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Quantentheorie molekularer Strukturen

Geboren 1935 in der Tschechoslowakei. Studium an der Karls-Universität Prag, 1961 C. Sc. (Ph. D.) an der Tschechoslowakischen Akademie der Wissenschaften. 1962-64 Postdoctoral Fellow, National Research Council of Canada, Ottawa. 1968 Emigration nach Kanada, seit 1975 o. Prof. für Angewandte Mathematik und Chemie an der University of Waterloo. Seit 1984 auch Adjunct Prof. an der University of Florida, Gainesville, Fla. Arbeitsgebiete: Quantentheorie, Struktur der Atome und Moleküle, methodologische Fragen der Quantenchemie, Gruppentheorie und ihre Anwendungen. Adresse: Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

My principle research interests center on *quantum theory of molecular electronic structure* and the related development and implementation of various quantum chemical methods. The main goal is to obtain the potential energy surfaces of existing and hypothetical molecular systems for both ground and excited states, the static properties at equilibrium geometries and, eventually, the dynamical properties. At the same time, we look for a novel exploitation of modern mathematical techniques, the presence of dynamical symmetries and a better understanding of the underlying mathematical structure of various physical and chemical phenomena.

We note in passing that this research is of a considerable interest in a broad spectrum of disciplines, ranging from astrophysics (structure, spectra and reactions of interstellar molecular species) to pharmacology (computational drug design). The knowledge of potential energy surfaces and of various physical and chemical properties (dipole and higher moments, harmonic and unharmonic force fields, ionization potentials and electron affinities, polarizabilities and hyperpolarizabilities, oscillator strengths, etc.) is essential for an understanding of many basic processes (e.*g.*, atmospheric pollution, chemical laser design, photosynthesis, heterogeneous catalysis, organic polymer conductors and photovoltaic devices, etc.) and, ultimately, for the development and design of various practical devices based on such phenomena and involving un-

conventional molecular systems (highly ionized or excited species, transition complexes, short-lived, highly-toxic or hypothetical species, etc.).

One of the key problems of achieving our goals is an appropriate treatment of many-electron correlation effects, as we now briefly explain. We recall that — as Dirac put it more than half a century ago — with the formulation of the Schrödinger equation, "the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed."

The basic approximation to the exact solution of the non-relativistic Schrödinger equation for atomic and molecular systems is provided by the independent particle model (IPM) within the Born-Oppenheimer approximation, which requires the solution of the Hartree-Fock (HF) equations. Nowadays, the latter equations can routinely be solved with great accuracy thanks to the availability of modern computing technology and the methodological developments following two decades after World War II. Although the HF approximation provides us with very accurate total energies (error is usually less than 0.1 %), this accuracy is not sufficient to describe most of the chemical phenomena where the relevant energy differences are very small (of the order of kcal) in comparison with the total electronic energy (10^2-10^5 eV). Consequently, the correlation energy, which corrects the inadequacies of the HF approximation, is essential for a reliable and accurate quantum mechanical description of molecular properties and phenomena, and is always included, in one way or another, in all state-of-the-art quantum chemical computations. However, in contrast to the IPM, an accurate assessment of the correlation effects is far from routine even though considerable progress has been made during the past decade. Particularly for the excited states and general open shell systems with more than 10 electrons, further work is sorely needed in order to achieve a more or less routine handling of correlation effects. In this regard, we pursue two different, yet related approaches, which show much promise and to which we made important contributions in the past, namely the configuration interaction (CI) and the coupled cluster (CC) approaches. While the latter technique is presently limited to closed-shell ground states, it has a great advantage over the universal CI method in being size extensive: an essential characteristic for applications to dissociative or associative chemical phenomena.

My goal at the Wissenschaftskolleg was to work on a multi-reference CC approach as well as on the Clifford algebra unitary group approach

(CAUGA) to CI and CC, to collaborate with Prof. Kouteckÿ's group at FU on the implementation of size-consistent approaches for the calculation of correlation energies of metal clusters, and to work on two monographs dealing with methodology of the correlation problem. The main results which were achieved in this direction are summarized below.

I. Research papers:

1. Parastatistics and the Clifford unitary group approach to the many-electron correlation problem (co-author M. D. Gould), Journal of Mathematical Physics (in press).

This paper shows that the CAUGA can be described in terms of parafermi algebra and discusses the possible applications for the development of efficient algorithms for explicit evaluation of UGA generator representatives.

2. Lie algebraic approach to many-electron correlation problem, Proceedings of the workshop on Atomic and Molecular Structure and Dynamics, IMA Series, Springer Verlag, New York (in press).

This paper reviews various UGAs to the many-electron correlation problem. Special attention is payed to recent exploitations of Green-Gould representation theory and to CAUGA.

3. Clifford algebra and unitary group formulations of the many-electron correlation problem (co-author B. Jeziorski), Theoretica Chimica Acta (submitted).

This paper clarifies the relationship between Clifford algebra matric units, the UGA generators and the higher order replacement or excitation operators, as well as between their first and second quantized realizations. The usefulness of higher order replacement operators is illustrated on the orthogonally spin-adapted CC approach. Natural connection with CAUGA is explored and new possibilities for its exploitation in large scale CI calculations are suggested.

4. Multi-reference coupled-cluster approach to many-electron correlation problem: Linear approximation for two closed-shell-type reference configurations (co-author B. Jeziorski), Journal of Chemical Physics (first draft available; final version in preparation).

An explicit form of the multi-reference CC formalism in the linear approximation was developed for the special case of a 2-dimensional model space involving only closed-shell type configurations. General problems of multi-reference CC approach, its relationship with CI formalism and problems of practical implementation are discussed.

5. Coupled-pair theories andDavidson-type corrections for quasidegenerate states: H_4 *model revisited* (co-authors P. E. S. Wormer and M. Bénard), Collection of Czechoslovak Chemical Communications (Festschrift for Prof. Zahradnrk) (to be submitted).

First draft of the account of various CI and CC results, using single- and multi-reference formalisms, for three model systems consisting of stretched hydrogen molecules

in trapezoidal, rectangular and linear configurations, has been finished. Different types of Davidson correction are also tested and evaluated.

The following three papers have been finalized by implementing referee comments:
1. Application of Lie algebraic methods to the perturbation theory of simple quantum systems (co-authors B. G. Adams and J. Cizek), Advances in Quantum Chemistry, Vol. 19 (in press).

A special camera-ready version of this paper was also prepared for the reprint and review volume on "Dynamical Groups and Spectrum Generating Algebras", edited by A.O. Barut, A. Böhm and Y. Ne'eman (World Scientific, Singapore, in press).
2. Clifford algebra unitary group approach to many-electron system partitioning (co-authors J. Q. Chen and M. J. Gao), Physical Reviews A *35,* 3197-3217 (1987).
3. Point group symmetry adaptation in Clifford algebra unitary group approach (co-authors J. Q. Chen and M.J. Gao), International Journal of Quantum Chemistry *32,* 133-147 (1987).

II. Books:

1. Group Theory of Many-Electron Systems (co-author P. E. S. Wormer), Academic Press (in preparation).

Final version of the following three chapters have been written: II. Algebras and their representation, III. Symmetric group and its group algebra, and VIII. SU(2) Wigner-Racah calculus and graphical methods of spin algebras. Work on Ch. VI is in progress and a material for a new draft of Ch. IV was prepared. Chapters I, VII and IX—XI remain to be written.
2. Diagrammatic Methods for Many-Electron Systems, Oxford University Press (in preparation).

Only Ch. I on Second quantization formalism was written; rough drafts of chapters on diagrammatic representation and the necessary material were prepared.

III. Collaboration with FU:

A joint work on the determination of size-consistent correlation energies of alkali metal clusters have been undertaken with Prof. Koutecký's group at FU (FB21, WE 3). Following a series of seminars (see below) the linear CC method for a single-reference case was implemented using the existing CI programs and calculation of correlation energies of Li and Na clusters have been carried out up to Li_{10}. Large clusters must await the implementation on the mainframe computer. The size-consistency effects were clearly identified by studying the dissociation of Li_4 and Li_b clusters into Li_e molecules along various paths of approach. The multi-reference version of an approximate linear CC approach is being currently implemented. In the meantime, the exact version of the linear CC approximation will be tested on various H_4 models at Waterloo. Furthermore, the basic theory for openshell (odd) clusters is being examined (ad

hoc use of CI based formalism was employed so far). In view of the quasi-lower-bound property of linear CC approach and the upper bound property of the variational CI approach, we hope to obtain reliable bounds for binding energies of small to medium size clusters. Collaboration will be continued in the future.

IV. Seminars, colloquia and lectures:

1. *Symmetry in the submolecular world: where mathematics, physics and chemistry meet* (Colloquium at Wissenschaftskolleg, 27.2. 1987).
2. *Many-electron correlation problem*
   - *I. Multireference coupled-cluster formalism: First steps* (26. 11. 1986 and 2. 12. 1986),
   - *II. UGA to large scale CI: Initiation and overview* (3. 12. 1986),
   - *III. Clifford algebra UGA and system partitioning* (19. 12. 1986),

   (Series of 4 Seminars in the series "Anwendung der Quantenchemie in der Theorie der Oberflächenerscheinungen and Mechanismen der Fotochemie", Free University, Berlin).
3. *Large order expansion and dynamical groups* (Joint FU and TU Mathematical Physics research seminar, 19. 1. 1987).
4. *Lie group theoretical approaches to molecular electronic structure* (University of Bonn, Theoretical Chemistry Seminar, 19. 5. 1987; University of Erlangen -Nürnberg, Theoretical Chemistry Seminar, 21. 5. 1987).
5. *Multi-reference coupled-cluster approach and perturbation theory* (University of Regensburg, Theoretical Chemistry Seminar, 22. 5. 1987).
6. *Algebraic approach to simple quantum-mechanical systems* (University of Braunschweig, Theoret. Chemistry Seminar, 19.6. 1987).
7. *Lie group theoretical aspects of the many-electron correlation problem* (3 lectures) (Fifth School on Advanced Methods of Quantum Chemistry, Nicholas Copernicus University in Torun, Bachotek, 31.5.-2.6. 1987)
8. *Lie algebraic approaches to many-electron correlation problem*

   I., II. Unitary group approach, III. CA UGA and system partitioning (Series of 3 lectures at the Workshop on Atomic and Molecular Structure and Dynamics, Institute for Mathematics and Its Application, University of Minnesota, Minneapolis, 29.6.-2.7. 1987).
9. *Davidson-type corrections for multi-reference CI approaches* (Meeting of the International Academy of Quantum Molecular Science, Menton, France, 18.-19.7. 1987).