

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

numerically far more important than the remaining non-EPV contributions (the genuine disconnected quadruples), and these EPV terms are included in both CEPA and CC theories, while maintaining size-extensivity. CC theory has other advantages; in particular it can be systematically extended to include higher excitations, while single-reference CEPA has never really seen these more advanced developments. Nonetheless, a small part of the community has always kept an active interest in CEPA, and in particular in multireference CEPA methods [47,56–59], which are thought to be somewhat easier to construct than multireference coupled cluster methods. In recent work, Mukherjee and co-workers presented several reductions of their state selective multireference coupled cluster theory [60–64] to multireference CEPA forms [65,66], and importantly in the context of this work, they designed an orbital invariant multireference CEPA approach.

In this work it is shown (in Section 2.1), how an orbital invariant form of CEPA can be derived straightforwardly in a single-reference context. This method shares many desirable properties with CCSD. It is exact for two-electron systems or for an arbitrary number of non-interacting subsystems, each containing two electrons. It consists of complete ‘connected diagrams’ only, and hence is size-extensive and size-consistent in the same way as CC theory, and it is, like CC theory, invariant to orbital rotations in the space of occupied (or virtual) orbitals. As in conventional CEPA, however, the procedure of selecting certain non-linear contributions is not uniquely determined by the requirement of exactness for two-electron systems. An alternative scheme, closely related to that discussed in this paper, is the so-called ACP-D45 (approximate coupled pair) approach introduced by Adams et al. [67] in 1981, while the so-called ACPQ scheme implicitly accounts for connected quadruple excitations [68–70] and has seen a number of interesting pilot applications. In this paper, we consider one particular variant of the orbital invariant CEPA family (ACP-D45 is another member of the family), and we refer to the methodology as a prototype version, using the name XCI (eXtensive configuration interaction) to emphasize the near-linear nature of the approach. In future work we plan to carry out a more systematic investigation of the complete family of orbital invariant CEPA methods. The ideas underlying orbital invariant CEPA can in principle be extended to higher-order excitations, and therefore, from a formal perspective, there seem to be few arguments (except for non-uniqueness, which may be more of a moral objection) for choosing between this form of CEPA and CC theory. Of course, the real test is how the orbital invariant CEPA approach holds up in practical calculations for many-electron systems.

As electron correlation methods restricted to single and double excitations are in general not quantitatively accurate, an orbital invariant and extensive formulation of a renormalized triples correction is derived in Section 2.2, based on an EPV argument, and a similar device is used as in Section 2.1, to include the EPV terms in an orbital invariant way. In Section 3, the new methods are put to the test, and potential energy curves are calculated for a variety of diatomics over a limited range of the internuclear distance. The selected diatomics span a wide

variety of chemical species including ionic and covalent bonding, radicals, triplet states and van der Waals molecules, and the breaking of chemical bonds is probed to some extent. To analyse the vast amount of data, vibrational energy levels in the $J=0$ rotational state are calculated and Dunham parameters [71] ω_e and $\omega_e x_e$ are extracted for the low-lying vibrational states. In addition, calculated rotational constants for each vibrational state are used to extract the parameters B_e, α_e . The vibrational calculations are performed using the Level 7.7 program [72]. The vibrational data are compared between CCSDT, CCSD(T) and the new p-RXCISD(T), p-RXCISD(M3) and the Brueckner orbital based p-RBXCISD(T) methods, all obtained using the same basis set. This comparison provides a fairly sensitive test of the new methodology. In Section 4, p-RBXCISD(T) results for the vibrational levels of the HF molecule are compared directly with experiment, and conclusions are presented in Section 5.

2. Theory

In this section, two topics will be discussed. The first is an orbital invariant single-reference CEPA theory restricted to single and double excitations. The second topic concerns a size-extensive renormalized triples correction.

2.1. Orbital invariant single-reference CEPA theory: eXtensive configuration interaction (XCI)

To avoid complications with single excitations, which are treated very satisfactorily at the coupled cluster level or using Brueckner orbitals [73], the wave function is parameterized in a hybrid form as

$$|\Psi\rangle = e^{\hat{T}_1}(1 + \hat{C})|0\rangle, \quad (1)$$

where $\hat{T}_1 = \sum_{i,a} t_i^a \hat{a}^\dagger \hat{i}$ represents single excitations, and the linear operator $\hat{C} = \hat{C}_2 + \hat{C}_3 + \dots$ represents higher excitations, e.g. $\hat{C}_2 = (1/4) \sum_{i,j,a,b} c_{ij}^{ab} \hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}$, and we employ the usual convention that i, j, k, l represent occupied spinorbitals in the reference determinant $|0\rangle$, while a, b, c, d denote virtual spinorbitals. Substituting this parameterization into the Schrödinger equation and multiplying by $e^{-\hat{T}_1}$, one obtains:

$$e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} (1 + \hat{C})|0\rangle = E(1 + \hat{C})|0\rangle \quad (2)$$

The energy can be written as

$$\begin{aligned} E &= \langle 0 | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} | 0 \rangle + \langle 0 | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} \hat{C}_2 | 0 \rangle = E_0 + E_S + E_D \\ &= E_0 + \left[\sum_{i,a} f_{a i}^i + \frac{1}{2} \sum_{i,j,a,b} v_{ab}^{ij} t_i^a t_j^b \right] + \frac{1}{4} \sum_{i,j,a,b} v_{ab}^{ij} c_{ij}^{ab} \end{aligned} \quad (3)$$

Writing the transformed Hamiltonian $e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1}$ in normal order [74], the constant term is precisely evaluated as $E_0 + E_S$, and the equation can be written as:

$$\hat{H}_{\text{open}}(1 + \hat{C})|0\rangle = E_D(1 + \hat{C})|0\rangle \quad (4)$$

The equation for singles is exactly equivalent to the singles equation in CC theory

$$\langle \Phi_i^a | \hat{H}_{\text{open}}(1 + \hat{C}) | 0 \rangle = 0, \quad (5)$$

and this equation can also be used to define Bruekner orbitals, for which Eq. (5) is satisfied, while $\hat{T}_1 = 0$.

The equation for double excitations requires further analysis. Let us first obtain a traditional CEPA type expression and define the so-called pair energies:

$$\varepsilon_{kl} = \frac{1}{2} \sum_{a,b} v_{ab}^{kl} c_{kl}^{ab}, \quad E_D = \frac{1}{2} \sum_{k,l} \varepsilon_{kl} \quad (6)$$

The projection of Eq. (4) against double excitations can be written as:

$$\langle \Phi_{ij}^{ab} | \hat{H}_{\text{open}}(1 + \hat{C}) | 0 \rangle = \left(\frac{1}{2} \sum_{k,l} \varepsilon_{kl} \right) c_{ij}^{ab} \quad (7)$$

The right-hand term in the above equation is responsible for the size-extensivity error in truncated CI calculations. If instead the right-hand term is replaced by

$$E_{ij} c_{ij}^{ab}, \quad E_{ij} = \frac{1}{2} \sum_{k,l \in (i,j)} \varepsilon_{kl} = \sum_k (\varepsilon_{ki} + \varepsilon_{kj}) - \varepsilon_{ij} \quad (8)$$

one particular variant of CEPA is obtained (called CEPA(3) [67]). This approach is exact for two-electron systems. Moreover, the approach is exact for a collection of non-interacting two-electron systems, provided localized orbitals are used. More generally, the approach is size-consistent for two non-interacting systems with an arbitrary number of electrons, provided the orbitals are localized in the individual subsystems.

The requirement of orbital localization is crucial. It is interesting to compare the energy of two N₂ molecules at large separation, stretched each to 1.3 Å, to the sum of two isolated N₂ molecules. If localized orbitals are used the CEPA approach is size-consistent, as anticipated. However, if the orbitals are delocalized over both fragments (for example, by arranging the overall geometry to have D_{2h} symmetry and using canonical MO's), the energy is lower by about 100 kcal/mol. This is a dramatic demonstration of the fact that CEPA methods are not invariant to rotations among the occupied and virtual orbitals amongst themselves. Moreover, one should not optimize orbitals using a variational principle in CEPA, as it would give rise to delocalized orbitals and to large size-consistency errors. While CEPA in this form can be used in conjunction with a well-defined prescription to localize orbitals, this is often inconvenient, and it complicates the calculation of analytical gradients, for example.

We will proceed slightly differently and obtain an orbital invariant form analogous to CEPA(3). Defining one-electron quantities

$$\omega_i^k = \frac{1}{4} \sum_{l,a,b} v_{ab}^{kl} c_{il}^{ab}, \quad (9)$$

such that $\sum_i \omega_i^i = E_D$, it is seen that the interpretation of the diagonal elements ω_i^i amounts to an average correlation energy for an electron in a particular orbital *i*. The CI equation for double excitations, Eq. (4), is modified accordingly to:

$$\langle \Phi_{ij}^{ab} | \hat{H}_{\text{open}}(1 + \hat{C}) | 0 \rangle - \sum_k (\omega_i^k c_{kj}^{ab} + \omega_j^k c_{ik}^{ab}) = 0 \quad (10)$$

As the summation labels in these equations are completely unrestricted, the equation can easily be shown to be invariant under rotations among the occupied (or virtual) orbitals. Likewise, it is easily seen that the equation is exact for two-electron systems. Finally, the equation is explicitly connected, implying that the results are size-extensive and a fortiori, size-consistent, provided that the occupied orbitals can be localized on individual subsystems. The term involving ω_k^i is similar to one of the quadratic contributions in CCSD, deriving from the 1/2 \hat{T}_2^2 term, except that the numerical factor in this term is reduced by a factor of 2, compared to CCSD. Hence, in this formulation all quadratic terms from CCSD are neglected but one, and this term is multiplied by a factor of (1/2). Note that the present approach to include the correlation energy contribution by using (part of) a quadratic contribution to the CCSD equations for two-electron systems is not unique. In particular, the so-called ACP-D45 approach by Paldus et al. [67] is a clear alternative, and the relation to CEPA type approaches is discussed in this early work. We will defer a more extensive investigation of the alternatives to the future, and focus on the above particular variant of orbital invariant CEPA.

The equations can be written slightly differently, defining

$$\hat{\omega} = \sum_{ij} \omega_i^j \hat{J}_i^{\dagger} \hat{i} = - \sum_{ij} \omega_i^j \hat{J}_j^{\dagger}, \quad (11)$$

where the matrix elements ω_i^j are defined as before, while $\{ \}$ indicates normal ordering with respect to $|0\rangle$. The orbital invariant CEPA doubles equation then reads:

$$\langle \Phi_{ij}^{ab} | \hat{H}_{\text{open}}(1 + \hat{C}) + \hat{\omega} \hat{C} | 0 \rangle = 0. \quad (12)$$

It may be instructive to point out that if one would define $\hat{\omega}' = \sum_{i,j} \omega_i^j \hat{J}_i^{\dagger} \hat{i} = E_D + \sum_{i,j} \omega_i^j \hat{J}_j^{\dagger} \hat{i}$, the equation could also be written as:

$$(\hat{H}_{\text{open}} + \hat{\omega}') (1 + \hat{C}) | 0 \rangle = E_D (1 + \hat{C}) | 0 \rangle \quad (13)$$

This equation is very much like a CI equation, where the single excitations are treated as in coupled cluster theory and an orbital invariant dressing is added, which depends on the doubles component of the CI vector.

It is perhaps illustrative to discuss to what extent the approach should be considered a variant of CEPA, in which the included modifications to the CI formulation are traditionally related to exclusion principle violating contributions. It appears that if $k \neq i$, $\omega_i^k c_{kj}^{ab} = \sum_{k,l,c,d} v_{cd}^{kl} c_{il}^{cd} c_{kj}^{ab}$ does not necessarily contain only EPV terms, in particular if (i,l) and (k,j) have no common indices. One can take a slightly extended view of this, by realizing that the equations are invariant under transformations of the occupied orbitals. In particular, it is possible to diagonalize the matrix ω_i^k . In the (biorthogonal)

diagonal basis, all terms would appear as EPV terms, as $i=k$ in non-zero contributions. From this generalized perspective, the current approach can be viewed as an orbital invariant member of the CEPA family, including a dressing in the CI matrix that is based on an inclusion of EPV terms.

While Eq. (13) is well defined for an arbitrary-order CI, it is only explicitly connected for the singles and doubles approach, and only exact for the limiting cases discussed above. It is possible to generalize the approach to higher-order excitations while maintaining size-extensivity, but these generalizations are not unique. In preliminary explorations (unpublished), approaches that yield satisfactory results become more and more reminiscent of coupled cluster theory, and some of the computational advantages underlying the orbital invariant CEPA approach are lost. In this paper, we will not consider full triples approaches, but rather focus on a perturbative inclusion of triple excitations, which is presumably most useful in practice. This is discussed in Section 2.2.

As shown in the results section, the present p-XCISD approach is often competitive with CCSD, although for highly correlated systems it appears more erratic. Even if the p-XCISD approach would yield results of comparable accuracy throughout, it would not be obvious that it would see a widespread use in the computational chemistry community in the future. It may be useful to reiterate the prime reasons for being interested in this variant of CEPA:

- (1) At a pedagogical level, the approach and derivation emphasizes the importance of a proper inclusion of EPV terms. This aspect is not often emphasized these days in rationalizations or explanations of CC theory, where it is more often emphasized that $e^{\hat{T}}$ includes higher excitation effects, in particular disconnected quadruple excitations. Historically, EPV arguments received far more attention, and we think it is worthwhile to reemphasize this point of view.
- (2) If the singles equations are used to arrive at a Brueckner theory, the equations are linear, except for the dependence of $\hat{\omega}$ on \hat{C}_2 . In addition, the calculation of the matrix-elements of $\hat{\omega}$ is almost as easy as calculating the correlation energy. This is only a small computational advantage in MO based calculations. However, it may turn out to be a major asset in local correlation calculations or calculations for extensive systems where the truncation of the non-linear CCSD or BCCD equations is non-trivial. Moreover, the near-linearity of the equations has advantages in parallel computations. It is far easier (and possibly intrinsically more effective) to parallelize CI (or CEPA) implementations than CC implementations.
- (3) Since, the approach is invariant under rotations of occupied and virtual orbital spaces, some of the prior objections to CEPA approaches disappear. Another objection might be that CEPA is arbitrary, as one can derive a number of different equations that are all exact for two-electron systems. In theoretical science, such freedom of choice is often regarded as undesirable, but it can also be exploited to advantage. At this point in time our investigations are

incomplete, but there are indications that it may be wise to designate the current approach as p-XCISD, as improvements appear possible.

- (4) It may be possible that suitable generalizations of this technique can be used to define multireference approaches. Likewise, response approaches for excitation energies might be developed that have similar advantages as the ground state version regarding local correlation approaches and parallelization. The simplicity of Eq. (13) is intriguing.
- (5) In Section 2.2, similar techniques are applied to obtain an orbital invariant form of rigorously size-extensive renormalized triples corrections.

A main disadvantage of the present approach is that the simple similarity transform picture of CC theory is lost. Moreover, the systematic treatment of higher-excitations is unclear in the present approach. It may be good to point out in this context that CC theory is highly systematic in the single-reference case, but its generalization to multireference situations is not unique, and one might learn something new from the orbital invariant CEPA or XCI perspective.

2.2. Extensive, orbital invariant, renormalized triples corrections

Following Kowalski and Piecuch [12], we use the formal device of defining an exact cluster operator \hat{T} , $|\Psi_{\text{exact}}\rangle = e^{\hat{T}}|0\rangle$, to obtain a correction to the approximate CCSD correlation energy based on $e^{\hat{T}}|0\rangle$, $\hat{T} = \hat{T}_1 + \hat{T}_2$. The derivation can be generalized fairly easily to higher-order CC methods. Let us emphasize here that the derivation in this section initially applies to genuine coupled cluster approaches. We will consider the modifications required for the correction to p-XCISD at the end of this section.

The exact energy is given by

$$\begin{aligned} E_{\text{exact}} &= \frac{\langle 0|e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}}|0\rangle}{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|0\rangle} = \frac{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}} e^{-\hat{T}} \hat{H} e^{\hat{T}}|0\rangle}{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|0\rangle} \\ &= \sum_k \frac{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|k\rangle \langle k|e^{-\hat{T}} \hat{H} e^{\hat{T}}|0\rangle}{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|0\rangle} \\ &= E_{\text{CCSD}} + \sum_{k \in T, Q, \dots} \frac{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|k\rangle \langle k|e^{-\hat{T}} \hat{H} e^{\hat{T}}|0\rangle}{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|0\rangle}, \end{aligned} \quad (14)$$

using the fact that the CCSD equations are satisfied regarding the projections on the 0, S(ingles) and D(oubles) manifolds. In the subsequent step, a diagrammatic argument is invoked to identify

$$\frac{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|k\rangle}{\langle 0|e^{\hat{T}^\dagger} e^{\hat{T}}|0\rangle} = \langle 0|(e^{\hat{T}^\dagger} e^{\hat{T}})_{\text{Linked}}|k\rangle \quad (15)$$

In brief, if one diagrammatically expands $e^{\hat{T}^\dagger} e^{\hat{T}}$ to obtain the pure de-excitation component, many closed parts are obtained that potentially can be factored from the result. The closed

parts precisely cancel between numerator and denominator, due to the exponential nature of the operators. It is important to note that while the identification made is formally exact, the expansion no longer terminates. This is not true for the original fraction, which has a finite expansion related to the number of electrons.

Using the above linked expression, the energy correction takes the form:

$$\delta E = \sum_{k \in T, Q, \dots} \langle 0 | (e^{\hat{T}^\dagger} e^{\hat{T}})_{\text{Linked}} | k \rangle \langle k | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle \quad (16)$$

This expression is explicitly connected because the right-hand term involving $\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ is connected, and a fully closed term is made by contracting this against a linked term, resulting in a connected diagram series. This expression for the energy correction is orbital invariant and rigorously extensive, because of the connectedness. However, it is rather expensive to evaluate accurately, particularly the factor on the left. Approximations are needed, and at this point the derivation starts to be somewhat ambiguous.

Let us consider explicitly various contributions to the Hermitian conjugate of the factor on the left:

$$\begin{aligned} & \langle k | (e^{\hat{T}^\dagger} e^{\hat{T}})_{\text{Linked}} | 0 \rangle \\ &= \langle k | \left(1 + \hat{T}_1^\dagger + \hat{T}_2^\dagger + \frac{1}{2} \hat{T}_1^{\dagger 2} + \dots \right) \\ & \quad \left(\tilde{T}_1 \tilde{T}_2 + \tilde{T}_3 + \tilde{T}_4 + \frac{1}{2} \tilde{T}_2^2 + \tilde{T}_3 \tilde{T}_2 + \dots \right) | 0 \rangle_{\text{Linked}} \end{aligned} \quad (17)$$

The exact \tilde{T} operator will have to be approximated (by low-order perturbation theory), and it is expected to contain the missing higher-rank cluster operators. This point will be addressed later. Moreover, $e^{\hat{T}} | 0 \rangle$ needs to be at least as highly excited as $| k \rangle$, and more highly so for terms in which the \hat{T}^\dagger operators are included. In this work, we will limit ourselves to the simplest approximations that provide reasonable results for even highly correlated systems, e.g. in the bond-breaking regime. Let us focus on a triples correction, so that $\langle k | \rightarrow \langle \Phi_{ijk}^{abc} |$. Moreover, let us assume for the moment that \hat{T}_1^\dagger is small and can be neglected. In that case, the expression (to leading orders) reduces to

$$\begin{aligned} & \langle k | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle_{\text{Linked}} \\ &= \langle k | (\tilde{T}_1 \tilde{T}_2 + \tilde{T}_3) | 0 \rangle + \langle k | \hat{T}_2^\dagger \tilde{T}_3 \tilde{T}_2 + \dots | 0 \rangle_{\text{Linked}} \end{aligned} \quad (18)$$

The first term is the leading term, while the second term will be approximated using an EPV argument. The second term involves a fivefold excitation $\tilde{T}_3 \tilde{T}_2$, and can be expected to be small in general, except if it is of EPV type, implying that \tilde{T}_3 and \tilde{T}_2 involve the same occupied orbital, such that $\tilde{T}_3 \tilde{T}_2 = 0$. There is a net contribution, however, from this EPV term, because only linked terms are retained. We can write:

$$\begin{aligned} & \langle \Phi_{ijk}^{abc} | \hat{T}_2^\dagger (\tilde{T}_3 \tilde{T}_2)_{\text{EPV}} | 0 \rangle_{\text{Linked}} \\ &= - \langle \Phi_{ijk}^{abc} | \hat{T}_2^\dagger (\tilde{T}_3 \tilde{T}_2)_{\text{EPV}} | 0 \rangle_{\text{Unlinked}} \\ &= - \left[\langle 0 | \hat{T}_2^\dagger \tilde{T}_2 | 0 \rangle \gamma_{ijk}^{abc} \right]_{\text{EPV}} \end{aligned} \quad (19)$$

If, by analogy with Section 2.2, a pair norm $\nu_{ij} = \frac{1}{2} \times \sum_{a,b} t_{ij}^{ab} \tau_{ij}^{ab}$ is defined, the EPV contribution can be written as $-N_{ijk} \gamma_{ijk}^{abc}$,

$$N_{ijk} = \nu_{ij} + \nu_{ik} + \nu_{jk} + \sum_{m \neq i,j,k} (\nu_{im} + \nu_{jm} + \nu_{km}), \quad (20)$$

where care is taken to avoid any double counting. The full renormalized triples correction takes the form:

$$\sum_{i < j < k} (1 - N_{ijk}) \left(\langle 0 | e^{\hat{T}^\dagger} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | e^{-\hat{T}} H e^{\hat{T}} | 0 \rangle \right)$$

$a < b < c$

As in the case of CEPA methods for the correlation energy discussed in Section 2.2, the restriction to EPV terms has the disadvantage that the result is not invariant under rotations of the occupied orbitals. However, as in the previous section, a result can be obtained that is rigorously invariant. Let us define $\mu_i^k = \frac{1}{4} \sum_{j,a,b} t_{ij}^{ab} t_{kj}^{ab}$, and obtain the EPV-like contribution as $-\sum_i (\mu_i^i \tau_{ijk}^{abc} + \mu_j^i \tau_{ilk}^{abc} + \mu_k^i \tau_{ijl}^{abc})$. This contribution is clearly orbital invariant, as the summations are unrestricted. To show that the present prescription amounts to an inclusion of EPV terms, consider an orbital basis in which μ_i^k is diagonal. This can always be done, as the matrix represented by the elements μ_i^k is symmetric (if $\tau_{ij}^{ab} = \tau_{ji}^{ab}$). The orbital invariant formulation in the diagonal basis can then be written as:

$$\begin{aligned} & -M_{ijk} \tau_{ijk}^{abc}; \quad M_{ijk} = \mu_i^i + \mu_j^j + \mu_k^k = \nu_{ij} + \nu_{ik} + \nu_{jk} \\ & + \frac{1}{2} \sum_{m \neq i,j,k} (\nu_{im} + \nu_{jm} + \nu_{km}) \end{aligned} \quad (21)$$

For a three-electron system the two formulations (Eqs. (20) and (21)) are identical, while they will differ for general multi-electron systems due to the factor of 1/2 in the summation in the orbital invariant formulation. If a small set of occupied orbitals dominates in the triple excitation amplitudes, the results can be expected to be similar. As in the previous section, it is convenient to define a one-particle normal-ordered operator $\hat{\mu} = \sum_{i,j} \mu_i^j \hat{t}_{ij}^\dagger$, and then the EPV diagrams can be evaluated as $\langle k | \hat{\mu} \tilde{T}_3 | 0 \rangle$, where the minus sign will emerge due to the contraction over the hole line.

In actual test calculations, it transpired that this approximation (using either the M or the N renormalization factor) is not good enough in the bond-breaking regime, as the factor N_{ijk} (or M_{ijk}) can become rather large. It works better to replace $(1 - N_{ijk})$ by $1/(1 + N_{ijk})$ or $\exp(-N_{ijk})$. The denominator form is reminiscent of the numerator-denominator connected form of Kowalski and Piecuch [22,23]. In our (granted, limited) experience the exponential factor seems to work somewhat better. In this case, the full term $\langle k | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle_{\text{Linked}}$ is represented

by $\langle k | e^{\hat{\mu}} e^{\hat{T}} | 0 \rangle$, which includes both the EPV and the leading non-EPV terms.

Let us summarize the precise working equations for the renormalized triples corrections for the CCSD method in the present formulation, including now also the singles excitations.

Define

$$\mu_i^k = \frac{1}{4} \sum_{j,a,b} [(t_{ij}^{ab} + t_i^a t_j^b) t_{kj}^{ab} + t_k^a t_j^b t_{ij}^{ab}] + \sum_a t_i^a t_k^a \quad (22)$$

This matrix is diagonalized to obtain eigenvalues λ_i and a corresponding set of rotated occupied orbitals. The eigenvalues of $\hat{\mu}$ are all greater than or equal to zero. In this basis of occupied orbitals in which $\hat{\mu}$ is diagonal, one calculates $L_{ijk}^{abc} = \langle \Phi_{ijk}^{abc} | e^{\hat{T}} | 0 \rangle$, $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$, where the triples are given by second order perturbation theory

$$\langle \Phi_{ijk}^{abc} | [\hat{H}_0, \hat{T}_3] + [\hat{V}, \hat{T}_2] | 0 \rangle = 0 \quad (23)$$

In the full triples moment correction, denoted $\langle M3 \rangle$, one obtains

$$R_{ijk}^{abc}(M3) = \langle \Phi_{ijk}^{abc} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle, \quad (24)$$

while in the somewhat simpler $\langle T \rangle$ approach the lowest second-order contribution

$$R_{ijk}^{abc}(T) = \langle \Phi_{ijk}^{abc} | [\hat{V}, \hat{T}_2] | 0 \rangle, \quad (25)$$

is calculated, which is also required in the calculation of t_{ijk}^{abc} , and this economizes the calculation. The renormalized triples corrections for the CCSD method are then defined as

$$E(\text{RCCSD} \langle T \rangle) = E_{\text{CCSD}} + \sum_{\substack{i < j < k \\ a < b < c}} e^{-(\lambda_i + \lambda_j + \lambda_k)} L_{ijk}^{abc} R_{ijk}^{abc}(T) \quad (26)$$

and

$$E(\text{RCCSD} \langle M3 \rangle) = E_{\text{CCSD}} + \sum_{\substack{i < j < k \\ a < b < c}} e^{-(\lambda_i + \lambda_j + \lambda_k)} L_{ijk}^{abc} R_{ijk}^{abc}(M3) \quad (27)$$

Test results for the $\text{RCCSD} \langle T \rangle$ and $\text{RCCSD} \langle M3 \rangle$ methods are to be reported in the future.

In this work, the calculation of \hat{T}_1 and $\hat{T}_2 (= \hat{C}_2)$ is based on p-XCISD, and this gives rise to an additional term in the p-RXCISD $\langle T \rangle$ and p-RXCISD $\langle M3 \rangle$ energy formulas. Using the same starting point as in Eq. (14), we note that the projection of \hat{H} onto double excitations does not vanish. There would be a (small) doubles residual as we do not solve the CCSD equations. The singles residual is zero in p-XCISD, however, as the equations are the same as in CCSD. The non-zero projection gives rise to a ‘doubles’ correction to the energy

$$\delta E(D) = \sum_{i < j, a < b} \langle 0 | (e^{\hat{T}} e^{\hat{T}^\dagger})_{\text{Linked}} | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle \quad (28)$$

in analogy to Eq. (16). This correction is evaluated by defining

$$L_{ij}^{ab} = \langle \Phi_{ij}^{ab} | e^{\hat{T}} | 0 \rangle, \quad \tilde{T} = \hat{T}_1 + \hat{T}_2 \quad (29)$$

$$R_{ij}^{ab}(M2) = \langle \Phi_{ij}^{ab} | e^{-\tilde{T}} \hat{H} e^{\tilde{T}} | 0 \rangle \quad (30)$$

and the result is transformed to the basis of occupied orbitals in which the norm-correction matrix $\hat{\mu}$ is diagonal, as before. The overall renormalized p-XCISD energy corrections are then given as

$$\begin{aligned} E(\text{p-RXCISD} \langle T \rangle) &= E_{\text{XCISD}} + \sum_{\substack{i < j \\ a < b}} e^{-(\lambda_i + \lambda_j)} L_{ij}^{ab} R_{ij}^{ab}(M2) \\ &+ \sum_{\substack{i < j < k \\ a < b < c}} e^{-(\lambda_i + \lambda_j + \lambda_k)} L_{ijk}^{abc} R_{ijk}^{abc}(T) \end{aligned} \quad (31)$$

and

$$\begin{aligned} E(\text{p-RXCISD} \langle M3 \rangle) &= E_{\text{XCISD}} + \sum_{\substack{i < j \\ a < b}} e^{-(\lambda_i + \lambda_j)} L_{ij}^{ab} R_{ij}^{ab}(M2) \\ &+ \sum_{\substack{i < j < k \\ a < b < c}} e^{-(\lambda_i + \lambda_j + \lambda_k)} L_{ijk}^{abc} R_{ijk}^{abc}(M3) \end{aligned} \quad (32)$$

The evaluation of the doubles part of the energy correction in p-XCISD requires the evaluation of the full CCSD residual vector, and this seems to imply that our sought for computational gains in local correlation and parallel calculations, as discussed in the introduction, are compromised. However, regarding parallelization, it seems advisable to distribute the t -amplitudes over all nodes before evaluating the triples correction, and so there are no extra communication costs related to the doubles evaluation. In local correlation approaches the issue of truncating intermediates does show up, but one can hope that the evaluation of the small quadratic correction term to the energy (of fourth order in typically small quantities) is not very sensitive to the truncation algorithm employed. At any rate the discussion is somewhat premature at this point of the development.

It may be pertinent to explain our nomenclature and to describe connections with other work. The bracket notation is used to denote energy corrections that are derived from an expectation value point of view, as in the starting point of the derivation (Eq. (14)). The $\langle T \rangle$ correction is closest to the $\langle T \rangle$ correction in CCSD $\langle T \rangle$, and to the so-called renormalized

corrections of Kowalski and Piecuch [12]. The difference with CCSD(*T*) is the use of

$$L_{ijk}^{abc} = t_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 | 0 \rangle \quad (33)$$

rather than the use of

$$L_{ijk}^{abc} = t_{ijk}^{abc} + \frac{1}{(\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c)} \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{V} | 0 \rangle, \quad (34)$$

as in CCSD(*T*). The latter can be viewed as a perturbative approximation to the singles term included in the $\langle T \rangle$ correction. Moreover, this term arises very naturally in the present derivation, while it is included in a somewhat ad hoc fashion in CCSD(*T*). The second type of triples correction, using the full moment of the CC equations $e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle$ projected on the triple excitations is denoted $\langle M3 \rangle$, in which M3 refers to the ‘triples moment’. Such an approach would be called a completely renormalized correction in the nomenclature by Piecuch et al. [12]. Using the present notation, it is fairly easy to designate precise definitions for higher order extensions, e.g. CCSD(*TQ*) or CCSD(*M3M4*). The above approaches would not yet be called renormalized, however.

The renormalization refers to the inclusion of the $e^{-\mu}$ (or $e^{-\lambda_i - \lambda_j - \dots}$) factor in our approach, while in the approaches by Kowalski and Piecuch [12] a denominator occurs, either of which serve to damp the growing perturbative triples correction in the bond breaking regime. In our nomenclature we use ‘R’ (e.g. RXCISD(*T*)) to indicate the inclusion of the renormalization factor. It may be noted that for well-behaved molecules around their equilibrium geometry, this renormalization factor is close to unity. The size-extensivity of the formula plays an important role here, as this statement is also true for very large molecules, which cause troubles for the original formulation of Kowalski et al., in which the renormalization factor included the complete norm, which can grow indefinitely and is the cause of the size-extensivity error.

The approaches have been implemented in the NWChem code [75] using the Tensor Contraction Engine developed by So Hirata [76,77] and building on the previous implementations of renormalized triples corrections by Hirata et al. [17]. In the current implementation, a particular block of triples amplitudes is obtained in memory, the transformation of the occupied labels to the μ -diagonal basis is carried out explicitly for all needed quantities, and the energy correction is then evaluated. The μ -diagonal basis retains the symmetry blocking of the original MO basis, which is an advantage over transformations to a local basis, which is needed in the NDC approach of Kowalski and Piecuch [22]. Moreover, results are invariant to degenerate rotations in the μ -diagonal basis, and this is an advantage for highly symmetric molecules. The scheme is stable and simple.

3. Benchmark results

In this section, benchmark results are presented for the p-XCISD approach and for the p-RXCISD(*T*), p-RXCISD(*M3*) and p-RBXCISD(*T*) approaches with renormalized triples

corrections for a variety of diatomic molecules, which exhibit a variety of binding characteristics. The results are compared to CCSDT results obtained either using the ACES2 [78] or NWChem [75] electronic structure packages, which provide sufficiently accurate reference values. In addition, we report CCSD and CCSD(*T*) results to enable comparisons with standard approaches. Table 1 below lists the diatomics considered, the basis set used for each, the ranges of internuclear distance considered, and a brief characterisation of the chemical binding and computationally interesting features of each species. Typically, the 1s core orbitals are dropped from the calculations, except for calculations involving Be. Also, for BF, BN and CN the core orbitals are included in the correlated calculations. For these species, Brueckner CCSDT calculations are performed because single excitations are large, and in the current version of ACES2, Brueckner CCSDT calculations require that the core orbitals be included in the calculation. In Table 1, this information on the frozen cores is included. For some molecules (HF, F₂, Be₂) a large portion of the potential energy curve (PEC) is scanned, but for most molecules only a limited range of the PEC is calculated, sufficient to obtain the lowest nine vibrational levels, with the exception of CN and BN, as will be discussed below. As will be evident from our results, the methodology is certainly not good enough to calculate complete potential energy curves, except for some relatively simple systems.

To analyse the extensive output from the calculations and to obtain an estimate of the accuracy and limitations of the XCI approaches, we proceed as follows. A first topic of interest is the comparison of CCSD with p-XCISD. Neither of these methods provides quantitative potential energy curves, and it therefore suffices to graphically compare the PEC at the CCSD,

Table 1
Diatomics included in the test set, and basic computational information

Diatomic	Basis set	Frozen core	R interval (Å)	Characteristics
HF	cc-pVDZ [79]	y	0.6–5.0	Single bond/ ionic-covalent
BF	6-311++ G(3DF,2DP) [80]	n	1.0–2.0	Single bond/ionic
F ₂	aug-cc-pVDZ [79]	y	1.0–5.0	Single bond/ covalent
BeO	6-311++ G(3DF,3PD) [80]	n	1.1–1.6	Ionic bond, large single excitations
BN	aug-cc-pVDZ [79]	n	1.0–1.6	Multiple bond, ionic, large singles
N ₂	aug-cc-pVDZ [79]	y	0.9–1.5	Triple bond, covalent
C ₂	aug-cc-pVDZ [79]	y	1.2–3.0	Double bond, strong correlation
Be ₂	6-311++ G(3DF,2DP) [80]	n	2.0–6.0	Van der Waals
CN	aug-cc-pVDZ [79]	n	0.9–1.4	Multiple bonded radical, large singles
O ₂	aug-cc-pVDZ [79]	y	1.0–1.7	Triplet state, covalent

p-XCISD and CCSDT levels for a number of representative molecules. A second topic concerns the quantitative comparison of the methods including triples corrections. Since, the curves themselves are close together, graphs containing the respective PECs would be hard to read, and therefore the difference in energy is displayed between the benchmark CCSDT results and the CCSD(*T*), p-RXCISD(*T*), p-RXCISD(*M3*) and p-RBXCISD(*T*) results, again using a representative set of examples. In a third group of comparisons, the PEC for each method and molecule included in the test set is used to obtain the lowest nine vibrational energy levels by solving the one-dimensional nuclear Schrödinger equation using Level 7.7 [72]. These nine lowest levels are fitted to a Dunham-type polynomial expansion [71] in $(\nu + 1/2)$. Moreover, the expectation value of $1/R^2$ is calculated for each vibrational level and used to obtain a fit of the average rotational constants as functions of $(\nu + 1/2)$. All of these calculations are carried out using the Level 7.7 suite of programs. The fitting procedure is exactly the same for each method applied to a given molecule, and hence the expansion coefficients obtained using the various electronic structure methods provide a proper comparison. These data are quite sensitive to the quality of the potentials, and provide a proper gauge of the methodology. The results will be discussed in three sections.

3.1. Comparison of potential energy curves at the CCSD and p-XCISD levels with the reference CCSDT PEC

In Fig. 1, the PEC comparison for the HF molecule is shown over a wide range of the internuclear distance. Both CCSD and p-XCISD provide smooth and qualitatively correct curves. Near the equilibrium geometry CCSD and p-XCISD are very close, but p-XCISD behaves significantly better near the asymptote. At 3.8 Å the energy difference with CCSDT is 24 mH for the CCSD approach and 7.5 mH for p-XCISD. Near equilibrium (e.g. $R=0.9$ Å) the CCSD error is 2.0 mH while p-XCISD is in error by 2.5 mH; hence, the parallelity error in p-XCISD is significantly reduced compared to CCSD for the

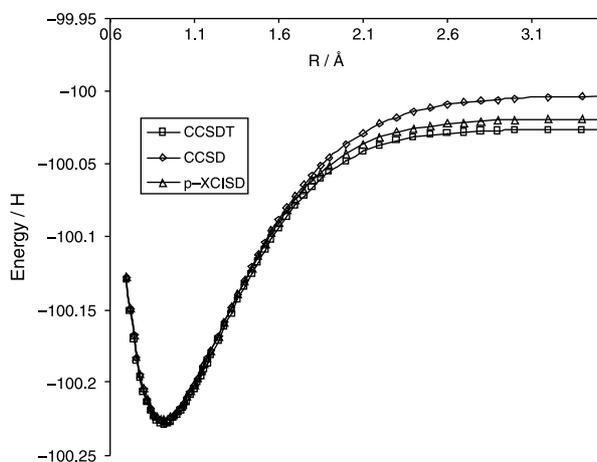


Fig. 1. Comparison of CCSD, p-XCISD and CCSDT potentials for the HF molecule in the cc-pVDZ basis set.

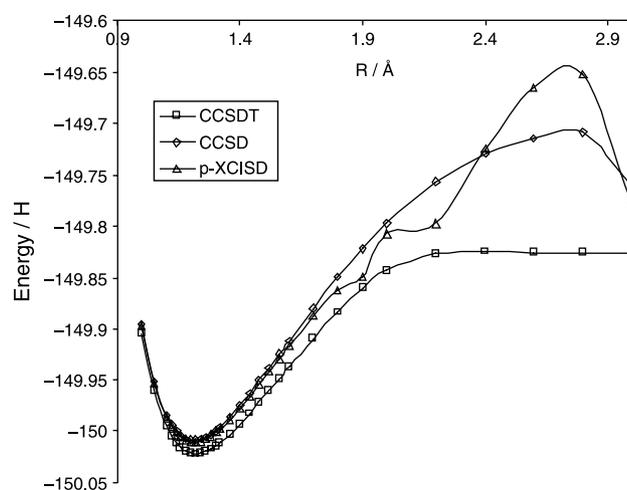


Fig. 2. Comparison of the CCSD, p-XCISD and CCSDT potentials for the O₂ molecule in the aug-cc-pVDZ basis set.

HF molecule. The results for the BF molecule (not shown) over a limited range of geometries indicate a similar good comparison between CCSD and p-XCISD, with curves running fairly parallel to the CCSDT benchmark. This will be confirmed by the Dunham coefficient analysis in Section 3.3.

In Fig. 2, the results for the triplet O₂ molecule are shown, illustrating prototypical behaviour that is also found for the N₂, BN, and BeO molecules (not shown). Near the equilibrium geometry, the CCSD and p-XCISD curves run fairly parallel, with p-XCISD being somewhat lower in energy than CCSD. However, at larger internuclear distances the p-XCISD method shows distinctly erratic oscillatory behaviour. The CCSD result is also not good at these geometries, but the result is far smoother than for p-XCISD. From this, we tentatively conclude that p-XCISD is less robust than CCSD when electron correlation effects are large.

Fig. 3 shows results for the F₂ molecule. The p-XCISD method shows distinctly erratic behaviour fairly close to the equilibrium geometry, between 1.5 and 2 Å, as emphasised in the inset of Fig. 3. This erroneous behaviour will be even

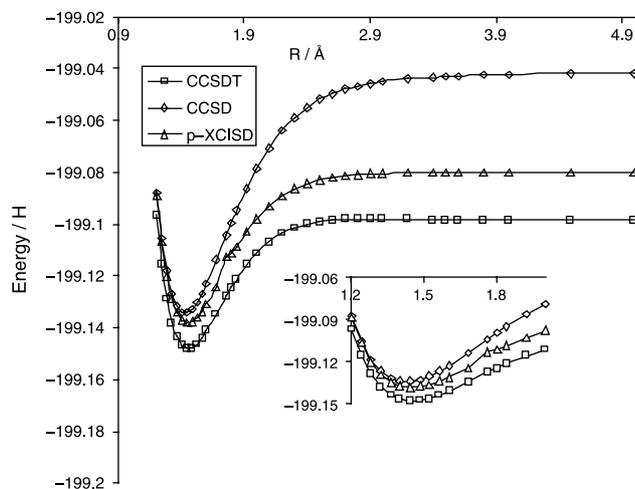


Fig. 3. Comparison of the CCSD, p-XCISD and CCSDT potentials for the F₂ molecule in the aug-cc-pVDZ basis set.

Table 2
Largest t_2 -amplitudes at various geometries for the F_2 molecule

	$R=1.40$	$R=1.56$	$R=1.76$	$R=2.00$	$R=4.00$
CCSDT	-0.134	-0.252	-0.389	-0.551	-0.996
	-0.086	-0.082	-0.080	-0.082	
			-0.050		
			-0.030		
p-XCISD	-0.131	-0.248	-0.388	-0.546	-0.9838
	-0.084	-0.080	-0.080	-0.082	
			-0.220		
			-0.216		
CCSD	-0.120	-0.220	-0.328	-0.454	-0.839
	-0.078	-0.073	-0.070	-0.071	

A comparison of the CCSDT, p-XCISD and CCSD results.

clearer if connected triple corrections are considered, as is shown in Section 3.2. Interestingly, in the asymptotic region the p-XCISD method is relatively well behaved, and the error (19 mH) is significantly smaller than for CCSD (57 mH). It is interesting to make a more detailed comparison of the largest t -amplitudes obtained at the CCSD, p-XCISD and CCSDT levels. These are reported in Table 2 for five different geometries (in Å).

The largest t_2 amplitudes describe the double excitation from the bonding σ_g to the antibonding σ_u orbital. The second coefficient, which is more or less constant at a value of -0.08 , is a similar double excitation into a higher lying σ_u orbital. Relative to CCSDT, the p-XCISD approach describes these coefficients better than does CCSD. However, in the troublesome region other coefficients in p-XCISD attain large values (-0.220 and -0.216), which correspond to a double excitation of the π orbitals into the antibonding σ_u orbital. These amplitudes never rise to a magnitude greater than 0.05 in the CCSDT calculations. This appears to be some kind of ‘singularity’ in the p-XCISD calculations that only shows up in a limited region of the potential. The effect is quite deleterious, however, and is poorly understood at the moment. Let us emphasize that this breakdown of the p-XCISD approach occurs where the wave function has substantial multireference character.

These results raise some other questions. The inclusion of triples would appear to be needed to achieve the proper primary double-excitation coefficients, gauging from a comparison of CCSD and CCSDT. However, the breaking of a single bond would naively be expected to be a two-electron phenomenon, and this is in fact confirmed by the p-XCISD results in which only disconnected triples play a (minor) role. The accurate asymptotic behaviour of p-XCISD is more intuitive than the CC result, and may point to an imbalance in CC theory itself. Unfortunately, this argument is far from convincing, as p-XCISD itself shows very anomalous behaviour in a limited, but important region of the PEC. While we shall not resolve this issue here, we can conclude that once again p-XCISD behaves erratically if electron correlation effects are large.

As our last example in this section, we consider the Be dimer. The basis set used is fairly large, yet inadequate to accurately describe the bonding in this weakly interacting

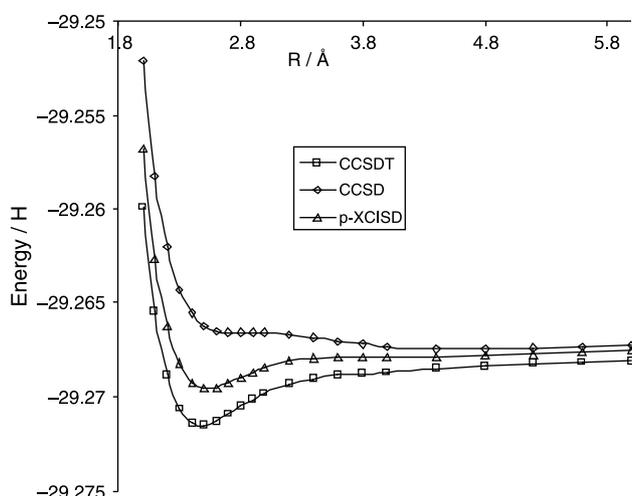


Fig. 4. Comparison of the CCSD, p-XCISD and CCSDT potentials for the Be_2 molecule in the 6-311++G(3DF,3DP) basis set.

system. As before, the focus is on the difference between accurate CCSDT results and CCSD and p-XCISD values, as depicted in Fig. 4. Interestingly, p-XCISD provides a qualitative description of the bonding, while CCSD is qualitatively in error predicting that the energy is lowest in the separated limit.

3.2. A comparison of $CCSD(T)$, $p-RXCISD(T)$, $p-RXCISD(M3)$, $p-RBXCISD(T)$ with $CCSDT$ potential energy curves for selected diatomics

Again, some representative examples are shown to examine the behaviour of the triples correction. In Fig. 5, the difference with respect to the CCSDT energy reference values are shown (in mH) for the HF molecule in the cc-pVDZ basis set. As is well established, the $CCSD(T)$ energy deteriorates as the bond breaks, at around 2 Å, and the energy difference with CCSDT

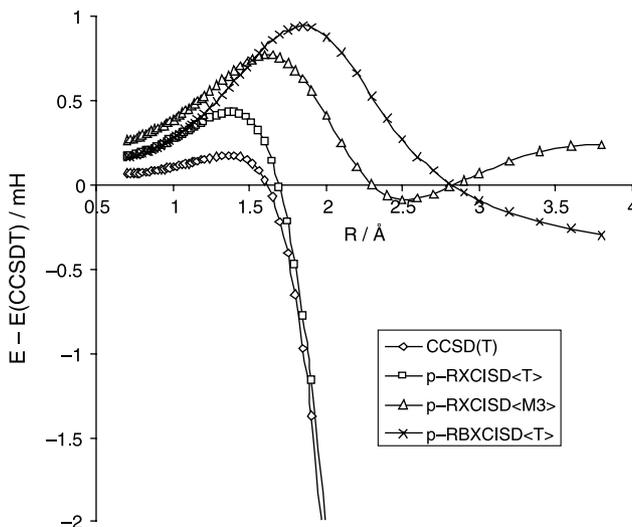


Fig. 5. Differences between $CCSD(T)$, $p-RXCISD(T)$, $p-RXCISD(M3)$, and $p-RBXCISD(T)$ results and $CCSDT$ total energies for the HF molecule in the cc-pVDZ basis set.

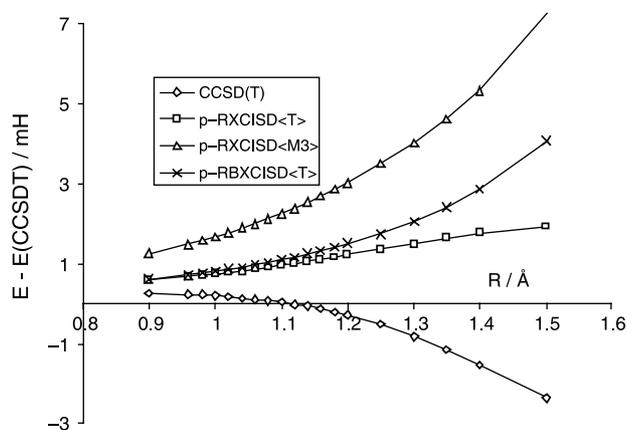


Fig. 6. Differences between CCSD(*T*), p-RXCISD(*T*), p-RXCISD(*M3*) and p-RBXCISD(*T*) results and CCSDT total energies for the N_2 molecule in the aug-cc-pVDZ basis set.

continues to grow negatively as R increases. Somewhat to our surprise, the p-RXCISD(*T*) method is almost as poorly behaved. At 3.8 Å the CCSD(*T*) error is -32 mH, compared to -17 mH at the p-RXCISD(*T*) level. In contrast, the p-RXCISD(*M3*) method, including the completely renormalized triples correction, is well-behaved and shows absolute errors less than 1 mH for the entire range of internuclear distances, the error being largest at intermediate bond distances. Results of a similar high quality are obtained using Brueckner orbitals, employing a (*T*) renormalized triples correction in the p-RBXCISD(*T*) approach. These results indicate that the single excitation coefficients require a delicate treatment in the triples correction. At the Hartree–Fock level the HF molecule separates erroneously to the ionic limit of $H^+ + F^-$, and consequently orbital rotation effects as described by the t_1 coefficients are important. From our results, we conclude that at least for the HF molecule the (*M3*) triples correction is essential to achieve accurate results if Hartree–Fock orbitals are employed, while the (*T*) triples correction suffices if Brueckner orbitals are used.

Fig. 6 shows the same comparisons for the N_2 molecule. All methods behave reasonably well for a limited range of internuclear separation (0.9–1.4 Å), and then rapidly deteriorate. Similar behaviour is observed for the O_2 molecule. For BF (not shown) the CCSD(*T*) results, with errors of consistently about 0.3 mH, are superior to those in p-RXCISD(*T*) and p-RBXCISD(*T*), whose errors range between 0.5 and 1.2 mH, which are in fact more typical ranges for the errors.

Fig. 7 shows the comparisons for the BeO molecule, using Brueckner CCSDT as a reference. It is evident that the results from all of the p-RXCISD triples methods are superior to the CCSD(*T*) results, as the error curves are considerably flatter. The BeO molecule has fairly large single excitation amplitudes, but for this case they apparently do not influence much the parallelism of the PEC comparing the p-RXCISD(*T*) or p-RXCISD(*M3*) levels of accuracy.

In Fig. 8, the PEC differences are displayed for the BN molecule. These error curves show a very distinct difference between CCSD(*T*) on the one hand and the RXCISD(*T*),

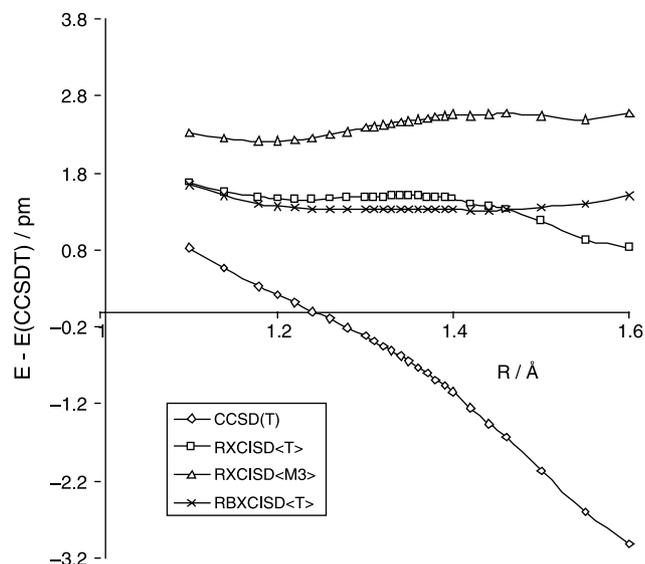


Fig. 7. Differences between CCSD(*T*), p-RXCISD(*T*), p-RXCISD(*M3*) and p-RBXCISD(*T*) results and CCSDT total energies for the BeO molecule in the 6-311 + +G(3DF,2DP) basis set.

RXCISD(*M3*) and RBXCISD(*T*) approaches on the other. The (restricted) Hartree–Fock reference provides a relatively poor description of the BN molecule, and this is hard to correct completely by inclusion of correlation. Once orbitals are optimized in the presence of dynamical correlation using Brueckner theory, BN becomes a more well-behaved system, at least for the limited range of geometries shown, as is clearly indicated by the p-RBXCISD(*T*) deviation curve in Fig. 8, which depicts that the corresponding potential energy curve is quite parallel to the CCSDT result for internuclear distances between 1 and 1.5 Å.

The results for the CN radical are shown in Fig. 9. Here again somewhat of a difference is observed between CCSD(*T*)

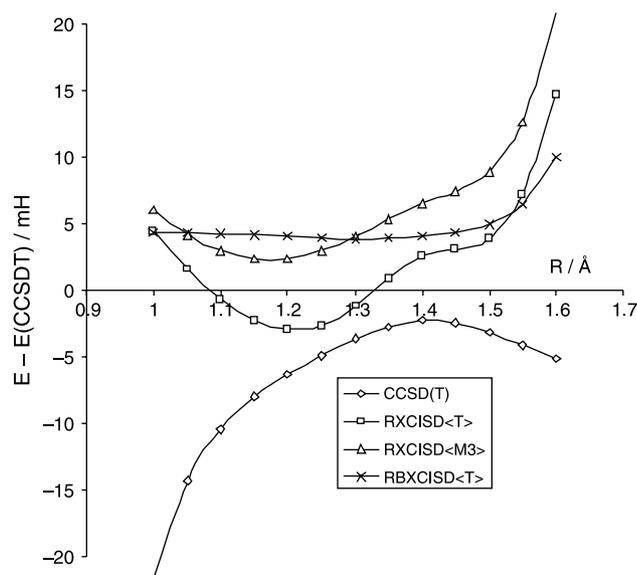


Fig. 8. Differences between CCSD(*T*), p-RXCISD(*T*), p-RXCISD(*M3*) and p-RBXCISD(*T*) results and CCSDT total energies for the BN molecule in the aug-cc-pVDZ basis set.

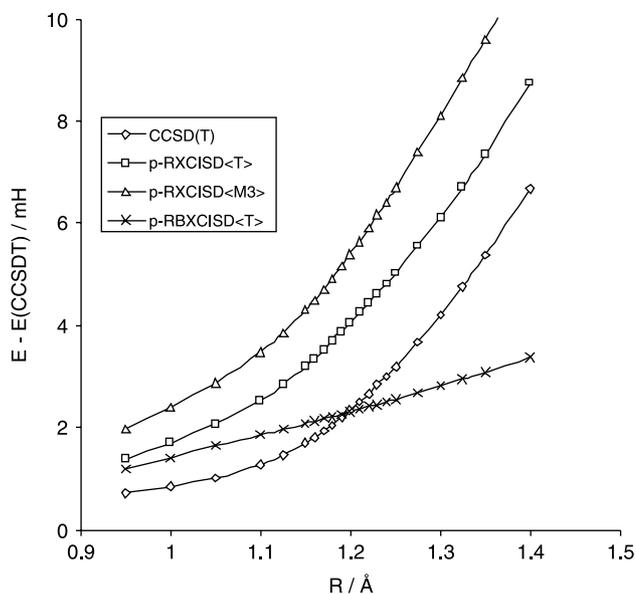


Fig. 9. Differences between CCSD(T), p-RXCISD(T), p-RXCISD(M3) and p-RBXCISD(T) results and CCSDT total energies for the CN radical in the aug-cc-pVDZ basis set.

and p-RXCISD(T)/p-RXCISD(M3) on the one hand, and the Brueckner based p-RBXCISD(T) on the other hand. The error curve for p-RBXCISD(T) is much better behaved compared to the others, indicating the importance of single excitations and the effectiveness of the use of Brueckner orbitals to stabilize the triples correction.

Our last example in this section is our *bête noir*, the F_2 molecule. As shown in Fig. 10, for the p-RXCISD(T) and p-RBXCISD(T) approaches the energy-deviation curves show large errors for a wide range of distances between 1.5 and 2.5 Å, and a sharp peak near 1.7 Å. The resulting potentials are clearly useless for applications in vibrational spectroscopy (see

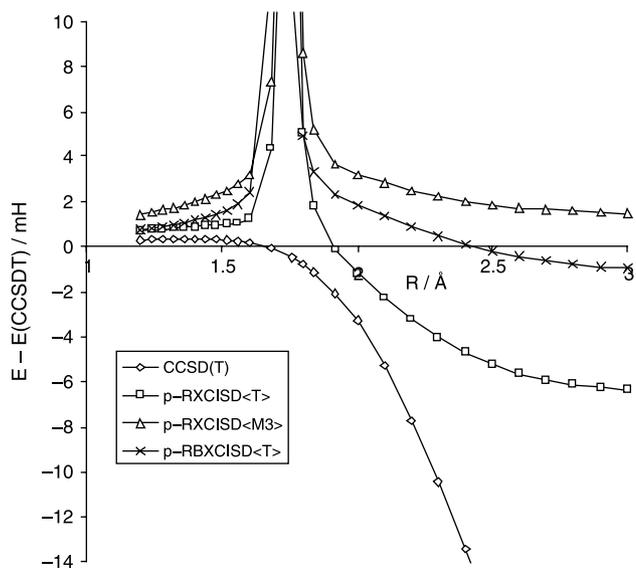


Fig. 10. Differences between CCSD(T), p-RXCISD(T), p-RXCISD(M3) and p-RBXCISD(T) results and CCSDT total energies for the F_2 molecule in the aug-cc-pVDZ basis set.

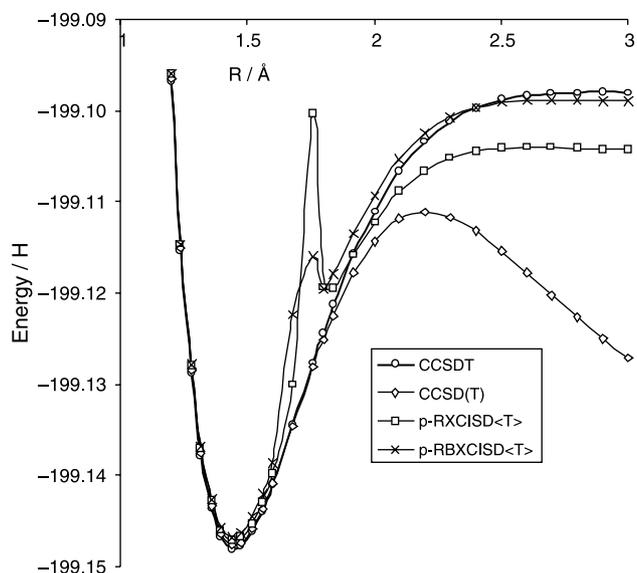


Fig. 11. Potential energy curves for the F_2 molecule obtained using the CCSDT, CCSD(T), p-RXCISD(T), and p-RBXCISD(T) methods and the aug-cc-pVDZ basis set.

Fig. 11). Most of this erratic behaviour should be attributed to the p-XCISD result for F_2 , as discussed before. Interestingly, the energy corrections at the troublesome geometries are positive, and this due to the doubles contribution to the energy correction (see Eqs. (31) and (32)). The triples correction itself is always negative. These results provide an indication that if the amplitudes in p-XCISD and CCSD are significantly different, then we can expect a large contribution to the energy corrections, from the doubles term and likely poor results. Note that the CCSD(T) potential energy curves for F_2 are quite reasonable out to about 2 Å, after which the method breaks down completely.

Similarly poor results are obtained for the C_2 molecule (not shown). The C_2 molecule is another example for which non-dynamical correlation effects are large for most internuclear distances, and p-XCISD has severe troubles coping with this situation.

3.3. Dunham analysis of vibrational frequencies and a comparison of CCSD(T), p-RXCISD(T), p-RXCISD(M3), and p-RBXCISD(T) to CCSDT

The potential energy curves for the molecules and basis sets described in Table 1 are used in vibrational energy calculations, except for F_2 and C_2 , for which no reasonable results are obtained using the p-XCISD method. Using the Level 7.7 program, the nine lowest vibrational levels in the $J=0$ rotational state are obtained by numerical solution of the radial Schrödinger equation on a grid. Computational parameters (the radial mesh and interpolation scheme) were chosen such that stable numerical results are obtained. The vibrational wave functions are used to calculate the expectation value of $1/R^2$ for each vibrational level, which in turn defines the rotational constant $B_v = \hbar^2/2\mu\langle 1/R^2 \rangle$, where μ is the reduced mass of the diatomic molecule. The nine lowest

vibrational energy levels are fitted to a polynomial in a Dunham expansion

$$E_v = E_0 + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots$$

and the B_v constants to the expression

$$B_v = B_e - \alpha_e(v + 1/2) + \gamma_e(v + 1/2)^2 + \dots$$

where all parameters and energies are expressed in per centimetre. The E_0 constant is of no particular importance, and is essentially arbitrary if no accurate value for the large R asymptote of the potential is available, as is the case in our examples. Comparison of the results of fits of various orders showed that (at best) stable values could only be determined for the two leading coefficients of each type, ω_e and $\omega_e x_e$ for vibration and B_e and α_e for rotation. This procedure for analysing and compressing the data was applied for the HF, BF, BeO, N₂ and O₂ molecules. For the BN molecule and the CN radical the range of internuclear distance for which the electronic structure methods gave reasonable results was too small to obtain nine vibrational levels, or a stable fit of the Dunham parameters. Likewise, for the weakly bound Be dimer the Dunham type compression of the vibrational data was not applicable. The BN and Be₂ molecules will be discussed explicitly below.

Table 3 presents the spectroscopic parameters for the HF, BF, BeO, N₂ and O₂ molecules, for which the Dunham analysis is applicable. Comparing CCSD and p-XCISD, we generally observe close agreement between the two methods, with p-XCISD in general being a little closer to the CCSDT values, particularly for the anharmonicity parameter $\omega_e x_e$ and α_e , which for all five molecules shows some improvement at the p-XCISD level. Comparing the various triples corrections, CCSD(T), p-RXCISD(T), p-RXCISD($M3$), and p-RBXCISD(T), in general good agreement is obtained among the various approaches. At the bottom of Table 3 we have collected statistics, and the various approaches including connected triples corrections are confirmed to behave quite similarly. The p-RBXCISD(T) method is a little more accurate than the others, which is presumably due to the use of Brueckner orbitals. The use of Brueckner orbitals may improve the singles and doubles result, but it also will likely improve the triples correction as all of the (renormalization) terms involving the t_1 amplitudes are zero. The statistical uncertainties for the vibrational anharmonicities $\omega_e x_e$ for p-RXCISD(T) are somewhat poorer than for the other methods, primarily due to the case of BeO.

As was shown in Fig. 7, the errors in the PEC for BeO, are substantially more constant for the XCI approaches than for CCSD(T), and it is of interest therefore to look at the energy

Table 3
Spectroscopic data for selected diatomics and comparison to the reference CCSDT values

Property (cm ⁻¹)	CCSD	p-XCISD	CCSD (T)	p-RXCISD (T)	pR-XCISD ($M3$)	p-RBXCISD (T)	CCSDT
<i>HF molecule, cc-pVDZ basis set</i>							
ω_e	4168	4164	4149	4151	4152	4152	4147
$\omega_e x_e$	90.7	91.9	92.1	92.1	91.9	91.8	92.1
B_e	20.858	20.859	20.816	20.821	20.823	20.822	20.812
α_e	0.798	0.803	0.804	0.804	0.804	0.803	0.805
<i>BF molecule, 6-311++(3DF, 2DP) basis set</i>							
ω_e	1418	1419	1400	1404	1405	1403	1400
$\omega_e x_e$	12.0	12.0	12.2	12.1	12.1	12.2	12.2
B_e	1.5247	1.5251	1.5159	1.5175	1.5181	1.5168	1.5156
α_e	0.0190	0.0191	0.0193	0.0192	0.0192	0.0192	0.0192
<i>BeO molecule, 6-311++(3DF, 2DP) basis set</i>							
ω_e	1533	1541	1432	1457	1465	1464	1466
$\omega_e x_e$	10.9	11.7	12.5	13.4	12.9	11.5	12.5
B_e	1.6559	1.6600	1.6182	1.6283	1.6312	1.6282	1.6284
α_e	0.0176	0.0174	0.0199	0.0200	0.0196	0.0188	0.0187
<i>N₂ molecule, aug-cc-pVDZ basis set</i>							
ω_e	2392	2385	2319	2332	2343	2336	2327
$\omega_e x_e$	13.3	13.7	14.4	14.1	13.8	14.2	14.1
B_e	1.9392	1.9373	1.9165	1.9199	1.9230	1.9207	1.9183
α_e	0.0159	0.0161	0.0168	0.0166	0.0164	0.0165	0.0166
<i>O₂ molecule, aug-cc-pVDZ basis set</i>							
ω_e	1641	1627	1564	1575	1585	1580	1569
$\omega_e x_e$	11.6	12.0	12.5	12.2	12.1	12.2	12.2
B_e	1.4385	1.4350	1.4152	1.4180	1.4208	1.4191	1.4159
α_e	0.0151	0.0154	0.0162	0.0160	0.0158	0.0158	.0160
<i>Average absolute relative deviation from CCSDT (%)</i>							
ω_e	2.65	2.61	0.61	0.32	0.45	0.31	–
$\omega_e x_e$	4.95	2.54	0.92	3.08	1.46	1.80	–
B_e	1.04	1.03	0.16	0.08	0.20	0.10	–
α_e	3.52	2.78	1.90	1.42	1.48	0.53	–

levels in some more detail. Fig. 12 shows the deviations from the benchmark CCSDT results for the vibration dependent rotational constants and the vibrational spacings $\Delta G_{v+1/2} = E_{v+1} - E_v$ for BeO, for all methods considered in Table 3. It is seen that for low energies (up to about $v=5$) the deviation between CCSDT and the XCI methods is small, but the deviations grow for the higher vibrational levels, except for RBXCISD(*T*) which is quite accurate throughout. For the lower energy levels, the triples corrected XCI approaches are more accurate than CCSD(*T*), as anticipated from Fig. 7. The higher vibrational levels sample part of the potential in which the RXCISD(*T*) and RXCISD(*M3*) approaches are less accurate, and CCSD(*T*) appears to be more stable as the bond is stretched. Part of the problem may again be the deviation

between CCSD and XCISD, leading to a relatively large contribution from the doubles correction to the XCISD energy.

Fig. 13 shows the rotational constants and the vibrational energy spacings for the BN molecule for levels up to $v=5$, obtained using various methods. While the data follows a nearly straight line for the CCSDT method, they show substantial curvature for other methods including triples corrections, and it is clear that the data are quite sensitive to the methodology used. None of the methods agree well with the CCSDT results for BN.

Our final example in this section is the Be dimer, whose calculated properties are shown in Fig. 14. The data shows some deviation between CCSD(*T*) on the one hand and the various p-XCISD + perturbative triples methods on the other,

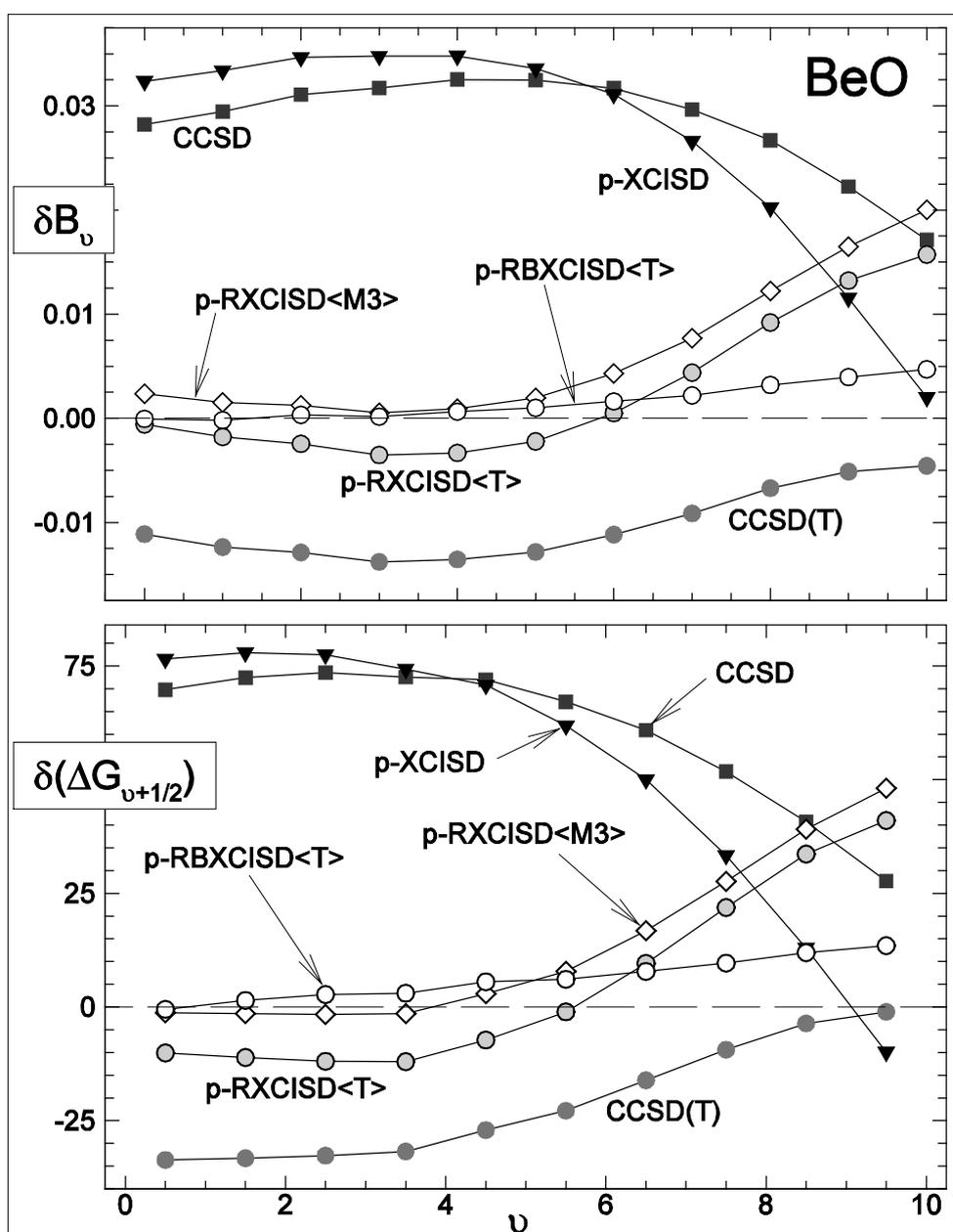


Fig. 12. Deviations (in cm^{-1}) from CCSDT results in 6-311 + +G(3DF,2DP) basis set for the BeO molecule. Top panel: deviations in vibrational dependence of the rotational constant. Bottom panel: deviations in vibrational level spacings.

which all closely lie together. The CCSD(T) curve is closer to the presumably accurate CCSDT curve. Also, the p-XCISD and CCSD data differ appreciably (in agreement with the potential energy curves depicted in Fig. 4). The doubles correction to the XCISD energy plays a substantial role, as there is a fairly large difference between the CCSD and XCISD amplitudes, and one might say that the poor CCSD results plague the energy corrections to XCISD. The basis set is not large enough to allow meaningful comparisons with experiment, but it is clear that the accurate calculation of the potential energy curve for the Be dimer is a challenging problem, and neither CCSD(T) nor p-RXCISD(T) seem to be quite good enough.

From our benchmark calculations we conclude the following. For reasonably well-behaved molecules, p-XCISD typically follows closely the CCSD result. This corroborates the hypothesis that a proper inclusion of the linear terms and the non-linear EPV terms is most important. The remaining non-EPV contributions arising from $\frac{1}{2}T_2^2$ are not nearly as important. However, as the results for the F_2 and the C_2 molecule (not shown) indicate, the p-XCISD method is not very robust when significant electron correlation occurs, and results quickly become erratic. This is also evident at the large R limits for many of the molecules in this study (O_2 was shown

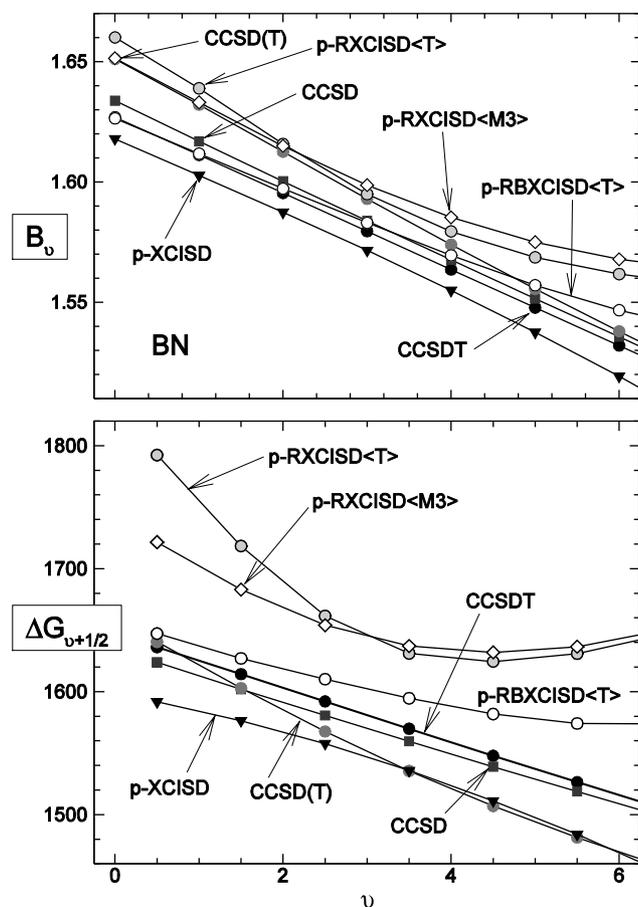


Fig. 13. Vibrational dependence of the rotational constant (in cm^{-1}) and the energy spacing between vibrational levels (in cm^{-1}) for the BN molecule (aug-cc-pVDZ basis).

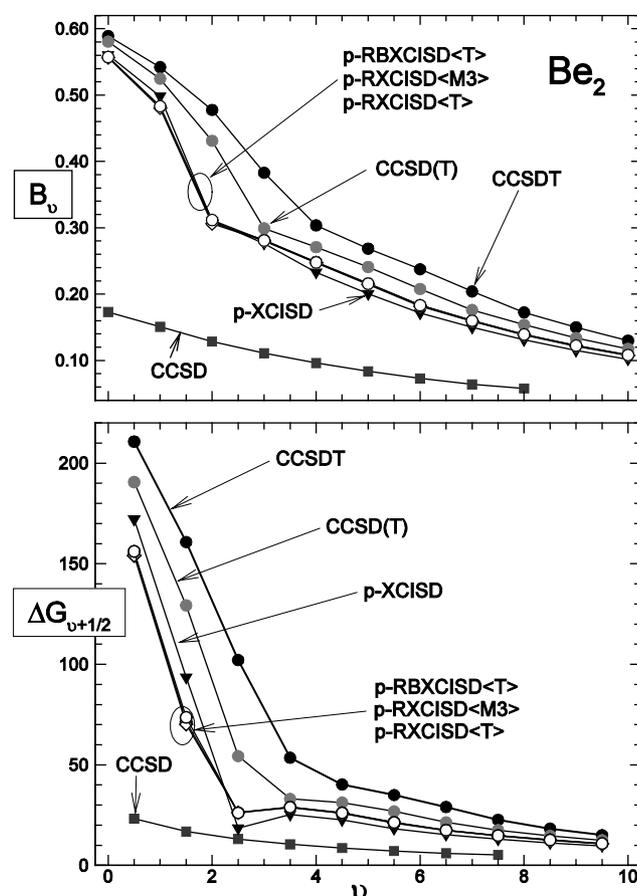


Fig. 14. Vibrational dependence of the rotational constant (in cm^{-1}) and the energy spacing between vibrational levels (in cm^{-1}) for the Be dimer (6-311++G** basis).

as an explicit example). F_2 is a curious molecule in this regard, as the large- R limit of p-XCISD is more accurate than CCSD, while the p-XCISD methodology clearly has troubles at intermediate distances. Likewise, for the HF molecule p-XCISD provides significantly better results at large R than does CCSD. Another interesting case is the Be dimer, for which CCSD results are surprisingly poor while p-XCISD results are reasonable.

Regarding the triples corrections, the comparison between renormalized triples corrections vs. the original triples corrections is somewhat obscured because p-RXCISD(T) is compared with CCSD(T). There are some cases in which the renormalized triples corrections are clearly effective, in particular for HF (if Brueckner orbitals are used or the completely renormalized correction is employed) and for F_2 at large internuclear distances. Also, for BeO the results are clearly much improved, particularly if Brueckner orbitals are used. It is unlikely, however, that the renormalized triples corrections have sufficient accuracy from a spectroscopic point of view for more highly correlated systems such as N_2 or BN at larger internuclear distances. It is worth emphasizing, however, that we have seen several examples where the use of Brueckner orbitals substantially improves the triples corrections, notably, HF, BeO, CN and BN.

Table 4
Comparison of calculated p-RXCISD(*T*) and p-RXCISD(*M3*)/aug-cc-pV[TZ/QZ] and experimental vibrational spacings ($J=0$) for the HF molecule (all quantities in cm^{-1})

<i>V</i>	Experimental		RBXCISD(<i>T</i>)		RBXCISD(<i>M3</i>)	
	Total energy	Vibrational spacing	Vibrational spacing	Deviation	Vibrational spacing	Deviation
0	2050.8					
1	6012.2	3961.4	3990.9	29.5	3995.2	33.7
2	9801.6	3789.4	3817.9	28.5	3822.2	32.8
3	13423.6	3622.0	3650.3	28.3	3654.6	32.6
4	16882.4	3458.8	3488.0	29.1	3492.2	33.4
5	20181.7	3299.3	3330.2	30.9	3334.4	35.1
6	23324.5	3142.8	3176.0	33.2	3180.2	37.4
7	26313.0	2988.5	3024.3	35.8	3028.6	40.1
8	29148.7	2835.7	2874.2	38.4	2878.6	42.9
9	31832.2	2683.5	2724.6	41.1	2729.2	45.8
10	34362.7	2530.5	2574.2	43.7	2579.4	48.9
11	36738.2	2375.5	2421.7	46.2	2427.6	52.1
12	38954.8	2216.6	2264.9	48.3	2272.1	55.6
13	41006.4	2051.7	2101.5	49.8	2110.7	59.0
14	42884.3	1877.9	1927.8	49.9	1940.0	62.2
15	44575.9	1691.6	1739.2	47.6	1756.0	64.4
16	46064.1	1488.2	1529.1	40.9	1552.7	64.6
17	47325.5	1261.4	1288.8	27.4	1322.8	61.3
18	48328.4	1002.9	1006.4	3.5	1056.0	53.1
19	49026.4	698.0	661.9	−36.1	732.7	34.7

4. Vibrational energies for the HF molecule and comparison to experiment

In this section, results from p-RBXCISD(*T*) and p-RBXCISD(*M3*) electronic structure calculations obtained with fairly large basis sets will be used in Level 7.7 calculations to obtain vibrational energies in the $J=0$ rotational state for the HF molecule that are compared to experiment. As discussed in Section 3.2, it appears that Brueckner orbitals are essential to provide the right results for the right reason for the HF molecule. Renormalized triples corrections are required to provide semi-quantitatively accurate curves at large internuclear distance, and both the $\langle T \rangle$ and $\langle M3 \rangle$ corrections are expected to be applicable in conjunction with Brueckner orbitals. In the p-RBXCISD(*T*) and p-RBXCISD(*M3*) calculations both the aug-cc-pVTZ and aug-cc-pVQZ basis sets were employed, while correlating the 1s orbital. The final electronic energies were obtained using extrapolation techniques. The Brueckner reference energy was obtained using fifth-order extrapolation, while the correlation energy was calculated using third-order extrapolation [81].

In a recent paper, Coxen and Hajigeorgiou [82] utilized all of the available experimental data for the HF ground state and first excited state of Σ symmetry, to obtain an analytical potential function, including Born–Oppenheimer breakdown functions. The reported accuracy for the $J=0$ vibrational levels in the ground electronic state is 10^{-3} cm^{-1} .

The experimental results for the vibrational energies and vibrational spacing between adjacent levels (in cm^{-1}) are presented in columns 2 and 3 in Table 4. Table 4 also shows the calculated vibrational spacings and their deviations from experiment for the p-RBXCISD(*T*) and p-RBXCISD(*M3*) approaches. In Table 5, the rotational constants are reported

for each vibrational level together with the percent deviation from experiment, and reasonable agreement is obtained between theory and experiment, except for the highest levels (from $v=16$ onwards).

From the data in Table 4, it is clear that the methods yield large errors of about 30–60 cm^{-1} in the calculated vibrational spacings, even for vibrational levels that only sample the region around the equilibrium geometry where the results

Table 5
Comparison of calculated p-RXCISD(*T*) and p-RXCISD(*M3*)/aug-cc-pVDZ/QZ to experimental rotational constants for each vibrational level ($J=0$) for the HF molecule

<i>V</i>	Experimental B_v (cm^{-1})	RBXCISD(<i>T</i>)		RBXCISD(<i>M3</i>)	
		B_v (cm^{-1})	% Deviation	B_v (cm^{-1})	% Deviation
0	20.56	20.63	0.36	20.65	0.42
1	19.79	19.87	0.40	19.88	0.47
2	19.03	19.12	0.43	19.13	0.50
3	18.30	18.39	0.46	18.40	0.54
4	17.58	17.67	0.51	17.69	0.59
5	16.88	16.97	0.57	16.99	0.65
6	16.19	16.29	0.64	16.31	0.73
7	15.50	15.62	0.73	15.63	0.83
8	14.83	14.95	0.83	14.97	0.94
9	14.15	14.28	0.95	14.30	1.07
10	13.47	13.61	1.08	13.63	1.22
11	12.78	12.94	1.23	12.96	1.40
12	12.07	12.24	1.39	12.26	1.62
13	11.33	11.50	1.56	11.54	1.89
14	10.54	10.72	1.71	10.77	2.20
15	9.69	9.86	1.79	9.93	2.55
16	8.74	8.89	1.68	8.99	2.92
17	7.65	7.73	1.14	7.90	3.28
18	6.34	6.30	−0.54	6.56	3.60
19	4.62	4.33	−6.35	4.70	1.69

from the electronic structure calculations are close to full CCSDT or Full CI calculations. We therefore tentatively conclude that this discrepancy is primarily a basis set effect, and that the extrapolated aug-cc-pV[TZ/QZ] basis set results are simply not accurate enough. In particular, the fact that we correlated the 1s electron while not including basis functions to account for core-valence effects, may have some deleterious effects. We also suspect that the basis set is still lacking in diffuse character. The fact that the error in the vibrational spacing is fairly constant means that the absolute error in the total vibrational energy grows nearly linearly with the vibrational quantum number. Interestingly, the same behaviour would be observed if a Dunham expansion was used in which the first term ω_e would be in error by about 30 cm^{-1} . This suggests that it might be meaningful to extract high-order Dunham expansion coefficients from the calculated vibrational energies and to compare these to experiment. Unfortunately, the values for the Dunham expansion coefficients are highly dependent on the order of polynomial used in obtaining the fit. This is also true for the experimental data, and we conclude therefore that a straightforward fitting procedure does not yield physically meaningful higher-order Dunham parameters when the vibrational levels are relatively sparse (as is true for most hydrides). Fig. 15 graphically displays the errors in the vibration dependent rotational constants and the error in the

vibrational spacings for the BXCISD, RBXCISD(T) and RBXCISD($M3$) approaches. It is seen that up to about $v=15$, these errors are fairly constant, while the approaches presumably break down for the highest vibrational levels ($v=16-19$), as the errors rapidly change there. It is interesting to note that the error is most constant for the BXCISD approach, which does not include a triples correction. It is difficult to extract a meaningful error analysis from the present results. The basis set is still simply not good enough to allow meaningful comparisons with experiment, and therefore basis set errors and methodological errors are lumped together and obscure the picture concerning the inherent accuracy of the electronic structure methods.

Renormalized triples corrections for the HF molecule have been compared to experimental results before in work by Piecuch et al. [11], where the aug-cc-pVTZ basis set was employed and the 1s core orbital was frozen. Piecuch et al. obtained excellent results using the renormalized CCSD(T) method, with errors in the total vibrational energy smaller than 10 cm^{-1} up to $v=13$. It is likely that this result was partly fortuitous, as the CCSDT results in the aug-cc-pVTZ basis set, also reported by Piecuch et al., showed a nearly linearly growing error, similar to that in the present work. In this context, an earlier study by Martin is revealing [83]. Martin focused on the lowest eight vibrational levels and performed a careful basis set study, including core-valence correlation effects, while the CCSD(T) results were adjusted using full CCSDT results in a smaller basis set. Using this approach, errors in the vibrational spacing well below 1 cm^{-1} were obtained, and this probably presents the state of the art in the field, although in that work a more limited number of vibrational levels were considered. At the wavenumber level of accuracy, non-Born–Oppenheimer effects start to be important. The basis sets used by Martin are significantly larger than the basis sets used in the present calculations, and they are essential to make a meaningful comparison between theory and experiment.

5. Summary

In this paper, two ideas are scrutinized. The orbital invariant CEPA or extensive configuration (p-XCISD) approach is a nearly linear approach (if Brueckner orbitals are used), and this is expected to be of great advantage both in local correlation treatments and in large-scale parallel implementations. The p-XCISD approach in general appears to be comparable in accuracy to CCSD, although it is less robust than CCSD and the results obtained for the F_2 and C_2 molecules are a significant cause for concern. It would be desirable to reformulate the p-XCISD method slightly, and if possible make it more robust. Nonetheless, the cases in which p-XCISD breaks down are fairly strongly correlated systems, and CCSD is not very reliable either. The results for the breaking of single bonds are intriguing, as p-XCISD seems to do a better job in the limit where the bond is broken, as judged by both the values of the t_2 amplitudes and the energetics. More test cases are needed to make a firm judgement on the prospects of this (or some

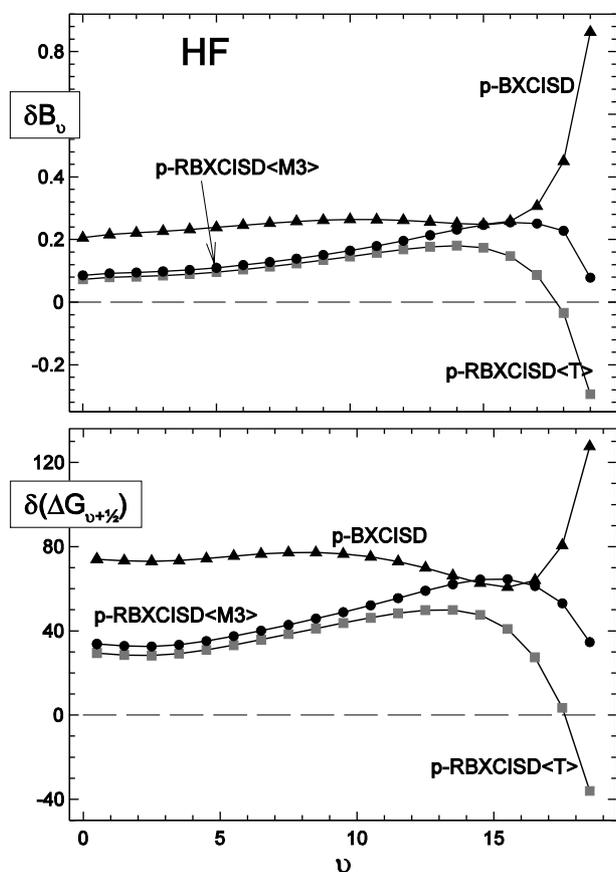


Fig. 15. Deviations from experiment for the BXCISD, p-RBXCISD(T) and p-RBXCISD($M3$) methods in the extrapolated aug-cc-pV[TZ/QZ] basis set for the HF molecule. Top panel shows deviation for vibration dependent rotational constants while bottom panel shows deviations for vibrational spacings (in cm^{-1}).

related) approach, and given the potential advantages, more research effort appears worthwhile.

The second idea concerns a new variety of extensive renormalized triples approaches, based on a partial summation of high-order EPV terms, which are designed to be rigorously invariant under rotations of occupied and virtual orbitals amongst themselves. These approaches can extend the applicability of the usual CCSD(*T*) approach to more highly correlated situations, such that the perturbative triples corrections are no longer the source of the breakdown of the approach. It is not yet clear whether such approaches would be accurate enough for spectroscopic studies, however, as basis set requirements are very demanding also in such studies, as discussed in Section 4. At present, we believe that the verdict is still out. The renormalized triples approaches are likely to be useful in the description of transition states, biradical species, and certain transition metal containing systems. From comparisons to CCSDT calculations, it appears that the renormalized triples correction presented here is of comparable accuracy to the NDC triple corrections introduced by Kowalski and Piecuch [22,23]. Both are a step forward compared to the size-extensivity violating renormalized corrections presented earlier. In particular, it means that the approaches reduce more or less to CCSD(*T*) for well-behaved systems, and moreover, weakly interacting systems are accessible using these extensive renormalized triples corrections. From the studies in this paper, the potential of the extensive, orbital invariant triples corrections is somewhat hard to gauge as the correction was combined with p-XCISD, and the latter methodology is less robust than CCSD; hence, few examples could be shown in which p-RXCISD(*T*) was applied to more highly correlated systems. For example, it was impossible to test the triples correction for the interesting and challenging F₂ molecule. The extensive triples, and likewise quadruples, corrections can be used equally well (perhaps better) in conjunction with CCSD, and this will be studied in future work. Finally, we have shown various examples in which it was of considerable advantage to use Brueckner orbitals in conjunction with renormalized triples corrections.

Acknowledgements

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