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Non-iterative coupled-cluster methods employing multi-reference perturbation theory wave functions

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Abstract

A new class of non-iterative coupled-cluster (CC) methods, which improve the results of standard CC and equation-of-motion (EOM) CC calculations for ground and excited-state potential energy surfaces along bond breaking coordinates and for excited states dominated by two-electron transitions, is explored. The proposed approaches combine the method of moments of coupled-cluster equations (MMCC), in which the a posteriori corrections due to higher-order correlations are added to standard CC/EOMCC energies, with the multi-reference many-body perturbation theory (MRMBPT), which provides information about the most essential non-dynamic and dynamic correlation effects that are relevant to electronic quasi-degeneracies. The performance of the basic MRMBPT-corrected MMCC approximation, in which inexpensive non-iterative corrections due to triple excitations are added to ground- and excited-state energies obtained with the CC/EOMCC singles and doubles approach, is illustrated by the results of a few test calculations, including bond breaking in HF and H_2O, and excited states of CH^+.

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1. Introduction

One of the most challenging problems in modern electronic structure theory, which is particularly important in studies of chemical reaction mechanisms and molecular electronic spectra, is the development of affordable ab initio methods that can provide an accurate description of ground- and excited-state molecular potential energy surfaces. In order to obtain a uniformly accurate description of reactants, products, reaction intermediates, and transition states, and electronic excitations in molecules, one has to come up with a well-balanced description of dynamic and non-dynamic correlation effects. The problem is that most of the existing quantum chemistry methods provide an accurate description of either the dynamic correlation effects that are the dominant correlations in closed-shell molecular systems or the non-dynamic correlation effects that play a significant role in quasi-degenerate electronic states characterizing bond breaking and the majority of excited states, but very few methods are capable of providing an equally accurate description of both dynamic and non-dynamic correlation effects required in studies of molecular potential energy surfaces along bond breaking coordinates. This is particularly true for larger many-electron systems, for which the potentially most accurate multi-reference configuration interaction (MRCI) or multi-reference coupled-cluster (MRCC) calculations are not feasible. For example, the highly successful and easy-to-use single-reference coupled-cluster (CC) theories [1–5] (cf. Refs. [6–11] for reviews), such as the popular CCSD(T) approximation [12] in which the dominant effects due to triply excited clusters are added to the CCSD (CC singles and doubles) [13–15] energies, and their iterative CCSDT-1 [16–18] and CC3 [19–22] analogs, provide an excellent description of closed-shell systems and dynamic correlation effects with the relatively low computer costs that scale as n^6-n^7 with the system size, but the CCSD, CCSD(T), CCSDT-1, CC3, and similar methods fail when potential energy surfaces involving bond breaking [8,10,23–48] and biradicals [49–51] are examined. Similar remarks apply to the excited-state analogs

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of the ground-state CCSD and CCSD(T) approximations, based on the linear-response CC theory [52–56], and the closely related equation-of-motion CC (EOMCC) [57–60] and symmetry-adapted cluster configuration interaction [61–65] methods. For example, the linear response CCSD [55,56] and EOMCCSD [57–59] approximations, which are characterized by the manageable computational steps that scale as n^6 with the system size, and their various extensions to triples of the EOMCCSD(T) [66,67], EOMCCSDT-*n* [66,67], and CC3 [19–22] type, provide reliable information about excited states dominated by one-electron transitions, but they cannot describe excited states having significant double excitation components and excited-state potential energy surfaces along bond breaking coordinates [19–22,33,34,40,43,48,66–78]. The high-level CC methods including higher-than-double excitations, such as CCSDT (CC singles, doubles, and triples approach) [79,80] and CCSDTQ (CC singles, doubles, triples, and quadruples approach) [81–84] and their recently formulated EOMCCSDT (EOMCC singles, doubles, and triples) [70,71,85,86] and EOMCCSDTQ (EOMCC singles, doubles, triples, and quadruples) [73,87] extensions to excited states, provide considerable improvements in the description of molecular potential energy surfaces along bond breaking coordinates and excited states dominated by doubles [24,26,27,30,34,40,70,71,73], but large costs of the CCSDT/EOMCCSDT and CCSDTQ/EOMCCSDTQ calculations, which are defined by the iterative steps that scale as n^8 and n^{10} with the system size, respectively, limit their applicability to small molecules with 2–3 light atoms and relatively small basis sets (the CC/EOMCC schemes with up to pentuple and even hextuple excitations have been implemented too [87,88], but the n^{12} and n^{14} scalings of the resulting CCSDTQP/EOMCCSDTQP and CCSDTQPH/EOMCCSDTQPH methods with the system size make these approaches completely impractical, since problems that one can tackle with such approaches are of the type of problems that can be handled by the full CI theory; moreover, the role of higher-than-quadruple excitations in the CC/EOMCC calculations of interest in chemistry is, in the vast majority of cases, virtually none [87,88]). Other, less expensive, ways of incorporating higher-than-double excitations in the CC and EOMCC/linear response CC formalisms must be developed in order to make these methods applicable to a wider range of molecular problems encountered in studies of reaction pathways and excited states dominated by either one- or two-electron transitions.

Several new ideas have been developed in the recent few years to improve the description of ground- and excited-state potential energy surfaces along bond breaking coordinates at the relatively low cost within the general framework of single-reference CC theory (see, e.g. Refs. [8,10,24,26–45,69–71,74–77,84,89–115] for the examples). In particular, we have demonstrated that considerable improvements in the description of ground- and excited-state potential energy surfaces along bond breaking coordinates can be obtained by using the completely renormalized (CR) CC/EOMCC approaches [10,28–35,37,38,40–44,76,77,116] or one of the externally corrected variants [10,33,34,36,40,74,75,113–115] of the method of moments of CC equations (MMCC) [10,28,29,33,34,40,74,75]. The CR-CC, CR-EOMCC, and other MMCC methods are based on a simple idea of improving the CCSD/EOMCCSD or other CC/EOMCC energies through the use of the suitably designed non-iterative corrections due to higher-order correlations that utilize the concept of the generalized moments of CC/EOMCC equations rather than the usual many-body perturbation theory (MBPT) arguments exploited in the standard CCSD(T)/EOMCCSD(T), CCSDT-*n*/EOMCCSDT-*n*, CC3, and similar approaches. The basic CR-CC, CR-EOMCC, and MMCC approximations preserve the relatively low, n^6-n^7-like, costs of the non-iterative methods of the CCSD(T)/EOMCCSD(T) type, while providing considerable improvements in the results of the standard CC and EOMCC calculations in the presence of electronic quasi-degeneracies [10,28–45,49–51,74–77,113–117]. The key to a successful description of ground- and excited-state potential energy surfaces by the CR-CC, CR-EOMCC, and other MMCC methods is a good control of accuracy that all of these methods offer by directly addressing the quantity of interest, which is the difference between the exact, full CI, and CC or EOMCC (e.g. CCSD or EOMCCSD) energies. The MMCC formalism provides us with precise information about the many-body structure of these differences, suggesting several useful types of non-iterative corrections to CCSD, EOMCCSD, and other CC/EOMCC energies.

The CR-CC and CR-EOMCC methods have an advantage over other MMCC approaches that they can be regarded as computational 'black-boxes', which are as easy to use as the single-reference CC/EOMCC methods of the CCSD(T) or EOMCCSD(T) type. There may be situations, however, where simple approximations invoked in the design of the CR-CC and CR-EOMCC methods are not sufficient to obtain the desired improvements. Examples of such situations might be provided by multiple bond breaking and excited-state potential energy surfaces of some quasi-degenerate systems (cf., e.g. Refs. [29,31,33,34,38–40,43,45]). In all these difficult situations, one can always switch to the CI-corrected MMCC (MMCC/CI) methods [10,33,34,36,40,74,75] (cf., also, Refs. [113–115]), which belong to a wider category of the externally corrected MMCC approaches, but computer costs of the MRCI-like calculations that are needed to generate the wave functions that enter the MMCC/CI corrections to CC or EOMCC energies can exceed the costs of the CC or EOMCC calculations which we are trying to improve. Undoubtedly, it would be useful to examine if we could use another, less expensive, multi-reference method to generate the wave functions that enter the MMCC corrections.

In this paper, we examine the possibility of replacing the relatively expensive MRCI-like wave functions in the MMCC/CI schemes by the wave functions obtained in the multi-reference MBPT (MRMBPT) [118–124] calculations. The low-order MRMBPT methods are known to provide a reasonable description of non-dynamic and leading dynamic correlation effects in the presence of electronic quasi-degeneracies (cf., e.g. Refs. [125–144]; see, also, Refs. [116,145] and references therein). At the same time, the