Energy levels by path integration

After a delay of more than 40 years, it seems that a gloss on Feynman's way of doing quantum mechanics will help in calculating atomic ground states.

WHEN the late Mark Kacs joined the Rockefeller Institute (now University) in the early 1960s, not all his new colleagues were as delighted as they should have been. Rumours (never confirmed) that Kacs's salary was roughly what that of a Harvard professor would be in 1992 led some to grumble that the institution was being run as if it were a baseball team. The more durable alarm was that the arrival of a mathematician of such stature made it seem possible that the resources of the university would be spread more widely than had previously been the case. (George Uhlenbeck, a physicist, was already there.) But Kacs quickly charmed his critics by his wit and versatility. His most endearing trait was his interest in other people's problems (not a common property of mathematicians).

One seed of that charitable frame of mind has now borne fruit, surprisingly in a new way of calculating the energy of the ground-states of atoms with more than one electron. The tale is that Kacs, moved by claims that Feynman's account of quantum mechanics was not mathematically rigorous, set out to rescue that appealing way of looking at things from the opprobrium it seemed destined to attract. If Kacs had published his solution more visibly than in the *Journal of Research of the National Bureau of Standards*, it would no doubt have had a more immediate impact.

The point at issue lies at the heart of Feynman's way of doing quantum mechanics, and of the quantum electrodynamics that followed from it. Start with Young's slit experiment in quantum mechanics: a sheet of impenetrable material with two parallel slits, a source of electrons on one side and a detector on the other, yielding an array of interference fringes just as in the original optical experiment. The interference fringes are quite distinct from the spot or the line-like pattern that would be produced if one or other slit is blanked off. Bohr's explanation of this is that, with two slits, electrons do not go through either one slit or the other, but through both. In other words, the two paths through the two slits contribute to the interference pattern at the detector according to the phase they carry when they reach there.

Feynman's generalization (forgetting about slits) of this argument to the motion of any quantum system, say a free electron moving in an electric potential, was to posit that all possible parts contribute to the evolution of the system. Instead of simply adding together two numbers (the contributions to the end result of the two slits), it was necessary to add together the outcomes of the infinite number of all possible paths, implying not summation but integration of some kind.

The underlying difficulty with Feynman's approach was that some of the possible paths from, say, A to B would inevitably be very strange. Along some paths, for example, a particle would change direction irregularly and frequently, and these paths would have to be given as much attention as more well ordered ways of making the transition. The trouble is that there must be even more irregular than well ordered paths — a multiply infinite rather than simply infinite number. How, in these circumstances, could people hope to rely on the results of some integration of the effects of all the separate paths? Kacs's resolution was to adapt to Feynman's problem a definition of path integration originally due to Wiener. The pure mathematicians were content and went back to what they had previously been doing.

How does this recondite argument lead to new solutions to the problem of the energy levels of atoms with several electrons? Kacs's argument seems to have what is called heuristic value as well as that of answering the purists. A. Korzeniowski, J. L. Fry, D. E. Orr and N. G. Fazleev from the University of Texas at Arlington have also seen it as a way of carrying through a computational scheme using a CM-2 model of the parallel computer called the Connection Machine (*Phys. Rev. Lett.* **69**, 893; 10 August 1992).

The difficulties of calculating the properties of many electron atoms have been known since the early days of quantum mechanics. At the outset, the solution of the hydrogen atom was a triumph, but then helium proved intractable. Those who would tackle such problems by solving the Schrödinger equation have a formidable task. Because the electrons repel each other, the simple wave functions describing the states of a hydrogen atom are no longer appropriate. Ideally, the states of the electrons in, say, helium could be represented as an infinite sum of all possible states of hydrogen-like atoms (with the nuclear charge doubled), and the repulsion between the electrons counted as a perturbation. The arithmetic, not to mention the algebra, is formidable.

But there is a further complication. The only allowable states of the two electrons of a helium atom are those in which the wave-function is antisymmetric with respect to the interchange of the two electrons, in accordance with Pauli's exclusion principle. The result is that people are required to calculate with wave-functions consisting of determinants with as many rows and columns as there are electrons and whose elements are single-electron hydrogen-like wave-functions. It is not surprising that the past half-century has seen the emergence of simpler ways.

The connection between Kacs' argument and parallel computers is necessarily more recent. Its essence is Kacs's proof that the lowest energy of a quantum system is linked with the expression for the position of a particle undergoing a random walk, and entails the integration of that expression along the length of some paths accessible to the system (which makes the energy of the ground-state not a function of, but a functional of, the expression.) What can be more appropriate than a parallel computer for calculating quantities like this? Dealing with random walks by computer is simply a matter of simulating them time and time again.

Indeed, a further refinement is possible. While the handling of the Slater determinants whose elements are one-electron wave-functions leads to endless algebraic complications in the computation of the lowest energy state, following Kacs's method it is possible to exclude the states of unwanted symmetry — those which are not antisymmetric on the exchange of any pair of electrons. It is simply necessary to specify that a random walk reaching such a state is promptly terminated and excluded from the calculation.

That sounds a little inelegant as does the technology. The parallel computer embodies some thousands of microprocessors, small groups of which are assigned to the parallel integration of the mathematical expressions along particular feasible paths, themselves random walks. But the outcome is impressive. The calculated ground-state energies of atoms from hydrogen to boron agree within the statistical errors of the computation with the measured values, which are themselves accurate to a fraction of a per cent.

The advantage of this computation method is not merely that it seems to work well but that it has the virtue of not requiring in advance guesses at the kinds of wave-functions that would make the most efficient starting points for computation. And although it may be argued that a strictly computational technique for the properties of atoms robs the process of clarity, that is how these calculations finish up in any case. Kacs would have been delighted that his work, more than 40 years after the event, promises to be so useful.

John Maddox