

When firsts come only second

Too many contributors to the scientific literature neglect the journalistic principle that the word "first" should prudently be avoided.

RESEARCHERS should learn from journalists the dangers of words such as "first". Those who describe some event as the first of its kind are almost certain to be assailed by readers saying that it is nothing of the kind. But to play safe by using qualifiers as in "the first recorded demonstration..." is merely to blunt the clarity of the message. Prudent people therefore stick to verifiable firsts.

Here is an illustration of the difficulties that may arise. In the issue of *Physical Review Letters* dated 24 November, R.P. Messmer and P.A. Schultz from the University of Pennsylvania contribute a fascinating account of their calculations of the electronic structure of C_2F_2 , acetylene in which the hydrogen atoms are replaced by fluorine atoms (57, 2653; 1086). The interest of the paper is its conclusion that the older valence bond description of atomic bonding may be a more accurate starting point for calculations of the electronic structures of molecules than the molecular orbital framework. A corollary is that the electrons participating in the carbon-carbon triple bond are more tightly localized on the two carbon atoms than the textbooks say.

Familiar? Even this brief description will prompt many to recall a recent paper by Cooper, Gerratt and Raimondi (*Nature* 323, 699; 1986). That was also an account of a valence bond calculation of an organic molecule, in that case benzene. Again the conclusion was that the valence-bond description can be the starting point for an accurate calculation of the electronic properties. Again it emerged that the electrons appear to be more tightly anchored to the carbon atoms than the textbooks say.

Both papers are important contributions to a reassessment of the utility of the alternative frameworks for molecular calculations.

The nearly simultaneous appearance of very similar pieces of work is not surprising. Sometimes, the explanation is that science has developed to the point at which a previously unformulated question cries out for an answer, whereupon several people independently design appropriate experiments.

On other occasions, a new technique may be the trigger for several parallel developments, which appears to be the case with the recalculation of the electronic properties of molecules. The work of Cooper, Gerratt and Raimondi and of

Messmer and Schultz has been made possible by computer programs capable of accommodating the very large numbers of alternative electronic configurations required for accurate valence-bond calculations and the availability of the computer power to implement them.

The dilemma of quantum chemistry is cruelly stated by the following string of simplifications. Chemical bonding is an essentially quantum phenomenon in which electron spin is crucial; if in the simplest of all natural molecules, H_2 , each atom is represented by a proton surrounded by a smeared-out electron but is otherwise dealt with classically, simple electrostatics will suggest that chemical bonding is impossible. Only the fact of electron spin allows electron wave-functions to overlap without an intolerable energetic penalty. If, for H_2 , the spatial wave-function is properly antisymmetrized with respect to an exchange of electrons, the electrostatic energy turns up with a minus sign if the electron spins are in opposite directions, implying chemical bonding in a state of zero total spin.

Both the valence-bond and molecular orbital schemes are ways of approximating to the wave functions of molecular electrons. In the valence-bond framework, molecular wave functions are built as linear combinations of products of pairs of atomic wave functions, not simply those with one electron attached to each nucleus but also those in which both electrons surround the same proton, leaving the other bare. Strictly speaking, excited states should play a part. For a complicated molecule, a horrendous number of configurations is usually required.

In the molecular orbital view of the world, the problem of H_2 can be dealt with almost exactly by means of the solution of Schrödinger's equation for the hydrogen molecule-ion; two electrons slot with opposite spins into the lowest electronic state, making molecular hydrogen a kind of binuclear helium atom. But only modestly more complicated molecules present fearsome problems; the simplest molecular orbital calculations start with approximations to molecular wave functions that are linear combinations of atomic wave functions, and yield useful results only by the empirical fitting of parameters. In neither scheme is the set of approximate wave functions an orthogonal set, which leads to further complications. Roy McWeeny made the compelling argu-

ment, in a *News and Views* article (*Nature* 323, 666; 1986) that there is no philosophical difference between the two approaches; what matters is merely which is the better starting point for calculation.

Much of the interest of what Cooper, Gerratt and Raimondi have done is their use of electronic spin as a way of classifying molecular electronic wave-functions, which is how they conclude that Kekulé's picture of benzene, as a structure in which different patterns of double bonds alternate, may be more realistic than the now-common view of benzene in which there is a static ring of electron density above and below the plane of the six-sided array of nuclei. Interestingly, their calculation starts with a set of old-fashioned molecular orbital functions on which they perform what is essentially a valence-bond calculation. The outcome is the surprising discovery that electrons are more nearly localized on the six carbon atoms than the conventional picture would have them.

Messmer and Schultz take a different tack, starting with the familiar way of dealing with carbon bonds which supposes that the four valence electrons of a carbon atom may occupy any hybrid mixture of the four independent wave-functions of the second electronic energy state. The conventional picture of the triple bond in C_2F_2 is that of two links between dumbbell-shaped electron orbits, at right angles to each other (called π bonds) and a direct link called a σ bond. By cleverly loosening the symmetry restrictions, they are able to show that the state of lowest energy is one in which the bonding electrons at each carbon atom are tetrahedrally arranged, and that the three carbon-carbon bonds are symmetrically arranged about the axis of the molecule. Again, the electrons are more localized than expected.

These developments are interesting and important. The only slightly jarring circumstance is that, admittedly with some qualification, Messmer and Schultz describe their work as a "first", a word whose use is belied by the appearance of Cooper, Gerratt and Raimondi roughly a month earlier.) The independence of the two pieces of work, which have only one reference in common, is plain, but the claim to be first makes one seem very mildly foolish. Should editors now seek to protect authors from themselves by banning the use of the word "first"?

John Maddox