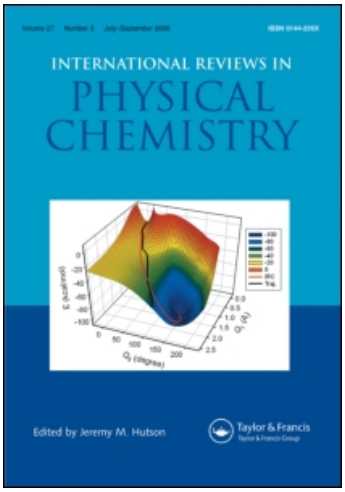

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BOOK REVIEWS

Geoffrey C. Maitland, Maurice Rigby, E. Brian Smith and W. A. Wakeham. *Intermolecular Forces*, Oxford: Clarendon Press, 1981. 616 pp. £39.50. ISBN 0–19–855611–X.

This book presents a simple but comprehensive account of the techniques which are currently being used to determine intermolecular potentials from molecular beam scattering and the spectroscopy of van der Waals dimers, as well as from thermally averaged macroscopic properties such as second virial coefficients and viscosity. The chapters on these topics are excellent and include a great deal of recent theoretical developments. The best feature of this book is that recent experimental data are used to illustrate most of the methods which are discussed. In this way the theory and the experiments are closely linked.

The jacket on its cover states that

> this important new book provides a definitive account of our present understanding of the forces between molecules. It deals with both the origins of such forces and their quantitative determination using a combination of theoretical and experimental techniques.

This is clearly an overstatement since it would be impossible at the present time for any one book to give a thorough treatment of *all* of the different types of intermolecular forces.

Instead, the authors state in the Preface: 'Naturally, we have given most attention to those systems (mainly monatomic) where the intermolecular potential is known with high accuracy....' As a result, only the simplest types of molecular interactions are considered in detail and very little attention is given to explaining the theory of more complicated sorts of interactions.

As experimental data becomes more precise, it becomes increasingly difficult to determine suitable analytical potential models. Thus a number of models for polyatomic molecule collisions are discussed and 27 pair potential models are given. For pairs, the authors prefer the many-constant Barker-Bobetic-Maitland-Smith (BBMS) potential. Of course, care must be used to ensure that extraneous wiggles do not result from using more empirical constants than is warranted by the experimental precision.

Considerable emphasis is placed on an inversion procedure first discovered by Hirschfelder and Eliason (Hirschfelder, J. O. and Eliason, M. A., *Ann. N.Y. Acad. Sci.*, *67*, 45 (1957)) and further developed by Gough, Maitland and Smith (Gough, D. W., Maitland, G. C. and Smith, E. B., *Mol. Phys.*, *24*, 151 (1972)). This makes possible a direct determination of the empirical constants in a model potential energy function, $U(r)$, from measurements of viscosity or any other thermophysical property, $P(T)$. The method is based upon the fact that the value of $P(T)$ is only sensitive to $U(r)$ in a small range of internuclear separations centred around $r_{P(T)}$. Furthermore, if we define a function $G_p(kT/\varepsilon)$ such that

$$U(r_p) = kT\, G_p(kT/\varepsilon)$$

then $G_p(kT/\varepsilon)$ is very insensitive to the functional form of the model potential which is assumed. However, both r_p and $G_p(kT/\varepsilon)$ depend considerably upon the property under consideration. Thus, it is difficult to make an accurate determination of a potential energy function on the basis of only one property. Whenever possible it is desirable to compare the potentials obtained from many different kinds of experimental measurements. [One minor comment: in Table 13.2 it would be helpful to include the parameters which were used in the calculation of the G_p.]

Since the authors have done such an excellent job presenting in this book the determination of intermolecular forces of ground-state inert-gas molecules and other simple molecular systems, we hope that as additional experimental data and new theoretical techniques warrant, they will write additional volumes which treat some of the topics which are not considered in detail in the present text, such as:

1. Intermolecular forces involving ions, molecules in excited states, or hydrogen-bonded molecules.
2. The role of resonant collisions in the transport properties and collision cross-sections of polar molecules (such as HCl).
3. The long range quadrupole–quadrupole interaction energy of non-S state atoms (such as the ground state of B, C, O, S, Cl, . . .) and its determination by means of spectroscopy).
4. The effects of potential energy curve crossings on transport properties and collision cross-sections.
5. Magnetic and current–current types of intermolecular forces.
6. The large effect of retardation on the long-range interaction of excited state molecules.

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G. S. Ezra. *Symmetry Properties of Molecules. Lecture Notes in Chemistry, Vol. 28*, Springer Verlag, 1982. 202 pp. $18.00, DM39.80. ISBN 3–540–11184–0.

In the early 1960s it became apparent that the standard procedures for classification of molecular states, which seemed acceptable when applied to ordinary 'rigid' molecules, failed to cope with 'non-rigid' molecules such as ethane and ammonia which have more than one readily accessible nuclear conformation. The failures in the non-rigid case showed that even the rigid case was not adequately handled by the existing machinery. Some of us recall the long and acrimonious arguments which ensued. Even at the time it was possible to see that much of the confusion was caused by failure to understand the way in which 'molecule-fixed' axes must be defined, and the way in which they were affected by such symmetry operations as the permutation of sets of identical nuclei. Since the rotational wavefunction depends on the orientation of the molecule-fixed axes relative to some arbitrary set of 'space-fixed' axes, this meant that the effect of symmetry operations on rotational wavefunctions was obscure. Another controversial issue was the concept of 'feasibility' introduced by Longuet-Higgins, who described a permutation of nuclei as feasible if the new configuration was not separated from the old by an excessively high energy barrier. Misinterpretation of this idea led to further disputes.

Dr Ezra has the advantage of coming to the subject a decade later, when most of the

passions have subsided. Nevertheless he is extremely skilful in picking his way through the minefield of conflicting definitions, in setting out the principles with remarkable clarity, and in weighing the merits of alternative approaches where alternatives are admissible. The four chapters deal with the molecular Hamiltonian, the symmetry properties of rigid molecules, the symmetry properties of non-rigid molecules, and non-rigid molecule symmetry groups. There are important appendices on rotational wavefunctions and on semi-direct product groups. The style is economical but clear. The book has been produced by photo-reproduction from an immaculate typescript, and is unusually legible for this type of work. I found only one misprint, and that was trivial. In common with other items in the series, it is relatively cheap, and it is essential reading for anyone seriously interested in the properties of non-rigid molecules, or in the symmetry classification of molecular wavefunctions when molecular rotation is important.

It is, in summary, an impressive piece of scholarship, and is all the more impressive in being, I understand, essentially a reprint of the author's Oxford D.Phil. thesis. It is no doubt because of this that it is marred by the lack of an index—a most unfortunate omission.

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