

# 1

## Introduction

By now the “chaos revolution” has reached nearly every branch of the natural sciences. In fact, chaos is everywhere. To name but a few examples, we talk about chaotic weather patterns, chaotic chemical reactions and the chaotic evolution of insect populations. Atomic and molecular physics are no exceptions. At first glance this is surprising since atoms and molecules are well described by the *linear* laws of quantum mechanics, while an essential ingredient of chaos is *nonlinearity* in the dynamic equations. Thus, chaos and atomic physics seem to have little to do with each other. But recently, atomic and molecular physicists have pushed the limits of their experiments to such high quantum numbers that it starts to make sense, in the spirit of Bohr’s correspondence principle, to compare the results of atomic physics experiments with the predictions of classical mechanics, which, for the most part, show complexity and chaos. The most striking observation in recent years has been that quantum systems seem to “know” whether their classical counterparts display regular or chaotic motion. This fact can be understood intuitively on the basis of Feynman’s version of quantum mechanics. In 1948 Feynman showed that quantum mechanics can be formulated on the basis of classical mechanics with the help of path integrals. Therefore it is expected that the quantum mechanics of an atom or molecule is profoundly influenced, but of course not completely determined, by the qualitative behaviour of its underlying classical mechanics. To be specific, we expect to see qualitatively different quantum behaviour in an atom or molecule depending on whether its classical mechanics is regular or chaotic.

The central theme of classical deterministic chaos is the occurrence of the most astonishing complexity in the simplest systems (see, e.g., Schuster (1988), Ott (1993)). And what could be simpler than, e.g., a hydrogen atom in a strong magnetic field? On second thought, however, we realize that on the classical level this system possesses the crucial

ingredient for the emergence of chaos: nonlinearity. In this case the nonlinearity consists in the combined interactions of the electron with the proton and the applied magnetic field. Sure enough, it was shown by many scientists (see, e.g., Friedrich (1990) and references therein) that chaos does indeed occur in the classical version of the hydrogen atom in a magnetic field. Therefore, we expect complex behaviour to appear in the quantum mechanics of this system. While complexity may reveal itself in many quantum observables, the most familiar observable is the energy. Fig. 1.1(a) shows the energy spectrum of the hydrogen atom as a function of the magnetic field in a range of principal quantum numbers around  $n = 40$ . At first glance the spectrum appears “wild” and “chaotic”. On second thought one might argue that Fig. 1.1(a) is merely “congested”, i.e. an assembly of many hydrogen lines, all in principle quite regular, but producing an irregular effect simply by plotting many of them in one single figure. To demonstrate that this is not so, i.e. that something fundamentally new is going on in Fig. 1.1(a), we show a magnification of the framed area of Fig. 1.1(a) in Fig. 1.1(b). The magnification reveals that Fig. 1.1(a) actually consists of hundreds of avoided crossings which force initially “regular” energy levels to bend in “erratic” ways as a function of the magnetic field strength producing considerable complexity in the energy spectrum. The bending of the energy levels makes it very hard, if not impossible, to assign quantum numbers to the individual energy levels at fixed magnetic field strength. In fact, it was argued by Percival in 1973 that one of the key quantum signatures of chaos is the loss of our ability to assign quantum numbers.

Chaos does not only wreak havoc in otherwise orderly atomic spectra, it also provides a natural framework, indeed a common language, in which one can discuss such seemingly unrelated systems as, e.g., ballistic electrons in mesoscopic semiconductor structures, the helium atom, and Rydberg atoms in strong external fields. All these systems have one feature in common: their classical counterparts are chaotic. Chaos imprints its presence on their spectra and manifests itself in spectral features which are very similar for all these systems (universality).

Especially in the highly excited semiclassical regime the quantum properties and dynamics of atomic and molecular systems are most naturally discussed within the framework of chaos. Not only does chaos theory help to characterize spectra and wave functions, it also makes specific predictions about the existence of new quantum dynamical regimes and hitherto unknown exotic states. Examples are the discovery of “frozen planet” states in the helium atom by Richter and Wintgen (1990a) and

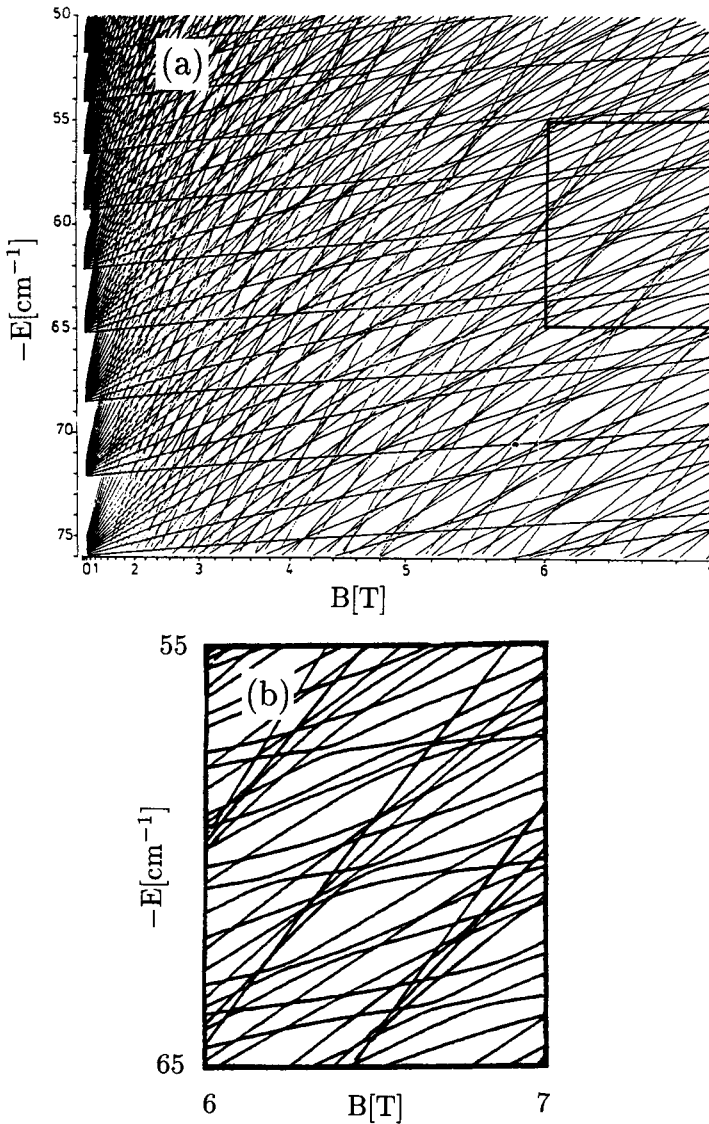


Fig. 1.1. Energy levels of the hydrogen atom as a function of magnetic field strength  $B$ . (a) Transition from order to “chaos” for increasing magnetic field strength (Friedrich and Wintgen (1989)). (b) A magnification of the framed detail in (a) resolves the complex behaviour of the energy levels in the  $E - B$  plane for high magnetic field strengths.

the prediction of a “gas of resonances” in doubly excited helium (see Chapter 10).

But chaos is more than a tool. There are as yet unsolved philosophical problems in its wake. While relativity and quantum mechanics necessitated – and in fact originated from – a careful analysis of the concepts of space, time and measurement, chaos, already on the classical level, forces us to re-think the concepts of determinism and predictability. Thus, classical mechanics could not be further removed from the dusty subject it is usually portrayed as. On the contrary: it is at the forefront of modern scientific research. Since path integrals provide a link between classical and quantum mechanics, conceptual and philosophical problems with classical mechanics are bound to manifest themselves on the quantum level. We are only at the beginning of a thorough exploration of these questions. But one fact is established already: chaos has a profound influence on the quantum mechanics of atoms and molecules. This book presents some of the most prominent examples.

Among the atomic systems discussed in this book we find the helium atom (Chapter 10). This topic rings a bell. It featured prominently in the final stages of the “old quantum mechanics”. The old pre-1925 quantum theory was based on classical notions such as periodic orbits. Periodic orbit quantization of the helium atom within the framework of the old quantum mechanics did not work out and presented an insurmountable problem (see, e.g., Van Vleck (1922)). But all the difficulties with the old quantum theory were solved with one blow when Heisenberg, Born, Jordan and Schrödinger developed the “new” quantum mechanics in 1925 and 1926. Heisenberg in particular was very proud of having eliminated the concept of classical orbits from the structure of quantum mechanics (Heisenberg (1969)). But his joy proved premature. Periodic orbits are very much alive! In fact, they currently enjoy a key role as one of the few known tools for the systematic semiclassical quantization of classically chaotic systems (Gutzwiller (1990)). Thus, the fall of the old quantum mechanics was not primarily due to the use of classical concepts, but to the inappropriate use of classical procedures, such as adding probabilities instead of amplitudes. Also, it was not known then how to incorporate properly the intricacies of classical mechanics, epitomized in the phenomenon of chaos. We note that the difficulties of incorporating the ideas of chaos into the old quantum theory were well appreciated by Paul Ehrenfest’s student Burgers (1916), Einstein (1917) and Dirac (1925).

In order to develop the mind set and methods needed to understand and use the fingerprints of chaos in quantum mechanics, we must set to work. Our journey through chaos in atomic physics begins head-on with a schematic, but physical, example of chaos in Section 1.1. The remaining

sections of Chapter 1 present a general discussion of some of the philosophical implications of the existence of chaos in the classical world. Formal tools and concepts, indispensable for a deeper understanding of chaos, are presented in Chapter 2. Chapter 3 is essentially an elementary review of Lagrangian and Hamiltonian mechanics with special emphasis on the role of chaos in classical mechanics. In Section 3.2, e.g., we present a simple physical system (the double pendulum) which shows many generic features of a chaotic Hamiltonian system. Chaos in quantum mechanics is discussed in Chapter 4. The main point here is to eliminate some of the confusion surrounding the topic of “quantum chaos” by proposing a classification of quantum systems into three categories: (I) systems whose quantum dynamics is not chaotic, but which “feel” the underlying classical chaos (“quantized chaos”); (II) systems whose quantum dynamics is fully chaotic, but which are coupled to at least one classical degree of freedom in the sense of a dynamic Born-Oppenheimer approximation (“semi-quantum chaos”); and (III) systems that are fully quantized and show fully developed chaos. While the existence of type I and type II systems is confirmed and their usefulness in atomic and molecular physics established, the very existence of type III systems is still much debated. Therefore, it may well be established by future research that category III, no doubt the most interesting of the three, is empty. With Chapter 4 we finish the introductory part of the book, whose main purpose is to provide the reader with the necessary tools and concepts for a thorough understanding of the remaining chapters of the book, which deal with the manifestations of chaos in specific atomic and molecular physics systems. Chapter 5, a study of the physics of an impulsively driven rotor, builds a bridge between the more formal introductory parts of the book and the applications. It links with the introductory chapters by providing further tools needed for the discussion of driven atomic physics systems, but also connects with the following more “applied” chapters by proposing a laboratory experiment with diatomic molecules driven into chaos by the application of a sequence of strong electric field pulses. In Chapters 6 – 10 the ideas of chaos and nonlinear systems developed in Chapters 1 – 5 are applied to actual atomic physics systems. Two different types of systems are discussed: driven and time independent (autonomous). Representatives of driven systems are discussed in Chapters 6 – 8. Chapter 6 presents the classical and quantum dynamics of surface state electrons. Surface state electrons are an essentially one-dimensional system whose physics is not encumbered with the presence of additional degrees of freedom. Moreover surface state electrons provide an excellent model for microwave-driven hydrogen Rydberg atoms discussed in Chapter 7. The importance of phase-space fractals for the properties of atomic decay is discussed in Chapter 8. With Chapter 8 we conclude the discussion of

time dependent atomic systems. Representatives of not explicitly time dependent atomic and molecular systems are discussed in Chapters 9 and 10. Chapter 9 is on chaotic scattering theory applied to molecular scattering in external fields. It prepares for a discussion of the helium atom (Chapter 10), which may be classified as an autonomous chaotic scattering system. The book concludes with Chapter 11, a discussion of status, trends and developments of chaos in atomic physics.

### 1.1 Chaos: a physical example

The difference between regular and chaotic motion is best explained with the help of a physical model. The model also illustrates one of the central messages of chaos theory: the possibility of complex motion in the simplest physical systems.

We assume Newtonian mechanics to be valid and consider a mass point  $M$  bouncing in a two-dimensional square box of side length 1 (see Fig. 1.2). The box shown in Fig. 1.2 is used to illustrate regular motion. Therefore, we call it “ $R$ ”. Another box is shown in Fig. 1.3. It is equipped with a hard stationary disk of radius  $r = 1/4$  at its centre. It serves to illustrate chaotic motion. Therefore, we call it “ $C$ ”. We assume that inside the boxes the mass point  $M$  travels on straight line trajectories subject only to specular reflection whenever it hits the walls of  $R$  or  $C$ , or the central disk of box  $C$ . Since the motion of  $M$  is free between bounces, the mass of  $M$  is irrelevant for the kinematics of  $M$ . Therefore,  $M$ 's velocity can be normalized to 1.

The walls of the boxes are labelled  $a$ ,  $b$ ,  $c$  and  $d$  as shown in Figs. 1.2 and 1.3. The mass point  $M$  is injected into the box at a launch point  $L$  located at  $x = 0, y = 1/2$ . The launch velocity of  $M$  is  $\vec{v} = (v_x, v_y) = (\cos(\varphi), \sin(\varphi))$  where  $\varphi$  is the initial inclination of the trajectory of  $M$

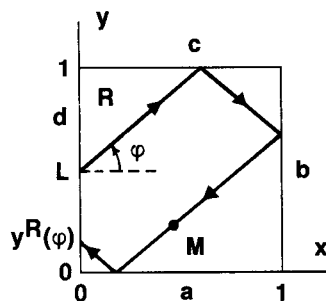


Fig. 1.2. Regular motion of a mass point  $M$  inside an empty square box labelled  $R$ . A trajectory launched at  $L$  with  $\varphi = 0.69$  returns to wall  $d$  after three bounces.



(see Figs. 1.2 and 1.3). In order for  $\vec{v}$  to point into the interior of the box, the angle  $\varphi$  may range from  $-\pi/2$  to  $\pi/2$ . Due to symmetry, and without loss of generality,  $\varphi$  may be restricted to the interval  $0 \leq \varphi < \pi/2$ .

At first sight the box systems may look dry and abstract. But adding a simple modification immediately converts the boxes into models for molecular reactions. We declare the wall *d* to be “sticky”. By this we mean that whenever the mass point *M* hits the wall *d* it is “absorbed”. This way its final position on the *y* axis, denoted by  $y^R$  ( $y^C$ , respectively), can be determined as a function of the initial angle  $\varphi$ . In analogy to the theory of molecular reactions, the functions  $y^R(\varphi)$ ,  $y^C(\varphi)$  are called *reaction functions*.

First, we discuss the motion of *M* in box *R*. Following its departure from *L*, the mass point *M* ricochets around inside *R*. Returning to Fig. 1.2, a sample trajectory launched at *L* with  $\varphi = 0.69$  is shown. The resulting motion is simple. The successive points of impact at the walls can be computed using only elementary geometry. As a result, the reaction function  $y^R(\varphi)$  can be calculated analytically. We obtain:

$$y^R(\varphi) = 1 - \left| 1 - \left[ \frac{1}{2} + 2 \tan(\varphi) \right] \bmod 2 \right|. \quad (1.1.1)$$

It is important to note that  $y^R(\varphi)$  can be expressed analytically with the help of elementary functions. This feature is characteristic for simple systems that do not show chaos. The simplicity of the reaction function (1.1.1) is reflected in the graph of  $y^R(\varphi)$ , shown in Fig. 1.4(a).

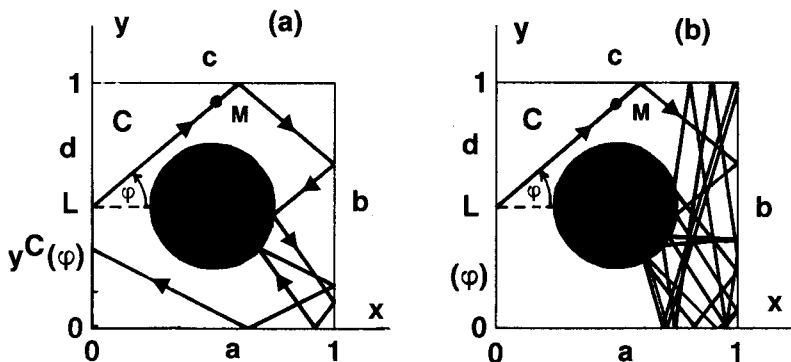


Fig. 1.3. Irregular motion in box *C*. This box is derived from box *R* by adding a totally reflecting disk at the centre of *R*. (a) A complicated but exiting trajectory is produced for the launch angle  $\varphi = 0.69$ . (b) Dynamically trapped trajectory for a launch angle close to  $\varphi \approx 0.692$ .

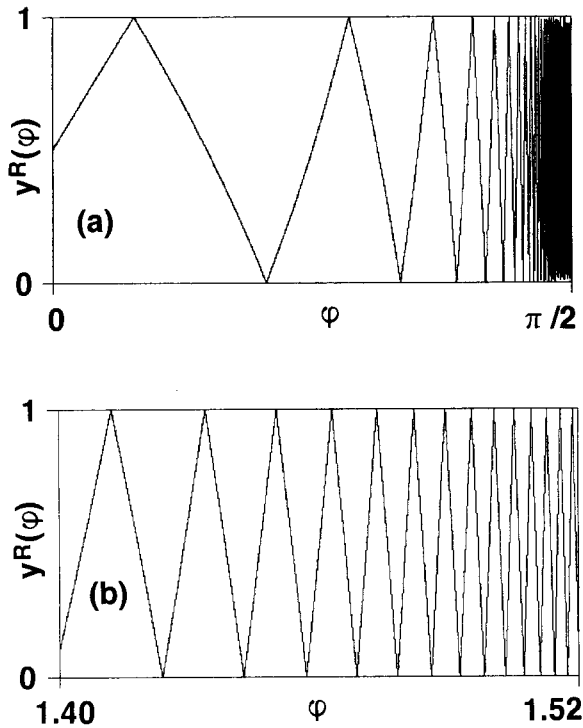


Fig. 1.4. Reaction function  $y^R(\varphi)$  for box  $R$ . (a) Full range of angles  $0 < \varphi < \pi/2$ . (b) Magnification of a detail of (a) in the interval  $1.4 \leq \varphi \leq 1.52$ .

The graph of  $y^R(\varphi)$  displays a regular, saw-tooth like behaviour. The cusps of the reaction function  $y^R(\varphi)$  occur at

$$\varphi_n = \arctan\left(\frac{2n-1}{4}\right), \quad n = 1, 2, \dots \quad (1.1.2)$$

The only “complication” in  $y^R(\varphi)$  is an accumulation point of “zig-zags” at  $\varphi = \pi/2$ . But this accumulation is perfectly regular. The positions of the accumulating cusps are predicted accurately by (1.1.2). In order to show that indeed nothing interesting is hidden in the “blur” in Fig. 1.4(a) close to  $\varphi = \pi/2$ , Fig. 1.4(b) shows a magnification of a detail of Fig. 1.4(a) ranging from  $\varphi = 1.4$  to  $\varphi = 1.52$ . It is important to note that any details which might be hidden in Fig. 1.4(a) close to  $\varphi = \pi/2$  can be *resolved* in any interval  $[a, b]$ ,  $a < b < \pi/2$ . No matter how closely we look, i.e. no matter how large the magnification factor, nothing interesting will ever be revealed about the functional behaviour of  $y^R(\varphi)$ . On the analytical level this is already clear from the simple analytical form (1.1.1) of  $y^R(\varphi)$  and the orderly position of its cusps according to (1.1.2).



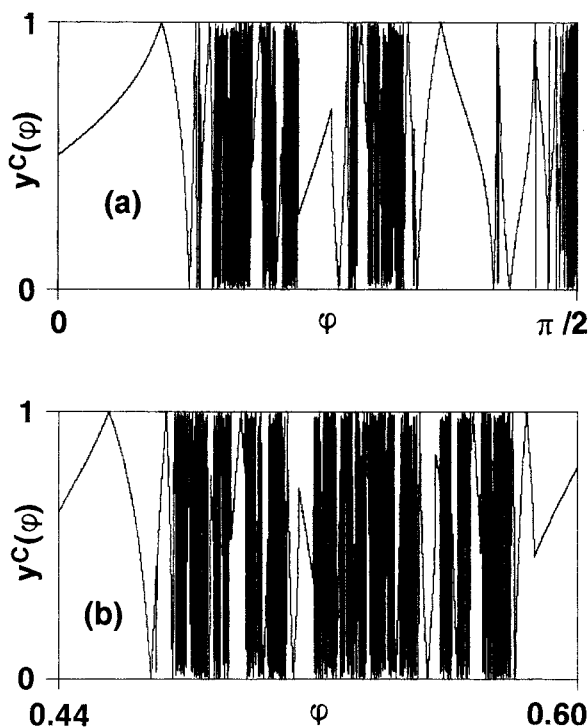


Fig. 1.5. Reaction function  $y^C(\varphi)$  for box  $C$ . (a) Full range of angles  $0 < \varphi < \pi/2$ . (b) Magnification of a detail of (a) in the range  $0.44 < \varphi < 0.60$ .

This situation changes drastically in the case of box  $C$ . The new reaction function  $y^C(\varphi)$  is shown in Fig. 1.5(a). This time the reaction function looks very complicated. The question is whether this complicatedness is only in degree or in quality. The answer is that the simple addition of a scattering disk at the centre of box  $R$  results in a profound qualitative change in the motion of  $M$ , so drastic, indeed, that the resulting motion can only be described as “chaotic”.

There are various indicators for this qualitatively new type of motion. First of all, an analytical formula for  $y^C(\varphi)$  is not known. By “analytical formula” we mean that  $y^C(\varphi)$  cannot be written down in finitely many steps with the help of the known special functions of mathematical physics. Furthermore, the unresolved structures apparent in the reaction function displayed in Fig. 1.5(a) *cannot be resolved in principle*, no matter how large the magnification factor. This is illustrated in Fig. 1.5(b), which shows a magnification of a detail of Fig. 1.5(a) in the range  $0.44 < \varphi < 0.60$ . Indeed, instead of appearing simpler, as was the case with magnifications of unresolved structures in  $y^R(\varphi)$ , the magnification shown in Fig. 1.5(b) appears to be even more complicated.

Further magnifications of Fig. 1.5(b) reveal generation after generation of additional structure *never resolving* the “spiky” behaviour of  $y^C(\varphi)$ . Obviously there is a fundamental difference between  $y^R(\varphi)$  and  $y^C(\varphi)$ . While Fig. 1.4(b) shows that the “blurry” structures in Fig. 1.4(a) can in fact be resolved, this is not true for the reaction function  $y^C(\varphi)$ . The reaction function  $y^C(\varphi)$  shows regions which exhibit structure on all length scales. Moreover, while  $y^R(\varphi)$  shows a mild type of “singularity”, called “cusps” above, the reaction function  $y^C(\varphi)$  exhibits genuine singularities in  $\varphi$ . The origin of these singularities is the phenomenon of *dynamical trapping*. Fig. 1.3(b) illustrates this phenomenon. There exist certain angles  $\varphi_s$  in the interval  $0 < \varphi < \pi/2$  of launch angles for which the resulting trajectory of the mass point  $M$  never returns to wall d of box  $C$ . As shown in Fig. 1.3(b) the particle bounces forever between the walls a, b, c and the central disk without ever reaching wall d. The important point about dynamical trapping is the fact that the particle is not hindered by any obvious means, such as physical obstacles, or energy considerations, from exiting the “reaction region”. It is free to leave at any time, but fails to do so, because of the details of its motion.

If a launch angle  $\varphi_s$  leads to dynamical trapping the value of the reaction function  $y^C(\varphi_s)$  is not defined. We collect all these special angles  $\varphi_s$  into a set  $S$  of *scattering singularities*. A way of visualizing the set  $S$  is to plot the number of bounces of  $M$  against the walls versus the launch angle  $\varphi$ . We call the number of bounces the *lifetime*  $l$  of a trajectory with launch angle  $\varphi$ . Fig. 1.6 shows the lifetime  $l(\varphi)$  as a function of  $\varphi$ . Smooth regions alternate with regions that contain “spikes” representing scattering singularities characterized by  $l = \infty$ . The singularities in  $l$  correspond to the exceptional angles  $\varphi_s$  collected in the set  $S$ . Since the singularities in  $l$  occur precisely at the places where  $y^C$  is not defined, we conclude that in analogy to Fig. 1.5 the spiky regions of Fig. 1.6 are not resolvable. This implies that the set  $S$  of scattering singularities has a very complicated structure. Moreover, since no degree of magnification yields an end to the hierarchy of scattering singularities, we conclude that  $S$  must have infinitely many members  $\varphi_s$ , i.e.  $S$  is an infinite set. Even more astonishing: it turns out that the elements of  $S$  are not countable. This means that no scheme exists according to which the singularities in  $y^C(\varphi)$  can be listed one by one. Therefore, paradoxically, the singularities of  $y^C(\varphi)$  ( $l(\varphi)$ , respectively) are just as numerous as the initial angles  $\varphi$  in the interval  $0 < \varphi < \pi/2$ . This fact is truly counterintuitive. Its precise meaning is explained in Chapter 2. We will return to a more detailed study of scattering singularities in Chapter 9, where we study a molecular physics example of chaotic scattering. In that chapter we