Theor Chem Acc (2012) 131:1086
DOI 10.1007/s00214-011-1086-6

REGULAR ARTICLE

Theoretical chemistry: current applications to photochemistry and thermochemistry

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Received: 7 August 2011 / Accepted: 11 August 2011 / Published online: 11 January 2012

Abstract A historical perspective is given contrasting challenges and advances in theoretical chemistry at the time the first issue of Theoretical Chemistry Accounts appeared in 1962 and the progress achieved since then as expressed in current state-of-the-art applications in photochemistry and thermochemistry.

Keywords Quantum chemistry and photochemistry · Quantum chemistry and thermochemistry · Applied quantum chemistry: future perspectives

The fertile change in paradigm brought forth by the quantum mechanical study of atoms and molecules provided many of the new tools and concepts, and it also presented a continued challenge to scientists to express the chemical concepts in the more mathematical language being developed. The early application of quantum mechanics to the ground state of He by Hylleraas [1] and to the ground state of H_2 by James and Coolidge, [2] although bringing some excitement about the accuracy one could obtain for these systems, has led to some frustration, since it was also soon realized that the explicit incorporation of the interelectronic distance in calculations of larger systems was not readily applicable.

In the meantime, since these earlier calculations appeared until 1962, when the first issue of Theoretica Chimica Acta was published, methodological advances like the Hartree–Fock and configuration interaction (CI) methods had already been made. Perturbational approaches like the one developed by Møller and Plesset, [3] although published as early as 1934, was largely unexploited until the work of Pople, Binkley and Seeger [4] later in 1976, and a general and straightforward application of multiconfigurational self-consistent field wavefunctions would only appear in the literature a decade later in the work of Das and Wahl [5].

Ab initio calculations were mostly restricted to atoms and diatomic molecules, since the evaluation of multicenter integrals over Slater functions was a major problem at the time, until the Gaussian-type functions introduced by Boys in 1950 replaced the Slater-type functions in calculations [6]. The contribution of Roothaan [7] where the molecular orbitals of the Hartree–Fock formalism were expressed in terms of a finite set of analytic functions leading to a rigorous matrix representation of the Hartree–Fock equation was almost simultaneous with the appearance of the first automatic computing machines in the academic environment. This combination of more easily implemented theoretical models and automatic computation seemed to indicate a brighter future for quantum chemistry. The attainment of the Hartree–Fock limit, thus, became a goal for some schools.

By 1960, a feeling of some of the hot issues in question can be appreciated in the collected papers from the Conference on Molecular Quantum Mechanics held at the University of Colorado the previous year [8]. It is interesting to recall that in his banquet speech summarizing the then present state of molecular structure calculations presented in this conference, Coulson [9], besides expressing

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Published as part of the special collection of articles celebrating the 50th anniversary of Theoretical Chemistry Accounts/Theoretica Chimica Acta.

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his opinion “that the whole group of theoretical chemists is on the point of splitting into two parts … almost alien to each other”, now known as the ab initio and semi-empirical theoretical chemists, also prophesized that “… the speeding up of calculations, and the design of even faster machines should enable us to extend the range of effectively exact solutions. I am inclined to think that the range of 6–20 electrons belongs to this picture.” Even considering the potential role that the large-scale use of electronic computers would have in the future, he again reemphasized that “It looks as if somewhere around 20 electrons there is an upper limit to the size of a molecule for which accurate calculations are ever likely to become practicable.” A few years later, the investigation of Pitzer and Lipscomb [10] on the barrier to internal rotational in ethane, performed at the self-consistent Hartree–Fock level of theory with a minimal basis represented a major step in obtaining reasonable accuracy and physical insights on the origin of the barrier. As part of Pitzer’s Ph.D. thesis, this project involved the development of an SCF program from scratch especially designed for this molecule [11]. Also, an early example of the predictive role that quantum chemical calculations would play in spectroscopy in the years to come was related to the structures and energy splitting of the singlet and triplet states in CH_2 [12]. For a critical review of the apparent conflict between theory and experiment, resolved in favor of quantum chemistry, the reader is referred to the survey of Shavitt [13]; a more recent account of studies on this system is given by Neugebauer and Häfelinger [14].

In this short and necessarily incomplete overview of some of the progress theoretical/computational chemistry had attained by the time the first issue of TCA came to be published, I am trying to convey to the younger generation of practitioners in this area that for a full appreciation of the progress we have achieved so far in the application of the methods of electronic structure, as presented in the articles that follow, they would benefit very much by getting acquainted with some of the landmark papers in the area. Fortunately for them, in the short monograph by Schaefer, a period of about 50 years since the very beginning of quantum chemistry has been covered in which his personal selection of 149 papers guides the reader to what he expresses as part of a necessarily “vigorous program of theoretical education” [15]. In this context, the young practitioner might be surprised to learn that in the 1970–1980s special installations were required to house huge mainframes with a computing power and disk storage much smaller than his or her desktop computer. This limitation of hardware required ingenuity to implement the various theoretical methods of electronic structure calculations, of which the determination of the eigenvalues of very large Hamiltonian matrices, the direct approach to the SCF-HF and CI methods, the transformation of atomic to molecular integrals, and the calculation of gradients of the energy with respect to the nuclear coordinates are a few examples. The new generation of vectorial computers appearing in the early 1980s brought new excitement to the quantum chemistry community, and since then the steep increase in computing power opened new frontiers to explore. Concomitantly, the progress made in the development of methods to solve the electronic Schrödinger equation and the availability of easy-to-use software packages made computational quantum chemistry a necessary field of study in every chemistry department.

In this section of the 50th anniversary issue of *TCA*, two contributions showing state-of-the-art applications of quantum chemistry to present day research make evident the enormous progress we have achieved in the last 50 years. The first paper by Lischka and collaborators [16] brings us to a complex, beautiful, and exciting universe never dreamed by Coulson in his 1959 speech. How to describe the significant physico-chemical changes that follow photoexcitation of molecular systems, what is the basic physics underlying these phenomena, and what are the quantum chemistry tools that can help us to reliably describe the excited state phenomenology are topics that only very recently could be successfully approached and that are treated in a state-of-the-art way by the authors. A survey of current possibilities and future challenges include topics related to nucleobases and nucleic acid fragments, model systems of retinal (the chromophore of rhodopsins), the fields of photovoltaics, photodevices, phototriggers, and molecular devices. For a realization of the immense advances made so far, one should contrast these subjects with the early problems of the internal rotation in C_2H_6, and the structure and energy splitting in CH_2, for example. Directions of as yet to be explored new territories are also presented as a challenge for future generations.

How much have we progressed in attaining increasingly accurate results since the first issue of Theoretica Chimica Acta came into press? The focus of the contribution of Peterson, Feller, and Dixon [17] on “chemical accuracy” leads us to an analysis and discussion of the intrinsic accuracy of highly correlated wavefunction-based electronic structure methods as applied in ab initio thermochemistry and spectroscopy. What to expect of increasing levels correlation treatment coupled with extensions of the 1-particle basis sets to the complete basis set limit in the characterization of molecular systems? How apparently small effects like scalar relativistic, spin–orbit (oute)core correlation effects, and zero point energies affect thermochemical properties like atomization energies and vibrational frequencies? What is an acceptable transition boundary between tractable and untractable systems for pushing the attainment of chemical and spectroscopic accuracy to their limits? How can we investigate these latter systems? And how "composite approaches" come to our rescue? By answering these questions, the authors conduct the readers through the state-of-the-art in this field in an authoritative way. Interesting to see in this arena, as in the old days, is the resurgence of the interelectronic coordinate (r_{12}) in explicitly correlated methods as an alternative approach to improve convergence, thus reducing the requirements of very large basis sets. Challenges to be overcome in the near future are finally presented for the accuracy seekers.

As a final remark in this introductory section, one should note that implicit in the calculations surveyed in these two contributions is the motto "Getting the Right Answer for the Right Reason" that should serve as a guide to all practitioners in the area.

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