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Recensio

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After the success of the first two volumes, P.-O. Löwdin now has edited the third volume of his series of advances in quantum chemistry containing the following papers.

R. K. Nesbet gives a survey of the present state of ab initio-calculations on small molecules in the framework of the Hartree-Fock-approximation. As in the last two years, especially in this field, an astonishing development has resulted, which gives new aspects concerning e. g. heterocycles, the paper is an example of how fast this field of research is developing. But the reviewer would suggest a more complete list of relevant papers, e. g. the method of pure gaussian functions, proposed by Preuss in 1956 is not even mentioned.

The long awaited chapter on single-center wavefunctions for molecules is written by D. Bishop. Though one has known for a long time that the one-center method is able to describe reasonably certain molecules from the viewpoint of the united atom and though one can retrace its origin nearly to the beginnings of quantum mechanics, there seems to be little progress in this field. Thus even D. Bishop discusses carefully and exclusively symmetrical polyatomic molecules where density at the light H-atoms is created by adding *d*- and *f*-functions centered at a heavy center. As no other cases are reported, one might get the impression that they are the only ones for which single center methods are appropriate; in reality this is due to the fact of using spherical harmonics as angular parts. Nevertheless, some new developments are included by giving references, without comment, in order to complete the survey of the field.

The title of the following paper by F. Harris sounds very general: Molecular Orbital Theory. Considering the paper in detail one recognizes that the author is engaged in elaborating formulae for matrix elements of spin-free and spin-dependent operators for closed- and open-shell and spin-projected cases. This chapter, very useful in practice, gives new formulae for spin-dependent operators. As the author is a specialist in matrix formalism, he can content himself with a few references. Nevertheless, it would be desirable to have in an introduction, which refers to Roothaan concerning closed-shell and to Pople and Nesbet concerning open-shell cases, in addition references to the papers of G. G. Hall and G. Berthier; e. g. in 1954 Berthier gave an important contribution to the open-shell problem.

H. Margenau and J. Stamper report on the non-additivity of intermolecular forces, which is based upon contributions of three- and many-body forces. The question of the convergence of the many-body series is raised. It is shown that in certain cases contributions of four-body forces to the energy are larger than those of three-body forces and have in any opposite sign. Jansen's model of three-body forces is subjected to a critical examination and the question concerning the stability of rare gas crystalline forms is illustrated from a new aspect. It is gratifying to find in this paper a careful and critical comment about a former similar paper of the series. This shows that the field is in a state of development and assures the series of continued interest of the readers.

The title of R. Daudel's chapter "Quantum Theory of Reactivity" is somewhat misleading, because until now quantum theory has played only a minor part in the field of reactivity which is so important for the chemist. Summarizing, the paper deals with transition state theory; quantum theory is involved primarily in calculations of delocalization energies in the Hückel- and PPP-approximation. However, as long as one excludes the statistical treatment, the explanation of temperature dependent reaction rates remains fragmentary. The topic is systematically presented.

In a brief, precise article, S. Bratoz surveys theories explaining hydrogen bonding. Starting from the classical electrostatic theories and continuing with the quantum theoretical attempts of VB, charge transfer and SCF MO CI methods, the author presents a living picture of the development in this field, interesting also outside of biochemistry. The explanation of the preservation of conjugation in coupled π-electron systems through π-orbitals at hydrogen, which seems to be proved by *ab* initio-

calculations on small systems, causes the author to indicate open questions and to suggest possible further developments.

K. Ohno emphasizes at the very beginning of his paper "Molecular Orbital Calculations of π-Electron Systems" that the content of his article is far from giving a complete picture of the present state of the theory and that mainly the non-empirical and Pariser-Parr-Pople calculational methods are to be dealt with. Nevertheless, the paper becomes rather long, not to the least because of an accumulation of elementary facts like a discussion of point groups, especially in connection with ethylene, the explicit formulae for the reduction of molecular integrals to atomic integrals, a table with Slater's rules for shielding constants etc. However, one finds interesting discussions on the calculation of W_{2p}, the explanation of the PPP method through orthogonalized atomic orbitals and remarks on σ—π-separation. The strength of the article consists in sections comparing different methods for the calculation of integrals or parameters, e.g. the choice of α- and β-values in Hückel theory. Then, in passing, the author might confuse the reader in the introduction with a definition of the molecular orbitals by the possibility of the diagonalization of the Hartree-Fock matrix. However, this would be valid only in the closed-shell case. The well-written paper is easy to read.

In his chapter on time-dependent phenomena, P.-O. Löwdin begins with a historical survey of the development of quantum mechanics emphasizing the relations between coordinate and momentum space. Against this background, he presents the method of the evolution operator which looks promising for the solution of time-dependent problems. Löwdin then proposes a reformulation of quantum mechanics on the basis of this operator by considering "constants of evolution". Reversible and irreversible processes, density matrices and perturbation theory are discussed from the viewpoint of the utility of this method. At last, considering quantum mechanics from the "integral" point of view instead of from the "differential" one, he forces the reader to reconsider the very bases of quantum mechanics.

From a practicle point of view, the reviewer would like to suggest to include the date of completion of the review articles in order to give the reader a more objective idea what to expect from a paper in the series.

On the whole, survey papers of recent developments in quantum mechanics are of great value and for this reason the series is again recommended.

K. Jug