Chaos on the Quantum Scale

Simulations of atomic-scale billiards reveal chaotic phenomena that expand theory and applications, especially in nanotechnology

Mason A. Porter and Richard L. Liboff

During the 20th century, two new ways of describing physical systems emerged to thwart scientists' hopes of ever completely predicting nature's behavior. First, the theory of quantum mechanics uncovered rampant uncertainty at the tiniest scales of matter—in the canonical example, an electron's precise position and momentum cannot simultaneously be known at any particular moment. The second body of thought is what we now call chaos theory. Some phenomena, it turns out, depend intimately on a system's initial conditions, so that an imperceptible change in the beginning value of a variable can make the outcome of a process impossible to predict. Chaos appears in examples as distinct as the frequency of drips from a faucet and the motion of planets.

Given the unpredictability that characterizes both chaos and quantum mechanics, one might well wonder what would happen if these phenomena were merged. Utter chaos, perhaps? Probably not; in fact we have tools for approaching the modeling of *quantum chaos*, or chaotic behavior on the quantum scale. Early attempts to understand this exotic realm have produced results that are both mathematically and scientifically important. Having found chaos at every larger scale, physicists cannot rule out the possibility of finding chaotic behavior in the devices they build at nanometer-scale dimensions—behavior that is bound to have the added uncertainty associated with the quantum world.

The trail of evidence toward a commingling of quantum mechanics and chaos started late in the 19th century, when the French mathematician, physicist and philosopher Henri Poincaré started working on equations to predict the positions of planets as they rotated around the sun. The task sounds easy enough. Note the starting positions and velocities, feed them into a set of equations based on Newton's laws of motion, and the results should predict future positions. But the outcome turned Poincaré's expectations upside down. With only two planets under consideration, he found that even tiny differences in the initial conditions—the starting values for position and velocity—elicited substantial changes in future positions. Although Poincaré didn't use the word "chaotic," that's just what such a system is called today.

The broader significance of Poincaré's work was recognized much later, in the 1960s, when Edward Lorenz, a meteorologist, discovered chaotic behavior in a simple set of equations he used to study atmospheric conditions. Soon examples of chaos seemed to appear wherever scientists looked. Chaos turned up in galactic orbits and in virtually every type of oscillator, from springs to electrical circuits.

Having found chaotic behavior in realms as small as the microscopic world, scientists still wonder how to profitably study chaos in the quantum world. That is, do events inside atoms and molecules display chaotic features? Through mathematical simulations, we take this universe-size idea of chaos and shrink it to make it fit into the quantum realm of atoms and electrons. In some cases, chaos never appears. In others, we show that life looms chaotic on this tiny scale. In still other situations, chaos grows more disordered under some conditions than others. From this work, new mathematical and physical theories are being developed. These theories can be applied to an exotic but growing range of applications—including quantum dots, nanotubes and superconducting quantum-interference devices.

An Idealized Game of Snooker

Systems that can behave chaotically (a complicated class of what are known as dynamical systems) often defy intuitive understanding. Therefore studies often start with very simple examples, such as the so-called particle in a box. A two-dimensional version of this scenario can be envisioned as a single billiard ball moving on a pocketless table, say a snooker table. Investigators further simplify this example by neglecting friction. This simple analogy helps us ease our way into the world of quantum chaos.

Imagine this ideal billiard table, whose geometry is rectangular just like a pool-hall table. Set a ball near one corner and shoot it toward the nearest rail. The ball hits the rail, bounces off with an angle of reflection equal to the angle of incidence, runs across the table until it hits another rail and bounces again, following the same rule. If no friction or any other force impedes the ball, it continues bouncing around the table forever. To compare the ball's path under slightly different initial conditions, the experimenter stops the simulated shot and returns the ball to almost the original starting point, offsetting it just

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Figure 1. Carbon nanotubes and a variety of other devices in the nanoworld exhibit chaotic characteristics on the quantum scale. The realms of chaos and quantum mechanics have proved difficult enough to understand on their own, but some mathematicians and physicists have pondered what would happen if these phenomena were merged. The authors describe a series of tools developed over the past quarter-century for modeling chaos on the quantum scale. These tools reveal vital characteristics behind some of the most advanced devices in small-scale technology, including quantum dots, superconducting quantum-interference devices and the aligned carbon nanotubes shown here, whose electronic properties show evidence of quantum-chaotic behavior. (Photomicrograph courtesy of Australia's Commonwealth Scientific and Industrial Research Organization.)

a bit. Cued just as before—at the same angle and with the same force—it follows virtually the same path as the first shot. If you plot the course of the two shots, though, the resulting lines differ gradually over time. This is called *linear divergence*, which means that the distance that separates the two trajectories increases at a rate proportional to the amount of time that passes. No shot on this table behaves chaotically.

Imagine using the same table, but add another rail, a circular one placed right in the center of the table. Line up a ball near the circular rail and take a shot. This time the ball will careen off the circular rail, bounce to an outside rail, roll to another outside rail, hit the circular one again, and so on. As before, return the ball to nearly (but not exactly) its starting position and hit the ball in the same manner. This ball could soon be traveling along an entirely different trajectory from the first—an example of *exponential divergence*, which means that over time the two trajectories diverge at a rate that is exponentially fast. Named after the mathematician Yakov Sinai of Princeton University, this billiard is chaotic.

The table with the circular rail in the middle depicts a fundamental characteristic of chaos called *sensitive dependence on initial conditions*. In other words, infinitesimally different initial conditions—here the starting location of a ball—yield wildly different outcomes. This is just what Poincaré discovered in analyzing the equations describing planetary motion. It also arises in other forms of billiards; shaping the outer boundary of the table like a stadium running track produces chaotic behavior. In a bit, we shall also show how such examples help us explore how chaos manifests in the quantum domain.

Tracking a Particle's Position

With just a few bounces in billiards, including one or more rails, an observer can easily keep track of a ball's trajectory. One might imagine laying out a replica of a billiard table on a two-dimensional grid and plotting points at some regular interval of time to record a trajectory. After many bounces, though, with a ball crossing, recrossing and in some cases even retracing its path, the plotted points turn into a mess that is often uninformative. Although many scientists might start with a conventional grid to record a ball's motion, that is not the only way to proceed.

Mathematicians and physicists often rely on another form of plotting that was inspired by work done by Sir Isaac Newton in the 17th century. In Newton's time, physicists often employed a pendulum to study nature's forces.

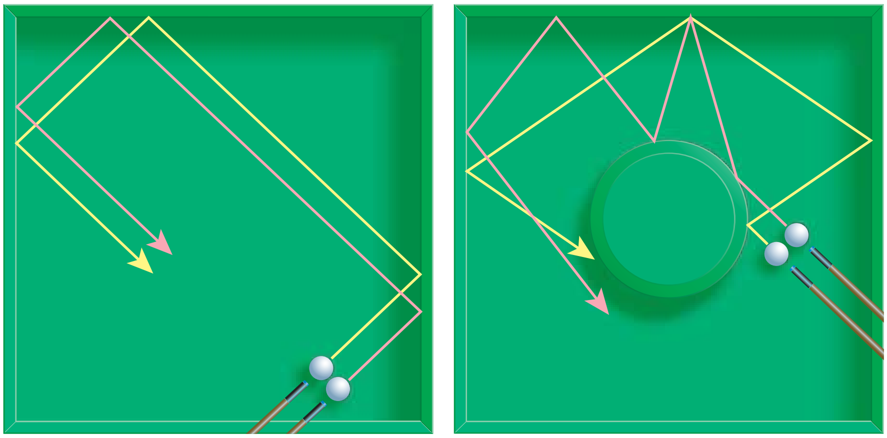

Figure 2. Chaotic behavior can be seen in an idealized game of snooker. On a rectangular, pocketless table *(left)*, a shot follows a trajectory that depends on the billiard's initial location and how it gets hit. After a slight change in the ball's starting position, a similar hit produces a similar trajectory. This is called linear divergence. Now, add a circular rail in the center of the table *(right)* to create a system called a Sinai billiard. A first shot hits the round rail and then bounces back and forth between the side and center rails a few times. Again, displace the ball slightly from its original position. This time the second trajectory is entirely different from the first. This example demonstrates exponential divergence; the two trajectories separate from one another at a rate that is exponentially fast, which is a fundamental characteristic of chaotic phenomena.

Newton found that he could completely describe a pendulum's state with two variables: its position and its momentum. Today's physicists and mathematicians also use these variables to describe the activity of subatomic particles. In other words, a particle's state, just like Newton's pendulum, can be described by its position in space and its momentum. Investigators plot these variables—momentum versus position—to create what is called *phase space*.

From a mathematical perspective, the use of phase space can solve several problems. It serves as a technique for tracking phenomena such as the activity of an electron. From an intuitive point of view, though, phase space can challenge your imagination. The trouble arises when a scientist wants to examine a particle in the real world, the three-dimensional world. Such a phase space has six dimensions: three dimensions for space—one for each axis of the three dimensions—and three for momentum. Anyone can generate a plot for just two dimensions, and even three can be created and understood fairly easily. But how does one imagine a plot with four or more dimensions?

Sometimes mathematicians solve such difficulties by sticking to simpler scenarios. For instance, the billiard examples above limit a ball to two-dimensional motion. That alone holds phase space to four dimensions. Still, it's not easy to plot a four-dimensional phenomenon on a sheet of paper. Luckily, a computer can imagine four dimensions, or many more. Thus, an investigator can enter position and momentum data into a computer in order to study the motion of particles even in high-dimensional spaces. The computer embodies this data in the form of equations that keep track of the myriad dimensions. Then, the software can "slice" through this multi-dimensional mass and cut out a piece—a section of phase space. This is called a *Poincaré section*, and it can be projected onto a two-dimensional space to create a set of points that can be viewed on a computer screen or printed on a piece of paper. Such a plot represents a series of snapshots of the system under investigation. The snapshots can give an understanding of the relation between conditions and outcomes; an investigator can, for instance, take a snapshot each time a certain condition occurs to examine a desired aspect of the system.

If a Poincaré map consists of a continuous line—no matter how curvy it might be—the system is not chaotic. If, on the other hand, a Poincaré map reveals an essentially random series of dots, a system is chaotic. So we can define a system—say, one of the billiard models above—describe it with mathematical equations, collect data on position and momentum over time and then generate a Poincaré map. The results, which are usually reliable, are used to distinguish chaotic from nonchaotic behavior.

Keeping a Particle in a Box

With the above tools in place, we can explain some of our research in quantum chaos. To get started, we turn to a slightly more complicated version of a particle in a box. Imagine a three-dimensional snooker table shaped like a sphere, and suppose that the particle confined within is an electron rather than a billiard ball. This system is an example of a *quantum billiard*. We can simulate this system to examine the motion of the electron as it collides with the walls of its spherical prison.

Given that this system resides in the quantum domain, we will describe this particle with an equation from quantum mechanics called the Schrödinger equation. This equation encompasses the bizarre features of quantum mechanics. For example, Heisenberg's uncertainty principle states that one cannot simultaneously determine the position and momentum of a particle. In other words, the more accurately one knows a particle's position, the less accurately one can determine its momentum. The Schrödinger equation incorporates this principle.

In addition, objects on the quantum scale exhibit characteristics of both particles and waves, what is often described as *particle-wave duality.* In fact, a solution to a Schrödinger equation is called a wavefunction. So the particle

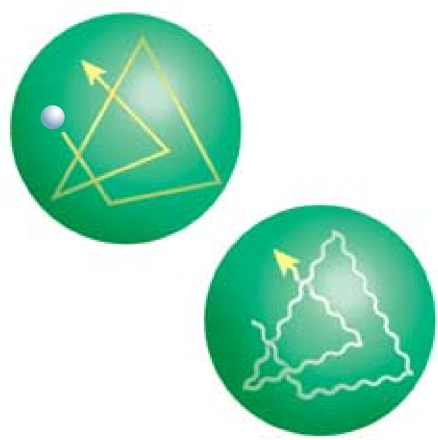

Figure 3. Particle trapped in a sphere serves as a simple model for developing mathematical simulations *(top)*. A particle bouncing inside a sphere can represent various physical phenomena, including a trapped electron. In quantum mechanics, particles exhibit some wavelike properties, and vice versa. Accordingly, a quantum simulation of a particle in a sphere can be replaced by a wave in a sphere *(bottom)*. The authors describe this wave with the Schrödinger equation, which represents a wave or particle's quantum features.

we imagined bouncing inside a sphere can also be conceptualized as a wave reflecting back and forth inside the spherical space. We don't need to add another equation to represent the sphere; instead, we define the Schrödinger equation in a way that makes a wave disappear to nothing when it reaches the sphere's boundary. We can describe the entire scenario—a particle, or a wave, in a sphere—with just one Schrödinger equation.

Waves serve as crucial elements for understanding the phenomena going on inside this sphere. Many ordinary waves—waves in the ocean or vibrations going back and forth along a plucked guitar string—consist of a summation of waves of various frequencies. A wave can also be composed of just one frequency, making a much simpler wave called a *normal mode*. We can pick a wave of an appropriate single frequency, plug it into the Schrödinger equation, and the results show how the wave would bounce around inside this sphere. We can then consider what happens in the presence of multiple normal modes.

In the billiard-table examples above, we looked for chaos by slightly changing the starting position of a ball and then following its trajectory. Here, instead of changing initial position, we add a second normal mode, one with a different frequency from the first. To get the complete solution to the Schrödinger equation, we would need to include an infinite series of normal modes, each distinguished by its energy and its geometry. To keep this simulation as simple as possible, however, we used only two modes in our wavefunction. When we did that, it reduced to a form of an equation that is known to never create chaos. Thus, there is no chaotic behavior in a particle moving inside a stationary sphere. We can also think of this system as being like the billiards mentioned earlier. The regular behavior of the wavefunctions corresponds to the linear divergence that is observed between nearby trajectories in a classical spherical billiard. We have not yet modeled a quantum-chaotic system.

Adding More Bounce to a Billiard

Now imagine the previous example of a quantum billiard, but with a small complication: The boundary of the sphere vibrates in and out. In this scenario, when a particle hits the vibrating wall of the sphere, the result depends on the states of the wall and the particle. This example takes a little more work, but it's a necessary complication to be able to simulate quantum chaos. (What we will be simulating is given the moniker *semiquantum* chaos, for reasons that will become clear.)

One starts to simulate this system just like the particle in a stationary sphere: Set up a Schrödinger equation for the particle. But this time there must also be an equation for the vibrating boundary. In this simulation, the particle's activity depends on its properties and those of the wall. The wall can be represented with mechanical motion, or a classical—as opposed to quantum mechanical—equation. In other words, this example of a particle in a vibrating sphere takes us to the interface between the quantum and classical worlds. Fortunately, a quantity called the *Hamiltonian* can be used to encode the dynamical behavior combining the Schrödinger equation for the particle and the mechanical equation for the wall. The Hamiltonian plays the role of conserved energy and produces the ordinary differential equations needed for this simulation.

As before, we tested this equation by inserting two normal modes. Then we conducted computer simulations of the differential equations obtained from the Hamiltonian to examine the behavior of the billiard system. After each run we changed the starting conditions a bit by, for instance, using a different

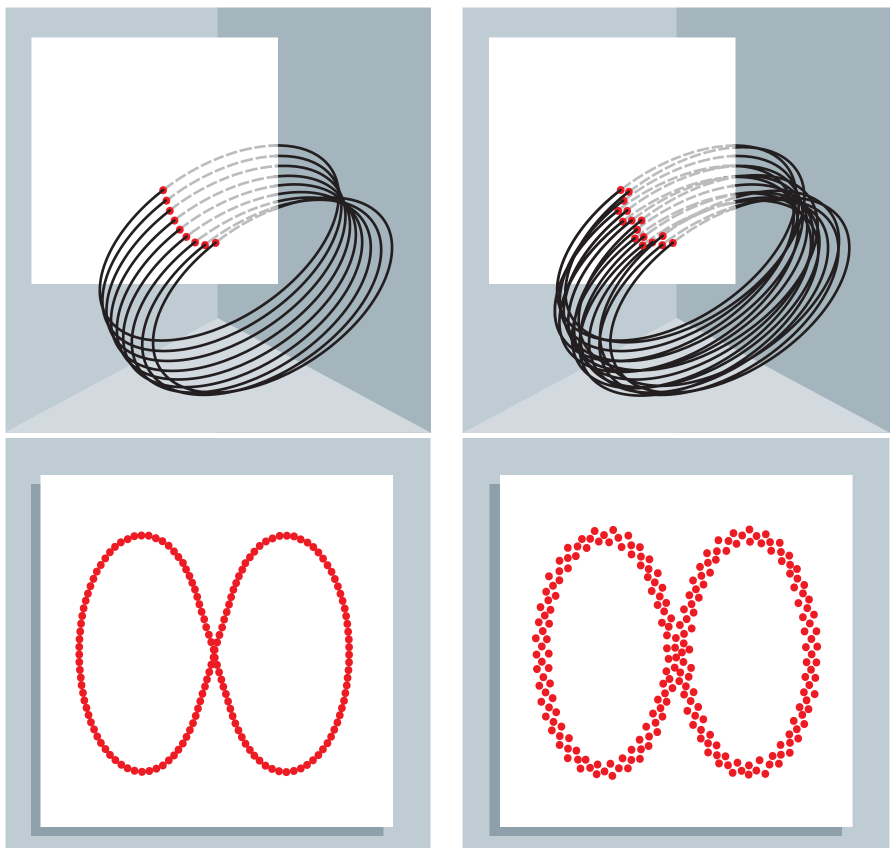

Figure 4. Poincaré sections reveal chaotic behavior. Imagine an electron bouncing around inside a sphere, as in Figure 3, but permit the radius of this sphere to vibrate in time. That is, the enclosed particle interacts with the pulsing spherical wall that surrounds it. The authors describe this system with a set of equations, provide starting data for the system and run it. The results might take the form of a loop in space *(upper left)*. The authors only collect data matching specific conditions, such as when one variable equals zero. If the data are collected in three dimensions, this is analogous to inserting a piece of paper to capture a two-dimensional plot, called a Poincaré section. In this case, it is projected into the plane describing the position and momentum of the sphere's radius. The resulting Poincaré section *(lower left)* contains only continuous curves, so it is not chaotic. By changing the system slightly—say, starting with a sphere with a slightly smaller or larger radius—this simulation would produce new data *(upper right)*. Although the original data sets *(upper panels)* might look virtually identical, they might create very different Poincaré sections. In this case, the second Poincaré section *(lower right)* includes smudged areas, so it does exhibit chaotic behavior.

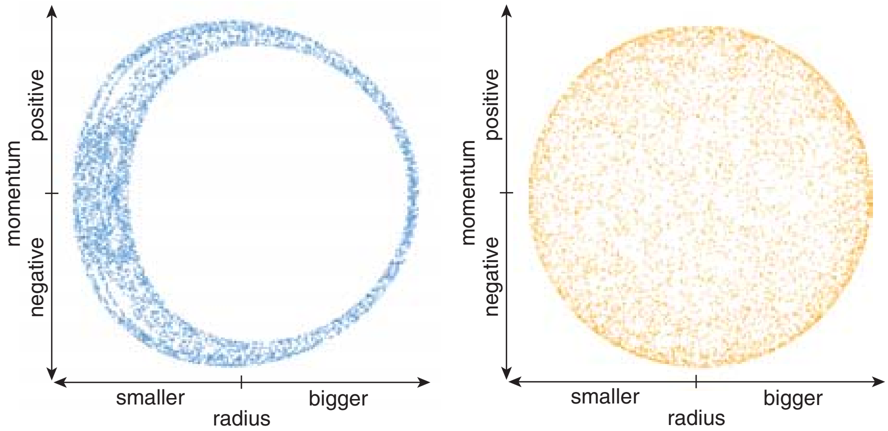

Figure 5. Chaos can exist in classical and quantum variables of vibrating quantum billiards. A plot showing a projection of a Poincaré section onto a plane described by a vibrating sphere's radius and momentum *(left)* consists of a distorted ring of data points. This is clearly not a continuous line, indicating the behavior is chaotic. A projection of a Poincaré section displaying the quantum variables for this system *(right)* also portrays chaos.

initial value for the time-varying radius. The data from each simulation were displayed in the form of a Poincaré section. In these simulations, which described the behavior of both the wall of the sphere and the enclosed particle, we examined Poincaré maps for each component of the system.

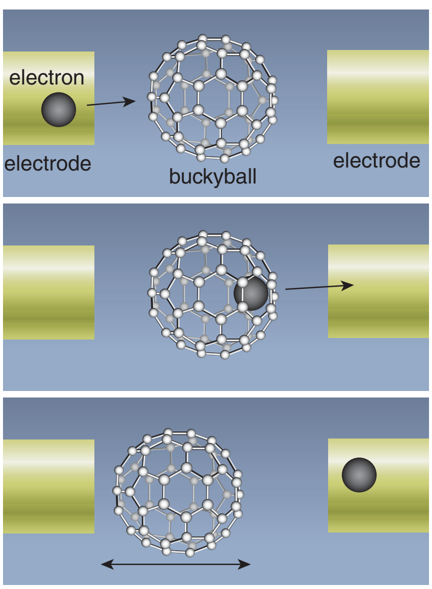

Figure 6. Unimolecular transistors are expected to exhibit semiquantum chaos, which refers to chaotic phenomena in systems with both classical and quantum components. Hongkun Park and his colleagues at the Lawrence Berkeley National Laboratory connected a carbon-60 molecule called a buckyball to a pair of gold electrodes *(top)*. As an electron jumps from the left electrode to the buckyball *(middle)* and then to the right electrode, the buckyball bounces back and forth *(bottom)*. This system can be modeled with tools that resemble the ones that the authors used for electrons trapped in pulsing spheres.

These mathematical simulations revealed chaos in a variety of flavors. For instance, some Poincaré maps of the classical variables—the radius of the wall and its momentum—consisted of a smeared ring of points, and the lack of a continuous line indicated chaotic phenomena. Other Poincaré maps showed a more ordered form of chaos in the classical variables. That is, some of the Poincaré maps from these simulations included areas with more structure—lines that were not quite continuous, but not as smeared in appearance as others. The quantum variables describing the particle in these simulations also produced chaotic characteristics in Poincaré maps.

This kind of system, where classical and quantum components both have chaotic aspects, may be said to exhibit *semiquantum chaos*. The classically chaotic motion of the radius leads to so-called *wave chaos* in the normal modes inside the radially vibrating spherical billiard. In other words, chaos arises in the waves bouncing inside the sphere because those waves depend on the sphere's radius; if the radius displays chaos, so will the associated waves.

It is possible to turn a vibrating billiard into an entirely quantum system. Doing this, however, requires stating the billiard boundary in quantum terms instead of classical ones. This results in a fully quantized system. So far, no one knows if nature includes a fully quantized system with a sensitive dependence on initial conditions. Most scientists reject the few examples of genuine quantum chaos that have been proposed.

Seeking Chaos at Small Scales

Our work on simulations in quantum chaos extends beyond mathematics and theoretical physics and into the world of applications. In fact, the techniques that have been developed in the study of quantum chaos can be used to model a wide variety of phenomena at the atomic scale. Such simulations can improve our understanding of how nanoscale systems work and perhaps translate into better control of such systems.

In some respects, these simulations might seem most applicable to quantum dots. A quantum dot is a nanometer-size structure composed of a semiconductor—such as indium arsenide, gallium arsenide or silicon—or a metal. The structure must be so small that it traps only a few electrons. Although vibrating quantum billiards may be useful for studying quantum dots, these structures are ordinarily studied using quantum billiards with stationary boundaries. When their shapes are irregular, like the classical stadium-shaped billiard and Sinai billiard described above, they exhibit another form of quantum chaos called *quantized chaos*, which describes the quantum signatures of classical chaos.

A quantum dot can be modeled as a particle, or a few particles, in a box. A better understanding of this phenomenon has the potential to improve the performance of quantum dots as binary switches.

In addition, the concepts of chaos at the quantum scale may eventually be used to improve conventional switches, or transistors, themselves, especially transistors made in unconventional ways. For example, Hongkun Park and his colleagues at the Lawrence Berkeley National Laboratory recently fabricated a unimolecular transistor by connecting a buckyball to gold electrodes. (A buckyball has a soccer-ball shape created from 60 carbon atoms and a diameter on the order of a single nanometer.)

Park's group studied the vibrations of these nanotransistors, through which just one electron at a time can flow. Imagine a buckyball at rest between two electrodes. The buckyball bounces as electrons hop on and off the molecule. To simplify matters, one can imagine the buckyball as a sphere, producing a system similar to what we have been discussing. However, the sphere in this system is bouncing rather than pulsing. The difference between this system and the one discussed previously is represented by the difference in form in the

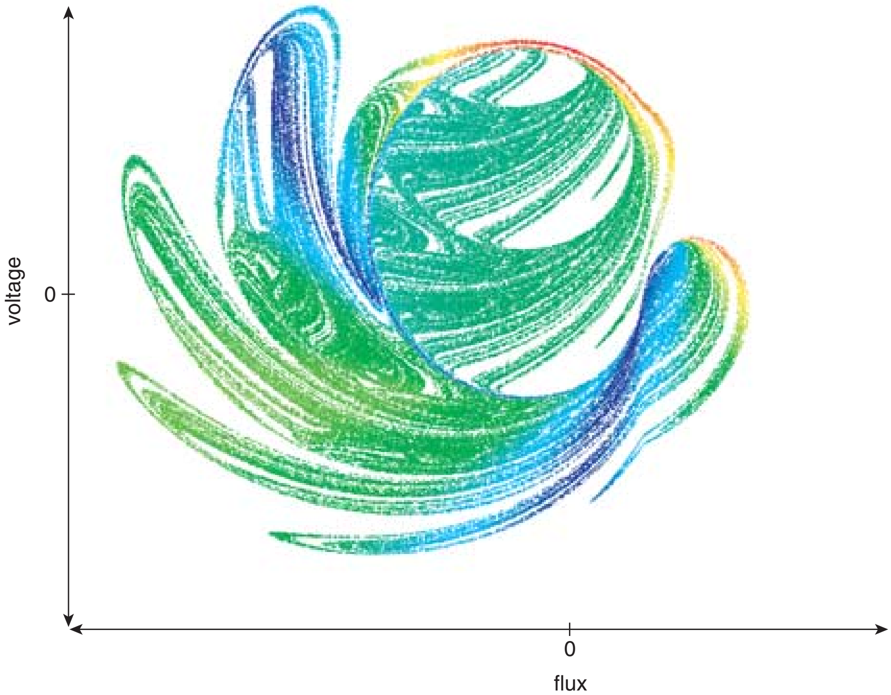

Figure 7. Superconducting quantum-interference devices, or SQUIDs, demonstrate semiquantum chaos. By coupling a superconducting ring and an alternating-current resonator, scientists at the University of Sussex generated chaotic behavior and were able to compute solutions capturing the observed dynamics of the system. The behavior of this circuit is captured in the Poincaré section above, which shows the relation between the voltage measured across the coupled classical resonator and the magnetic flux in the coil, or tank-circuit inductor. The cover image was generated by changing the system parameters. (Image courtesy of T. D. Clark, University of Sussex.)

Hamiltonian one obtains. There are still both classical and quantum-mechanical components. Considering the buckyball's actual geometry adds several further complications.

Techniques from quantum chaos can also be applied to carbon nanotubes, which are like buckyballs with repeating patterns that yield a long tube rather than a ball. These tubes can be micrometers to millimeters long and roughly a nanometer or so in diameter. Their dimensions—both length and diameter—can vibrate, similar to the pulsing sphere in our simulations. Nanotubes can also vibrate like a plucked guitar string, the entire tube oscillating back and forth but retaining its shape. Many of these aspects of nanotubes have not been explored through modeling like ours. Nevertheless, we do know that a pillbox-like nanotube—essentially a cylinder with spherical caps at both ends—should create chaotic phenomena for a trapped electron. Additionally, we expect that the use of quantum billiards might enhance the study of horn-shaped nanobugles, which are also carbon-based.

Switching gears a bit, we can examine another class of real-world systems whose behavior can be modeled as semiquantum chaos. This type of behavior has been observed in a so-called superconducting quantum-interference device, or SQUID. SQUIDs make the world's most sensitive measurements of magnetic fields. These devices don't take up much room—usually not more than a millimeter. Nevertheless, that millimeter holds a fair number of components. To make a SQUID one first needs a superconductor, a material that has no electrical resistance and therefore can carry a current without losing energy, assuming it is cooled enough. A SQUID includes a circular, or sometimes a square-shaped, superconductor that is energized by an electrical oscillator. The oscillator applies current to the superconductor, eventually creating a voltage across the SQUID. When a SQUID is exposed to a magnetic field, the voltage changes, and the magnitude of the voltage change provides a measurement of the magnetic field's strength. To better understand the overall operation of a SQUID, Joseph Diggins and his colleagues at the University of Sussex modeled the motion of electrons in the superconducting ring using quantum mechanics and again found chaotic phenomena in this atomic-scale system.

As scientists continue to search, we expect aspects of chaos to emerge repeatedly throughout the quantum realm. This mystical beast, however, may prove a beneficent one. Moreover, better understanding of phenomena at the nanometer scale may assist designers in creating devices that are easier to manipulate. In any case, much work—on both theory and applications—lies ahead in this relatively new field, as numerous problems have not even been considered. As we have shown, though, this theory possesses beautiful mathematical structure and the potential to aid progress in several areas of physics—both in theory and in practice.

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