Problems of more than one electron

The spectrum of helium and other atoms with two electrons has been a bother since the early days of quantum mechanics. And there are perplexing issues outstanding still.

THE darkest days of the quantum theory must have been the decade or so between the appearance of Bohr's semi-classical theory of electron orbits and the first appearance of modern quantum theory more than a decade later. Bohr had given a persuasive account of the hydrogen atom, accounting for the regularities of the Periodic Table in the process, but despite the efforts of people such as Sommerfeld, nobody could make much sense of the measured spectrum of helium, the simplest electron configuration after hydrogen. Was Bohr's account of the hydrogen atom flawed in its assumptions?

By the mid-1920s, after Heisenberg and Schrödinger, the origin of the difficulty (but not its resolution) must have been plain. With helium just as with hydrogen, there will indeed be a series of states in which a helium atom can exist, but calculating them from first principles is a bother because of the need to take account of the electrostatic repulsion between the two electrons.

Even enumerating the states accurately is not straightforward. The obvious classifiers to use are the total angular momentum of a state and its projection along some axis, but who could guess which one-electron states must be mixed together to make the states the spectroscopists observe?

Formally, there is no great difficulty. Simply take a complete set of wavefunctions representing electrons in a hydrogen atom, mix them all together with undetermined coefficients, substitute that mixture in the relevant Schrödinger's equation and solve the resulting linear algebraic equations. There are two important snags. Experience has shown that it is necessary to use hundreds, even thousands, of wavefunctions to get reasonably accurate results — and the size of the matrix equation that must be solved is identical with the number of wavefunctions, say M, used as a starting point.

The second and more serious difficulty is that somebody has to evaluate $M(M-1)/2$ integrals, one for each distinct pair of the basis functions, in which the integrand is the product of the pair of wavefunctions, each of which is a function of the space coordinates of one or other of the two electrons in a helium atom; that product is then divided by the geometrical distance between the two coordinate points and the integration is carried out over all six coordinates from zero to infinity. Even when it is commonplace to use simplified wavefunctions in the calculations, who can wonder that serious attempts at the accurate calculation of atoms beyond hydrogen began only in the 1970s (when computers began to make their mark)?

Now, there seem to be two approaches to the problem: computational and reflective. S.P. Goldman from the University of Western Ontario, seems to have struck oil in the search for better ways of computing electronic states (*Phys. Rev. Lett.* **73**, 2547–2550; 1994). For one thing, he has found a neat way of dealing with the especially brutish feature of the integrals occurring in these problems, which consists of a cusp-like feature in the electrostatic potential when the two electrons are equidistant from the helium nucleus and which comes about because the potential energy would be literally infinite if the two electrons occupied the same point. He has also modified the standard set of simplified wavefunctions due to J.C. Slater to give the inner and outer electrons different distributions in space.

The immediate result is that many fewer wavefunctions are needed to win accurate results. Goldman reckons to have calculated the energy of the ground state of helium to within 4.6 parts in 10^9, at least three orders of magnitude better than previous results, by using "only" 305 starting functions. For good measure, he used only a desk-top workstation for the arithmetic.

The reflective one is Michael E. Kellman from the University of Oregon at Eugene, and almost literally so. Not often, these days, is an author given space to rehearse his past contributions to the literature of his subject, but Kellman seems to have won that privilege from a journal notoriously tight-fisted with paper (*Phys. Rev. Lett.* **73**, 2543–2547; 1994). But the circumstances are exceptional; Kellman has had an important afterthought 20 years after the event.

He and D.R. Herrick were pioneers in the 1970s of the pursuit of the two-electron atom and its spectra. Unlike many others, they had a physical model to guide them. As electrons repel each other, will they not tend to be found on the opposite sides of the nucleus? That makes a helium atom a kind of triatomic molecule, but one in which the supposed bonds holding the outlying electrons to the nucleus are simply their mutual electrostatic repulsion. So the bonds, on this analogy, have very small force constants.

Herrick, Kellman and their contemporaries in the early 1970s made much of this analogy. Vastly improving on what Sommerfeld has attempted half a century earlier, they were able to conjecture what states would arise in helium if each of the electrons were excited above the ground state, not necessarily to the same degree.

They predicted multiplets of states and groupings thereof (called supermultiplets), finding confirmation in the data.

And the afterthought? It should be possible to classify the states of a two-electron atom by the choice of an appropriate symmmetry group. That is how group theory, without the intervention of conventional algebra, can by itself be used to show that the states of one-electron atoms are precisely those found in the laboratory or by solving the appropriate Schrödinger equation algebraically.

In the 1970s, Herrick and Kellman were already guessing that the three-dimensional rotation group that accounts for the properties of the angular momentum of one-electron orbits would not suffice for their floppy triatomic molecules, and were guessing that they would have to use the four-dimensional orthogonal group called O(4) instead. The use of the three-dimensional analogue, O(3), which works well enough for one-electron atoms, leads directly to the slow convergence and poor approximation that Goldman is seeking to circumvent.

The more tangible part of what Kellman has now done is to apply the formalism of classification by O(4) to cases in which, in the approximation in which the classification at first ignores the electrostatic repulsion between electrons, two electrons have different principal quantum numbers. More multiplets and supermultiplets fall out of that. It turns out that the classification is best represented by quantities such as the momentum (quantized, of course) locked up in the bending vibrations of the floppy triatomic molecules, which quantities function as quantum numbers for the multiplets and supermultiplets. People working in the field will be waiting eagerly for the details.

Meanwhile, there is a puzzle: the O(4) group, or more strictly its unitary equivalent U(4), keeps throwing up extra terms, which seem not to fit in well with the classification of the states of two-electron atoms and which have no obvious physical meaning. Could they represent some collective motion of two electrons bound to a nucleus that nobody has yet thought of? Kellman thinks that unlikely, but there is no other obvious way round the difficulty. Is this one of the rare cases in which mathematics has failed to be ready with a solution to physicists' problems? Or is the model of the triatomic molecule inappropriate? The conjuction of the two papers by Kellman and Goldman will send many people scurrying in search of an explanation. **John Maddox**