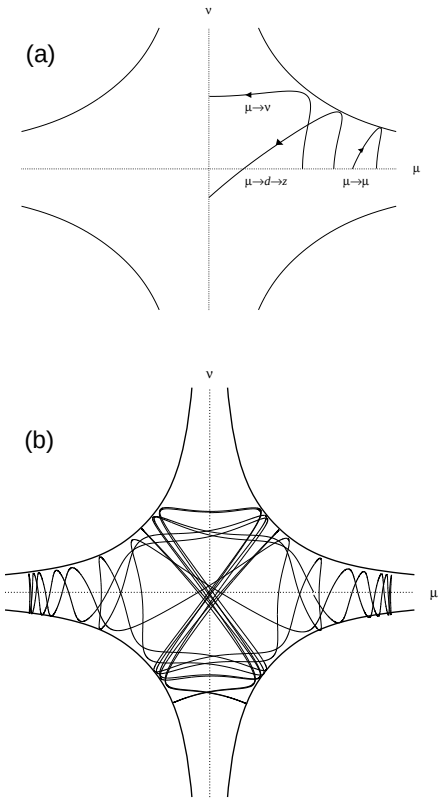

FIG. 1. (a) In the multi-shooting algorithm each orbit is split into short segments starting and ending on one of the axes. The concatenation of various types of segments is guided by the symbolic code of the orbit. (b) Periodic orbit with symbol length $L = 30$ and stability eigenvalue $\lambda = -3.041 \times 10^{17}$ of the diamagnetic hydrogen atom at scaled energy $\tilde{E} = E\gamma^{-2/3} = 0.5$.

The multi-shooting algorithm for the periodic orbit search basically works as follows. Each periodic orbit is split into segments, with the number of segments equal to the string length L of the symbolic code. The segments start on either the μ or the ν axis and end on one of the axes as illustrated in Fig. 1 (a). Starting all segments with initial guesses chosen in accordance with the symbolic code the orbit is discontinuous between the end point of one and the starting point of the next segment. Now the initial conditions of all

segments are iteratively changed to remove the discontinuities. This problem can be formulated as a $2L$-dimensional root search. (Note that two parameters can be changed for each segment to vary the initial conditions on one of the axes.)

Because the segments are short the multi-shooting algorithm usually converges rapidly and uniquely to the periodic orbit selected by the symbolic code, provided the orbit is not pruned or very close to bifurcation. The method works very well even for very long and unstable orbits. As an example a periodic orbit with symbol length $L = 30$ and stability eigenvalue $\lambda = -3.041 \times 10^{17}$ at scaled energy $\tilde{E} = 0.5$ is presented in Fig. 1 (b).

At the field-free ionization threshold $E = 0$ the dynamics is pruned, i.e., for certain code strings a corresponding physical orbit does not exist. Nevertheless, the multi-shooting algorithm works very well at energy $E = 0$. The pruning of orbits is indicated by a failure of the root search. Only when orbits are very close to bifurcations it may happen that an existing orbit is either not found or an orbit is obtained where the symbolic code differs from the initially chosen string.

The pruning of orbits can be revealed using the well-ordered symbolic code introduced in Ref. [13] for the four-disk and hyperbola billiards. From the symbol string of orbits two real numbers $\{\gamma, \delta\} \in [0, 1]$ are determined, which for a selected starting point describe the past and the future of the orbit. Without pruning the periodic orbits densely fill the (γ, δ)-plane, whereas empty areas indicate an incomplete symbolic dynamics. The lines surrounding the empty areas are called pruning fronts. The (γ, δ)-plane for the diamagnetic hydrogen atom at energy $E = 0$ is shown in Fig. 2. Pruning fronts are clearly visible. Qualitatively, they resemble the pruning fronts of the closed four-disk billiard investigated in [13].

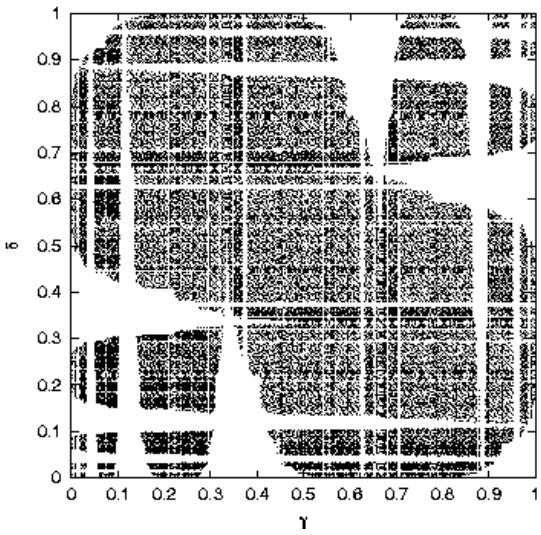

FIG. 2. Well-ordered symbolic dynamics of the diamagnetic hydrogen atom at energy $E = 0$. The black regions mark the existing periodic orbits. The white areas indicate pruning.

4. Results and discussion

For the periodic orbit quantization of the diamagnetic hydrogen atom we employ the scaling properties of the classical and quantum Hamiltonian. At fixed energy $E = 0$ Schrödinger's equation can be written as a generalized eigenvalue problem

$$\left[\frac{1}{4}(\mu^4\nu^2 + \mu^2\nu^4) - 4\right]\Psi = w^{-2}(\Delta_\mu + \Delta_\nu)\,\Psi \tag{13}$$

for discrete eigenvalues w_n of the parameter $w \equiv \gamma^{-1/3}$. The quantum level density is given as $\varrho(w) = \sum_n \delta(w - w_n)$. The scaling of the classical and semiclassical expressions results in the replacement of energy and time $\{E, t\}$ with the set $\{w, s\}$, in the equations of Sec. 2, where $s = \gamma^{1/3} S$ is the scaled action of the classical trajectories.

To apply the harmonic inversion method with constraints the complete set of periodic orbits with scaled action $s \leq s_{\max}$ is required. For $s_{\max} = 40$ we found 1784 primitive periodic orbits. The absolute values of the stability eigenvalues λ as functions of the scaled action are presented in Fig. 3. For some series of orbits the action grows very slowly with increasing cycle length. E.g., along the line with accumulating orbits approaching $|\lambda| \approx 2000$ at $s = 40$, which is clearly visible in Fig. 3, the

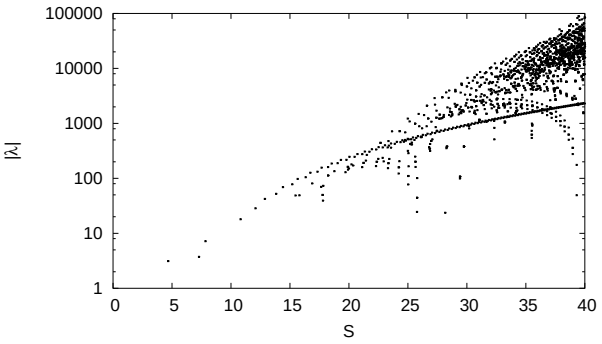

FIG. 3. Absolute values of the stability eigenvalues λ as functions of the scaled action s for the periodic obits of the diamagnetic hydrogen atom at energy $E = 0$.

string length of the symbolic code increases up to $L = 76$. Note that for a ternary symbolic code about $3^{76}/76 = 2.4 \times 10^{34}$ code words with length $L = 76$ exist, and therefore a good strategy is necessary to find the "short" orbits with $s \leq s_{\max}$.

From the periodic orbit data of the 1784 orbits with $s \leq 40$ a band-limited semiclassical signal $C_{\rm bl}^{\rm sc}(s)$ can be constructed as a function of the scaled action in a similar same way as the time signal in Eq. (5). The signal is analyzed via harmonic inversion with constraints to obtain the semiclassical eigenvalues $w_n = \gamma_n^{-1/3}$. In Fig. 4 the semiclassical eigenvalues are compared with exact quantum states obtained by numerical diagonalization of the Hamiltonian using a complete Sturmian type basis set. Fig. 4 (a) and (b) present the results for states with magnetic quantum number $m = 0$ and even and odd z-parity, respectively. The semiclassical and exact quantum spectra show good, though not perfect agreement.

5. Conclusion

We have introduced a novel method for periodic orbit quantization, viz. harmonic inversion with constraints. The method has been applied to the diamagnetic hydrogen atom. Using an efficient multi-shooting algorithm for the periodic

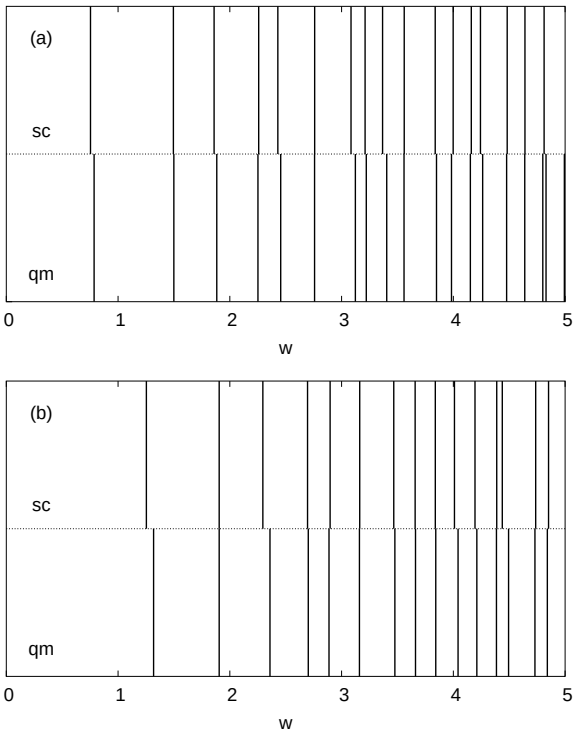

FIG. 4. Scaled energy spectra of the diamagnetic hydrogen atom at the field-free ionization threshold $E = 0$. States with magnetic quantum number $m = 0$ and (a) even, (b) odd z-parity. The semiclassical eigenvalues (sc) are compared with exact quantum computations (qm).

orbit search and the new quantization technique we obtained, for the first time, semiclassical spectra at the field-free ionization threshold $E = 0$.

Harmonic inversion with constraints will also be a powerful tool for the efficient periodic orbit quantization of other bound systems with pruned symbolic dynamics, such as the closed three-disk or the hyperbola billiard.

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