Chemical Physics 356 (2009) vii–ix

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Editorial

Electron correlation, molecular properties and relativity – A tribute to Werner Kutzelnigg

The contributions to this special issue of *Chemical Physics* report on new developments in the quantum-chemical calculation of electron correlation, relativistic effects and/or molecular properties. The 75th birthday of Professor Werner Kutzelnigg, which was celebrated a few months ago, triggered the idea to dedicate a special issue of *Chemical Physics* to these topics. The idea has been made real by the guest editors of this special issue together with, of course, the contributors. To the three research fields just mentioned, Werner Kutzelnigg has made important contributions throughout his scientific career, which becomes obvious when we go through the list of his 20 most-cited papers. We feel tempted to do so although Werner Kutzelnigg himself has expressed a rather critical attitude toward measuring scientific output with bibliometric tools [1].

When looking at these 20 papers [2–21] (in decreasing order by the number of citations, as of the end of 2008), we see several contributions from the 1970s to the electron correlation problem [6,8,11,14,17,21] based on a pair (or pseudo) natural orbital (PNO) expansion of the wave function, which allows for rather economical configuration-interaction (CI) calculations as well as for size-consistent variants thereof such as the various CEPA (coupled electron pair approximation) models. PNOs can be viewed as an optimized virtual orbital pair space for a fast convergence (w.r.t. the size of a truncated virtual space) of a CI calculation. These methods allowed, at that time, to recover 80–90% of the correlation energy with very compact CI wave functions, which really boosted the accuracy. Work along the same lines was done by Meyer [22] and the two groups, which were geographically very close (Kutzelnigg/Ahlrichs in Karlsruhe, Meyer in Mainz and Kaiserslautern) were competing for some time for the most accurate calculations. These methods have been extensively used for about two decades, mostly by German groups, but did not become “mainstream” quantum chemistry for reasons that are not easy to understand. Of course, the PNO-CI correlation energy is always a little smaller than a CI calculation which uses the full virtual space, and it also depends on the choice and the truncation of the PNOs. This introduces only small errors but can introduce jumps in potential energy surfaces. CEPA (which is akin to coupled cluster theory from today’s perspective) was later replaced by coupled cluster methods, but initially met some reservation because it is not variational and can give more than 100% of the correlation energy (as coupled cluster does). Since the PNOs are optimized individually for each pair of occupied orbitals, the CI basis becomes non-orthogonal. All these “drawbacks” (as it was considered in the 1970s) are also there in modern methods that make the correlation problem tractable by using localized orbitals, so one could even state that the “German” correlation methods from the 1970s faced acceptance problems because they were ahead of the time.

The most fundamental problem in electron correlation, namely the correlation cusp and the slow convergence of an expansion of the wave function in orbital products, was analyzed [10] and a practical solution (“r_{12}” methods) was worked out and combined with standard electron correlation approaches such as Møller–Plesset perturbation theory and coupled cluster methods [5,7,16,18]. The paper [5] actually marks the birth of the “r_{12}” methods. It was known that the convergence of the partial-wave expansion was extremely slow, even for a two-electron atom. If one truncates the one-electron basis at some angular quantum number ℓ, then the error is of the order ℓ^{-3}. However, this slow convergence can be much improved by using basis functions that explicitly depend on the interelectronic distance r_{12}. Although this insight was certainly not new at the time – since r_{12}-dependent wave functions had been used since many years – the main message of Ref. [5] was that one can avoid “difficult” integrals even in the multi-electron case and get very good results nevertheless. The key idea was to insert a completeness relation (resolution of the identity, RI) into the “difficult” integrals such as those over the operator products $r_{12}r_{13}^{-1}$, $r_{12}r_{23}^{-1}r_{34}$ and $r_{12}r_{23}^{-1}r_{13}$. In this spirit, first results obtained at the level of second-order Møller–Plesset perturbation theory were published in 1987 [16]. The general theory for configuration-interaction-type approaches was published in Ref. [7] and for coupled cluster-type expansions in Ref. [18].

The “r_{12}” methods have attracted renewed interest since Klopper and Samson [23] introduced an auxiliary basis for Kutzelnigg’s RI approximation, and even more so since Ten-No suggested to use a Slater-type geminal (STG) of the form $\exp(-\gamma r_{12})$ in place of the linear r_{12} term [24]. Today, a number of research groups are developing various variants of coupled cluster theory with STGs [25–34], and in view of these recent works, we expect that Kutzelnigg’s “r_{12}” methods will become even more important and more widely used in the future.

Werner Kutzelnigg’s most important contribution to the calculation of molecular properties is without any doubt the IGLO (individual gauge for localized orbitals) method for the calculation of magnetic shieldings and magnetic susceptibilites. The heart of the problem is that the electromagnetic potentials are not uniquely defined, but there is a freedom to choose the gauge. While this does not affect any observable quantities, it *does* change the wave

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doi:10.1016/j.chemphys.2009.01.011

function if magnetic fields are involved. For an unsuitable gauge, it may be very difficult to accurately represent the wave function with a given basis set. It now turns out that *any* choice of the gauge origin of a homogenous magnetic field is unsuitable in this respect, if the spatial extent of the molecule is large, so one has to implement some sort of distributed gauge origins. The work on IGLO [3,4,12,13] began around 1980 and was at that time a major breakthrough, as it introduced distributed gauge origins in a very economical way, that is, without the need to calculate any non-standard two-electron integrals. IGLO has meanwhile by and large been superseded by GIAO approaches (gauge-including atomic orbitals). These two methods are actually very similar [35], IGLO introduces distributed gauge origins for localized molecular orbitals while GIAO does so for the atom-centered basis functions. The GIAO approach is much older than IGLO. It goes back to London [36] and was first used in a coupled Hartree–Fock scheme by Ditchfield [37,38]. At that time, the limiting factor in Hartree–Fock calculations was the calculation and the processing of the two-electron integrals. Since the GIAO method involves additional (new types of) two-electron integrals, this method was computationally not very efficient and IGLO, not needing those integrals, could overtake. Moreover, the interpretation of magnetic properties in terms of localized orbitals (although possible both with GIAO and IGLO) comes in more naturally with IGLO, and this added probably much to the popularity the IGLO method quickly gained. IGLO was not only used with the Hartree–Fock method, but also extended to multireference Hartree–Fock [39,40], and it also found much use in combination with density functional theory [41–43]. One must note that there are some disadvantages when using IGLO: for highly symmetrical molecules, the localized orbitals often break the symmetry and the magnetic shielding of symmetry-equivalent nuclei is not necessarily the same. IGLO with MCSCF suffers from the fact the orbital localization is only possible for certain types of MCSCF wave functions (CASSCF functions, often using a full-valence CAS), which makes this approach less flexible than MCSCF-GIAO which is meanwhile also available [44]. In the 1990s, new GIAO implementations could profit from modern techniques to evaluate two-electron integrals which had meanwhile been developed. Probably the first such implementation came from Pulay [45], others quickly followed. At the same time, a much more efficient implementation of IGLO based on integral-direct techniques (and other improvements) was presented [46], but IGLO could no longer outperform GIAO in terms of computational efficiency.

Kutzelnigg's contributions to relativistic quantum chemistry come from different periods of his career. An early contribution was an investigation of the behavior of the Dirac operator in an algebraic approximation [9]. This work addresses the problem of *variational collapse* which plagued relativistic calculations at that time. This variational collapse can largely be eliminated by the famous *kinetic-balance condition*, a term coined by Stanton and Havriliak [47] at about the same time. But not only the kinetic-balance condition is written down explicitly in Kutzelnigg's paper, also the so-called *modified Dirac equation*, popularized much later by Dyall [48], can be found here. Two papers of Kutzelnigg's "top twenty" started his efforts in the area of the *direct perturbation theory* (DPT) of relativistic effects. Although the presentation is quite different, the results are very similar to those obtained by Rutkowski three years earlier [49]. The most recent work on relativistic quantum chemistry is concerned with the so-called two-component Hamiltonians and how to reach good accuracy with them. Although these papers are not (yet) in Kutzelnigg's "top twenty", they probably will steadily climb the rungs. The background here is that the energy gap between the positive- and negative-energy eigenstates of the Dirac operator is so large compared to "chemical" energies that for "chemical" applications, a description with a fixed number of particles is sufficient and one does not need to go to field theoretical approaches. In other words, pair creation and annihilation does not happen in chemistry. Taking this for granted, the negative-energy states are of no concern in many cases such that one simply does not want to have them in the calculation. This is the realm of the so-called two-component quasi-relativistic Hamiltonians, which Kutzelnigg has given the nice name Hamiltonians "for electrons only" [50] in the title of a paper which reviews the field as well as bringing new ideas. It remains to be seen whether the development of two-component Hamiltonians has come to an end, since within a finite basis set representation, it is not very difficult to find the exact (finite-dimensional) two-component Hamiltonian. This has recently been stressed by Kutzelnigg [51–54] but has discussed and/or used by other groups as well [48,55–57]. The negative-energy states are of course still there, and they raise their head, for example, in the calculation of second-order properties. While they make a small contribution for electric properties because of the large energy gap, they contribute substantially to magnetic second-order properties such as magnetic susceptibilities and magnetic shieldings. Kutzelnigg suggested a reformulation of the problem that drastically reduces the second-order contribution of the negative-energy states [58], a highly influential paper that lead to new attempts at relativistic magnetic shielding in several groups.

Several of the very important ideas of Werner Kutzelnigg did not elicit the attention they deserved, but are well worth mentioning. In the many-body approaches to electron correlation for quasi-degenerate systems, it was shown by Mukherjee [59] that one can use a 'valence universal' wave operator to generate eigenstates of the Fock space many-electronic Hamiltonian with different number of 'valence' (or active) electrons simultaneously. A related development was also suggested by Lindgren [60]. Reitz and Kutzelnigg [61] used a common unitary many-body transformation of the Hamiltonian in Fock space to generate direct methods of studying ionization potentials. All these formulations used wave functions in different sectors of various n-valence Hilbert spaces, and served as the fore-runners to the elegant, compact, insightful and unifying concept of 'Quantum chemistry in Fock space' [62–64]. Kutzelnigg emphasized that various quasi-degenerate valence sectors of the Fock space Hamiltonian H can be simultaneously treated in effective-Hamiltonian formalism if H is brought to block-diagonal (or lower block-diagonal) form by a unitary/similarity transformation defined also in Fock space at the operator level. The concept of valence universality of the wave operator [59] assumes a natural significance in this approach, and his concise and comprehensive classification of the various components of a Fock space operator [62–64] facilitated the analysis of size-extensivity of the associated formalisms tremendously.

Maintenance of size-extensivity for a many-body-formalism using incomplete model spaces (IMS) was a notorious problem, since it was believed that any effective-Hamiltonian based approach will lead to size-inextensive energies when the effective-Hamiltonian is diagonalized in an IMS. Mukherjee [65] showed that one can restore size-extensivity by abandoning the customary intermediate normalization. Once this was realized, Kutzelnigg with his collaborators [66,67] rapidly came up with a very comprehensive book-keeping procedure within the framework of "quantum chemistry in Fock space" which gave a thorough survey of the problems involved. Another important contribution of Kutzelnigg is the analysis of the importance of density cumulants in generating theories of electron correlation via the density equation of Nakatsuji [68,69] (also known as the contracted Schrödinger equation) and the irreducible Brillouin conditions [70–73].

No appreciation of the corpus of work by Werner Kutzelnigg can be complete without a mention of his very influential pedagogical papers which are at once very profound and original, yet very accessible to a wider audience with varied theoretical background. Two such papers [2,15] are devoted to the analysis of the chemical bond based on quantum-chemical calculations. While this topic does not fall within the scope of the present special issue, it is noteworthy that Ref. [2] is actually Kutzelnigg's most-cited paper. His analysis of the physical origin of the chemical bond [74], critiques on the famous Royal Society paper of Dirac [75] and the works of Hückel [76] are gems in their clarity and incisiveness, and places Kutzelnigg as also a master in elucidating chemical concepts which are difficult to quantify. His book reviews [77–79] are characterized by great scholarship, a deep sense of historicity and the genuine admiration of his distinguished peers.

Many of us, the guest editors included of course, must have felt over our long associations with Werner Kutzelnigg that he is a natural leader of the quantum chemistry community because of many sterling qualities: deep insight, high originality, effortless mastery in absorbing new concepts and morphing them to understand newer vistas, encyclopedic knowledge of various aspects of culture, science being just one of them, and not the least of all, his kind and caring persona revealed to all those who scientifically and socially interacted with him. Beneath his apparent formal exterior resides a very compassionate soul of a unique nature. It has been a privilege and a pleasure to have known him, and this special issue is a mark of tribute to his many lasting and important contributions to quantum chemistry on the occasion of his reaching 75. For this patriarch, the 'autumn' is nowhere in horizon; he is forever in his 'spring' and we are sure to see him thus in the years ahead.

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