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Classical and quantum chaos in atomic systems

CLASSICAL AND QUANTUM CHAOS IN ATOMIC SYSTEMS

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I. Introduction	85
A. Classical and Quantum Chaos	85
B. Chaotic Atomic Systems	87
C. Ionization: A Complication or a Useful Tool?	90
D. Scaling Properties	91
E. Laboratory Experiments versus Numerical Experiments	92
II. Time Scales—Energy Scales	94
A. Classical Scales	94
B. Quantum Scales	95
III. Spectroscopy	97
A. Properties of Individual Energy Levels	97
B. Widths of Resonances	101
C. Periodic Orbit Spectroscopy	103
D. From Classical to Quantum Mechanics	108
IV. Wave Functions: Localization and Scars	109
A. Localization in the Regular Regime	110
B. Localization in the Chaotic Regime	111
C. Localization in the Mixed Regular—Chaotic Regime	113
D. Relationship between Localization and Lifetime	115
V. Dynamics	115
A. Time-Independent Systems	115
B. Time-Dependent Systems	116
VI. Conclusions	121
References	121

I. Introduction

A. CLASSICAL AND QUANTUM CHAOS

Atomic systems played a major role in the birth and growth of quantum mechanics. One central idea was to relate the well-known classical motion of the electron of a hydrogen atom—an ellipsis around the nucleus—to

the experimentally observed quantization of the energy levels. This is the aim of the Bohr and Bohr-Sommerfeld models. These simple *semiclassical* models were unable to make any reliable prediction on the energy spectrum of the next simplest atom, helium.

Because of the great success of quantum mechanics, the problem of correspondence between the classical and the quantal dynamics has not received much attention in the last 60 years. The fundamental question is (Gutzwiller, 1990): How can classical mechanics be understood as a limiting case within quantum mechanics?

For systems with time-independent one-dimensional dynamics like the harmonic oscillator and the hydrogen atom, the correspondence is well understood. The restriction to such simple cases creates the erroneous impression that the classical behavior of simple systems is entirely comprehensible and easily described. During the last 20 years it has been recognized that this is not true and that a complex behavior can be obtained from simple equations of motion. This usually happens when the motion is *chaotic*, that is, unpredictable on a long time scale although perfectly deterministic (Henon, 1983).

A major problem is that of understanding how the regular or chaotic behavior of the classical system is manifest in its quantum properties, especially in the semiclassical limit. This is the subject of *quantum chaos*. More precisely, typical questions we would like to answer are as follows (Gutzwiller, 1990):

- What are the appropriate observables to detect the regular or chaotic behavior of the system in the classical limit?
- More precisely, how is chaotic or regular behavior expressed in the energy levels and eigenstates of a quantum system?
- What kind of semiclassical approximations can be used if the system is not separable?
- What is the long-term behavior of a quantum system?

A relatively nonintuitive result is that chaos may take place in low-dimensional systems. Because atoms are simple microscopic low-dimensional systems that have to be described by quantum mechanics, they are among the best available prototypes for studying quantum chaos. The goal of this chapter is to present and discuss the most important progress in this area.

When chaos is present, it is generally impossible to obtain analytic expressions (even approximate ones) for the time evolution of the system. Hence, chaotic systems are intrinsically *complex* systems lying beyond any traditional analytic description. On the other hand, complex systems are not necessarily chaotic, but may have similar statistical properties. For example,

recent experimental results on *mesoscopic* systems (Bouchiat and Montabaux, 1990; Al'tshuler *et al.*, 1991) suggest that the universal fluctuations observed could have the same origin as the spectral fluctuations (see Section III.A) of quantum chaotic systems. In that sense, quantum chaos can also be thought of as a first step in the direction of complex systems.

B. CHAOTIC ATOMIC SYSTEMS

Compared with other microscopic complex systems (nuclei, atomic clusters, semiconductors, etc.), atoms have the great advantage that all the basic components are well understood: These are essentially point particles interacting through a Coulomb static field. Hence, it is possible to write an explicit expression of the Hamiltonian.

A definite advantage of atomic systems is that they can be studied theoretically and *experimentally*. The word *experiment* must be understood here to mean traditional laboratory experiments, but also numerical experiments. Indeed, currently available computers make it possible to compute numerically properties of complex systems described by simple Hamiltonians. During the last 10 years, the constant interaction between the experimental results and numerical simulations led to major advances in the field of quantum chaos, as is shown later.

A crucial result is that classical chaos can only exist in systems where different degrees of freedom are *strongly* coupled. [this is a consequence of the celebrated KAM theorem (Lichtenberg and Liberman, 1983).] This implies that a small perturbation added to a regular system cannot make it chaotic. In other words, atomic systems where chaos is supposed to play an important role require *nonperturbative* situations, where, in addition to the Coulomb binding force, the electrons are submitted to additional forces of comparable strength. This can be easily realized on the simplest atom, hydrogen, by applying to it an external field. Different situations can be realized depending on the type of field used (magnetic, electric, or both) and on its time dependence.

We first consider the case of a hydrogen atom in a static external electric field. Small corrections to the pure Coulomb potential in the hydrogen atom (finite mass of the nucleus, relativistic corrections, spin effects, QED corrections, spontaneous emission, etc.) do not affect the global (regular or chaotic) behavior of the system and can be neglected. Throughout this chapter, we use atomic units, where the mass, the absolute value of the charge of the electron, and the Planck's constant are equal to 1. In these units, the Hamiltonian is (Delande, 1991):

$$H = H_0 + \mathbf{F} \cdot \mathbf{r} \quad (1)$$

where H_0 is the field-free Hamiltonians:

$$H_0 = \frac{\mathbf{p}^2}{2} - \frac{1}{r} \quad (2)$$

$\mathbf{p}$ and $\mathbf{r}$ are, respectively, the momentum and position of the electron, and F is the electric field in atomic units of 5.14×10^9 V/cm. Fortunately (unfortunately as far as chaos is concerned!), this Hamiltonian is separable in parabolic coordinates (Harmin, 1982) and the motion is fully regular.

The case of the static magnetic field is more interesting. In cylindrical coordinates, and using the symmetric gauge $\mathbf{A} = \frac{1}{2}\mathbf{r} \times \mathbf{B}$ for the vector potential, the Hamiltonian is given by:

$$H = H_0 + \frac{\gamma}{2}L_z + \frac{\gamma^2\rho^2}{8} \quad (3)$$

where γ denotes the magnetic field (along the z axis) in atomic units of 2.35×10^5 T, and L_z the z component of the angular momentum.

Because of the azimuthal symmetry around the magnetic field axis, the paramagnetic term $\gamma L_z/2$, responsible for the usual Zeeman effect, is just a constant. The diamagnetic term, $\gamma^2\rho^2/8$, is directly responsible for the onset of chaos in the system. The competition between the Coulomb potential with spherical symmetry and diamagnetic potential with cylindrical symmetry governs the dynamics. As a crude criterion, chaos is most developed when these two terms have the same order of magnitude. For a quantum state of principal quantum number n , this gives:

$$\gamma n^3 \simeq 1 \quad \text{that is, } Bn^3 \simeq 2.35 \times 10^5 \text{ T} \quad (4)$$

This can be realized in a laboratory experiment with Rydberg states $n \simeq 40$ to 150 (Iu *et al.*, 1991; Holle *et al.*, 1988; van der Veldt *et al.*, 1993).

When written in cylindrical coordinates, the Hamiltonian (3) describes a time-independent two-dimensional system belonging to the class of the simplest possible chaotic systems (Lichtenberg and Leiberman, 1983). This makes this system an almost ideal prototype for the study of quantum chaos (Friedrich and Wintgen, 1989).

A combination of static electric and magnetic fields can also be used. When the two fields are not parallel (for example, perpendicular), the system is fully three dimensional and described by the Hamiltonian:

$$H = H_0 + \frac{\gamma}{2}L_z + \frac{\gamma^2\rho^2}{8} + \mathbf{F} \cdot \mathbf{r} \quad (5)$$

Again, the nonperturbative regime is reached when the impact of the three fields (Coulomb field of the nucleus, external magnetic field, and electric field) is comparable. In addition to Eq. (4), this implies:

$Fn^4 \simeq 1$ in atomic units, that is

$$Fn^4 \simeq 1 \times 10^9 \text{ V/cm in laboratory units} \quad (6)$$

which is relatively easy to realize in laboratory experiments (Raithel *et al.*, 1991).

Finally, it is possible to replace the external field with the internal field due to another electron of the same atom. This brings back the three-body problem (helium or helium-like atoms) described by the following Hamiltonian (Z is the charge of the nucleus):

$$H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (7)$$

From the chaos point of view, an interesting situation arises when the two electrons have comparable excitations. Strong dynamical correlations between the two electrons are expected, leading to a breakdown of the independent electron picture. The corresponding doubly excited states, lying very close to the *double* ionization threshold, are autoionizing states with weak optical excitation probabilities from low excited states, which does not make it easy to observe them (Domke *et al.*, 1992; Eichmann *et al.*, 1992; Camus *et al.*, 1989).

Different dynamical properties are expected for systems whose Hamiltonian shows an explicit time dependence. The easiest way to introduce such a dependence is to apply an external oscillating electric field on a hydrogen atom. For a monochromatic field of amplitude F and angular frequency ω , polarized along the z axis, the Hamiltonian in the length gauges is

$$H = H_0 + Fz \cos \omega t \quad (8)$$

Because of the azimuthal symmetry around the electric field axis, the system is effectively two dimensional. In numerical experiments and theoretical investigations, a simplified one-dimensional model of the atom has been widely used (Casati *et al.*, 1988; Galvez *et al.*, 1988; Bayfield *et al.*, 1989; Sauer *et al.*, 1992; Jensen *et al.*, 1989).

Chaotic dynamics can be observed only in a nonperturbative regime, that is, when the amplitude and frequency of the external field are comparable

to the amplitude of the Coulomb field on the n 'th Bohr orbit and to the classical Kepler frequency of the electron. This gives:

$$\begin{cases} Fn^4 \simeq 1 \\ \omega n^3 \simeq 1 \end{cases} \text{ in atomic units, or} \quad \begin{cases} Fn^4 \simeq 1 \times 10^9 \text{ V/cm} \\ \omega n^3 \simeq 5 \times 10^{15} \text{ Hz} \end{cases} \text{ in laboratory units} \quad (9)$$

Such a situation can be obtained by applying a strong infrared laser to a weakly excited state. However, the spatio-temporal characteristics of the laser pulse are then extremely important for the dynamics of the atoms, ions, and electrons produced. Such complications usually hide the regular or chaotic aspects (L'Huillier *et al.*, 1991).

Another possibility is to employ highly excited states ($n \simeq 60$) and a microwave field. This system led to numerous important experimental and theoretical results and is discussed in Section V.

For a circular polarization of the external electric field, classical studies have shown that the system is mainly regular and of poor interest as long as chaos is concerned (Zakrzewski *et al.*, 1993).

C. IONIZATION: A COMPLICATION OR A USEFUL TOOL?

Chaos or regularity manifest themselves during the long-term behavior of the system. For this reason, it is often studied (in classical mechanics) for bounded systems where the different components may interact during an indefinitely long time. Atoms do not belong to this type of systems, because they can *ionize*. Hence, they are prototypes for studying the effect of *transient chaos*, that is, chaos *on a finite time scale* (fixed by the lifetimes of the resonances).

A complementary point of view is given by scattering experiments, when the dynamics near the scatterer is chaotic. Clearly, the physics is the same, although the language is somewhat different (Smilansky, 1991).

On the other hand, ionization provides a simple tool for analyzing the electron dynamics. Experimentally, we can easily detect whether an atom is ionized after interaction with an external field, whereas it is much more complicated to measure its internal state. Ionization is a by-product of the underlying quantum dynamics. Although it is only a very rough measure of the final state of an atom, it can provide much physical insight. The most striking example is the dynamics of the hydrogen atom in a microwave field where most experiments just measure the ionization probability.

D. SCALING PROPERTIES

One of the main difficulties in the study of the semiclassical limit $\hbar \rightarrow 0$ is that the value of the Planck constant is fixed in laboratory experiments. One can get around this difficulty in atomic systems thanks to the existence of scaling laws. Indeed, the Coulomb potential and other interaction potentials discussed earlier are power functions of the position and momentum. Thus, a convenient scaling of all variables and external fields leaves the equations of motion invariant. This scaling transformation is (Delande, 1991):

$$\begin{aligned} \mathbf{r} &\rightarrow \lambda^{-1} \mathbf{r} \\ \mathbf{p} &\rightarrow \lambda^{1/2} \mathbf{p} \\ H &\rightarrow \lambda H \\ t &\rightarrow \lambda^{-3/2} t \\ F &\rightarrow \lambda^2 F \\ \omega &\rightarrow \lambda^{3/2} \omega \\ \gamma &\rightarrow \lambda^{3/2} \gamma \end{aligned} \tag{10}$$

where λ is any positive real number. This means that different initial conditions with different external fields may have exactly the same classical dynamics. A simple example is the field-free motion of the electron, which is an elliptic trajectory whatever its (negative) energy. This is no longer true in quantum mechanics, because of the absolute scale imposed by the Planck constant $\hbar$. Different scaled situations observed experimentally correspond to the same classical dynamics with different effective values of the Planck constant.

Hence, in a real (or numerical) experiment, the semiclassical limit $\hbar \rightarrow 0$ can be studied by tuning simultaneously toward higher excited states the energy and the characteristics of the external fields according to Eq. (10). This possibility is extremely important for understanding the classical-quantal correspondence. The best example is so-called “scaled spectroscopy,” where the wavelength of the exciting laser (which determines the energy of the excited state under study) is scanned together with the external static electric and/or magnetic field (see Section III.C).

The scaled variables are those quantities defined in Eq. (10) that are invariant under the scaling transformation. An example is the scaled energy ε of a hydrogen atom in a magnetic field (Delande, 1991; Friedrich and Wintgen, 1989; Hasegawa *et al.*, 1989):

$$\varepsilon = E\gamma^{-2/3} \tag{11}$$

which measures the energy of the electron in units of magnetic field. Because of the scaling law, the classical dynamics, instead of depending both on E

and γ , actually depends only on ε , whereas quantum properties depend *a priori* on both quantities.

In the crossed magnetic and electric fields, an additional scaled quantity, measuring the electric field in "units of magnetic field" has to be introduced. It is $f = F\gamma^{-4/3}$. For helium-like atoms, the situation is even simpler. Whatever the (negative) total energy, the entire dynamics is fixed and depends only on the discrete parameter Z . This is in sharp contrast with the quantum properties, which clearly depend on whether the total energy is above or below the first ionization threshold.

For time-dependent systems, the situation is somewhat more complicated, because the energy is no longer conserved. However, a standard experiment consists of preparing a Rydberg state with principal quantum number n and applying a microwave field to it. The convenient scaled quantities are the scaled field amplitude and frequency (Casati *et al.*, 1988), defined through [see Eq. (10)]:

$$\begin{cases} F_0 = Fn^4 \\ \omega_0 = \omega n^3 \end{cases} \quad (12)$$

In any case, the use of scaled variables is necessary for a correct understanding of the classical-quantal correspondence.

E. LABORATORY EXPERIMENTS VERSUS NUMERICAL EXPERIMENTS

From a conceptual point of view, experiments on chaotic atomic systems should be done on excited states of the simplest atoms, hydrogen (in external field) or helium. Because of the high density of Rydberg states, a selective excitation requires the use of lasers. Unfortunately, the desired wavelengths are not always easily obtained with current laser technology. For this reason, many experiments have also been done on Rydberg states of different atomic species. It is reasonable to expect that the perturbation induced by the presence of the atomic core on the Rydberg electron will not affect too much its regular/chaotic properties. However, this does not go beyond a questionable assumption. The atomic core is a small object with a radius of a few Bohr radii; whether any semiclassical approximation can be used to represent its effect is far from obvious. The simplest way is to use an effective potential $V_c(r)$ in addition to the Coulomb potential, replacing the zero-field Hamiltonian by:

$$H_0 = \frac{\mathbf{p}^2}{2} - \frac{1}{r} + V_c(r) \quad (13)$$

The core potential is chosen so that it reproduces the observed quantum defects of the different l series of Rydberg states. However, different model potentials give roughly the same quantum defects, but different classical dynamics. This shows that the atomic core is a *pure quantum object*, which

does not have any straightforward classical counterpart.

The main effect of the core potential is to break the Coulomb degeneracy of the energy levels. In most cases, in the strong field regime where all hydrogenic states are supposed to be strongly mixed, this effect is probably weak (see Section III.A). However, in the case of the microwave ionization, there are strong experimental and numerical indications that this assumption is not true (Blümel *et al.*, 1991; Arndt *et al.*, 1991; Buchleitner, 1993).

From the theoretical point of view, the hydrogen atom is entirely calculable using its dynamical group $SO(4,2)$. The use of group theory allows extremely efficient numerical experiments (Delande, 1991; Friedrich and Wintgen, 1989; Hasegawa *et al.*, 1989). The Hamiltonian of an atom in an external field, when expressed in a basis adapted to its internal dynamical properties, can be represented as a sparse matrix. Using an efficient diagonalization algorithm, one is able to compute very accurately, highly excited energy levels and wave functions. For example, computing the 1000'th excited state of a hydrogen atom in a magnetic field of a few teslas with 8 significant digits is nowadays an easy task! It is even more surprising when it is found to be in exact agreement with the (less accurate) experimental measurement (see Fig. 3 later in this chapter)!

This method makes it also possible to compute the dynamics of a hydrogen atom in a time-dependent external field (Buchleitner and Delande, 1993). In addition, use of the complex coordinate method allows for the full inclusion of the effect of ionization and atomic continua (Delande *et al.*, 1991). Recently, it has been successfully extended to the helium atom, taking into account the *exact* interelectronic repulsion (Wintgen *et al.*, 1992). Another recent advance is the extension to nonhydrogenic atoms, by inclusion of a core potential (Halley *et al.*, 1993).

The main advantage of numerical experiments is their flexibility and their ability to give information that is extremely difficult or even impossible to measure (for example, a wave function). On the other hand, they require big and expensive computers. For two-dimensional time-independent or one-dimensional time-dependent problems, the numerical experiments are now possible in realistic conditions. In higher dimensions, this is more difficult—at the border of feasibility—and experimental results are of major importance.

From the ensemble of recent experimental and theoretical results, one has to choose subjectively the most interesting ones. From our point of view, the main concern in quantum chaos is to establish an understandable connection between traditional quantum properties—energy levels, eigenstates, wave functions, etc.—and the rather novel point of view of time-dependent dynamics, which is more suitable for comparison with classical dynamics. These different aspects are studied in the following sections. First, we discuss what we think is the skeleton of the classical and quantal dynamics, the existence and ordering of the different *time scales* of the system. We then

turn to the *spectroscopic* (in an extended sense) aspects, including wave functions, ionizations, and excitation probabilities. Finally, we discuss the dynamics of classical and quantum regular and irregular systems, with an emphasis on time-dependent systems.

II. Time Scales—Energy Scales

A. CLASSICAL SCALES

Depending on the nature of the classical dynamics, there may be different time scales in the evolution of an atomic system. The first one is the typical period, which can be characterized, for example, by the period T_0 of the shortest periodic orbit. Typically, for a Rydberg atom with principal quantum number around 50, it is of the order of a few picoseconds (Delande, 1991).

For a chaotic system, neighboring initial conditions diverge exponentially with time. The associated time constant T_{chaos} is a second time scale, which describes the typical time on which the memory of the initial condition is lost. For a typical strongly chaotic system, this time scale is of the order of the shortest period.

An additional complication arrives when the motion is not bounded, that is, when the atom ionizes. The additional time scale T_{ion} is then the lifetime of the atom. If $T_{\text{ion}} \ll T_{\text{chaos}}$, chaos is beaten by ionization; a discussion in terms of regularity or chaos is irrelevant in this case. This is experimentally observed for atoms in ultrastrong, pulsed laser fields (L'Huillier *et al.*, 1991) and not discussed in this chapter. Except in this situation, all experiments in chaotic atomic systems have been performed under conditions where the ionization time is reasonably long, of the order of nanoseconds or microseconds.

The most complicated situation is observed when the classical dynamics is in the mixed regular-chaotic regime, depending on the initial conditions. There, one observes classical structures that can trap some trajectories or strongly inhibit the diffusive-like chaotic motion. The exact nature of these classical structures is not extremely clear (Percival, 1991). They seem to be remnants of the invariant tori existing in the regular regime. They are known as *vague tori* or *cantori* and apparently have a fractal structure. Contrary to invariant tori, they are not impermeable and a trajectory can escape from such a structure. The associated leaking time is another time constant for these mixed systems. It seems that, in fact, different time scales exist (at various scales). To our knowledge, these phenomena are not well understood even in the classical context. The hydrogen atom in a microwave field provides an example of such a system with mixed dynamics and several

time scales. This makes the detailed interpretation of the quantum results very difficult.

B. QUANTUM SCALES

Additional time scales, depending on $\hbar$, exist for quantum dynamics. This can be understood from the following example. Consider a time-independent bound quantum system with Hamiltonian H in an arbitrary initial state $|\psi(t=0)\rangle$. It obeys the Schrödinger time evolution equation:

$$H|\psi(t)\rangle = i\hbar \frac{d|\psi(t)\rangle}{dt} \quad (14)$$

The solution of this equation can be expressed using the discrete eigenstates and eigenvalues of the Hamiltonian H :

$$H|\phi_i\rangle = E_i|\phi_i\rangle \quad (15)$$

with the following expressions:

$$|\psi(t)\rangle = \sum_i c_i \exp\left(-i\frac{E_i t}{\hbar}\right) |\phi_i\rangle \quad (16)$$

where the constant coefficients c_i are computed from the initial state by means of

$$c_i = \langle \phi_i | \psi(t=0) \rangle \quad (17)$$

The autocorrelation function of the quantum system is a diagonal element of the time-evolution operator $U(t) = \exp(-iHt/\hbar)$:

$$\begin{aligned} C(t) &= \langle \psi(0) | \psi(t) \rangle = \langle \psi(0) | U(t) | \psi(0) \rangle \\ &= \sum_i |c_i|^2 \exp\left(-i\frac{E_i t}{\hbar}\right) \end{aligned} \quad (18)$$

It is a discrete sum of oscillating terms and, consequently, a quasiperiodic function of time. This is *extremely different* from a classical autocorrelation function for a chaotic system, which is decreasing on the characteristic time scale T_{chaos} and does not show any revival at longer times (Lichtenberg and Liberman, 1983).

The time-evolution operator is the Fourier transform of the Green's function (Gutzwiller, 1990; Balian and Bloch, 1974):

$$G^+(E) = \frac{1}{E + i\eta - H} = \sum_i \frac{|\phi_i\rangle \langle \phi_i|}{E + i\eta - E_i} \quad (19)$$

$$U(t) = -\frac{1}{2i\pi} \int_{-\infty}^{\infty} G^+(E) \exp(-iEt/\hbar) dE \quad (20)$$

[This expression is valid for $t > 0$ provided a small imaginary part η is added to the energy so that integrals are well defined; a similar expression can be written for $t < 0$ with $G^-(E)$.]

The Fourier transform of the autocorrelation function

$$\tilde{C}(E) = \int_{-\infty}^{\infty} \exp(iEt/\hbar) C(t) dt = \sum_i 2\pi\hbar |c_i|^2 \delta(E - E_i) \quad (21)$$

is thus a diagonal term of the Green's function:

$$\tilde{C}(E) = i\hbar \langle \psi(0) | G^+(E) - G^-(E) | \psi(0) \rangle \quad (22)$$

If we now consider the Fourier transform over a finite time interval, instead of over the whole range of time from $-\infty$ to $+\infty$, we obtain a smoothed version of the quantum spectrum:

$$\tilde{C}_T(E) = \int_{-T}^T \exp(iEt/\hbar) C(t) dt = \sum_i 2\pi\hbar |c_i|^2 \frac{\sin \frac{T(E - E_i)}{\hbar}}{\frac{T(E - E_i)}{\hbar}} \quad (23)$$

For short T , the different broadened peaks centered at energy levels E_i overlap, and $\tilde{C}_T(E)$ is a globally smooth function as its classical counterpart. In such a situation, it is possible (although nothing proves that it is always the case) that the quantum $\tilde{C}_T(E)$ mimics classical chaotic behavior. The important point is that, for large T , the different peaks do not overlap and the discrete nature of the energy spectrum *must* appear in $\tilde{C}_T(E)$, regardless of the initial state. The typical time needed for resolving individual quantum energy levels is simply related to the mean level spacing ΔE through

$$T_{\text{break}} = \frac{\hbar}{\Delta E} \quad (24)$$

After this break time, the quantum system *cannot* mimic the classical chaotic behavior, which has a continuous spectrum. Since T_{break} depends on $\hbar$, one can understand how quantum dynamics tends to classical dynamics as $\hbar$ goes to zero. The mean level spacing is given by the Thomas-Fermi approximation and scales as $\hbar^f$, with f the number of degrees of freedom. For two- (or higher) dimensional systems, T_{break} tends to infinity as $\hbar \rightarrow 0$. Hence, on a *fixed* interval of time, the quantum dynamics may tend to the classical one as $\hbar$ goes to 0, although the convergence is not uniform with time. This statement has to be understood in its strict mathematical sense: Different values of the fixed interaction time t demand in general different values of $\hbar$ in order to achieve the desired approximation of the classical limit by the real quantum system. The longer the interval of time, the smaller the $\hbar$ needed to obtain the convergence of the mean value of a quantum observable to the value of the corresponding classical quantity. This

illustrates the noncommuting character of the limits $t \rightarrow \infty$ and $\hbar \rightarrow 0$.

In some sense, after the break time, the quantum system “knows” that the energy spectrum is discrete, it has resolved all individual peaks, and the future evolution cannot bring any essential new information. As a consequence, the system cannot explore a new part of the phase space, so it freezes its evolution, repeating forever the same type of dynamics. Any diffusive-like dynamics is then prohibited by pure quantum effects after the break time. This is the origin of the *dynamical localization* (Casati *et al.*, 1988; Fishman *et al.*, 1982) experimentally observed for the dynamics of Rydberg states in a microwave field (see Section V). Since the density of states strongly depends on the number of degrees of freedom, T_{break} may vary over many orders of magnitude in atomic systems. Typical orders of magnitude are nanoseconds to microseconds for atomic Rydberg states studied experimentally.

Whether an intermediate time scale exists that is shorter than T_{break} and limits the quantum-classical correspondence is mainly unknown.

Finally, the natural lifetimes (due to spontaneous emission) are usually of the order of hundreds of microseconds, much longer than any time scale relevant to regular or chaotic behavior. This is why the system can be considered to be governed by a nondissipative Hamiltonian.

III. Spectroscopy

In this section, we discuss the basic spectroscopic properties of chaotic atomic systems, including positions of the different energy levels and related properties like oscillator strengths and lifetimes of resonances. We show that the onset of chaos is characterized by well-defined properties of the quantum spectrum, which have important experimental consequences.

A. PROPERTIES OF INDIVIDUAL ENERGY LEVELS

The goal of traditional spectroscopy is to assign quantum numbers to the different energy levels in order to obtain a complete classification of the spectrum. Good quantum numbers are associated with conserved quantities, that is, operators commuting with the Hamiltonian. In a classically ergodic system, the trajectories generically explore uniformly all the available phase space, which discards the existence of conserved quantities (except energy for time-independent systems). The same is valid in quantum mechanics: Quantum chaos is characterized by the *destruction of good quantum numbers*.

This is illustrated in Fig. 1, which shows the evolution of the energy levels

FIG. 1. Energy levels of a hydrogen atom versus magnetic field for typical Rydberg states ($L_z = 0$, even parity series). At low field (left part of the figure), the classical dynamics is regular and the energy levels (quasi-) cross. The quantum eigenstates are defined by a set of good quantum numbers. In the right part of the figure, the classical dynamics is chaotic, the good quantum numbers are lost, and the energy levels strongly repel each other. The strong fluctuations in the energy levels are a characteristic of chaotic behavior.

of a hydrogen atom as a function of the magnetic field strength. At low magnetic field, when the classical motion is regular, approximate good quantum numbers exist. States with different sets of good quantum numbers do not (or weakly) interact. A given eigenstate can be unambiguously followed in a wide range of field strength, since it crosses (or has very small avoided crossings with) the other energy levels. In this regular regime, it can be shown that, because of the existence of conserved quantities, a given classical trajectory does not explore the entire phase space, but only a subspace known as an *invariant torus*, almost like a separable system. It is possible to quantize semiclassically such a system using the EBK procedure (Gutzwiller, 1990; Ozorio, 1988). This is a natural extension of the usual WKB quantization rule along each almost separated coordinate and provides an efficient semiclassical quantization scheme for individual energy levels in association with good quantum numbers (see also Section IV.A for the wave functions in the regular regime). Actually, the energy levels predicted from the EBK quantization should not be distinguishable from the exact quantum result in the left part of Fig. 1.

When chaos invades the major part of the classical phase space (right part of Fig. 1), this quantization scheme cannot be used: The sizes of the avoided crossings increase and individual states progressively lose their identities and the associated good quantum numbers.

In the fully chaotic regime, the energy levels and the eigenstates strongly

FIG. 2. Two numerical simulations of an excitation spectrum of hydrogen atoms in a magnetic field γ from the ground state. Although the magnetic field changes by only 3 parts in 1000, the spectra are completely different. This shows the extreme sensitivity of chaotic spectra on small changes of parameters.

fluctuate when the magnetic field is changed. An example is given in Fig. 2 where a relative change of 0.3% in the magnetic field is enough to scramble the spectrum. In that sense, the quantum system shows a high sensitivity on a small perturbation as its chaotic classical equivalent. The energy spectrum of a classically chaotic system displays an extreme *intrinsic* complication, which means the death of traditional spectroscopy.

Such extremely complex spectra have been observed experimentally in several atomic systems in external fields (magnetic field, crossed electric and magnetic fields) and numerically on virtually all chaotic systems. It is probably the simplest and most universal property. Figure 3 shows an experimental spectrum of the lithium atom in a magnetic field, compared with the numerical simulation on hydrogen. Both display the same complicated reproducible details and the agreement is excellent (Iu *et al.*, 1991).

FIG. 3. Comparison between the experimental spectrum of the lithium atom in a magnetic field $B \simeq 6.113$ T ($L_z = 0$, even parity series) and the theoretical spectrum of the hydrogen atom computed using the complex coordinate method, shown as mirrors of each other. The agreement is excellent. Aside from an overall intensity scale factor, there is *no* adjustable parameter.

This also proves that the atomic core is only a small perturbation.

This qualitative property has been put on firm ground by a study of the statistical properties of energy levels (Bohigas, 1991). The simplest quantity is the distribution of nearest neighbor spacings (energy difference between two consecutive levels, normalized to the mean level spacing). In the regular regime [see Fig. 4(a)], consecutive energy levels generally have different sets of good quantum numbers and do not interact. The distribution of spacings is one of uncorrelated levels, that is, a Poisson distribution:

$$P(s) = e^{-s} \quad (25)$$

which nicely reproduces the numerical results obtained on different systems and the experimental results on Rydberg atoms in a magnetic field (Delande and Gay, 1986; Friedrich and Wintgen, 1989; Hasegawa *et al.*, 1989).

In the chaotic regime, the strong level repulsion induces a completely different result [see Fig. 4(b)], with practically no small spacing. A simple model is able to predict the statistical properties of energy levels. It assumes a maximum disorder in the system and therefore models the Hamiltonian by a set of random matrices, which couple any basis state to all of the other ones. Depending on the symmetry properties of the Hamiltonian (especially with respect to time reversal), different ensembles of random matrices have to be considered (Bohigas, 1991). For all atomic systems studied, the Gaussian orthogonal ensemble of real symmetric matrices is convenient. The predicted spacing distribution agrees very well with the numerical results for various atomic systems. It is very close to the so-called Wigner distribution:

$$P(s) = \frac{\pi s}{2} \exp\left(-\frac{\pi s^2}{4}\right) \quad (26)$$

FIG. 4. Distribution of energy level spacings (normalized to the mean level spacing) for the hydrogen atom in a magnetic field, obtained from numerical diagonalization of the Hamiltonian. (a) In the classically regular regime, the distribution is maximum at 0 and well fitted by a Poisson distribution (dashed line). (b) In the classically chaotic regime, the probability of finding almost degenerate levels is very small (level repulsion). The results are well reproduced by the Wigner distribution (dashed line) and random matrix theory (Delande and Gay, 1986).

The transition from a Poisson distribution in the classically regular regime to a Wigner distribution in the chaotic regime gives a *characterization* of quantum chaos, at least for highly excited states.

Other statistical properties of the energy levels in the chaotic regime have been studied and are in good agreement with the predictions of random matrix theory (Delande and Gay, 1986). From an experimental point of view, fully resolved clean spectra are needed for extracting spacing distributions. These are difficult to obtain because of the high density of states in the regions of interest and because of possible experimental imperfections (stray fields, etc.), which rapidly spoil the results. Although there is no doubt that the spacing distribution should be Wigner, it has not yet been verified in a real experiment on a chaotic atomic system. Recently, dynamic properties involving different values of an external parameter have been studied and put the sensitivity on external perturbations on a quantitative ground (Zakrzewski *et al.*, 1993b; Zakrzewski and Delande, 1993).

Finding universal properties in the local statistical properties of energy levels for chaotic systems is not a real surprise. As discussed in the preceding section, this range of energy (mean level spacing ΔE) corresponds to a long time behavior ($\hbar/\Delta E \gg T_{\text{chaos}}$), where chaos classically fully develops with its universal properties. Universality is also observed in the corresponding quantum dynamics. On the other hand, at shorter times of the order of T_{chaos} , nonuniversal properties exist in the classical behavior. This implies also a deviation from the predictions of random matrix theory on a large energy scale, as has been numerically and experimentally observed (Delande, 1991).

B. WIDTHS OF RESONANCES

The model of random matrices describes bound spectra and does not take into account the possible autoionization of the atom. If the typical autoionization time is longer than the break time:

$$T_{\text{ion}} \gg T_{\text{break}} \quad (27)$$

the atom does not ionize significantly during the time needed to develop the detailed quantum dynamics. Hence, the energy spectrum and the eigenstates will be essentially well described by random matrix theory. Autoionization comes into play after, as a small perturbation. Each eigenstate is thus coupled to the continua through some operator, which can be modeled by a random matrix. The resulting width of the eigenstate results from the superposition of all the decay channels. As a first approximation, all decay channels have roughly the same importance and the statistical distribution of the widths depends only on the number of open channels. If this number is small, pure quantum effects are very important. This is especially the case

for the hydrogen atom in a magnetic field. In such a case, the magnetic field confines the transverse motion of the electron: Immediately above this first ionization threshold, the electron can ionize only in the magnetic field direction and is left in the lowest Landau level. There is only one channel and the prediction of random matrix theory for the widths Γ of the resonances is the so-called Porter-Thomas distribution (Grémaud *et al.*, 1993):

$$P(\Gamma) = \frac{1}{\sqrt{2\pi\Gamma\bar{\Gamma}}} \exp\left(-\frac{\Gamma}{2\bar{\Gamma}}\right) \quad (28)$$

where $\bar{\Gamma}$ is the average width, which can be obtained from classical dynamics. This formula implies that the small widths are by far the most probable. This nonintuitive result means that the strong statistical fluctuations in the random matrix model tend to compensate each other, the most probable value of any matrix element being zero. This prediction has been checked using numerical experiments (Grémaud *et al.*, 1993). The resulting cumulative distribution $\int P(\Gamma) d\Gamma$ is shown in Fig. 5 in comparison with the Porter-Thomas prediction.

The experimental observation of extremely narrow resonances in the spectrum of the lithium atom in a magnetic field between the first two Landau ionization thresholds (Iu *et al.*, 1991) confirms the predominance of small widths and its extreme sensitivity (as any completely destructive interference process) to a small change of parameter. The agreement between theory and numerical experiment in Fig. 5 for a nontrivial phenomenon clearly shows the relevance of quantum chaos for the understanding of complex atomic systems.

FIG. 5. Cumulative probability of the normalized widths (solid line) compared with the cumulative probability obtained from the Porter-Thomas distribution (dashed line). The agreement is very good, especially for the smallest values. The infinite slope at the origin (square root behavior) is characteristic of only one open channel. The narrow resonances are by far the most probable.

When condition (27) is not satisfied, the different resonances overlap. The ionization process has to be fully, that is, nonperturbatively, included in the classical and quantal dynamics. Such a situation is probably encountered in the experiments on the hydrogen atom in crossed fields as well as in the microwave ionization experiments. Unfortunately, no clean experimental data in this region have been published. Numerical experiments in crossed fields have reached this regime. The random matrix theory here predicts a well-defined signature in the ionization cross section—the so-called Ericson fluctuations (Ericson, 1960)—which are observed in the numerical spectra (Main and Wunner, 1992). This is one more piece of evidence for the relevance of quantum chaos.

C. PERIODIC ORBIT SPECTROSCOPY

The two previous subsections have demonstrated the *universal* character of fluctuations. This also implies that a detailed analysis of all energy levels and eigenstates does not make sense: No interesting information can be brought to the physics of chaotic phenomena beyond the statistical aspects. On the other hand, this does *not* mean that these energy levels do not carry any information; it is just that this information has to be extracted in a different way. More precisely, as the individual specificity of a chaotic system manifests at relatively short times, before universal chaotic features dominate, it has to be found in the long energy range characteristics of the quantum spectra.

From the analysis of Section II, the comparison between quantum and classical properties is more clearly expressed by a Fourier transform of an experimental spectrum, hereby passing from the energy to the more suitable time domain. Indeed, in a typical spectroscopic experiment, a laser is shined on the atoms, and the absorption probability (or related quantities such as the excitation cross section) is measured. The experimental spectrum is close to

$$\tilde{C}(E) = \sum_i |\langle \phi_i | T | g \rangle|^2 \delta(E - E_i) \quad (29)$$

where $|\phi_i\rangle$ are the eigenstates with energy E_i , $|g\rangle$ represents the initial state of the atom, and T is the transition operator, depending on the polarization and properties of the laser used. The finite resolution of the spectra can be accounted for through a simple convolution with the line profile.

A straightforward comparison with Eqs. (14) to (23) shows that the Fourier transform of the spectrum is simply a diagonal element of the time-evolution operator [see Eq. (18)] with the initial state:

$$|\psi(0)\rangle = T|g\rangle \quad (30)$$

where $T|g\rangle$ is not a stationary state of the Hamiltonian, but rather a wave packet. Therefore, performing the Fourier transform of the experimental spectrum is tantamount to studying the time dynamics of this wave packet. In other words, this allows for the investigation of wave packet dynamics with cw lasers. In the specific case of excitation of atomic Rydberg states from a low lying state, $T|g\rangle$ is a small (on the typical scale of Rydberg states) wave packet starting very close to the nucleus. After absorption of a laser photon, the wave packet expands from the nucleus and eventually returns after some time. For such short times, it is reasonable to assume that the wave packet propagates semiclassically along the classical paths. Hence, $C(t)$ should first decrease very rapidly, as the wave packet explodes from the nucleus, then display a bump after the period of a closed orbit, that starts and ends at the nucleus. The amplitude of the bump is directly related to the angular localization of the initial wave packet and thus depends on the initial state and polarization of the laser. Indeed, Fourier transforms of experimental spectra obtained for the hydrogen atom in electric (Harmin, 1982), magnetic (Delande, 1991; Friedrich and Wintgen, 1980) and crossed fields show these bumps at the periods of closed orbits.

The full theory of the effect of closed and periodic orbits on quantum spectra is beyond the scope of this chapter, but certainly among the major achievements of the last years (Bogomolny, 1988; Gao and Delos, 1992). It relies on the qualitative arguments given earlier. The starting point is the Feynman path integral formalism, which is strictly equivalent to the usual formulation of quantum mechanics. It expresses the quantum propagator as a sum over all paths (including unphysical trajectories) connecting the initial to the final point, each path contributing with a factor $\exp(i\int L dt/\hbar)$ where L is the classical Lagrangian. In the semiclassical limit $\hbar \rightarrow 0$, the sum over all paths is calculated with the stationary phase approximation, which selects only classical trajectories (along which the action $\int L dt$ is precisely stationary). This gives the semiclassical approximation to the propagator, known as the Van Vleck propagator. In the next step, the Green function at energy E , Fourier transform of the propagator, is computed with one further stationary phase approximation. The dominant contributions then come from the classical orbits with energy E . The experimentally measured spectra can be computed using this semiclassical Green's function. The simplest quantity is the density of states:

$$d(E) = \sum_i \delta(E - E_i) \quad (31)$$

Considering our previous notation [see Eq. (21)], it corresponds to the case where $|c_i| = 1$, and is nothing but the trace of the Green's function:

$$d(E) = -\frac{1}{\pi} \text{Tr} \text{Im} G^+(E) = -\frac{1}{\pi} \int \langle \mathbf{r} | \text{Im} G^+(E) | \mathbf{r} \rangle d\mathbf{r} \quad (32)$$

If the trace is evaluated again by the stationary phase approximation, one obtains the famous trace formula (Gutzwiller, 1990; Balian and Bloch, 1974) (here written for a two-dimensional time-independent system):

$$d(E) = d_0(E) + \text{Im} \sum_j \frac{T_j}{\pi \hbar} \frac{\exp[i(S_j/\hbar - \alpha_j \pi/2)]}{[\det(M_j - 1)]^{1/2}} \quad (33)$$

which expresses the density of states as a sum over all periodic orbits j with action $S_j(E)$, period $T_j(E)$, and their repetitions (same orbit traveled several times). Here M_j is the monodromy matrix describing the linearized motion around the periodic orbit; α_j is the Morse index (an integer); and $d_0(E)$ is the smooth density of states obtained from the Thomas-Fermi model:

$$d_0(E) = \frac{1}{(2\pi\hbar)^2} \iint \delta[E - H(\mathbf{r}, \mathbf{p})] \, d\mathbf{r} \, d\mathbf{p} \quad (34)$$

Related quantities, such as the density of oscillator strengths observed experimentally, can also be expressed as sums over periodic or closed trajectories.

The trace formula and related formulas establish an intuitive link from quantum to classical mechanics. A difficulty is that the characteristics (period, action, etc.) of the periodic orbits smoothly evolve with the energy E . Thus, the positions and intensities of the peaks in the Fourier transform of a spectrum move with energy, which broadens and smears out the peaks. One can get around this problem using scaled spectra (see Section I.D) obtained from fixed classical dynamics. From Eq. (33), a Fourier transform of the density of states with respect to the effective value of $1/\hbar$ will display δ peaks at exactly the *actions*—instead of the *periods* in the usual spectra—of the periodic orbits.

This periodic orbit spectroscopy of scaled spectra is actually the best method we know for extracting information from chaotic spectra, where a detailed analysis of the individual lines is not particularly enlightening. An example of periodic orbit spectroscopy is given in Fig. 6 for the spectrum of the helium atom in a magnetic field (van der Veldt *et al.*, 1993). The *quantum* spectrum contains 3000 energy levels without any apparent order. Its Fourier transform reveals about 50 peaks at the actions of *classical* periodic orbits. The comparison with the synthetic spectrum obtained from a semiclassical theory inspired by the trace formula (Gao and Delos, 1992) is very impressive. Most of the peaks are reproduced at exactly the right position with a satisfactory intensity.

Those splendid spectra have been obtained in a regime where the dynamics is mainly regular. Other spectra have been recorded on the hydrogen atom in the chaotic regime, at much lower resolution (Holle *et al.*, 1988). Figure 7 shows a series of Fourier transforms of scaled spectra,

FIG. 6. (a) Fourier transform of an experimental spectrum of the helium atom in a magnetic field γ , at constant scaled energy $\varepsilon = -0.7$. It displays peaks at the actions of the classical periodic orbits. Comparison with the semiclassical prediction in (b) shows an extremely good agreement. This proves the major role of classical periodic orbits in quantum spectra. (Courtesy of T. van der Veldt.)

obtained at different values of the scaled energy ε , in comparison with the actions of the periodic orbits. Each peak can be clearly attributed to a periodic orbit and its evolution with ε . The same kind of results have been obtained on scaled spectra of the rubidium atom in crossed electric and magnetic fields (which requires a simultaneous sweep of the laser frequency and the strengths of the two external fields). Again, some peaks are unambiguously related to periodic orbits (Fig. 8) (Raithel *et al.*, 1991). This is an experimental indication that periodic orbits, which are one-dimensional structures, also play a major role in six-dimensional phase space.

The experimental data are not of comparable quality for doubly excited states. Numerical experiments on a two-dimensional simplified model of the helium atom, which assumes the two electrons to be localized in opposite directions with respect to the nucleus, have shown equally the importance of periodic orbits. More importantly, the study of Wintgen *et al.* (1992) shows that the most important orbit is the one where the two electrons have the same excitation, but opposite phases (one electron collides with the nucleus while the other one is at its maximum distance and vice versa). This

FIG. 7. Fourier transform of the experimental spectra of the hydrogen atom in a strong magnetic field γ , obtained at constant scaled energy ε . The different spectra, plotted in (a) for various ε (here denoted by $\bar{E}$), display peaks at the actions of the classical periodic orbits, plotted in (b). The agreement between the experimental *quantum* Fourier transform and the *classical* periodic orbits shows their importance for understanding the long range correlations in the chaotic spectra. (Courtesy of K. H. Welge.)

asymmetric stretch is much less unstable than the symmetric one and consequently dominates the spectra (Ezra *et al.*, 1991). This invalidates the traditional approach (Fano, 1983), in which the two electrons are supposed to lie in the symmetric configuration (the so-called “motion” on the Wannier ridge). This important and unexpected result is typical of how the classical mechanics of complex systems can improve our understanding of quantum spectra.

Recently, it has been shown on the basis of theoretical and numerical work that the periodic orbits are not the only relevant structures in chaotic spectra. A complete description must also include *complex* orbits, where time, position, and momentum are made complex (Kus *et al.*, 1993). The relatively small peak at action $S = 3.93$ in Fig. 6 does not correspond to any real periodic orbit, but to a “ghost” (complex) periodic orbit. The inclusion

FIG. 8. Fourier transform of an experimental scaled spectrum of rubidium atoms in crossed electric and magnetic fields. It displays peaks at the actions of classical closed orbits. [Courtesy of Raithel *et al.* (1991).]

of these complex orbits, especially in the vicinity of classical bifurcations, should improve the efficiency of periodic orbit expansions.

D. FROM CLASSICAL TO QUANTUM MECHANICS

The set of preceding figures (Figs. 6 to 8) shows how some collective (not related to a specific energy level) properties of quantum chaotic spectra can be interpreted in terms of classical orbits. Because periodic orbits are dense in a fully chaotic phase space, it can be argued that they contain all the information. However, we basically do not know how this information is shared and structured in the different orbits. It seems that some hierarchy exists, at least for systems where a systematic coding of the periodic orbits is known: Most of the information contained in the very long orbits can be essentially extracted from shorter periodic orbits (Wintgen *et al.*, 1992).

The best way to clarify this issue is to try to compute a quantum spectrum from the knowledge of as many classical periodic orbits as possible. It has been found numerically that this is an extremely difficult problem because of the proliferation of long periodic orbits and because of subtle relations and compensations between them. Resolving individual peaks requires the inclusion in the sum at least all of the orbits of a period shorter than the break time $T_{\text{break}} = \hbar/\Delta E$. For typical Rydberg states, this means billions of orbits, which is, of course, impossible. Thus the trace formula and related formulas are of no practical use for computing semiclassical approximations to the energy levels. Partially successful attempts to overcome this difficulty have been made. In practice, although the trace formula is supposed to be asymptotically valid for highly excited states, it is able to give satisfactory values for the energies of the *lowest states* only! For example, inclusion of 13 periodic orbits allows us to compute correct values for the lowest 10 states of the hydrogen atom in a magnetic field (Wintgen, 1988).

TABLE I
ENERGY LEVELS OF $1S^e$ SERIES OF HELIUM ATOM

State	Periodic Orbit	Cycle Expansion	Exact quantum
1s1s	-3.097	-2.932	-2.904
2s2s	-0.804	-0.777	-0.778
3s3s	-0.362	-0.353	-0.354
4s4s	-0.205	-0.199	-0.201
5s5s	-0.131	-0.129	-0.129

Note. Some energy levels of the $1S^e$ series of the helium atom, compared to the simple semiclassical quantization using only the assymetric stretch periodic orbit and the more refined "cycle expansion," which includes a set of unstable periodic orbits. The agreement is remarkable, which proves the efficiency of semiclassical methods for this chaotic system. (Courtesy of D. Wintgen.)

A very interesting example in this context is the helium atom, for which the use of cycle expansion (an improvement of the periodic orbit expansion) gives a remarkable value for the energy of the ground state (see Table I). This shows how modern semiclassical mechanics (which is aware of chaos and of the properties of periodic orbits) can solve a simple problem having been discussed for more than 70 years (Wintgen *et al.*, 1992).

Yet, we are far from the goal of computing individual, highly excited states of a chaotic system from the knowledge of its classical dynamics. Using periodic orbits, we can at most compute low-resolution spectra.

IV. Wave Functions: Localization and Scars

In this section, we discuss the general properties of the wave functions of a classically chaotic system, with emphasis on the localization properties. As for individual energy levels, the wave functions are extremely sensitive to any change of a parameter or any perturbation. In a first approximation, random matrix theory predicts that the wave functions are random waves, uniformly distributed over the entire phase space. This is the quantum equivalent of an ergodic classical trajectory. However, because of quantum interference effects, differences *must* exist, especially at long times. Any eigenstate of a quantum Hamiltonian is invariant under time evolution and not uniformly distributed over the phase space. Hence, *quantum ergodicity* is possibly observable in the wave functions only on a scale larger than the typical oscillations, that is, the de Broglie wavelength. The most ergodic wave function one can imagine is then composed of random oscillations at

the de Broglie wavelength superimposed on a smooth uniform background.

Beside the previous general description of chaotic wave functions, specific structures might exist that are related to peculiarities of the system, exactly as periodic orbits are responsible for specific structures in the energy spectrum.

The simplest manifestation of such a specificity is a preferential localization (enhancement) of the wave function in some region of phase space. Unfortunately, there is a large amount of confusion in the current literature regarding different types of localization, which have different physical origin. Among them, the following ones have been discussed and (numerically) observed or predicted:

- Localization in the vicinity of invariant tori in a classically regular system (see Section IV.A)
- Localization on residual structures (such as cantori) in systems with mixed regular-chaotic dynamics (see Section IV.C)
- Localization in the vicinity of *unstable* orbits in globally chaotic systems. Such a localization has been baptized a “scar” (Heller, 1984) of the unstable periodic orbit (see Section IV.B).

In atomic systems, direct experimental observation of wave functions is almost impossible. Hence, we have only indirect proofs of totally or partially localized wave functions. Such proofs rely on measurements of matrix elements involving highly excited chaotic states, which are, of course, affected by the localization. Because of the lack of experimental data in atomic systems, we will mainly present results of numerical experiments.

A. LOCALIZATION IN THE REGULAR REGIME

For a regular system, the EBK quantization predicts a localization of the regular wave functions on the invariant tori of the classical motion (Ozorio, 1988; Gutwiller, 1990). This has been confirmed numerically on several quantum regular systems. The simplest one is the hydrogen atom in a static electric field. Using its separability in parabolic coordinates and semiclassical quantization along these coordinates, we can compute absorption spectra (and consequently wave functions) in excellent agreement (Harmin, 1982) with the experimental observations.

Another example has been recently discovered in the dynamics of the helium atom: There are eigenstates localized on classical invariant tori for the “frozen planet” configuration (Richter *et al.*, 1992).

Similar phenomena have been found in the hydrogen atom in a microwave field. The wave functions of the Floquet states evolve at the period of the microwave field. In the simplified one-dimensional model, there is a resonance between the electronic Kepler motion and the microwave external

field when their two frequencies are equal. The nonlinear terms create the following standard phenomenon: There is a stable periodic trajectory where the electron motion is locked on the external frequency (with a well-defined phase) surrounded by invariant tori and an unstable periodic trajectory with opposite phase embedded in a stochastic separatrix layer (Buchleitner, 1993). Figure 9 shows the time evolution of a quantum wave function associated with an invariant torus. It is clearly an atomic wave packet oscillating back and forth at the frequency of the external microwave. Contrary to normal atomic wave packets, which spread rapidly because of dispersion, this wave packet is *nondispersive* and reproduces itself identically after one period. This is a typical nonlinear stabilization phenomenon, which might be of interest in the context of wave packet studies.

B. LOCALIZATION IN THE CHAOTIC REGIME

The localization of chaotic wave functions in the vicinity of unstable periodic orbits, although it might appear a little surprising at first sight, is after all extremely natural if one comes back to the equations describing the quantum dynamics. For times of the order of the shortest periods, the

FIG. 9. Wave functions of Floquet eigenstates of a one-dimensional hydrogen atom in a microwave field. The states evolve in time with the periodicity of the external microwave field. We show the wave packets at phases 0, $\pi/2$, and π (from left to right). *Top*: When the classical motion is regular, the quantum wave packet is localized in phase space, locked on the external frequency, and *nondispersive*. *Bottom*: When the classical motion is chaotic, the quantum wave packet may be partially localized on complex phase space structures, with a quasirandom background. Note the phase difference of π s between the regular and chaotic wave packets.

semiclassical Van Vleck propagator can be used, which means that a localized wave packet essentially evolves classically. Let us consider an initial wave packet $|\psi(0)\rangle$ lying close to the classical orbit with an initial momentum close to the classical momentum on the orbit, for example, a coherent state. Its localization is limited by the Heisenberg inequalities, but in the semiclassical limit $\hbar \rightarrow 0$, an accurate localization is possible. For short times, it will evolve as a dispersing wave packet approximately following the classical periodic orbit. On the other hand, its time evolution can also be described by the quantum equations (14) to (23). This has two consequences:

- Because the modulus of the overlap between the wave packet $|\psi(t)\rangle$ and an eigenstate $|\phi_i\rangle$ is constant with time, the latter cannot be localized only on one point or one part of the periodic orbit. It is either scarred by the whole orbit or not scarred at all.
- The autocorrelation function $C(t) = \langle \psi(0) | \psi(t) \rangle$ displays peaks at multiples of the period T , because the wave packet comes back at its initial point. Of course, because of the dispersion of the wave packet, the returning peaks get smaller and smaller and finally disappear. However, the low-resolution Fourier transform of $C(t)$ will display peaks at the inverse period $2\pi\hbar/T$. From Eq. (23), these peaks are unresolved superpositions of the contributions of the various energy levels. Consequently, some of the eigenstates must have enhanced values of $|c_i| = |\langle \phi_i | \psi(0) \rangle|$. In other words, some wave functions of eigenstates must have an enhanced amplitude on the initial position, that is, a scar of the periodic orbit.

Moreover, these arguments make it possible to predict quantitatively where the peaks are located and thus where scars are expected to be. The resulting condition is known as the scar quantization condition (Delande, 1991; Gutzwiller, 1990):

$$S(E) = \oint \mathbf{p} \cdot d\mathbf{r} = 2\pi\hbar \left(n + \frac{\alpha}{4} \right) \quad (35)$$

where $S(E)$ is the action of the periodic orbit, α its Morse index, and n a non-negative integer. This formula, although it is strongly reminiscent of the WKB quantization condition, is of a different nature. It is only an approximate indication of where scarred states have the highest probability of being. Indeed, nothing proves that the different unresolved states lying under the peaks of the low-resolution Fourier transform are democratically scarred. All we know is that *collectively* they carry a well-defined scar strength. The detailed repartition depends on the long-term behavior of the wave packet and cannot be estimated with this approach.

The existence of scars makes the difference between real wave functions and random waves. Scars appear because they are the only possible intense manifestations of chaotic fluctuations compatible with the dynamics.

The scarring phenomenon is nothing but intrinsic fluctuations plus semiclassical propagation.

It also follows that scars are stronger if the orbit is short and weakly unstable. An example of a scar, obtained in a numerical experiment for the hydrogen atom in a magnetic field, is shown in Fig. 10.

An indirect experimental proof of the existence of partial localization of chaotic wave functions has been obtained on the rubidium atom in crossed electric and magnetic fields. It uses an inhomogeneous electric field to induce deflection of an atomic beam proportionally to the static electric atomic dipole moment. If the wave functions were purely random waves, the electric dipole moment would be close to an average fixed value (classical average over the accessible phase space). On the contrary, experimental results, displayed in Fig. 11, indicate the existence of large electric dipole moments and large variations with the different parameters (Raithel *et al.*, 1993). Although it is not obvious that we should associate the large dipole moment with a specific classical structure (saddle fixed point, periodic orbits, etc.), this nevertheless proves that localization phenomena exist in this real chaotic system.

C. LOCALIZATION IN THE MIXED REGULAR-CHAOTIC REGIME

Localization phenomena are much more difficult to analyze in mixed systems. Indeed, contributions come from the remaining invariant tori

FIG. 10. Wave function of the hydrogen atom in a magnetic field. We show the 474th excited state ($L_z = 0$, odd parity series) at scaled energy $\varepsilon = -0.2$, scarred by the classical almost circular unstable periodic orbit shown in superimposition. The dotted line is the line of classical turning points.

FIG. 11. Experimental measurements showing the dipole-deflection pattern as a function of a scaled electric field. The variations of the average electric dipole moment are probably related to localization of the eigenstates on classical structures (Courtesy of Raithel *et al.*, 1993.)

together with various structures of the phase space. The latter cannot be reduced to isolated periodic orbits, as in a fully chaotic system. The main reason is the existence of lots of different time scales, which strongly prevents the quantum system from approaching ergodicity. Additional information is needed to interpret the quantum spectra properly, such as sizes and geometrical shapes of the unstable regions surrounding unstable orbits, geometries of separatrices between different types of motion, existence and geometries of partial barriers, etc.

A typical example is the one-dimensional hydrogen atom in a microwave field. The phase space is mixed and structured by the different resonances between the atomic and the external frequencies. Figure 9 shows an atomic state, evolving periodically with the microwave frequency, localized near the unstable periodic orbit, in phase opposition with the stable resonance, and the surrounding phase space. It is the counterpart to the quantum state localized on the principal resonance discussed earlier. One clearly sees the wave packet oscillating back and forth emerging from a rather erratic background. Analysis of phase space plots of such a state shows that it contains essential contributions from the stochastic layer surrounding the unstable periodic orbit. Hence, analyzing such a system in terms of the scar of an unstable periodic orbit (Jensen *et al.*, 1989; Sauer *et al.*, 1992) is an

adventurous extrapolation and certainly an oversimplified view of localization in mixed systems. Note also that strictly analogous localized wave packets, periodic in time with *no dispersion*, have also been observed in numerical simulations of three-dimensional atoms (Buchleitner, 1993).

D. RELATIONSHIP BETWEEN LOCALIZATION AND LIFETIME

An important question is one of whether the localization of atomic wave functions on bound phase space structures implies some stability versus ionization. In general ionization takes place in an outer region of the atom, where the binding Coulomb field is relatively weak, while significant phase space structures are localized in the inner part, where all interactions have the same order of magnitude. Thus, any relation between localization and the ionization rate indicates the existence of a long-range correlation in phase space. This certainly happens in regular systems where the relevant structures, invariant tori, extend throughout phase space, as has been demonstrated for the hydrogen atom in a static electric field (Harmin, 1982) and for the frozen planet configuration of the helium atom (Richter *et al.*, 1992).

For a strongly chaotic system, long-range correlations are not expected, and scarring by an unstable periodic orbit should not increase (or decrease) significantly the lifetime of an atomic state. Strong numerical evidence of this decorrelation exists for the case of atoms in a magnetic field above the ionization threshold (see Section III.B). This explains why residual regularities as scars are not relevant for the ionization rate and the success of the random matrix predictions.

Mixed regular-chaotic systems are much more complicated. Residual long-range correlations exist, but not in a systematic way. Hence, scarring might favor low ionization rates, as suggested by Jensen *et al.* (1989), but there is no systematic one-to-one correspondence. It is certainly oversimplified and essentially wrong to associate a reduced ionization rate with an individual scar of an unstable periodic orbit.

V. Dynamics

A. TIME-INDEPENDENT SYSTEMS

Although the study of the temporal dynamics of a quantum system provides us with the clues for understanding quantum chaos (see Section II), very few

direct measurements have been done in the chaotic regime. Actually, as shown earlier, Fourier transforms of spectra obtained with cw lasers allow for the same information in an easier way. Furthermore, there is no equivalent of scaled spectroscopy in the time domain. Any wave packet excited in a real experiment by a short laser pulse has a certain dispersion in energy and will consequently spread quite rapidly, which is avoided in scaled spectroscopy. Consequently, it is not very likely that new interesting physical information can be obtained from such time-resolved experiments on time-independent systems.

B. TIME-DEPENDENT SYSTEMS

For explicitly time-dependent Hamiltonian systems, the situation is completely different. Experimental results are badly needed, especially for the long-time dynamics, which is difficult to study in numerical experiments. The present status of technology allows us to excite and probe atomic systems on very short time scales, of the order of 1 ps or less. For excited Rydberg states, this is shorter than the Kepler period of the electron. A new generation of experiments in atomic physics is born. Most probably, fascinating unexpected results on quantum chaotic dynamics will be discovered in the near future.

The hydrogen atom in a microwave field is a first step in this direction, because it contains an explicit time dependence, but can also be reduced to a static problem by use of the Floquet theorem as a consequence of its time periodicity. The exchange of energy between the different degrees of freedom, which is usually difficult to measure in a microscopic multidimensional system, is equivalent here to the number of photons exchanged between the atom and the external field, a much more accessible quantity. A rough estimation of the energy exchange is the ionization probability of the atom, by far the easiest quantity to measure in an experiment. It contains some information on the dynamics, but in a strongly convoluted form.

In view of the success of spectroscopy of chaotic time-dependent systems, it should be interesting to perform the spectroscopy of the Floquet states of the microwave problem, eventually followed by a Fourier transform. Although in principle feasible, Floquet spectroscopy has not yet been performed.

In a typical experiment, the atoms are prepared in an excited Rydberg state, then exposed to the microwave for a finite well-defined interaction time and finally analyzed. The analysis can simply be the ionization probability or, in a more refined experiment, the internal state of the atom is analyzed by (static) field ionization. The shape of the ionization signal versus the static field strength is sensitive to the values of the principal

FIG. 12. Experimental ionization probability of hydrogen atoms after interaction with a microwave field versus the field amplitude. The curve has a typical threshold behavior, a signature of a classical phenomenon. (Courtesy of P. Koch.)

quantum number populated after the interaction with the microwave.

Figure 12 shows a typical experimental result: The ionization probability plotted versus the microwave field strength displays a threshold behavior (Sauer *et al.*, 1992). The field strength at which 10% of the atoms is ionized, defines the *10% ionization threshold*, which, in turn, is a smooth function of the microwave frequency. This behavior is in sharp contrast to the standard photoeffect where the threshold behavior is observed on the *frequency* dependence of the ionization probability, independently of the field amplitude. The latter is a signature of a quantum effect, whereas the former is rather characteristic of a classical phenomenon. The key observation is that the gross features of the ionization process depend only on the scaled variables of Eq. (12): Different ionization curves for different initial states, but at the same scaled frequency and plotted versus the scaled amplitude, do approximately coincide. As explained in Section I.D, this is a clear signature of a classical phenomenon. It does not discard the possibility of finding a quantum interpretation, but it proves that a classical one, without specific quantum interferences, has to exist. Conversely, any deviations from this scaling behavior are the signature of a quantum effect.

Figure 13 shows the scaled 10% ionization threshold versus the scaled frequency, as observed experimentally (Bayfield *et al.*, 1989). In the low-frequency regime, the threshold tends to the static threshold, as it should. At larger frequencies, it decreases up to a scaled frequency $\omega_0 \simeq 1$ where it starts to increase again. For the classical system, the phase space is mixed regular-chaotic, because of various resonances between the atomic and external frequencies. The classical ionization threshold is associated with the disappearance of the last invariant torus separating the initial state of the

FIG. 13. Scaled 10% ionization threshold versus the scaled frequency, from the experimental results of Bayfield *et al.* (1989). Above $\omega_0 = 1$, the experimental results (symbols, dashed line) significantly deviate from the classical result (dotted line). This supports the theory of dynamic localization, whose prediction is indicated by the solid line. (Courtesy of I. Guarneri.)

atom from the continuum. Above this value, the classical dynamics is essentially a diffusive-like motion leading to relatively fast ionization. The comparison between the classical threshold and the quantum experimental results shows a globally excellent agreement up to $\omega_0 \simeq 1$; above, the experimental result lies systematically higher, which signifies that the quantum system is *more stable* than the classical one.

Strong experimental and numerical proofs show that this phenomenon is of quantum origin:

- Starting from higher values of the principal quantum number n_0 , at the *same* value of ω_0 , leads to a quantum threshold a little lower. At fixed ω_0 , the threshold tends to the classical prediction with increasing n_0 , as it should do in the semiclassical limit (Buchleitner, 1993).
- When broadband noise is added to the microwave field, the threshold decreases and tends to the classical one (Arndt *et al.*, 1991). The noise amplitude needed to induce such an effect is very small, not sufficient to affect strongly the classical dynamics. The correct interpretation is that noise destroys the subtle phase coherence effects in the quantum system.
- Numerical experiments show that the ionization probability is very sensitive to small changes (of the order of 10^{-3}) of the scaled frequency at a fixed value of n_0 . This has been related to the sensitivity of individual Floquet states on small changes of parameters (Casati *et al.*, 1988; Buchleitner, 1993), a *quantum* consequence of classical chaos, as shown in Section III.A.

FIG. 14. Scaled 10% ionization threshold of a one-dimensional hydrogen atom (initial principal quantum number $n_0 = 23$) in a microwave field versus the interaction time t (numerical experiment). The different curves correspond to different values of the scaled frequency (from top to bottom, $\omega_0 = 2.7, 3.0, 2.0, 1.43, 1.3, 0.6$, and 0.8). This shows a weak dependence over more than 4 orders of magnitude in the interaction time, apparently of the algebraic type. This result strongly supports the theory of dynamical localization.

- Numerical experiments where the interaction time with the microwave is changed over several orders of magnitude show a very weak dependence of the 10% threshold with the interaction time (see Fig. 14) without displaying a systematic dependence on ω_0 (Buchleitner, 1993). This is inconsistent with the diffusive-like chaotic excitation and ionization predicted by classical dynamics. It agrees with an experimental observation on rubidium atoms (Arndt *et al.*, 1991).

We currently interpret these results to be an effect of *dynamical localization* due to the relatively long interaction time between the atom and the microwave (few hundreds periods): The quantum time dynamics initially follows the diffusive classical one, but “freezes” after the break time (Casati *et al.*, 1988; Fishman *et al.*, 1982; Blümel *et al.*, 1991). Of course, this is only a qualitative argument: Ionization does not stop after the break time, but it is strongly reduced.

A direct experimental observation on rubidium Rydberg states, analyzed by static field ionization, effectively shows this freezing of the atomic evolution after some break time (see Fig. 15) and supports the theory of dynamic localization (Blümel *et al.*, 1991). By means of simplified classical

FIG. 15. Field ionization signal of rubidium Rydberg states. (a) Initial state $8p_{3/2}$. (b) The same initial state after interaction with a microwave field during 100 ns. (c) Same as (b), but interaction time equal to 1000 ns. The absence of evolution between (b) and (c) strongly supports the theory of dynamic localization (Blümel *et al.*, 1991).

time dynamics and a simplified one-dimensional model of the atom, quantitative predictions on the effect of dynamical localization on the threshold behavior (Casati *et al.*, 1988) have been obtained, which agree quite well with experimental results (see Fig. 13). Numerical experiments (Buchleitner and Delande, 1993) also show that the same phenomenon exists for a three-dimensional atom as well as for a simplified one-dimensional model. In the former situation, because of the additional degree of freedom, the mean level spacing between Floquet eigenstates is much smaller and the simple expression for the break time [Eq. (24)] predicts a much longer time for the manifestation of dynamical localization. The reason is probably that Eq. (24) is valid for a strongly chaotic system, but not for mixed systems. In the real experiments, the influence of remaining structures in phase space on the break time is not known.

VI. Conclusions

We believe that the experimental, theoretical, and numerical results discussed in this review clearly show how the concepts of classical chaos in low-dimensional Hamiltonian systems provide one with new and interesting physical insights into the dynamics of complex quantum systems. The general behavior of a chaotic quantum system may have different complementary aspects depending on which physical quantities are probed:

- On a narrow energy interval—roughly at the level of individual eigenstates—the quantum structures display strong apparently random fluctuations and a high sensitivity to any small change of an external parameter. This is the quantum counterpart of the classical sensitivity to initial conditions on long time scales.
- On a large energy scale, where spectral properties are averaged over several states, the individual features of the studied system become manifest, the best example being the importance of periodic orbits and scars.

The two preceding aspects are well separated in the semiclassical limit, that is, for highly excited states. A major unsolved problem is to understand what happens for weakly excited states, far from the semiclassical limit. There, the standard characterization of quantum chaos by the statistical properties of the energy levels breaks down. This is highly relevant for experimental systems such as molecular physics, where the complexity comes not from the strong excitation of a few degrees of freedom, but from the simultaneous excitation of many different degrees of freedom.

A second very difficult problem is the quantum behavior of systems with mixed regular-chaotic dynamics—by far the most common ones. Theoretical guides are lacking here. It is likely that progress will be achieved in this direction in the near future.

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CLASSICAL AND QUANTUM CHAOS IN ATOMIC SYSTEMS

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I. Introduction	85
A. Classical and Quantum Chaos	85
B. Chaotic Atomic Systems	87
C. Ionization: A Complication or a Useful Tool?	90
D. Scaling Properties	91
E. Laboratory Experiments versus Numerical Experiments	92
II. Time Scales—Energy Scales	94
A. Classical Scales	94
B. Quantum Scales	95
III. Spectroscopy	97
A. Properties of Individual Energy Levels	97
B. Widths of Resonances	101
C. Periodic Orbit Spectroscopy	103
D. From Classical to Quantum Mechanics	108
IV. Wave Functions: Localization and Scars	109
A. Localization in the Regular Regime	110
B. Localization in the Chaotic Regime	111
C. Localization in the Mixed Regular—Chaotic Regime	113
D. Relationship between Localization and Lifetime	115
V. Dynamics	115
A. Time-Independent Systems	115
B. Time-Dependent Systems	116
VI. Conclusions	121
References	121

I. Introduction

A. CLASSICAL AND QUANTUM CHAOS

Atomic systems played a major role in the birth and growth of quantum mechanics. One central idea was to relate the well-known classical motion of the electron of a hydrogen atom—an ellipsis around the nucleus—to

the experimentally observed quantization of the energy levels. This is the aim of the Bohr and Bohr-Sommerfeld models. These simple *semiclassical* models were unable to make any reliable prediction on the energy spectrum of the next simplest atom, helium.

Because of the great success of quantum mechanics, the problem of correspondence between the classical and the quantal dynamics has not received much attention in the last 60 years. The fundamental question is (Gutzwiller, 1990): How can classical mechanics be understood as a limiting case within quantum mechanics?

For systems with time-independent one-dimensional dynamics like the harmonic oscillator and the hydrogen atom, the correspondence is well understood. The restriction to such simple cases creates the erroneous impression that the classical behavior of simple systems is entirely comprehensible and easily described. During the last 20 years it has been recognized that this is not true and that a complex behavior can be obtained from simple equations of motion. This usually happens when the motion is *chaotic*, that is, unpredictable on a long time scale although perfectly deterministic (Henon, 1983).

A major problem is that of understanding how the regular or chaotic behavior of the classical system is manifest in its quantum properties, especially in the semiclassical limit. This is the subject of *quantum chaos*. More precisely, typical questions we would like to answer are as follows (Gutzwiller, 1990):

- What are the appropriate observables to detect the regular or chaotic behavior of the system in the classical limit?
- More precisely, how is chaotic or regular behavior expressed in the energy levels and eigenstates of a quantum system?
- What kind of semiclassical approximations can be used if the system is not separable?
- What is the long-term behavior of a quantum system?

A relatively nonintuitive result is that chaos may take place in low-dimensional systems. Because atoms are simple microscopic low-dimensional systems that have to be described by quantum mechanics, they are among the best available prototypes for studying quantum chaos. The goal of this chapter is to present and discuss the most important progress in this area.

When chaos is present, it is generally impossible to obtain analytic expressions (even approximate ones) for the time evolution of the system. Hence, chaotic systems are intrinsically *complex* systems lying beyond any traditional analytic description. On the other hand, complex systems are not necessarily chaotic, but may have similar statistical properties. For example,

recent experimental results on *mesoscopic* systems (Bouchiat and Montabaux, 1990; Al'tshuler *et al.*, 1991) suggest that the universal fluctuations observed could have the same origin as the spectral fluctuations (see Section III.A) of quantum chaotic systems. In that sense, quantum chaos can also be thought of as a first step in the direction of complex systems.

B. CHAOTIC ATOMIC SYSTEMS

Compared with other microscopic complex systems (nuclei, atomic clusters, semiconductors, etc.), atoms have the great advantage that all the basic components are well understood: These are essentially point particles interacting through a Coulomb static field. Hence, it is possible to write an explicit expression of the Hamiltonian.

A definite advantage of atomic systems is that they can be studied theoretically and *experimentally*. The word *experiment* must be understood here to mean traditional laboratory experiments, but also numerical experiments. Indeed, currently available computers make it possible to compute numerically properties of complex systems described by simple Hamiltonians. During the last 10 years, the constant interaction between the experimental results and numerical simulations led to major advances in the field of quantum chaos, as is shown later.

A crucial result is that classical chaos can only exist in systems where different degrees of freedom are *strongly* coupled. [this is a consequence of the celebrated KAM theorem (Lichtenberg and Liberman, 1983).] This implies that a small perturbation added to a regular system cannot make it chaotic. In other words, atomic systems where chaos is supposed to play an important role require *nonperturbative* situations, where, in addition to the Coulomb binding force, the electrons are submitted to additional forces of comparable strength. This can be easily realized on the simplest atom, hydrogen, by applying to it an external field. Different situations can be realized depending on the type of field used (magnetic, electric, or both) and on its time dependence.

We first consider the case of a hydrogen atom in a static external electric field. Small corrections to the pure Coulomb potential in the hydrogen atom (finite mass of the nucleus, relativistic corrections, spin effects, QED corrections, spontaneous emission, etc.) do not affect the global (regular or chaotic) behavior of the system and can be neglected. Throughout this chapter, we use atomic units, where the mass, the absolute value of the charge of the electron, and the Planck's constant are equal to 1. In these units, the Hamiltonian is (Delande, 1991):

$$H = H_0 + \mathbf{F} \cdot \mathbf{r} \quad (1)$$

where H_0 is the field-free Hamiltonians:

$$H_0 = \frac{\mathbf{p}^2}{2} - \frac{1}{r} \quad (2)$$

$\mathbf{p}$ and $\mathbf{r}$ are, respectively, the momentum and position of the electron, and F is the electric field in atomic units of 5.14×10^9 V/cm. Fortunately (unfortunately as far as chaos is concerned!), this Hamiltonian is separable in parabolic coordinates (Harmin, 1982) and the motion is fully regular.

The case of the static magnetic field is more interesting. In cylindrical coordinates, and using the symmetric gauge $\mathbf{A} = \frac{1}{2}\mathbf{r} \times \mathbf{B}$ for the vector potential, the Hamiltonian is given by:

$$H = H_0 + \frac{\gamma}{2}L_z + \frac{\gamma^2\rho^2}{8} \quad (3)$$

where γ denotes the magnetic field (along the z axis) in atomic units of 2.35×10^5 T, and L_z the z component of the angular momentum.

Because of the azimuthal symmetry around the magnetic field axis, the paramagnetic term $\gamma L_z/2$, responsible for the usual Zeeman effect, is just a constant. The diamagnetic term, $\gamma^2\rho^2/8$, is directly responsible for the onset of chaos in the system. The competition between the Coulomb potential with spherical symmetry and diamagnetic potential with cylindrical symmetry governs the dynamics. As a crude criterion, chaos is most developed when these two terms have the same order of magnitude. For a quantum state of principal quantum number n , this gives:

$$\gamma n^3 \simeq 1 \quad \text{that is, } Bn^3 \simeq 2.35 \times 10^5 \text{ T} \quad (4)$$

This can be realized in a laboratory experiment with Rydberg states $n \simeq 40$ to 150 (Iu *et al.*, 1991; Holle *et al.*, 1988; van der Veldt *et al.*, 1993).

When written in cylindrical coordinates, the Hamiltonian (3) describes a time-independent two-dimensional system belonging to the class of the simplest possible chaotic systems (Lichtenberg and Leiberman, 1983). This makes this system an almost ideal prototype for the study of quantum chaos (Friedrich and Wintgen, 1989).

A combination of static electric and magnetic fields can also be used. When the two fields are not parallel (for example, perpendicular), the system is fully three dimensional and described by the Hamiltonian:

$$H = H_0 + \frac{\gamma}{2}L_z + \frac{\gamma^2\rho^2}{8} + \mathbf{F} \cdot \mathbf{r} \quad (5)$$

Again, the nonperturbative regime is reached when the impact of the three fields (Coulomb field of the nucleus, external magnetic field, and electric field) is comparable. In addition to Eq. (4), this implies:

$Fn^4 \simeq 1$ in atomic units, that is

$$Fn^4 \simeq 1 \times 10^9 \text{ V/cm in laboratory units} \quad (6)$$

which is relatively easy to realize in laboratory experiments (Raithel *et al.*, 1991).

Finally, it is possible to replace the external field with the internal field due to another electron of the same atom. This brings back the three-body problem (helium or helium-like atoms) described by the following Hamiltonian (Z is the charge of the nucleus):

$$H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (7)$$

From the chaos point of view, an interesting situation arises when the two electrons have comparable excitations. Strong dynamical correlations between the two electrons are expected, leading to a breakdown of the independent electron picture. The corresponding doubly excited states, lying very close to the *double* ionization threshold, are autoionizing states with weak optical excitation probabilities from low excited states, which does not make it easy to observe them (Domke *et al.*, 1992; Eichmann *et al.*, 1992; Camus *et al.*, 1989).

Different dynamical properties are expected for systems whose Hamiltonian shows an explicit time dependence. The easiest way to introduce such a dependence is to apply an external oscillating electric field on a hydrogen atom. For a monochromatic field of amplitude F and angular frequency ω , polarized along the z axis, the Hamiltonian in the length gauges is

$$H = H_0 + Fz \cos \omega t \quad (8)$$

Because of the azimuthal symmetry around the electric field axis, the system is effectively two dimensional. In numerical experiments and theoretical investigations, a simplified one-dimensional model of the atom has been widely used (Casati *et al.*, 1988; Galvez *et al.*, 1988; Bayfield *et al.*, 1989; Sauer *et al.*, 1992; Jensen *et al.*, 1989).

Chaotic dynamics can be observed only in a nonperturbative regime, that is, when the amplitude and frequency of the external field are comparable

to the amplitude of the Coulomb field on the n 'th Bohr orbit and to the classical Kepler frequency of the electron. This gives:

$$\begin{cases} Fn^4 \simeq 1 \\ \omega n^3 \simeq 1 \end{cases} \text{ in atomic units, or} \quad \begin{cases} Fn^4 \simeq 1 \times 10^9 \text{ V/cm} \\ \omega n^3 \simeq 5 \times 10^{15} \text{ Hz} \end{cases} \text{ in laboratory units} \quad (9)$$

Such a situation can be obtained by applying a strong infrared laser to a weakly excited state. However, the spatio-temporal characteristics of the laser pulse are then extremely important for the dynamics of the atoms, ions, and electrons produced. Such complications usually hide the regular or chaotic aspects (L'Huillier *et al.*, 1991).

Another possibility is to employ highly excited states ($n \simeq 60$) and a microwave field. This system led to numerous important experimental and theoretical results and is discussed in Section V.

For a circular polarization of the external electric field, classical studies have shown that the system is mainly regular and of poor interest as long as chaos is concerned (Zakrzewski *et al.*, 1993).

C. IONIZATION: A COMPLICATION OR A USEFUL TOOL?

Chaos or regularity manifest themselves during the long-term behavior of the system. For this reason, it is often studied (in classical mechanics) for bounded systems where the different components may interact during an indefinitely long time. Atoms do not belong to this type of systems, because they can *ionize*. Hence, they are prototypes for studying the effect of *transient chaos*, that is, chaos *on a finite time scale* (fixed by the lifetimes of the resonances).

A complementary point of view is given by scattering experiments, when the dynamics near the scatterer is chaotic. Clearly, the physics is the same, although the language is somewhat different (Smilansky, 1991).

On the other hand, ionization provides a simple tool for analyzing the electron dynamics. Experimentally, we can easily detect whether an atom is ionized after interaction with an external field, whereas it is much more complicated to measure its internal state. Ionization is a by-product of the underlying quantum dynamics. Although it is only a very rough measure of the final state of an atom, it can provide much physical insight. The most striking example is the dynamics of the hydrogen atom in a microwave field where most experiments just measure the ionization probability.

D. SCALING PROPERTIES

One of the main difficulties in the study of the semiclassical limit $\hbar \rightarrow 0$ is that the value of the Planck constant is fixed in laboratory experiments. One can get around this difficulty in atomic systems thanks to the existence of scaling laws. Indeed, the Coulomb potential and other interaction potentials discussed earlier are power functions of the position and momentum. Thus, a convenient scaling of all variables and external fields leaves the equations of motion invariant. This scaling transformation is (Delande, 1991):

$$\begin{aligned} \mathbf{r} &\rightarrow \lambda^{-1} \mathbf{r} \\ \mathbf{p} &\rightarrow \lambda^{1/2} \mathbf{p} \\ H &\rightarrow \lambda H \\ t &\rightarrow \lambda^{-3/2} t \\ F &\rightarrow \lambda^2 F \\ \omega &\rightarrow \lambda^{3/2} \omega \\ \gamma &\rightarrow \lambda^{3/2} \gamma \end{aligned} \tag{10}$$

where λ is any positive real number. This means that different initial conditions with different external fields may have exactly the same classical dynamics. A simple example is the field-free motion of the electron, which is an elliptic trajectory whatever its (negative) energy. This is no longer true in quantum mechanics, because of the absolute scale imposed by the Planck constant $\hbar$. Different scaled situations observed experimentally correspond to the same classical dynamics with different effective values of the Planck constant.

Hence, in a real (or numerical) experiment, the semiclassical limit $\hbar \rightarrow 0$ can be studied by tuning simultaneously toward higher excited states the energy and the characteristics of the external fields according to Eq. (10). This possibility is extremely important for understanding the classical-quantal correspondence. The best example is so-called “scaled spectroscopy,” where the wavelength of the exciting laser (which determines the energy of the excited state under study) is scanned together with the external static electric and/or magnetic field (see Section III.C).

The scaled variables are those quantities defined in Eq. (10) that are invariant under the scaling transformation. An example is the scaled energy ε of a hydrogen atom in a magnetic field (Delande, 1991; Friedrich and Wintgen, 1989; Hasegawa *et al.*, 1989):

$$\varepsilon = E\gamma^{-2/3} \tag{11}$$

which measures the energy of the electron in units of magnetic field. Because of the scaling law, the classical dynamics, instead of depending both on E

and γ , actually depends only on ε , whereas quantum properties depend *a priori* on both quantities.

In the crossed magnetic and electric fields, an additional scaled quantity, measuring the electric field in "units of magnetic field" has to be introduced. It is $f = F\gamma^{-4/3}$. For helium-like atoms, the situation is even simpler. Whatever the (negative) total energy, the entire dynamics is fixed and depends only on the discrete parameter Z . This is in sharp contrast with the quantum properties, which clearly depend on whether the total energy is above or below the first ionization threshold.

For time-dependent systems, the situation is somewhat more complicated, because the energy is no longer conserved. However, a standard experiment consists of preparing a Rydberg state with principal quantum number n and applying a microwave field to it. The convenient scaled quantities are the scaled field amplitude and frequency (Casati *et al.*, 1988), defined through [see Eq. (10)]:

$$\begin{cases} F_0 = Fn^4 \\ \omega_0 = \omega n^3 \end{cases} \quad (12)$$

In any case, the use of scaled variables is necessary for a correct understanding of the classical-quantal correspondence.

E. LABORATORY EXPERIMENTS VERSUS NUMERICAL EXPERIMENTS

From a conceptual point of view, experiments on chaotic atomic systems should be done on excited states of the simplest atoms, hydrogen (in external field) or helium. Because of the high density of Rydberg states, a selective excitation requires the use of lasers. Unfortunately, the desired wavelengths are not always easily obtained with current laser technology. For this reason, many experiments have also been done on Rydberg states of different atomic species. It is reasonable to expect that the perturbation induced by the presence of the atomic core on the Rydberg electron will not affect too much its regular/chaotic properties. However, this does not go beyond a questionable assumption. The atomic core is a small object with a radius of a few Bohr radii; whether any semiclassical approximation can be used to represent its effect is far from obvious. The simplest way is to use an effective potential $V_c(r)$ in addition to the Coulomb potential, replacing the zero-field Hamiltonian by:

$$H_0 = \frac{\mathbf{p}^2}{2} - \frac{1}{r} + V_c(r) \quad (13)$$

The core potential is chosen so that it reproduces the observed quantum defects of the different l series of Rydberg states. However, different model potentials give roughly the same quantum defects, but different classical dynamics. This shows that the atomic core is a *pure quantum object*, which

does not have any straightforward classical counterpart.

The main effect of the core potential is to break the Coulomb degeneracy of the energy levels. In most cases, in the strong field regime where all hydrogenic states are supposed to be strongly mixed, this effect is probably weak (see Section III.A). However, in the case of the microwave ionization, there are strong experimental and numerical indications that this assumption is not true (Blümel *et al.*, 1991; Arndt *et al.*, 1991; Buchleitner, 1993).

From the theoretical point of view, the hydrogen atom is entirely calculable using its dynamical group $SO(4,2)$. The use of group theory allows extremely efficient numerical experiments (Delande, 1991; Friedrich and Wintgen, 1989; Hasegawa *et al.*, 1989). The Hamiltonian of an atom in an external field, when expressed in a basis adapted to its internal dynamical properties, can be represented as a sparse matrix. Using an efficient diagonalization algorithm, one is able to compute very accurately, highly excited energy levels and wave functions. For example, computing the 1000'th excited state of a hydrogen atom in a magnetic field of a few teslas with 8 significant digits is nowadays an easy task! It is even more surprising when it is found to be in exact agreement with the (less accurate) experimental measurement (see Fig. 3 later in this chapter)!

This method makes it also possible to compute the dynamics of a hydrogen atom in a time-dependent external field (Buchleitner and Delande, 1993). In addition, use of the complex coordinate method allows for the full inclusion of the effect of ionization and atomic continua (Delande *et al.*, 1991). Recently, it has been successfully extended to the helium atom, taking into account the *exact* interelectronic repulsion (Wintgen *et al.*, 1992). Another recent advance is the extension to nonhydrogenic atoms, by inclusion of a core potential (Halley *et al.*, 1993).

The main advantage of numerical experiments is their flexibility and their ability to give information that is extremely difficult or even impossible to measure (for example, a wave function). On the other hand, they require big and expensive computers. For two-dimensional time-independent or one-dimensional time-dependent problems, the numerical experiments are now possible in realistic conditions. In higher dimensions, this is more difficult—at the border of feasibility—and experimental results are of major importance.

From the ensemble of recent experimental and theoretical results, one has to choose subjectively the most interesting ones. From our point of view, the main concern in quantum chaos is to establish an understandable connection between traditional quantum properties—energy levels, eigenstates, wave functions, etc.—and the rather novel point of view of time-dependent dynamics, which is more suitable for comparison with classical dynamics. These different aspects are studied in the following sections. First, we discuss what we think is the skeleton of the classical and quantal dynamics, the existence and ordering of the different *time scales* of the system. We then

turn to the *spectroscopic* (in an extended sense) aspects, including wave functions, ionizations, and excitation probabilities. Finally, we discuss the dynamics of classical and quantum regular and irregular systems, with an emphasis on time-dependent systems.

II. Time Scales—Energy Scales

A. CLASSICAL SCALES

Depending on the nature of the classical dynamics, there may be different time scales in the evolution of an atomic system. The first one is the typical period, which can be characterized, for example, by the period T_0 of the shortest periodic orbit. Typically, for a Rydberg atom with principal quantum number around 50, it is of the order of a few picoseconds (Delande, 1991).

For a chaotic system, neighboring initial conditions diverge exponentially with time. The associated time constant T_{chaos} is a second time scale, which describes the typical time on which the memory of the initial condition is lost. For a typical strongly chaotic system, this time scale is of the order of the shortest period.

An additional complication arrives when the motion is not bounded, that is, when the atom ionizes. The additional time scale T_{ion} is then the lifetime of the atom. If $T_{\text{ion}} \ll T_{\text{chaos}}$, chaos is beaten by ionization; a discussion in terms of regularity or chaos is irrelevant in this case. This is experimentally observed for atoms in ultrastrong, pulsed laser fields (L'Huillier *et al.*, 1991) and not discussed in this chapter. Except in this situation, all experiments in chaotic atomic systems have been performed under conditions where the ionization time is reasonably long, of the order of nanoseconds or microseconds.

The most complicated situation is observed when the classical dynamics is in the mixed regular-chaotic regime, depending on the initial conditions. There, one observes classical structures that can trap some trajectories or strongly inhibit the diffusive-like chaotic motion. The exact nature of these classical structures is not extremely clear (Percival, 1991). They seem to be remnants of the invariant tori existing in the regular regime. They are known as *vague tori* or *cantori* and apparently have a fractal structure. Contrary to invariant tori, they are not impermeable and a trajectory can escape from such a structure. The associated leaking time is another time constant for these mixed systems. It seems that, in fact, different time scales exist (at various scales). To our knowledge, these phenomena are not well understood even in the classical context. The hydrogen atom in a microwave field provides an example of such a system with mixed dynamics and several

time scales. This makes the detailed interpretation of the quantum results very difficult.

B. QUANTUM SCALES

Additional time scales, depending on $\hbar$, exist for quantum dynamics. This can be understood from the following example. Consider a time-independent bound quantum system with Hamiltonian H in an arbitrary initial state $|\psi(t=0)\rangle$. It obeys the Schrödinger time evolution equation:

$$H|\psi(t)\rangle = i\hbar \frac{d|\psi(t)\rangle}{dt} \quad (14)$$

The solution of this equation can be expressed using the discrete eigenstates and eigenvalues of the Hamiltonian H :

$$H|\phi_i\rangle = E_i|\phi_i\rangle \quad (15)$$

with the following expressions:

$$|\psi(t)\rangle = \sum_i c_i \exp\left(-i\frac{E_i t}{\hbar}\right) |\phi_i\rangle \quad (16)$$

where the constant coefficients c_i are computed from the initial state by means of

$$c_i = \langle \phi_i | \psi(t=0) \rangle \quad (17)$$

The autocorrelation function of the quantum system is a diagonal element of the time-evolution operator $U(t) = \exp(-iHt/\hbar)$:

$$\begin{aligned} C(t) &= \langle \psi(0) | \psi(t) \rangle = \langle \psi(0) | U(t) | \psi(0) \rangle \\ &= \sum_i |c_i|^2 \exp\left(-i\frac{E_i t}{\hbar}\right) \end{aligned} \quad (18)$$

It is a discrete sum of oscillating terms and, consequently, a quasiperiodic function of time. This is *extremely different* from a classical autocorrelation function for a chaotic system, which is decreasing on the characteristic time scale T_{chaos} and does not show any revival at longer times (Lichtenberg and Liberman, 1983).

The time-evolution operator is the Fourier transform of the Green's function (Gutzwiller, 1990; Balian and Bloch, 1974):

$$G^+(E) = \frac{1}{E + i\eta - H} = \sum_i \frac{|\phi_i\rangle \langle \phi_i|}{E + i\eta - E_i} \quad (19)$$

$$U(t) = -\frac{1}{2i\pi} \int_{-\infty}^{\infty} G^+(E) \exp(-iEt/\hbar) dE \quad (20)$$

[This expression is valid for $t > 0$ provided a small imaginary part η is added to the energy so that integrals are well defined; a similar expression can be written for $t < 0$ with $G^-(E)$.]

The Fourier transform of the autocorrelation function

$$\tilde{C}(E) = \int_{-\infty}^{\infty} \exp(iEt/\hbar) C(t) dt = \sum_i 2\pi\hbar |c_i|^2 \delta(E - E_i) \quad (21)$$

is thus a diagonal term of the Green's function:

$$\tilde{C}(E) = i\hbar \langle \psi(0) | G^+(E) - G^-(E) | \psi(0) \rangle \quad (22)$$

If we now consider the Fourier transform over a finite time interval, instead of over the whole range of time from $-\infty$ to $+\infty$, we obtain a smoothed version of the quantum spectrum:

$$\tilde{C}_T(E) = \int_{-T}^T \exp(iEt/\hbar) C(t) dt = \sum_i 2\pi\hbar |c_i|^2 \frac{\sin \frac{T(E - E_i)}{\hbar}}{\frac{T(E - E_i)}{\hbar}} \quad (23)$$

For short T , the different broadened peaks centered at energy levels E_i overlap, and $\tilde{C}_T(E)$ is a globally smooth function as its classical counterpart. In such a situation, it is possible (although nothing proves that it is always the case) that the quantum $\tilde{C}_T(E)$ mimics classical chaotic behavior. The important point is that, for large T , the different peaks do not overlap and the discrete nature of the energy spectrum *must* appear in $\tilde{C}_T(E)$, regardless of the initial state. The typical time needed for resolving individual quantum energy levels is simply related to the mean level spacing ΔE through

$$T_{\text{break}} = \frac{\hbar}{\Delta E} \quad (24)$$

After this break time, the quantum system *cannot* mimic the classical chaotic behavior, which has a continuous spectrum. Since T_{break} depends on $\hbar$, one can understand how quantum dynamics tends to classical dynamics as $\hbar$ goes to zero. The mean level spacing is given by the Thomas-Fermi approximation and scales as $\hbar^f$, with f the number of degrees of freedom. For two- (or higher) dimensional systems, T_{break} tends to infinity as $\hbar \rightarrow 0$. Hence, on a *fixed* interval of time, the quantum dynamics may tend to the classical one as $\hbar$ goes to 0, although the convergence is not uniform with time. This statement has to be understood in its strict mathematical sense: Different values of the fixed interaction time t demand in general different values of $\hbar$ in order to achieve the desired approximation of the classical limit by the real quantum system. The longer the interval of time, the smaller the $\hbar$ needed to obtain the convergence of the mean value of a quantum observable to the value of the corresponding classical quantity. This

illustrates the noncommuting character of the limits $t \rightarrow \infty$ and $\hbar \rightarrow 0$.

In some sense, after the break time, the quantum system “knows” that the energy spectrum is discrete, it has resolved all individual peaks, and the future evolution cannot bring any essential new information. As a consequence, the system cannot explore a new part of the phase space, so it freezes its evolution, repeating forever the same type of dynamics. Any diffusive-like dynamics is then prohibited by pure quantum effects after the break time. This is the origin of the *dynamical localization* (Casati *et al.*, 1988; Fishman *et al.*, 1982) experimentally observed for the dynamics of Rydberg states in a microwave field (see Section V). Since the density of states strongly depends on the number of degrees of freedom, T_{break} may vary over many orders of magnitude in atomic systems. Typical orders of magnitude are nanoseconds to microseconds for atomic Rydberg states studied experimentally.

Whether an intermediate time scale exists that is shorter than T_{break} and limits the quantum-classical correspondence is mainly unknown.

Finally, the natural lifetimes (due to spontaneous emission) are usually of the order of hundreds of microseconds, much longer than any time scale relevant to regular or chaotic behavior. This is why the system can be considered to be governed by a nondissipative Hamiltonian.

III. Spectroscopy

In this section, we discuss the basic spectroscopic properties of chaotic atomic systems, including positions of the different energy levels and related properties like oscillator strengths and lifetimes of resonances. We show that the onset of chaos is characterized by well-defined properties of the quantum spectrum, which have important experimental consequences.

A. PROPERTIES OF INDIVIDUAL ENERGY LEVELS

The goal of traditional spectroscopy is to assign quantum numbers to the different energy levels in order to obtain a complete classification of the spectrum. Good quantum numbers are associated with conserved quantities, that is, operators commuting with the Hamiltonian. In a classically ergodic system, the trajectories generically explore uniformly all the available phase space, which discards the existence of conserved quantities (except energy for time-independent systems). The same is valid in quantum mechanics: Quantum chaos is characterized by the *destruction of good quantum numbers*.

This is illustrated in Fig. 1, which shows the evolution of the energy levels

FIG. 1. Energy levels of a hydrogen atom versus magnetic field for typical Rydberg states ($L_z = 0$, even parity series). At low field (left part of the figure), the classical dynamics is regular and the energy levels (quasi-) cross. The quantum eigenstates are defined by a set of good quantum numbers. In the right part of the figure, the classical dynamics is chaotic, the good quantum numbers are lost, and the energy levels strongly repel each other. The strong fluctuations in the energy levels are a characteristic of chaotic behavior.

of a hydrogen atom as a function of the magnetic field strength. At low magnetic field, when the classical motion is regular, approximate good quantum numbers exist. States with different sets of good quantum numbers do not (or weakly) interact. A given eigenstate can be unambiguously followed in a wide range of field strength, since it crosses (or has very small avoided crossings with) the other energy levels. In this regular regime, it can be shown that, because of the existence of conserved quantities, a given classical trajectory does not explore the entire phase space, but only a subspace known as an *invariant torus*, almost like a separable system. It is possible to quantize semiclassically such a system using the EBK procedure (Gutzwiller, 1990; Ozorio, 1988). This is a natural extension of the usual WKB quantization rule along each almost separated coordinate and provides an efficient semiclassical quantization scheme for individual energy levels in association with good quantum numbers (see also Section IV.A for the wave functions in the regular regime). Actually, the energy levels predicted from the EBK quantization should not be distinguishable from the exact quantum result in the left part of Fig. 1.

When chaos invades the major part of the classical phase space (right part of Fig. 1), this quantization scheme cannot be used: The sizes of the avoided crossings increase and individual states progressively lose their identities and the associated good quantum numbers.

In the fully chaotic regime, the energy levels and the eigenstates strongly

FIG. 2. Two numerical simulations of an excitation spectrum of hydrogen atoms in a magnetic field γ from the ground state. Although the magnetic field changes by only 3 parts in 1000, the spectra are completely different. This shows the extreme sensitivity of chaotic spectra on small changes of parameters.

fluctuate when the magnetic field is changed. An example is given in Fig. 2 where a relative change of 0.3% in the magnetic field is enough to scramble the spectrum. In that sense, the quantum system shows a high sensitivity on a small perturbation as its chaotic classical equivalent. The energy spectrum of a classically chaotic system displays an extreme *intrinsic* complication, which means the death of traditional spectroscopy.

Such extremely complex spectra have been observed experimentally in several atomic systems in external fields (magnetic field, crossed electric and magnetic fields) and numerically on virtually all chaotic systems. It is probably the simplest and most universal property. Figure 3 shows an experimental spectrum of the lithium atom in a magnetic field, compared with the numerical simulation on hydrogen. Both display the same complicated reproducible details and the agreement is excellent (Iu *et al.*, 1991).

FIG. 3. Comparison between the experimental spectrum of the lithium atom in a magnetic field $B \simeq 6.113$ T ($L_z = 0$, even parity series) and the theoretical spectrum of the hydrogen atom computed using the complex coordinate method, shown as mirrors of each other. The agreement is excellent. Aside from an overall intensity scale factor, there is *no* adjustable parameter.

This also proves that the atomic core is only a small perturbation.

This qualitative property has been put on firm ground by a study of the statistical properties of energy levels (Bohigas, 1991). The simplest quantity is the distribution of nearest neighbor spacings (energy difference between two consecutive levels, normalized to the mean level spacing). In the regular regime [see Fig. 4(a)], consecutive energy levels generally have different sets of good quantum numbers and do not interact. The distribution of spacings is one of uncorrelated levels, that is, a Poisson distribution:

$$P(s) = e^{-s} \quad (25)$$

which nicely reproduces the numerical results obtained on different systems and the experimental results on Rydberg atoms in a magnetic field (Delande and Gay, 1986; Friedrich and Wintgen, 1989; Hasegawa *et al.*, 1989).

In the chaotic regime, the strong level repulsion induces a completely different result [see Fig. 4(b)], with practically no small spacing. A simple model is able to predict the statistical properties of energy levels. It assumes a maximum disorder in the system and therefore models the Hamiltonian by a set of random matrices, which couple any basis state to all of the other ones. Depending on the symmetry properties of the Hamiltonian (especially with respect to time reversal), different ensembles of random matrices have to be considered (Bohigas, 1991). For all atomic systems studied, the Gaussian orthogonal ensemble of real symmetric matrices is convenient. The predicted spacing distribution agrees very well with the numerical results for various atomic systems. It is very close to the so-called Wigner distribution:

$$P(s) = \frac{\pi s}{2} \exp\left(-\frac{\pi s^2}{4}\right) \quad (26)$$

FIG. 4. Distribution of energy level spacings (normalized to the mean level spacing) for the hydrogen atom in a magnetic field, obtained from numerical diagonalization of the Hamiltonian. (a) In the classically regular regime, the distribution is maximum at 0 and well fitted by a Poisson distribution (dashed line). (b) In the classically chaotic regime, the probability of finding almost degenerate levels is very small (level repulsion). The results are well reproduced by the Wigner distribution (dashed line) and random matrix theory (Delande and Gay, 1986).

The transition from a Poisson distribution in the classically regular regime to a Wigner distribution in the chaotic regime gives a *characterization* of quantum chaos, at least for highly excited states.

Other statistical properties of the energy levels in the chaotic regime have been studied and are in good agreement with the predictions of random matrix theory (Delande and Gay, 1986). From an experimental point of view, fully resolved clean spectra are needed for extracting spacing distributions. These are difficult to obtain because of the high density of states in the regions of interest and because of possible experimental imperfections (stray fields, etc.), which rapidly spoil the results. Although there is no doubt that the spacing distribution should be Wigner, it has not yet been verified in a real experiment on a chaotic atomic system. Recently, dynamic properties involving different values of an external parameter have been studied and put the sensitivity on external perturbations on a quantitative ground (Zakrzewski *et al.*, 1993b; Zakrzewski and Delande, 1993).

Finding universal properties in the local statistical properties of energy levels for chaotic systems is not a real surprise. As discussed in the preceding section, this range of energy (mean level spacing ΔE) corresponds to a long time behavior ($\hbar/\Delta E \gg T_{\text{chaos}}$), where chaos classically fully develops with its universal properties. Universality is also observed in the corresponding quantum dynamics. On the other hand, at shorter times of the order of T_{chaos} , nonuniversal properties exist in the classical behavior. This implies also a deviation from the predictions of random matrix theory on a large energy scale, as has been numerically and experimentally observed (Delande, 1991).

B. WIDTHS OF RESONANCES

The model of random matrices describes bound spectra and does not take into account the possible autoionization of the atom. If the typical autoionization time is longer than the break time:

$$T_{\text{ion}} \gg T_{\text{break}} \quad (27)$$

the atom does not ionize significantly during the time needed to develop the detailed quantum dynamics. Hence, the energy spectrum and the eigenstates will be essentially well described by random matrix theory. Autoionization comes into play after, as a small perturbation. Each eigenstate is thus coupled to the continua through some operator, which can be modeled by a random matrix. The resulting width of the eigenstate results from the superposition of all the decay channels. As a first approximation, all decay channels have roughly the same importance and the statistical distribution of the widths depends only on the number of open channels. If this number is small, pure quantum effects are very important. This is especially the case

for the hydrogen atom in a magnetic field. In such a case, the magnetic field confines the transverse motion of the electron: Immediately above this first ionization threshold, the electron can ionize only in the magnetic field direction and is left in the lowest Landau level. There is only one channel and the prediction of random matrix theory for the widths Γ of the resonances is the so-called Porter-Thomas distribution (Grémaud *et al.*, 1993):

$$P(\Gamma) = \frac{1}{\sqrt{2\pi\Gamma\bar{\Gamma}}} \exp\left(-\frac{\Gamma}{2\bar{\Gamma}}\right) \quad (28)$$

where $\bar{\Gamma}$ is the average width, which can be obtained from classical dynamics. This formula implies that the small widths are by far the most probable. This nonintuitive result means that the strong statistical fluctuations in the random matrix model tend to compensate each other, the most probable value of any matrix element being zero. This prediction has been checked using numerical experiments (Grémaud *et al.*, 1993). The resulting cumulative distribution $\int P(\Gamma) d\Gamma$ is shown in Fig. 5 in comparison with the Porter-Thomas prediction.

The experimental observation of extremely narrow resonances in the spectrum of the lithium atom in a magnetic field between the first two Landau ionization thresholds (Iu *et al.*, 1991) confirms the predominance of small widths and its extreme sensitivity (as any completely destructive interference process) to a small change of parameter. The agreement between theory and numerical experiment in Fig. 5 for a nontrivial phenomenon clearly shows the relevance of quantum chaos for the understanding of complex atomic systems.

FIG. 5. Cumulative probability of the normalized widths (solid line) compared with the cumulative probability obtained from the Porter-Thomas distribution (dashed line). The agreement is very good, especially for the smallest values. The infinite slope at the origin (square root behavior) is characteristic of only one open channel. The narrow resonances are by far the most probable.

When condition (27) is not satisfied, the different resonances overlap. The ionization process has to be fully, that is, nonperturbatively, included in the classical and quantal dynamics. Such a situation is probably encountered in the experiments on the hydrogen atom in crossed fields as well as in the microwave ionization experiments. Unfortunately, no clean experimental data in this region have been published. Numerical experiments in crossed fields have reached this regime. The random matrix theory here predicts a well-defined signature in the ionization cross section—the so-called Ericson fluctuations (Ericson, 1960)—which are observed in the numerical spectra (Main and Wunner, 1992). This is one more piece of evidence for the relevance of quantum chaos.

C. PERIODIC ORBIT SPECTROSCOPY

The two previous subsections have demonstrated the *universal* character of fluctuations. This also implies that a detailed analysis of all energy levels and eigenstates does not make sense: No interesting information can be brought to the physics of chaotic phenomena beyond the statistical aspects. On the other hand, this does *not* mean that these energy levels do not carry any information; it is just that this information has to be extracted in a different way. More precisely, as the individual specificity of a chaotic system manifests at relatively short times, before universal chaotic features dominate, it has to be found in the long energy range characteristics of the quantum spectra.

From the analysis of Section II, the comparison between quantum and classical properties is more clearly expressed by a Fourier transform of an experimental spectrum, hereby passing from the energy to the more suitable time domain. Indeed, in a typical spectroscopic experiment, a laser is shined on the atoms, and the absorption probability (or related quantities such as the excitation cross section) is measured. The experimental spectrum is close to

$$\tilde{C}(E) = \sum_i |\langle \phi_i | T | g \rangle|^2 \delta(E - E_i) \quad (29)$$

where $|\phi_i\rangle$ are the eigenstates with energy E_i , $|g\rangle$ represents the initial state of the atom, and T is the transition operator, depending on the polarization and properties of the laser used. The finite resolution of the spectra can be accounted for through a simple convolution with the line profile.

A straightforward comparison with Eqs. (14) to (23) shows that the Fourier transform of the spectrum is simply a diagonal element of the time-evolution operator [see Eq. (18)] with the initial state:

$$|\psi(0)\rangle = T|g\rangle \quad (30)$$

where $T|g\rangle$ is not a stationary state of the Hamiltonian, but rather a wave packet. Therefore, performing the Fourier transform of the experimental spectrum is tantamount to studying the time dynamics of this wave packet. In other words, this allows for the investigation of wave packet dynamics with cw lasers. In the specific case of excitation of atomic Rydberg states from a low lying state, $T|g\rangle$ is a small (on the typical scale of Rydberg states) wave packet starting very close to the nucleus. After absorption of a laser photon, the wave packet expands from the nucleus and eventually returns after some time. For such short times, it is reasonable to assume that the wave packet propagates semiclassically along the classical paths. Hence, $C(t)$ should first decrease very rapidly, as the wave packet explodes from the nucleus, then display a bump after the period of a closed orbit, that starts and ends at the nucleus. The amplitude of the bump is directly related to the angular localization of the initial wave packet and thus depends on the initial state and polarization of the laser. Indeed, Fourier transforms of experimental spectra obtained for the hydrogen atom in electric (Harmin, 1982), magnetic (Delande, 1991; Friedrich and Wintgen, 1980) and crossed fields show these bumps at the periods of closed orbits.

The full theory of the effect of closed and periodic orbits on quantum spectra is beyond the scope of this chapter, but certainly among the major achievements of the last years (Bogomolny, 1988; Gao and Delos, 1992). It relies on the qualitative arguments given earlier. The starting point is the Feynman path integral formalism, which is strictly equivalent to the usual formulation of quantum mechanics. It expresses the quantum propagator as a sum over all paths (including unphysical trajectories) connecting the initial to the final point, each path contributing with a factor $\exp(i\int L dt/\hbar)$ where L is the classical Lagrangian. In the semiclassical limit $\hbar \rightarrow 0$, the sum over all paths is calculated with the stationary phase approximation, which selects only classical trajectories (along which the action $\int L dt$ is precisely stationary). This gives the semiclassical approximation to the propagator, known as the Van Vleck propagator. In the next step, the Green function at energy E , Fourier transform of the propagator, is computed with one further stationary phase approximation. The dominant contributions then come from the classical orbits with energy E . The experimentally measured spectra can be computed using this semiclassical Green's function. The simplest quantity is the density of states:

$$d(E) = \sum_i \delta(E - E_i) \quad (31)$$

Considering our previous notation [see Eq. (21)], it corresponds to the case where $|c_i| = 1$, and is nothing but the trace of the Green's function:

$$d(E) = -\frac{1}{\pi} \text{Tr} \text{Im} G^+(E) = -\frac{1}{\pi} \int \langle \mathbf{r} | \text{Im} G^+(E) | \mathbf{r} \rangle d\mathbf{r} \quad (32)$$

If the trace is evaluated again by the stationary phase approximation, one obtains the famous trace formula (Gutzwiller, 1990; Balian and Bloch, 1974) (here written for a two-dimensional time-independent system):

$$d(E) = d_0(E) + \text{Im} \sum_j \frac{T_j}{\pi \hbar} \frac{\exp[i(S_j/\hbar - \alpha_j \pi/2)]}{[\det(M_j - 1)]^{1/2}} \quad (33)$$

which expresses the density of states as a sum over all periodic orbits j with action $S_j(E)$, period $T_j(E)$, and their repetitions (same orbit traveled several times). Here M_j is the monodromy matrix describing the linearized motion around the periodic orbit; α_j is the Morse index (an integer); and $d_0(E)$ is the smooth density of states obtained from the Thomas-Fermi model:

$$d_0(E) = \frac{1}{(2\pi\hbar)^2} \iint \delta[E - H(\mathbf{r}, \mathbf{p})] \, d\mathbf{r} \, d\mathbf{p} \quad (34)$$

Related quantities, such as the density of oscillator strengths observed experimentally, can also be expressed as sums over periodic or closed trajectories.

The trace formula and related formulas establish an intuitive link from quantum to classical mechanics. A difficulty is that the characteristics (period, action, etc.) of the periodic orbits smoothly evolve with the energy E . Thus, the positions and intensities of the peaks in the Fourier transform of a spectrum move with energy, which broadens and smears out the peaks. One can get around this problem using scaled spectra (see Section I.D) obtained from fixed classical dynamics. From Eq. (33), a Fourier transform of the density of states with respect to the effective value of $1/\hbar$ will display δ peaks at exactly the *actions*—instead of the *periods* in the usual spectra—of the periodic orbits.

This periodic orbit spectroscopy of scaled spectra is actually the best method we know for extracting information from chaotic spectra, where a detailed analysis of the individual lines is not particularly enlightening. An example of periodic orbit spectroscopy is given in Fig. 6 for the spectrum of the helium atom in a magnetic field (van der Veldt *et al.*, 1993). The *quantum* spectrum contains 3000 energy levels without any apparent order. Its Fourier transform reveals about 50 peaks at the actions of *classical* periodic orbits. The comparison with the synthetic spectrum obtained from a semiclassical theory inspired by the trace formula (Gao and Delos, 1992) is very impressive. Most of the peaks are reproduced at exactly the right position with a satisfactory intensity.

Those splendid spectra have been obtained in a regime where the dynamics is mainly regular. Other spectra have been recorded on the hydrogen atom in the chaotic regime, at much lower resolution (Holle *et al.*, 1988). Figure 7 shows a series of Fourier transforms of scaled spectra,

FIG. 6. (a) Fourier transform of an experimental spectrum of the helium atom in a magnetic field γ , at constant scaled energy $\varepsilon = -0.7$. It displays peaks at the actions of the classical periodic orbits. Comparison with the semiclassical prediction in (b) shows an extremely good agreement. This proves the major role of classical periodic orbits in quantum spectra. (Courtesy of T. van der Veldt.)

obtained at different values of the scaled energy ε , in comparison with the actions of the periodic orbits. Each peak can be clearly attributed to a periodic orbit and its evolution with ε . The same kind of results have been obtained on scaled spectra of the rubidium atom in crossed electric and magnetic fields (which requires a simultaneous sweep of the laser frequency and the strengths of the two external fields). Again, some peaks are unambiguously related to periodic orbits (Fig. 8) (Raithel *et al.*, 1991). This is an experimental indication that periodic orbits, which are one-dimensional structures, also play a major role in six-dimensional phase space.

The experimental data are not of comparable quality for doubly excited states. Numerical experiments on a two-dimensional simplified model of the helium atom, which assumes the two electrons to be localized in opposite directions with respect to the nucleus, have shown equally the importance of periodic orbits. More importantly, the study of Wintgen *et al.* (1992) shows that the most important orbit is the one where the two electrons have the same excitation, but opposite phases (one electron collides with the nucleus while the other one is at its maximum distance and vice versa). This

FIG. 7. Fourier transform of the experimental spectra of the hydrogen atom in a strong magnetic field γ , obtained at constant scaled energy ε . The different spectra, plotted in (a) for various ε (here denoted by $\bar{E}$), display peaks at the actions of the classical periodic orbits, plotted in (b). The agreement between the experimental quantum Fourier transform and the classical periodic orbits shows their importance for understanding the long range correlations in the chaotic spectra. (Courtesy of K. H. Welge.)

asymmetric stretch is much less unstable than the symmetric one and consequently dominates the spectra (Ezra *et al.*, 1991). This invalidates the traditional approach (Fano, 1983), in which the two electrons are supposed to lie in the symmetric configuration (the so-called “motion” on the Wannier ridge). This important and unexpected result is typical of how the classical mechanics of complex systems can improve our understanding of quantum spectra.

Recently, it has been shown on the basis of theoretical and numerical work that the periodic orbits are not the only relevant structures in chaotic spectra. A complete description must also include *complex* orbits, where time, position, and momentum are made complex (Kus *et al.*, 1993). The relatively small peak at action $S = 3.93$ in Fig. 6 does not correspond to any real periodic orbit, but to a “ghost” (complex) periodic orbit. The inclusion

FIG. 8. Fourier transform of an experimental scaled spectrum of rubidium atoms in crossed electric and magnetic fields. It displays peaks at the actions of classical closed orbits. [Courtesy of Raithel *et al.* (1991).]

of these complex orbits, especially in the vicinity of classical bifurcations, should improve the efficiency of periodic orbit expansions.

D. FROM CLASSICAL TO QUANTUM MECHANICS

The set of preceding figures (Figs. 6 to 8) shows how some collective (not related to a specific energy level) properties of quantum chaotic spectra can be interpreted in terms of classical orbits. Because periodic orbits are dense in a fully chaotic phase space, it can be argued that they contain all the information. However, we basically do not know how this information is shared and structured in the different orbits. It seems that some hierarchy exists, at least for systems where a systematic coding of the periodic orbits is known: Most of the information contained in the very long orbits can be essentially extracted from shorter periodic orbits (Wintgen *et al.*, 1992).

The best way to clarify this issue is to try to compute a quantum spectrum from the knowledge of as many classical periodic orbits as possible. It has been found numerically that this is an extremely difficult problem because of the proliferation of long periodic orbits and because of subtle relations and compensations between them. Resolving individual peaks requires the inclusion in the sum at least all of the orbits of a period shorter than the break time $T_{\text{break}} = \hbar/\Delta E$. For typical Rydberg states, this means billions of orbits, which is, of course, impossible. Thus the trace formula and related formulas are of no practical use for computing semiclassical approximations to the energy levels. Partially successful attempts to overcome this difficulty have been made. In practice, although the trace formula is supposed to be asymptotically valid for highly excited states, it is able to give satisfactory values for the energies of the *lowest states* only! For example, inclusion of 13 periodic orbits allows us to compute correct values for the lowest 10 states of the hydrogen atom in a magnetic field (Wintgen, 1988).

TABLE I
ENERGY LEVELS OF $1S^e$ SERIES OF HELIUM ATOM

State	Periodic Orbit	Cycle Expansion	Exact quantum
1s1s	-3.097	-2.932	-2.904
2s2s	-0.804	-0.777	-0.778
3s3s	-0.362	-0.353	-0.354
4s4s	-0.205	-0.199	-0.201
5s5s	-0.131	-0.129	-0.129

Note. Some energy levels of the $1S^e$ series of the helium atom, compared to the simple semiclassical quantization using only the asymmetric stretch periodic orbit and the more refined "cycle expansion," which includes a set of unstable periodic orbits. The agreement is remarkable, which proves the efficiency of semiclassical methods for this chaotic system. (Courtesy of D. Wintgen.)

A very interesting example in this context is the helium atom, for which the use of cycle expansion (an improvement of the periodic orbit expansion) gives a remarkable value for the energy of the ground state (see Table I). This shows how modern semiclassical mechanics (which is aware of chaos and of the properties of periodic orbits) can solve a simple problem having been discussed for more than 70 years (Wintgen *et al.*, 1992).

Yet, we are far from the goal of computing individual, highly excited states of a chaotic system from the knowledge of its classical dynamics. Using periodic orbits, we can at most compute low-resolution spectra.

IV. Wave Functions: Localization and Scars

In this section, we discuss the general properties of the wave functions of a classically chaotic system, with emphasis on the localization properties. As for individual energy levels, the wave functions are extremely sensitive to any change of a parameter or any perturbation. In a first approximation, random matrix theory predicts that the wave functions are random waves, uniformly distributed over the entire phase space. This is the quantum equivalent of an ergodic classical trajectory. However, because of quantum interference effects, differences *must* exist, especially at long times. Any eigenstate of a quantum Hamiltonian is invariant under time evolution and not uniformly distributed over the phase space. Hence, *quantum ergodicity* is possibly observable in the wave functions only on a scale larger than the typical oscillations, that is, the de Broglie wavelength. The most ergodic wave function one can imagine is then composed of random oscillations at

the de Broglie wavelength superimposed on a smooth uniform background.

Beside the previous general description of chaotic wave functions, specific structures might exist that are related to peculiarities of the system, exactly as periodic orbits are responsible for specific structures in the energy spectrum.

The simplest manifestation of such a specificity is a preferential localization (enhancement) of the wave function in some region of phase space. Unfortunately, there is a large amount of confusion in the current literature regarding different types of localization, which have different physical origin. Among them, the following ones have been discussed and (numerically) observed or predicted:

- Localization in the vicinity of invariant tori in a classically regular system (see Section IV.A)
- Localization on residual structures (such as cantori) in systems with mixed regular-chaotic dynamics (see Section IV.C)
- Localization in the vicinity of *unstable* orbits in globally chaotic systems. Such a localization has been baptized a “scar” (Heller, 1984) of the unstable periodic orbit (see Section IV.B).

In atomic systems, direct experimental observation of wave functions is almost impossible. Hence, we have only indirect proofs of totally or partially localized wave functions. Such proofs rely on measurements of matrix elements involving highly excited chaotic states, which are, of course, affected by the localization. Because of the lack of experimental data in atomic systems, we will mainly present results of numerical experiments.

A. LOCALIZATION IN THE REGULAR REGIME

For a regular system, the EBK quantization predicts a localization of the regular wave functions on the invariant tori of the classical motion (Ozorio, 1988; Gutwiller, 1990). This has been confirmed numerically on several quantum regular systems. The simplest one is the hydrogen atom in a static electric field. Using its separability in parabolic coordinates and semiclassical quantization along these coordinates, we can compute absorption spectra (and consequently wave functions) in excellent agreement (Harmin, 1982) with the experimental observations.

Another example has been recently discovered in the dynamics of the helium atom: There are eigenstates localized on classical invariant tori for the “frozen planet” configuration (Richter *et al.*, 1992).

Similar phenomena have been found in the hydrogen atom in a microwave field. The wave functions of the Floquet states evolve at the period of the microwave field. In the simplified one-dimensional model, there is a resonance between the electronic Kepler motion and the microwave external

field when their two frequencies are equal. The nonlinear terms create the following standard phenomenon: There is a stable periodic trajectory where the electron motion is locked on the external frequency (with a well-defined phase) surrounded by invariant tori and an unstable periodic trajectory with opposite phase embedded in a stochastic separatrix layer (Buchleitner, 1993). Figure 9 shows the time evolution of a quantum wave function associated with an invariant torus. It is clearly an atomic wave packet oscillating back and forth at the frequency of the external microwave. Contrary to normal atomic wave packets, which spread rapidly because of dispersion, this wave packet is *nondispersive* and reproduces itself identically after one period. This is a typical nonlinear stabilization phenomenon, which might be of interest in the context of wave packet studies.

B. LOCALIZATION IN THE CHAOTIC REGIME

The localization of chaotic wave functions in the vicinity of unstable periodic orbits, although it might appear a little surprising at first sight, is after all extremely natural if one comes back to the equations describing the quantum dynamics. For times of the order of the shortest periods, the

FIG. 9. Wave functions of Floquet eigenstates of a one-dimensional hydrogen atom in a microwave field. The states evolve in time with the periodicity of the external microwave field. We show the wave packets at phases 0, $\pi/2$, and π (from left to right). *Top*: When the classical motion is regular, the quantum wave packet is localized in phase space, locked on the external frequency, and *nondispersive*. *Bottom*: When the classical motion is chaotic, the quantum wave packet may be partially localized on complex phase space structures, with a quasirandom background. Note the phase difference of π s between the regular and chaotic wave packets.

semiclassical Van Vleck propagator can be used, which means that a localized wave packet essentially evolves classically. Let us consider an initial wave packet $|\psi(0)\rangle$ lying close to the classical orbit with an initial momentum close to the classical momentum on the orbit, for example, a coherent state. Its localization is limited by the Heisenberg inequalities, but in the semiclassical limit $\hbar \rightarrow 0$, an accurate localization is possible. For short times, it will evolve as a dispersing wave packet approximately following the classical periodic orbit. On the other hand, its time evolution can also be described by the quantum equations (14) to (23). This has two consequences:

- Because the modulus of the overlap between the wave packet $|\psi(t)\rangle$ and an eigenstate $|\phi_i\rangle$ is constant with time, the latter cannot be localized only on one point or one part of the periodic orbit. It is either scarred by the whole orbit or not scarred at all.
- The autocorrelation function $C(t) = \langle \psi(0) | \psi(t) \rangle$ displays peaks at multiples of the period T , because the wave packet comes back at its initial point. Of course, because of the dispersion of the wave packet, the returning peaks get smaller and smaller and finally disappear. However, the low-resolution Fourier transform of $C(t)$ will display peaks at the inverse period $2\pi\hbar/T$. From Eq. (23), these peaks are unresolved superpositions of the contributions of the various energy levels. Consequently, some of the eigenstates must have enhanced values of $|c_i| = |\langle \phi_i | \psi(0) \rangle|$. In other words, some wave functions of eigenstates must have an enhanced amplitude on the initial position, that is, a scar of the periodic orbit.

Moreover, these arguments make it possible to predict quantitatively where the peaks are located and thus where scars are expected to be. The resulting condition is known as the scar quantization condition (Delande, 1991; Gutzwiller, 1990):

$$S(E) = \oint \mathbf{p} \cdot d\mathbf{r} = 2\pi\hbar \left(n + \frac{\alpha}{4} \right) \quad (35)$$

where $S(E)$ is the action of the periodic orbit, α its Morse index, and n a non-negative integer. This formula, although it is strongly reminiscent of the WKB quantization condition, is of a different nature. It is only an approximate indication of where scarred states have the highest probability of being. Indeed, nothing proves that the different unresolved states lying under the peaks of the low-resolution Fourier transform are democratically scarred. All we know is that *collectively* they carry a well-defined scar strength. The detailed repartition depends on the long-term behavior of the wave packet and cannot be estimated with this approach.

The existence of scars makes the difference between real wave functions and random waves. Scars appear because they are the only possible intense manifestations of chaotic fluctuations compatible with the dynamics.

The scarring phenomenon is nothing but intrinsic fluctuations plus semiclassical propagation.

It also follows that scars are stronger if the orbit is short and weakly unstable. An example of a scar, obtained in a numerical experiment for the hydrogen atom in a magnetic field, is shown in Fig. 10.

An indirect experimental proof of the existence of partial localization of chaotic wave functions has been obtained on the rubidium atom in crossed electric and magnetic fields. It uses an inhomogeneous electric field to induce deflection of an atomic beam proportionally to the static electric atomic dipole moment. If the wave functions were purely random waves, the electric dipole moment would be close to an average fixed value (classical average over the accessible phase space). On the contrary, experimental results, displayed in Fig. 11, indicate the existence of large electric dipole moments and large variations with the different parameters (Raithel *et al.*, 1993). Although it is not obvious that we should associate the large dipole moment with a specific classical structure (saddle fixed point, periodic orbits, etc.), this nevertheless proves that localization phenomena exist in this real chaotic system.

C. LOCALIZATION IN THE MIXED REGULAR-CHAOTIC REGIME

Localization phenomena are much more difficult to analyze in mixed systems. Indeed, contributions come from the remaining invariant tori

FIG. 10. Wave function of the hydrogen atom in a magnetic field. We show the 474th excited state ($L_z = 0$, odd parity series) at scaled energy $\varepsilon = -0.2$, scarred by the classical almost circular unstable periodic orbit shown in superimposition. The dotted line is the line of classical turning points.

FIG. 11. Experimental measurements showing the dipole-deflection pattern as a function of a scaled electric field. The variations of the average electric dipole moment are probably related to localization of the eigenstates on classical structures (Courtesy of Raithel *et al.*, 1993.)

together with various structures of the phase space. The latter cannot be reduced to isolated periodic orbits, as in a fully chaotic system. The main reason is the existence of lots of different time scales, which strongly prevents the quantum system from approaching ergodicity. Additional information is needed to interpret the quantum spectra properly, such as sizes and geometrical shapes of the unstable regions surrounding unstable orbits, geometries of separatrices between different types of motion, existence and geometries of partial barriers, etc.

A typical example is the one-dimensional hydrogen atom in a microwave field. The phase space is mixed and structured by the different resonances between the atomic and the external frequencies. Figure 9 shows an atomic state, evolving periodically with the microwave frequency, localized near the unstable periodic orbit, in phase opposition with the stable resonance, and the surrounding phase space. It is the counterpart to the quantum state localized on the principal resonance discussed earlier. One clearly sees the wave packet oscillating back and forth emerging from a rather erratic background. Analysis of phase space plots of such a state shows that it contains essential contributions from the stochastic layer surrounding the unstable periodic orbit. Hence, analyzing such a system in terms of the scar of an unstable periodic orbit (Jensen *et al.*, 1989; Sauer *et al.*, 1992) is an

adventurous extrapolation and certainly an oversimplified view of localization in mixed systems. Note also that strictly analogous localized wave packets, periodic in time with *no dispersion*, have also been observed in numerical simulations of three-dimensional atoms (Buchleitner, 1993).

D. RELATIONSHIP BETWEEN LOCALIZATION AND LIFETIME

An important question is one of whether the localization of atomic wave functions on bound phase space structures implies some stability versus ionization. In general ionization takes place in an outer region of the atom, where the binding Coulomb field is relatively weak, while significant phase space structures are localized in the inner part, where all interactions have the same order of magnitude. Thus, any relation between localization and the ionization rate indicates the existence of a long-range correlation in phase space. This certainly happens in regular systems where the relevant structures, invariant tori, extend throughout phase space, as has been demonstrated for the hydrogen atom in a static electric field (Harmin, 1982) and for the frozen planet configuration of the helium atom (Richter *et al.*, 1992).

For a strongly chaotic system, long-range correlations are not expected, and scarring by an unstable periodic orbit should not increase (or decrease) significantly the lifetime of an atomic state. Strong numerical evidence of this decorrelation exists for the case of atoms in a magnetic field above the ionization threshold (see Section III.B). This explains why residual regularities as scars are not relevant for the ionization rate and the success of the random matrix predictions.

Mixed regular-chaotic systems are much more complicated. Residual long-range correlations exist, but not in a systematic way. Hence, scarring might favor low ionization rates, as suggested by Jensen *et al.* (1989), but there is no systematic one-to-one correspondence. It is certainly oversimplified and essentially wrong to associate a reduced ionization rate with an individual scar of an unstable periodic orbit.

V. Dynamics

A. TIME-INDEPENDENT SYSTEMS

Although the study of the temporal dynamics of a quantum system provides us with the clues for understanding quantum chaos (see Section II), very few

direct measurements have been done in the chaotic regime. Actually, as shown earlier, Fourier transforms of spectra obtained with cw lasers allow for the same information in an easier way. Furthermore, there is no equivalent of scaled spectroscopy in the time domain. Any wave packet excited in a real experiment by a short laser pulse has a certain dispersion in energy and will consequently spread quite rapidly, which is avoided in scaled spectroscopy. Consequently, it is not very likely that new interesting physical information can be obtained from such time-resolved experiments on time-independent systems.

B. TIME-DEPENDENT SYSTEMS

For explicitly time-dependent Hamiltonian systems, the situation is completely different. Experimental results are badly needed, especially for the long-time dynamics, which is difficult to study in numerical experiments. The present status of technology allows us to excite and probe atomic systems on very short time scales, of the order of 1 ps or less. For excited Rydberg states, this is shorter than the Kepler period of the electron. A new generation of experiments in atomic physics is born. Most probably, fascinating unexpected results on quantum chaotic dynamics will be discovered in the near future.

The hydrogen atom in a microwave field is a first step in this direction, because it contains an explicit time dependence, but can also be reduced to a static problem by use of the Floquet theorem as a consequence of its time periodicity. The exchange of energy between the different degrees of freedom, which is usually difficult to measure in a microscopic multidimensional system, is equivalent here to the number of photons exchanged between the atom and the external field, a much more accessible quantity. A rough estimation of the energy exchange is the ionization probability of the atom, by far the easiest quantity to measure in an experiment. It contains some information on the dynamics, but in a strongly convoluted form.

In view of the success of spectroscopy of chaotic time-dependent systems, it should be interesting to perform the spectroscopy of the Floquet states of the microwave problem, eventually followed by a Fourier transform. Although in principle feasible, Floquet spectroscopy has not yet been performed.

In a typical experiment, the atoms are prepared in an excited Rydberg state, then exposed to the microwave for a finite well-defined interaction time and finally analyzed. The analysis can simply be the ionization probability or, in a more refined experiment, the internal state of the atom is analyzed by (static) field ionization. The shape of the ionization signal versus the static field strength is sensitive to the values of the principal

FIG. 12. Experimental ionization probability of hydrogen atoms after interaction with a microwave field versus the field amplitude. The curve has a typical threshold behavior, a signature of a classical phenomenon. (Courtesy of P. Koch.)

quantum number populated after the interaction with the microwave.

Figure 12 shows a typical experimental result: The ionization probability plotted versus the microwave field strength displays a threshold behavior (Sauer *et al.*, 1992). The field strength at which 10% of the atoms is ionized, defines the *10% ionization threshold*, which, in turn, is a smooth function of the microwave frequency. This behavior is in sharp contrast to the standard photoeffect where the threshold behavior is observed on the *frequency* dependence of the ionization probability, independently of the field amplitude. The latter is a signature of a quantum effect, whereas the former is rather characteristic of a classical phenomenon. The key observation is that the gross features of the ionization process depend only on the scaled variables of Eq. (12): Different ionization curves for different initial states, but at the same scaled frequency and plotted versus the scaled amplitude, do approximately coincide. As explained in Section I.D, this is a clear signature of a classical phenomenon. It does not discard the possibility of finding a quantum interpretation, but it proves that a classical one, without specific quantum interferences, has to exist. Conversely, any deviations from this scaling behavior are the signature of a quantum effect.

Figure 13 shows the scaled 10% ionization threshold versus the scaled frequency, as observed experimentally (Bayfield *et al.*, 1989). In the low-frequency regime, the threshold tends to the static threshold, as it should. At larger frequencies, it decreases up to a scaled frequency $\omega_0 \simeq 1$ where it starts to increase again. For the classical system, the phase space is mixed regular-chaotic, because of various resonances between the atomic and external frequencies. The classical ionization threshold is associated with the disappearance of the last invariant torus separating the initial state of the

FIG. 13. Scaled 10% ionization threshold versus the scaled frequency, from the experimental results of Bayfield *et al.* (1989). Above $\omega_0 = 1$, the experimental results (symbols, dashed line) significantly deviate from the classical result (dotted line). This supports the theory of dynamic localization, whose prediction is indicated by the solid line. (Courtesy of I. Guarneri.)

atom from the continuum. Above this value, the classical dynamics is essentially a diffusive-like motion leading to relatively fast ionization. The comparison between the classical threshold and the quantum experimental results shows a globally excellent agreement up to $\omega_0 \simeq 1$; above, the experimental result lies systematically higher, which signifies that the quantum system is *more stable* than the classical one.

Strong experimental and numerical proofs show that this phenomenon is of quantum origin:

- Starting from higher values of the principal quantum number n_0 , at the *same* value of ω_0 , leads to a quantum threshold a little lower. At fixed ω_0 , the threshold tends to the classical prediction with increasing n_0 , as it should do in the semiclassical limit (Buchleitner, 1993).
- When broadband noise is added to the microwave field, the threshold decreases and tends to the classical one (Arndt *et al.*, 1991). The noise amplitude needed to induce such an effect is very small, not sufficient to affect strongly the classical dynamics. The correct interpretation is that noise destroys the subtle phase coherence effects in the quantum system.
- Numerical experiments show that the ionization probability is very sensitive to small changes (of the order of 10^{-3}) of the scaled frequency at a fixed value of n_0 . This has been related to the sensitivity of individual Floquet states on small changes of parameters (Casati *et al.*, 1988; Buchleitner, 1993), a *quantum* consequence of classical chaos, as shown in Section III.A.

FIG. 14. Scaled 10% ionization threshold of a one-dimensional hydrogen atom (initial principal quantum number $n_0 = 23$) in a microwave field versus the interaction time t (numerical experiment). The different curves correspond to different values of the scaled frequency (from top to bottom, $\omega_0 = 2.7, 3.0, 2.0, 1.43, 1.3, 0.6$, and 0.8). This shows a weak dependence over more than 4 orders of magnitude in the interaction time, apparently of the algebraic type. This result strongly supports the theory of dynamical localization.

- Numerical experiments where the interaction time with the microwave is changed over several orders of magnitude show a very weak dependence of the 10% threshold with the interaction time (see Fig. 14) without displaying a systematic dependence on ω_0 (Buchleitner, 1993). This is inconsistent with the diffusive-like chaotic excitation and ionization predicted by classical dynamics. It agrees with an experimental observation on rubidium atoms (Arndt *et al.*, 1991).

We currently interpret these results to be an effect of *dynamical localization* due to the relatively long interaction time between the atom and the microwave (few hundreds periods): The quantum time dynamics initially follows the diffusive classical one, but “freezes” after the break time (Casati *et al.*, 1988; Fishman *et al.*, 1982; Blümel *et al.*, 1991). Of course, this is only a qualitative argument: Ionization does not stop after the break time, but it is strongly reduced.

A direct experimental observation on rubidium Rydberg states, analyzed by static field ionization, effectively shows this freezing of the atomic evolution after some break time (see Fig. 15) and supports the theory of dynamic localization (Blümel *et al.*, 1991). By means of simplified classical

FIG. 15. Field ionization signal of rubidium Rydberg states. (a) Initial state $84p_{3/2}$. (b) The same initial state after interaction with a microwave field during 100 ns. (c) Same as (b), but interaction time equal to 1000 ns. The absence of evolution between (b) and (c) strongly supports the theory of dynamic localization (Blümel *et al.*, 1991).

time dynamics and a simplified one-dimensional model of the atom, quantitative predictions on the effect of dynamical localization on the threshold behavior (Casati *et al.*, 1988) have been obtained, which agree quite well with experimental results (see Fig. 13). Numerical experiments (Buchleitner and Delande, 1993) also show that the same phenomenon exists for a three-dimensional atom as well as for a simplified one-dimensional model. In the former situation, because of the additional degree of freedom, the mean level spacing between Floquet eigenstates is much smaller and the simple expression for the break time [Eq. (24)] predicts a much longer time for the manifestation of dynamical localization. The reason is probably that Eq. (24) is valid for a strongly chaotic system, but not for mixed systems. In the real experiments, the influence of remaining structures in phase space on the break time is not known.

VI. Conclusions

We believe that the experimental, theoretical, and numerical results discussed in this review clearly show how the concepts of classical chaos in low-dimensional Hamiltonian systems provide one with new and interesting physical insights into the dynamics of complex quantum systems. The general behavior of a chaotic quantum system may have different complementary aspects depending on which physical quantities are probed:

- On a narrow energy interval—roughly at the level of individual eigenstates—the quantum structures display strong apparently random fluctuations and a high sensitivity to any small change of an external parameter. This is the quantum counterpart of the classical sensitivity to initial conditions on long time scales.
- On a large energy scale, where spectral properties are averaged over several states, the individual features of the studied system become manifest, the best example being the importance of periodic orbits and scars.

The two preceding aspects are well separated in the semiclassical limit, that is, for highly excited states. A major unsolved problem is to understand what happens for weakly excited states, far from the semiclassical limit. There, the standard characterization of quantum chaos by the statistical properties of the energy levels breaks down. This is highly relevant for experimental systems such as molecular physics, where the complexity comes not from the strong excitation of a few degrees of freedom, but from the simultaneous excitation of many different degrees of freedom.

A second very difficult problem is the quantum behavior of systems with mixed regular-chaotic dynamics—by far the most common ones. Theoretical guides are lacking here. It is likely that progress will be achieved in this direction in the near future.

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