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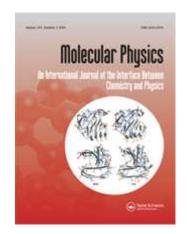https://hal.science/hal-00629951

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RESEARCH ARTICLE

Towards the Full Coupled Cluster Model with Triples: A Retrospective after 25 Years

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The CCSD+T(CCSD) approach was proposed 25 years ago together with a suggestion of a coupled cluster hierarchy including triply excited configurations, known as CCSDT-n. This retrospective recapitulates the essence of those approaches in the contemporary context. Finally, the relation to other developments in this field is briefly outlined with emphasis on work perfomed at the Quantum Theory Project.

Keywords: coupled cluster theory; triple excitations; non-iterative correction; many body perturbation theory; one-particle relaxation

1. Introduction

More than fourty years ago, using diagrammatic techniques Čížek [1–3] worked out the exponential ansatz of Coester and Kümmel [4, 5] in a manageable way for many-fermion systems. Thus, he fully opened the door into the world of quantum chemistry for what is nowadays known as the coupled cluster (CC) theory. Restricting ourselves to a single Slater determinant reference $|\Phi\rangle$, the exact wave function Ψ is expressed as

$$|\Psi\rangle = \exp(\hat{T})|\Phi\rangle. \tag{1}$$

Here, in general,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... \tag{2}$$

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is a global excitation operator. Since, due to the Thouless theorem [6], $\exp(\hat{T}_1)|\Phi\rangle$ represents again a single Slater determinant, minimization of the energy functional

$$E(\hat{T}_1^\dagger, \hat{T}_1) = \frac{\langle\Phi|e^{\hat{T}_1^\dagger}\hat{H}e^{\hat{T}_1}|\Phi\rangle}{\langle\Phi|e^{\hat{T}_1^\dagger}e^{\hat{T}_1}|\Phi\rangle} \tag{3}$$

is not only equivalent to the Hartree-Fock (HF) method, but, as shown recently, it also provides a very practical and efficient alternative to solve the HF problem [7, 8]. Consequently, with a HF reference a CC approach restricted to mere singles (CCS) brings zero energy change and the most important contribution to the post HF correction (correlation energy) comes from double (pair) substitutions (i. e. $\hat{T}=\hat{T}_2$), to which the operator of Eq. (2) was restricted in the original work of Čížek. Accordingly, he named the method Coupled Pair Many Electron Theory (CPMET) [1, 2].

Undoubtedly, throughout the years the power of the CC approach has been convincingly proved in calculations of highly accurate energies and properties of molecules [9–17]. Although it is not explicitly seen in the original work, in order to obtain the wave function, one is solving a wave equation

$$\tilde{H}|\Phi\rangle = E|\Phi\rangle \tag{4}$$

with a single reference determinant $|\Phi\rangle$ and similarity transformed Hamiltonian

$$\tilde{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}} = \left(\hat{H}e^{\hat{T}}\right)_C. \tag{5}$$

The CC equations, either with doubles only [2, 18–20] (CCD) or singles and doubles (CCSD) [21] involve steps whose computational complexities formally scale as $\propto N^6$ where N is the number of molecular orbitals. Including triples in full CCSDT [22] means a jump to $\propto N^8$ scaling, including full quadruple excitations in CCSDTQ causes another jump to $\propto N^{10}$ [23, 24]. More generally, each excitation level of the $\hat{T}$ operator increases the computational complexity by N^2, starting with CCS that scales as $\propto N^4$, i. e. similarly to the HF method.

A particularly important step was accomplished in QTP by introducing the CCSD with full consideration of single and double excitation operators in the exponential ansatz of Eq. (1) [21], i. e. using $\hat{T}=\hat{T}_1+\hat{T}_2$. Bearing in mind the Thouless theorem, it is clear that this ansatz introduces the important orbital relaxation effects. Nevertheless, soon after introducing the CC method in "large scale" codes it became clear that in order to obtain higly accurate results inclusion of triple excitations into the wave function ansatz, more precisely to the excitation operator expressed by Eq. (2), is inevitable. Contribution due to triple excitations appears already at the second order in the wave function expansion in terms of the many body perturbation theory (MBPT), similarly as for the single excitations when a HF reference is considered. Consequently, the aforementioned excitations contribute to fourth order in the energy expansion. In fact, the first report of the inclusion of triples and also singles into the wave function ansatz derived from Eq. (1) goes back to the work of Paldus, Čížek and Shavitt [25] who introduced an Extended CPMET (E-CPMET) in which in addition to CCD (CPMET) the $\hat{T}_1$ and $\hat{T}_3$ containing terms in the expansion of $\tilde{H}$ were restricted to $(\hat{H}\hat{T}_1)_C$ and $(\hat{H}\hat{T}_3)_C$. The performace of this method, including the importance of demanding triples was shown for the BH_3 molecule using minimal basis. The cost and complexity of E-CPMET was essentially the same as if would have the full CCSDT.

This fact, combined with fairly limited available computer power prevented the authors from demonstrating the ability of E-CPMET on larger molecular systems. Nevertheless, their work showed that there was a need for development of efficient approaches and algorithms allowing full consideration of triples or eventually even higher excitation operators.

More practical implementations of triples within the framework of MBPT intended for "larger" molecules were reported from a few laboratories at the beginning of eighties [26–30]. At the same time Purvis and Bartlett [21] showed that the fourth order contribution from triples combined with the energy from their newly developed CCSD approach provided a reasonable approximation to full configuration interaction (FCI). Soon after, Lee, Kucharski and Bartlett introduced the simplest iterative extension of CCSD by triples within the framework of the CC theory [31] that is at present denoted as CCSDT-1a. They pointed out that unlike CI, connected triple excitations were the most important new terms to add to CCSD, which already accounts for the disconnected triple and quadruple contributions.

Being involved in similar projects in Bratislava, at this stage the present authors started an active collaboration with Quantum Theory Project (QTP), namely with the group of Rodney Bartlett, where both authors spent some time as research associates in the 1980s of the last century. It was the time when quantum chemists and general users of quantum chemistry methods started to believe that the coupled cluster approach could be useful. Of course, this was also a time when the practical applicability of CC (similarly as other highly correlated ab-initio wave function methods) was restricted to rather small systems due to much more limited computer resources than today.

Independently, in Bratislava we had been developing MBPT codes since the late 1970s [29, 32], eventually including an efficient algorithm for triples that implicitly used molecular symmetry [28]. Combining our codes with the program developed at QTP [21] enabled a prompt implementation of the methods described below and helped much in debugging both of the codes.

This retrospective summarizes essential results of the joint effort dating back to 1984 and 1986. There were two directions proposed in papers resulting from this period. First, we suggested a hierarchy of CC methods involving triple excitations known as CCSDT-n methods [33, 34] eventually leading to the full treatment within FCCSDT [22]. Secondly, a substantial improvement over the aforementioned MBPT correction for triples to CCSD was offered by a modified a posteriori non-iterative correction introduced as CCSD+T(CCSD) [33]. Although some of the proposed approximations are currently not so frequently used in practical applications, some of them remain topical, or served as essential foundations for even better approximations.

2. The CCSDT-n Hierarchy

The standard way of solving Eq. (4) is provided by its subsequent projection onto the reference –giving the energy— and onto excitation subspaces that are created by the action of operator (2) on the reference determinant resulting in a set of non-linear equations that determine the amplitudes of $\hat{T}$. These sets of coupled equations are then solved iteratively. The driving force behind the development of the CCSDT-n hierarchy was to keep the slowest step in a single iteration at the computational complexity corresponding to the 4th order MBPT, i. e. $\propto N^7$. Little was then known about the higher order corrections and their possible mutual cancellations. Our philosophy was to provide a hierarchy that would be "exactly"

4   *J. Noga and M. Urban*

formulated with $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$ when the Eq. (4) was projected onto single (Φ_1) and double (Φ_2) substitutions, i. e.

$$\langle\Phi_\mu| \left(\hat{H}e^{\hat{T}_1+\hat{T}_2+\hat{T}_3}\right)_C |\Phi\rangle = 0, \qquad \mu = 1, 2 \tag{6}$$

while (at least from the formal point of view) gradually improving the exponential expansion when projecting onto triply excited states (Φ_3). Hence, in addition to Eq. (6) the following equations:

$$\langle\Phi_3| \left(\hat{H}\hat{T}_2\right)_C |\Phi\rangle = 0, \tag{7}$$

$$\langle\Phi_3| \left(\hat{H}e^{\hat{T}_2}\right)_C |\Phi\rangle = 0, \tag{8}$$

$$\langle\Phi_3| \left(\hat{H}e^{\hat{T}_1+\hat{T}_2}\right)_C |\Phi\rangle = 0, \tag{9}$$

define CCSDT-1b, CCSDT-2 and CCSDT-3, respectively [33, 34]. If we consider the amplitudes in terms of the perturbation theory in a generalized sense [35, 36] then Eq. (7) involves second order, Eq. (8) third order, and Eq. (9) fourth order contributions in the wave function expansion. One has to add, however, that third and higher orders are not included in full, i. e. the energy is only correct to fourth order in MBPT. In fact, prior to suggesting this hierarchy, an approach originally called CCSDT-1 had been implemented at QTP by Lee Kucharski and Bartlett [31] which differs from CCSDT-1b in projection onto double excitations, when in CCSDT-1 the disconnected clusters involving $\hat{T}_3$ are disregarded in Eq. (6) and which was also correct to fourth order in the MBPT energy expansion. The latter method was renamed to CCSDT-1a in Ref. [33]. Implementation of the CCSDT-2 and CCSDT-3 has been reported in Ref. [34] together with results for BH, HF, NH_3, CO, C_2H_2 at equilibrium geometries, and H_2O for equilibrium bond distance (R_e) together with symmetrically stretched bonds with $R = 1.5R_e$ and $R = 2.0R_e$. Except for CO and C_2H_2 the FCI benchmarks were available. Somewhat surprisingly, for equilibrium geometries the methods that are "higher" in the CCSDT-n hierarchy provided results which deviated from the FCI ones more than CCSDT-1. Nevertheless, with substantially stretched geometry ($2R_e$), CCSDT-3 energy was closest to FCI. When we extended the hierarchy with CCSDT-4 –including $(\hat{H}\hat{T}_3)_C$ into Eq. (9)– and to full CCSDT [22] led us to conclude that, generally, linear terms in the exponential expansion lower the energy while nonlinear terms act in the opposite direction. A short note regarding the correction added to our original paper a year later is appropriate at this point. Despite careful checking, it happened that a seventh order contribution of $(\hat{H}\hat{T}_1^3)_C$ was accounted twice in CCSDT. This was identified after a discussion and numerical comparisons with Gustavo Scuseria whom one of us (JN) met at the Sanibel Symposium in 1988 and who was just finishing implementation of CCSDT at the Center for Computational Quantum Chemistry, University of Georgia [37].

3.   Non-iterative correction for triples.

After a quarter of a century, it is now clear that the main impact of Ref. [33] to the field of practical quantum chemistry was not provided by the suggested CCSDT-n hierarchy, but instead by a rather simple approximation to the energy contribution stemming from triply excited configurations that was simply added 'a posteriori' to the CCSD energy. This approximation was originally named "CCSD+T(CCSD)", later a shorthand notation "CCSD[T]" was suggested [38].

What was the essence of T(CCSD)? Even though in CCSDT-1 – CCSDT-3 the computational scaling of the most demanding step is the same as in MBPT(4), i. e. $\propto N^7$, such a step has to be repeated in the iterative procedure of solving the nonlinear Eqs. (6)-(9) twice in each iteration. This is, of course, not very favorable, and any plausible approximation that would improve upon such unfavorable scaling was more than welcome. Hence, shortly after introducing the CCSD approach it was suggested to "complete" the energy in order to be correct to the fourth order of MBPT simply by adding the triple-excitation contribution from MBPT(4) to the CCSD energy [30]. The aforementioned contribution can be expressed as

$$E_T^{[4]} = -\langle \Phi | (\hat{T}_3^\dagger \hat{F} \hat{T}_3)_C | \Phi \rangle, \tag{10}$$

where $\hat{F}$ is the Fock operator. In the spinorbital basis, $\hat{F}$ can be always made diagonal . Hence, having $\hat{T}_3$, this particular contribution involves $\propto N_{T_3}$ algebraic operations, where N_{T_3} is the number of independent triple-excitation amplitudes. Having

$$\hat{H} = \hat{F} + \hat{W} \tag{11}$$

$\hat{T}_3$ is obtained from

$$-\langle \Phi_3 | (\hat{F} \hat{T}_3)_C | \Phi \rangle = \langle \Phi_3 | (\hat{W} \hat{T}_2^{(1)})_C | \Phi \rangle. \tag{12}$$

On the r.h.s the $\hat{T}_2^{(1)}$ amplitudes come from the first order wave function within MBPT. Let us remind that if $\hat{F}$ is a diagonal operator, $\hat{T}_3$ is obtained in a single step simply by dividing the r.h.s. matrix elements by the pertinent energy denominator.

The idea behind CCSD[T] consists in substituting the first order double excitation amplitudes in Eq. (12) by converged double excitation amplitudes from CCSD. Formally, and computationally Eq. (12) remains the same. However, through the $\hat{T}_2$ amplitudes arising from CCSD, the inherently hidden higher order information is also transfered to triples.

Indeed, this idea had been partially prompted by an incidental observation. During the development of CCSDT-1b, we used a checking output number from Eq. (10) using $\hat{T}_2$ of the current iteration in Eq. (12). In our iteration scheme the first iteration provided exactly $E_T^{[4]}$ when we started from the first order MBPT wave function. Surprisingly, when we started from the $\hat{T}_2$-amplitudes after converged CCSD equations, we noticed that if we added the initial "check" number to the CCSD energy, we approximately obtained the CCSDT-1 energy (in this context, "1a" or "1b" is immaterial). Hence, the idea of CCSD[T] was born. In the reasoning supporting this approach we have argued in terms of a symmetrical energy

6   *J. Noga and M. Urban*

functional [2] related to the CC ansatz of Eq. (1)

$$E(\hat{T}^{\dagger}, \hat{T}) = \frac{\langle\Phi|e^{\hat{T}^{\dagger}}\hat{H}e^{\hat{T}}|\Phi\rangle}{\langle\Phi|e^{\hat{T}^{\dagger}}e^{\hat{T}}|\Phi\rangle} = \langle\Phi|\left(e^{\hat{T}^{\dagger}}\hat{H}e^{\hat{T}}\right)_C|\Phi\rangle. \tag{13}$$

Čížek has shown that for exact $\hat{T}$

$$\langle\Phi|\left(\hat{H}e^{\hat{T}}\right)_C|\Phi\rangle = \langle\Phi|\tilde{H}|\Phi\rangle = \langle\Phi|\left(e^{\hat{T}^{\dagger}}\hat{H}e^{\hat{T}}\right)_C|\Phi\rangle. \tag{14}$$

With $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$ and after expanding the exponential in a Taylor series Eq. (13) can be rewritten as:

$$E(\hat{T}^{\dagger}, \hat{T}) = \langle\Phi|(1 + \hat{T}_1^{\dagger} + \hat{T}_2^{\dagger})(\hat{H}e^{\hat{T}_1+\hat{T}_2})_C|\Phi\rangle \tag{15}$$

$$+ \langle\Phi|\hat{T}_3^{\dagger}(\hat{F}\hat{T}_3 + \hat{W}\hat{T}_2)_C|\Phi\rangle \tag{16}$$

$$+ \langle\Phi|(\hat{T}_2^{\dagger}\hat{W}\hat{T}_3)_C|\Phi\rangle \tag{17}$$

$$+ \langle\Phi|(\hat{T}_2^{\dagger}\hat{F}\hat{T}_3)_C|\Phi\rangle \tag{18}$$

$$+ \langle\Phi|(\hat{T}_1^{\dagger}\hat{W}\hat{T}_3)_C|\Phi\rangle \tag{19}$$

$$+ \text{...other fifth and higher order terms}$$

The first term (15) corresponds to the asymmetric functional of Arponen's type [39] from which the CCSD equations can be derived by making it stationary with respect to $\hat{T}_1^{\dagger}$ and $\hat{T}_2^{\dagger}$. Hence, if we start from CCSD amplitudes this term is exactly equal to the CCSD energy. In T(CCSD) we replace in Eq. (12) the first order amplitudes by those from the converged CCSD. Due to the validity of Eq. (12) the contribution (16) is zero and the term (17) becomes equivalent with Eq. (10). What remains (for closed shell systems or the UHF reference) are fifth and higher order terms.

Independently, and in parallel to our work on T(CCSD), Raghavachari [40] used a non-iterative correction due to single and triple excitations added to the CCD energy. The method was named CCD+ST(CCD) and the *a posteriori* energy corrections were calculated exactly as in our case, using fourth order formulae with converged $\hat{T}_2$ amplitudes, which has been often an improvement over the CCD+ST(MP4) used earlier at QTP [9, 21]. The better performance of T(CCSD) originates mainly from the much better recovering of the orbital relaxation (vide infra) that results from the interplay between the $\hat{T}_1$ and $\hat{T}_2$ amplitudes.

3.1.   *Towards a more accurate approximation*

The CCSD[T] approximation was the forerunner of the currently widely used CCSD(T) approximation [41] – often denoted as a "golden standard" of ab initio quantum chemistry. In the latter the contribution of (19) $[E_{ST}^{(5)}]$ is taken into account in addition to the T(CCSD) correction with the closed shell and the UHF references. One of the arguments for using this particular $\hat{T}_1$-containing fifth order contribution was the fact that this term participates in the final CCSDT-n energies twice, i. e. as in 5th order MBPT,

$$\langle\Phi|T_1^{\dagger}\hat{H}\hat{T}_3|\Phi\rangle + \langle\Phi|T_3^{\dagger}\hat{H}\hat{T}_1|\Phi\rangle, \tag{20}$$

when $\hat{T}_1^\dagger$ and $\hat{T}_3^\dagger$ are implicitly restricted to second order in the MBPT wave function expansion. In CCSD[T] only half of the total contribution is inherently included via CCSD. Thus, the CCSD(T) energy includes all the fifth order terms that are present in CCSDT-1. In fact, there are many fifth order terms [42] that are comparable and often larger [43, 44]. In our opinion, the most plausible reason for including of $E_{ST}^{(5)}$ together with T(CCSD) was given by Stanton somewhat later [45]. Instead of focusing on the missing contributions in terms of MBPT he concentrated on a perturbation approach based on the CCSD reference. This automatically accounts for the asymmetric nature of the (approximated) coupled cluster theory and the aforementioned contributions represent the leading-order corrections.

The original T(CCSD) approximation was based on arguments using a symmetrical energy functional, while the amplitudes are obtained using a non-Hermitian similarity transformed Hamiltonian Eq. (5), i. e. the symmetry in T(CCSD) is forced. For critical cases, when this approximation starts to be inappropriate, significantly improved results are obtained using the left vector amplitudes, instead of assuming that the amplitudes of $\hat{T}^\dagger$ are equivalent to amplitudes of $\hat{T}$ [46–48].

As follows from the Thouless theorem mentioned in Sec. 1, the action of $\exp(\hat{T}_1)$ on $|\Phi\rangle$ in the coupled cluster treatment takes care of the orbital relaxation, i.e. transforms the the original reference to a different Slater determinant that is closer to an optimal reference within the given CC ansatz, while the "closeness" depends on the specific evaluation of $\hat{T}_1$. Hence, as mentioned already in the context of CCSD [21] the $\exp(\hat{T}_1)$ could be included in the reference. Then, however, the $|\Phi\rangle$ has to be determined self consistently. Consequently, integral transformation is needed in each iteration step. This has been done in the so-called Brueckner doubles theory [49]. Since the $\hat{T}_1 = 0$, with this reference the non-iterative correction for triples [BD(T)] is calculated exactly as in ST(CCD) or T(CCSD), though the actual 5th order content (as compared to the HF reference) differs somewhat from CCSD(T). Comparison of results using CC hierarchy up to triples using both HF and Brueckner orbitals has been given somewhat later as a QTP contribution [50].

3.2. *Starting from open shell ROHF reference*

In CC calculations, the use of an ROHF reference for open–shell molecules was first reported in 1988 by Rittby and Bartlett [51]. For the latter reference or more general reference wave functions created from non-canonical orbitals the CCSD[T] (and accordingly also CCSD(T)) approximation has to be modified. First, if the Brillouin theorem is not obeyed, the occupied-virtual block of $\hat{F}$ is not zero and hence the contribution of (18) is non-zero, as well. If the pertinent block of the Fock matrix is treated as a perturbation then the latter term contributes in the 4th order of the MBPT energy expansion and it has to be included in order to stay within arguments behind T(CCSD). This term is, however, easy to calculate and, computationally, it only requires a small fraction of the cost needed for the evaluation of $\hat{T}_3$ via Eq. (12). More problems are caused by the off-diagonal elements of the occupied-occupied ($\hat{F}_{oo}$) and virtual-virtual ($\hat{F}_{vv}$) blocks of $\hat{F}$. With these terms the accurate solution of Eq. (12) requires an iterative procedure involving $\propto N^7$ steps in each iteration, which is undesired. Alternatively, one can abandon the frame of ROHF orbitals and separately diagonalize the $\hat{F}_{oo}$ and $\hat{F}_{vv}$ blocks. Afterwards, one works with semicanonical orbitals leading to different orbitals for different spins. Careful analysis of the problem of triples within iterative and non-iterative CC procedures was presented by Watts, Gauss and Bartlett [52] who prefer the semicanonical

approach. If one decides to stay within the spin-restricted scheme, the $\hat{T}_3$ in Eq. (12) has to be obtained iteratively in order to arrive at results that are invariant to rotations within the blocks of occupied and/or virtual orbitals [52]. In this case the whole $\hat{F}_{oo}$ and $\hat{F}_{vv}$ blocks are treated as the unperturbed Hamiltionian. For the efficient treatment of triples which takes the advantage of having the same spatial orbitals for different spins in the restricted part of the ROHF reference one can eventually give up the orbital invariance and restrict the procedure to its first iteration fully neglecting the off-diagonal part of $\hat{F}$ with two options [53]: i) using the orbital energies instead of the full diagonal elements in contributions calculated according to Eqs. (10) and (12), which would correspond to "traditional" perturbational viewpoint or ii) using the complete diagonal part of $\hat{F}$ that is in open shell ROHF different from orbital energies. Although such approaches are not invariant with respect to orbital rotations, it has been numerically demonstrated that the differences from invariant values were small, in particular for $CCSD(T)_d$ [53].

One has to realize that even when using the ROHF reference which is a proper wave function of the spin operators, the resulting CCSD wave function and the triples contribution in CCSD(T) is not. Approximate spin adaptation of the double excitation amplitudes used for the triples was suggested by Neogrady and one of us (MU) [53]. For a rigorous treatment of the open–shell molecules and the spin adaptation see e.g. Refs. [54, 55].

3.3.   *Prompting alternative ansätze*

As mentioned, the T(CCSD) approximation was based on arguments related to the expansion of the expectation value Eq. (13) in terms of MBPT. Accordingly, we had also investigated the one-particle properties as expectation values of the pertinent operators [56], showing that the error was relatively small, as soon as singles were included. The paper was in press as I (JN) revisited QTP in 1988 for a short time. One night, we started to discuss the details with Rod Bartlett spending about two hours at the blackboard drawing tens of diagrams, while our discussion went far beyond the initial issue. Not far from the early morning we ended understanding how and to which order the terms mutually cancel. To my surprise, the next day Rod came in with the handwritten first draft of the manuscript on the expectation value CC [XCC(n)] hierarchy [35]. Soon after, this was followed by a fruitful collaboration with Staszek Kucharski resulting in a hierarchy based on the Unitary CC method [57] and methods involving 5th order energy terms, including the fifth order MBPT [43], the first implementation of quadruples within the CC methods, namely within the XCC(5) ansatz [58], or non-iterative corrections [44] based on the generalized PT scheme [36]. Methods including quadruple and higher excitations emerged from QTP subsequently [24, 59–61].

4.   Conclusions

Presently, CC methods have developed as a most powerfull method for accurate calculations of molecular properties. The hierarchical structure of the CC theory, the possibility of controlling the applicability of a single determinant reference, e. g. through checking the magnitudes of excitation amplitudes, enables obtaining "good results for a good reason". We believe that the work done 25 years ago at QTP and reminded in this retrospective has significantly contributed to the former statement. Besides, the suggested T(CCSD) approach that had been a forerunner

of the pragmatic and widely used CCSD(T), we tried to suggest a systematic hierarchy that eventually led to full inclusion of triples within the coupled cluster treatment. In the mean time, there are certainly new hierarchies suggested. Among them the CCn hierarchy [62, 63] is based on the argument the orbital relaxation and hence particularly suited for molecular properties. Another interesting concept is the hierarchy based on the method of moments in coupled cluster theory [64–66] that builds a common roof above the variety of CC approximations. Along with the progress related to molecules well represented by a single determinant reference we are witnessing a progression of CC methods applicable for more general molecules, particularly those which show some extent of quasidegeneracy. Either in the treatment via higher excitations [43, 46, 67–69] or in the treatment via multireference approaches [12, 15, 70–73]. In several of these approaches the ideas put forward in our original paper on approximations to iterative as well to non-iterative triples were further extended.

Improved theoretical formulations transformed into sophisticated computer codes with high level of parallelism [74–77], employing localized orbitals [78–81], or the possibility of reducing the virtual space by methods like OVOS (also initiated at QTP) [82, 83] contribute to making gradually larger molecules tractable by the CC methods.

Acknowledgements

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