Orbital update

Patrick Fowler

Methods of Molecular Quantum Mechanics, 2nd edn. By R. McWeeny. Academic: 1989. Pp.573. £65, \$130.

THEORETICAL chemistry is a peculiar subject. It is based on an equation that can hardly ever be solved. It deals in chemical concepts and qualitative rationalizations and yet its practitioners are amongst the biggest users wherever computer time and disk space are to be had. The new edition of a classic textbook offers a useful chance to see just how this odd activity has been changing. "McWeeny and Sutcliffe" has lost an author and gained several hundred pages. It remains a beautifully clear exposition of quantum chemistry written for the graduate student but useful for more experienced researchers, with newly added and sometimes tough problems at the end of each chapter. Quite deliberately, it concentrates on the conceptual and mathematical development of the subject and touches only lightly on computational aspects. In content and emphasis it is significantly different from the first edition which was issued about 20 years ago.

Since 1969 there have been several shifts in the subject. The enormous growth in computer power has, of course, extended the horizon of what is possible, but methods are also changing rapidly. Techniques and language lifted from theoretical nuclear and solid-state physics are beginning to make an impact on the everyday practice of molecular physics. Second quantization, Greens functions, propagators and diagrammatic techniques are becoming accepted as practical tools and not just ways to restate conventional results in what has sometimes seemed to the uninitiated to be wilfully esoteric form. The new edition contains an elementary account of diagrams which (almost) convinced me, at least, of their usefulness. Many-body perturbation treatments of correlation energy seem intuitively appealing and yet fail to deliver quantitative results in so many contexts that it is interesting to speculate whether they will still be prominent in textbooks of 20 years hence.

Since the early days of quantum mechanics the controversy between proponents of molecular-orbital (MO) and valence-bond (VB) theories has afforded good, clean, knockabout fun for the disinterested spectator. Because these theories start from the same equation, and converge in the limit to the same result, it is sometimes hard to see why they can have aroused such passions over the years. As used to be well known to undergraduate chemists, VB theory aims to construct

wavefunctions in which all possible chemical bonds are represented in terms of spin-pairing of the electrons in atomic valence orbitals. This inevitably leads to formidable practical difficulties with non-orthogonal orbitals, calculations that grow factorially with the number of electrons, and embarrassing 'ionic' and 'charge-transfer' contributions in the descriptions of ordinary covalent molecules. The basic MO approach is mathematically simpler and physically more appealing to many with its description of orbitals which extend over the whole nuclear framework and give an obvious rationalization of electron delocalization in π -systems and electron-deficient clusters. MO theory is much more readily translated into workable computer algorithms and came to eclipse VB both in calculation and in the descriptive language of theoretical, inorganic and eventually organic chemists. But in the pursuit of ever greater accuracy, MO calculations moved beyond the single-determinant self-consistent-field wavefunction to use vast configuration expansions which are almost as difficult to handle as giant VB functions and which rapidly lose physical interpretation in a welter of small energy terms. At the same time technical developments in VB theory mean that calculations on slightly larger molecules are now feasible and VB is enjoying something of a revival. The

controversy is not dead yet. The new edition of *Molecular Quantum Mechanics* gives more space to VB and an extensive discussion of modern approaches to the configuration-interaction problem.

Quantum chemistry used to deal exclusively with questions of electronic structure and valence. Nowadays, prompted partly by new experiments and partly by expanded computational possibilities, the study of more general molecular properties is on the increase. Electric and magnetic properties of single molecules are intimately linked to electronic structure, give information on intermolecular forces and properties of materials in bulk, and are probed by numerous sophisticated spectroscopic techniques. This book gives an excellent introduction to the theory of static and, in a new chapter, time- and frequency-dependent response of molecules to perturbation by fields and other molecules. For practical purposes, this would need to be supplemented by a discussion of multipole moments and multipole expansions which, mathematically unsatisfactory though they may be, are used in most current calculations and theoretical treatments of intermolecular forces. All in all, this is an excellent new version of an important textbook. □

Patrick Fowler is in the Department of Chemistry, Exeter University, Exeter EX4 4QD, UK.

The African zebras and Eurasian pygmy mouse, above and right, are reproduced from *Grzimek's Encyclopedia of Mammals*. This five volume set was produced by B. Grzimek in collaboration with more than 200 naturalists, zoologists, biologists and ecologists, and is a comprehensive study of animals in their natural environments. The volumes are beautifully illustrated, containing more than 3,000 colour photographs. Published by McGraw-Hill, price \$500, £325.