EXPLICITLY CORRELATED WAVE FUNCTIONS IN CHEMISTRY AND PHYSICS
Theory and applications

Edited by
JACEK RYCHLEWSKI
A. Mickiewicz University and IChB PAN, Poznań, Poland

Kluwer Academic Publishers
Boston/Dordrecht/London

Contents

Dedicated to the memory of Włodzimierz Kołos

Contributing Authors

E. Bednarz N. Copernicus University, Toruń, Poland

R. Bukowski University of Delaware, Newark, DE, USA

M. Bylicki N. Copernicus University, Toruń, Poland

W. Cencek University of Delaware, Newark, DE, USA

H. Chojnacki University of Technology, Wrocław, Poland

R. Jaquet University of Siegen, Siegen, Germany

B. Jeziorski Warsaw University, Warsaw, Poland

J. Karwowski N. Copernicus University, Toruń, Poland

W. Klopper Utrecht University, Utrecht, Netherlands

J. Komasa Adam Mickiewicz University, Poznań, Poland

W. Kutzelnigg Ruhr University, Bochum, Germany

J. Noga Slovak Academy of Sciences, Bratislava, Slovakia

G. Pestka N. Copernicus University, Toruń, Poland

J. Rychlewski Adam Mickiewicz University, Poznań, Poland and Institute of Bioorganic Chemistry PAN, Poznań, Poland

K. Strasburger University of Technology, Wrocław, Poland

K. Szalewicz University of Delaware, Newark, DE, USA

Introduction

Jacek Rychlewski

Quantum chemistry has established its usefulness for theoretically oriented chemists for a long time and now it evolves quickly into a powerful tool for experimentalists studying structure, reactivity, dynamics, and biological activity of chemical systems. The amazing computer revolution which still seems to gain pace makes it possible not only to shift our interest towards more and more complex systems, but also to employ more computationally demanding, and hence more adequate and accurate, theoretical models. While only some 20 years ago simple semiempirical approaches dominated the research of medium-size and large organic molecules, now large scale ab-initio calculations and density-functional methods are slowly becoming standards even in theoretical bioorganic chemistry. Ultimately, we can be faced with the situation which already occurs for few-electron molecules, namely that it is the intrinsic accuracy of available methods rather than computation time that limits the quality of the results. Indeed, all commonly used methods dealing with the ubiquitous electronic correlation problem are extremely slowly convergent. Algorithms treating algebraic expansions counting currently in billions of terms are pretty spectacular, but because of the slow l^{-3} convergence of the error, these algorithms are not capable of reaching very high levels of accuracy even for small systems. For example, a one-electron basis set with a maximum angular momentum $l_{\max} \cong 30$ should be employed in the CI procedure to calculate the ground state energy of helium atom with a prescribed accuracy of 1 microhartree or $l_{\max} \cong 300$ to achieve nanohartree accuracy, the latter basis set having dozens of millions of orbitals, which is completely unrealistic. Thus, it is unlikely that very accurate results can be obtained using the CI like methods. Hence, we need fast computers as well as a better theory. Such a theory has actually existed since the early days of quantum mechanics. The idea is to use the wave functions that depend explicitly on the interelectronic distance, r_{12}. Explicit inclusion of the r_{12} term into the wave function leads to a much faster convergence of the CI expansion. This is due to the fact that the correlation factor favours electrons being far apart. The ability of these *explicitly correlated* (EC) wave functions to give accurate energies for atomic and molecular systems has been demonstrated first in 1929 by Hylleraas for the helium atom and in 1933 by James and Coolidge for the hydrogen molecule. In 1960's the latter function has been generalized by Kołos and Wolniewicz in order to describe properly the process of dissociation. These wave functions improve dramatically the accuracy of the energy of the above mentioned systems but bring about two problems. First, the resulting algorithms are much more cumbersome and difficult to implement. Secondly, they are incompatible with such deeply rooted concepts as "orbital" and "electronic configuration" since they avoid the one-electron approximation from the very beginning. Great successes of the explicitly correlated calculations for the helium atom and the hydrogen molecule are beyond question. However, in the mind of an average chemist (and even of a large number of quantum chemists) the EC wave functions are limited to these two systems and represent an interesting, but rather exotic case with mainly historical importance. However, for the last two decades the theory and application of these functions have evolved and rapidly grown. The original idea of the explicit correlation was based on the wave functions constructed from Slater type functions, power series expansion and linear correlation term. Later Gaussian functions combined with the linear correlation factor have been considered. In 1960 a new type of EC wave function has been proposed by Boys and Singer. This function is constructed from one-electron Gaussian function and exponential correlation factor of the form $\exp(-\gamma r_{12}^2)$. These types of wave functions have been implemented into standard quantum chemistry schemes such as configuration interaction and coupled cluster, and thanks to a very efficient method of avoiding many-electron integrals, applied to quite large systems. The direct variational ansatz has been successfully extended from 2-electron to 3- and 4-electron atoms and molecules. In all these cases the EC functions have proven capable of yielding significantly (often dramatically) better results than traditional approaches.

On the other hand, it has to be said that this extremely promising field is investigated by merely a handful of research groups worldwide and has not yet received a wider attention it certainly deserves. The prime example of this is an absence of a book dealing entirely with the EC functions.

There are a number of reasons for this:

- As already mentioned, the theory is complicated and its efficient implementation is difficult.
- Computational resources are still not sufficient to allow for computations for large molecules.
- There is no black-box EC program which could be used by a non-specialist.

The aim of our project is to fill up the above mentioned gap and present a book devoted entirely to the theory and applications of EC wave functions. This book was born as a result of cooperation of the leading European groups working on this subject within the COST Chemistry Actions D9 and D26.

The first part of the book is dedicated to the theory of EC wave functions. It starts with the Chapter by Werner Kutzelnigg on the general theory of electron correlation. In this Chapter various aspects of this theory are reviewed, from a traditional description of electron correlation to modern approaches taking into account this effect. The EC wave functions are applied to solve the nonrelativistic electronic Schrödinger equation and therefore in the next three chapters, which deal with the fundamental theory of EC wave functions, the Born-Oppenheimer (BO) approximation is assumed. Chapter 2 covers the theory of different types of EC wave function within the variational approach. Among these function the Hylleraas type functions, James-Coolidge and Kołos-Wolniewicz functions, as well as Hylleraas-CI and Hylleraas-CIVB wave functions are considered. All the above mentioned functions contain as a correlation term the linear r_{12} or its powers, r_{12}^{v}. Another very promising form of EC function, namely exponentially correlated Gaussian functions (ECG) containing $\exp(-\gamma r_{12}^2)$ expression as the correlation term, have also been considered. The BO energies for 2-, 3- and 4-electron atomic and molecular systems computed using the above mentioned wave functions are reviewed and their accuracy is discussed. Chapter 3 is devoted to the R12 theory which has been developed in the late 1980's and early 1990's by Kutzelnigg and his co-workers. In this Chapter an overview of the R12 theory is presented both at the MP2 (MP2-R12) and coupled-cluster (CCSD-R12 and CCSD(T)-R12) levels. These methods have been applied to such large systems as the ferrocene molecule. Next Chapter (Ch.4) gives a review of the theory of the correlated Gaussian geminals within the framework of the CC and MBPT theories. The application of this method for 2- and 4-electron atoms and molecules and for larger systems such as Ne and H_2O is described.

The next four chapters concern the effects that go beyond the BO approximation. Chapter 5 describes methods that can be used to calculate adiabatic corrections using EC functions (KW and ECG functions). The importance of these corrections has been addressed since 1960's. It is due to the fact that the contribution of the adiabatic corrections to the dissociation energy is considerably larger than experimental error. The calculations of these corrections and their importance for the dissociation energy of the ground and excited states of H_2 and some larger molecules are reviewed. The state of art of the relation between theory and experiment is given.

Chapter 6 gives an overview of the direct perturbation theory of relativistic effects. The next Chapter (Ch.7) describes Hylleraas CI approach to the Dirac-Coulomb equation. In the last Chapter (Ch.8) of this part a discussion is given on the application of the ECG wave function in the calculations of lowest-order relativistic corrections to the electronic energy and static polarizability within the frameworks of the Pauli approximation and direct perturbation theory.

The second part of the book is devoted to the selected applications of the EC wave functions. Chapter 9 is concerned with the applications of the KW and ECG wave functions to determine very accurately atomic and molecular properties of 2- and 4-electron systems. The next Chapter (Ch.10) is devoted to the application of EC wave function in calculations of positronic systems. These systems are interesting as for some of them the BO approximation cannot be applied due to the equal masses of all N particles forming them. Thus, the appropriate nonrelativistic Schrödinger equation has to be solved as an N-body problem.

Chapter 11 presents another very interesting field of applications of EC wave function, namely atomic resonance states. Due to the strong correlation effects for such states, which are multiple-excited, the use of EC wave functions is effective and desired.

In the last Chapter (Ch.12) an overview of the spectroscopy and dynamics of the simplest polyatomic molecule, H_3^+, is presented. Special attention is given to the accuracy of the potential energy surface and how this accuracy depends on the quality of the wave functions used. In this analysis including adiabatic, nonadiabatic and relativistic effects, CISD-R12 and ECG wave functions are used.

We hope that this book will attract readers attention towards the methods based on EC wave functions which are able to reproduce experimental data with accuracy not reachable by other methods. We express our hope that applying a new more advanced theory and more advanced computer's technology we shall move the area of applications of EC wave functions towards more complex atomic and molecular systems.

I would like to thank everybody who has contributed to our project, especially the members of the working groups WGD9/0013/98 and WGD26/0012/02, and COST Chemistry D9 and D26 Actions for encouragement to form the team working on the explicitly correlated wave functions problem and for financial support of our cooperation. I would like to acknowledge also a support from Polish State Committee for Scientific Research within the SPUB-M scheme and T09A17118 grant.

† † †

Just before this volume was completed, Professor Rychlewski died unexpectedly at the age of only 55, leaving all of us deeply shocked and in great grief. He was working on the book till the very last hours of his life, dedicating to this task his admirable energy and enthusiasm. We pay him our tribute by finishing this book and we can only regret that he couldn't live to see his idea taking the final form.

The contributors