

Quantum chaos

A beginning or an end?

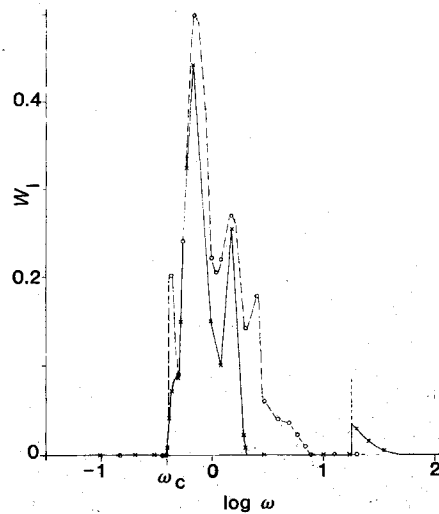
Joseph Ford

Two recent publications by Giulio Casati, Boris Chirikov, Italo Guarneri and Dima Shepelyansky (*Phys. Rev. Lett.* **53**, 2525; 1984 and **57**, 823; 1986) greatly lengthen the shadows of doubt which play across the existence of chaos in quantum mechanics. The significance of these results is but heightened by the indisputable reality of chaos in classical dynamics — games of chance, for example, as well as turbulence in all its guises. For, given that quantum mechanics is universally accepted as our most fundamental and all-inclusive description of nature, the undeniable existence of chaos in nature clearly implies that chaos must also occur in quantum mechanics. And yet the evidence exposed in these two reports indicates that it does not!

To place the new evidence in context, recall that newtonian systems are universally regarded as deterministic because their orbits have been proved to exist and to be unique. Moreover, perhaps because of a widely held, almost mystical belief that any orbit that has been proved to exist can actually be computed, newtonian systems are also presumed to be completely predictable. On the other hand, contemporary nonlinear dynamics, although affirming the notion of determinism, nonetheless establishes that deterministic chaotic motion is totally unpredictable and fully random. But what of quantum mechanics: is the quantal description of a classically chaotic system also fully random?

To understand the full import of this question, it is crucial to recall that, by definition, the term 'quantum chaos' refers only to that randomness in quantum mechanics which occurs over and above that contained in the wavefunction itself or in probabilities derived therefrom. Hence, aside from the long-debated and

still unverified possibility that chaos arises from measurement-induced collapse of the wavefunction, only two possibilities for quantum chaos exist: randomness in



A plot of classical (circles) and quantal (crosses) ionization probabilities W_1 versus the logarithm of normalized microwave frequency ω for the microwave-driven hydrogenic electron obtained from numerical integration of Newton's and Schrödinger's equations. Far right is the conventional photoelectric peak. The much higher, broader and previously unsuspected peak that begins at the critical frequency (ω_c) owes its existence to chaos. Nonetheless, it is only the classical motion that is chaotic.

the deterministic Schrödinger time evolution of the wavefunction; and randomness in the deterministic eigenvalue/eigenfunction equations. It is these two possibilities that Casati *et al.* address.

Because the energy spectrum of spatially bounded, finite-particle-number, conservative quantum systems is rigorously known to be discrete, the associated wavefunctions or density matrices are almost periodic functions of time. Such predictably repetitive behaviour in the time evolution of these systems clearly precludes chaos. Consequently, Casati *et al.* have looked at finite, time-driven systems. In particular, they have numerically integrated both Newton's and Schrödinger's equations for a highly excited hydrogen atom being driven to ionization by a microwave field. Classically, they find that under suitable conditions the hydrogenic electron exhibits a truly random, diffusive absorption of energy. Quantum mechanically, the corresponding Schrödinger time evolution indicates that the electron is mimicking the classical diffusion, but more detailed inspection reveals striking deviations. First, a critical microwave

field strength has been discovered below which the quantum electron ceases its 'diffusion-like' absorption of energy even though the classical electron still continues its random walk toward the continuum. This striking numerical prediction of a quantum suppression of classical diffusion can and will be subjected to laboratory investigation. But much more damaging to the notion of quantum chaos is the fact that, even when the calculated ionization probabilities for classical and quantal electron agree quite nicely, the underlying diffusive classical motion cannot be numerically time-reversed without invoking almost 'infinite' calculational precision, whereas the apparently similar quantum motion is easily reversed using only limited accuracy. This easy time reversal clearly reveals that the quantum motion, as opposed to the classical, is not diffusive and therefore not chaotic.

In summary, despite extensive searching, no chaos has yet been found in the quantum time evolution of any classically chaotic system. In consequence, when these negative results are added to earlier ones, the shadows on the face of quantum chaos and even on quantum mechanics itself grow quite long indeed.

But it must be emphasized that Casati *et al.* also report significant positive results. Specifically, their theoretical investigations expose a previously unsuspected, quite large photoelectric ionization peak in the microwave-driven hydrogen atom. To appreciate the surprise of this result, recall that the standard photoelectric effect requires each incoming microwave photon to have an energy sufficient to raise the electron from its initial state up to the continuum. In consequence, as the microwave photon energy is decreased below that required to ionize the electron via absorption of a single photon, only unlikely multiphoton events would be expected to yield ionization.

However, these arguments do not reckon with chaos. Indeed, ionization of the hydrogenic electron was actually observed some years ago at frequencies much below those required by the conventional photoelectron effect provided that sufficiently large microwave field strengths were used. Subsequent theoretical calculations of orbits for the classical hydrogenic electron, independently performed by several investigators, then revealed this ionization to be a consequence of a transition to chaos which can be observed even at low-microwave frequency as the field strength is increased through sufficiently large values. Specifically, a critical field strength was found above which the classical hydrogenic electron absorbs energy chaotically (diffusively) and below which it absorbs energy 'almost periodically'.

Because this transition to chaos is most easily discussed using microwave frequency (or energy) rather than field strength as



100 years ago

EXTREME partisans of one school assume that the hedge-sparrow lays a blue egg because every egg that was not blue was tried in the high court of Evolution, under the clause relative to the survival of the fittest, and condemned, a hungry magpie or crow being the executioner. The extreme partisans of the other school regard the little hedge-sparrow, not only as a free agent, but as a highly intelligent one, who lays blue eggs because the inherited experience of many generations has convinced her that blue is the most suitable colour for eggs.

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the variable, let us imagine the microwave field strength to be held fixed at some suitably large value, and then inquire what theory predicts regarding ionization as a function of frequency when each electron initially has the same energy. Note that, with this change of variable, the transition to chaos will appear at a critical frequency rather than a critical field strength.

Typical theoretical results are presented in the figure where curves of classical and quantal ionization probabilities at a fixed time are plotted against the logarithm of a normalized microwave frequency. Below the critical frequency for the transition to classical chaos, both classical and quantal calculations predict the expected negligible absorption of microwave energy by the electron. But now come the surprises numerically discovered by Casati and colleagues. First, above the critical frequency both classical and quantal curves rise steeply together and then 'level off' onto a peak much wider and higher than the conventional photoelectric peak seen on the right in the figure. Second, when these previously unsuspected ionization peaks do begin to fall,

the quantum curve drops rapidly to zero long before the classical curve does. In essence, a frequency window is predicted inside which the classical electron ionizes whereas the quantum electron does not. Because here the electron is always initiated in a highly excited, 'semi-classical' state where quantal and classical results might be expected to agree, a remarkable question now arises. Can theory predict before the experiment whether the electron perceives itself as classical or quantal in this circumstance?

In this article I have sought to convey the excitement contained in the results of Casati *et al.*, the implications of which extend from applications of the new photoelectric peak to modifications in the foundations of physics resulting from chaos. But in a deeper sense, the true excitement of these papers lies not so much in their explicit content as in the tantalizingly brief glimpse they provide of competent scientists working on problems that count. □

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Resonance ion spectroscopy

Counting molecules one by one

Keith Boyer

TUNABLE lasers are rapidly entering the business of identifying, counting and concentrating atoms or molecules of specific chemical or isotope species, even in the presence of large backgrounds of very similar types such as neighbouring isotopes or chemical isomers. This technique has been dubbed resonance ionization spectroscopy (RIS), and it involves the ionization of free atoms or molecules, thus converting them to a detectable form through the absorption of two or more laser quanta. One of these quanta is resonant to provide selectivity; subsequent photons, which complete the ionization process, generally have different wavelengths. Some form of mass spectrometry is often used to increase selectivity, when because of its great sensitivity, the process has been called single-atom detection. The results described at a recent meeting* show clearly that RIS is a rapidly maturing discipline of great importance.

Several outstanding accomplishments were reported at the symposium, but the most exciting was the extension of the technique to the identification and counting of both small and large complex molecules, despite the conclusion reached at the previous symposium in 1984 that molecules, as opposed to atoms, were not good candidates for the RIS technique. It

now seems that a major role of the technology will be the selective detection of molecules in science, industry and medicine.

For the application of RIS techniques to molecular species, the molecules must be prepared in a free state, and the 'hot band' rotational and vibrational contributions to their spectra eliminated. For non-volatile molecules such as chlorophyll, mesoporphrin and tripeptides, ultraviolet laser ablation can be used to introduce free molecules into a supersonic gas stream from a nozzle, thus cooling the molecules of interest and causing them to populate their lowest vibrational state (U. Bösel, Technical University, Munich). Other volatile molecules such as xylene isomers (R.J. Donovan, University of Edinburgh) and acetamide (E. Benedetti, University of Naples) can be simply evaporated into the nozzle gas stream. Acetamide is of interest as it is a basic component of peptides and proteins, whereas the ability to determine the relative amounts of different isomers of compounds such as xylene has important industrial applications.

An extraordinarily sensitive device has been developed that can detect and count 1,000 atoms in a background of 10^{15} atoms of other krypton isotopes (N. Thonnard, Atom Sciences, Oak Ridge, Tennessee). The first application of this device will be to measure the quantity of ^{85}Kr and ^{87}Kr in hydrological, oceanographical and atmos-

pheric samples to date ground water and polar ice, and to determine circulation patterns in the deep ocean or the atmosphere. Another significant achievement is the measurement, on a production basis, of impurities with a high degree of reproducibility in semiconductor substrates at the 10^{-9} level (J. Parks, Atom Sciences). Bioassays of trace elements and uranium can also be made with similar sensitivity using tiny samples of blood or urine. The medical applications are of great importance, as these are techniques which could provide rapid analysis of trace amounts of a wide variety of substances using very small samples. Small size also has the advantage of reducing the effect of reagent contamination on detection sensitivity when a chemical step is required.

The preparation of free sources of atoms for RIS measurements is being investigated both experimentally and theoretically (N. Winograd, Pennsylvania State University). Ion sputtering and electron and photodesorption of atoms indicates that both bond breaking and momentum transfer are effective mechanisms in producing free atoms from surfaces.

Various types of mass spectrometry are now being used together with RIS to improve selectivity. Descriptions were presented at the meeting of time-of-flight mass spectrometers, magnetic and electrostatic mass spectrometers and the 'Reflecton' device used to improve time-of-flight spectroscopy. Other techniques include double resonance, hyperfine structure discrimination and the use of synchronized pulsed-atom sources, detectors and lasers. Many of these techniques permit the analysis of very small samples including airborne particles, oil and blood samples, and others, allowing the detection of nanogram quantities of copper, uranium and other elements of interest. An RIS system is in use for geological and mineral exploration in China (Keling Wen, Quinghua University).

Isotope and isomer separation techniques now often involve RIS (for example, J.K. Crane, Lawrence Livermore National Laboratory). The presentations describing these techniques were limited to atomic vapour techniques to produce separations of isotopes, such as those of uranium and mercury, in large quantity although molecular techniques using flow cooling have also been demonstrated. If cost-effective, many isotopes could have great commercial value when produced in quantity in this way. One of the more exotic uses of RIS is in the search for quarks and heavy atoms, but the results to date are, unfortunately, negative. □

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*The Third Resonance Ionization Symposium, Swansea, UK, 7-12 September 1986. Proceedings to be published by Hilger.