Chapter 1

Introduction

Ever since the early days of quantum mechanics, the correspondence between classical trajectories and atomic spectra has been a question of fundamental interest and importance. The "old" quantum theory suffered from the severe drawback that the Bohr-Sommerfeld quantization rules could only be applied to integrable systems. Although it had already been noted by Einstein [1] that integrable systems are exceptional, the question of how to quantize classically non-integrable systems remained unsolved. After the advent of the "exact" quantum mechanics, quantum mechanical calculations no longer relied on the underlying classical mechanics, so that the interest in the correspondence between classical and quantum mechanics declined. It was only after the development of periodic-orbit theory [2] and, as a variant for the photo-excitation spectra of atomic systems, closed-orbit theory [3, 4], that techniques were available to explore the intimate connections between quantum spectra and the underlying classical dynamics. These theories triggered an enormous upsurge of interest in the long-standing problem of developing what is now called a semiclassical quantization procedure for classically non-integrable systems, i.e. a quantization scheme based on the underlying classical dynamics.

The hydrogen atom in external electric and magnetic fields has become a prototype example for semiclassical studies. Whereas the hydrogen atom in an electric field is classically integrable, in a magnetic field it shows a transition from regular to completely chaotic behaviour, so that it is ideally suited to investigate the impact of classical regularity or chaos on quantum mechanical spectra. Closed-orbit theory provides a semiclassical approach to atomic photo-absorption spectra [3, 4]. It gives the oscillator-strength density as a sum of two terms, one a smoothly varying part (as a function of energy) and the other a superposition of sinusoidal oscillations. Each oscillation is associated with a "closed" classical orbit starting at and returning to the nucleus. It is therefore possible to analyse a given photo-absorption spectrum in terms of the closed orbits contributing to it. For the hydrogen atom in a magnetic field, a comprehensive classification of closed orbits exists, and in this framework the large-scale structures of the spectrum found a convincing semiclassical interpretation. Conversely, atomic energy levels and the corresponding transition strengths could be calculated from classical orbits [5].

Because the hydrogen atom in a purely magnetic field possesses a rotational symmetry around the magnetic field axis, the angular momentum component along this axis is conserved. Therefore, the dynamics can be reduced, effectively, to two degrees of freedom. If, to the contrary, the atom is subjected to the combined influences of perpendicular magnetic and electric fields, all continuous symmetries are broken and three non-separable degrees of freedom have to be dealt with. In addition, the dynamics depends on two external parameters, viz. the field strengths, instead of only one. Hence, both the classical and quantum dynamics of the crossed-fields hydrogen atom is significantly more complex than in a magnetic field. Even after ten years of intense study, this complex behaviour is far from being completely understood.

Although a closed-orbit theory can be derived for the crossed-fields [6,7] as well as for the magnetized hydrogen atom, and the large-scale structures of crossed-fields photo-absorption spectra have been interpreted successfully in terms of individual closed orbits [7–11], only contributions of rather short orbits have been identified, and a general overview of the closed orbits in the crossed-fields system is not yet available. What is more, closed orbits are known to proliferate through bifurcations as the external field strengths are increased. As a crucial step towards a classification of closed orbits, therefore, one needs a bifurcation theory describing the generic types of bifurcations one should expect to find. A bifurcation theory for periodic orbits in Hamiltonian systems was developed long ago by Mayer [12]. Nevertheless, an analogue for closed orbits is still unavailable.

Much effort has been spent since the advent of the modern semiclassical theories on the construction of a general semiclassical quantization scheme (see, e.g., [13–19]). Although closed-orbit theory provides a means of calculating smoothed spectra, it does not readily lend itself to a calculation of individual energy levels because the sum over all closed orbits is divergent. Periodic-orbit theory, which gives a semiclassical approximation to the density of states of a quantum system, is formally analogous to closed-orbit theory and shares this fundamental difficulty. A number of different techniques have been proposed to overcome the convergence problems of the semiclassical theories. All of them are limited in their applicability because they make certain assumptions about the underlying classical dynamics. In particular, no method proposed to date can be used if bifurcations of classical orbits must be taken into account.

Most of the work on semiclassical quantization was restricted to systems having two degrees of freedom. It is of fundamental importance to assess the applicability of semiclassical schemes to systems with three or more degrees of freedom. Nevertheless, due to the additional complications brought about by the third degree of freedom, previous studies [20–25] have been restricted to billiard systems. A full semiclassical quantization has so far been achieved for the three-dimensional Sinai billiard [20] and the N-sphere scattering system [23] only. As it exhibits a transition from regular to chaotic dynamics, the hydrogen atom in crossed fields is considerably more complicated than billiard systems, and a semiclassical quantization has not even been attempted to date. To achieve a quantization, a number of rather diverse problems must be solved. First, a thorough understanding of the closed orbits in the crossed-fields system is required. Second, bifurcations of closed orbits will turn out to play an important role in the crossed-fields hydrogen atom. They introduce divergences into the semiclassical spectrum, and suitable uniform approximations smoothing these divergences must be found. Third, a semiclassical quantization procedure capable of dealing with uniform approximations must be developed. All of these problems will be tackled in the course of this work.

In chapter 2, the basic properties of the crossed-fields hydrogen atom will be described and the fundamental formulae of closed-orbit theory will be derived. Recently, Granger and Greene [26] proposed a novel formulation of closed-orbit theory for atoms in magnetic fields based on semiclassical S-matrices. Their formulation appears to be more flexible than the conventional treatment when applied to non-hydrogenic atoms or molecules. I have extended it to the case of crossed external fields. For the case of a magnetic field, I discuss and clarify some misleading conclusions arrived at by Granger and Greene.

The semiclassical investigations presented here are largely based on the method of harmonic inversion, which was introduced [19, 27] as a general technique for both semiclassical quantization and the semiclassical analysis of quantum spectra. Several variants of the method have been proposed in the literature. I will summarize these in chapter 3 and apply them to two simple example systems to compare their numerical efficiencies. Finally, I will generalize the method to the semiclassical quantization of systems without a classical scaling property. This generalization is relevant beyond the realm of closed-orbit theory, because it can also be applied in connection with semiclassical trace formulae. It is the first truly universal semiclassical quantization scheme proposed in the literature, because it does not make any assumptions whatsoever about the underlying classical dynamics.

The numerical integration of the classical equations of motion for the crossed-fields hydrogen atom is plagued by the presence of the Coulomb singularity. As is well-known, this singularity can be regularized by means of a Kustaanheimo-Stiefel transformation [28]. A novel formulation of the transformation in the language of geometric algebra was introduced by Hestenes [29]. It offers the advantages of greater calculational simplicity and a clearer geometric interpretation than provided by a matrix-based approach. In this formalism, I will develop Lagrangian and Hamiltonian formulations of the Kustaanheimo-Stiefel transformation in chapter 4. I will then discuss the problems specific to the description of closed orbits and demonstrate that the geometric algebra allows a particularly clear exposition.

In chapter 5, the general framework for a local theory of closed-orbit bifurcations will be set up and the codimension-one generic bifurcations will be identified. It will be shown that the presence of reflection symmetries in the crossed-fields hydrogen atom has a significant impact on the possible types of bifurcations. Subsequently, I will describe the actual closed orbits and their bifurcations at low scaled energies. The simple elementary bifurcations will be seen to form a surprisingly rich structure of complicated bifurcation scenarios. Finally, I will propose a classification scheme for closed orbits which is inspired by the case of a pure magnetic field, and I will demonstrate that it is applicable for electric field strengths at least up to half the strength of the magnetic field (in atomic units).

Chapter 6 discusses the semiclassics of the crossed-fields system. I will present both low-resolution and high-resolution semiclassical photo-absorption spectra. In the latter case, the strongest spectral lines are resolved. The observation that the high-resolution spectra cannot easily be improved so as to yield more spectral lines leads to a closer inspection of the semiclassical signal. Semiclassical recurrence spectra reveal that closed-orbit theory can be applied in principle for long as well as for short closed orbits, but the semiclassical spectrum is marred by missing orbits and, in particular, by the presence of bifurcations of closed orbits. Bifurcations lead to a divergence of the usual closed-orbit formula and must be treated by uniform semiclassical approximations. I will propose a heuristic, easy-to-apply technique for the construction of uniform approximations and derive these for the two types of codimension-one bifurcations. I will then show how uniform approximations can be included in the semiclassical quantization by harmonic inversion.

As the bifurcation scenarios occurring in crossed fields turn out to be too complex for a semiclassical quantization to be actually carried out, I will focus my discussion, in chapter 7, on the hydrogen atom in an electric field. This system is integrable, hence its classical mechanics is easy to understand. I will derive semi-analytical formulae describing the closed orbits which have not been given before in the literature. In spite of its apparent simplicity, the system still exhibits a multitude of closed-orbit bifurcations, that have so far precluded a semiclassical quantization based on closed-orbit theory. A uniform approximation describing a single bifurcation in the Stark system has been given before [30, 31]. Using the general method of chapter 6, I will re-derive it in a form which is much easier to apply in practice and supplement it with a uniform approximation for a more complicated bifurcation scenario. The latter is of fundamental interest because it is the first uniform approximation described in the literature which depends on a topologically non-trivial configuration space. The uniform approximations will then be used for a semiclassical quantization in a spectral region where the conventional closed-orbit formula would be completely useless due to an abundance of bifurcations. In this way, it is demonstrated that the quantization scheme introduced in chapters 3 and 6 indeed permits the inclusion of uniform approximations into a semiclassical quantization, which has so far been impossible.

Because of their high topicality, part of the results in this work have been published in advance [32].