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Manifestations of chaos in atoms, molecules and quantum wells

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The role of atoms and related systems in external fields in the study of the manifestations of classical chaos in quantum systems is reviewed. Periodic orbit theory is a major theoretical framework for the interpretation of the irregular atomic spectra that are observed when the corresponding classical motion is chaotic: quantum spectra are modulated and 'scarred' by unstable periodic orbits, isolated in a surrounding 'sea' of chaotic paths. Recent work has additionally highlighted contributions from other, classically forbidden types of paths, for example, diffractive orbits in non-hydrogenic atoms, 'ghost' periodic orbits near bifurcations, tunnelling orbits which allow quantum transport through potential barriers and dynamical barriers such as tori, and also orbits of a new type—saddle orbits—that are important in experiments probing localized observables. Techniques of atomic physics such as R-matrix and Floquet methods and scaled-energy spectroscopy have been important in exposing some of these effects.

Keywords: atoms; chaos; quantum chaos; semiclassical methods; mesoscopic physics

1. Introduction to quantum chaos

(*a*) *Quantum chaos on short time-scales: periodic orbits and beyond*

Quantum spectra for which the corresponding classical motion is chaotic are extremely irregular in appearance. Individual quantum states defy classification in terms of quantum numbers since in general there is no conserved quantity, other than the energy. Hence one impetus to quantum chaology has been the need for a means to interpret and classify such dense and disordered spectra. The earliest approach involved the study of statistical distributions of energy levels in order to identify 'universal' properties common to very different dynamical systems, but atomic experiments in particular singled out a formula derived by Gutzwiller as a powerful tool for the interpretation of the spectra of highly excited atoms in external fields.

In the Feynman picture, the quantum dynamical behaviour is obtained as a sum of interfering paths each associated with a phase, given by its action S and an amplitude A, $\sim \sum A \exp \mathrm{i}S/\hbar$. At high energies, in the semiclassical limit, the phases $S/\hbar$ associated with different paths are large (this is referred to as $\hbar \to 0$ limit). Hence, neighbouring paths rapidly fall out of phase and their rapidly oscillating contributions cancel by destructive interference. The most important contributions come from paths for which the action is stationary; in other words, where neighbouring paths interfere constructively.

By evaluating the relevant oscillating Feynman path integrals by stationary phase, Gutzwiller was able to relate a chaotic quantum spectrum to a sum over certain classical paths. These are the classical trajectories that are isolated and unstable but retrace themselves repeatedly: periodic orbits. The importance of this work became clear in experiments and theory in atomic physics in the 1980s (Wintgen 1987; Holle *et al*. 1988; Friedrich & Wintgen 1989). Apparently, random atomic energy level spectra and photoabsorption spectra were shown to have underlying regularities corresponding to periodic orbits. When certain scaling transformations are exploited these can easily be exposed by a simple Fourier transform, as seen in figure 1. We can see that the Fourier transformed spectra are very cleanly modulated by oscillations at well-defined frequencies. These frequencies correspond to the actions of classical periodic orbits. The heights of the peaks are determined accurately by the stability of the classical orbits. The photoabsorption peaks are different from the eigenvalue modulations since photoabsorption spectra are not described by the Gutzwiller formula but by a related semiclassical theory: closed orbit theory (Du & Delos 1988; Alber 1989; Bogomolny 1989; Gao *et al*. 1992). Some of the peaks correspond to stable orbits, others to unstable orbits. In the latter case the stability parameter (Liapunov exponent) determines the rate at which neighbouring paths diverge exponentially. A periodic orbit can be stabilized or destabilized at a bifurcation.

Figure 2 illustrates the quantal manifestation of the loss of stability of an important periodic orbit (R_1) of a hydrogen atom in a magnetic field. The figures show a cut through phase space. In the classical case the global phase space structure is shown. For the quantum case three individual quantum states (their Wigner functions) showing high intensity on the periodic orbit R_1 are shown for the stable, bifurcating and unstable case. For the latter case we see that the classical phase space seems featureless, while the quantum probability is still highly concentrated on the isolated unstable periodic orbit. This phenomenon is termed quantum 'scarring' (Heller 1984), and is one of the best studied phenomena of quantum chaology.

The applications of periodic orbits and related theories to interpret spectral features, not just of atoms but also small electronic devices such as quantum wells in tilted fields or quantum dots (Marcus *et al*. 1992; Fromhold *et al*. 1994; Muller *et al*. 1995), molecular vibrational spectra (Weston & Child 1996; Huppert *et al*. 1997; de Polavieja *et al*. 1994; Pollak 1990), and even optical properties of laser resonators in the chaotic regime (Gmachl *et al*. 1998), have multiplied.

A host of advances have also followed in studies of atoms in static fields. The first fully quantal calculation on hydrogen in a field was by Clark & Taylor (1982). Theoretically, a major step was the application of R-matrix theory (Burke *et al*. 1971) to calculations of fully quantal spectra of atoms and molecules in fields (O'Mahony & Taylor 1986; Monteiro & Taylor 1990). The R-matrix method was combined with the scaling transformations which enable reliable comparison with periodic and closed orbit theories (Monteiro & Wunner 1990; Jans *et al*. 1993; Delande *et al*. 1994) and showed that non-hydrogenic Rydberg atoms differed strongly in their periodic orbit behaviour and statistics from hydrogen. In particular, the statistical distributions indicated that they were near the chaotic limit even at energies where hydrogen is regular. Monteiro & Wunner (1990) found new spectral modulations not seen in hydrogen.

Since the classical dynamics was expected to be similar for all atoms, this posed a problem. After all, hydrogen in magnetic fields is well described by the Gutzwiller for-

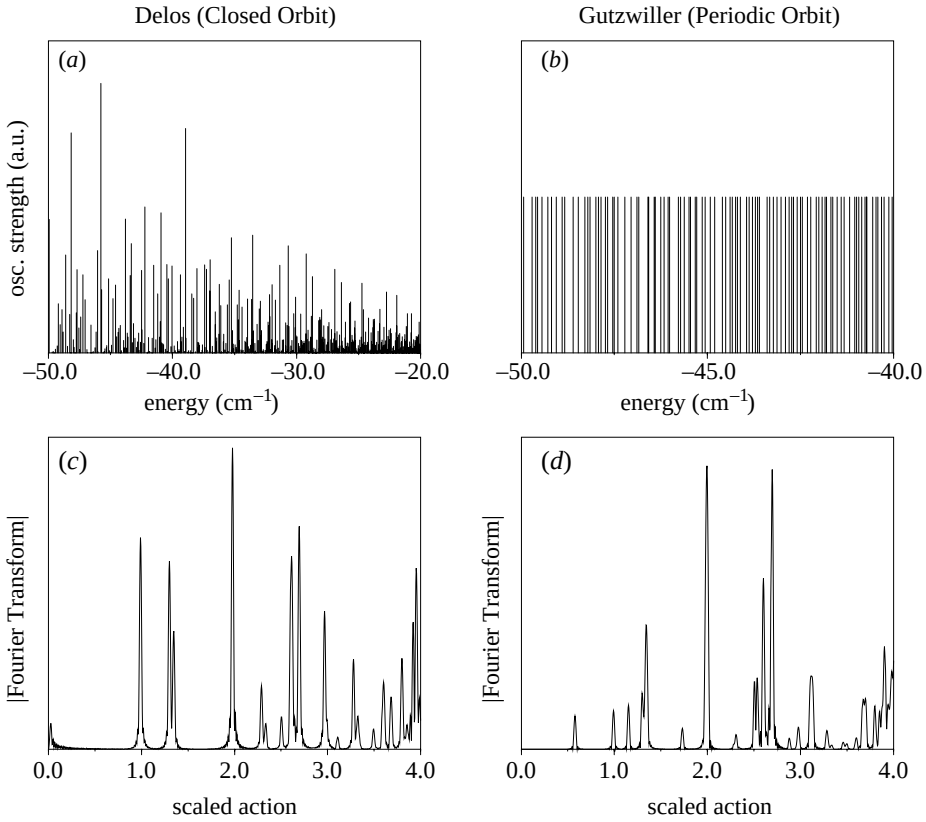

Figure 1. Comparison between calculated $m = 0$, even parity (a) photoabsorption and (b) energy level spectra for hydrogen in a magnetic field. (c), (d) The corresponding Fourier transforms that reveal the periodicities in the spectral modulations. While the actual spectra are very irregular, the Fourier transformed spectra are very cleanly modulated at specific frequencies. The energy level spectra are modulated by periodic orbits while photoabsorption spectra are modulated by closed orbits.

mula. Recently, we were able to show that the Gutzwiller trace formula can be made to work for all atoms by allowing for a 'failure' of the stationary phase approximation analogous to optical diffraction (Dando *et al*. 1998). Corrections to the semiclassical theory of the photoabsorption spectrum were also made (Dando *et al*. 1995).

The R-matrix-type approach for the solution of non-hydrogenic systems was improved by an efficient method using a Schneider term on the boundary (Delande *et al*. 1994). This technique, combined with a Lanczos algorithm for diagonalization of the Hamiltonian matrix, meant the highest Rydberg states that could be calculated went up from $n \sim 50$ to $n \sim 500$. Improvements in experimental techniques meant that scaled spectra resolving the finest detail—individual quantum states—were now possible. These developments meant that very stringent quantitative tests of closed-orbit modulations became possible in quantal and experimental atomic photoabsorption spectra.

Figure 3 shows a comparison between experimental and theoretical modulations

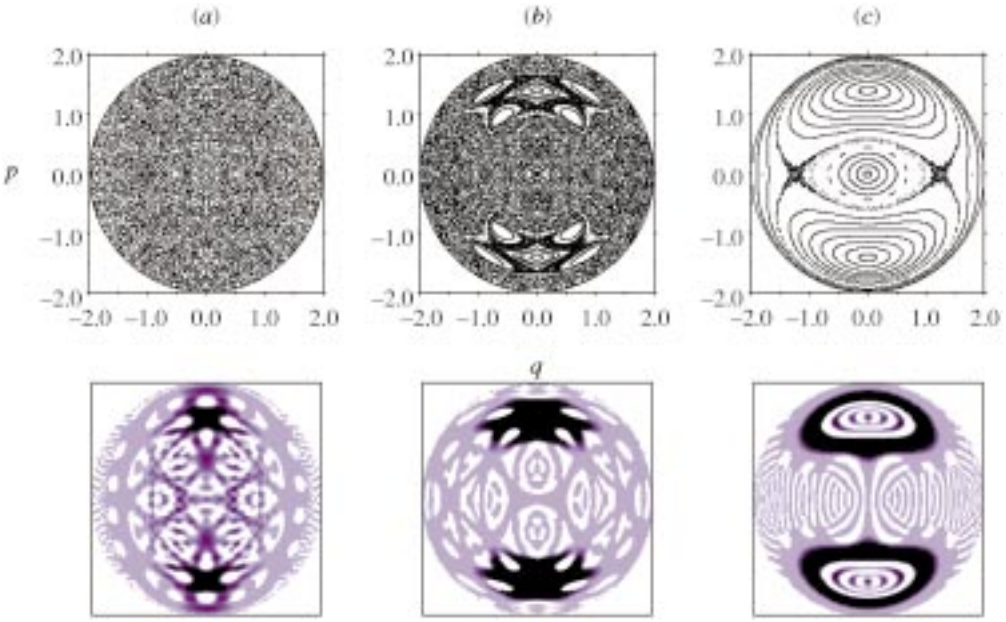

Figure 2. This figure shows the transition from regular to chaotic dynamics for hydrogen in a magnetic field B as the scaled energy $\varepsilon = EB^{-2/3}$ is increased. Above are shown three Wigner functions and classical Poincaré surfaces-of-section for hydrogen atoms in a magnetic field at scaled energies (a) $\varepsilon = -0.1$ (scarred state), (b) $\varepsilon = -0.316$ (bifurcation) and (c) $\varepsilon = -0.5$ (torus quantization on an island of stability).

for Rydberg helium in a magnetic field. The spectra show diffractive effects (additional peaks not seen in hydrogen atoms) as well as a peak that is due to another contribution termed a 'ghost'.

A 'ghost' is a modulation associated with a periodic orbit that has not yet been born (Kuś *et al*. 1993). A new quantum spectral oscillation is seen to appear at energies below a 'tangent' bifurcation at which a pair of new periodic orbits (one stable, the other unstable), is born. Below the bifurcation energy one finds contributions from complex periodic orbits. In an interesting connection with atomic scattering, the correction to the Gutzwiller formula at a tangent bifurcation (the formula diverges) is along similar lines to the correction for coalescing stationary points in semiclassical rainbow scattering (Child 1991) in atomic collisions.

In these studies one cannot stress enough the importance of scaling, where in both experiment and theory the fields and energy are adjusted simultaneously so as to keep the classical dynamics constant. Atoms in both static and oscillating fields have this property. The technique of fixed, scaled-energy spectroscopy was pioneered by Wintgen (1987) for atoms in static fields.

Some mesoscopic systems also have this property. Mesoscopic systems are electronic devices small enough that wave-like interference effects become important. Quantum dots which, like atoms, also exhibit shell structure and spin effects have been even termed 'artificial atoms' (McEuen 1997). Much of the current interest in quantum chaos centres on mesoscopic systems. Oscillations in the conductance from coherent recurrences along periodic orbits have been demonstrated for quantum dots where electrons are confined in circular or stadium-shaped enclosures (Marcus *et al*.

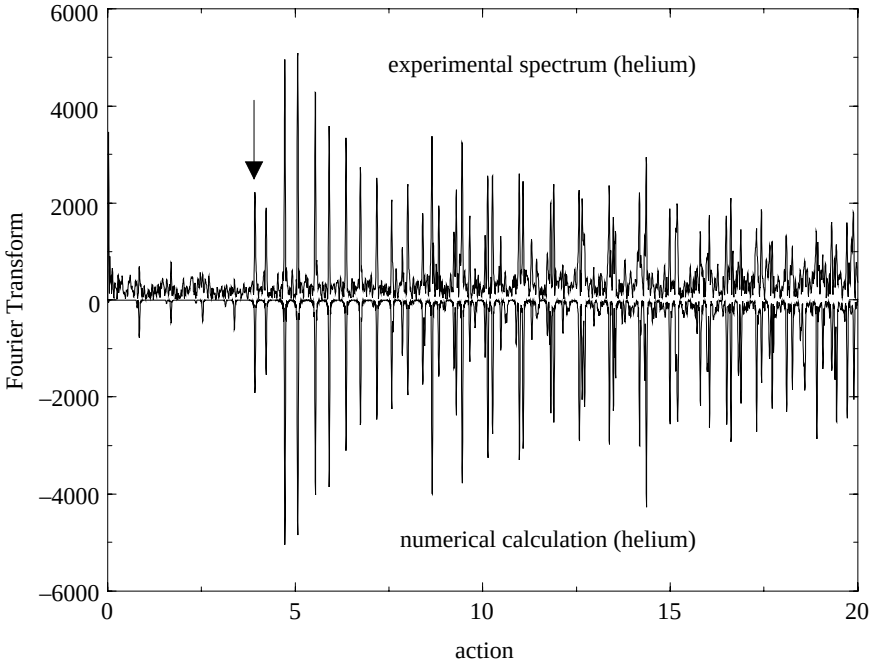

Figure 3. Figure shows a comparison between fully quantal and experimental closed-orbit modulations for helium atoms in magnetic fields (Delande *et al*. 1994). The arrow indicates the contribution of a 'ghost', a complex periodic orbit that appears in the quantum spectrum at an energy below the bifurcation at which it is born.

1992). For periodic orbit phenomena, quantum wells in fields (Fromhold *et al*. 1994) really stand out. These are a type of realization of a two-dimensional particle in a box problem, in the presence of electric and magnetic fields. Coherence times in these experiments are short: only about 1 in 10 electrons survive coherently each circuit along a periodic orbit, so these systems are most suitable for the short-time regime. In a set of experiments at Bell Laboratories, Muller *et al*. (1995) obtained a large amount of data, comprising tens of thousands of oscillations (a few are shown in figure 5 below) spanning a wide set of dynamical regimes and enabling one to analyse the results with quantum scaled spectra (Monteiro *et al*. 1997*b*). This showed oscillations that were not well described by periodic orbits, but rather with a new and peculiar type of complex path, a saddle orbit (Saraga & Monteiro 1998).

In addition to 'ghosts' and saddle orbits, complex periodic orbits also occur when tunnelling through potential barriers is involved. For example, Creagh & Whelan (1997) investigated a two-dimensional tunnelling problem, with a symmetric double-well potential. They calculated periodic orbit modulations of the tunnelling-induced energy splittings of eigenstates in a symmetric double-well potential by including the complex periodic orbits that cross the barrier. For atoms in electric fields there is a potential barrier for energies close to the Stark saddle for which the tunnelling has recently been investigated semiclassically in the fully regular ('integrable') regime (Beims *et al*. 1998). An interesting type of tunnelling phenomenon is dynamical tunnelling, which involves quantum transport across phase-space barriers. An con-

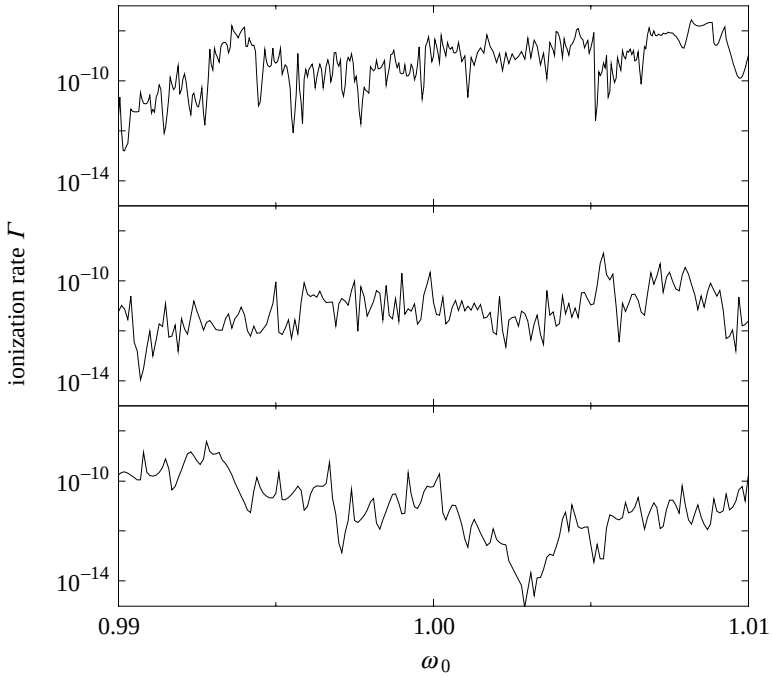

Figure 4. Fluctuations in multiphoton ionization of hydrogen atoms in microwave fields obtained by diagonalization of the Floquet Hamiltonian (Zakrzewski *et al*. 1995). The ionization rates as a function of field from are shown for eigenstates trapped inside stable islands. They show fluctuations analogous to universal conductance fluctuations seen in chaotic mesoscopic systems. These appear in a three-dimensional model (top), two-dimensional model (middle) and even one-dimensional model (bottom).

sequence of this effect has been identified, from fully quantal Floquet calculations by Zakrewski *et al*. (1995), in quasi-random fluctuations in the multiphoton ionization of certain states of atoms in oscillating fields. These states are non-spreading wave packets 'trapped' inside islands of stability at resonances between the Kepler frequency and the field. Escape to the continuum occurs by tunnelling out of this island into the surrounding chaotic 'sea'. These observed fluctuations are analogous in origin to a well-known mesoscopic effect, universal conductance fluctuations due to interference between different paths in the chaotic regime.

In sum, non-classical additions to the basic semiclassical models (such as diffractive orbits, ghosts and bifurcations, tunnelling effects and saddle orbits) are valuable tools for the interpretation of novel features in quantum spectra in the chaotic regime. These are detailed in the following sections, but first we briefly outline some other key areas in the field.

(*b*) *Quantum chaos on long time-scales*

The effects discussed above (including the corrections to periodic orbit theory) all appear as low-resolution features in the experimental energy spectra of atoms and mesoscopic devices. This is tantamount to restricting oneself to short time-scales. In

other words, they are accounted for by a small subset (about 3 for the mesoscopic system and about 100 for atoms) of periodic orbits. These are the shortest orbits, also responsible for the strongest 'scarring'.

Including longer orbits has the effect of resolving finer and finer details of the semiclassically computed spectrum. One might thus hope to obtain fully resolved eigenvalue spectra obtained purely from periodic orbits and their classical stabilities. Unfortunately, the number of periodic orbits proliferates exponentially with increasing period. The Gutzwiller formula is a non-convergent infinite sum. Any semiclassical calculation of a quantum spectrum in the chaotic regime will eventually be overwhelmed by this exponential 'wall' of unstable periodic orbits.

In the problem termed the 'quantization of chaotic systems' the aim is to extract actual eigenvalues by improving the convergence of the Gutzwiller formula. Nowadays this approach is seldom of practical value, since new powerful algorithms mean that computational solutions of the Schrödinger equation are preferable, but there are interesting and deep issues in the connection between classical and quantum behaviour in the chaotic regime. Much effort has in fact been expended by quantum chaologists in addressing this problem and pushing semiclassical methods deep into the long-time limit with (Berry 1989; Keating 1993) or even without (Bogomolny 1992) periodic orbits. However, many quantum chaologists have switched over to quantum field theoretical methods as a tool for the study of spectral statistics or spectral 'correlations' of disordered mesoscopic systems (see the textbook on the subject of supersymmetric methods by Efetov (1997)).

An often addressed question is, 'on what time-scales will quantum and semiclassical dynamics part company?' One early answer was the 'log-time', $t_{\log}$. A minimum uncertainty wave packet launched along a classical orbit will spread rapidly if the underlying trajectories are diverging exponentially with time as $\exp \lambda t$. Observed effects from constructive interference as a wave packet recurs along a periodic path and interferes with itself decay exponentially. The time-scale for a wave packet to spread over the available phase space is $t_{\log} \sim 1/\lambda \log \hbar^{-1}$. Another, much longer time-scale is the Heisenberg time, $t_{\mathrm{H}} \sim \hbar/\Delta E$, where ΔE is the typical spacing between eigenenergies. The time-evolution of a quantum system cannot exhibit exponential divergence indefinitely, since a normal quantum eigenstate is a superposition of discrete eigenfrequencies. On a long enough time-scale its evolution must be quasi-periodic; hence there can be no chaos in the classical sense, in a quantum system. The discreteness of a quantum system becomes apparent on the time-scale t_{H}. However, quantum suppression of chaos can appear on an intermediate time-scale, t_{B}, the so-called 'break-time', which is of much interest. t_{B} depends strongly on the dimensionality of the system. An important, unresolved issue is whether one can estimate this very quantal parameter, the break-time, which has its origin in wave interference effects, from classical periodic orbits. The explanation may (see, for example, Cohen 1998) involve considering correlations between the actions of long periodic orbits.

In atomic physics there are two especially important problems associated with chaotic dynamics on longer time-scales: dynamical localization and spectral statistics. Dynamical localization was an effect first identified in a model problem, a quantum kicked rotor (Casati *et al.* 1979). For a periodically driven rotating particle subjected to a regular sequence of impulses the classical dynamics is chaotic and the energy grows diffusively. The quantum equivalent will follow this classical behaviour up to the break-time, t_{B}, after which the chaotic diffusion is arrested. The quantum

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particle's energy becomes exponentially localized about the initial energy with a distribution width characteristic of the particular system. This in effect is a mechanism for the quantum suppression of chaos. Fishman *et al*. (1982) showed that it is analogous to Anderson localization, the exponential localization of electron wave functions in disordered materials—a destructive interference effect that restricts conductivity. The ionization of Rydberg atoms by a microwave field was shown to manifest localization and so became the archetypal example for the experimental and theoretical study of chaos (Casati *et al*. 1987). Only recently though have accurate quantal calculations been undertaken for the full two- or three-dimensional case by diagonalization of the Floquet Hamiltonian with complex coordinate rotation (Zakrzewski *et al*. 1995). Also recently, an extremely clean and convincing experimental demonstration of dynamical localization in cold atoms in traps (Moore *et al*. 1996) was carried out.

2. Periodic orbits and irregular spectra

The Gutzwiller trace formula (see, for example, Gutzwiller 1990) and periodic orbit theory have provided a powerful framework for the analysis of chaotic spectra. The trace formula makes use of the relation between the quantal spectrum (the density of states),

$$N(E) = \sum_n \delta(E - E_n), \tag{2.1}$$

and the trace of the retarded Green's function,

$$N(E) = -(1/\pi)\,\mathrm{Im}\,\mathrm{Tr}\,\hat{G}(E) \tag{2.2}$$

$$= -(1/\pi)\,\mathrm{Im}\int \mathrm{d}q\,\mathrm{d}q'\,\delta(q-q')G(q,q',E). \tag{2.3}$$

The semiclassical form for the Green's function,

$$G(q,q',E) \sim \sum_\gamma \frac{\exp[\mathrm{i}(S_\gamma(q,q',E)/\hbar - \nu_\gamma\pi/2)]}{|D_\gamma|^{1/2}}, \tag{2.4}$$

as a sum over all classical paths γ starting and returning to point q is then substituted into the integral in equation (2.3), where, for a classical path γ, S_γ is the classical action, $S = \int p\,\mathrm{d}q$, D_γ is a matrix of derivatives of S, and ν is a phase that keeps a count of turning points and caustics.

Gutzwiller chose a local reference frame where the components of position $\boldsymbol{q}$ are parallel and transverse to the trajectory (for the simplest case, a two-dimensional system). Then he evaluated the integral equation (2.3) by Taylor expanding the action near closed paths $\boldsymbol{q} = \boldsymbol{q'}$ up to quadratic order transverse to the orbit in order to describe the behaviour of the neighbouring trajectories. In the semiclassical limit $S/\hbar$ is very large, $\exp\mathrm{i}(S/\hbar)$ oscillates violently, so the integral must be evaluated at points where the phase is stationary. In the integral in equation (2.3), this selects those paths for which $\partial S/\partial q - \partial S/\partial q' = 0$, i.e. $P = P'$, initial and final momenta must be equal. This implies that only periodic trajectories—which start and finish with the same momentum at the same point and hence go on to retrace themselves—are involved, rather than the much larger set of closed paths that start and finish at the same point but then do not retrace themselves.

The result is the Gutzwiller trace formula: $N(E)$ is written as the sum of a smooth background term together with an oscillatory part of the form,

$$N_{\mathrm{osc}}(E) = \frac{1}{\pi}\,\mathrm{Im}\sum_n \frac{T_n}{\mathrm{i}\hbar}\sum_j \frac{\exp(\mathrm{i}j(S_n(E)/\hbar - \mu_n\pi/2))}{|\det(M_n^j - I)|^{1/2}}, \tag{2.5}$$

where n is an index representing each periodic orbit, j indicates the number of circuits (traversals) around each orbit, S_n is the classical action, T_n the period, and M_n^j is the classical stability matrix ('monodromy matrix'), which describes the behaviour of neighbouring trajectories. For the two-dimensional atomic, molecular and mesoscopic systems M is a simple 2×2 matrix obtained by considering a small displacement in position and momentum $\delta q, \delta P$ transverse from the periodic orbit (PO) on a surface of section through phase space. The next intersection of the displaced trajectory with the surface of section is at $\delta q_1, \delta P_1$ to the PO. M is obtained by the linearized relation between the two displacements:

$$\begin{pmatrix}\delta q_1\\ \delta P_1\end{pmatrix} = \begin{bmatrix}m_{11}m_{12}\\ m_{21}m_{22}\end{bmatrix}\begin{pmatrix}\delta q\\ \delta P\end{pmatrix}.$$

In the Gutzwiller formula each path is weighted by the diagonal elements of the stability matrix $\sim 1/|m_{11}+m_{22}-2|^{1/2}$. For an unstable orbit the amplitude of each periodic orbit can be re-expressed in terms of a classical parameter the Liapunov exponent, λ_n, which quantifies the rate at which paths in the neighbourhood diverge exponentially from each other, since in equation (2.5) $|\det(M_n^j - I)|^{1/2} = \sinh T_n\lambda_n/2$.

Hence the Gutzwiller formula makes an important and subtle connection between the exponential divergence characteristic of chaos and the properties of the quantum spectrum. As seen below, the theory of photoabsorption involves a different semiclassical theory since the spectrum is weighted by an oscillator strength. In that case each orbit is weighted by an off-diagonal element of M, i.e. $\sim 1/|m_{12}|^{1/2}$.

3. Beyond periodic orbits

An increasing number of failures of the basic assumptions made above—that the stationary phase treatment is valid and that periodic orbits are isolated—have been identified in atomic and mesoscopic experiments. They are often termed '$\hbar$-dependent corrections' since they appear at different powers of $\hbar$ relative to the leading order (periodic or closed orbit) term. The examples discussed below are not systematic failures of the semiclassical approximation, affecting all POs uniformly, but rather failures due to specific dynamical properties of the atoms or related systems. Below we describe these more exotic contributions and the dynamical conditions which give rise to them. We concentrate on the phenomena needed to interpret real atomic and mesoscopic spectra.

(*a*) *Bifurcations and ghosts*

A critical assumption in the derivation of the Gutzwiller formula is that the stationary phase points are isolated. In the neighbourhood of a periodic orbit, there should not be another periodic orbit of similar action. However, at a bifurcation, new periodic orbits originate from the bifurcating orbit and this assumption is no longer valid.

At the bifurcation M tends to the identity so in the Gutzwiller trace formula the amplitudes become infinite since $m_{11} + m_{22} - 2$ tend to zero. In bifurcations of atoms in magnetic fields too m_{12} goes to zero, so closed-orbit theory diverges. This divergence represents a failure of the semiclassical approximation since the corresponding modulation of the quantum spectrum for small $\hbar$ merely becomes large (increasingly so as the semiclassical limit is approached).

The procedure for removing the divergence due to a bifurcation is well known (Ozorio de Almeida & Hannay 1987), but is specific to each type of bifurcation: there are five main types for well-behaved Hamiltonian systems. Perhaps the simplest type is a tangent bifurcation: a stable periodic orbit and an unstable periodic orbit coalesce and vanish. Classically, it appears to be a case of mutual annihilation. In the quantum case, ghost modulations persist, associated with periodic orbits in complex phase space. The technique for removing the divergence is analogous to the treatment of rainbow scattering in atomic physics (Child 1991). Near the energy of the bifurcation ϵ_{b}, a normal form for the action is used, where the action is expanded to cubic order, rather than quadratic as for the ordinary trace formula. It now contains terms (in appropriately scaled coordinates) like $(\epsilon - \epsilon_{\mathrm{b}})\delta q + (\delta q)^3$, where ϵ is a dynamical parameter like a scaled energy. This functional form will yield two stationary phase points, for $\delta q^2 = (\epsilon - \epsilon_{\mathrm{b}})/3$. This implies two real roots above the bifurcation and two complex roots below (the 'ghosts' (Kuś *et al*. 1993)). An improved treatment, to quartic order 'uniform approximation', was given by Schomerus & Sieber (1997).

Ghosts can be found by solving Hamilton's classical equations in complex phase space and looking for periodic orbits. They are generally very weak contributions to a quantum spectrum, only visible very close to a bifurcation since the complex part of the action ensures that their contribution $\exp \mathrm{i}(S_{\mathrm{r}} + \mathrm{i}S_{\mathrm{i}})/\hbar$ is damped exponentially; typically, S_{i} increases rapidly for energies ϵ below the bifurcation. They have been investigated theoretically in atoms in magnetic fields by Main & Wunner (1997).

However, experiments in quantum wells revealed surprisingly persistent 'ghosts' (Monteiro *et al*. 1997*a*; Saraga & Monteiro 1998*a*). Current oscillations due to coherent recurrences of electrons 'bouncing' back and forth between the walls of a quantum well are shown in figure 5. The dynamics can be accurately related to the characteristic shape and frequency of the oscillations; corresponding quantal calculations are shown. A 'ghost' region of oscillations is indicated where we can find no real periodic orbit that can account for these oscillations. In Saraga *et al*. (1998), the standard procedure of locating complex periodic orbits was followed. A ghost orbit was found, but its contribution decayed far faster than the experimental oscillations. Several other problematic experimental regions were similarly identified. As explained below, the puzzle of these 'long-lived' ghosts led to a redevelopment of the semiclassical theory for this system, in terms of complex, non-periodic paths, which we termed 'saddle orbits'.

(*b*) *Observed spectra: periodic paths, closed paths or saddle paths?*

Typical atomic, molecular and mesoscopic experiments do not detect the density of states

$$N(E) = \sum_n \delta(E - E_n).$$

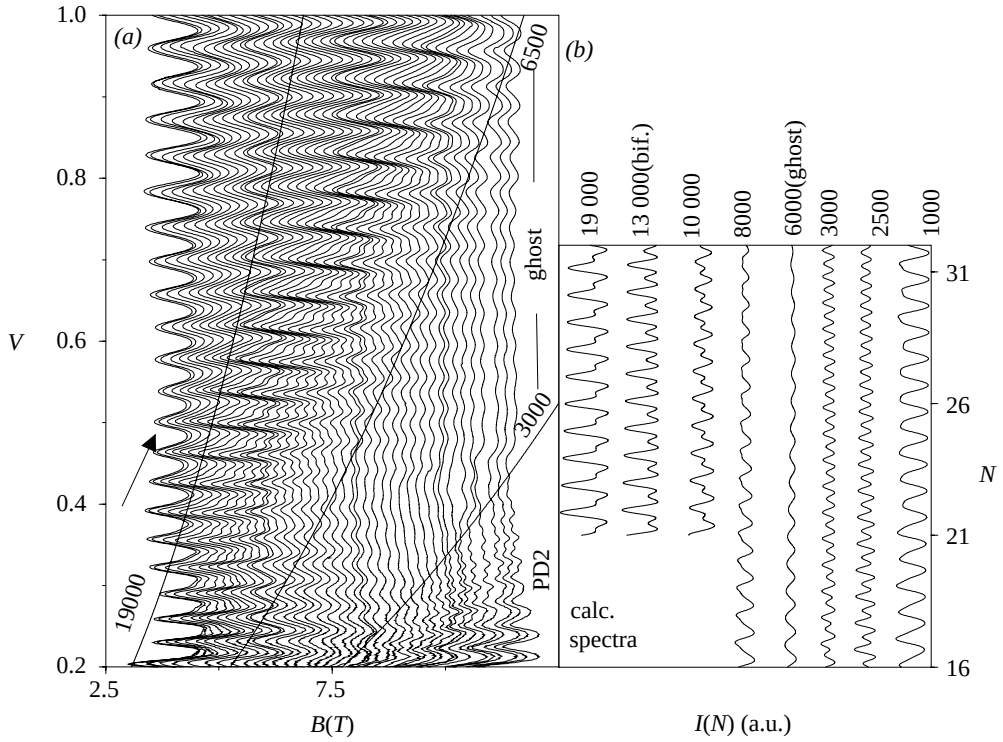

Figure 5. Comparison between experimental and theoretical current oscillations for quantum wells in magnetic B and electric F fields tilted at $\theta = 11^\circ$ to each other. The dynamics is roughly constant along parabolas of constant $\epsilon = V/LB^2$, where V is voltage drop and L is the width of the well. The ghost region below the bifurcation at 6500 is indicated.

They detect rather a quantum spectrum weighted by some observable $\hat{A}$ like an oscillator strength or a current,

$$I(E) = \sum_n \langle n|\hat{A}|n\rangle \delta(E - E_n).$$

In this case, instead of the Gutzwiller formula, a separate semiclassical theory incorporating the relevant matrix element for the expectation value of $\hat{A}$ must be employed. Now the trace must include $\hat{A}$:

$$I(E) = -(1/\pi)\,\mathrm{Im}\,\mathrm{Tr}\,\hat{G}(E)\hat{A}. \tag{3.1}$$

As previously (in a two-dimensional system), the semiclassical form of

$$G(E) \sim \sum_\gamma \frac{1}{m_{12}^{1/2}} \exp[\mathrm{i}(S(q,q')/\hbar - \nu\pi/2)]$$

as a sum over paths from an initial point q to final point q' is used.

Often the weighting involves a projection over some initial state ϕ, i.e. $\hat{A} = |\phi\rangle\langle\phi|$. In many cases one assumes a simple Gaussian form $\phi \sim \exp(-\beta q^2/2)$. This has been used for the semiclassical description of Franck–Condon factors in the excitation of molecules from a ground vibrational state (Zobay & Alber 1994; Huppert *et al.*

1997). A similar form is used for the calculation of the oscillations in the tunnelling current of quantum wells in external fields, since the experiments involve tunnelling from an initial ground Landau state.

There is already a considerable body of work on semiclassical theories of observed spectra in the chaotic regime. Depending on the dynamics and the degree of localization of $\hat{A}$ (i.e. the width of the Gaussian), one can class these calculations into four distinct 'categories'.

(1) The usual formulation of the theory was proposed by Eckhardt *et al.* (1992). In this case $\hat{A}$ was assumed to be smooth in phase space and very slowly varying relative to G, which oscillates rapidly in the semiclassical limit as $\sim \exp \mathrm{i}(S_{path})/\hbar$.

Eckhardt *et al.* evaluated the trace in phase space rather than position space by taking Wigner transforms of $\hat{A}$ and $\hat{G}$. Then the trace in equation (3.1) is an integral over all of phase space:

$$I(E) = -(1/\pi)\,\mathrm{Im}\int \mathrm{d}Q\,\mathrm{d}P\,A(P,Q)G(P,Q). \tag{3.2}$$

The phase-space form (Wigner function) of a the ground harmonic oscillator is especially simple: $A(P,Q) \sim \exp -\beta Q^2 - P^2/\beta$. The semiclassical Green's function in phase space takes the standard form:

$$G(P,Q) \sim \int \mathrm{d}X \sum_{\gamma} \frac{1}{m_{12}^{1/2}} \exp[\mathrm{i}(S(Q-X/2, Q+X/2)/\hbar - \mathrm{i}PX/\hbar - \nu_\gamma \pi/2)].$$

To calculate our spectrum we now have to consider three separate integrals involving rapidly oscillating functions (over P, Q, X). These will yield three separate stationary phase conditions. If we disregard the variation in A, the stationary points are then obtained solely from the oscillations in the Green's function. For the integral over P, the phase must be stationary with respect to variations in P so $X = 0$. This means that the orbit is closed. The integral over X yields the average of the initial and final momenta p, p', but does not require them to be equal, i.e. $\nabla_X(\text{phase}) = P - (p+p')/2 = 0$. The final integral yields $-\partial S/\partial Q = p = p' = \partial S/\partial Q'$, i.e. periodic orbits.

If A is very smooth transverse to the periodic orbit, Eckhardt *et al.* found that the trace could be evaluated in the same manner as Gutwiller.

The result is a weighted spectrum, which is a sum over periodic orbits:

$$N_{\mathrm{osc}}(E) = \frac{1}{\pi}\,\mathrm{Im}\sum_n \frac{A_n}{\mathrm{i}\hbar}\sum_j \frac{\exp(\mathrm{i}j(S_n(E)/\hbar - \mu_n\pi/2))}{|\det(M_n^j - I)|^{1/2}}. \tag{3.3}$$

The only difference from the standard Gutzwiller formula is that each periodic orbit is now weighted by the average of the observable over one period of the orbit, i.e. $A_n = \int_0^T \mathrm{d}t\,A$.

This formula has been applied to Franck–Condon spectra of chaotic molecules like water (see, for example, Huppert *et al.* 1997).

(2) A second, intermediate type of theory was adopted by Zobay & Alber (1994), Narimanov *et al.* (1998) and Bogomolny & Rouben (1998). In rough terms the method is as follows: the observable does not determine the paths around which the quantum spectrum will be constructed (the stationary phase points). These are still chosen by considering only the variation in S. However, having chosen these paths, one then considers explicitly the variation of the observable $\hat{A}$ in the integral in equation (3.2). These theories still yield spectra as sums of periodic orbits but with a weighting different from the Gutzwiller formula.

Zobay & Alber applied this to a molecular photoabsorption problem (with CO_2). In this case the observable $\hat{A}$ is sufficiently smooth that the stationary phase points were obtained by considering only oscillations in the Green's function. As in the previous case this implies periodic orbits for the stationary phase points so $q = q'$ and $p = p'$. In the usual semiclassical procedure they carried out a Taylor expansion of the phases up to quadratic order about the periodic orbits. However, in this case the explicit functional form initial state $A(P, Q) \sim \exp(-\beta Q^2 - P^2/\beta)$ was included in the integrals over P and Q in equation (3.2). The result is a more accurate expression for the Franck–Condon factors, which has the added bonus of not diverging at bifurcations.

The intense interest generated by experiments on quantum wells in tilted fields (Fromhold *et al.* 1994; Muller *et al.* 1995; Wilkinson *et al.* 1996) led to a search for a semiclassical periodic-orbit-type theory that describes the oscillations in the tunnelling current. Narimanov *et al.* (1998) proposed a periodic theory for the current, also following this phase-space approach. Bogomolny & Rouben (1998) derived a simple analytical expression for the current, starting from the position space Green's functions.

However, comparisons with fully quantal results and the experiments showed that the periodic orbit expressions failed drastically over wide regimes of the experiment. One example is the regime shown in figure 5 above where the only accessible periodic orbits with the right period vanish intermittently into the complex plane leaving 'ghosts', which are replaced subsequently by new real orbits that appear elsewhere. Periodic orbit theories, even 'patched' with the normal forms described in the previous section, give poor results.

(3) The third approach to the observable $\hat{A}$ is needed in the case where $\hat{A}$ is so localized that one must take it into account even when choosing the important paths (the stationary phase points). The quantum well problem represents a good example of this case, since the initial state is a narrow Gaussian. One could follow the phase-space approach as above, but a formulation in coordinate space (Bogomolny & Rouben 1998) gives the quickest route to the key results. For paths from x, z to x', z' the quantum well matrix element yields oscillatory integrals of the form,

$$\sim \int \mathrm{d}z \int \mathrm{d}z' \sum_{\mathrm{cl}} \mathrm{e}^{\mathrm{i}S(z,z')/\hbar - \beta(z^2+z'^2)/2\hbar}. \tag{3.4}$$

There are the path-dependent oscillations $\mathrm{e}^{\mathrm{i}S(z,z')/\hbar}$ due to the Green's function and Gaussians $\exp(-\beta(z^2 + z'^2)/2\hbar)$ due to the initial state $|\phi\rangle$ in the matrix

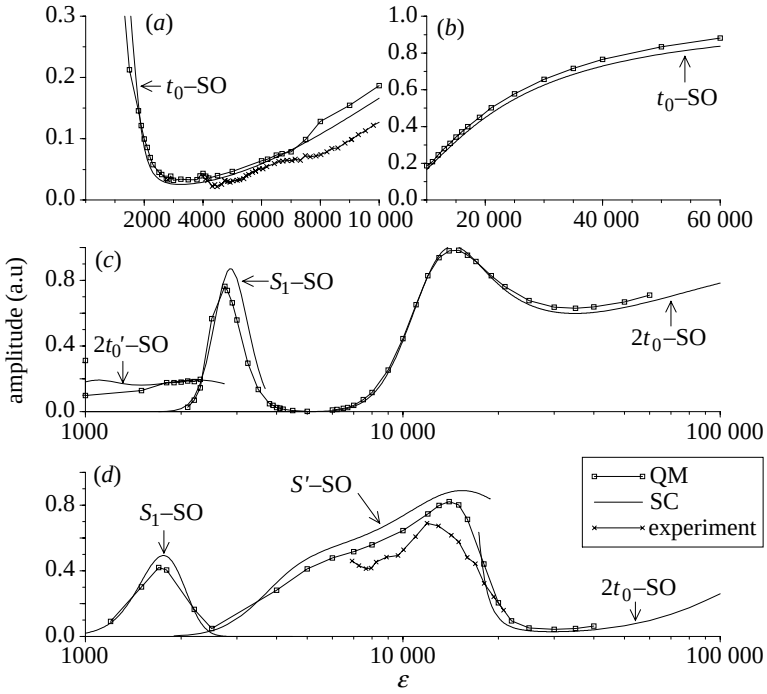

Figure 6. Quantal, experimental and semiclassical amplitudes for quantum wells in fields. The semiclassical theory, which uses complex, non-periodic paths called saddle orbits (SOs) instead of periodic orbits, gives excellent agreement with results and experiment, while periodic orbit theory in this instance does not. The figure shows amplitudes of period-one oscillations of the current at $\theta = 11^\circ$ for low (a) and high (b) values of V/LB^2. (c) Amplitudes of period-two oscillations at $\theta = 11^\circ$. (d) Amplitudes of period-two oscillations at $\theta = 27^\circ$.

elements. If the variation of the Gaussian is as fast as the oscillations from the action, then, instead of POs, one has a saddle point condition defined by

$$\mathrm{i}\frac{\partial S}{\partial z} = \beta z, \qquad \mathrm{i}\frac{\partial S}{\partial z'} = \beta z'. \tag{3.5}$$

These conditions define paths that are complex and non-periodic. These saddle orbits (Saraga & Monteiro 1998*b*) were obtained by solving classical equations of motion allowing time and position to have imaginary values. One can obtain a simple analytical expression, in terms of saddle orbits for the experimental current of quantum wells in tilted fields, that gives excellent agreement with both experiment and quantal calculations as seen in figure 6. Unlike ghosts, saddle orbits are not periodic. Like ghosts they are complex, but are peculiar because they can contribute substantially even when the imaginary component of the action is large. An additional complex amplitude partly cancels the $\mathrm{e}^{-\mathrm{i}S/\hbar}$ damping so their contribution can decay much more slowly with $\hbar$. Hence, they solve the puzzle of the excessively large 'ghost' oscillations seen in the experiments.

We expect that saddle orbits will potentially be relevant in molecular spectra (Franck–Condon spectra) involving photoabsorption from a ground vibrational state.

(4) Photoabsorption spectra of atoms in strong fields exemplify a fourth type of semiclassical theory. The static field eigenstates ψ_n are also weighted by an oscillator strength $|\langle\psi_n D\psi_{1s}\rangle|^2$. In this case our initial state $|\phi>=|D\psi_{1s}>$ will be something like the ground state of an atom, acted on by D, a dipole operator. One can, as above, use the Green's function form for the oscillator strength $\langle\phi|\hat{G}|\phi\rangle$.

This initial state is extremely localized, more so than even the quantum well case. Only paths that start and end near the nucleus can contribute. The important difference relative to the three types of theory described above is that the semiclassical form of the Green's function is not valid near the nucleus. Du & Delos (1988) and Gao *et al*. (1992) instead employed the full quantal Green's function over a small region near the multielectron core. Fortunately, the effects of a magnetic or electric field are negligible near the core, so the exact Green's function is given in terms of regular and irregular Coulomb functions and quantum defect theory. Far from the nucleus Du & Delos employed semiclassical waves along classical orbits that return to the nucleus (closed orbits) and were matched to the waves at the core.

The basic closed-orbit theory has had tremendous success in interpreting quantitatively features of the experimental photoabsorption spectra of hydrogen in external fields (Main *et al*. 1994). The need for the full quantal treatment near the multielectron core is reflected in 'diffractive' corrections to the pure semiclassical treatment (Dando *et al*. 1995, 1998).

To summarize, we have shown that current semiclassical theories used to interpret observed spectra for chaotic or at least non-integrable atomic, molecular and related systems can be grouped together depending on the degree of localization of the relevant observable.

(*c*) *Diffractive orbits: atoms in fields*

Periodic orbit theory represents a sort of ray-optics limit to the full quantum wave behaviour. Geometric optics becomes a poor approximation in certain situations such as the rim of a disc, where 'creeping paths' can illuminate areas that should be dark, or when the light strikes a sharp corner or a vertex. In the atomic case, the small electronic core is about the same size as the de Broglie wavelength of the Rydberg electron *ca*. 1 au. Hence, new modulations in addition to the usual periodic orbits appear in the quantum spectrum and the strengths of all contributions differ from atom to atom.

R-matrix type calculations on non-hydrogenic atoms in magnetic fields showed additional peaks not corresponding to known closed orbits. In addition, the statistical distributions of energy levels indicated that non-hydrogenic atoms were much more 'chaotic' (Monteiro & Wunner 1990; Jans *et al*. 1993).

At first sight it seemed that the effect of a non-hydrogenic core was to induce chaos in a non-hydrogenic atom or molecule, even at low energies, where hydrogen

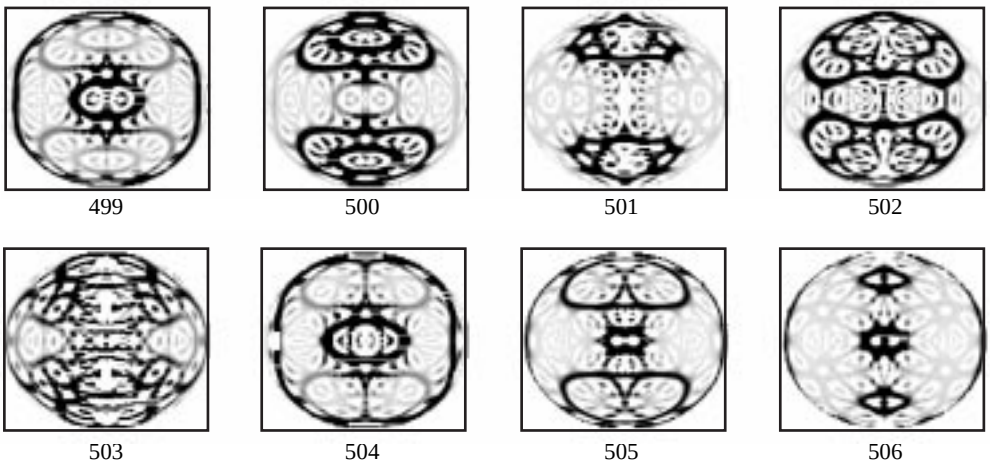

Figure 7. Quantum phase-space distributions (Wigner functions) for a set of levels of a non-hydrogenic atom (even l, $m = 0$, $\delta_{l=0} = 0.5$; the level number, counting from the ground state, is shown) in a magnetic field for scaled energy $\epsilon = -0.5$. Black indicates high intensity. In this regime the classical dynamics is regular and states of hydrogen are localized on single tori as shown in figure 2*c*. The non-hydrogenic states shown in the figure are typically well localized on two or three 'torus-like' structures. This behaviour differs from the typical distribution in the classically chaotic regime, where quantum states will not show 'torus' structures and unless strongly scarred will be more 'ergodic' (more evenly distributed over phase space).

is regular. However, the quantum wave functions did not seem typical of a chaotic system. They remained concentrated on regular torus-like structures. But while for hydrogen in the regular regime each quantum state may be assigned a single torus, in the non-hydrogenic case, the typical state is a set of two or three connected 'tori' (Jans *et al*. 1993). This is illustrated in figure 7.

The classical dynamics corresponds to a process we termed 'torus-hopping' (Dando *et al*. 1994). While away from the nucleus, the motion is entirely regular and confined to a torus. Hence the localization on tori reflects the short-time dynamics, analogous to quantum scarring. Intermittently, the particle is scattered at the core. For quantitative results this process cannot be described semiclassically.

The periodic orbit theory of diffraction was developed recently for quantum particles moving in billiards (Vattay *et al*. 1994; Primack *et al*. 1996; Bruus & Whelan 1996). If the potential has a discontinuity or a structure smaller than the de Broglie wavelength of the particle, the geometric optics corresponding the Gutzwiller trace formula is insufficient. In the atomic case this means that the trace formula fails to describe atoms other than hydrogen. What is needed is a procedure to combine the Gutzwiller formula with quantum defect theory in a simple way.

For our purposes, a good example of a diffractive system is the cardioid billiard (Bruus & Whelan 1996), which has a single sharp vertex. In that case, periodic orbits that miss the vertex will simply involve specular reflection at the walls of the enclosure, like an ordinary billiard. But paths that strike the vertex provide a new source of amplitude that can 'feed' trajectories in 'unexpected' directions. The Green's function from which the quantum density of states is obtained now has two components, a geometric contribution $G_{\mathrm{g}}(E)$ analogous to the trajectories in the

Gutzwiller formula and a new, diffractive contribution $G_{\mathrm{D}}(E)$:

$$N(E) = \underbrace{-\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,G_{\mathrm{g}}(E)}_{\text{geometric}} - \underbrace{\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,G_{\mathrm{D}}(E)}_{\text{diffractive}}. \tag{3.6}$$

An important result due to Vattay *et al.* (1994) is that the trace integral taken between the nth and $(n+1)$th diffractive points is proportional to the semiclassical Green's function between those points. The trace over the second (diffractive) contribution is

$$\mathrm{Tr}\,G_{\mathrm{D}}(E) = \sum_p \frac{T_p}{\mathrm{i}\hbar} \prod_n d_n G(q_n, q_{n+1}; E), \tag{3.7}$$

where T_p is the sum of periods taken over the paths between the vertices and d_n is the diffraction constant specific to each dynamical system.

In order to adapt the theory to a Rydberg atom like lithium, the non-hydrogenic core must be represented as a diffractive source (Dando *et al.* 1998). The crucial step is to obtain an expression for the diffractive constant, d, in terms of quantum defects. To this end, we considered an incoming Coulomb wave, $\psi^{(-)}_{\mathrm{Coul}}$, which approaches the atomic core from infinity at an angle θ_{f} to the z-axis. On reaching the core, $\psi^{(-)}_{\mathrm{Coul}}$ produces a scattered wave, ψ_{scatt}, which feeds outgoing semiclassical waves along periodic orbits; ψ_{scatt} can be decomposed into an outgoing Coulomb wave together with a core-scattered wave, as in Gao *et al.* (1992):

$$\psi_{\mathrm{scatt}}(r,\theta) = \psi^{(+)}_{\mathrm{Coul}}(r,\theta) + \psi^{\theta_{\mathrm{f}}}_{\mathrm{core}}(r,\theta).$$

Our first approximation consisted of equating $\psi^{(+)}_{\mathrm{Coul}}$ with the source for geometric paths (i.e. the usual Gutzwiller trace formula). The core-scattered wave $\psi^{\theta_{\mathrm{f}}}_{\mathrm{core}}$, arising from the incoming wave at angle θ_{f}, was equated with the source of diffractive semiclassical waves. For a small atom like lithium or helium in a magnetic field, it takes the form of a simple s-wave since only quantum defects $\delta_{l<2}$ are non-negligible. The theory is general, but we illustrate it with the pure s-wave case. The diffractive constant d was taken to be the fractional amplitude scattered by the core:

$$d(\delta_0, \theta_{\mathrm{i}}, \theta_{\mathrm{f}}) = \psi^{\delta_0,\theta_{\mathrm{f}}}_{\mathrm{core}}(r_0, \theta_{\mathrm{i}}) / \psi^{(-)}_{\mathrm{Coul}}(r_0, \theta_{\mathrm{f}}). \tag{3.8}$$

Substituting for this diffractive constant, which is a function of δ_0, the quantum defect for $l = 0$ in equation (3.7) gives us a connection between the trace formula with diffraction and quantum defect theory. Analytical expressions can easily be obtained for the periodic orbit amplitudes for each atom. They now depend not just on the stability matrix but also on the quantum defects.

Figure 8 shows a comparison between fully quantal calculations on hydrogen and lithium and the diffractively corrected Gutzwiller formula. Away from bifurcations the new formula agrees with the quantal results to within 1%. New pure diffractive modulations are indicated with a D. Modulations due to combinations of periodic orbits (another diffractive phenomenon not seen in hydrogen) are also seen. The analogous photoabsorption effect (combinations of closed orbits) were seen in several atomic experiments (Delande *et al.* 1994; Raithel *et al.* 1994; Courtney *et al.* 1994).

There is an especially important difference between the model cardioid billiard and a real atom. In the former, orbits are either geometric or diffractive. In the atomic

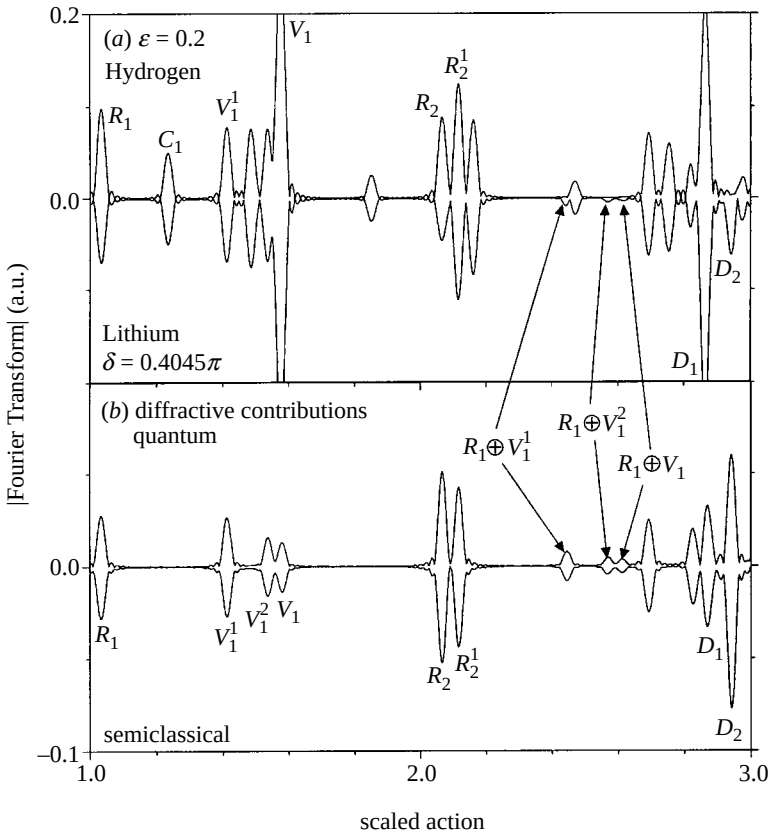

Figure 8. (*a*) Comparison of Fourier transforms of the density of states for hydrogen and lithium ($\delta = 0.4045\pi$) in a static magnetic field at constant scaled energy $\varepsilon = -0.2$ from a fully quantal calculation with average $\hbar = 1/90$. Note the changes in amplitudes of periodic orbits and new modulations due to diffractive orbits in the lithium case. (*b*) Comparison between quantal and semiclassical difference spectra obtained by coherently subtracting the Fourier transforms shown in (*a*). This exposes the diffractive contributions to the spectrum and eliminates contributions from orbits that do not pass through the core. Shown are changes in periodic orbit amplitudes due to diffraction, diffractive combinations of two periodic orbits and pure diffractive orbits, marked D_1 and D_2. Away from bifurcations, which affect V_1 and D_2, the agreement between quantum and semiclassical calculations, shown in (*b*), is excellent.

case, orbits that approach the nucleus are treated as pair of trajectories which coincide, one of which is diffractive, the other geometric. They are de-phased relative to each other. The interference between the two trajectories explained puzzling features seen in the quantum spectra, where as a function of quantum defect some periodic orbit amplitudes would *increase* while others would decrease.

To summarize, we conclude that although the behaviour of non-hydrogenic spectra in external fields mimics some signatures of chaos at low energies, the dynamics is best understood as regular motion with diffraction (Dando *et al*. 1998). We recall that the statistics for the lowest few thousand states were found to be nearer the 'chaotic' (GOE) for non-hydrogenic atoms (Monteiro & Wunner 1990; Monteiro *et al*. 1992; Jans *et al*. 1993). This was confirmed by a recent experiment, resolving

individual quantum states (Held 1997). However, it has now been found that nearer the semiclassical limit, the statistical signature of the spectra non-hydrogenic atoms in magnetic fields tends to a new form (Jonckheree *et al*. 1998), termed 'half-Poisson' (Bogomolny *et al*. 1998). The nearest-neighbour spacings are characterized by short-range level repulsion but with a long-range 'Poissonian' tail characteristic of regular systems.

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