PHYSICAL REVIEW A VOLUME 59, NUMBER 4 APRIL 1999

Semiclassical calculation of transition matrix elements for atoms in external fields

Jörg Main[1] and Günter Wunner[2]
[1]*Institut für Theoretische Physik I, Ruhr-Universität Bochum, D-44780 Bochum, Germany*
[2]*Institut für Theoretische Physik und Synergetik, Universität Stuttgart, D-70550 Stuttgart, Germany*
(Received 15 September 1998)

Closed-orbit theory is generalized to the semiclassical calculation of cross-correlated recurrence functions for atoms in external fields. The cross-correlation functions are inverted by a high-resolution spectral analyzer to obtain the semiclassical eigenenergies and transition matrix elements. The method is demonstrated for dipole transitions of the hydrogen atom in a magnetic field. This is an alternative semiclassical calculation of individual quantum transition strengths from closed-orbit theory. [S1050-2947(99)51104-9]

PACS number(s): 32.60.+i, 03.65.Sq, 32.70.Cs

In 1925, Heisenberg [1] pushed open the door to quantum mechanics when he proposed a quantum theory consisting only of ''in principle observable'' quantities—matrix elements $A(n,m)$—whose physical meaning was hinged upon the correspondence principle: For high quantum numbers n and $|n-m| \ll n$ the matrix elements were to turn into the Fourier amplitudes of the corresponding physical observable $A(t)$ associated with a classical periodic orbit, viz., $A(n,m)\exp[i(E(n)-E(m))t/\hbar] \Leftrightarrow A_\tau(n)\exp[i\tau\omega(n)]$, with $\tau = n-m$ and $\omega(n)$ the frequency of the periodic orbit. By a consistent application of the translation rules to the quantization condition for actions, $\Delta S/\Delta n = h$, he arrived at the canonical commutation relations underlying the whole of quantum mechanics. Thus establishing the connection between the information encoded in classical orbits and quantum-mechanical transition amplitudes, he proved one of the fundamental questions of quantum physics.

The correspondence principle is silent about transition amplitudes involving low-lying states. It was, therefore, a great success when, more than 60 years later, *closed-orbit theory*—a variant of periodic orbit theory [2]—came up with the discovery that there exists an intimate connection between classical orbits and transition amplitudes even in cases where one of the states lies in the deep quantum regime. In closed-orbit theory, developed by Du and Delos [3] and Bogomolny [4], the transition amplitudes are given as the sum of two terms, one a smoothly varying part (as a function energy) and the other a superposition of sinusoidal modulations. The frequencies, amplitudes, and phases of the modulations are directly obtained from information contained in the closed classical orbits. When the resulting transition amplitudes are Fourier transformed the sinusoidal modulations produce sharp peaks in the Fourier-transform recurrence spectra. Closed-orbit theory has been applied to the interpretation of photoabsorption spectra of atoms in external fields and has been most successful in explaining the quantum-mechanical recurrence spectra qualitatively and even quantitatively in terms of the closed orbits of the underlying classical system [5–7].

However, up to now practical applications of closed-orbit theory have always been restricted to the semiclassical calculation of *low-resolution* spectra for two reasons. First, the closed-orbit sum requires, in principle, the knowledge of all orbits up to infinite length, which are not normally available from a numerical closed-orbit search; and, second, the infinite closed-orbit sum suffers from fundamental convergence problems [3,4]. It is therefore usually believed that the calculation of *individual* transition matrix elements, e.g., of the dipole operator D, $\langle \phi_i|D|\psi_f\rangle$, which describe the transition strengths from the initial state $|\phi_i\rangle$ to final states $|\psi_f\rangle$, is a problem beyond the applicability of the semiclassical closed-orbit theory, i.e., is the domain of quantum-mechanical methods.

It is the purpose of this Rapid Communication to demonstrate that high-precision quantum transition amplitudes between low-lying and highly excited states can be obtained within the framework of closed-orbit theory using solely the information contained in closed classical orbits. In this way we can establish a connection between classical orbits and quantum-mechanical matrix elements that goes far beyond what was conceived of in the early days of quantum mechanics. To that end, we slightly generalize closed-orbit theory to the semiclassical calculation of cross-correlated recurrence functions. We then adopt the method of Refs. [8–10] to harmonically invert the cross-correlated recurrence signal and to extract the semiclassical eigenenergies and transition matrix elements. Results will be presented for the photoexcitation of the hydrogen atom in a magnetic field.

The oscillator strength f for the photoexcitation of atoms in external fields can be written as

$$f(E) = -\frac{2}{\pi}(E-E_i)\,\mathrm{Im}\,\langle \phi_i|DG_E^+D|\phi_i\rangle, \tag{1}$$

where $|\phi_i\rangle$ is the initial state at energy E_i, D is the dipole operator, and G_E^+ the retarded Green's function of the atomic system. The basic steps for the derivation of closed-orbit theory are to replace the quantum-mechanical Green's function in Eq. (1) with its semiclassical Van Vleck–Gutzwiller approximation and to carry out the overlap integrals with the initial state $|\phi_i\rangle$. Here we go one step further by introducing a cross-correlation matrix

$$g_{\alpha\alpha'} = \langle \phi_\alpha|DG_E^+D|\phi_{\alpha'}\rangle, \tag{2}$$

with $|\phi_\alpha\rangle$, $\alpha = 1,2,\ldots,L$ a set of independent initial states. As will be shown below, the use of cross-correlation matrices can considerably improve the convergence properties of

the semiclassical procedure. In the following we will concentrate on the hydrogen atom in a magnetic field (for reviews see [11–13]), with $\gamma = B/(2.35\times 10^5\,\mathrm{T})$ the magnetic field strength in atomic units. The system has a scaling property, i.e., the shape of periodic orbits does not depend on the scaling parameter, $w=\gamma^{-1/3}=\hbar_{\mathrm{eff}}^{-1}$, and the classical action scales as $S=sw$, with s the scaled action. As, e.g., in Ref. [5], we consider scaled photoabsorption spectra at constant scaled energy $\tilde{E}=E\gamma^{-2/3}$ as a function of the scaling parameter w. We choose dipole transitions between states with magnetic quantum number $m=0$. Note that the following ideas can be applied in an analogous way to atoms in electric fields. Following the derivation of Refs. [3,4] the semiclassical approximation to the fluctuating part of $g_{\alpha\alpha'}$ in Eq. (2) reads

$$g^{\mathrm{SC}}_{\alpha\alpha'}(w)=w^{-1/2}\sum_{\mathrm{CO}}\frac{-(2\pi)^{5/2}}{\sqrt{|m^{\mathrm{CO}}_{12}|}}\sqrt{\sin\vartheta^{\mathrm{CO}}_i\sin\vartheta^{\mathrm{CO}}_f}\,\mathcal{Y}_\alpha(\vartheta^{\mathrm{CO}}_i)\times\mathcal{Y}_{\alpha'}(\vartheta^{\mathrm{CO}}_f)e^{i(s_{\mathrm{CO}}w-(\pi/2)\mu_{\mathrm{CO}}+\pi/4)},\tag{3}$$

with s_{CO} and μ_{CO} the scaled action and Maslov index of the closed orbit (CO), m^{CO}_{12} an element of the monodromy matrix, and $\vartheta^{\mathrm{CO}}_i$ and $\vartheta^{\mathrm{CO}}_f$ the initial and final angles of the trajectory with respect to the magnetic-field axis. The angular functions $\mathcal{Y}_\alpha(\vartheta)$ depend on the states $|\phi_\alpha\rangle$ and the dipole operator D, and are given as a linear superposition of Legendre polynomials, $\mathcal{Y}_\alpha(\vartheta)=\Sigma_l\mathcal{B}_{l\alpha}P_l(\cos\vartheta)$. For low-lying initial states with principal quantum number n only a few coefficients $\mathcal{B}_{l\alpha}$ with $l\leqslant n$ are nonzero. Explicit formulas for the calculation of the coefficients can be found in Refs. [3,4]. The problem now is to extract the semiclassical eigenenergies and transition matrix elements from Eq. (3) because the closed-orbit sum does not converge. We therefore adopt the idea of Ref. [14] where we proposed to adjust the Fourier transform of a nonconvergent Dirichlet series like the semiclassical expression (3) to the functional form of its quantum-mechanical analogue. The Fourier transformation of $w^{1/2}g^{\mathrm{SC}}_{\alpha\alpha'}(w)$ yields the cross-correlated recurrence signals

$$C^{\mathrm{SC}}_{\alpha\alpha'}(s)=\sum_{\mathrm{CO}}\mathcal{A}^{\mathrm{CO}}_{\alpha\alpha'}\delta(s-s_{\mathrm{CO}}),\tag{4}$$

with the amplitudes

$$\mathcal{A}^{\mathrm{CO}}_{\alpha\alpha'}=\frac{-(2\pi)^{5/2}}{\sqrt{|m^{\mathrm{CO}}_{12}|}}\sqrt{\sin\vartheta^{\mathrm{CO}}_i\sin\vartheta^{\mathrm{CO}}_f}\,\mathcal{Y}_\alpha(\vartheta^{\mathrm{CO}}_i)\times\mathcal{Y}_{\alpha'}(\vartheta^{\mathrm{CO}}_f)e^{i(-(\pi/2)\mu_{\mathrm{CO}}+\pi/4)}\tag{5}$$

being determined exclusively by closed-orbit quantities. The corresponding quantum-mechanical cross-correlated recurrence functions, i.e., the Fourier transforms of $w^{1/2}g^{\mathrm{QM}}_{\alpha\alpha'}(w)$ read

$$C^{\mathrm{QM}}_{\alpha\alpha'}(s)=-i\sum_k b_{\alpha k}b_{\alpha' k}e^{-iw_k s},\tag{6}$$

with w_k the eigenvalues of the scaling parameter, and

$$b_{\alpha k}=w_k^{1/4}\langle\phi_\alpha|D|\psi_k\rangle\tag{7}$$

proportional to the transition matrix element for the transition from the initial state $|\phi_\alpha\rangle$ to the final state $|\psi_k\rangle$.

The method to adjust Eq. (4) to the functional form of Eq. (6) for fixed states $|\phi_\alpha\rangle$ and $|\phi_{\alpha'}\rangle$ is that of harmonic inversion as discussed in Ref. [14]. However, information theoretical considerations then yield an estimate for the required signal length, $s_{\max}\sim 4\pi\overline{\varrho}(w)$ [14], which may result in an unfavorable scaling because of a rapid proliferation of closed orbits with increasing period. Moreover, it is a special problem to resolve nearly degenerate states and to detect states with very low transition strengths from the harmonic inversion of a *single* function $C^{\mathrm{SC}}_{\alpha\alpha'}(s)$. Note also that the element of the monodromy matrix m_{12} and the values of the angular functions $\mathcal{Y}_\alpha(\vartheta_i)$ and $\mathcal{Y}_{\alpha'}(\vartheta_f)$ are intrinsically intertwined in Eq. (5) for the amplitudes $\mathcal{A}^{\mathrm{CO}}_{\alpha\alpha'}$, i.e., a single function $C^{\mathrm{SC}}_{\alpha\alpha'}(s)$ does not contain independently the information from the monodromy matrix and the starting and returning angles ϑ_i and ϑ_f of the closed orbits.

In this Rapid Communication we therefore propose to apply an extension of the method to the harmonic inversion of cross-correlation functions [8–10], which has recently also served as a powerful tool for the semiclassical calculation of tunneling splittings [15]. The idea is that the informational content of an $L\times L$ time signal is increased roughly by a factor of L as compared to a 1×1 signal. The additional information is gained with the set of linearly independent angular functions $\mathcal{Y}_\alpha(\vartheta)$, $\alpha=1,2,\ldots,L$ in Eq. (5) evaluated at the starting and returning angles ϑ_i and ϑ_f of the closed orbits. Note that the cross-correlation matrix (4) is constructed by using independently the information of the closed-orbit quantities, i.e., the elements m_{12} of the monodromy matrix and the angles ϑ_i and ϑ_f. For a given number of closed orbits the accuracy of semiclassical spectra can be significantly improved with the help of the cross-correlation approach, or, alternatively, spectra with similar accuracy can be obtained from a closed-orbit cross-correlation signal with a significantly reduced signal length.

Here we only give a qualitative and brief description of the method. The details of the numerical procedure of solving the generalized harmonic inversion problem (6) have been presented in Refs. [8–10]. The idea is to recast the nonlinear fit problem as a linear algebraic problem [8]. This is accomplished by associating the signal $C_{\alpha\alpha'}(s)$ (to be inverted) with a time cross-correlation function between an initial state Φ_α and a final state $\Phi_{\alpha'}$,

$$C_{\alpha\alpha'}(s)=\langle\Phi_{\alpha'}|e^{-is\hat{H}_{\mathrm{eff}}}\Phi_\alpha\rangle,\tag{8}$$

where the fictitious quantum-dynamical system is described by an effective Hamiltonian $\hat{H}_{\mathrm{eff}}$. The latter is defined implicitly by relating its spectrum to the set of unknown spectral parameters w_k and $b_{\alpha k}$. Diagonalization of $\hat{H}_{\mathrm{eff}}$ would yield the desired w_k and $b_{\alpha k}$. This is done by introducing an appropriate basis set in which the matrix elements of $\hat{H}_{\mathrm{eff}}$ are available only in terms of the known signals $C_{\alpha\alpha'}(s)$. The Hamiltonian $\hat{H}_{\mathrm{eff}}$ is assumed to be complex symmetric even in the case of a bound system, which makes the harmonic

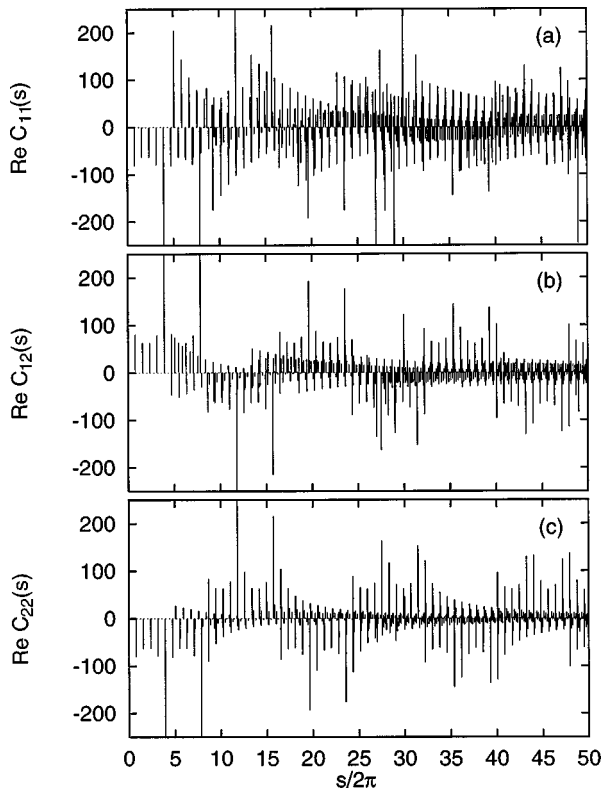

FIG. 1. Real parts of the semiclassical cross-correlated recurrence functions for the hydrogen atom in a magnetic field at constant scaled energy $\tilde{E}=-0.7$ as functions of the classical action s (in dimensionless scaled units). The graphs of the imaginary parts (not shown) qualitatively resemble those of the real parts.

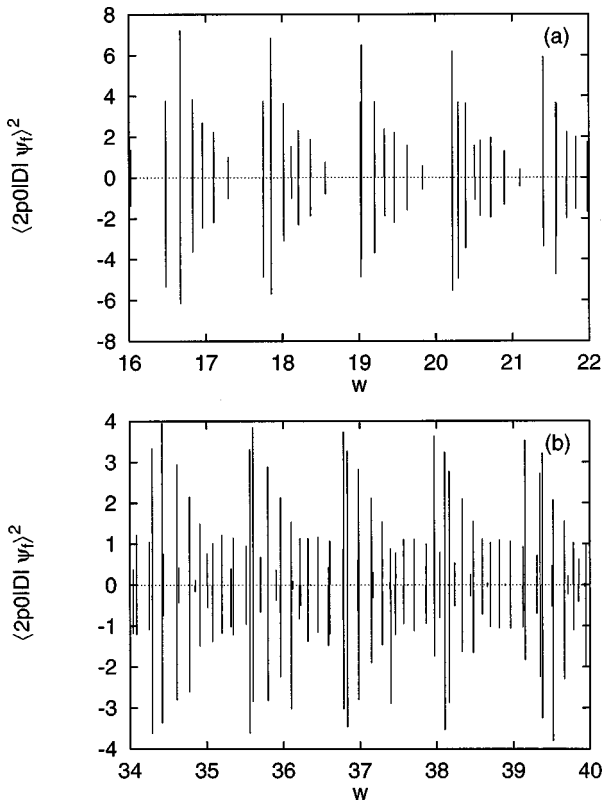

FIG. 2. Quantum (upper part) and semiclassical (lower part) photoabsorption spectra of the hydrogen atom in a magnetic field at scaled energy $\tilde{E}=-0.7$ as functions of the dimensionless scaling parameter $w=\gamma^{-1/3}$: Transition matrix elements $\langle 2p0|D|\psi_f\rangle^2$ for dipole transitions with light polarized parallel to the magnetic field axis.

inversion stable with respect to ''noise'' due to the imperfections of the semiclassical approximation.

We now demonstrate the method of harmonic inversion of the cross-correlated closed-orbit recurrence functions (4) for the example of the hydrogen atom in a magnetic-field at constant scaled energy $\tilde{E}=-0.7$. This energy was also chosen for detailed experimental investigations of the helium atom [6]. We investigate dipole transitions from the initial state $|\phi_1\rangle=|2p0\rangle$ with light polarized parallel to the magnetic-field axis to final states with magnetic quantum number $m=0$. For this transition the angular function in Eq. (5) reads $\mathcal{Y}_1(\vartheta)=(2\pi)^{-1/2}2^7e^{-4}(4\cos^2\vartheta-1)$. For the construction of a 2×2 cross-correlated recurrence signal we use for simplicity, as a second transition, formally an outgoing s-wave, i.e., $D|\phi_2\rangle\propto Y_{0,0}$, and thus $\mathcal{Y}_2(\vartheta)=\text{const}$. A numerical closed-orbit search yields 1395 primitive closed orbits (2397 orbits including repetitions) with scaled action $s/2\pi<100$. With the closed-orbit quantities at hand it is straightforward to calculate the cross-correlated recurrence functions in Eq. (4). The real parts of the functions $C_{11}^{\mathrm{SC}}(s)$, $C_{12}^{\mathrm{SC}}(s)$, and $C_{22}^{\mathrm{SC}}(s)$ with $s/2\pi<50$ are presented in Fig. 1. The imaginary parts are not shown because they qualitatively resemble the real parts. Note that for symmetry reasons $C_{21}^{\mathrm{SC}}(s)=C_{12}^{\mathrm{SC}}(s)$.

We have inverted the 2×2 cross-correlated recurrence functions in the region $0<s/2\pi<100$. The resulting semiclassical photoabsorption spectrum is compared with the exact quantum spectrum in Fig. 2(a) for the region $16<w<21$ and in Fig. 2(b) for the region $34<w<40$. The upper and lower parts in Fig. 2 show the exact quantum spectrum and the semiclassical spectrum, respectively. Note that the region of the spectrum presented in Fig. 2(b) belongs well to the experimentally accessible regime with laboratory field strengths $B=6.0\,\mathrm{T}$ to $B=3.7\,\mathrm{T}$. The overall agreement between the quantum and semiclassical spectrum is impressive, even though a line-by-line comparison still reveals small differences for a few matrix elements. It is important to note that the high quality of the semiclassical spectrum could only be achieved by our application of the cross-correlation approach. For example, the two nearly degenerate states at $w=36.969$ and $w=36.982$ cannot be resolved and the very weak transition at $w=38.894$ with $\langle 2p0|D|\psi_f\rangle^2=0.028$ is not detected with a single (1×1) recurrence signal of the same length. However, these hardly visible details are indeed present in the semiclassical spectrum in Fig. 2(b) obtained from the harmonic inversion of the 2×2 cross-correlated recurrence functions.

In conclusion, we have demonstrated that closed-orbit theory is not restricted to describe long-range modulations in quantum-mechanical photoabsorption spectra of atoms in external fields but can well be applied to extract individual eigenenergies and transition matrix elements from the closed-orbit quantities. This is achieved by a high-resolution spectral analysis (harmonic inversion) of cross-correlated closed-orbit recurrence signals. For the hydrogen atom in a

magnetic field we have obtained transition matrix elements between low-lying and highly excited Rydberg states using exclusively classical closed orbit data. It will be straightforward, and rewarding, to apply the method to atoms in electric fields.

We acknowledge fruitful discussions with V. Mandelshtam. This work was supported in part by the Sonderforschungsbereich No. 237 of the Deutsche Forschungsgemeinschaft. J.M. thanks the Deutsche Forschungsgemeinschaft for a Habilitandenstipendium (Grant No. Ma 1639/3).

[1] W. Heisenberg, Z. Phys. **33**, 879 (1925); M. Born, W. Heisenberg, and P. Jordan, *ibid.* **35**, 557 (1926).

[2] M. C. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer, New York, 1990).

[3] M. L. Du and J. B. Delos, Phys. Rev. Lett. **58**, 1731 (1987); Phys. Rev. A **38**, 1896 (1988); **38**, 1913 (1988).

[4] E. B. Bogomolny, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 445 (1988) [JETP Lett. **47**, 526 (1988)]; Zh. Eksp. Teor. Fiz. **96**, 487 (1989) [Sov. Phys. JETP **69**, 275 (1989)].

[5] J. Main, G. Wiebusch, and K. H. Welge, Comments At. Mol. Phys. **25**, 233 (1991); J. Main, G. Wiebusch, K. H. Welge, J. Shaw, and J. B. Delos, Phys. Rev. A **49**, 847 (1994).

[6] T. van der Veldt, W. Vassen, and W. Hogervorst, Europhys. Lett. **21**, 903 (1993).

[7] M. Courtney, H. Jiao, N. Spellmeyer, and D. Kleppner, Phys. Rev. Lett. **73**, 1340 (1994); M. Courtney, N. Spellmeyer, H. Jiao, and D. Kleppner, Phys. Rev. A **51**, 3604 (1995).

[8] M. R. Wall and D. Neuhauser, J. Chem. Phys. **102**, 8011 (1995).

[9] E. Narevicius, D. Neuhauser, H. J. Korsch, and N. Moiseyev, Chem. Phys. Lett. **276**, 250 (1997).

[10] V. A. Mandelshtam, J. Chem. Phys. **108**, 9999 (1998).

[11] H. Friedrich and D. Wintgen, Phys. Rep. **183**, 37 (1989).

[12] H. Hasegawa, M. Robnik, and G. Wunner, Prog. Theor. Phys. Suppl. **98**, 198 (1989).

[13] S. Watanabe, *Review of Fundamental Processes and Applications of Atoms and Ions*, edited by C. D. Lin (World Scientific, Singapore, 1993).

[14] J. Main, V. A. Mandelshtam, and H. S. Taylor, Phys. Rev. Lett. **79**, 825 (1997); J. Main, V. A. Mandelshtam, G. Wunner, and H. S. Taylor, Nonlinearity **11**, 1015 (1998).

[15] V. A. Mandelshtam and M. Ovchinnikov, J. Chem. Phys. **108**, 9206 (1998).