CORRECTION FOR TRIPLES IN REDUCED MULTIREFERENCE COUPLED-CLUSTER APPROACHES

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> *Vita mortuorum in memoria vivorum est posita.*
> *Verba volant, scripta manet.*
> *Supremum aeternum vale.*

The performance of the recently proposed version of the reduced multireference (RMR) coupled-cluster (CC) method with singles and doubles (SD), which employs a modest-size configuration interaction wave function as an external source for a small subset of approximate connected three- and four-body cluster amplitudes that are primarily responsible for the nondynamic correlation effects, and which has been perturbatively corrected for the remaining triples along the same line as in the standard CCSD(T) method (Li X., Paldus J.: *J. Chem. Phys.* **2006**, *124*, 174101), referred to by the acronym RMR CCSD(T), is being tested by evaluating equilibrium spectroscopic constants for a demanding system of the beryllium dimer, as well as by computing atomization energies for several di- and triatomics. The focus is on the equilibrium properties, since it has been demonstrated earlier that the RMR CCSD method corrects well for the nondynamic correlation in bond-breaking situations. We find that in all the cases we have examined, the RMR CCSD(T) method does in fact improve the performance of CCSD(T) even in the vicinity of the equilibrium geometry. For states possessing a moderate multireference character, the improvement in computed thermochemical properties relative to CCSD(T) amounts to a few kJ/mol, a meaningful amount when striving for chemical accuracy.

Keywords: Coupled-cluster method; Externally-corrected coupled-cluster methods; Reduced multireference coupled-cluster method; Correction for triples; Beryllium dimer; Atomization energies; Size-extensivity; Ab initio calculations.

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An account of many-electron correlation effects is essential in any quantum-chemical approach that strives for a quantitative description of the electronic structure of molecular systems and of their various properties. The coupled-cluster (CC) approach[1,2] that exploits the exponential Ansatz for the wave operator plays here an important role, since it can efficiently account for the so-called dynamic correlation and, in turn, guarantees the size-extensivity of the computed energies, a highly desirable property that is lacking in truncated configuration interaction (CI) type approaches (for reviews, see refs[3–12]; for a historical account, see refs[13,14]). The dynamic correlation arises due to a large number of higher-than-doubly-excited configurations that are missing in the standard single reference (SR) CI with singles (S) and doubles (D), namely the SR CISD method, while these are automatically accounted for through the disconnected clusters in the corresponding SR CCSD method (or, in fact, at any level of truncation) via the exponential Ansatz. In the absence of quasidegeneracy, these disconnected components provide a satisfactory description of higher-than-doubly-excited configuration state functions (CSFs), since the four- or higher-body connected clusters are negligible in comparison with the corresponding disconnected components.

In most actual applications that rely on a realistic ab initio model, characterized by a large basis set of at least a triple-zeta quality, it is imperative to truncate either the CI or CC expansion at the two-body level, lest the computational requirements become overwhelming. In the CI case, the lack of higher than doubly-excited CSFs is usually overcome by reverting to a multireference (MR) version of the formalism, i.e., to MR CISD. This in turn enables an easy account of the size-consistency requirement, which is necessary for a proper description of various dissociation processes or, generally, of the degeneracy or quasidegeneracy of considered states, as well as when handling transition states, radicaloid species, and open-shell systems in general, not to mention the facility of spin or other symmetry adaptation of CI approaches. Yet, CI approaches are not generally size-extensive, a shortcoming that is usually corrected ex post via various Davidson-type empirical corrections.

In contrast, the SR CC-type methods are automatically size-extensive at any level of truncation. However, in view of the requirement that the single-determinantal reference configuration they employ be nondegenerate, these SR CC approaches often lack the size-consistency property. This shortcoming is generally not essential when considering closed-shell molecular systems in their equilibrium geometry, yet becomes crucially important when we wish to describe various dissociation channels involving open-shell fragments, as is invariably the case when breaking genuine chemical bonds and computing the respective potential energy surfaces (PESs) or curves (PECs). An alternative way of striving for size-consistency employs the unrestricted Hartree–Fock (UHF) reference which, however, brings about the spin contamination into the formalism and causes other problems (see, e.g., ref.[9]). While in the ideal case the higher-than-two-body connected cluster components play a negligible role, so that the SR CCSD method represents a very good approximation, their importance increases with increasing quasidegeneracy of the reference. In fact, the connected three-body clusters (T_3) play already a non-negligible role even when considering molecular systems in their equilibrium geometry, and have to be taken into account if we wish to achieve the "chemical accuracy" of 1 kcal/mol (for more detail, see, e.g., ref.[15]).

Nonetheless, in standard situations, the size of the three-body connected cluster amplitudes is sufficiently small, enabling their handling via perturbation theory rather than by invoking a higher-level CCSDT method, which soon becomes computationally unaffordable when considering larger systems or basis sets. The resulting SR CCSD(T) method[16,17] does indeed yield very accurate results, and is offen used as a method of choice, or even as a benchmark, when a high accuracy is called for (cf. ref.[15]). Unfortunately, with increasing quasidegeneracy that is brought about when considering nonequilibrium geometries with stretched genuine chemical bonds, the CCSD(T) method invariably fails, yielding highly unrealistic potentials with a huge "hump" and completely breaks down in the dissociation limit. We must also note that for some "delicate" molecular systems, as represented for example by the BN molecule, CCSD(T) fails even at the equilibrium geometry and predicts an incorrect ground state[18]. In this type of systems, even the full CCSDT gives quantitatively unsatisfactory results for the singlet–triplet separation[19].

QUASIDEGENERACY AND CC APPROACHES

An obvious remedy for the quasidegeneracy and size-consistency problems of the SR CC approaches would seem to be a transition to their MR version, as in the CI case. Unfortunately, in contrast to CI, the generalization of the SR CC methods to the MR case is highly nontrivial, and not even unambiguous, since it admits different types of MR CC cluster Ansätze (for more detail, see, e.g., refs[20–24] or reviews[3,5,9,12]). Moreover, these methods generally suffer from severe problems, or even a complete breakdown, due to the presence of the so-called "intruder states". Even though these problems can be overcome to a large extent via various modifications, most recently, e.g., via the so-called C-conditions[25,26] that enable the use of general model spaces (GMSs), there has been a tendency to focus on one state at a time via the state-selective or state-specific (SS) MR CC approaches (see, e.g., refs[7,27–29]). This is also the case of the Brillouin–Wigner version of the MR CCSD method[30], which a priori disregards size-extensivity, but avoids the problem of intruders. Although some of the SS CC methods are designed to handle any state associated with the chosen model space, most attention has been paid to approaches that focus on the lowest state of a given symmetry species, including the ground state (see, e.g., SS MR CC approaches due to Adamowicz, Piecuch, and co-workers[31], which were also extended to equations-of-motion (EOM) CC for excited states[32]).

At this stage we must also mention several remedies to overcome the failure of the CCSD(T) method in the presence of quasidegeneracy that have been recently formulated and tested. Thus, Gwaltney and Head–Gordon[33] proposed the so-called CCSD(2) method that computes the second-order perturbative correction based on the CCSD as a reference, rather than using the standard independent-particle-model (IPM) reference. This approach yields improved results relative to the standard CCSD(T), assuming that CCSD itself is well behaved, which is not always the case.

A much more universal and robust approaches to this problem were formulated by Piecuch and co-workers[29,34], as represented by the renormalized (R) and completely renormalized (CR) CCSD(T), and lately by the so-called CR-CC(2,3) method[35]. These approaches are based on the so-called method of moments[29,36] and represent a great improvement over the standard CCSD(T), yielding qualitatively correct potentials. The only minor shortcoming, at least for the renormalized versions, seems to be the fact that in the vicinity of the equilibrium geometry they produce slightly less accurate results than does the standard CCSD(T) method, so that the computed harmonic frequencies, and other equilibrium properties, are inferior to the CCSD(T) ones. In the entire region of internuclear separations, however, these methods represent an enormous improvement over the standard CCSD(T) and produce results that closely approximate those rendered by the full CCSDT method. Nonetheless, neither of these methods accounts for connected quadruples.

EXTERNALLY-CORRECTED CC APPROACHES

In our work we have employed an alternative way of accounting for the quasidegeneracy in the SR CCSD method (as well as for the related problem of intruder states in MR CC approaches of the state-universal (SU) type[21]; see ref.[37]), which is based on the idea of the so-called external corrections[38,39]. Thus, rather than relying on the perturbation theory when assessing the contribution due to triples (and, possibly, quadruples), the externally corrected (ec) CC methods approximate the three- and four-body connected cluster amplitudes by relying on some external source wave function. Such source should be effective in accounting for the nondynamic correlation, computationally affordable, and its cluster analysis (that is required to extract the desired cluster amplitudes) should be easy to carry out.

The ecCC approach has a rather long history; it originated with the exploitation of the singlet-projected UHF (or PUHF) wave function as a source of approximate four-body clusters[40,41] (note that the PUHF wave function cannot provide three-body clusters). This in turn led to the so-called ACPQ (approximate coupled-pair theory with quadruples) method[40], which is closely related to the ACC(S)D approach pursued by Dykstra's group[42] and to the so-called ACP-45 (approximate coupled-pair method accounting for important exclusion-principle-violating or EPV diagrams, labeled as diagrams 4 and 5; see ref.[43]) as well as to other methods that emphasize the special role played by the EPV terms, which also play an important role in CEPA-type approaches. In fact, none of these CC methods actually evaluates the approximate four-body cluster amplitudes and simply discards certain $\frac{1}{2}T_2^2$ terms (labeled as diagrams 1, 2, and 3 in ref.[43]) – actually, computationally the most demanding quadratic terms. It was shown later on when formulating the ACPQ approach[40] that under certain conditions these terms are cancelled by the terms arising from the T_4 clusters. Only later on were the t_4 amplitudes actually extracted from the PUHF wave function, resulting in the CCSD' method[41].

The inability of these approaches to account for triples was justly criticized by Bartlett's group[44]. Nonetheless, a number of actual applications to various systems, including a rather demanding H_4-type models as H4, P4, etc.[43], cyclic polyenes[40,45] and other quasidegenerate systems[42,46–48], as well as the extension of the ACPQ method to SU MR CCSD [49], clearly indicated the potential usefulness of these approaches, particularly in view of the fact that they invariably produce results superior to the standard CCSD, while being computationally more efficient, since they avoid the evaluation of the most demanding algebraic expressions arising from the $\frac{1}{2}T_2^2$ term in the CCSD equations. Very recently the attention has been again turned to this topic, be it in the empirical-type handling of various quadratic terms in the CCSD equations[50], or in the so-called 2CC method[51]. The formulation of the latter provides yeat another viewpoint on this type of approaches (see also ref.[52] for related matters).

Realizing the importance of connected three- and four-body clusters in the presence of quasidegeneracy, we have turned our attention to other types of ecCCSD approaches, in which a relatively small subset of these clusters was explicitly accounted for by extracting them from a suitable external-source wave function via cluster analysis. These developments were in particular stimulated by the realization that in the SR formalism (i) the energy is fully determined by one- and two-body CC clusters or CI coefficients and (ii) that SR CCSD equations arise from the full CC chain by neglecting the t_3 and t_4 amplitudes that otherwise contribute via the T_3, T_4, and T_1T_3 terms. Indeed, extracting the three- and four-body amplitudes t_3 and t_4, respectively, from the full CI (FCI) wave function – representing the exact solution for a given ab initio model – and using them to correct the CCSD equations for the absence of just mentioned T_3, T_4, and T_1T_3 terms, we achieve the exact decoupling of the full CC chain of equations at the pair-cluster level, and thus corrected CCSD formalism renders back the exact FCI result.

In addition to earlier trials exploiting the PUHF wave function, we have explored various other options as external sources, namely those that can also provide approximate triples, in particular the VB, CAS FCI, and CAS SCF wave functions[38,53]. An exploitation of the latter option was also independently proposed by Stolarczyk[39], though we are not aware of any actual exploitation. The VB-type wave functions represent indeed an ideal external source in view of their numerous desirable properties, in particular thanks to the fact that they correctly describe all dissociation channels already in its simplest perfect-pairing version. Unfortunately, there are no general-purpose codes that generate VB wave functions at the ab initio level, so that we were able to test this source only for semi-empirical PPP-type Hamiltonians[54].

The CAS-type wave function, particularly the CAS SCF one, also represents a very desirable source, since it also brings with it molecular orbitals (MOs) that are adapted to the problem at hand. This source also seems to be essential for the recently proposed tailored CCSD (TCCSD) method[55] (see also ref.[56]). However, to generate a suitable CAS FCI or CAS SCF wave function requires the use of rather large active spaces, rapidly increasing the cost.

Thus, the most appropriate external source for our purposes turned out to be a modest size MR CISD wave function. As already implied above, there exists a definite complementarity between the CC and CI descriptions in their ability to handle, respectively, the dynamic and nondynamic or static correlation effects. Moreover, thanks to its linear nature, the cluster analysis of the CI or MR CI wave functions is straightforward and computationally trivial[57]. A suitable choice of the model (or reference) space for MR CISD then warrants a proper account of size-consistency. The t_3 and t_4 amplitudes that are extracted in such a way from the MR CISD wave function constitute only a very small subset of all tree- and four-body amplitudes (for example, in the simplest two-reference (2R) CISD case, the number of t_4 amplitudes is the same as that of the t_2 amplitudes), yet they represent the most important terms of this type, are easy to handle computationally, and account to an excellent degree for the nondynamic or static correlation that is missing in the SR CCSD approach. Moreover, these three- and four-body amplitudes implicitly account for all higher-order cluster contributions, as is apparent from the fact that by using the FCI t_3 and t_4 amplitudes, the ecCCSD yields again the FCI result. Needless to say that in the N-electron limit, both FCI and full CC (FCC) yield an identical exact result. The exploitation of the MR CISD wave function as an external source thus led to the formulation of the so-called reduced MR (RMR) CCSD method[27]. The usefulness of this approach has been demonstrated by a host of various applications[58] (see also ref.[59]).

We also note here that the same idea can be employed in the MR context, particularly within the general-model space (GMS) CCSD, relying on the so-called C-conditions enabling us to employ an arbitrary reference space[25,26], since the quasidegeneracy problem that we encounter in SR formalism is not unlike the intruder state problem of MR theories: both are due to a strong interaction with states that are not included in the model space M_0 (which, in the SR case, is one-dimensional). Basically, there are at least two ways to eliminate, or at least moderate, the undesirable effect of intruders: (i) By employing a GMS, rather than the complete model space (CMS), we can exclude references leading to intruders, and (ii) we can exploit external source wave functions. In this latter case, we consider an M-dimensional GMS for SU CCSD, while exploiting an N-dimensional reference space MR CISD that accounts for intruders as an external source ($N \geq M$). Using the MR CISD three- and four-body cluster amplitudes for the M relevant states, we then carry out ec SU CCSD. This approach is referred to as the (N,M)-CCSD method[60].

Clearly, the RMR or (N,M)-CCSD methods account for the missing nondynamic correlation via a small subset of t_3 and t_4 cluster amplitudes. However, this leaves a large number of such amplitudes unaccounted for. Although individually such amplitudes (or corresponding CSFs) contribute very little, they provide a non-negligible contribution in their entirety, as in the standard SR CCSD(T). We also recall that, in contrast to the four-body terms, in which case the disconnected $\frac{1}{2}T_2^2$ clusters are much more important (by one order in perturbation theory) than the connected T_4 clusters, the reverse is true for the three-body terms (see ref.[2]). It thus should be worthwhile to consider those connected three-body clusters that are not accounted for via external corrections in RMR CCSD. These amplitudes should be sufficiently small to allow a perturbative treatment as in the standard CCSD(T) method.

We have thus recently formulated[61] the triple-corrected RMR CCSD method, designated by the acronym RMR CCSD(T) (see also ref.[62]). Some preliminary tests clearly indicate the usefulness of this undertaking. It is the objective of this paper to provide a further evidence in this direction. First, however, we briefly outline the formalism we employ.

METHOD

The SR CC formalism relies on the exponential cluster Ansatz for the exact wave function $|\Psi\rangle$,

$$|\Psi\rangle = \exp(T)|\Phi_0\rangle, \quad T = \sum_{k=1}^{N} T_k , \tag{1}$$

where $|\Phi_0\rangle$ represents a single-determinantal IPM reference and T_k designates a k-body component of the cluster operator T. The T_k component is then determined by the cluster amplitudes $t_i^{(k)}$,

$$T_k = \sum_i t_i^{(k)} G_i^{(k)} , \tag{2}$$

each amplitude $t_i^{(k)}$ being associated with the k-fold excitation operator $G_i^{(k)}$ that generates k-times excited IPM CSF $|\Phi_i^{(k)}\rangle$ when acting on $|\Phi_0\rangle$, $|\Phi_i^{(k)}\rangle = G_i^{(k)}|\Phi_0\rangle$.

The cluster amplitudes are determined by solving the energy-independent CC equations,

$$\langle\Phi_i^{(k)}|\overline{H}|\Phi_0\rangle = 0 , \tag{3}$$

where $\overline{H}$ is a similarity-transformed Hamiltonian in its normal-product form, $H_\mathrm{N} = H - \langle\Phi_0|H|\Phi_0\rangle$,

$$\overline{H} = \exp(-T)\,H_N \exp(T). \qquad (4)$$

The energy relative to that of the reference is then fully determined by one- and two-body clusters, namely

$$\Delta E = \langle\Phi_0|H(T_1 + T_2 + \tfrac{1}{2}T_1^2)|\Phi_0\rangle. \qquad (5)$$

Truncating T at the two-body level, $T_\mathrm{CCSD} = T_1 + T_2$, we arrive at the SR CCSD method. We write CC equations (*3*) projected onto the singly- and doubly-excited CSFs as follows

$$\langle\Phi_i^{(1)}|\overline{H}_\mathrm{CCSD} + [H, T_3^{(0)}]|\Phi_0\rangle = 0\,, \qquad (6)$$

$$\langle\Phi_i^{(2)}|\overline{H}_\mathrm{CCSD} + [H, T_3^{(0)} + T_4^{(0)}] + [[H, T_1], T_3^{(0)}]|\Phi_0\rangle = 0\,, \qquad (7)$$

where now $\overline{H}_\mathrm{CCSD} = \exp(-T_\mathrm{CCSD})\, H_\mathrm{N} \exp(T_\mathrm{CCSD})$. Here we indicated by the superscript (0) higher-than-pair clusters that couple these equations to the rest of the CC chain. Setting these components to zero, $T_3^{(0)} = T_4^{(0)} = 0$, we obtain the CCSD equations.

Clearly, a physically more meaningful truncation of the CC chain can be achieved when we use some approximate values for the $T_3^{(0)}$ and $T_4^{(0)}$ clusters. In fact, should we use for $T_3^{(0)}$ and $T_4^{(0)}$ their FCI values, then solving so corrected CCSD equations yields back the exact FCI result, as already pointed out above. In the RMR CCSD we employ a modest-size MR CISD wave function as the external source for a small subset of important $t_i^{(3)}$ and $t_i^{(4)}$ amplitudes. The ground-state (or the lowest state of a given symmetry species) MR CISD wave function can be easily expressed in the intermediately normalized form relative to the reference $|\Phi_0\rangle$ and subsequently cluster-analyzed (see, e.g., refs[27,57]). Once these cluster amplitudes are known, we compute the $T_3^{(0)}$ and $T_4^{(0)}$ dependent terms in Eqs (*6*) and (*7*) (for a noniterative handling of the $[[H, T_1], T_3^{(0)}]$ term, see refs[27,38,53]) and correct the absolute term in CCSD equations, which are then solved as in the standard CCSD method. Note that the $T_3^{(0)}$ and $T_4^{(0)}$ dependent terms are evaluated only once.

In order to take into account those triples that were not accounted for via RMR CCSD, we employ the same perturbative procedure as in the standard CCSD(T) method, while relying on the RMR CCSD amplitudes. Thus, each triply-excited configuration $|\Phi_i^{(3)}\rangle$ (relative to the reference $|\Phi_0\rangle$) will contribute to the correlation energy the amount $e(i)$,

$$e(i) = \left(\sum_{k=1}^{2} \sum_{l \in M_k} \right) \sum_{d \in M_2} D(i)^{-1} t_l^{(k)} t_d^{(2)} \langle \Phi_l^{(k)} | H | \Phi_i^{(3)} \rangle \langle \Phi_i^{(3)} | H | \Phi_d^{(2)} \rangle . \tag{8}$$

Here we designate the set of singly-, doubly-, triply-, and higher-excited configurations relative to $|\Phi_0\rangle$ by, respectively, M_1, M_2, M_3, etc., while the perturbation-theory-type denominator $D(i)$ is given by the difference of the diagonal matrix elements of the Fock operator (or, when $|\Phi_0\rangle$ is a Hartree–Fock reference, by the difference of orbital energies) that are associated with the triply-excited configuration $|\Phi_i^{(3)}\rangle$.

Now, while in the standard SR CCSD(T) approach the correction due to triples is given by the sum of the individual $e(i)$ contributions for all triples in M_3, the appropriate correction for RMR CCSD should only involve those triples that are not already accounted for via the external corrections in RMR CCSD. In this way we avoid the overcounting of triple corrections and, most importantly, consider only those triples that can be safely handled by perturbation theory.

To be more specific, assume that the RMR CCSD, or the corresponding MR CISD, M-dimensional model space P is spanned by a set M_P of quasi-degenerate configurations $|\Phi_i\rangle$, $i = 0, 1, 2, \ldots, M - 1$,

$$M_P = \{ |\Phi_0\rangle, |\Phi_1\rangle, \ldots, |\Phi_{M-1}\rangle \} , \tag{9}$$

with $|\Phi_0\rangle$ representing the SR CCSD reference. The external source MR CISD wave function then involves, in addition to the references in M_P, the set M_Q of singles and doubles relative to the configurations spanning the model space P. Configurations in M_Q thus span the first-order interacting space Q. Clearly, all singles and doubles relative to $|\Phi_0\rangle$, constituting the set $\{M_1 \cup M_2\}$, are contained in the MR CISD space $P \oplus Q$, which, moreover, contains also configurations from M_3, M_4, etc., which are singles or doubles relative to some configuration in M_P, but higher-than-doubles relative to $|\Phi_0\rangle$.

Thus, generally,

$$\{M_1 \cup M_2\} \subset \{M_P \cup M_Q\} \quad \text{and} \quad \{M_3 \cup M_4\} \cap \{M_P \cup M_Q\} \neq \varnothing . \tag{10}$$

We thus isolate those triples relative to $|\Phi_0\rangle$ that are in $\{M_P \cup M_Q\}$, constituting a subset Θ_3,

$$\Theta_3 = \{M_P \cup M_Q\} \cap M_3 , \qquad \Theta_3 \subset M_3 , \tag{11}$$

and consider only those triples from M_3 that are not in $\{M_P \cup M_Q\}$, forming a subset Ω_3,

$$\Omega_3 = M_3 \setminus \Theta_3 . \tag{12}$$

Thus, while SR CCSD(T) computes the correction for triples by relying on the entire set M_3,

$$E_{\text{CCSD(T)}} = E_{\text{CCSD}} + \sum_{i \in M_3} e(i) , \tag{13}$$

only those triples that are not accounted for via RMR CCSD are taken into account in RMR CCSD(T), namely

$$E_{\text{RMR–CCSD(T)}} = E_{\text{RMR–CCSD}} + \sum_{i \in \Omega_3} e(i) . \tag{14}$$

RESULTS AND DISCUSSION

Very recently we have tested the performance of a truncated version of RMR CCSD(T) by considering the PEC for the F_2 molecule in a wide range of internuclear separations as well as the equilibrium geometry and dissociation energies of nickel carbonyls[56]. Particularly in the latter case the use of a truncated version of the method was essential when large basis sets were employed.

As a particularly delicate, yet rather unique, test we have considered the singlet–triplet separation of the lowest-lying states of the isoelectronic C_2 and BN molecules[18]. We recall that the standard SR CCSD(T) method fails to predict the correct ground state of BN, and even the full CCSDT gives a grossly inadequate value for the singlet–triplet separation energy[19], while RMR CCSD(T) predicts a correct ground state for both species and yields realistic singlet–triplet separation energies.

In this paper we have thus decided to carry out a few additional tests, addressing some difficult cases. For reasons of economy, we focus on the equilibrium geometry properties, since the ability of RMR CCSD to account for a nondynamic correlation – which arises when stretching genuine chemical bonds – has been amply demonstrated earlier[58]. As already mentioned, the utter failure of the standard CCSD(T) in this regard can also be efficiently handled by the R- or CR-CCSD(T) and CR-CC(2,3) methods[34,35] which, however, provide slightly inferior results than CCSD(T) in the region of equilibrium geometries. We thus wish to examine precisely the performance of RMR CCSD(T) relative to that of SR CCSD(T) in this region of geometries.

Beryllium Dimer

We first turn our attention to the Be_2 molecule, which is well-known to represent a difficult case due to the near-degeneracy of the 2s and 2p atomic orbitals in Be. In its ground state, it represents a weakly bound system, in which both the σ bonding and antibonding MOs are doubly occupied. Many papers have been devoted to this problem (see below), and only a very limited experimental data are available. In a recently published paper by Røeggen and Veseth[63] that deals with the Be_2 ground state potential, we read: "... practically all methods failed in predicting a reliable interatomic potential. Even though the more recent works (see below) yield results that are more consistent, the question concerning the correct form of the potential cannot be considered settled."

The Be_2 ground state represents a particularly crucial test for CC-type approaches in view of a very poor performance of both MP2 and SR CCSD methods[64–68] (see also ref.[69]). We thus compare our test results with both the experimental[70,71] and recent theoretical, highly-accurate, results, 'girded' by those based on the extended geminal model[72] (EXGM), namely on ref.[73] and the more recent ref.[63], referred to by the acronyms EXGM and (r)EXGM, respectively. We also refer the reader to the former reference[73] for a very exhaustive list of 45 earlier papers on the subject. Thus, in addition to the just given references, we compare in Table I our results with those listed below (in a chronological order), which are based on widely different approaches: The MR-CISD (or MRD-CI, see ref.[74]) method[75], MR averaged quadratic CC (MR-AQCC) method[76], all-electron SCF/valence-shell MR-CI with effective core polarization potential (MC-SCF/MR-CI/CPP) method[77], MR internally-contracted CISD [(IC)MRSDCI] method[78], averaged coupled-pair functional (ACPF) with full valence CAS(4/8) method[68] and, finally, an explicitly-correlated r_{12}-MR-CI method[79]. The last two very accurate potentials were very recently used by Špirko[80] to construct Be_2 PEC by 'morphing'

TABLE I
A comparison of computed and experimental spectroscopic constants for Be_2: Equilibrium bond length R_e (in Å), harmonic frequency ω_e (in cm^{-1}), rotational constant B_e (in cm^{-1}), and dissociation energy D_e (in cm^{-1})

Method	Basis	R_e	ω_e	B_e	D_e
CCSD(T)	cc-pVDZ	4.511	32.3	0.184	69
	cc-pVTZ	2.493	240.7	0.602	698
	cc-pVQZ	2.467	240.6	0.615	650
(2R)RMR CCSD(T)	cc-pVDZ	4.478	32.4	0.186	58
	cc-pVTZ	2.473	256.8	0.611	792
	cc-pVQZ	2.453	252.2	0.621	716
EXGM[a]	GTO[a]	2.47	224.7	–	812
MRD-CI[b]	[s,p,d][b]	2.498	258	0.603	766
MR-AQCC[c]	WMR[c]	2.446	–	–	864
MC-SCF/MR-CI[d]	GTO/CPP[d]	2.448	268.2	0.6213	893
(IC)MRSDCI[e]	cc-pVQZ	2.41	293	–	1050
ACPF[f]	cc-pV5Z[f]	2.4397	267.93	0.6285	944 ± 25
r_{12}-MR-CI[g]	[19s11p6d4f3g2h][g]	2.443	269.9	0.6258	898 ± 8
(r)EXGM[h]	[23s10p8d6f3g2h][h]	2.452	–	–	945 ± 15
RPC[i]		2.4382	277.4[j]	–	921.5–922.9
Exp.[k]		2.45	~250	0.618[l]	750–800[m]
Exp.[n]		2.450	275.8	0.623	790 ± 30

[a] From ref.[73]; [b] from ref.[75]; [c] from ref.[76]; [d] from ref.[77]; [e] from ref.[78]; [f] from ref.[68]; [g] from ref.[79]; [h] from ref.[63]; [i] from ref.[80]; [j] using expansion[82] $E = \omega_e(v + \frac{1}{2}) - x_e(v + \frac{1}{2})^2 + y_e(v + \frac{1}{2})^3$; [k] from ref.[70]; [l] B_0 value; [m] given as 839 ± 10 cm^{-1} in ref.[78]; [n] from ref.[71]

them (i.e., by fitting them to experimental data) within the framework of the reduced potential curve (RPC) approach of Jenč and Plíva[81].

In addition to the standard CCSD(T) results, we present in Table I those obtained with the two-reference (2R) RMR CCSD(T) method. The second reference is a doubly-excited HOMO to LUMO CSF and the resulting 2R space represents in this case a CMS involving both frontier MOs (i.e., HOMO and LUMO), which transform according to distinct symmetry species, since we deal with a homonuclear molecule. We note, in particular, a qualitative change in the equilibrium bond length when going beyond the basis of a double-zeta quality (cc-pVDZ). Likewise, we find a very long equilibrium bond length when using a 6-31G* basis with CCSD and, in fact, even with the 6-311G* basis set. Correspondingly, the harmonic frequencies indicate a very flat PEC in these cases, yielding ω_e = 4.5 cm^{-1} for CCSD(T)/6-31G* (correlating either 4 or all 8 electrons), and CCSD/6-311G* value is also most unreasonable (22.2 cm^{-1}). However, CCSD(T) gives already 177.3 cm^{-1} for the same basis set (correlating all 8 electrons). This clearly indicates the importance of triples, as do the 6-311G* results obtained by the 2R RMR CCSD and 2R RMR CCSD(T) methods, which give for ω_e the values 134.1 and 203.3 cm^{-1}, respectively (again, correlating all 8 electrons).

The data obtained with correlation-consistent (cc) polarized (p) VXZ (X = D, T, Q) basis sets using both CCSD(T) and 2R RMR CCSD(T) methods (Table I) clearly indicate the improvement brought about by the latter method. The 2R RMR CCSD(T) bond length R_e, and the related rotational constant B_e, obtained with the cc-pVQZ basis set agree well with the experimental values, and with highly accurate theoretical ones as well. The 2R RMR CCSD(T) harmonic frequency values for both cc-pVTZ and cc-pVQZ basis sets are also very reasonable, considering a rather large spread of both theoretical and experimental values. In any case, these values represent an improvement over the CCSD(T) ones, primarily due to the inclusion of connected quadruples, which are doubles relative to the second reference, and which are lacking in CCSD(T).

It is also worth noting that the computed results are rather sensitive to the type of basis set atomic orbitals (AOs) that we employ. The results presented in Table I were obtained with Cartesian Gaussians. The use of spherical Gaussians leads to a slightly shorter bond lengths R_e, and correspondingly larger harmonic frequencies ω_e (for the cc-pVXZ, X = D, T, and Q, basis sets, the 2R RMR CCSD(T) values for R_e are 4.550, 2.331 and 2.422 Å, and 31.1, 380.1 and 280.2 cm^{-1} for ω_e, respectively, all 8 electrons being correlated).

Finally, an account of connected quadruples significantly lowers the dimer energy, so that the dissociation energies D_e, as obtained by the 2R RMR CCSD(T) method, are considerably closer to the experimental values than are the CCSD(T) ones, even though they lie below most of the theoretical values. Again, in spite of a large scatter of both theoretical and experimental results, 2R RMR CCSD(T) is an improvement over the standard CCSD(T). Unfortunately, all quantities obtained with a basis of a double-zeta quality are grossly inadequate, so that it would be meaningless to employ them in a three-point extrapolation toward the complete basis set (CBS) limit. In any case, the data presented in Table I must be regarded as a preliminary test and we hope to carry out a much more detailed study in the future.

Atomization Energies

As another test of triple-corrected RMR CCSD we consider atomization energies for several typical systems, involving several first row di- and triatomics (Table II), as well as the more challenging MgO molecule (Table III). Both zero-point energies (unscaled) and spin-orbit correlations have been taken into account. It is well-known that CCSD(T) yields generally very good and reliable results for atomization energies (cf. ref.[15]), so that it is meaningful to check how RMR CCSD(T) fares in this case and how much improvement can be achieved by using the RMR CCSD(T) method.

In Table II we present the standard CCSD and RMR CCSD results, as well as the triple-corrected CCSD(T) and RMR CCSD(T) ones. For the high-spin states, our calculations are based on the ROHF MOs. The results so obtained differ only slightly from those relying on the UHF-based CC method. For the HF molecule, whose ground state has a strong SR character, the difference between the CCSD and RMR CCSD results, as well as between the CCSD(T) and RMR CCSD(T) ones, is very small. For the ground states of other molecules that are included in Table II, the MR effects play already a definite role, particularly for ozone. In general, the differences between the triple-uncorrected values are larger than for the triple-corrected ones. Indeed, the difference between the CCSD(T) and RMR CCSD(T) atomization energies is very small, amounting to a few kJ/mol. The largest difference is found for O_3, in which case RMR CCSD(T) improves the CCSD(T) value by 6.3 kJ/mol. The RMR CCSD(T) values, which in all the cases considered (Table II) are slightly larger than the CCSD(T) ones, lie always closer to the experiment.

TABLE II
Atomization energies (0 K; in kJ/mol) computed with various CC methods and cc-pVTZ basis set

System	CCSD	RMR CCSD	*N*[a]	CCSD(T)	RMR CCSD(T)	Exp.[b]
HF	539.0	540.6	4	546.1	546.2	566.6
F_2	108.7	128.7	2	136.4	139.8	154.5
CS	630.6	643.8	3	668.0	670.3	712.9
C_2H	1000.5	1007.0	3	1032.8	1034.0	1073.4
HCN	1181.8	1190.1	3	1217.3	1218.9	1265.7
O_3	422.2	475.2	2	533.4	539.7	595.9

[a] Number of references used in the RMR CCSD approach for a molecule. For atoms, SR approach is employed, except for the C atom, in which case a 2-reference approach is used; [b] from ref.[83]

The same conclusion holds for the MgO results (Table III), even though in this case the RMR CCSD(T) values are slightly smaller than the CCSD(T) ones. Yet again, however, the shift is in the right direction, RMR CCSD(T) energies being closer to the experimental value of 241.7 cm^{-1}, although the very close agreement between the experiment and 4R RMR CCSD(T)/cc-pVQZ result (241.7 vs 241.2 kJ/mol) must be considered as fortuitous.

TABLE III
Atomization energies (0 K; in kJ/mol) for MgO as obtained with SR CCSD(T) and 4R RMR CCSD(T) methods and different basis sets. The second row indicates number of electrons that are correlated

Method	CCSD(T)		4R RMR CCSD(T)	
	8-e	16-e	8-e	16-e
cc-pVDZ	166.9	167.1	166.3	166.4
cc-pVTZ	217.6	220.8	216.0	218.7
cc-pVQZ	237.8	243.9	235.5	241.2
Exp.[a]	241.7	241.7	241.7	241.7

[a] From ref.[83]

CONCLUSIONS

The recently formulated RMR CCSD(T) method[61] clearly represents a useful extension of the standard SR CCSD(T) approach, since it makes it possible to overcome the near-degeneracy effects that are always present when breaking genuine chemical bonds, or when handling certain open-shell systems. These quasidegeneracy effects lead to the breakdown, or at least to a very poor performance, of the otherwise so successful and useful standard CCSD(T) method. This breakdown is due to the presence of those triply-excited CSFs that significantly contribute to the exact wave function, having significant weights. These CSFs are thus responsible for the increased role of the nondynamic correlation effects. It is thus highly desirable to treat these CSFs via the ec RMR CCSD method (note that RMR CCSD also accounts for important quadruples). Having accounted for these triply-excited CSFs via external corrections to CCSD, we are thus left with those triples (very large in number compared with those that require RMR CCSD handling), which can be safely treated via perturbative (T)-type corrections, as in the standard CCSD(T).

As mentioned earlier, RMR CCSD represents an alternative approach to the renormalized R- or CR-CCSD(T) methods[34,35], which also overcome the CCSD(T) breakdown in quasidegenerate situations. Nonetheless, these methods slightly underperform CCSD(T) in an important region of equilibrium geometries (see, e.g., ref.[61]). For this reason we have focused in this paper on equilibrium properties, considering spectroscopic constants for a very challenging beryllium dimer, where the standard CCSD method fails, as well as on atomization energies, where CCSD(T) usually works very well. It is thus gratifying to find that the RMR CCSD(T) method cannot only overcome the shortcomings or failure of the standard CCSD(T) when near-degeneracy effects become significant, but also represents an improvement in the region of equilibrium geometries, where generally CCSD(T) works very well. Even for molecules with a moderate MR character, the improvement of RMR CCSD(T) over CCSD(T) is of the order of a few kJ/mol. Although these improvements are relatively small, they are nonetheless larger than the accuracy of thermochemical data, and thus deserve to be pursued further. We can thus conclude that the RMR CCSD(T) method does achieve a better accuracy than CCSD(T), which is already considered to be rendering results of the chemical accuracy and, moreover, is applicable to a considerably wider range of molecular systems.

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REFERENCES

1. a) Čížek J.: *J. Chem. Phys.* **1966**, *45*, 4256; b) Čížek J.: *Adv. Chem. Phys.* **1969**, *14*, 35; c) Čížek J., Paldus J.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1971**, *5*, 359.
2. Paldus J., Čížek J., Shavitt I.: *Phys. Rev. A* **1972**, *5*, 50.
3. Paldus J.: *NATO ASI Ser., Ser. B* **1992**, *293*, 99.
4. Bartlett R. J., Stanton J. F. in: *Reviews in Computational Chemistry* (K. B. Lipkowitz and D. B. Boyd, Eds), Vol. 5, p. 65. VCH, New York 1994.
5. Paldus J.: *NATO ASI Ser., Ser. B* **1994**, *318*, 207.
6. Bartlett R. J. in: *Modern Electronic Structure Theory* (D. R. Yarkony, Ed.), Part I, p. 1047. World Scientific, Singapore 1995.
7. Mahapatra U. S., Datta B., Mukherjee D. in: *Recent Advances in Coupled Cluster Methods* (R. J. Bartlett, Ed.), p. 155. World Scientific, Singapore 1997.
8. Gauss J. in: *Encyclopedia of Computational Chemistry* (P. von R. Schleyer, Ed.), Vol. 1, p. 615. Wiley, New York 1998.
9. Paldus J., Li X.: *Adv. Chem. Phys.* **1999**, *110*, 1.
10. Crawford T. D., Schaefer III H. F. in: *Reviews in Computational Chemistry* (K. B. Lipkowitz and D. B. Boyd, Eds), Vol. 14, Chap. 2, p. 33. Wiley, New York 2000.
11. Stanton J. F., Gauss J.: *Int. Rev. Phys. Chem.* **2000**, *19*, 61.
12. Paldus J. in: *Handbook of Molecular Physics and Quantum Chemistry* (S. Wilson, Ed.), Vol. 2, Part 3, Chap. 19, p. 272. Wiley, Chichester 2003.
13. Paldus J. in: *Theory and Applications of Computational Chemistry: The First Forty Years* (C. F. Dykstra, G. Frenking, K. S. Kim and G. E. Scuseria), Chap. 7, p. 115. Elsevier, Amsterdam 2005.
14. Bartlett R. J. in: *Theory and Applications of Computational Chemistry: The First Forty Years* (C. F. Dykstra, G. Frenking, K. S. Kim and G. E. Scuseria), Chap. 42, p. 1191. Elsevier, Amsterdam 2005.
15. Lee T. J., Scuseria G. E. in: *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy* (S. R. Langhoff, Ed.), p. 47. Kluver, Dordrecht 1995.
16. a) Raghavachari K.: *J. Chem. Phys.* **1985**, *82*, 4607; b) Raghavachari K., Trucks G. W., Pople J. A., Head–Gordon M.: *Chem. Phys. Lett.* **1989**, *157*, 479.
17. Urban M., Noga J., Cole S. J., Bartlett R. J.: *J. Chem. Phys.* **1985**, *83*, 4041.
18. Li X., Paldus J.: *Chem. Phys. Lett.* **2006**, *431*, 179.
19. Watts J. D. in: *Computational Chemistry: Reviews of Current Trends* (J. Leszczynski, Ed.), Vol. 7, p. 89. World Scientific, Singapore 2002.
20. a) Lindgren I.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1978**, *12*, 33; b) Mukherjee D., Moitra R. K., Mukhopadhyay A.: *Mol. Phys.* **1977**, *33*, 955.
21. Jeziorski B., Monkhorst H. J.: *Phys. Rev. A* **1981**, *24*, 1668.
22. a) Lindgren I., Morrison J.: *Atomic Many-Body Theory*. Springer-Verlag, Berlin 1982; b) Lindgren I., Mukherjee D.: *Phys. Rep.* **1987**, *151*, 93.
23. Mukherjee D., Pal S.: *Adv. Quantum Chem.* **1989**, *20*, 292.
24. Jeziorski B., Paldus J.: *J. Chem. Phys.* **1989**, *90*, 2714.

25. Li X., Paldus J.: *J. Chem. Phys.* **2003**, *119*, 5320.
26. a) Li X., Paldus J.: *Int. J. Quantum Chem.* **2004**, *99*, 914; b) Paldus J., Li X.: *Collect. Czech. Chem. Commun.* **2004**, *69*, 90; c) Paldus J., Li X., Petraco N. D. K.: *J. Math. Chem.* **2004**, *35*, 215.
27. Li X., Paldus J.: *J. Chem. Phys.* **1997**, *107*, 6257.
28. Mahapatra U. S., Datta B., Mukherjee D.: *J. Chem. Phys.* **1999**, *110*, 6171.
29. Piecuch P., Kowalski K. in: *Computational Chemistry: Review of Current Trends* (J. Leszczynski, Ed.), Vol. 5, p. 1. World Scientific, Singapore 2000.
30. a) Mášik J., Hubač I., Mach P.: *J. Chem. Phys.* **1998**, *108*, 6571; b) Pittner J., Nachtigall P., Čársky P., Mášik J., Hubač I.: *J. Chem. Phys.* **1999**, *110*, 10275; c) Hubač I., Pittner J., Čársky P.: *J. Chem. Phys.* **2000**, *112*, 8779; d) Sancho-Garcia J. C., Pittner J., Čársky P., Hubač I.: *J. Chem. Phys.* **2000**, *112*, 8785; e) Petraco N. D. K., Horný L., Schaefer III H. F., Hubač I.: *J. Chem. Phys.* **2002**, *117*, 9580; f) Kerkines I. S. K., Pittner J., Čársky P., Mavridis A., Hubač I.: *J. Chem. Phys.* **2002**, *117*, 9733; g) Pittner J.: *J. Chem. Phys.* **2003**, *118*, 10876.
31. Piecuch P., Oliphant N., Adamowicz L.: *J. Chem. Phys.* **1993**, *99*, 1875; and references therein.
32. Gour J. R., Piecuch P., Włoch M.: *J. Chem. Phys.* **2005**, *123*, 134113.
33. Gwaltney S. R., Head–Gordon M.: *J. Chem. Phys.* **2001**, *115*, 2014.
34. a) Kowalski K., Piecuch P.: *J. Chem. Phys.* **2000**, *113*, 18; b) Kowalski K., Piecuch P.: *J. Chem. Phys.* **2000**, *113*, 5644; c) Kowalski K., Piecuch P.: *J. Chem. Phys.* **2000**, *113*, 8490; d) Kowalski K., Piecuch P.: *Chem. Phys. Lett.* **2001**, *334*, 89; e) Kowalski K., Piecuch P.: *Chem. Phys. Lett.* **2001**, *344*, 165; f) Kowalski K., Piecuch P.: *J. Chem. Phys.* **2001**, *115*, 643; g) Kowalski K., Piecuch P.: *J. Chem. Phys.* **2001**, *115*, 2966; h) Piecuch P., Kowalski K., Pimienta I. S. O., Fan P.-D., Lodriguito M. D., McGuire M. J., Kucharski S. A., Kuś T., Musiał M.: *Theor. Chem. Acc.* **2004**, *112*, 349; i) Kowalski K., Piecuch P.: *J. Chem. Phys.* **2004**, *120*, 1715.
35. a) Piecuch P., Włoch M.: *J. Chem. Phys.* **2005**, *123*, 224105; b) Piecuch P., Włoch M., Gour J. R., Kinal A.: *Chem. Phys. Lett.* **2005**, *418*, 463; c) Włoch M., Lodriguito M. D., Piecuch P., Gour J. R.: *Mol. Phys.* **2006**, *104*, 2149.
36. Kowalski K., Piecuch P.: *J. Chem. Phys.* **2001**, *115*, 643.
37. a) Li X., Paldus J.: *J. Chem. Phys.* **2003**, *119*, 5334; b) Li X., Paldus J.: *J. Chem. Phys.* **2004**, *120*, 5890.
38. a) Paldus J., Planelles J.: *Theor. Chim. Acta* **1994**, *89*, 13; b) Planelles J., Paldus J., Li X.: *Theor. Chim. Acta* **1994**, *89*, 33; c) Planelles J., Paldus J., Li X.: *Theor. Chim. Acta* **1994**, *89*, 59.
39. Stolarczyk L.: *Chem. Phys. Lett.* **1994**, *217*, 1.
40. a) Paldus J., Čížek J., Takahashi M.: *Phys. Rev. A* **1984**, *30*, 2193; b) Paldus J., Takahashi M., Cho R. W. H.: *Phys. Rev. B* **1984**, *30*, 4267; c) Takahashi M., Paldus J.: *Phys. Rev. B* **1985**, *31*, 5121.
41. Piecuch P., Toboła R., Paldus J.: *Phys. Rev. A* **1996**, *54*, 1210.
42. a) Chiles R. A., Dykstra C. E.: *Chem. Phys. Lett.* **1981**, *80*, 69; b) Bachrach S. M., Chiles R. A., Dykstra C. E.: *J. Chem. Phys.* **1981**, *75*, 2270; c) Liu S.-Y., Daskalakis M. F., Dykstra C. E.: *J. Chem. Phys.* **1986**, *85*, 5877; d) Bernholdt D. E., Liu S.-Y., Dykstra C. E.: *J. Chem. Phys.* **1986**, *85*, 5120; e) Dykstra C. E., Liu S.-Y., Daskalakis M. F., Lucia J. P., Takahashi M.: *Chem. Phys. Lett.* **1987**, *137*, 266; f) Dykstra C. E.: *Ab Initio Calculation of the Structure and Properties of Molecules*. Elsevier, Amsterdam 1988.

43. a) Jankowski K., Paldus J.: *Int. J. Quantum Chem.* **1980**, *18*, 1243; b) Paldus J., Wormer P. E. S., Bénard M.: *Collect. Czech. Chem. Commun.* **1988**, *53*, 1919; c) Adams B. G., Jankowski K., Paldus J.: *Phys. Rev. A* **1981**, *24*, 2316; d) Adams B. G., Jankowski K., Paldus J.: *Phys. Rev. A* **1981**, *24*, 2330.
44. Kucharski S. A., Balková A., Bartlett R. J.: *Theor. Chim. Acta* **1991**, *80*, 321.
45. Piecuch P., Čížek J., Paldus J.: *Int. J. Quantum Chem.* **1992**, *42*, 165.
46. Piecuch P., Toboła R., Paldus J.: *Int. J. Quantum Chem.* **1995**, *55*, 133.
47. Finley J. P., Chaudhuri R. K., Freed K. F.: *J. Chem. Phys.* **1995**, *103*, 4990.
48. Piecuch P., Kondo A. E., Špirko V., Paldus J.: *J. Chem. Phys.* **1996**, *104*, 4699.
49. Piecuch P., Toboła R., Paldus J.: *Chem. Phys. Lett.* **1993**, *210*, 243.
50. a) Nooijen M., Le Roy R. J.: *J. Mol. Struct. (THEOCHEM)* **2006**, *768*, 25; b) Nooijen M.: Private communication.
51. Bartlett R. J., Musiał M.: *J. Chem. Phys.* **2006**, *125*, 204105.
52. Paldus J., Čížek J., Jeziorski B.: *J. Chem. Phys.* **1990**, *93*, 1485.
53. a) Li X., Peris G., Planelles J., Rajadell F., Paldus J.: *J. Chem. Phys.* **1997**, *107*, 90; b) Peris G., Planelles J., Paldus J.: *Int. J. Quantum Chem.* **1997**, *62*, 137; c) Peris G., Rajadell F., Li X., Planelles J., Paldus J.: *Mol. Phys.* **1998**, *94*, 235.
54. a) Paldus J., Li X.: *Israel J. Chem.* **1991**, *31*, 351; b) Li X., Paldus J.: *J. Mol. Struct. (THEOCHEM)* **1991**, *229*, 249; c) Li X., Paldus J.: *Int. J. Quantum Chem.* **1992**, *41*, 117; d) Paldus J., Li X. in: *Group Theory in Physics*, AIP Conference Proceedings (A. Frank, T. H. Seligman and K. B. Wolf, Eds), No. 266, p. 159. American Institute of Physics, New York 1992; e) Paldus J., Li X. in: *Pauling's Legacy: Modern Modelling of the Chemical Bond, Theoretical and Computational Chemistry Series* (Z. B. Maxić and W. J. Orville-Thomas, Eds), Vol. 6, Chap. 17, p. 481. Elsevier, Amsterdam 1999; f) Paldus J., Li X. in: *Symmetries in Science VI: From the Rotation Group to Quantum Algebras* (B. Gruber, Ed.), p. 573. Plenum Press, New York 1993.
55. a) Kinoshita T., Hino O., Bartlett R. J.: *J. Chem. Phys.* **2005**, *123*, 074106; b) Hino O., Kinoshita T., Chan G. K.-L., Bartlett R. J.: *J. Chem. Phys.* **2006**, *124*, 114311.
56. Li X., Paldus J.: *J. Chem. Phys.* **2006**, *125*, 164107.
57. Paldus J., Li X.: *J. Chem. Phys.* **2003**, *118*, 6769.
58. a) Li X., Paldus J.: *J. Chem. Phys.* **1998**, *108*, 637; b) Li X., Paldus J.: *Chem. Phys. Lett.* **1998**, *286*, 145; c) Li X., Paldus J.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 1381; d) Li X., Paldus J.: *J. Chem. Phys.* **1999**, *110*, 2844; e) Li X., Paldus J.: *Mol. Phys.* **2000**, *98*, 1185; f) Li X., Paldus J.: *J. Chem. Phys.* **2000**, *113*, 9966; g) Li X., Paldus J.: *Int. J. Quantum Chem.* **2000**, *80*, 743; h) Li X.: *J. Mol. Struct. (THEOCHEM)* **2001**, *547*, 69; i) Li X., Paldus J.: *J. Chem. Phys.* **2002**, *117*, 1941; j) Li X., Paldus J.: *J. Chem. Phys.* **2003**, *118*, 2470.
59. a) Paldus J., Li X.: *Top. Curr. Chem.* **1999**, *203*, 1; b) Li X., Paldus J.: *J. Chem. Phys.* **2001**, *115*, 5759; c) Li X., Paldus J.: *J. Chem. Phys.* **2001**, *115*, 5774; d) Paldus J., Li X. in: *Advances in Quantum Many Body Theory* (R. F. Bishop, T. Brandes, K. A. Gernoth, N. R. Walet and Y. Xian, Eds), Vol. 5, p. 393. World Scientific, Singapore 2002; e) Li X., Paldus J.: *ACS Symp. Ser.* **2002**, *828*, 10; f) Paldus J., Li X.: *Collect. Czech. Chem. Commun.* **2003**, *68*, 554.
60. Li X., Paldus J.: *J. Chem. Phys.* **2003**, *119*, 5334.
61. a) Li X., Paldus J.: *J. Chem. Phys.* **2006**, *124*, 174101; b) Li X., Paldus J.: *Mol. Phys.* **2006**, *104*, 2047.
62. Li X., Paldus J.: *J. Chem. Phys.* **2006**, *124*, 034112.
63. Røeggen I., Veseth L.: *Int. J. Quantum Chem.* **2005**, *101*, 201.

64. Chiles R. A., Dykstra C. F.: *J. Chem. Phys.* **1981**, *74*, 4544.
65. a) Lee Y. S., Bartlett R. J.: *J. Chem. Phys.* **1984**, *80*, 4371; b) Sosa C., Noga J., Bartlett R. J.: *J. Chem. Phys.* **1988**, *88*, 5974.
66. Černušák I., Noga J., Diercksen G. H. F., Sadlej A. J.: *Chem. Phys.* **1988**, *125*, 255.
67. Noga J., Kutzelnigg W., Klopper W.: *Chem. Phys. Lett.* **1992**, *199*, 497.
68. Martin J. M. L.: *Chem. Phys. Lett.* **1999**, *303*, 399.
69. Lotrich V. F., Bartlett R. J., Grabowski I.: *Chem. Phys. Lett.* **2005**, *405*, 43.
70. Bondybey V. E., English J. H.: *J. Chem. Phys.* **1984**, *80*, 568.
71. Bondybey V. E.: *Chem. Phys. Lett.* **1984**, *109*, 436.
72. a) Røeggen I.: *J. Chem. Phys.* **1983**, *79*, 5520; b) Røeggen I.: *Int. J. Quantum Chem.* **1990**, *38*, 585.
73. Røeggen I., Almlöf J.: *Int. J. Quantum Chem.* **1996**, *60*, 453.
74. a) Buenker R. J., Peyerimhoff S. D.: *Theor. Chim. Acta* **1975**, *39*, 217; b) Buenker R. J., Peyerimhoff S. D., Butscher W.: *Mol. Phys.* **1978**, *35*, 771; c) Buenker R. J., Phillips R. A.: *J. Mol. Struct. (THEOCHEM)* **1985**, *123*, 291.
75. Bruna P. J., Wright J. S.: *Can. J. Chem.* **1996**, *74*, 998.
76. Füsti-Molnár L., Szalay P. G.: *Chem. Phys. Lett.* **1996**, *258*, 400.
77. Stärck J., Meyer W.: *Chem. Phys. Lett.* **1996**, *258*, 421.
78. Kaledin L. A., Kaledin A. L., Heaven M. C., Bondybey V. E.: *J. Mol. Struct. (THEOCHEM)* **1999**, *461–462*, 177.
79. Gdanitz R. J.: *Chem. Phys. Lett.* **1999**, *312*, 578.
80. Špirko V.: *J. Mol. Spectrosc.* **2006**, *235*, 268.
81. Jenč F.: *Adv. At. Mol. Phys.* **1983**, *19*, 265.
82. Špirko V.: Private communication.
83. http://srdata.nist.gov/cccbdb; section II, Experimental data.