Quantum Chaos

Does chaos lurk in the smooth, wavelike quantum world? Recent work shows that the answer is yes—symptoms of chaos enter even into the wave patterns associated with atomic energy levels

by Martin C. Gutzwiller

In 1917 Albert Einstein wrote a paper that was completely ignored for 40 years. In it he raised a question that physicists have only recently begun asking themselves: What would classical chaos, which lurks everywhere in our world, do to quantum mechanics, the theory describing the atomic and subatomic worlds? The effects of classical chaos, of course, have long been observed—Kepler knew about the irregular motion of the moon around the earth, and Newton complained bitterly about the phenomenon. At the end of the 19th century, the American astronomer George William Hill demonstrated that the irregularity is the result entirely of the gravitational pull of the sun. Shortly thereafter, the great French mathematician-astronomer-physicist Henri Poincaré surmised that the moon's motion is only a mild case of a congenital disease affecting nearly everything. In the long run, Poincaré realized, most dynamic systems show no discernible regularity or repetitive pattern. The behavior of even a simple system can depend so sensitively on its initial conditions that the final outcome is uncertain [see "The Amateur Scientist," page 144].

At about the time of Poincaré's seminal work on classical chaos, Max Planck started another revolution, which would lead to the modern theory of quantum mechanics. The simple systems that Newton had studied were investigated again, but this time on the atomic scale. The quantum analogue of the humble pendulum is the laser; the flying cannonballs of the atomic world consist of beams of protons or electrons, and the rotating wheel is the spinning electron (the basis of magnetic tapes). Even the solar system itself is mirrored in each of the atoms found in the periodic table of the elements.

Perhaps the single most outstanding feature of the quantum world is its smooth and wavelike nature. This feature leads to the question of how chaos makes itself felt when moving from the classical world to the quantum world. How can the extremely irregular character of classical chaos be reconciled with the smooth and wavelike nature of phenomena on the atomic scale? Does chaos exist in the quantum world?

Preliminary work seems to show that it does. Chaos is found in the distribution of energy levels of certain atomic systems; it even appears to sneak into the wave patterns associated with those levels. Chaos is also found when electrons scatter from small molecules. I must emphasize, however, that the term "quantum chaos" serves more to describe a conundrum than to define a well-posed problem.

Considering the following interpretation of the bigger picture may be helpful in coming to grips with quantum chaos. All our theoretical discussions of mechanics can be somewhat artificially divided into three compartments [*see illustration on page 80*]—although nature recognizes none of these divisions.

Elementary classical mechanics falls in the first compartment. This box contains all the nice, clean systems exhibiting simple and regular behavior, and so I shall call it R, for regular. Also contained in R is an elaborate mathematical tool called perturbation theory, which is used to calculate the effects of small interactions and extraneous disturbances, such as the influence of the sun on the moon's motion around the earth. With the help of perturbation theory, a large part of physics is understood nowadays as making relatively mild modifications of regular systems. Reality, though, is much more complicated; chaotic systems lie outside the range of perturbation theory, and they constitute the second compartment.

Since the first detailed analyses of the systems of the second compartment were done by Poincaré, I shall name this box P in his honor. It is stuffed with the chaotic dynamic systems that are the bread and butter of science [see "Chaos," by James P. Crutchfield, J. Doyne Farmer, Norman H. Packard and Robert S. Shaw; SCIENTIFIC AMERICAN, December 1986]. Among these systems are all the fundamental problems of mechanics, starting with three, rather than only two, bodies interacting with one another, such as the earth, moon and sun, or the three atoms in the water molecule, or the three quarks in the proton.

Quantum mechanics, as it has been practiced for about 90 years, belongs in the third compartment, called Q. After the pioneering work of Planck, Einstein and Niels Bohr, quantum mechanics was given its definitive form in four short years, starting in 1924. The seminal work of Louis de Broglie, Werner Heisenberg, Erwin Schrödinger, Max Born, Wolfgang Pauli and Paul Dirac has stood the test of the laboratory without the slightest lapse. Miraculously, it provides physics with a mathematical framework that, according to Dirac, has yielded a deep understanding of "most of physics and all of chemistry." Nevertheless, even though most

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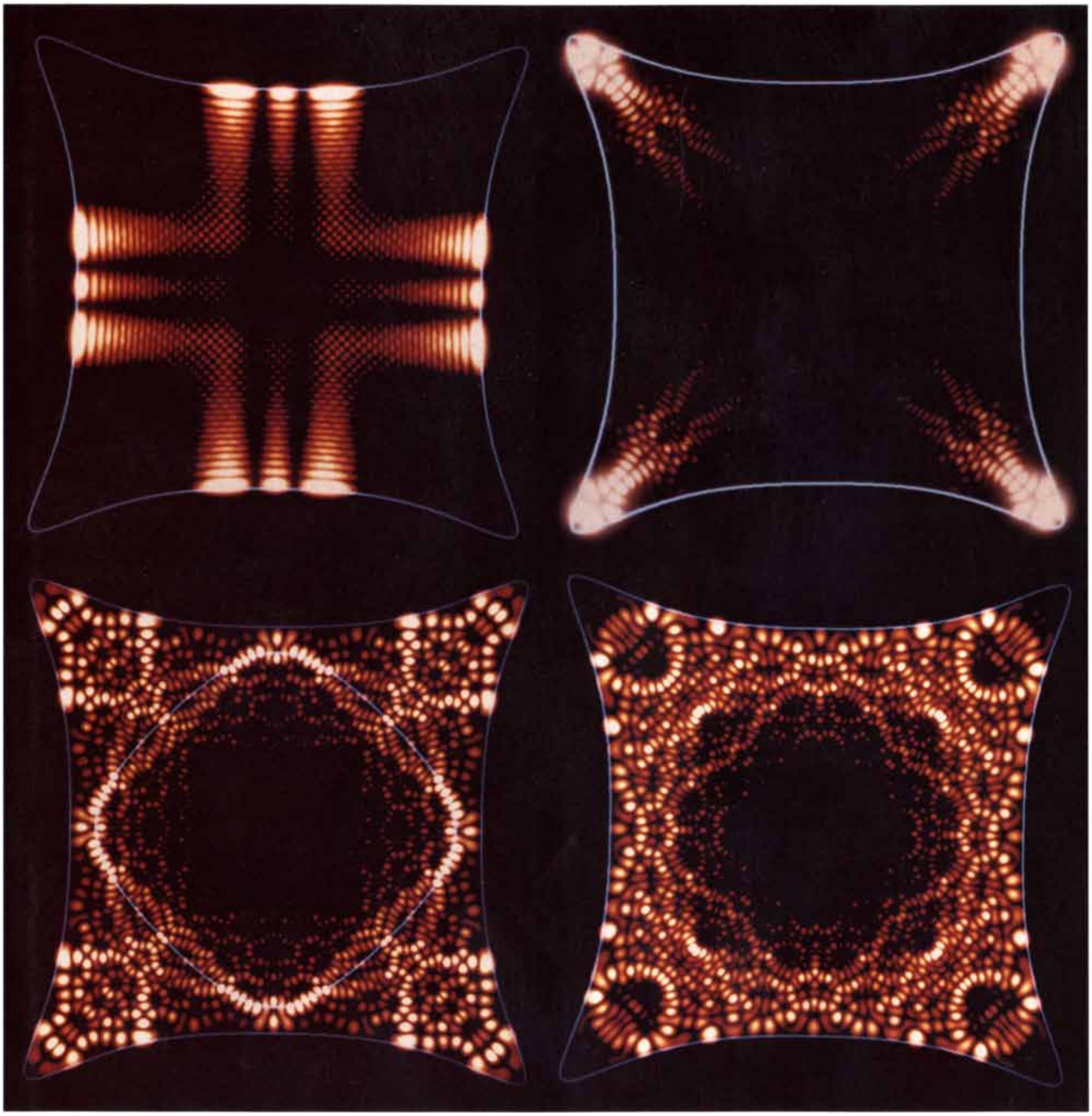
physicists and chemists have learned how to solve special problems in quantum mechanics, they have yet to come to terms with the incredible subtleties of the field. These subtleties are quite separate from the difficult, conceptual issues having to do with the interpretation of quantum mechanics.

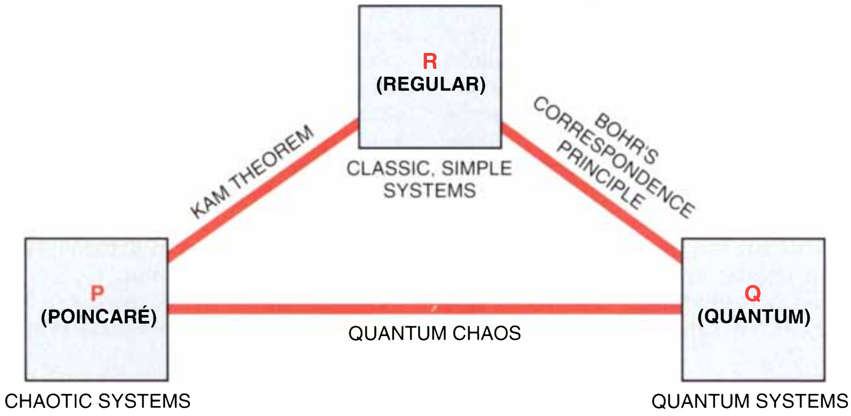
The three boxes R (classic, simple systems), P (classic chaotic systems) and Q (quantum systems) are linked by several connections. The connection between R and Q is known as Bohr's correspondence principle. The correspondence principle claims, quite reasonably, that classical mechanics must be contained in quantum mechanics in the limit where objects become much larger than the size of atoms. The main connection between R and P is the Kolmogorov-Arnold-Moser (KAM) theorem. The KAM theorem provides a powerful tool for calculating how much of the structure of a regular system survives when a small perturbation is introduced, and the theorem can thus identify perturbations that will cause a regular system to undergo chaotic behavior.

Quantum chaos is concerned with establishing the relation between boxes P (chaotic systems) and Q (quantum systems). In establishing this relation, it is useful to introduce a concept called phase space. Quite amazingly, this concept, which is now so widely exploited by experts in the field of dynamic systems, dates back to Newton.

The notion of phase space can be found in Newton's *Mathematical Princi-*



STATIONARY STATES, or wave patterns, associated with the energy levels of a Rydberg atom (a highly excited hydrogen atom) in a strong magnetic field can exhibit chaotic qualities. The states shown in the top two images seem regular; the bottom two are chaotic. At the bottom left, the state lies mostly along a periodic orbit; at the bottom right, it does not and is difficult to interpret, except for the four mirror symmetries with respect to the vertical, horizontal and two diagonal lines.



MECHANICS is traditionally (and artificially) divided into the three compartments depicted here, which are linked together by several connections. Quantum chaos is concerned with establishing the relation between boxes P and Q.

ples of Natural Philosophy, published in 1687. In the second definition of the first chapter, entitled "Definitions," Newton states (as translated from the original Latin in 1729): "The quantity of motion is the measure of the same, arising from the velocity and quantity of matter conjointly." In modern English, this means that for every object there is a quantity, called momentum, which is the product of the mass and velocity of the object.

Newton gives his laws of motion in the second chapter, entitled "Axioms, or Laws of Motion." The second law says that the change of motion is proportional to the motive force impressed. Newton relates the force to the change of momentum (not to the acceleration, as most textbooks do).

Momentum is actually one of two quantities that, taken together, yield the complete information about a dynamic system at any instant. The other quantity is simply position, which determines the strength and direction of the force. Newton's insight into the dual nature of momentum and position was put on firmer ground some 150 years later by two mathematicians, William Rowan Hamilton and Karl Gustav Jacob Jacobi. The pairing of momentum and position is no longer viewed in the good old Euclidean space of three dimensions; instead it is viewed in phase space, which has six dimensions, three dimensions for position and three for momentum.

The introduction of phase space was a wonderful step from a mathematical point of view, but it represents a serious setback from the standpoint of human intuition. Who can visualize six dimensions? In some cases, fortunately, the phase space can be reduced to three or, even better, two dimensions.

Such a reduction is possible in examining the behavior of a hydrogen atom in a strong magnetic field. The hydrogen atom has long been a highly desirable system because of its simplicity: a lone electron moves around a lone proton. And yet the classical motion of the electron becomes chaotic when the magnetic field is turned on. How can we claim to understand physics if we cannot explain this basic problem?

Under normal conditions, the electron of a hydrogen atom is tightly bound to the proton. The behavior of the atom is governed by quantum mechanics. The atom is not free to take on any arbitrary energy; it can take on only discrete, or quantized, energies. At low energies, the allowed values are spread relatively far apart. As the energy of the atom is increased, the atom grows bigger, because the electron moves farther from the proton, and the allowed energies get closer together. At high enough energies (but not too high, or the atom will be stripped of its electron!), the allowed energies get very close together into what is effectively a continuum, and it now becomes fair to apply the rules of classical mechanics.

Such a highly excited atom is called a Rydberg atom [see "Highly Excited Atoms," by Daniel Kleppner, Michael G. Littman and Myron L. Zimmerman; SCIENTIFIC AMERICAN, May 1981]. Rydberg atoms inhabit the middle ground between the quantum and the classical worlds, and they are therefore ideal candidates for exploring Bohr's correspondence principle, which connects boxes Q (quantum phenomena) and R (classic phenomena). If a Rydberg atom could be made to exhibit chaotic behavior in the classical sense, it might provide a clue as to the nature of quantum chaos and thereby shed light on the middle ground between boxes Q and P (chaotic phenomena).

A Rydberg atom exhibits chaotic behavior in a strong magnetic field, but to see this behavior we must reduce the dimension of the phase space. The first step is to note that the applied magnetic field defines an axis of symmetry through the atom. The motion of the electron takes place effectively in a two-dimensional plane, and the motion around the axis can be separated out; only the distances along the axis and from the axis matter. The symmetry of motion reduces the dimension of the phase space from six to four.

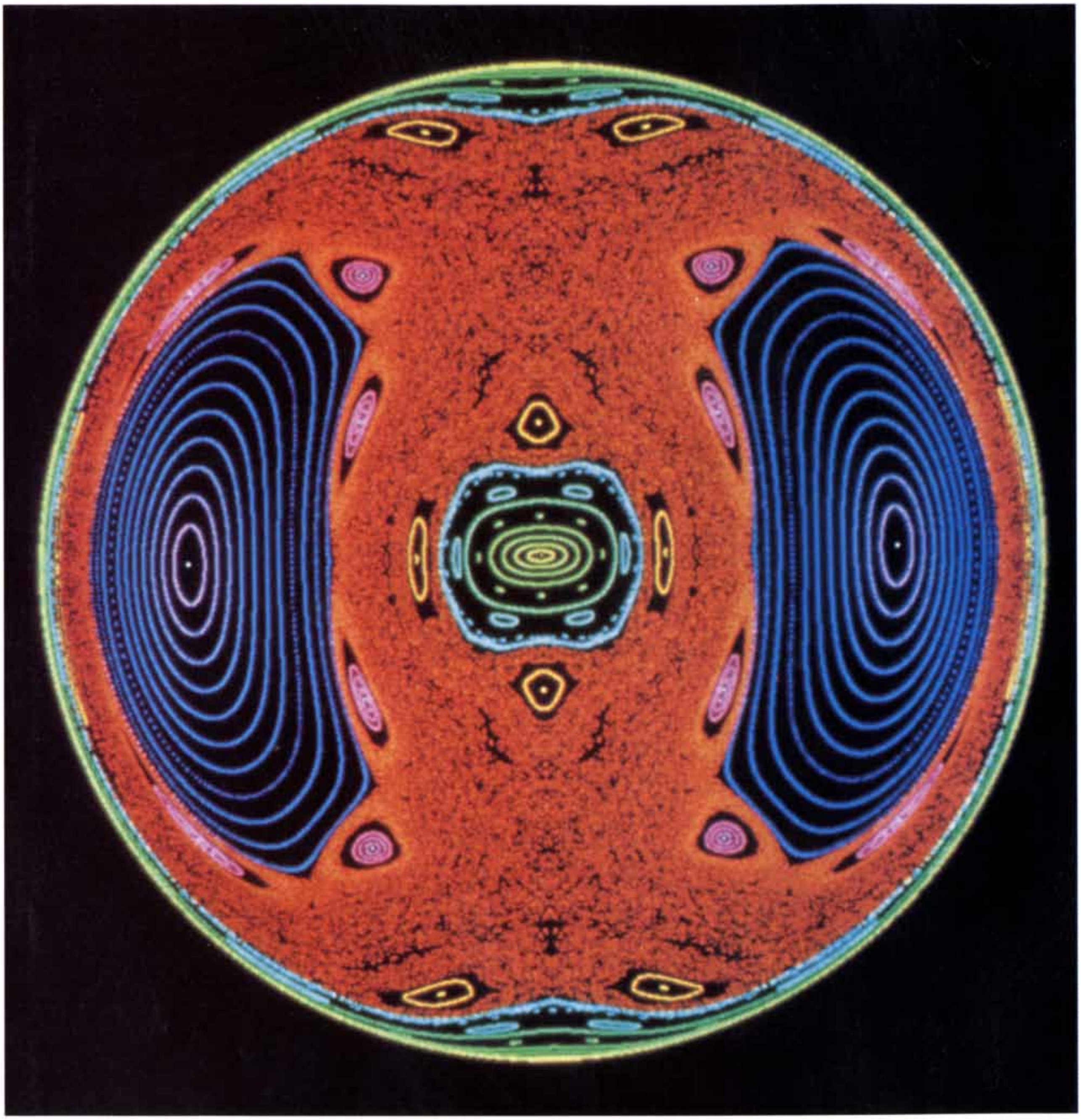
Additional help comes from the fact that no outside force does any work on the electron. As a consequence, the total energy does not change with time. By focusing attention on a particular value of the energy, one can take a three-dimensional slice—called an energy shell—out of the four-dimensional phase space. The energy shell allows one to watch the twists and turns of the electron, and one can actually see something resembling a tangled wire sculpture. The resulting picture can be simplified even further through a simple idea that occurred to Poincaré. He suggested taking a fixed two-dimensional plane (called a Poincaré section, or a surface of section) through the energy shell and watching the points at which the trajectory intersects the surface. The Poincaré section reduces the tangled wire sculpture to a sequence of points in an ordinary plane.

A Poincaré section for a highly excited hydrogen atom in a strong magnetic field is shown on the opposite page. The regions of the phase space where the points are badly scattered indicate chaotic behavior. Such scattering is a clear symptom of classical chaos, and it allows one to separate systems into either box P or box R.

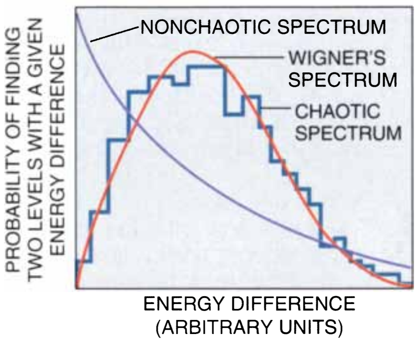
What does the Rydberg atom reveal about the relation between boxes P and Q? I have mentioned that one of the trademarks of a quantum mechanical system is its quantized energy levels, and in fact the energy levels are the first place to look for quantum chaos. Chaos does not make itself felt at any particular energy level, however; rather its presence is seen in the spectrum, or distribution, of the levels. Perhaps somewhat paradoxically, in a nonchaotic quantum system the energy levels are distributed randomly and without correlation, whereas the energy levels of a chaotic quantum system exhibit strong correlations [*see top illustration on page 82*]. The levels of the regular system are often close to one another, because a regular system is composed of smaller subsystems that are completely decoupled. The energy levels of the chaotic system, however, almost seem to be aware of one another and try to keep a safe distance. A chaotic system cannot be decomposed; the motion along one coordinate axis is always coupled to what happens along the other axis.

The spectrum of a chaotic quantum system was first suggested by Eugene P. Wigner, another early master of quantum mechanics. Wigner observed, as had many others, that nuclear physics does not possess the safe underpinnings of atomic and molecular physics; the origin of the nuclear force is still not clearly understood. He therefore asked whether the statistical properties of nuclear spectra could be derived from the assumption that many parameters in the problem have definite, but unknown, values. This rather vague starting point allowed him to find the most probable formula for the distribution. Oriol Bohigas and Marie-Joya Giannoni of the Institute of Nuclear Physics in Orsay, France, first pointed out that Wigner's distribution happens to be exactly what is found for the spectrum of a chaotic dynamic system.

Chaos does not seem to limit itself to the distribution of quantum energy levels, however; it even appears to work its way into the wavelike nature of the quantum world. The position of the electron in the hy-



POINCARÉ SECTION OF A HYDROGEN ATOM in a strong magnetic field has regions (*orange*) where the points of the electron's trajectory scatter wildly, indicating chaotic behavior. The section is a slice out of phase space, an abstract six-dimensional space: the usual three for the position of a particle and an additional three for the particle's momentum.



ENERGY SPECTRUM, or distribution of energy levels, differs markedly between chaotic and nonchaotic quantum systems. For a nonchaotic system, such as a molecular hydrogen ion (H_2^+), the probability of finding two energy levels close to each other is quite high. In the case of a chaotic system such as a Rydberg atom in a strong magnetic field, the probability is low. The chaotic spectrum closely matches the typical nuclear spectrum derived many years ago by Eugene P. Wigner.

drogen atom is described by a wave pattern. The electron cannot be pinpointed in space; it is a cloudlike smear hovering near the proton. Associated with each allowed energy level is a stationary state, which is a wave pattern that does not change with time. A stationary state corresponds quite closely to the vibrational pattern of a membrane that is stretched over a rigid frame, such as a drum.

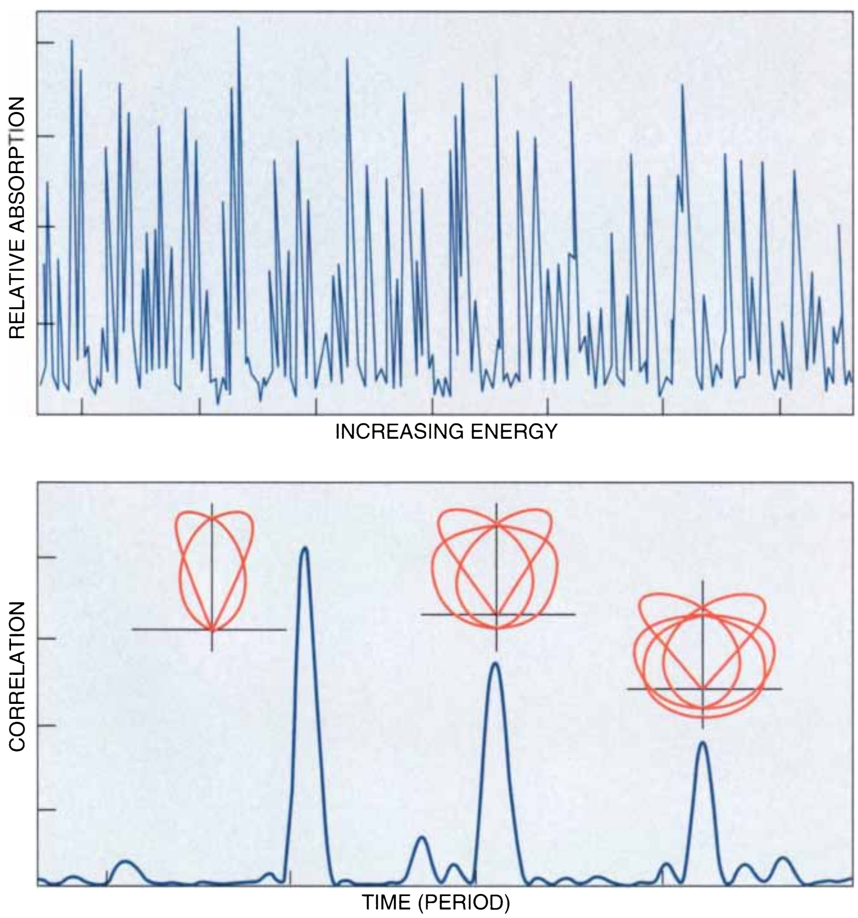
The stationary states of a chaotic system have surprisingly interesting structure, as demonstrated in the early 1980s by Eric Heller of the University of Washington. He and his students calculated a series of stationary states for a two-dimensional cavity in the shape of a stadium. The corresponding problem in classical mechanics was known to be chaotic, for a typical trajectory quickly covers most of the available ground quite evenly. Such behavior suggests that the stationary states might also look random, as if they had been designed without rhyme or reason. In contrast, Heller discovered that most stationary states are concentrated around narrow channels that form simple shapes inside the stadium, and he called these channels "scars" [*see illustration on opposite page*]. Similar structure can also be found in the stationary states of a hydrogen atom in a strong magnetic field [*see illustration on page 79*]. The smoothness of the quantum wave forms is preserved from point to point, but when one steps back to view the whole picture, the fingerprint of chaos emerges.

It is possible to connect the chaotic signature of the energy spectrum to ordinary classical mechanics. A clue to the prescription is provided in Einstein's 1917 paper. He examined the phase space of a regular system from box R and described it geometrically as filled with surfaces in the shape of a donut; the motion of the system corresponds to the trajectory of a point over the surface of a particular donut. The trajectory winds its way around the surface of the donut in a regular manner, but it does not necessarily close on itself.

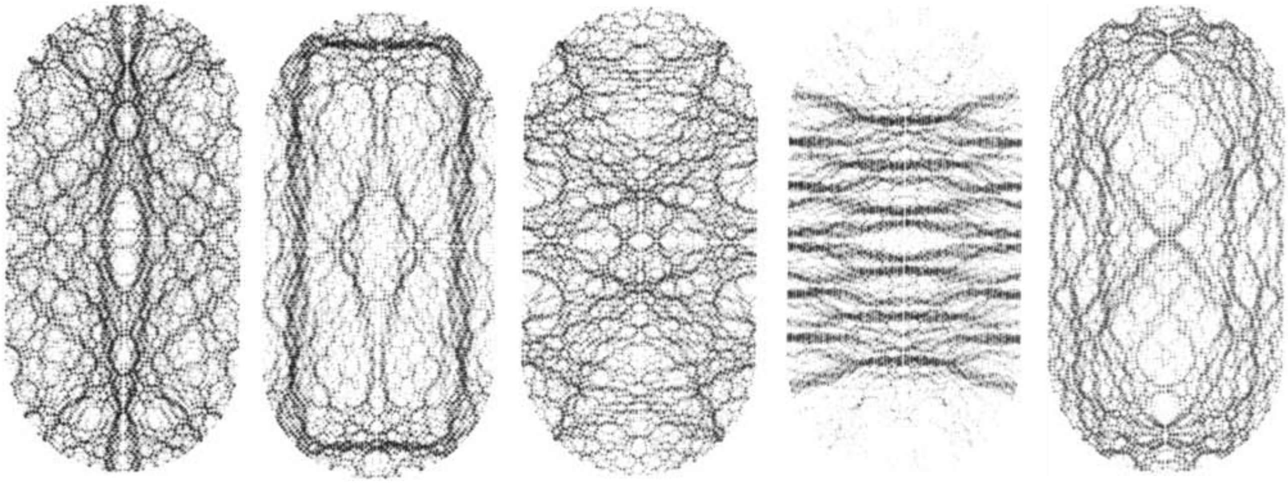
In Einstein's picture, the application of Bohr's correspondence principle to find the energy levels of the analogous quantum mechanical system is simple. The only trajectories that can occur in nature are those in which the cross section of the donut encloses an area equal to an integral multiple of Planck's constant, h (2π times the fundamental quantum of angular momentum, having the units of momentum multiplied by length). It turns out that the integral multiple is precisely the number that specifies the corresponding energy level in the quantum system.

Unfortunately, as Einstein clearly saw, his method cannot be applied if the system is chaotic, for the trajectory does not lie on a donut, and there is no natural area to enclose an integral multiple of Planck's constant. A new approach must be sought to explain the distribution of quantum mechanical energy levels in terms of the chaotic orbits of classical mechanics.

Which features of the trajectory of classical mechanics help us to understand quantum chaos? Hill's discussion of the moon's irregular orbit because of the presence of the sun provides a clue. His work represented the first instance where a particular periodic orbit is found to be at the bottom of a difficult mechanical problem. (A periodic orbit is like a closed track on which the system is made to run; there are many of them, although they are isolated and unstable.) Inspiration can also be drawn from Poincaré, who emphasized the



ABSORPTION OF LIGHT by a hydrogen atom in a strong magnetic field appears to vary randomly as a function of energy (*top*), but when the data are analyzed according to the mathematical procedure called Fourier analysis, a distinct pattern emerges (*bottom*). Each peak in the bottom panel has associated with it a specific classical periodic orbit (*red figures next to peaks*).



PARTICLE IN A STADIUM-SHAPED BOX has chaotic stationary states with associated wave patterns that look less random than one might expect. Most of the states are concentrated around narrow channels that form simple shapes, called scars.

general importance of periodic orbits. In the beginning of his three-volume work, *The New Methods of Celestial Mechanics,* which appeared in 1892, he expresses the belief that periodic orbits "offer the only opening through which we might penetrate into the fortress that has the reputation of being impregnable." Phase space for a chaotic system can be organized, at least partially, around periodic orbits, even though they are sometimes quite difficult to find.

In 1970 I discovered a very general way to extract information about the quantum mechanical spectrum from a complete enumeration of the classical periodic orbits. The mathematics of the approach is too difficult to delve into here, but the main result of the method is a relatively simple expression called a trace formula. The approach has now been used by a number of investigators, including Michael V. Berry of the University of Bristol, who has used the formula to derive the statistical properties of the spectrum.

I have applied the trace formula to compute the lowest two dozen energy levels for an electron in a semiconductor lattice, near one of the carefully controlled impurities. (The semiconductor, of course, is the basis of the marvelous devices on which modern life depends; because of its impurities, the electrical conductivity of the material is halfway between that of an insulator, such as plastic, and that of a conductor, such as copper.) The trajectory of the electron can be uniquely characterized by a string of symbols, which has a straightforward interpretation. The string is produced by defining an axis through the semiconductor and simply noting when the trajectory crosses the axis. A crossing to the "positive" side of the axis gets the symbol +, and a crossing to the "negative" side gets the symbol –.

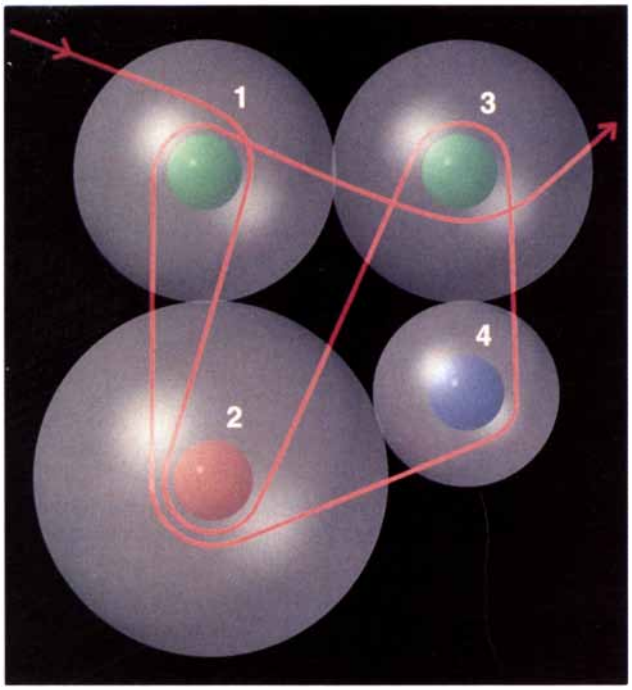
A trajectory then looks exactly like the record of a coin toss. Even if the past is known in all detail—even if all the crossings have been recorded—the future is still wide open. The sequence of crossings can be chosen arbitrarily. Now, a periodic orbit consists of a binary sequence that repeats itself; the simplest such sequence is (+ –), the next is (+ + –), and so on. (Two crossings in a row having the same sign indicate that the electron has been trapped temporarily.) All periodic orbits are thereby enumerated, and it is possible to calculate an approximate spectrum with the help of the trace formula. In other words, the quantum mechanical energy levels are obtained in an approximation that relies on quantities from classical mechanics only.

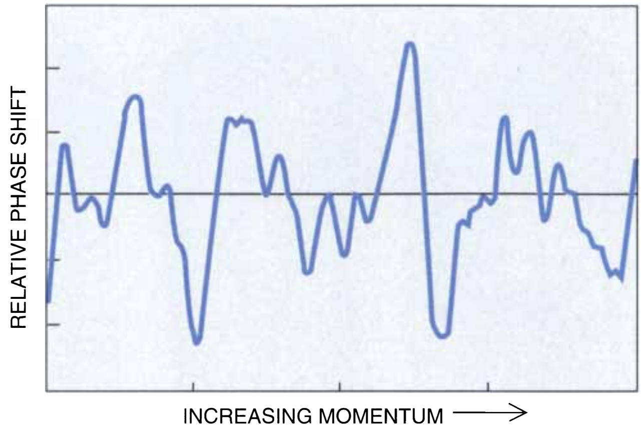
The classical periodic orbits and the quantum mechanical spectrum are closely bound together through the mathematical process called Fourier analysis [see "The Fourier Transform," by Ronald N. Bracewell; SCIENTIFIC AMERICAN, June 1989]. The hidden regularities in one set, and the frequency with which they show up, are exactly given by the other set. This idea was used by John B. Delos of the College of William and Mary and Dieter Wintgen of the Max Planck Institute for Nuclear Physics in Heidelberg to interpret the spectrum of the hydrogen atom in a strong magnetic field.

Experimental work on such spectra has been done by Karl H. Welge and his colleagues at the University of Bielefeld, who have excited hydrogen atoms nearly to the point of ionization, where the electron tears itself free of the proton. The energies at which the atoms absorb radiation appear to be quite random [*see upper part of bottom illustration on opposite page*], but a Fourier analysis converts the jumble of peaks into a set of well-separated peaks [*see lower part of bottom illustration on opposite page*]. The important feature here is that each of the well-separated peaks corresponds precisely to one of several standard classical periodic orbits. Poincaré's insistence on the importance of periodic orbits now takes on a new meaning. Not only does the classical organization of phase space depend critically on the classical periodic orbits, but so too does the understanding of a chaotic quantum spectrum.

So far I have talked only about quantum systems in which an electron is trapped or spatially confined. Chaotic effects are also present in atomic systems where an electron can roam freely, as it does when it is scattered from the atoms in a molecule. Here energy is no longer quantized, and the electron can take on any value, but the effectiveness of the scattering depends on the energy.

Chaos shows up in quantum scattering as variations in the amount of time the electron is temporarily caught inside the molecule during the scattering process. For simplicity, the problem can be examined in two dimensions. To the electron, a molecule consisting of four atoms looks like a small maze. When the electron approaches one of the atoms, it has two choices: it can turn left or right. Each possible trajectory of the electron through the molecule can be recorded as a series of left and right turns around the atoms, until the particle finally emerges. All of the trajectories are unstable: even a





TRAJECTORY OF AN ELECTRON through a molecule during scattering can be recorded as a series of left and right turns around the atoms making up the molecule (*left*). Chaotic variation (*above*) characterizes the time it takes for a scattered electron of known momentum to reach a fixed monitoring station. Arrival time varies as a function of the electron's momentum. The variation is smooth when changes in the momentum are small but exhibits a complex chaotic pattern when the changes are large. The quantity shown on the vertical axis, the phase shift, is a measure of the time delay.

minute change in the energy or the initial direction of the approach will cause a large change in the direction in which the electron eventually leaves the molecule.

The chaos in the scattering process comes from the fact that the number of possible trajectories increases rapidly with path length. Only an interpretation from the quantum mechanical point of view gives reasonable results; a purely classical calculation yields nonsensical results. In quantum mechanics, each classical trajectory of the electron is used to define a little wavelet that winds its way through the molecule. The quantum mechanical result follows from simply adding up all such wavelets.

Recently I have done a calculation of the scattering process for a special case in which the sum of the wavelets is exact. An electron of known momentum hits a molecule and emerges with the same momentum. The arrival time for the electron to reach a fixed monitoring station varies as a function of the momentum, and the way in which it varies is what is so fascinating about this problem. The arrival time fluctuates smoothly over small changes in the momentum, but over large changes a chaotic imprint emerges, which never settles down to any simple pattern [*see right part of illustration above*].

A particularly tantalizing aspect of the chaotic scattering process is that it may connect the mysteries of quantum chaos with the mysteries of number theory. The calculation of the time delay leads straight into what is probably the most enigmatic object in mathematics, Riemann's zeta function. Actually, it was first employed by Leonhard Euler in the middle of the 18th century to show the existence of an infinite number of prime numbers (integers that cannot be divided by any smaller integer other than one). About a century later Bernhard Riemann, one of the founders of modern mathematics, employed the function to delve into the distribution of the primes. In his only paper on the subject, he called the function by the Greek letter zeta.

The zeta function is a function of two variables, x and y (which exist in the complex plane). To understand the distribution of prime numbers, Riemann needed to know when the zeta function has the value of zero. Without giving a valid argument, he stated that it is zero only when x is set equal to $1/2$. Vast calculations have shown that he was right without exception for the first billion zeros, but no mathematician has come even close to providing a proof. If Riemann's conjecture is correct, all kinds of interesting properties of prime numbers could be proved.

The values of y for which the zeta function is zero form a set of numbers that is much like the spectrum of energies of an atom. Just as one can study the distribution of energy levels in the spectrum, so can one study the distribution of zeros for the zeta function. Here the prime numbers play the same role as the classical closed orbits of the hydrogen atom in a magnetic field: the primes indicate some of the hidden correlations among the zeros of the zeta function.

In the scattering problem the zeros of the zeta function give the values of the momentum where the time delay changes strongly. The chaos of the Riemann zeta function is particularly apparent in a theorem that has only recently been proved: the zeta function fits locally any smooth function. The theorem suggests that the function may describe all the chaotic behavior a quantum system can exhibit. If the mathematics of quantum mechanics could be handled more skillfully, many examples of locally smooth, yet globally chaotic, phenomena might be found.

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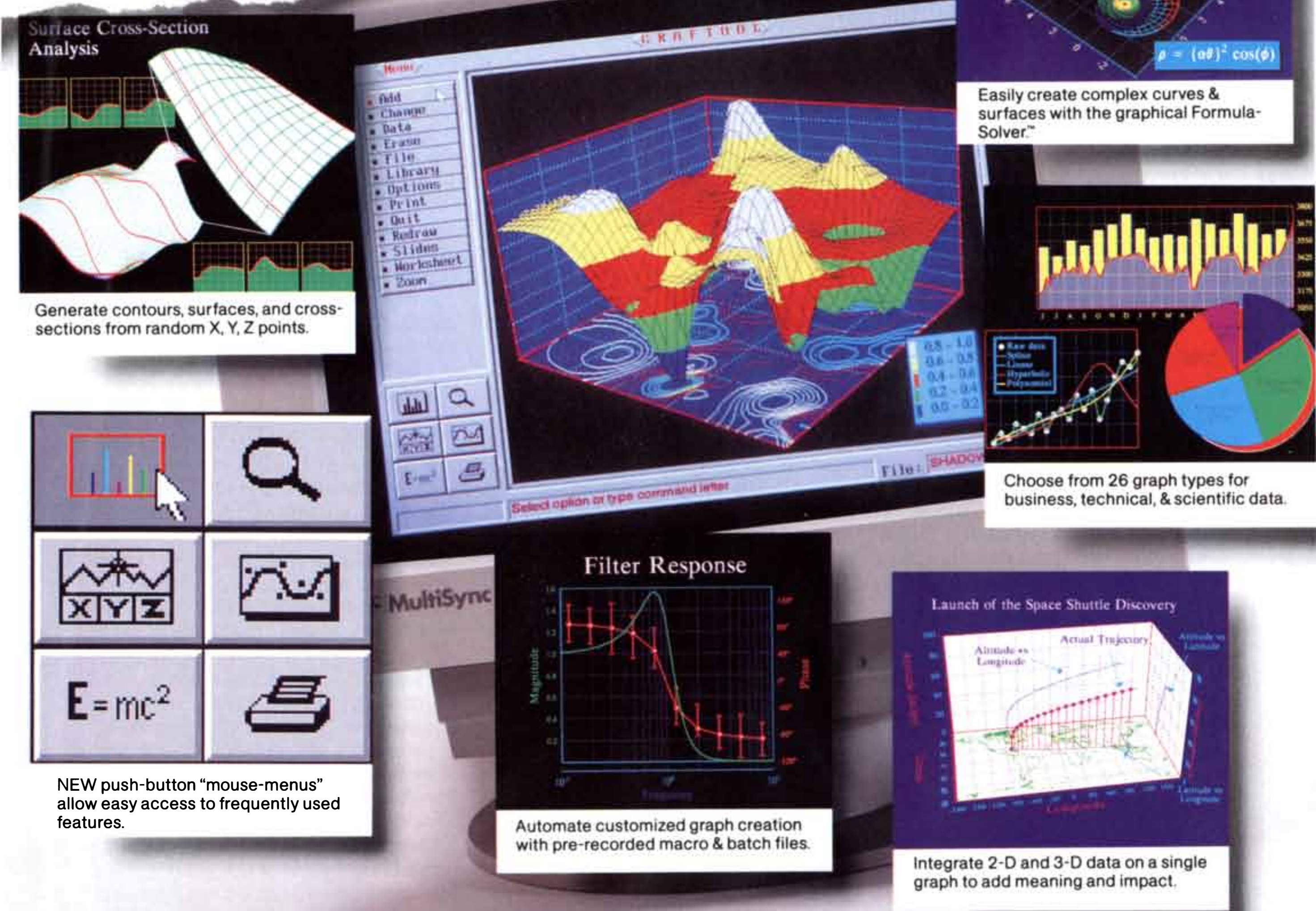

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