

Molecular physics and the correlation problem: Two books

Introduction to the Electron Theory of Small Molecules

A. C. Hurley
329 pp. Academic, London, 1977. \$26.25

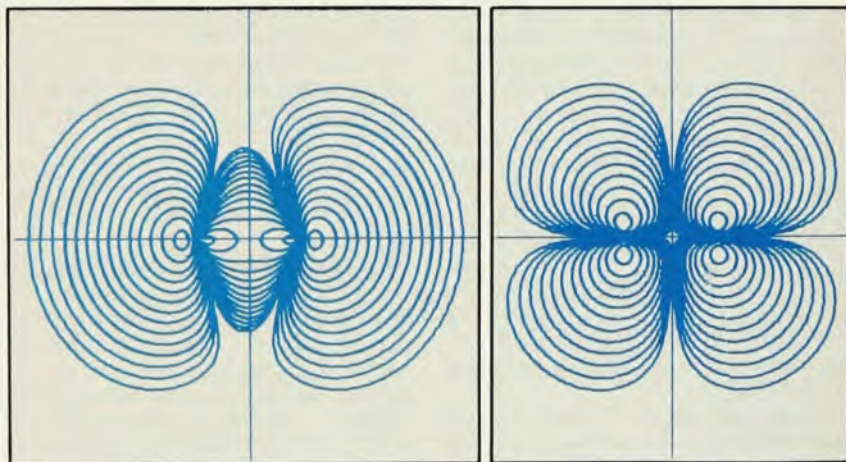
Electron Correlation in Small Molecules (Theoretical Chemistry, No. 6)

A. C. Hurley
276 pp. Academic, London, 1977. £10.50

Reviewed by Nils Yngve Ohrn

Andrew C. Hurley, molecular physicist at the Commonwealth Scientific and Industrial Research Organization in Melbourne, Australia, has written two books on the electron theory of small molecules. This field of many-particle physics lies on the interface with chemistry, so much so that sometimes one refers to the subject as quantum chemistry. The application of quantum-mechanical methods to the detailed quantitative treatment of general molecular systems is one of the most challenging areas of research in theoretical physics. One must deal with systems that possess neither the simplifying spherical symmetry of the isolated atom nor the translational symmetry of the perfect solid, yet at the same time one seeks to obtain accurate results for binding energies (within fractions of a kcal/mole) as well as qualitative and quantitative interpretation of the subtleties of molecular spectroscopy (by now, a highly developed endeavor). The electron theory of molecules requires the use of sophisticated many-particle methods in a manner that yields practical calculations.

Hurley is eminently qualified to write on this topic. He has contributed actively to this field of theoretical physics since the early 1950's. The book *Introduction to the Electron Theory of Small Molecules* is the more elementary of the two texts, but the level of presentation presumes the reader to have had one to two semesters of quantum mechanics. The second book, *Electron Correlation in Small Molecules* is a research-level monograph on electron-pair theories, a



Contour diagrams of electron densities for the O_2 molecule. The diagram at left represents the $3\sigma_g$ -state orbital density, while the figure at right is for the $1\pi_g$ state. Both have the same lowest contour value, $6.1 \times 10^{-5} e^-/\text{bohr}^3$. Figures by A. C. Wahl, *Science* **151**, 961 (1966).

part of molecular theory to which the author currently is an active contributor. This means that the non-specialist probably would benefit from reading the more elementary text before trying to work through the maze of current electron-pair theories, while the quantum-chemistry specialist will enjoy the more advanced material and find a self-contained presentation.

In the case of the introductory volume, the presentation is lucid although somewhat terse. Practical aspects of the application of the theory are sprinkled throughout the text. The topics treated include a brief review of the separation of nuclear and electronic motion and the adiabatic approximation. This is done following the work of Max Born and Robert Oppenheimer, which means that the separation of the translational motion is not considered before defining the concept of electronic energy. Hurley discusses the construction of empirical potential surfaces and reviews the semiclassical methods of Dunham and Rydberg-Klein-Rees. These methods are still viable, although being improved upon, and this is a very useful introduction to these important techniques for drawing information from spectroscopic data.

Great clarity distinguishes the author's

treatment of variational methods for solving the Schrödinger equation, and a very valuable account is given of the Hellman-Feynman formulae and theorems.

A detailed treatment of the hydrogen-molecule ion and the hydrogen molecule takes about 130 pages, better than one-third of the text. Most of this material can be found in other texts, but Hurley's style of presentation and the detailed comparisons between different approximate methods make these chapters very enjoyable and informative reading. A chapter on the use of determinantal wavefunctions and spin projectors precedes a chapter on molecular orbitals and the Hartree-Fock method. Considerable detail is given in the discussion of the unrestricted and the restricted cases and the concept of localized orbitals, and there are many examples of actual calculations. The short chapter on symmetry of molecular electronic states contains an amazing amount of information and group-theoretical facts, with the most interesting part being the examples given of the so-called "symmetry dilemma," namely, that a properly symmetrized approximate wavefunction often yields a poorer variational bound to the total energy than an asymmetrical one.

Now let us turn to the more advanced

text. The error inherent in the Hartree-Fock model for the many-electron molecular system is usually referred to as the correlation error. This deficiency in a simple model is employed as a basis for analyzing the details of chemical bonding and spectra. Hurley starts out by discussing the more obvious corrections, namely those which are necessary in order to give qualitatively correct behavior at dissociation. This discussion leads to an instructive comparison of the molecular-orbital and the valence-bond methods and to detailed applications to diatomic and polyatomic molecules. The treatment, although abstract in nature, is very close to actual calculations. In particular, I find the discussion of the dissociation of the ethylene molecule into two methylene radicals very instructive.

A chapter entitled "The Correlation Problem" makes up the bulk of the text (190 pages). Hurley's discussion of reduced-density matrices and natural orbitals draws heavily on the work by Per-Olov Löwdin during 1955-59. The problem of selecting a determinantal basis for a superposition-of-configurations calculation is treated in great depth, but the discussion lacks references to work published after 1970.

Particular emphasis is given to the electron-pair theories, for the calculation of correlation energies. Separated-pair theory, independent-pair theory and their extensions are worked out with numerous examples of applications to molecular systems, particularly for the ground state.

It should be valuable for the quantum chemist to get the alphabetical zoo of methods (IPA, IPEA, IPNO-CI, IPNSO and so on) sorted out. Hurley's presentation explains the sometimes subtle differences between these schemes in a clear and elegant manner using consistent notation.

The works by Harold Conroy and by Niclas C. Handy and the late S. Francis Boys using interelectronic coordinates are also briefly reviewed.

I do not mean this as any criticism, but it should be noted that some of the important recent work on electron correlation in molecules is not mentioned in this text. For instance, the work on the calculation of excited states, excitation energies, ionization energies and various transition properties using bracketing functions, many-body perturbation theory, Green's function theory and the EOM methods are not mentioned. Still, the text is a very valuable and welcome account of what goes on in the world of electrons in molecules.

* * *

Yngve Öhrn is a Professor of Physics and of Chemistry at the University of Florida at Gainesville, where he also serves as associate director of the Quantum Theory Project. His

research interests have included such topics as the electronic structure, properties and spectra of atoms; molecules and solids, and quantum-mechanical properties of matter.

Asymptotic Structure of Space-Time

F. P. Esposito, L. Witten, eds.

442 pp. Plenum, New York, 1977. \$42.50

There are few working on the frontiers of gravitation physics and relativity today who will not find this book a valuable guide in their investigations, and of those who rather want simply a flavor of the latest in the field, there are few who will not get from the volume at least some impression of the topics of central interest today.

I can imagine many who will buy *Asymptotic Structure of Space-Time* simply for Robert Geroch's more than 100-page treatise of the same title. Others will read it for Leonard Parker's 120-page paper, "The Production of Elementary Particles by Strong Gravitational Fields," and still others will find indispensable the work by E. T. Newman and K. P. Tod on the calculus of spin weight functions, not to mention the ensuing development of that topic contributed by other distinguished authors further on in the volume.

One could only hope that the editors will take the good outcome of the present enterprise as stimulus to edit an annual series of books on recent developments in general relativity.

JOHN A. WHEELER

The University of Texas at Austin

Science Development: The Building of Science in Less Developed Countries

M. J. Moravcsik

262 pp. Pasitum, Bloomington, Ind., 1975. \$6.00 in Europe, Australia, Canada, the US and Japan—free elsewhere on individual request

This book is the first one in English about science in underdeveloped countries. The number of papers devoted to this problem has been growing steadily; however this is the first systematic attempt to cover a whole range of problems in the field. The author, Michael Moravcsik, is an American physicist who has spent several years in less-developed countries. He has drawn his information from his own experience and from almost 500 papers, which are quoted in an impressive bibliography. He has been trained as a physicist, but the field belongs in my opinion to the social sciences: Science policy should be considered a part of political science. This is, therefore, not just

a book for physicists or natural scientists, but for social scientists and for all those interested in the harmonic and rational development of the less-developed countries, including the scientists of the developed countries who might be willing to help in this development by contributing their particular expertise; the numbers of these last, unfortunately, have been so far very small.

The importance of the subject can hardly be overestimated. Science policy is needed if a scientific and technological system is going to develop in the less-developed countries. Such a policy is a necessary tool for building up their higher education (and their educational systems in general), public health and production, and thus for breaking away from their underdeveloped dependent situation. The importance of the subject is not appreciated in the advanced countries, as is witnessed by the fact that Moravcsik got no support for writing his book and did not find it easy to publish. On the other hand, at least in two Spanish-American countries, Argentina and México, a strong interest has arisen in this subject. Two symposia were held in 1973 and 1974, in Buenos Aires and Mexico City. The initiatives were totally local, and no foreign participants were invited, not for chauvinistic reasons but because the means available and organizing capabilities were modest. Five anthologies on the subject of science and technology development were published in 1974 and 1975 in Buenos Aires and Mexico City. (The four published in Buenos Aires were edited by Oscar Varsavsky, Jorge A. Sabato, Francisco Suárez and Gregorio Klimovsky, the last with the rather misleading title of *Ciencia e ideología*; Luis Cañedo edited the Mexican volume.) As a result of the current purge of Argentine intellectuals, the anthology edited by Varsavsky has become a collector's item, and many of the authors probably share the fate of most Argentine scientists—slaughtered, kidnapped, fired from their jobs or forced to emigrate. These facts show quite clearly how difficult and tragic life might be for intellectuals in underdeveloped countries.

The best of Moravcsik's work is his description of the real situation of science and scientists in the underdeveloped countries. This is a subject on which a number of authors—such as John Ziman, Antoine Zahlan, Philip Altbach, N. Singh and others—have written good papers, sometimes in journals not widely read. Moravcsik's merit lies in his having put together all this valuable information in a more systematic way and for a larger audience. The book gives a good list of obstacles to science development: formalist teaching, scientists prejudiced against experimental work, scientists with a "non-functional" understanding of science and narrow ranges of competence that make them a kind of dead wood in