Ground-state diatomic systems summarized in two volumes

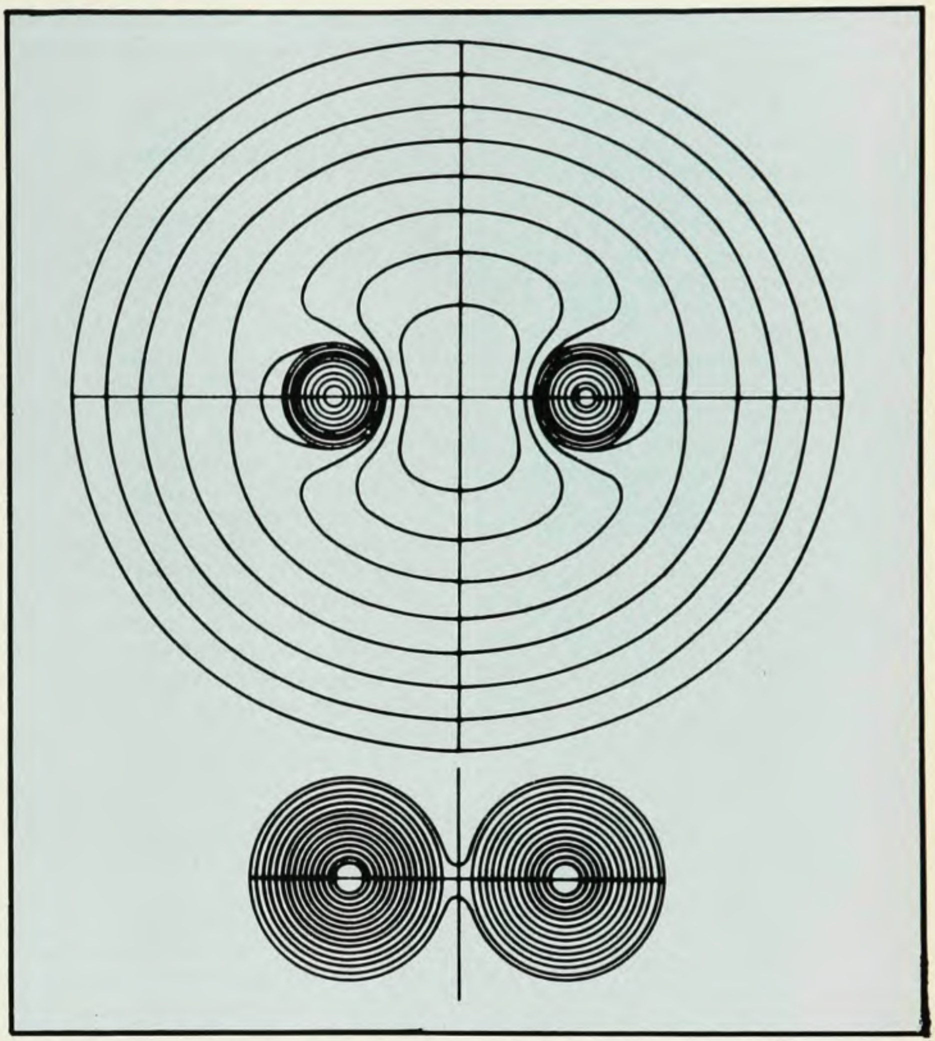
Diatomic Interaction Potential Theory: Vol. 1, Fundamentals; Vol. 2, Applications

J. Goodisman
311 pp.; 423 pp. Academic, New York, 1973. Vol. 1, $24.00; Vol. 2, $34.00

Reviewed by Samuel O. Colgate

The advent of methods for high-speed electronic computation coupled with the rapid growth in the ranks of research personnel has during recent years led to a proliferation of scientific calculations that could not have been foreseen a relatively short time ago and which to most of us appears mind boggling even today.

From time to time a dauntless spirit invades the mountainous literature to return with a report summarizing the more significant achievements in some limited area. Jerry Goodisman is such a spirit. He has braved the literature dealing with calculations of the intermolecular potential and, after severely limiting the scope of his report to interactions of ground-state diatomic systems by methods generally applicable to many electron systems, found it necessary to write two volumes for an adequate summarization of his findings.



Electron density contour maps of the homogeneous diatomic lithium molecule. The adjacent contours, generated by computer, differ in electron density by a factor of two. The 2sσ bonding orbital is shown at the top and the 1sσ bonding orbital at the bottom. The diagrams were prepared by Arnold C. Wahl of the Argonne National Lab.

That, as a frequent contributor to this literature, Goodisman is eminently qualified to perform such a service, is generally borne out by the quality of the manuscript. The first volume is concerned principally with presentation of the various quantum-mechanical methods that have been developed for calculation of interaction potentials. The introductory material on the form of the potential and the many different analytical functions that have been proposed to emulate that form is very good. The section on determination of the potential from experimental measurements is necessarily brief, but Goodisman does direct the reader to recent comprehensive reviews.

The bulk of volume one comprises a survey of theoretical models from which potential information can be computed. The material is presented in a concise, but coherent, manner and includes techniques based on the variation principle, perturbation theory, the virial theorem, the Hellmann–Feynman theorem, local-energy methods and quantum-statistical calculations. That the level of presentation is consistent throughout these various topics testifies to the obvious care with which the manuscript was prepared. One does not get the feeling that some topics were included to give the appearance of completeness without being as well researched as others.

Volume two consists of a survey of $U(R)$ values calculated by application of the methods presented in volume one. The author considers the problems of calculating the potential for large, intermediate, and small values of R separately. His treatment of the Casimir–Polder relation and its use to establish bounds on van der Waals constants is particularly interesting, although he does not explain clearly how reliable the resulting tolerances are or justify presentation of calculations that yield results lying outside the computed bounds. For interactions between atoms at intermediate distances, methods based on the self-consistent field and configuration interaction are emphasized. The final chapter reviews semi-empirical calculations derived from modified molecular orbital theories, pseudopotentials, and the atoms in molecules approximation, and concludes with consideration of some simple models and correlations between potentials. The author frequently cites comparisons of calculated values with experimental results.

The completion of so exhaustive a two-volume study is truly a monumental achievement. Goodisman has cited some 1300 papers including at the end of each chapter a list of papers published too late to be included in the main manuscript. For each of these the reader is directed to the section of the chapter to which the content of the paper is most relevant. The author claims that a knowledge of quantum mechanics equal to that which would be obtained from a one-semester course is sufficient for users of this work. He directs the student reader to standard texts for clarifying details. It appears likely that considerable use of such reference material would be needed by students with only one semester of quantum mechanics, but more advanced students should find the work to be quite lucid.

The only substantial disappointment that comes from reading the work is that the expectation of success generated by early statements in the text ["... quantum chemists can now produce reliable interaction potentials for diatomic systems in their ground states," (preface) and " ... the derivation of the potential *U(R)* from calculated energies for a series of values of *R* ... is considered, as well as the correction of the results of Hartree–Fock calculations to give accurate potential curves." (volume one, page 4)] is not fulfilled by the actual results given. In volume two, page 263 one finds: "It appears that one can perform approximate Hartree–Fock calculations leading to *U(R)* for any diatomic system desired. The resulting potential constants and other features, however, will generally be reliable only qualitatively, unless one has an idea of (a) the expansion error ... and (b) the correlation error ... These questions can be answered when one has available similar calculations on a set of related molecules, for which exact Hartree–Fock and exact results are known." This information of course, is generally not available. Later (page 285) he writes "One would like to have a set of rules for constructing configurations which could easily be implemented for a variety of new systems, and which yields a potential curve in which one can be confident. It does not appear from the preceeding discussion that theoretical analysis suffices to derive such a method." Although the material offered falls short of one's hopes, it remains an outstanding review of the state of the art up to the date of publication.

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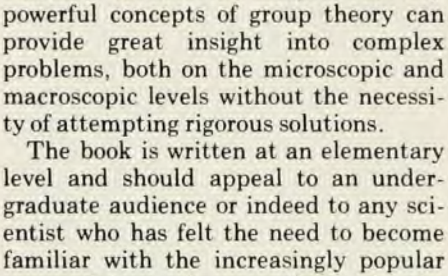
Symmetry and its Applications in Science

A. D. Boardman, D. E. O'Connor, P. A. Young
305 pp. Halsted, New York, 1973. $14.95

This book by A. D. Boardman, D. E. O'Connor, and P. A. Young is a welcome addition to the literature on the application of group-theoretical principles to physics and chemistry. The authors have produced a well planned introductory text, which aims primarily to provide the reader with an understanding of how the simple but very powerful concepts of group theory can provide great insight into complex problems, both on the microscopic and macroscopic levels without the necessity of attempting rigorous solutions.

The book is written at an elementary level and should appeal to an undergraduate audience or indeed to any scientist who has felt the need to become familiar with the increasingly popular nomenclature of group theory in the realm of atomic, molecular and solid-state physics and chemistry. Although there are many existing books on group theory and its applications; most of them are encumbered by varying degrees of rigorous mathematical background and abstract group concepts that, although of great value to the serious student of the formal theory, have perhaps scared away that great body of scientists who would prefer to use the theory as a tool (or at least learn its language), but have looked in vain for a simple textbook that would enable them to acquire this facility in a limited time and without significant previous knowledge. The present book appears to fill this void admirably. Avoiding rigorous proofs, it introduces the essential concepts and relationships of basic group theory and the manner in which they may be used to extract the maximum amount of information from the inherent symmetry properties of physical phenomena. The later chapters contain many applications such as crystal symmetry, tensors, energy bands in solids, atomic orbitals, molecular orbitals, selection rules, normal modes and vibrational spectra.



Symmetry abounds in benzene ring where sigma bonding occurs in the x–y plane.

To a large extent the several chapters on the various applications can be read independently, each chapter supplying its own preamble of background material. In addition, each chapter contains a handful of well chosen problems that enable the reader to assess his grasp of the material (and his ability to use the knowledge acquired) at frequent intervals. The solutions are supplied together with the detailed working at the end of the book.

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Physical Fluid Dynamics

P. D. McCormack, L. Crane
487 pp. Academic, New York, 1973.
$17.50

It sometimes seems as though all of the scores of fluid mechanics books except that by Landau and Lifshitz were written primarily for applied mathematicians and/or engineers, so the appearance of this one, *Physical Fluid Dynamics*, is an event of interest to readers of PHYSICS TODAY.

The bad news is that this book is in many ways less "physical" than many others on the subject. Evidently the first adjective of the title was justified in the minds of the authors by presence of a chapter on the hydrodynamics of superfluids, a topic researched more by "physicists" than by "applied mathematicians" or "engineers." The inclusion of this subject is the principal good news. But there is more bad news: the book has more than its fair share of misprints, errors, misleading omissions, and generally slipshod exposition.

The shortcomings can be categorized as follows:

- misprints and undefined symbols,