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Editorial

Throughout his entire scientific career – from the very beginning in the 1960s till his retirement in 1998 – Werner Kutzelnigg was one of the most ingenious and broadly interested quantum chemists, not only in Germany but also on the international scene. He flooded the whole field of quantum chemistry with numerous new concepts and ideas, he developed new numerical schemes and approximate methods for accurate calculations of the electronic structure of atoms and molecules, and he found new ways to analyse the numerical results and to characterise the 'chemical bond'. All this gained him a very high international reputation. His main contributions to quantum chemistry can be briefly summarised as follows: the direct determination of pair natural orbitals (PNOs) and their use in configuration interaction (CI) and coupled cluster (CC) calculations; the IGLO method ('individual gauge for localised orbitals') for reliable calculations of NMR chemical shifts; quantum chemistry in Fock Space; the incorporation of interelectronic coordinates ('r12-method') into electronic wavefunctions; direct perturbation theory (DPT) to treat relativistic effects. All this has been described several times, for instance in the editorials to previous special issues in his honour, and it is not necessary to repeat it here.

But also after his retirement in 1998 – the German law forced him to retire at the age of 65 – Kutzelnigg remained very active scientifically. Of course, there were quite some changes in the way he could continue working. He had to replace his luxurious office of a German full professor with a much smaller room for a professor emeritus. He was no longer heading a large group, but was working mostly by himself and with some distinguished guests, like Debashis Mukherjee, Wenjian Liu, Josef Noga and Ralph Jaquet. He had no teaching duties any more, but he was and still is attending the weekly Theoretical Chemistry Colloquia in Bochum. And, maybe most importantly, he is now free from administration and time-consuming committee meetings, so he has probably more time for science than before his retirement.

Apart from these more technical changes there also some changes in his scientific interests and in the way he is working. He is no more performing large-scale calculations or plain applications to challenging chemical problems, but is more interested – even more than ever before – in the fundamental concepts and the mathematical background of the molecular quantum science. That means that he is more and more focusing on formal developments and on analytical rather than numerical methods. His aim is always to

better understand what he is doing and to open up new ways for more accurate approximations and advanced numerical methods.

At the same time, Kutzelnigg is also turning a little – owing to his long experience in the whole field – to historical remarks and to critical discussions of the current trends in quantum chemistry. He has written several review-type papers and given many invited talks, most of which deal with the electron correlation problem and contain the characterisation of different post-Hartree–Fock methods (CI, CEPA, CC, MP perturbation theory, and to some extent also DFT), possible future extensions of them and the relationships between them. We only mention his perspective view on 'electron correlation at the dawn of the 21st century', his discussion of the 'difficult partnership between density functional theory and *ab initio* quantum chemistry', and the paper on the impact that many-body perturbation theory (MBPT) has had on chemistry. The papers on the half-forgotten Hückel theory and on DFT in terms of a Legendre transformation belong to this type of papers .

In the following we will briefly discuss the main fields of Kutzelnigg's scientific interest after his retirement.

Of course, a person who has dedicated almost his entire scientific work to the problem of electron correlation cannot easily abandon this field. Today, CCSD(T) is established as the 'gold standard' of quantum chemistry and many colleagues are convinced that they can solve all chemically relevant problems with this approach (maybe except for a few odd multi-reference cases) and the only challenge is to extend the method to larger systems and make it competitive with DFT. Is this really the end of the story? Kutzelnigg is trying to go beyond this limit in several ways. The most promising of them seems to be the 'cumulant expansion of the reduced density matrices' that he and D. Mukherjee developed over the past 15 years. The first steps were rather formal, but eventually a set of working equations and different reasonable ways to approximately overcome the 'N-representability' problem emerged. Recently, these approaches were implemented as 'density cumulant functional theory' (DCFT) in a numerical electronic structure code by the group of H.F. Schaefer, with quite nice and promising results. Another question that kept Kutzelnigg and Mukherjee busy is that of contracted Schrödinger equations. In conventional CI and CC expansions the electronic wavefunctions contain many more parameters (amplitudes) than the Hamiltonian itself. Methods aiming at a minimal

parametrisation have been proposed by several authors, but they lead to highly non-linear equations for these amplitudes. In a series of rather formal papers Mukherjee and Kutzelnigg tackled this problem using concepts like irreducible Brillouin conditions, Wick's theorem and generalised normal ordering. It seems still too early to decide whether these ideas will lead to new competitive numerical methods.

Kutzelnigg's second central field of interest is the treatment of relativistic effects. The first problem one encounters in relativistic quantum chemistry is that the one-electron Dirac operator is not bound from below, therefore one easily ends up in a 'variational collapse' when applying blindly conventional basis set expansions. Kutzelnigg and Liu solved this problem by introducing 'kinetically balanced' Gaussian basis sets and transforming the operators in the Dirac equation from the very beginning into finite matrices constructed by means of such basis sets. Using this approach they successfully formulated a quasirelativistic theory by incorporating the effects of the small component of the Dirac spinor into the equations for the large component. But the majority of their work is still devoted to the direct perturbation theory (DPT), which is the 'natural' perturbation expansion of relativistic effects in terms of c^2, c being the velocity of light. The equations for the second-order terms are quite simple, but they become more and more complicated for higher-order corrections and in particular whenever not only the energy but also other properties are to be calculated. Kutzelnigg and Liu developed the formal theory for properties like NMR and EPR parameters or diamagnetism, and numerical codes partly based on these ideas have been implemented and are currently used by younger colleagues for several applications.

There are also some smaller research areas, not so closely connected to the two major subjects. One of them addresses the question, which masses are vibrating and rotating in molecules. R. Jaquet is calculating the rovibrational spectra of H_3^+, starting from very accurate potential energy surfaces. If one is trying to reach an accuracy of 0.1 to 0.5 cm^{-1} – such an accuracy is indeed necessary for a unique assignment of the measured spectra – one has of course to include adiabatic and non-adiabatic corrections to the Born–Oppenheimer surface, but there is also the question whether the reduced masses for vibrations and rotations should be derived from the nuclear or the atomic masses of the constituent atoms. Kutzelnigg treated this problem analytically for H_2^+ by analysing a full nine-dimensional wavefunction (for two nuclei and one electron) in the LCAO approximation and found that the masses to be used are somewhere between pure nuclear and full atomic masses, and, even more complicated, they are different for vibrations and rotations and depend also on the internuclear distance. Later on this concept was extended to more sophisticated wavefunctions and larger systems and now the correct reduced masses are evaluated on a pure numerical basis.

More recently, Kutzelnigg came back to an old topic analysing in detail the convergence behaviour of the expansion of atomic or molecular orbitals in Gaussian basis sets. Again, he is not pursuing the conventional way of performing numerical calculations with larger and larger basis sets containing carefully optimised parameters, but he is analysing analytically how the parameters of 'even-tempered' Gaussian basis sets depend on the expansion length and how the errors – of the energy and the wavefunction – behave asymptotically for large basis sets.

This brief overview shows that Kutzelnigg did not cease to work during the past 15 years and continued to provide both critical discussions and stimulating new ideas to the community of quantum chemists. The papers collected in this special issue of *Molecular Physics* and the talks given at the scientific symposium in his honour, '40 Years of Concepts in Theoretical Chemistry from the Bochum Perspective' scheduled for 24 October 2013 in Bochum, show that many of these ideas are being pursued by the colleagues from the younger generations.

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