

Orbital invariant single-reference coupled electron pair approximation with extensive renormalized triples correction

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Abstract

A single-reference coupled electron pair approximation is proposed that is exact for two-electron systems, rigorously size-extensive, and invariant under rotations of the occupied and virtual orbitals amongst themselves. In addition, an alternative framework is presented to derive renormalized perturbative corrections to single and double excitation approaches, which are likewise rigorously extensive and invariant under rotations of occupied and virtual orbitals. The new methodology, which is still in a prototype phase at the time of writing this paper, is baptised eXtensive Configuration Interaction with renormalized connected triples corrections, p-RXCISD(*T*), where ‘p’ indicates the preliminary, prototype stage of its development. A few variations on the theme are discussed, notably the completely renormalized p-RXCISD(*M3*) and the Brueckner orbital based p-RBXCISD(*T*). The methodology is applied to obtain potential energy curves and low lying vibrational energy levels (up to $v=8$) for a variety of closed-shell and open-shell diatomics that exhibit a range of chemical bonding patterns (HF, BF, F₂, N₂, BeO, BN, CN, O₂, and Be₂). Low-order Dunham expansions of the vibrational data are compared between reference CCSDT, CCSD(*T*), and the newly developed p-RXCISD(*T*), p-RXCISD(*M3*) and p-RBXCISD(*T*) methods. In addition, for the HF molecule the complete set of $J=0$ vibrational levels, obtained from p-RBXCISD(*T*) and p-RBXCISD(*M3*) calculations using basis set extrapolation based on the aug-cc-pVTZ/aug-cc-pVQZ basis sets, are compared to experiment.

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1. Introduction

Single-reference coupled cluster theory [1–3] including a non-iterative perturbative connected triples correction, CCSD(*T*) [4], is widely used today as a routinely applicable electronic structure method, which in general yields high accuracy results, provided high quality basis sets are used [5–7]. The methodology has its limitations, as it breaks down for highly correlated systems, as occur for example when describing bond-breaking processes [6]. The onset of the breakdown is ascribed to the use of the perturbative triples correction, although CCSD itself also has its limitations. Moreover, CCSD(*T*) calculations scale with the 7th power of the basis set size, and this, in conjunction with the demands on the quality of the basis set, severely limits the size of the molecule that can be treated.

In recent years, progress has been made in pushing the boundaries of applicability of CCSD(*T*) in both regards. In their work, on the method of moments coupled cluster approach [8–10], Kowalski and Piecuch have pioneered renormalized corrections built on CCSD and CCSDT, which postponed the breakdown of single-reference methods, or, in some cases, eliminated the breakdown completely [11,12]. Other groups have also achieved significant progress in this regard [13–17]. Hence, it has become possible to provide a substantially improved treatment of processes in which single bonds are broken, and the potential benefits for describing reaction profiles, biradicals and transition metal species are under active investigation [18–21].

The early proposals for renormalized triples corrections by Kowalski and Piecuch were not size-extensive, and this presents a drawback, even for systems that are not very large. For example, it prohibits the accurate description of the interaction energy of weakly bound systems using these methods. In addition, as a consequence of the size-extensivity problem, the method can deviate substantially from CCSD(*T*) for well-behaved systems, and the renormalization factor in the

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triples correction can have substantial and undesirable basis set dependence. Recently, Kowalski and Piecuch introduced the numerator–denominator connected (NDC) approach to renormalized triples and quadruples corrections, which is explicitly extensive and size-consistent, provided the occupied orbitals are localized [22,23]. This alleviates the earlier drawbacks, but it introduces another: results will depend (slightly) on the localization scheme used. Moreover, for systems with high degrees of symmetry, the choice of localized orbitals can have some arbitrariness, and this creates complications when developing analytical gradients, or even when evaluating vibrational frequencies numerically. In this work, an alternate track is followed to derive extensive renormalized triples corrections in which exclusion principle violating (EPV) contributions are summed to high order. The selection of EPV terms in the renormalized triples corrections is analogous to the treatment of EPV terms in coupled electron pair approximations (CEPA) [24,25], which are in general not invariant under rotations of occupied orbitals. We will employ a strategy to circumvent this problem, which is similar both in the renormalized triples and in our orbital invariant CEPA approach (to be discussed), and arrive at a formulation that is rigorously extensive (implying the equations contain manifestly connected terms only) and invariant under rotation of occupied (or virtual) orbitals amongst themselves. This is discussed in Section 2.2.

At the other end of the spectrum, various groups have been working on high-accuracy local correlation methods [26–38], in which a localized orbital representation is used to screen contributions to dramatically speed up the cost of calculations, and linear scaling has been achieved for large molecules [28,29]. In the most advanced treatments, a judicious choice is made to treat certain wave function amplitudes at a low-order perturbation level (MP2), while other more sizeable amplitudes are included at the coupled cluster (CCSD) level. Finally, only a small fraction of possible triple excitation amplitudes is included in the connected triples correction. In the approach developed by Ayala and Scuseria [30,38] and also in our own work [39], the selection of methodology for different amplitudes is done dynamically: the level of computation to be used to treat the various amplitudes is selected as the calculation proceeds. This is in principle more satisfactory than basing the selection on a rigid a priori protocol. While this dynamical decision can presumably be made in an effective manner, coupled cluster methods are non-linear in the amplitudes, and for this reason similar screening in principle is needed for each intermediate that arises in the combined CC/PT approach. This is a difficult problem, which likely will affect the robustness and systematics of the implementation. Similar problems arise in local correlation treatment of excitation energies in a coupled cluster linear response framework: approximations have to be designed regarding how to calculate and screen transformed matrix elements of $\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ that enter the diagonalization procedure [40–43]. The non-linearity of the coupled cluster and coupled cluster linear response equations complicates the problems.

The same non-linearity of coupled cluster approaches is also somewhat of a complication in designing effective parallel

coupled cluster codes [44]. Intermediate quantities calculated on one processor may have to be transferred to another processor, and communication costs rise. In recent work, an effective loop fusion approach was described to parallelize CCSD, in which the communication of intermediates is completely avoided, but in this scheme all of the t -amplitudes need to be duplicated, while the residual vector is accumulated in every iteration. As a result, the performance of the parallelized code deteriorates with an increasing number of computational nodes, since although computational costs are reduced, communication costs rise [45]. While it may be possible to design effective parallelization strategies for coupled cluster methods that work on massively parallel computers, it is again a difficult problem, and the origin of the problem is the essential non-linearity of the coupled cluster equations.

For these reasons, it may be very worthwhile to explore methods simpler than coupled cluster theory in the context of local correlation and/or parallel computations. Coupled electron pair approximations (CEPA) [24,25,46,47] have particular appeal as they are nearly linear (as is CI), while they rival CC methods in accuracy; for large scale multi-reference calculations the MR-ACPF [48–50] and MR-AQCC methods [51–54], which can be viewed as variants of CEPA, are among the most accurate tools currently available. Historically, single-reference CEPA can be viewed as a precursor to coupled cluster theory [55], and CEPA includes the linear terms from CC theory and a selection of exclusion principle violating (EPV) non-linear contributions, which are typically easy to include. CEPA methods are designed to be exact for two-electron systems or for a set of non-interacting two-electron systems, and they are extensive. The main drawback of CEPA approaches is that they are not invariant to rotations of the occupied orbitals amongst one other, and they lead to size-consistent results for non-interacting systems only if localized orbitals are used. Another formal theoretical discomfort is that CEPA methods are not unique. Different selections of EPV terms can be made that all give rise to exact results for two-electron systems. Both the lack of orbital invariance and the theoretical ambiguity are reasons that genuine single-reference CEPA approaches never became very popular in the computational chemistry community. In ACPF [48], the averaged coupled pair functional approach, the EPV terms are included in an average way. This renders the approach invariant to orbital rotations, but it is somewhat less sophisticated and only nearly size-extensive.

Our interest in CEPA is partially for computational reasons, but partially also because CEPA is of fundamental interest. The terms included in CEPA are of vital importance for accuracy, and as a corollary, ‘our sacred coupled cluster theory might be viewed merely as a convenient orbital invariant form of CEPA’. The reason coupled cluster theory works so well is not so much the fact that $1/2\hat{T}_2^2$ includes the most important disconnected quadruple excitations. Rather, it is that the terms that derive from the EPV part of $1/2\hat{T}_2^2$, which is zero as an operator, still contribute if only connected terms are retained upon contraction with the Hamiltonian. These EPV terms are

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