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Explicit-r_{12} Correlation Methods and Local Correlation Methods

Guest Editors: Hans-Joachim Werner and Peter Gill

Editorial

Explicit-r_{12} correlation methods and local correlation methods
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Papers

Implementation of the CCSD(T)-F12 method using cusp conditions
Denis Bokhan, Seiichiro Ten-no and Jozef Noga, *Phys. Chem. Chem. Phys.*, 2008
DOI: 10.1039/b803426p

Analysis of non-covalent interactions in (bio)organic molecules using orbital-partitioned localized MP2
Stefan Grimme, Christian Mück-Lichtenfeld and Jens Antony, *Phys. Chem. Chem. Phys.*, 2008
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The principle-quantum-number (and the radial-quantum-number) expansion of the correlation energy of two-electron atoms
Werner Kutzelnigg, *Phys. Chem. Chem. Phys.*, 2008
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Explicit-r_{12} correlation methods and local correlation methods

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Quantum chemistry is the discipline in which quantum mechanical principles are used to rationalize and predict chemical behaviour. For most purposes, Schrödinger's conceptual framework is the one best suited to the paradigms of chemistry and his famous equation

$$H\Psi = E\Psi$$

is the tool by which chemical questions are reduced to problems in applied mathematics. The philosophical recognition that such a reduction is possible, as well as the gloomy prospects for practical calculations, were tersely captured by Dirac's famous 1929 aphorism: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

However, despite a relatively slow start, the subject developed rapidly during the second half of the 20th century, fueled largely by breathtaking improvements in computer technology and, by 1998, when the Nobel prize for Chemistry was awarded jointly to Walter Kohn and John Pople, it was widely held that computational chemistry had matured into a useful partner of experiment.

Nonetheless, as we beat a path into the 21st century significant obstacles remain, preventing the routine use of quantum mechanics to provide quantitative understanding of complicated chemical systems. The nub of the problem is the fact that each of the electrons in a system repels every one of the other electrons and, as a result, the details of many-electron electronic structures are extremely complicated. In principle, these details are embodied in a configuration interaction wavefunction using a large one-electron basis set but, in practice, the computational expense of generating such a wavefunction grows so rapidly with the number of electrons that it is (and will remain) intractable for all but the smallest of systems. This is the infamous electron correlation problem.

Three seminal advances, introduced during the mid-eighties and early nineties, provided the conceptual bedrock to many of the developments that are described in the present Themed Issue.

First, Pulay showed that it is profitable to partition the total correlation energy into contributions from electrons that are nearby, moderately separated and distant, and that different treatments can be applied within each of these regions. The various approaches that are now called the local correlation methods are founded on this intuitively appealing principle and a number of recent advances are discussed in this issue.

The paper by Grimme uses local MP2 to obtain a greater understanding of intramolecular dispersion effects in large molecules; Doser *et al.* discuss rigorous estimates of small, potentially negligible integrals in local MP2 calculations; Russ and Crawford describe a systematic partitioning approach in local coupled-cluster theory; and Goll *et al.* explore local correlation in the context of DFT–wavefunction hybrid models.

Second, Kutzelnigg revisited Hylleraas' brilliant suggestion that it is both very natural and highly effective to work with trial wavefunctions that explicitly include the interelectronic distance r_{ij}. Through the ingenious use of the resolution of the identity, Kutzelnigg showed how one can avoid the three- and four-electron integrals that had bedevilled earlier attempts to apply the Hylleraas approach to many-electron systems and the various approaches that are now called the R12 (or F12) methods stem from this work. Several developments in this and cognate areas are presented in this issue.

The paper by Shiozaki *et al.* describes the use of computer algebra to generate the equations of R12 coupled-cluster theory; Bande and Lüchow apply the quantum Monte Carlo method and explicitly correlated wavefunctions to study vanadium oxides; Dahle *et al.* use calculations with Gaussian geminals to obtain an accurate estimate of the exact MP2 energy of the H_2O molecule; Bokhan *et al.* implement CCSD(T)-F12 and explore the importance of cusp conditions; Komasa uses exponentially correlated Gaussian functions to study excited states of the H_2 molecule; Höfener *et al.* report the implementation of Slater-type geminals within the TURBOMOLE package; Marchetti and Werner discuss the results of MP2-F12 calculations and new efficient CCSD(T)-F12 approximations on intermolecular interaction energies; and Torheyden and Valeev present a variational formulation of the CCSD(2)-R12 method.

Third, Almlöf demostrated that remarkable simplifications follow if the energy denominators that arise in Rayleigh–Schrödinger (and therefore Møller–Plesset) perturbation theory are replaced by their Laplace transform representations. This 'trick' is especially effective in conjunction with the local correlation methods and the only downside is the introduction of a one-dimensional integral that is usually handled by a simple quadrature. In this issue, Izmaylov and Scuseria present an improved version of the atomic-orbital Laplace-transformed MP2 method and Kats *et al.* present a new Laplace-based version of the local MP2 method.

The remaining papers in this Themed Issue address other related topics. The papers by Gori-Giorgi *et al.* and Bernard *et al.* are concerned with the probability distribution of r_{12} and its time derivative; Chan reports a Lagrangian formulation that will be valuable in DMRG response theory; and Kutzelnigg examines a novel decomposition of the correlation energy of the helium-like ions.

We hope that *PCCP* readers will find much to savour in this snapshot of the field.

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