Reviews of Books

Reduced Density Matrices in Quantum Chemistry. By E. R. DAVIDSON. (Academic Press, New York, 1976). Pp. viii+135. Price £9.35/$17.00.

Density-matrix theory is an important part of modern theoretical chemistry. It was developed to account for the properties of systems which are not in a pure state but which can be described by a representative ensemble. The density matrix is more satisfactory than the wavefunction since it is applicable both to pure states and to statistical ensembles. The same basic theory applies to the N-electron molecule in a stationary state. The diagonal elements of the pth-order reduced density matrix in the coordinate representation give the p-electron distribution function, where $N \geqslant p \geqslant 1$. Löwdin's natural spin orbitals are the one-electron functions which diagonalise the first-order reduced density matrix. Knowledge of the second-order reduced density matrix is sufficient to determine the energy and this apparent simplification of the N-electron problem has prompted much recent work on density matrices.

The author is well-known for his work on natural orbitals and the present book evolved from a course he taught at the Ohio State University. The book contains seven short chapters on the properties of the first- and second-order reduced density matrices. The natural orbitals of He and H_2 are considered in detail and there are diagrams of the natural orbitals of HF in its ground state.

Those theoretical chemists who are concerned with the problem of electron correlation will find this book helpful and enlightening. However, the terse style and the absence of an elementary introduction imply that it is unlikely to be useful to those with only a little knowledge of the subject. A few minor errors were detected, including misspellings of Hellmann and Linnett.

A. D. BUCKINGHAM

Received 24th September, 1976

Molecular Spectroscopy, Vol. 4. Senior reporters R. F. BARROW, D. A. LONG and J. SHERIDAN. (Specialist Periodical Report, The Chemical Society, London, 1976). Pp. viii+279. Price £17.25. ISBN 0 85186 536 4.

This fourth volume of the annual series devoted to " Molecular Spectroscopy " contains chapters on microwave spectroscopy, electronic structure of diatomic transition-metal molecules, Rayleigh and Raman scattering of polarised light, biological applications of Raman spectroscopy, ionic and molecular electronic Raman spectroscopy, and on non-linear Raman effects. The articles themselves are of very good quality and are written by well known authors but, taking into account the nature of the different chapters and their subject matter, it is clear that in this year's volume only the microwave spectroscopists and particularly the Raman spectroscopists come off well. The infrared spectroscopists have nothing directly offered to them, and the chapter on electronic spectroscopy is somewhat specialized. Also unfortunately the sub-title of the volume " a Review of the Literature published during 1974 and early 1975 " only really applies to the chapter on microwave spectroscopy which continues an annual systematic review of the literature in that field. The four chapters on Raman spectroscopy provide a good cover of aspects of the literature over a longer period.

The somewhat unbalanced choice of subject matter in this volume led the reviewer to analyse the contents of all 4 volumes to date. These have provided 4 chapters on microwave spectroscopy, 7 on electronic spectra (with surprisingly no coverage of photoelectron spectroscopy), 7 on infrared (and far infrared) spectroscopy, 10 on Raman spectroscopy, and 3 on special techniques or fields of application, *e.g.* matrix isolation spectroscopy. It can be seen, that over the 4 year period, electronic and infrared spectroscopy have been given much more balanced coverage than is provided by the particular volume under review. Also the above analysis does cover a number of chapters where, advantageously, certain topics of infrared and Raman spectroscopy are treated together. The magnetic resonance spectroscopies are provided for in other series of Reports.

The present reviewer is in general an enthusiastic supporter of the Chemical Society series of Specialist Periodical Reports. He felt comparatively cut-off from the recent literature when last year he worked in an overseas library which contained few of them. However, for this purpose, he strongly prefers the systematic and uniformly-structured type of annual review such as has been provided for microwave spectroscopy in the present series of Reports, and would hope that it might be possible to cover more of the literature of the electronic and vibrational spectroscopies in this manner.

N. SHEPPARD

Received 27th September, 1976

Advances in Chemical Physics. Vol. 34 and 35. Ed. I. PRIGOGINE and S. A. RICE (John Wiley, New York, 1976.) Pp. ix+324 and ix+358. Prices £21.50/$36.60 and £22.00/$37.40 respectively.

The first of these volumes deals with the physics of fluids and, although untitled, it could be regarded as a companion to last year's volume 31 which was called " Non-Simple Liquids ". It opens with a long article by W. A. Steele on the Rotation of Molecules in Dense Phases, a subject which has much interest in that it can be studied by many different experimental methods. H. C. Andersen, D. Chandler and J. D. Weeks discuss the Roles of Repulsion and Attractive Forces in Liquids, the former by the particular perturbation techniques which they have developed, and the latter by some interesting summations of graphical expansions. This is followed by two reviews of X-ray diffraction, J. F. Karnicky and C. J. Pings on experimental methods principally for monatomic fluids, and L. Blum and A. H. Narten on diffraction by molecular liquids. Finally, N. G. van Kampen takes what he calls a mesoscopic view of transport phenomena, that is, one which is neither molecular nor macroscopic, and in which his chosen tool is the so-called " master equation ".

Volume 35 has no theme; indeed one of the reviews, although a fascinating topic, has no chemical content—M.J. Haggerty and G. Severne on the Kinetic Theory of Gravitational Systems. Such thermodynamically divergent forces concern those whose laboratories are on the galactic scale. The remaining articles are more in the mainstream of chemical physics. P. W. Atkins and G. T. Evans write lucidly on the two principal theories of chemically induced electron spin polarization, and C. F. Curtiss, R. B. Bird and O. Hassager write an article of much greater length and difficulty on the Kinetic Theory and Rheology of Macromolecular Solutions. The latter contains more original work than most reviews, and is an article intended for use rather than for casual reading. P. J. Stephens writes on Magnetic Circular Dichroism, restricting himself to the theory of electronic transitions of impurities in crystals. Finally D. R. Dion and J. O. Hirschfelder review a classic topic, the Time-dependent Perturbation of a Two-state Quantum System by a Sinusoidal Field.

Both volumes maintain the high standard of this series and, alas, their ever higher prices.

J. S. ROWLINSON

Received 1st October, 1976

Advances in Infrared and Raman Spectroscopy. Vol. 2. Ed. R. J. H. CLARK and R. E. HESTER. (Heyden and Son, London, 1976). Pp. xv+343. Price £17.50/$35.00/DM 112.00.

Vibrational infrared and Raman spectroscopy are among the most important spectroscopic techniques on account of their wide applicability and the high information content of a vibrational spectrum. The rapid growth of electro-optical technology in the form of visible and infrared lasers and signal detection and processing systems has enabled vibrational spectroscopy to be applied in situations quite undreamed of a decade ago. There is certainly a need for an ongoing series of authoritative accounts of both the new techniques and their application in physics, chemistry and biology. The present volume is the second in just such a series, which so far appears to meet this need admirably.

Vibrational spectroscopy is expected to be a powerful probe of the structure of matrix isolated species, and chapter one discusses the vibrational energy levels of such species, emphasising applications to metal carbonyls. Chapter two is concerned with the information that can be extracted from the vibrational fine structure of the electronic absorption and emission spectra of transition metal coordination compounds (another related example of the fruitful union of electronic and vibrational spectroscopy being resonance Raman scattering). Infrared and Raman spectroscopy appear to be the best spectroscopic techniques for on-line analysis of chemical plant processes, which is the subject of chapter three: as well as much useful information for industrial chemists, it contains many examples for teachers who wish to inject some technological relevance into their undergraduate spectroscopy courses. Chapter four describes gadgetry which enable complete Raman spectra to be taken with a time resolution as high as 1 ps, together with an account of a Raman microscope for the study of heterogeneous systems. The last two chapters, which take up about half of the volume, are concerned with the minutiae of recent applications of infrared and Raman spectroscopy to the study of, respectively, ionic vapours, liquids and glasses, and electrolytes.

The book is well-produced, and while the price would have seemed outrageous a year or two ago, it is not excessive by the standards of today.

L. D. BARRON

Received 20th December, 1976