Localizing electrons in atomic orbits

A simple technique for preparing atoms in such a way that a distant electron behaves for several periods of revolution as if it were a particle may be the most vivid illustration yet of the Correspondence Principle.

DECADES have passed since people pictured electrons orbiting around atoms as if they were point electrical charges moving in keplerian ellipses around the central nucleus. Bohr's first attempt at an understanding of atomic structure in 1913 was, after all, nothing more than an account of the solution of a problem in classical mechanics constrained by the empirically derived (or guessed) quantum conditions. A decade later, with the Uncertainty Principle (but the same quantum conditions), people took to heart the doctrine that an electron in an atom is a probability distribution of charge. Keplerian orbits were gone for good.

What follows is a piece of fun, a demonstration that the old concept of semi-classical Bohr orbits may not be entirely untenable. Those concerned are Z. D. Gaeta, Michael W. Noel and D. R. Stroud from the University of Rochester, New York. What they have done is to suggest how it would be possible to prepare the state of a hydrogen atom in such a way that the single electron would be seen (by suitably fast laser pulses) to be moving in a kind of orbit. The argument appears in what must be a vintage issue of *Physical Review Letters* (**73**, 636; 1 August 1994).

For what it's worth, the objectives underlying this kind of trickery are not entirely the maximization of collective amusement. It is at least conceivable that the controlled preparation of the electronic states of molecules by well-judged laser excitation may make particular chemical reactions more feasible than they would otherwise be. But that prospect is still some way off.

What Gaeta and his colleagues are for the time being concerned with is somehow to arrange that wave packets of electron density will move unchanged in arbitrary elliptical orbits around a hydrogen nucleus. They expect that they will be able to do this only if the electrons are relatively far from the nucleus, meaning that they will have a principal quantum number, *n*, that is relatively large, or that the atom is in a Rydberg state. That is the semi-classical regime, where electrons behave more or less as if they were classical entities. Then it is possible to use classical arguments to reach some kind of explanation of how the trick may be accomplished.

Because quantum theory is an exact description and classical mechanics only an approximation in restricted conditions, it is important to be clear what is going on in these experiments (which can be done in the laboratory as well as the head). The *s* states of electrons around hydrogen atoms are, of course, represented by spherically symmetrical wave-functions whose algebraic form is well known. So why not take groups of them together in linear combinations to form atoms in which the electron distribution is a spherical annulus? There is nothing in principle to prevent that being done.

It is even possible to go further and, by taking linear combinations of orbitals that have no projection of angular momentum in some arbitrary direction, to construct orbitals (not pure states) that are ring-shaped. But this is not mere hand-waving. It is possible to prepare atoms in just those states in the laboratory, for example by using a static electric field and a laser tuned to the energy of the ring-like state. Inevitably, of course, there are limits (determined by the Uncertainty Principle) on the narrowness of such a ring; the greater the quantum number *n*, the relatively narrower the ring can be.

Gaeta and his colleagues first set out to show that it is possible to turn a ring-like Rydberg state into one in which there is a bunch of electron density moving around a circular orbit. Their recipe simply entails subjecting these atoms to a brief but relatively strong electric pulse for a picosecond or less. Because the ring-like states are already semi-classical, it is possible to use classical arguments to understand why this works.

Suppose, for example, that there are several (classical) electrons in the same circular orbit about a nucleus, and then arrange that there is a uniform electric field in the plane of the orbit for a brief interval of time, a small fraction of the period of the electrons in their orbit. Then particles instantaneously in the direction of the field will be accelerated, those moving in the opposite direction will be decelerated and those moving transversely to the field will not be affected.

The result of that velocity dispersion is that, eventually, all the electrons will bunch together briefly at some point in the orbit. So brief pulses of electric field are the means by which electrons are localized in circular orbits. Gaeta and colleagues show these bunches of electron density (each representing a single electron) persisting for several orbital periods, eventually decaying into gaussian smudges which then become uniform distributions about the circular orbit again. That the bunches of electron distribution last for even a single period is, of course, the surprise in this observation.

So why not go further, and make elliptical orbits by the same techniques? This is what proves possible. First, it appears, the ring-like orbits can be simply made into elliptical orbits by a steady electric field, whereupon the electrons can be made to travel around them by means of a short sharp field, as in the preparation of bunched circular orbits. The motion of the electrons has even been observed (with the help of femtosecond lasers).

As Kepler (or at least Heisenberg) might have predicted, an electron moves most quickly, and is less tightly bunched together, when near the nucleus, and is most tightly localized and most slowly moving at the other end of the orbit.

The immediate importance of these developments is, for the time being, pedagogical. They illustrate as vividly as anybody could ask the importance of the Correspondence Principle by which Bohr first grounded his semi-classical theory on observation, and which has since become the means of telling when a system has to be dealt with by quantum rather than classical mechanics. Here one can see electrons in that half-way stage between classical and quantum behaviour, making several orbits around a nucleus in a localized condition before eventually smearing out into a uniform distribution around the orbit.

Beyond that, the localized electron in orbit is a telling measure of how much has been learned of Rydberg atoms in the past decade or so. It is not merely that they have been powerful tests of atomic theory, but they have also been the proving-ground of the interaction of magnetic fields with atoms. In reality, for technical reasons and especially the lack of easily usable and tunable lasers in the ultraviolet, most studies have been made with Rydberg-like atoms, in which one of several electrons in a multi-electron atom has been excited into a state with large quantum number. But that may yet change.

Meanwhile, the fun and games mostly lie ahead, with the studies yet to come of the behaviour of Rydberg-like molecules. That is when it may be possible to learn something of the degree to which simple exposure to electric fields may bring about chemical reactions at present only possible in much more extreme conditions.

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