

Editorial

Wilfried Meyer

This issue of *Theoretical Chemistry Accounts* is dedicated to the pioneering contributions of Professor Wilfried Meyer to electronic structure theory. His life is a mirror of the eventful history of Europe in the second half of the twentieth century. The Berlin Wall had just been erected as he completed his physics studies at the University of Leipzig, in the former German Democratic Republic (East Germany), in 1961. Surprised by the events, he was luckily able to escape to the West where he began his graduate studies in Munich in philosophy and physics, the latter with Prof. F. Bopp. This study was interrupted by a year-long involuntary stay in East Germany, when he went to see his family. He was lucky again, and was released to the West where he joined the newly established quantum chemistry group at the Max Planck Institute for Physics and Astrophysics, headed by Dr. H. Preuss.

These were exciting times in electronic structure theory. Powerful computers were just becoming accessible to nonmilitary research, and a plethora of techniques was waiting to be invented and tried. Meyer approached the problem with his characteristic intensity and, within a year or so, created a program system which was unique for the time: it had open and closed shell SCF, the former both restricted and unrestricted, approximate extended Hartree-Fock, CI with optimized correlation orbitals, various analysis programs, and a program for determining vibrational energy levels of anharmonic potential curves. Indeed, the seed of much of his seminal work was already there. For some reason he had to use the old Zuse G3 electron tube computer, which could be programmed only in a primitive assembler language. Thus, only his ideas could be used in later work, not the programs. His doctoral dissertation deals with the first successful UHF-based calculation of the Fermi contact hyperfine splittings for first-row atoms and the radicals NH_2 and CH_3 at a uniform level. In addition, bending potential curves and spectroscopic properties of different electronic states of BH_2 , CH_2 , and NH_2 were calculated and some experimental misassignments could be corrected.

He also took a keen interest in the then (1968–1969) new ab initio gradient techniques, and, with his extensive physics background, provided much support for me. This was the beginning of our life-long friendship. I recall vividly the excitement felt when the first ab initio gradient program, coded in ALGOL for the IBM 7090 but attached to Meyer's machine-code SCF program, produced correct results on 17 August, 1968. (The excitement turned into depression when, 2 days later, Soviet tanks rolled into Prague, setting back our hopes for the end of the cold war by 20 years.) Within a year, we had reprogrammed both parts of the code in FORTRAN. This program, which we called MOLPRO, used the Gaussian lobe basis functions introduced by Preuss, and was the forerunner of several successful quantum chemistry programs, most notably a set of MCSCF and CI programs, which led to the current MOLPRO of H.-J. Werner and P. Knowles, and my TEXAS, although little actual code remains in the current programs. With the then new gradient capability, we were in a position to be able to calculate full harmonic force fields of polyatomic molecules. In a series of papers, we have shown that the ab initio SCF method can provide reasonably accurate force constants and vibrational spectra, and that its systematic errors can be corrected by empirical scaling. The work on accurate theoretical potential surfaces was taken up later by several of Meyer's students and coworkers.

Meyer spent a fruitful year at IBM's San Jose Research Center in 1971, working in the research group headed by E. Clementi. Between 1969 and 1974 he worked at the University of Stuttgart in the group of Prof. H. Preuss. His postdoctoral dissertation (1973) dealt with CI using nonorthogonal orbitals, and is the basis of his classic series of papers entitled "PNO-CI and CEPA studies of electron correlation effects" (1973–1978). Besides having the most accurate CI wave functions at that time, these papers also introduced the first practical approximate coupled-cluster technique, the coupled electron pair approximation, and focused the attention of chemists on the fatal shortcoming of variational CI with fixed excitation level, a problem later

named the size consistency error by J. A. Pople, and size extensivity error by R.J. Bartlett.

In 1973, Meyer was appointed Professor at the University of Mainz. Several important scientific projects, resulting in major advances, started here. P. Rosmus (now at the Université de Marne-la-Vallée, France) joined his group as a postdoctoral associate and achieved notable success with the accurate calculation of the spectroscopic constants of diatomic hydrides. P. Botschwina (now at the University of Göttingen) came as a graduate student from Stuttgart and began applying the new accurate correlation and gradient methods for reactive surfaces and for accurate theoretical spectroscopy of small polyatomic molecules. This was the beginning of some very successful work, highly appreciated by experimentalists, which is still continuing. H.-J. Werner (now at the University of Stuttgart) joined Meyer's group as an undergraduate and promptly achieved notable success in calculating accurate electric polarizabilities. A little later C.E. Dykstra (now at Purdue in Indianapolis), then a graduate student at Berkeley with H.F. Schaefer, came and started programming the theory of self-consistent electron pairs (SCEP). This compact matrix formulation of the single-reference correlation problem allows the use of nonorthogonal external orbitals, and is computationally efficient because of the use of matrix arithmetic. This was the first direct CISD method which eliminated all complicated coupling coefficients. SCEP became important as a basis of local correlation methods and, most importantly, of the matrix-formulated multiconfigurational extensions. In a 1977 review, Meyer suggested "internal contraction" for the efficient calculation of highly accurate wavefunctions. This method reduces the immense number of configurations needed to account for dynamical electron correlation in the presence of a nondynamical one, e.g., for reactive potential surfaces, to a manageable set. He also began a collaboration with E. Reinsch at nearby Frankfurt University. Meyer was always more interested in new techniques than in chemical applications. This fact plus the relative scarcity of computer resources in Europe at that time were responsible for the fact that the new techniques, e.g., PNO-CI and PNO-CEPA, although the best at that time, were less widely applied than they deserved to be.

In 1976, Meyer was appointed Professor of Physical Chemistry at the University of Kaiserslautern, in the beautiful Palatinate region of Germany, a position he has held ever since, interrupted only by a sabbatical semester in 1984 in the United States and Australia, a Visiting Professorship in the Physics Department of The University of Texas at Austin in 1988, and a Visiting Fellowship at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado in 1991. A productive working relationship started between Meyer, Werner, who, after receiving a doctoral degree in a different field, became a postdoctoral associate in Frankfurt, and Reinsch. In 1979, Werner and Meyer developed a second-order MCSCF program with fast and stable convergence. A little later Werner and Reinsch, using the idea put

forward by Meyer a few years earlier, developed the first internally contracted multireference CI program. This program was notable for its generality and efficiency, and the inclusion of the difficult but important semi-internal configurations. The work was carried on by Werner and Knowles in Cambridge, leading to the current MOLPRO. Although greatly extended over the years, the most essential and unique parts of this program system are still based on the ideas first proposed by Meyer. MOLPRO is probably the most efficient and complete program system for highly accurate quantum chemical calculations and is widely used around the world.

In Kaiserslautern, Meyer's focus shifted toward application of accurate electronic structure theory to important problems in atomic and molecular physics, although characteristically most of these required the development of new methods. Several topics stand out among these lines of investigation:

1. Potential surfaces of small systems containing alkali atoms. The experimental investigations have been conducted in the laboratories of I. V. Hertel, W. Demtröder, and K. Bergmann in the Physics Department at Kaiserslautern, and the theoretical investigations by Meyer and his associates, in particular W. Müller and I. Schmidt-Mink, with important contributions from R. Schinke (now at Göttingen) to the scattering aspects. These are rich systems that exhibit a number of interesting features, such as the first clear experimental evidence for the Berry phase which was found recently. The high accuracy of these calculations was achieved through the development of an efficient treatment of core-valence electron correlation by means of core polarization potentials.
2. Very accurate calculations, with M. Movre, on systems containing excited He atoms, experimentally investigated by H. Hotop and coworkers, also in the Physics Department at Kaiserslautern.
3. Collision-induced transitions. This led to a very productive working relationship with L. Frommhold (University of Texas at Austin). The results are important, among other things, for the understanding of planetary atmospheres.
4. Numerical calculation of rovibrational energy levels, in collaboration with S. Carter, another long-standing interest of Meyer.
5. The calculation of weak intermolecular interactions. Owing to its close connections both with accurate correlation calculations and with (dynamic) polarizabilities, this has been of interest to Meyer for a long time. Recent results obtained in collaboration with D. Spelsberg are particularly promising.

The main characteristics of Meyer's work are his fresh and intuitive approach to complex mathematical problems and the search for definitive answers. His work has greatly enriched quantum chemistry and serves as an inspiration to us all.

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