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Perspective

Multireference many-body methods. Perspective on "Linked-cluster expansions for the nuclear many-body problem"

Bradow BH (1967) Rev Mod Phys 39: 771

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Abstract. The role of the title paper in the history of multireference many-body methods is reviewed. Subsequent developments are described, and unsolved outstanding problems are also discussed.

Key words: Many-body methods – Multireference – Coupled cluster

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Many-body methods, based on the linked-cluster expansion (LCE), were first developed by Brueckner [1] and Goldstone [2] in the 1950s for nuclear physics problems. Perturbation-theory applications to atomic and molecular systems (in a numerical, one-center frame) were pioneered by Kelly [3] in the early 1960s. Basis sets were later introduced, first in second-order [4] and then in third-order [5]. The 1970s saw a proliferation of molecular applications with basis sets, under the names of many-body perturbation theory (MBPT) [6] or the Møller-Plesset method [7]. Nowadays, many-body methods offer some of the most powerful tools in the quantum chemistry arsenal, in particular the coupled-cluster (CC) method, and are available in many widely used quantum chemistry program packages.

All the early applications, as well as the vast majority of many-body calculations performed to this day, are single-reference in character. They start from an appropriate single determinant, usually (but not necessarily) Hartree–Fock, and include correlation by finite-order perturbation or infinite-order summation of certain perturbation terms (the CC approach). The starting determinant may be closed-shell or open-shell: the latter leads to contaminated spin states and occasionally to broken spatial symmetry [8], but acceptable results are obtained in most cases. States involving degeneracy or quasidegeneracy, where a single determinant does not provide an adequate starting point, are not amenable to this treatment.

The early 1960s saw several attempts to extend the linked-cluster expansion to multireference cases, to make possible the treatment of general open-shell systems. These attempts met with partial success, and it was Brandow [9] who first proved the LCE for multireference methods in his 1967 paper, opening the way to new types of applications. The first (short) part of the article is an elegant time-independent proof of the linked-cluster theorem for single-reference cases using diagrammatic methods (previous proofs used time-dependent evolution operators and infinite time integrations). Most of the paper is devoted to a detailed discussion of the degenerate case. A novel type of diagram is described; the so-called "folded" diagrams solved the difficulties which had stymied earlier attempts. It was now possible for the first time to have a linked-cluster, energy-independent expansion for degenerate systems (it is interesting to note that Sandars [10] came up with a similar solution 2 years later, apparently unaware of Brandow's paper: he used the term "backward" diagrams). A detailed proof of the LCE is given, rules for application are described, and subjects such as calculation of properties other than energy and handling of quasidegeneracy (as distinct from exact degeneracy) are also discussed in this comprehensive landmark paper.

The route to applications involving states of multireference character was now open. The first application of Brandow's method in molecular physics treated the excited states of H_2 at several internuclear separations [11]. Several other molecules followed. In the coming years, emphasis in the high-accuracy small-molecules end of quantum chemistry shifted from finite-order MBPT to the all-order CC method, thanks largely to the work of Bartlett, Pople and their coworkers [12]. Here the problem of degeneracy or quasidegeneracy and the need for multireference methods appeared again. Brandow's folded diagrams were used by Lindgren [13] to derive a linked (and therefore size-extensive) multireference CC method. Shavitt [14] proposed in a 1983 workshop that "a multireference CC formalism is probably the single most promising approach" to molecular computations.

What is the current situation in multireference many-body methods? On the low-order side, the second-order CASPT2 method [15] based on a large active space is highly successful. At the high-order or CC end, several methods exist, each with its advantages and shortcomings (for a review see Ref. [16]). The Fock-space method, which starts from a closed-shell state and reaches the state(s) of interest by adding and/or removing electrons from the reference, is the most widely used [17]. Its strong point is preservation of the full symmetry (both spin and spatial) of the system. The method has been particularly successful in calculating spectra of heavy atoms in the relativistic regime [18]. The main drawback is the existence of so-called "spectator" lines, with the same (valence) orbital going into and coming out of the diagram, creating terms which are formally *n*-excited but physically describe lower excitation numbers. The Hilbert-space approach [19] does not suffer from this problem, but it breaks symmetry and may generate substantially different energies for states which should be degenerate (e.g., $M_s = 1$ and 0 states of a triplet) [20]. A widely used alternative for open-shell systems which may be described by a single determinant is to start from the UHF or ROHF function. This may be problematic, leading in some cases to breaking geometrical symmetry of open-shell molecules [8]. The QRHF-CC method [21] starts from an uncorrelated function with correct spin and spatial symmetry, but breaks symmetry in the correlation part. It should be noted that different approaches yield, in general, different energies and other properties for the same system.

To conclude, much progress has been achieved in applying multireference many-body methods in quantum chemistry since Brandow made it possible by proving the linked-cluster expansion, but the problem cannot be considered fully solved. Further work is needed to realize the hope expressed by Shavitt [14] 15 years ago.

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