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Quantum Theory of Matter: Introduction

Slater chose the title "Quantum Theory of Matter" for his summary volume on the electronic structure of atoms, molecules, and solids. This ambitious title might apply also to this issue of *Chemical Reviews*. Since 1970, the revolution in computers has made it possible to develop and test quantitative models of the structure of all types of chemical matter. There are now a vast array of numerical results, and a few new ideas, which could not have been foreseen 20 years ago. Unfortunately, the growth in this field has also led to repeated bifurcations into microfields, so that it is now nearly impossible for one person to comprehend the whole field. It is hoped that the present review will put a few of these microfields into perspective.

Each of the authors for this volume was invited to review an area of application of quantum theory in chemistry. The results are remarkable. The range of applications made possible with modern computers, and the depth of understanding of complex phenomena which has resulted, make typical textbook treatments of quantum theory seem dated and superficial. The challenge for the future will be how to incorporate this new knowledge into the training of the next generation of chemists. Meanwhile, these reviews document some of the uses to which theory has been put during the last two decades. They also illustrate the major tools of quantum theory—ab initio calculations, semiempirical models, density functionals, molecular mechanics, and formal derivation of equations for model situations.

Two of the reviews cover material of importance to biochemistry. A. Pullman has reviewed calculations on ion transport through membranes using a molecular modeling method with parameters from ab initio theory. This review makes clear the open theoretical questions in ion transport. Newton has reviewed the numerous approximate models of electron transfer and has shown the relation of these models to ab initio calculations.

Three of the reviews relate to material science. Whangbo and Canadell review the results from extended Hückel theory for one-, two-, and three-dimensional solids with emphasis on $A_xMo_yO_z$ and $A_xW_yO_z$ compounds. Bonačič-Koutecký, Fantucci, and Koutecký have discussed large clusters of metal atoms and the approach to the metallic limit. Andrē and Delhalle discuss organic materials which may be important in optoelectronics because of their large nonlinear polarizability.

The theory of transition-metal chemistry has lagged behind the quantum theory of organic chemistry because quantitative wave functions are more complicated. Five papers in this volume deal with aspects of organometallic bonding. Morokuma and Koga review some important reactions catalyzed by a metal center. Bursten and Pepper review results on the actinides where relativistic effects cannot be ignored. Veillard critically reviews the ab initio literature on transition metal–ligand binding and concludes that the SCF method is inadequate while better methods are very costly. Zerner and Cory emphasize that much of the spectra of these molecules is best understood from the viewpoint of ligand field split atomic levels coupled to excited ligand energy levels. Ziegler shows that the density functional method produces better results than the SCF method for the ground states of organometallic molecules. This is an important alternative approach to describing the energy and charge density of large systems.

In spite of the focus in these reviews on large molecules, the chemical physics of small molecules is still an active field. Bauschlicher and Langhoff have reviewed the accuracy achievable in describing the spectra—energy and intensity—of diatomic molecules. Simons and Gutowski have reviewed the field of resonances in small anions in which two electrons are excited into Rydberg orbitals. The review by Orlandi, Zerbetto, and Zgierski on the spectra of "short" polyenes bridges the gap between small molecules and larger molecules of importance in biochemistry and material science.

Bader reviews his methods for defining atoms in molecules and computing their properties. Cooper, Gerratt, and Raimondi review spin-coupled valence-bond theory as an alternative method for obtaining and interpreting electronic structure. Both of these reviews face up to one difficulty of modern calculations: Too often, only the energy is reported, but the wave function is discarded without interpretation.

Clementi and collaborators have attempted to overview his approach to describing matter from small atoms to simulations of liquids. This "vertical" review shows the dependence of other branches of theoretical chemistry on the solutions to the Schrödinger equation. This paper focuses almost exclusively on work done in his laboratory, since a comprehensive review of this broad subject would be too voluminous. The Editors felt that the unique perspective provided by this contribution rounds off the thematic issue and justifies the exception to a rule to which the journal otherwise adheres religiously.

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