Back to the Quantum Future

Evading chaos to make quantum predictions

By IVARS PETERSON

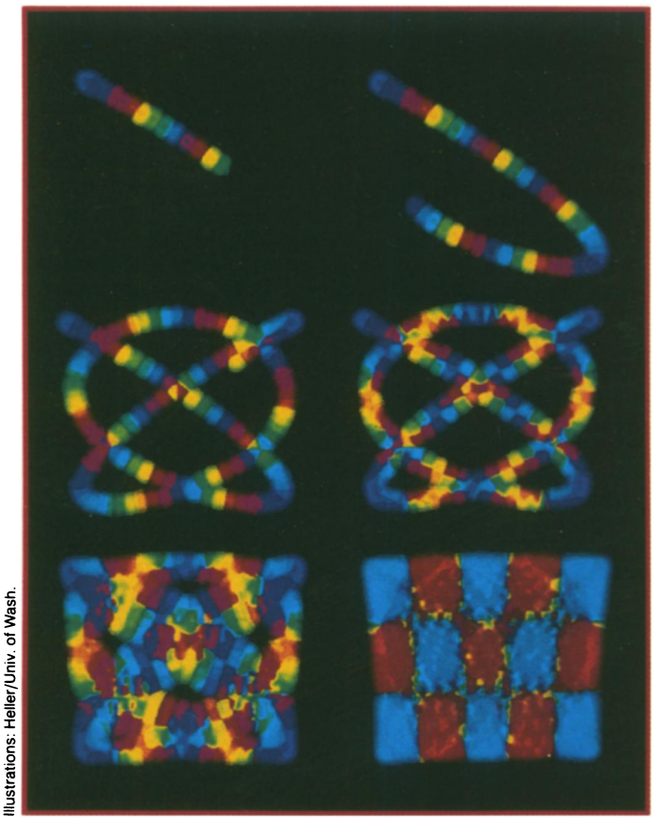
Resembling a disheveled butterfly, the benzophenone molecule flutters in the glare of ultraviolet light. Absorbing radiation, its pair of bent wings—wrinkled, hydrogen-loaded rings of carbon atoms affixed to a carbon-atom body—twist and flap in specific, characteristic ways.

Each kind of contortion absorbs a certain wavelength of light, taking particular bites out of a broad band of ultraviolet radiation to produce the distinctive peaks and valleys of its absorption spectrum. These spectral features represent the energies that correspond to different types of molecular motions that result when a molecule absorbs energy and its electrons shift from one arrangement, or state, to another.

Quantum mechanics normally provides the framework within which scientists can deduce or predict how a molecule or an atom responds to radiation and thus produces a characteristic spectrum. But solving the equations of quantum mechanics to predict the heights and locations of peaks in a given spectrum poses serious difficulties.

To handle such recalcitrant cases, researchers are beginning to turn back to ideas from classical mechanics, applying equations similar to those used to calculate planetary orbits or describe the oscillations of a pendulum. By marrying classical mechanics with quantum concepts, they have evolved a hybrid "semiclassical" mechanics that affords a simpler path toward prediction than the full paraphernalia of quantum theory.

Theorists have now discovered that semiclassical methods provide surprisingly useful predictions, even when a system's underlying behavior is chaotic. These techniques unexpectedly seem to paper over the wild, intricately detailed irregularities, which a chaotic system normally displays, to produce a remarkably accurate prediction of the long-term behavior of an equivalent quantum system.



Illustrations: Heller/Univ. of Wash.

Classical mechanics describes how a particle, whether an electron or a planet, moves in response to forces acting on it. By adding information about the particle's wavelength and phase (shown as bands of color along its trajectory), researchers can build up a "semiclassical" picture of its behavior (depicted as a color patchwork, lower right), which matches the purely quantum-mechanical description of this motion.

"Many people had doubted that this was possible, even in principle," says theoretical chemist Eric J. Heller of the University of Washington in Seattle.

Heller and his collaborators have now used this kind of semiclassical technique to compute the ultraviolet absorption spectrum of benzophenone, accurately reproducing the spikes and dips observed in the laboratory. This success suggests the possibility that by using appropriate semiclassical methods, researchers can rapidly compute the behavior of a wide variety of chemical systems presently too complicated to be handled by quantum mechanics, such as the spectra produced by organic molecules.

The picture of an atom as a miniature solar system in which electrons orbit a nucleus represents one of the simplest examples of a semiclassical description of a quantum system. Like planets, the electrons revolve about a central object. Unlike planets, however, they must follow orbits corresponding to multiples of a certain, fundamental angular momentum, which expresses the rate at which an object of a given mass rotates.

This blend of classical mechanics (planet-like orbits) and quantum restrictions (only certain orbits allowed) provided a useful model of atomic behavior during the early days of quantum theory, more than 70 years ago. But this "old" quantum theory was swept aside in the 1920s by the "new" quantum mechanics of Erwin Schrödinger, in which the wave-like behavior of matter plays a key role.

As a result, attention shifted from classical analogs to purely quantum-mechanical systems. Theorists concentrated on finding approximate solutions of Schrödinger's wave equation to predict the behavior of atoms and molecules.

But scientists quickly discovered that operating the machinery of quantum mechanics was quite troublesome, and they often found it provided little insight into atomic and molecular behavior. They had great difficulty developing an intuitive understanding of the whys and wherefores of quantum mechanics.

That remains the situation today. "Although quantum mechanics provides a correct description of nature, it does not

hold the intuitive appeal of classical theories, which are easier to implement," write Ahmet T. Uzer of the Georgia Institute of Technology in Atlanta and his coauthors in the July 5 SCIENCE.

The growing appreciation over the last two decades that physical laws expressed by simple mathematical equations can nonetheless yield an astonishing array of complex dynamical behavior has revived interest in semiclassical approaches to quantum mechanics. Now aided by high-speed computers, physicists and chemists are again probing the fuzzy, perplexing boundary between quantum and classical systems.

"Combining nonlinear dynamics, group theory, and semiclassical methods provides a powerful way of determining the underlying structure and trends in either experimental data or detailed numerical simulations," Uzer and his colleagues contend.

One of the most promising approaches involves a semiclassical, mathematical formula originally introduced in 1928 by U.S. physicist John H. Van Vleck. His formula, or "propagator," in effect encapsulates the overall dynamical behavior of a given system, making it possible to calculate quickly what happens over time to a small disturbance starting anywhere within the system.

Heller likens the Van Vleck propagator to the map generated in an acoustic experiment in which someone goes around to every point in a room, claps her hands, and records the echoes. This record, representing the net effects of the way sound travels as it bounces around the room, can then be used to calculate and predict what happens to any new sound introduced within the room.

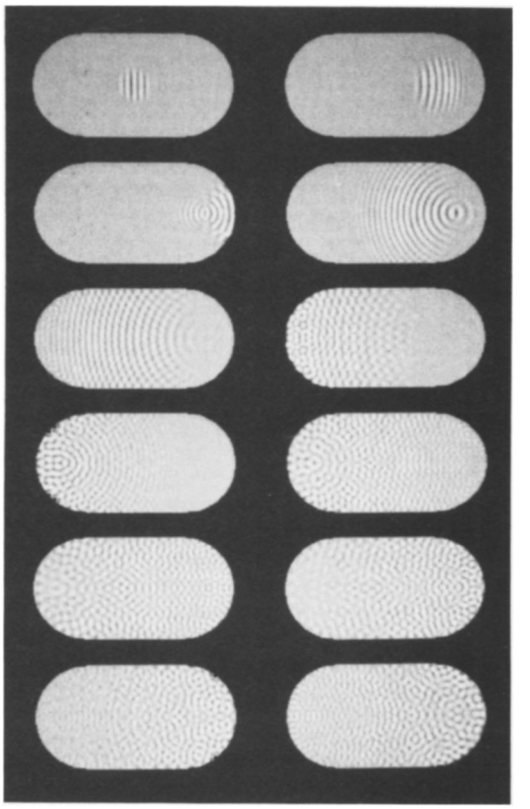
Similarly, the Van Vleck propagator provides a map from which it's possible to calculate and predict the future course of any disturbance introduced into a system, whether a room or a molecule. "If we create a disturbance at one point, it [the propagator] tells us what's going to happen at another point later on," Heller says.

In reviving Van Vleck's semiclassical formula, Heller and his colleague Steven Tomsovic modified the method slightly to make it easier to compute the required map. They mathematically track the paths followed by imaginary particles as they move in response to any forces acting within the system under consideration, whether a molecule or simply a box with reflecting walls. Such trajectories, governed by the rules of classical mechanics, are relatively easy to compute.

The scheme preserves a system's quantum-mechanical aspects by associating with each trajectory a wave property known as phase. "You get a trajectory which has both classical and wave-like properties," Heller says.

That duality has important consequences. Just as water waves cancel each other when crest meets trough or reinforce each other when crest meets crest, crossing trajectories also cancel or reinforce one another. Theorists can build up a map of a system's dynamical behavior simply by adding together the contributions of all trajectories that happen to pass through any given point within the system.

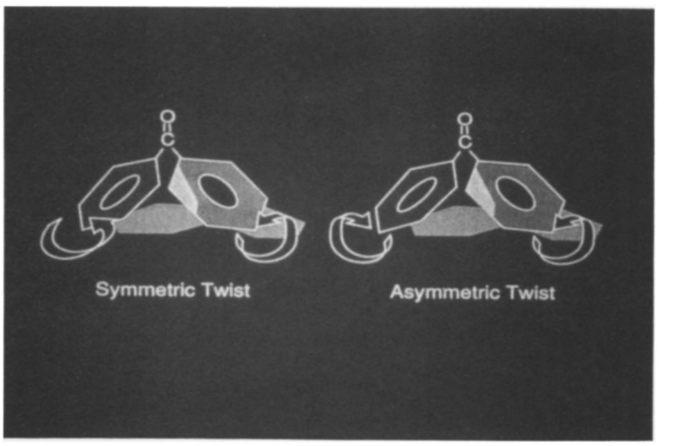
Such a technique allows researchers to compute the behavior of a quantum system and make predictions much more easily than if they used pure quantum mechanics. "One of our interests is to develop computational techniques that allow us to compute things that are much too difficult to compute exactly [using quantum mechanics]," Heller says.

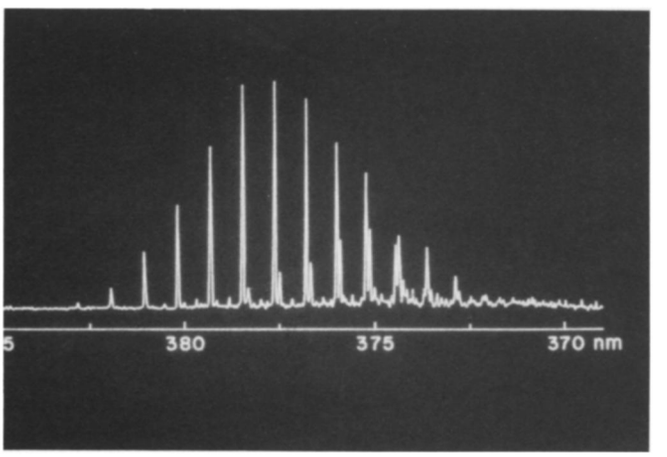


Frames from a movie showing how a small "packet" of waves spreads out and echoes within a stadium-shaped chamber. Semiclassical calculations generate a complicated tapestry that closely resembles the wave pattern predicted by quantum theory.

Heller and Tomsovic's version of the Van Vleck propagator, however, is more than simply a faster way of computing a system's quantum properties. It works even when a system's classical behavior is chaotic.

For example, consider the endless motion of a billiard ball across a frictionless, stadium-shaped table having two semicircular ends connected by a pair of straight sides. In such a geometry, two balls that start out next to each other end up following very different trajectories as they ricochet from cushion to cushion. Such sensitive dependence on ini-





Shifts in energy corresponding to two particular twisting motions in a benzophenone molecule (top) produce a distinctive ultraviolet absorption spectrum (left).

tial position means that a given ball's long-term motion is essentially unpredictable. This type of unstable dynamical behavior is one of the hallmarks of a chaotic system.

But using the modified Van Vleck propagator to trace trajectories and keep track of phases within the same geometry produces a different result. Reporting in the Aug. 5 PHYSICAL REVIEW LETTERS, Heller and Tomsovic show that a small wave packet (see illustration p.283) starting in the middle of the stadium rapidly spreads out to cover the entire surface with an apparently unruly sea of waves. Nonetheless, their analysis reveals patterns in the wave amplitudes from point to point that closely match the fluctuating quantum behavior expected when the equations of quantum mechanics are applied to the stadium problem.

"The surprise is that every detail of the fluctuating quantum behavior is captured by the semiclassical prediction," Heller and Tomsovic say. Somehow, the underlying chaotic behavior evident in the classical version of the system doesn't overwhelm or interfere with the Van Vleck propagator's utility for making quantum predictions.

"The Van Vleck formula, which goes back to the old quantum theory, is amazingly accurate," Heller says. "[Furthermore], chaos doesn't ruin our ability to describe the quantum world with classical mechanics. It was thought that it would, but it doesn't."

These results open up the possibility of simulating atomic and molecular behavior on a scale not possible with just quantum mechanics. Heller's student Miguel Sepulveda has already used the Van Vleck propagator to trace trajectories across a geometric form representing the forces within a benzophenone molecule to derive its ultraviolet absorption spectrum.

"You can simulate the entire spectrum line by line simply by running classical trajectories," Heller says. Even at moderate and high energies, where the classical motions of the molecule are chaotic, "we were able to power right through all that chaos to get the correct spectrum," he says.

The results achieved by Heller's group represent more than just a new, potentially faster tool for chemists and physicists to simulate atomic and molecular behavior. Scientists now have some assurance that they can apply classical and semiclassical approximations to quantum theory more broadly than they had previously thought.

"What Heller showed is that if you start with classical mechanics and do it right, you can go a long way," says quantum-chaos pioneer Martin C. Gutzwiller of the IBM Thomas J. Watson Research Center in Yorktown Heights, N.Y. The chaos evident in classical systems doesn't stop one from making quantum predictions based on semiclassical techniques.

Because it's easier to picture orbits and billiard balls, semiclassical techniques enable researchers to obtain deeper insights into the behavior of molecules and materials at the microscopic level than those afforded by the wave functions and probabilities of quantum mechanics.

"For better or for worse, if you really want to understand a quantum-mechanical system, you almost always have to fall back on classical mechanics," Gutzwiller explains.

"Classical mechanics fits our mode of thinking best," agrees Georgia Tech's Uzer. "There are some quantum-mechanical phenomena that are just very, very difficult to understand except in a classical way."

"But," he cautions, "you always have to raise the question of how correct [these approximations] are."

Nonetheless, the future of semiclassical methods in quantum mechanics seems assured. "The old quantum theory is indeed experiencing a resurgence and is stronger and more useful than ever," Heller maintains.

This renewed activity marks what chemist Robert Harris of the University of California, Berkeley, has described, only partly tongue-in-cheek, as the birth of "postmodern quantum mechanics." □