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Analysis of coupled cluster methods*

IV. Size-extensive quadratic CI methods – quadratic CI with triple and quadruple excitations

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Summary. A procedure is developed that leads from CI to size-extensive CI (ECI) by stepwise cancellation of disconnected terms in the CI equations. The ECI methods thus obtained are identical with the corresponding coupled cluster (CC) methods with the exception of CISD and CISDT, which convert to size-extensive quadratic CI (QCISD) and ECISDT. The latter method has similar properties as CCSDT, but does not offer any significant time-savings as compared to CCSDT. Therefore, the idea of extending CI methods to size-extensive CI methods does not lead to a hierarchy of independent CC methods. However, the procedure of obtaining ECI methods lays the basis for deriving QCI methods that are truly size-extensive. This is accomplished by (a) deleting the first linear term of the p-fold CI excitation equations ($p \geqslant 3$) since this term always represents a disconnected term and (b) including just the connected part of appropriate quadratic correction terms in all but the energy equation. In this way, size-extensive QCISDT and QCISDTQ are obtained and their properties are discussed in comparison with QCISD(T) and CCSDT.

Key words: Coupled cluster methods – Size-extensive CI – Quadratic CI – QCISDT – QCISDTQ

1 Introduction

Coupled cluster (CC) theory [1–3] has attracted much attention in recent years since it provides one of the most powerful ways to include electron correlation in an *ab initio* calculation. Since CC methods are size-extensive and since they cover infinite order effects, they lead to better results than either configuration interaction (CI) or many-body perturbation theory (MBPT) methods. CC results are the more accurate the more excitations are included, for example double excitations (D) in CCD [4], single (S) and D excitations in CCSD [5], S, D, and triple (T) excitations in CCSDT [6], S, D, T, and quadruple (Q) excitations in CCSDTQ [7], etc. While

* This paper is dedicated to Prof. Werner Kutzelnigg on the occasion of his sixtieth birthday

CCD and CCSD are $O(M^6)$ methods (M: number of basis functions) and, therefore, are used for routine calculations on small and medium-sized molecules, CCSDT and CCSDTQ are $O(M^8)$ and $O(M^{10})$ methods that can be applied only for small molecules.

Because of the success of the CC methods there have been many attempts to simplify them in such a way that their accuracy is maintained while at the same time their computational costs are reduced. For example, Pople, Head-Gordon, and Raghavachari (PHR) [8] have suggested a new CC method that they derived from CISD by adding quadratic terms to the CI projection equations. In this way, the method becomes size-extensive at the cost of loosing the variational character of CI. PHR coined the method quadratic CI with S and D excitations (QCISD) and discussed its relationship to CCSD. They pointed out that QCISD is a simplified CCSD method that does not contain cubic and quartic terms and, therefore, is easier to carry out. Also, PHR compared QCISD energies with the corresponding CISD and CCSD values and found that the former are closer to full CI energies than the latter. QCISD energies can be substantially improved by adding T excitations in a perturbative way to QCISD, thus leading to QCISD(T) [8]. QCISD(T) energies compare even better with full CI energies as QCISD energies do.

With QCISD, PHR introduced a new series of methods which they considered to be intermediate between CI and CC methods. For the case that all excitations up to n-fold are included, the corresponding QCI method is obtained from the CI method by adding just quadratic terms to the n and $(n-1)$ excitation equations. In this way, PHR expected to get a hierarchy of size-extensive QCI methods that provide computational advantages both with regard to CI and CC [8].

The QCI approach has met considerable criticism from various authors. For example, Paldus, Cizek, and Jeziorski [9] pointed out that QCISDT as suggested by PHR is no longer size-extensive even though the QCI methods were developed to restore size-extensiveness in CI. Scuseria and Schaefer [10] compared the time requirements of QCISD and CCSD and found that QCISD has essentially the same computational requirements as the more complete CCSD method [11]. In a recent investigation, we compared CC and QCI methods in terms of 5th, 6th, and infinite order MBPT [12–14]. Our analysis clearly showed that QCI methods are inferior to CC methods and that the energy comparisons carried out by PHR are somewhat misleading. In addition, it has to be noted that the simplicity of the QCI equations vanishes if one starts from a general reference wavefunction which is not based on canonical Hartree-Fock orbitals. It is also worth noting that, unlike CC, QCI does not possess a well-defined wavefunction.

Nevertheless, the QCI methods QCISD and QCISD(T) are widely used in *ab initio* investigations and, probably, it is just a matter of time when QCI will be extended to a full inclusion of T effects. Therefore, one has to ask whether a size-extensive QCISDT method with just quadratic corrections added to the linear CISDT terms is possible at all and how such a method will differ from the non-size-extensive QCISDT method originally proposed by PHR [8]. We will answer this question in the present paper and by doing so we will look into the more general question whether there exists a hierarchy of size-extensive QCI methods that is in line with the original idea of PHR, namely a simple improvement of CI by just including quadratic correction terms.

Our investigation will proceed in the following way. In Sect. 2, we will develop a systematic procedure that restores size-extensiveness in the CI approach. We will apply this procedure to CID, CISD, CISDT, and CISDTQ and compare the resulting size-extensive CI (ECI) [14] with existing QCI and CC methods (Sect. 3).

In Sects. 4 and 5, we will focus on the question whether there is a hierarchy of size-extensive QCI methods. In particular, we will concentrate on size-extensive QCISDT and QCISDTQ and derive the projection equations for these methods.

2 Systematic development of size-extensive CI methods

The procedure applied by PHR [8] to derive QCISD from CISD can be generalized in the following way:

The physically not meaningful terms in the projection equations of truncated CI show up in a diagrammatic description in form of unlinked diagrams. The unlinked diagrams result from disconnected terms in the CI equations of a given truncation level. In order to obtain a size-extensive CI energy we have to eliminate all disconnected terms from the CI projection equations. This implies that we have:

a) to analyze the disconnected terms, then b) to find the simplest way of cancelling disconnected terms by adding new terms and, finally, c) to check whether the addition of appropriated terms to the CI equations does not lead to new disconnected terms.

If new disconnected terms appear, one has to add further terms until all disconnected terms disappear. In the most general case one has to loop through the sequence a), b), and c) several times before a size-extensive procedure is obtained. This is illustrated in Fig. 1 which contains a flow-chart diagram for a systematic development of ECI projection equations from the corresponding equations of a CI method of given truncation level.

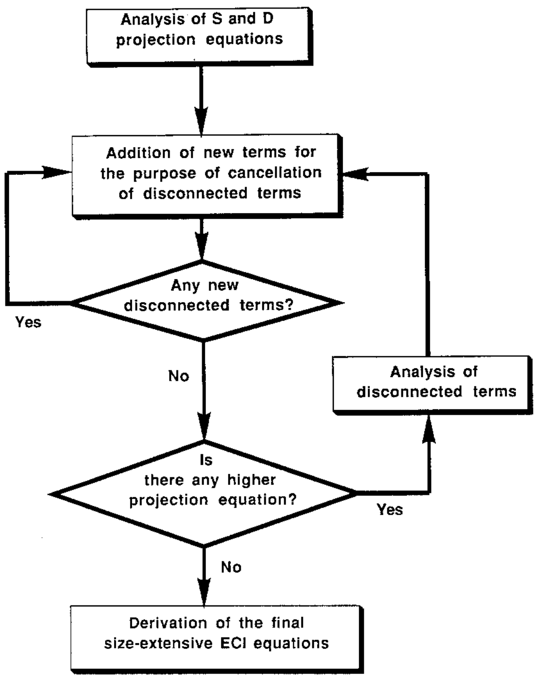


Fig. 1. Flow-chart diagram for the conversion of CI methods to size-extensive ECI methods

According to this procedure, *an ECI method can be considered as a CI method, to which a minimum number of terms have been added to restore size-extensiveness, or better as an approximated CC method that differs from the corresponding CI method by a minimal number of terms.* If the CI space is restricted to S and D excitations, the new terms to be added are quadratic as has been shown by PHR [8]. However, if higher excitations are included, e.g. T excitations at the CISDT level, size-extensiveness will require the inclusion of both quadratic and cubic terms as will be shown in the following. Accordingly, one would have to speak of cubic CI, quadratic CI, etc. However, we will refrain from introducing a new terminology and, instead, stick to the term ECI [15].

We will apply in the following the procedure outlined in Fig. 1 to CID, CISD, CISDT, and CISDTQ in order to get the corresponding ECI procedures. Although this has been done for CID and CISD before, we will include these methods in our analysis in order to establish our procedure and to introduce the necessary nomenclature.

2.1 From CID to ECID

The CID wavefunction is given by:

$$|\Phi_{CID}\rangle = (1 + \hat{T}_2)|\Phi_0\rangle \tag{1}$$

where $|\Phi_0\rangle$ is a reference function (for simplicity, we take here and in the following the Hartree-Fock (HF) wavefunction as a reference function) and $\hat{T}_2$ a double excitation cluster operator:

$$\hat{T}_2 = \tfrac{1}{4}\sum_{ij}\sum_{ab} c_{ij}^{ab}\hat{b}_a^+\hat{b}_i\hat{b}_b^+\hat{b}_j \tag{2a}$$

or, in general:

$$\hat{T}_n = \frac{1}{(n!)^2}\sum c_{ijk\ldots}^{abc\ldots}\hat{b}_a^+\hat{b}_i\hat{b}_b^+\hat{b}_j\hat{b}_c^+\hat{b}_k\cdots. \tag{2b}$$

We refrain from using different symbols for CI and CC cluster operators (e.g., $\hat{C}$ and $\hat{T}$). Instead, we distinguish between CI and CC cluster operators by denoting CI amplitudes by $c_{ijk\ldots}^{abc\ldots}$ and CC (QCI, ECI) amplitudes by $a_{ijk\ldots}^{abc\ldots}$. Subscripts $i, j, k, \ldots, (a, b, c, \ldots)$ denote occupied (virtual) spin orbitals while subscripts $p, q, r, \ldots$ are used for general spin orbitals. The operators $\hat{b}^+$ and $\hat{b}$ are creation and annihilation operators. With Eq. (2a) the CID projection equations can be written as:

$$\langle\Phi_0|\bar{H}\hat{T}_2|\Phi_0\rangle = E_{corr}^{CID} \tag{3}$$

$$\langle\Phi_{ij}^{ab}|\bar{H}(1 + \hat{T}_2)\Phi_0\rangle = c_{ij}^{ab}E_{corr}^{CID}, \tag{4}$$

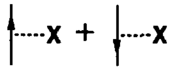
in which $\bar{H}$ denotes the normal-order Hamiltonian:

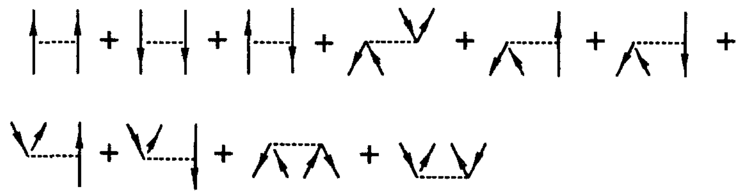
$$\begin{aligned}\bar{H} &= \hat{H} - E(HF) = \bar{H}_0 + \bar{V}\\ &= \sum_{rs}\{\hat{b}_r^+\hat{b}_s\}\langle r|\hat{F}|s\rangle + \tfrac{1}{4}\sum_{rstu}\{\hat{b}_r^+\hat{b}_s^+\hat{b}_t\hat{b}_u\}\langle rs\|tu\rangle\end{aligned} \tag{5}$$

and $|\Phi_{ij}^{ab}\rangle$ a doubly excited wavefunction. E_{corr}^{CID} corresponds to the CID correlation energy:

$$E_{corr}^{CID} = E^{CID} - E(HF). \tag{6}$$

With $|\Phi_0\rangle$ as the HF reference function, operators $\bar{H}_0$ and $\bar{V}$ are expressed by the following diagrams [16]:

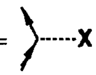
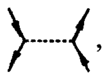
$\bar{H}_0 =$  (7)

$\bar{V} =$  (8)

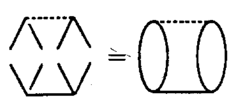
and the cluster operator $\hat{T}_2$ by:

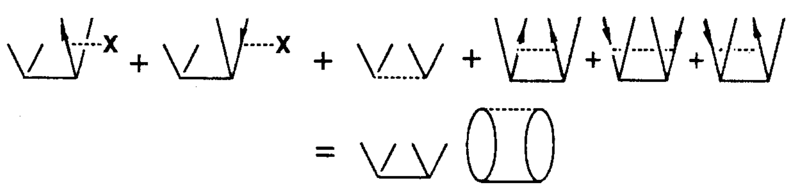
$\hat{T}_2 =$  (9)

where

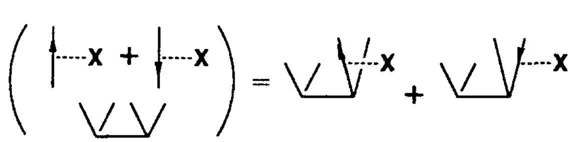
$\langle b|\hat{F}|a\rangle =$  , $\langle ja\|ib\rangle =$  , $c_{ij}^{ab} =$ 

We get for Eqs. (3) and (4) the diagrammatic representations (10) and (11):

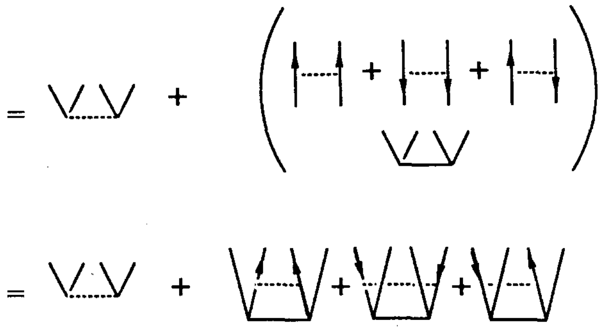
$E_{corr}^{CID} =$  (10)

 (11)

which can be verified with the matrix elements (12) and (13):

$\langle \Phi_{ij}^{ab}|\bar{H}_0\hat{T}_2|\Phi_0\rangle =$  (12)

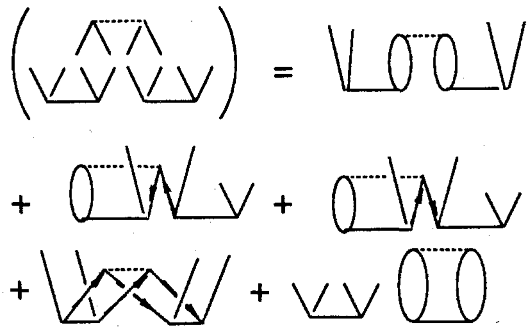
$$\langle \Phi_{ij}^{ab} | \bar{V}(1 + \hat{T}_2) | \Phi_0 \rangle =$$



(13)

Equation (11) reveals that $c_{ij}^{ab} E_{corr}^{CID}$ represents a disconnected term that leads to unlinked diagrams. Hence, the CID method is not size-extensive. The simplest matrix element that contains the same unlinked diagram is $\langle \Phi_{ij}^{ab} | \bar{H} \frac{1}{2} \hat{T}_2^2 | \Phi_0 \rangle$ as is shown by (14).

$$\langle \Phi_{ij}^{ab} | \bar{H} \hat{T}_2^2/2 | \Phi_0 \rangle =$$



(14)

Hence, by inserting $\langle \Phi_{ij}^{ab} | \bar{H} \frac{1}{2} \hat{T}_2^2 | \Phi_0 \rangle$ on the left side of Eq. (4), the unlinked diagram due to the disconnected term $c_{ij}^{ab} E_{corr}^{ECID}$ is cancelled. In this way, size-extensive ECID is obtained:

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECID} \tag{15}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_2 + \tfrac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} E_{corr}^{ECID} \tag{16}$$

where a_{ij}^{ab} is used to distinguish ECI or CC amplitudes from CI amplitudes. Inspection of Eqs. (15) and (16) reveals that ECID is identical with QCID, which in turn is identical with CCD as has been noted before [8]. Therefore, size-extensiveness corrections lead right away from CID to CCD [17].

2.2 *From CISD to ECISD*

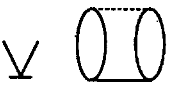
The CISD projection equations are given by Eqs. (17)–(19):

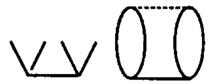
$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{CISD} \tag{17}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle = c_i^a E_{corr}^{CISD} \tag{18}$$

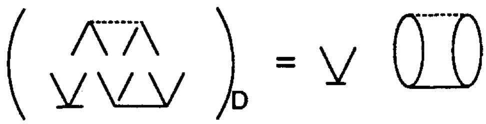
$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle = c_{ij}^{ab} E_{corr}^{CISD} \tag{19}$$

The disconnected terms, which lead to unlinked diagrams, are:

$$c_i^a E_{corr}^{CISD} =$$  (20)

$$c_{ij}^{ab} E_{corr}^{CISD} =$$  (21)

By adding $\langle \Phi_i^a | \bar{H} \hat{T}_1 \hat{T}_2 | \Phi_0 \rangle_D$:

$$\langle \Phi_i^a | \bar{H} \hat{T}_1 \hat{T}_2 | \Phi_0 \rangle_D =$$  (22)

and $\langle \Phi_{ij}^{ab} | \bar{H} \frac{1}{2} \hat{T}_2^2 | \Phi_0 \rangle$ (compare with Eq. (14)) on the left side of Eqs. (18) and (19), respectively, unlinked diagrams resulting from $c_i^a E_{corr}^{CISD}$ and $c_{ij}^{ab} E_{corr}^{CISD}$ are cancelled and the ECISD projection equations are obtained.

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECISD} \tag{23}$$

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle = a_i^a E_{corr}^{ECISD} \tag{24}$$

$$\langle \Phi_{ij}^{ab} | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} E_{corr}^{ECISD} \tag{25}$$

ECI is identical with QCISD, but contrary to QCID, QCISD is not identical with the corresponding CC method, CCSD. Thus, QCISD is the first independent method in the QCI series [8]. We will investigate in the following whether there are any further QCI methods.

2.3 From CISDT to ECISDT

The CISDT projection equations are given by Eqs. (26)–(29)

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{CISDT} \tag{26}$$

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_i^a E_{corr}^{CISDT} \tag{27}$$

$$\langle \Phi_{ij}^{ab} | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_{ij}^{ab} E_{corr}^{CISDT} \tag{28}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_{ijk}^{abc} E_{corr}^{CISDT}. \tag{29}$$

From Eqs. (27) and (28) the S and D equations of ECISDT are obtained in the same way as the corresponding ECISD equations:

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECISDT} \tag{30}$$

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle = a_i^a E_{corr}^{ECISDT} \tag{31}$$

$$\langle \Phi_{ij}^{ab} | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \tfrac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} E_{corr}^{ECISDT} \tag{32}$$

Equations (31) and (32) can be rewritten in the connected form, thus leading to Eqs. (33) and (34):

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_c = 0 \tag{33}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_c = 0, \tag{34}$$

where the subscript "c" indicates a restriction to connected terms.

Contrary to the S and D projection equations, the T Eq. (29) contains two disconnected terms, which lead to the following disconnected diagrams:

$$\langle \Phi_{ijk}^{abc} | \bar{H} \hat{T}_1 | \Phi_0 \rangle =$$  (35a)

$$c_{ijk}^{abc} E_{corr}^{CISDT} = \langle \Phi_{ijk}^{abc} | \hat{T}_3 | \Phi_0 \rangle \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle$$

$$=$$  (35b)

By applying $\hat{T}_2 \hat{T}_3$ the disconnected term $c_{ijk}^{abc} E_{corr}^{CISD}$ is cancelled:

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_2 \hat{T}_3) | \Phi_0 \rangle = a_{ijk}^{abc} E_{corr}^{ECISDT}, \tag{36}$$

where the disconnected part of $\hat{T}_2 \hat{T}_3$ is given by:

$$\langle \Phi_{ijk}^{abc} | (\bar{H} \hat{T}_2 \hat{T}_3)_D | \Phi_0 \rangle = \langle \Phi_{ijk}^{abc} | \hat{T}_3 (\bar{H} \hat{T}_2)_C | \Phi_0 \rangle + \langle \Phi_{ijk}^{abc} | \hat{T}_2 (\bar{H} \hat{T}_3)_C | \Phi_0 \rangle \tag{37a}$$

$$= \langle \Phi_{ijk}^{abc} | \hat{T}_3 | \Phi_0 \rangle \langle \Phi_0 | (\bar{H} \hat{T}_2)_C | \Phi_0 \rangle + \sum_s^S \langle \Phi_{ijk}^{abc} | \hat{T}_2 | \Phi_s \rangle \langle \Phi_s | (\bar{H} \hat{T}_3)_C | \Phi_0 \rangle \tag{37b}$$

$$= a_{ijk}^{abc} E_{corr}^{ECISDT} + \sum_s^S \langle \Phi_{ijk}^{abc} | \hat{T}_2 | \Phi_s \rangle \langle \Phi_s | (\bar{H} \hat{T}_3)_C | \Phi_0 \rangle. \tag{37c}$$

In Eq. (37) we have used the fact that:

$$\langle \Phi_n | (\bar{H} \hat{T}_m \hat{T}_k)_D | \Phi_0 \rangle = \langle \Phi_n | \hat{T}_m (\bar{H} \hat{T}_k)_C | \Phi_0 \rangle + \langle \Phi_n | \hat{T}_k (\bar{H} \hat{T}_m)_C | \Phi_0 \rangle \tag{38}$$

and, in addition, we have inserted the identity operator $\sum_p^\infty | \Phi_p \rangle \langle \Phi_p |$ (with p as general substitution index) into the matrix elements $\langle \Phi_{ijk}^{abc} | \hat{T}_3 (\bar{H} \hat{T}_2)_C | \Phi_0 \rangle$ and $\langle \Phi_{ijk}^{abc} | \hat{T}_2 (\bar{H} \hat{T}_3)_C | \Phi_0 \rangle$. However, by cancelling $a_{ijk}^{abc} E_{corr}^{ECISDT}$ we get a new disconnected term, namely $\langle \Phi_{ijk}^{abc} | \hat{T}_2 (\bar{H} \hat{T}_3)_C | \Phi_0 \rangle = \sum_s^S \langle \Phi_{ijk}^{abc} | \hat{T}_2 | \Phi_s \rangle \langle \Phi_s | (\bar{H} \hat{T}_3)_C | \Phi_0 \rangle$ that requires the inclusion of further terms into Eq. (36). For this purpose, we use the single excitations Eq. (33) and multiply it with $\hat{T}_2$. Obviously, the addition of $\hat{T}_2 \hat{T}_1, \frac{1}{2}\hat{T}_2^2$, and $\frac{1}{2}\hat{T}_1 \hat{T}_2^2$ to $\hat{T}_2 \hat{T}_3$ will lead to cancellation of disconnected S excitation terms, but not necessarily of other disconnected terms resulting from D excitations. To check this we have to analyze Eq. (39):

$$\langle \Phi_{ijk}^{abc}|\bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_1 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1\hat{T}_2^2)|\Phi_0\rangle = (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc}|\hat{T}_2\hat{T}_1|\Phi_0\rangle)E_{corr}^{ECISDT}, \tag{39a}$$

which can be rewritten in the form of Eq. (39b):

$$\langle \Phi_{ijk}^{abc}|(\bar{H} - E_{corr}^{ECISDT})(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_1 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1\hat{T}_2^2)|\Phi_0\rangle = 0. \tag{39b}$$

For the analysis, we dissolve the disconnected part of Eq. (39a) with the help of Eq. (38):

$$\begin{aligned}
&\langle \Phi_{ijk}^{abc}|[\bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_1 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1\hat{T}_2^2)]_D|\Phi_0\rangle \\
&= \langle \Phi_{ijk}^{abc}|[\bar{H}(\hat{T}_1 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_1 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1\hat{T}_2^2)]_D|\Phi_0\rangle \\
&= \langle \Phi_{ijk}^{abc}|\hat{T}_1[\bar{H}(1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2)_C]|\Phi_0\rangle + \langle \Phi_{ijk}^{abc}|\hat{T}_2[\bar{H}(\hat{T}_1 + \hat{T}_2 \\
&\quad + \hat{T}_3 + \hat{T}_1\hat{T}_2)]_C|\Phi_0\rangle + \langle \Phi_{ijk}^{abc}|\hat{T}_3(\bar{H}\hat{T}_2)_C|\Phi_0\rangle + \langle \Phi_{ijk}^{abc}|\hat{T}_1\hat{T}_2(\bar{H}\hat{T}_2)_C|\Phi_0\rangle \\
&= \sum_d^D \langle \Phi_{ijk}^{abc}|\hat{T}_1|\Phi_d\rangle\langle \Phi_d|\bar{H}(1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2)|\Phi_0\rangle_C \\
&\quad + \sum_s^S \langle \Phi_{ijk}^{abc}|\hat{T}_2|\Phi_s\rangle\langle \Phi_s|\bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2)|\Phi_0\rangle_C \\
&\quad + (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc}|\hat{T}_1\hat{T}_2|\Phi_0\rangle)\langle \Phi_0|\bar{H}\hat{T}_2|\Phi_0\rangle
\end{aligned} \tag{40a}$$

$$\begin{aligned}
&= \sum_d^D \langle \Phi_{ijk}^{abc}|\hat{T}_1|\Phi_d\rangle\langle \Phi_d|\bar{H}(1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2)|\Phi_0\rangle_C \\
&\quad + (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc}|\hat{T}_1\hat{T}_2|\Phi_0\rangle)E_{corr}^{ECISDT},
\end{aligned} \tag{40b}$$

where we have inserted Eq. (33) into Eq. (40a). Equation (40b) reveals that the remaining disconnected terms indeed involve D excitations and, therefore, it is reasonable to cancel them with the help of Eq. (34) (actually, Eq. (34) being multiplied by $\hat{T}_1$). For this purpose, we introduce the terms $\frac{1}{2}\hat{T}_1^2$ and $\hat{T}_1\hat{T}_3$ into Eq. (39a). Since the disconnected part of $\langle \Phi_{ijk}^{abc}|\bar{H}(\frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_3)|\Phi_0\rangle$ can be written as:

$$\begin{aligned}
&\langle \Phi_{ijk}^{abc}|[\bar{H}(\tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_3)]_D|\Phi_0\rangle \\
&= \langle \Phi_{ijk}^{abc}|\hat{T}_1[\bar{H}(\hat{T}_1 + \hat{T}_3)]_C|\Phi_0\rangle \\
&= \sum_d^D \langle \Phi_{ijk}^{abc}|\hat{T}_1|\Phi_d\rangle\langle \Phi_d|\bar{H}(\hat{T}_1 + \hat{T}_3)|\Phi_0\rangle_C
\end{aligned} \tag{41}$$

with

$$\begin{aligned}
&\langle \Phi_{ijk}^{abc}|\hat{T}_3(\bar{H}\hat{T}_1)_C|\Phi_0\rangle \\
&= \langle \Phi_{ijk}^{abc}|\hat{T}_3|\Phi_0\rangle\langle \Phi_0|(\bar{H}\hat{T}_1)_C|\Phi_0\rangle = 0,
\end{aligned} \tag{42}$$

it is easy to see that after adding $\frac{1}{2}\hat{T}_1^2$ and $\hat{T}_1\hat{T}_3$ the disconnected part of Eq. (40b) vanishes. Hence, the desired projection equations of a size-extensive ECISDT method are given by:

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECISDT} \tag{30}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle = a_i^a E_{corr}^{ECISDT} \tag{31}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} E_{corr}^{ECISDT} \tag{32}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \tfrac{1}{2}\hat{T}_1 \hat{T}_2^2 + \hat{T}_2 \hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle$$
$$= (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 \rangle) E_{corr}^{ECISDT} \tag{43}$$

or, alternatively, by:

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_c = 0 \tag{33}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_c = 0, \tag{34}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \hat{T}_2 \hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1 \hat{T}_2^2) | \Phi_0 \rangle_C = 0 \tag{44}$$

Clearly, *ECISDT is not identical with the QCISDT method suggested by PHR*. Since ECISDT is also not identical with CCSDT, it is intermediate between QCISDT and CCSDT, but closer to the latter than the former method. *ECISDT and CCSDT are both size-extensive while QCISDT is not.*

2.4 From CISDTQ to ECISDTQ

The CISDTQ projection equations are given by Eqs. (45) to (49):

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{CISDTQ} \tag{45}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_i^a E_{corr}^{CISDTQ} \tag{46}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_{ij}^{ab} E_{corr}^{CISDTQ} \tag{47}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_{ijk}^{abc} E_{corr}^{CISDTQ} \tag{48}$$

$$\langle \Phi_{ijkl}^{abcd} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_{ijkl}^{abcd} E_{corr}^{CISDTQ}. \tag{49}$$

The disconnected terms $c_i^a E_{corr}^{CISDTQ}$ and $c_{ij}^{ab} E_{corr}^{CISDTQ}$ in the S and D excitation Eqs. (46) and (47) can be cancelled in the same way as this was done for ECISD and ECISDT. Accordingly, the first three equations of ECISDTQ are given by:

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECISDTQ} \tag{50}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle = a_i^a E_{corr}^{ECISDTQ} \tag{51a}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} E_{corr}^{ECISDTQ} \tag{52a}$$

where Eqs. (51a) and (52a) can be rewritten as:

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_C = 0 \tag{51b}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C = 0 \tag{52b}$$

To find the appropriate ECISDTQ triple excitation equation, we follow the same procedure as applied for CISDT. First, we introduce $\hat{T}_2 \hat{T}_3$ into Eq. (48) to cancel the disconnected term $c_{ijk}^{abc} E_{corr}^{CISDTQ}$ and, then, the terms $\hat{T}_1 \hat{T}_2$, $\frac{1}{2}\hat{T}_2^2$, and $\frac{1}{2}\hat{T}_1 \hat{T}_2^2$ to cancel the disconnected term resulting from the addition of $\hat{T}_2 \hat{T}_3$. In this way, we obtain Eq. (53).

$$\begin{aligned}\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_2 \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1 \hat{T}_2^2) | \Phi_0 \rangle \\ = (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 | \Phi_0 \rangle) E_{corr}^{ECISDTQ}. \end{aligned} \tag{53}$$

The disconnected part of Eq. (53) can be rewritten as:

$$\begin{aligned}&\langle \Phi_{ijk}^{abc} | [\bar{H}(\hat{T}_1 + \hat{T}_2 \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1 \hat{T}_2^2)]_D | \Phi_0 \rangle \\ &= \langle \Phi_{ijk}^{abc} | \hat{T}_1 [\bar{H}(1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2)]_C | \Phi_0 \rangle + \langle \Phi_{ijk}^{abc} \hat{T}_3 (\bar{H} \hat{T}_2)_C | \Phi_0 \rangle \\ &\quad + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 (\bar{H} \hat{T}_2)_C | \Phi_0 \rangle \end{aligned} \tag{54a}$$

$$\begin{aligned}&= \sum_d^D \langle \Phi_{ijk}^{abc} | \hat{T}_1 | \Phi_d \rangle \langle \Phi_d | \bar{H}(1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C \\ &\quad + (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 | \Phi_0 \rangle) E_{corr}^{ECISDTQ}, \end{aligned} \tag{54b}$$

which reveals that the disconnected part $\langle \Phi_{ijk}^{abc} | \hat{T}_1 [\bar{H}(1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2)]_C | \Phi_0 \rangle$ can be cancelled with the help of the D excitation Eq. (52b) provided the terms $\frac{1}{2}\hat{T}_1^2$, $\hat{T}_1 \hat{T}_3$ and $\hat{T}_1 \hat{T}_4$ are added to Eq. (54). Accordingly, the T excitation equation of ECISDTQ takes the form of Eq. (55a).

$$\begin{aligned}\langle \Phi_{ijk}^{abc} | \bar{H}(&\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \hat{T}_1 \hat{T}_4 \\ &+ \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_2 \hat{T}_3 + \tfrac{1}{2}\hat{T}_1 \hat{T}_2^2) | \Phi_0 \rangle \\ &= (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 | \Phi_0 \rangle) E_{corr}^{ECISDTQ} \end{aligned} \tag{55a}$$

or

$$\begin{aligned}\langle \Phi_{ijk}^{abc} | \bar{H}(&\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \hat{T}_1 \hat{T}_4 \\ &+ \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_2 \hat{T}_3 + \tfrac{1}{2}\hat{T}_1 \hat{T}_2^2) | \Phi_0 \rangle_C = 0 \end{aligned} \tag{55b}$$

To cancel the disconnected term $c_{ijkl}^{abcd} E_{corr}^{CISDTQ}$ in Eq. (49), $\hat{T}_2 \hat{T}_4$ is added thus leading to Eq. (56).

$$\langle \Phi_{ijkl}^{abcd} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_2 \hat{T}_4) | \Phi_0 \rangle = a_{ijkl}^{abcd} E_{corr}^{ECISDTQ} \tag{56}$$

With the term $\hat{T}_2 \hat{T}_4$ a new disconnected term $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2 (\bar{H} \hat{T}_4)_C | \Phi_0 \rangle$ is brought in as is revealed by Eq. (57).

$$\begin{aligned}\langle \Phi_{ijkl}^{abcd} | (\bar{H} \hat{T}_2 \hat{T}_4)_D | \Phi_0 \rangle &= \langle \Phi_{ijkl}^{abcd} | \hat{T}_4 (\bar{H} \hat{T}_2)_C | \Phi_0 \rangle + \langle \Phi_{ijkl}^{abcd} | \hat{T}_2 (\bar{H} \hat{T}_4)_C | \Phi_0 \rangle \\ &= a_{ijkl}^{abcd} E_{corr}^{ECISDTQ} + \sum_d^D \langle \Phi_{ijkl}^{abcd} | \hat{T}_2 | \Phi_d \rangle \langle \Phi_d | (\bar{H} \hat{T}_4)_C | \Phi_0 \rangle. \end{aligned} \tag{57}$$

In the next step, Eq. (56) is extended to Eq. (58) by adding $\hat{T}_2 \hat{T}_1$, $\frac{1}{2}\hat{T}_2^2$, $\hat{T}_2 \hat{T}_3$, and $\frac{1}{6}\hat{T}_2^3$ according to the D excitation Eq. (52b).

$$\begin{aligned}&\langle \Phi_{ijkl}^{abcd} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_2 \hat{T}_4 + \hat{T}_2 \hat{T}_1 + \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_2 \hat{T}_3 + \tfrac{1}{3!}\hat{T}_2^3) | \Phi_0 \rangle \\ &= (a_{ijkl}^{abcd} + \langle \Phi_0 | \tfrac{1}{2}\hat{T}_2^2 | \Phi_0 \rangle) E_{corr}^{ECISDTQ} \end{aligned} \tag{58}$$

The disconnected part on the left-hand side can be written as shown in Eq. (59):

$$\begin{aligned}
&\langle \Phi_{ijkl}^{abcd} | [\bar{H}(\hat{T}_2 + \hat{T}_2\hat{T}_1 + \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_4 + \tfrac{1}{3!}\hat{T}_2^3)]_D | \Phi_0 \rangle \\
&= \langle \Phi_{ijkl}^{abcd} | \hat{T}_2 [\bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2)]_C | \Phi_0 \rangle \\
&\quad + \langle \Phi_{ijkl}^{abcd} | \hat{T}_1 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle + \langle \Phi_{ijkl}^{abcd} | \hat{T}_3 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle \\
&\quad + \langle \Phi_{ijkl}^{abcd} | \hat{T}_4 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle + \langle \Phi_{ijkl}^{abcd} | \tfrac{1}{2}\hat{T}_2^2 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle \qquad (59a) \\
&= \sum_d^D \langle \Phi_{ijkl}^{abcd} | \hat{T}_2 | \Phi_d \rangle \langle \Phi_d | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C \\
&\quad + \sum_t^T \langle \Phi_{ijkl}^{abcd} | \hat{T}_1 | \Phi_t \rangle \langle \Phi_t | (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle \\
&\quad + \sum_s^S \langle \Phi_{ijkl}^{abcd} | \hat{T}_3 | \Phi_s \rangle \langle \Phi_s | (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle \\
&\quad + \langle \Phi_{ijkl}^{abcd} | \hat{T}_4 | \Phi_0 \rangle \langle \Phi_0 | (\bar{H}\hat{T}_2) | \Phi_0 \rangle \\
&\quad + \langle \Phi_{ijkl}^{abcd} | \tfrac{1}{2}\hat{T}_2^2 | \Phi_0 \rangle \langle \Phi_0 | (\bar{H}\hat{T}_2) | \Phi_0 \rangle \qquad (59b) \\
&= \sum_t^T \langle \Phi_{ijkl}^{abcd} | \hat{T}_1 | \Phi_t \rangle \langle \Phi_t | (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle \\
&\quad + \sum_s^S \langle \Phi_{ijkl}^{abcd} | \hat{T}_3 | \Phi_s \rangle \langle \Phi_s | (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle \\
&\quad + (a_{ijkl}^{abcd} + \langle \Phi_{ijkl}^{abcd} | \tfrac{1}{2}\hat{T}_2^2 | \Phi_0 \rangle) E_{corr}^{ECISDT}, \qquad (59c)
\end{aligned}$$

where Eqs. (50) and (52b) have been used in Eq. (59c). According to Eq. (59c), there are two new disconnected terms in Eq. (58), namely:

$$\langle \Phi_{ijkl}^{abcd} | \hat{T}_1 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle = \sum_t^T \langle \Phi_{ijkl}^{abcd} | \hat{T}_1 | \Phi_t \rangle \langle \Phi_t | (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle \qquad (60)$$

and

$$\langle \Phi_{ijkl}^{abcd} | \hat{T}_3 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle = \sum_s^S \langle \Phi_{ijkl}^{abcd} | \hat{T}_3 | \Phi_s \rangle \langle \Phi_s | (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle. \qquad (61)$$

The disconnected terms (60) and (61) can be cancelled according to Eqs. (51b) and (55b) by adding to Eq. (58) $\hat{T}_1\hat{T}_3$, $\hat{T}_1\hat{T}_4$, $\hat{T}_1\hat{T}_2\hat{T}_3$, $\frac{1}{2}\hat{T}_1^2\hat{T}_2$, $\frac{1}{2}\hat{T}_1^2\hat{T}_3$, $\frac{1}{2}\hat{T}_1^2\hat{T}_4$, $\frac{1}{4}\hat{T}_1^2\hat{T}_2^2$, $\frac{1}{2}\hat{T}_1\hat{T}_2^2$, and $\frac{1}{2}\hat{T}_3^2$:

$$\begin{aligned}
&\langle \Phi_{ijkl}^{abcd} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_1\hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_4 \\
&\quad + \tfrac{1}{3!}\hat{T}_2^3 + \hat{T}_1\hat{T}_3 + \hat{T}_1\hat{T}_4 + \hat{T}_1\hat{T}_2\hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_3 \\
&\quad + \tfrac{1}{2}\hat{T}_1^2\hat{T}_4 + \tfrac{1}{4}\hat{T}_1^2\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_3^2) | \Phi_0 \rangle \\
&\quad = (a_{ijkl}^{abcd} + \langle \Phi_{ijkl}^{abcd} | \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 | \Phi_0 \rangle) E_{corr}^{ECISDTQ}. \qquad (62)
\end{aligned}$$

With Eq. (62) the disconnected terms $a_{ijkl}^{abcd} E_{corr}^{ECISDTQ}$, $\langle \Phi_{ijkl}^{abcd} | \bar{H}\hat{T}_2 | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_1 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle$, and $\langle \Phi_{ijkl}^{abcd} | \hat{T}_3 (\bar{H}\hat{T}_2)_C | \Phi_0 \rangle$, are cancelled, but again new disconnected terms have entered the equation: $\langle \Phi_{ijkl}^{abcd} | \hat{T}_4 (\bar{H}\tfrac{1}{2}\hat{T}_1^2)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_3 (\bar{H}\tfrac{1}{2}\hat{T}_1^2)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2 (\bar{H}\tfrac{1}{2}\hat{T}_1^2)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2 (\bar{H}\hat{T}_1\hat{T}_2)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2 (\bar{H}\hat{T}_1\hat{T}_3)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2 (\bar{H}\tfrac{1}{2}\hat{T}_1^2\hat{T}_2)_C | \Phi_0 \rangle$.

These terms can only be cancelled if energy, S, and D Eqs. (50), (51a), and (52a) are extended by appropriate terms: a) The term $\frac{1}{2}\hat{T}_1^2$ has to be added to the energy Eq. (50) so that $\langle \Phi_{ijkl}^{abcd} | \hat{T}_4(\bar{H}\frac{1}{2}\hat{T}_1^2)_C | \Phi_0 \rangle$ is cancelled in Eq. (62).
b) The term $\frac{1}{2}\hat{T}_1^2$ has also to be added to the S Eq. (51a) so that

$$\langle \Phi_{ijkl}^{abcd} | \hat{T}_3(\bar{H}\tfrac{1}{2}\hat{T}_1^2)_C | \Phi_0 \rangle = \sum_s^S \langle \Phi_{ijkl}^{abcd} | \hat{T}_3 | \Phi_s \rangle \langle \Phi_s | \bar{H}\tfrac{1}{2}\hat{T}_1^2)_C | \Phi_0 \rangle \tag{62a}$$

is cancelled.

c) The terms $\frac{1}{2}\hat{T}_1^2$, $\hat{T}_1\hat{T}_2$, and $\hat{T}_1\hat{T}_3$, $\frac{1}{2}\hat{T}_1^2\hat{T}_2$ have to be included into the D Eq. (52a) to eliminate $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2(\bar{H}\frac{1}{2}\hat{T}_1^2)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2(\bar{H}\hat{T}_1\hat{T}_2)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2(\bar{H}\hat{T}_1\hat{T}_3)_C | \Phi_0 \rangle$, $\langle \Phi_{ijkl}^{abcd} | \hat{T}_2(\bar{H}\frac{1}{2}\hat{T}_1^2\hat{T}_2)_C | \Phi_0 \rangle$. With a), b) and c) one gets Eqs. (63), (64), and (65).

$$E_{corr}^{ECISDTQ} = \langle \Phi_0 | \bar{H}(\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2) | \Phi_0 \rangle \tag{63}$$

$$\begin{aligned}\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \tfrac{1}{3!}\hat{T}_1^3) | \Phi_0 \rangle \\ = a_i^a E_{corr}^{ECISDTQ} \qquad &(64a)\\ = a_i^a \langle \Phi_0 | \bar{H}(\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2) | \Phi_0 \rangle \qquad &(64b)\end{aligned}$$

$$\begin{aligned}\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3 \\ + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^3 + \tfrac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle \\ = (a_{ij}^{ab} + \langle \Phi_{ij}^{ab} | \tfrac{1}{2}\hat{T}_1^2 | \Phi_0 \rangle) E_{corr}^{ECISDTQ} \qquad &(65a)\\ = (a_{ij}^{ab} + \langle \Phi_{ij}^{ab} | \tfrac{1}{2}\hat{T}_1^2 | \Phi_0 \rangle)(\langle \Phi_0 | \bar{H}(\hat{T}_2 + \tfrac{1}{2}T_1^2) | \Phi_0 \rangle) \qquad &(65b)\end{aligned}$$

These equations are identical with the corresponding CCSDTQ equations. The same holds for the T and Q ECISDTQ equations so that we come to the surprising conclusion that *ECISDTQ in the same way as ECID is identical with the corresponding CC method* (compare with Eqs. (66)–(70)):

$$E_{corr}^{CCSDTQ} = \langle \Phi_0 | \bar{H}(\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2) | \Phi_0 \rangle \tag{66}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \tfrac{1}{3!}\hat{T}_1^3) | \Phi_0 \rangle = a_i^a E_{corr}^{CCSDTQ} \tag{67}$$

$$\begin{aligned}\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3 \\ + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^3 + \tfrac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle \\ = (a_{ij}^{ab} + \langle \Phi_{ij}^{ab} | \tfrac{1}{2}\hat{T}_1^2 | \Phi_0 \rangle) E_{corr}^{CCSDTQ}\end{aligned} \tag{68}$$

$$\begin{aligned}\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3 + \hat{T}_1\hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_2\hat{T}_3 \\ + \tfrac{1}{3!}\hat{T}_1^3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_4 + \tfrac{1}{2}\hat{T}_1\hat{T}_2^2 + \hat{T}_1\hat{T}_2\hat{T}_3 + \tfrac{1}{3!}\hat{T}_2^3 \\ + \tfrac{1}{4!}\hat{T}_1^4 + \tfrac{1}{3!}\hat{T}_1^3\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^3\hat{T}_3 + \tfrac{1}{4}\hat{T}_1^2\hat{T}_2^2 + \tfrac{1}{5!}T_1^5 + \tfrac{1}{6!}\hat{T}_1^6) | \Phi_0 \rangle \\ = (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^3 | \Phi_0 \rangle) E_{corr}^{CCSDTQ}\end{aligned} \tag{69}$$

$$\begin{aligned}\langle \Phi_{ijkl}^{abcd} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3 + \hat{T}_1\hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_4 \\ + \tfrac{1}{2}\hat{T}_3^2 + \tfrac{1}{3!}\hat{T}_1^3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_4 + \tfrac{1}{2}\hat{T}_1\hat{T}_2^2 + \hat{T}_1\hat{T}_2\hat{T}_3 + \tfrac{1}{3!}\hat{T}_2^3 \\ + \tfrac{1}{4!}\hat{T}_1^4 + \tfrac{1}{3!}\hat{T}_1^3\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^3\hat{T}_3 + \tfrac{1}{4}\hat{T}_1^2\hat{T}_2^2 + \tfrac{1}{5!}\hat{T}_1^5 + \tfrac{1}{4!}\hat{T}_1^4\hat{T}_2 + \tfrac{1}{6!}\hat{T}_1^6) | \Phi_0 \rangle \\ = (a_{ijkl}^{abcd} + \langle \Phi_{ijkl}^{abcd} | \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{4!}\hat{T}_1^4 | \Phi_0 \rangle) E_{corr}^{CCSDTQ}\end{aligned} \tag{70}$$

We conclude that there does not exist any intermediate method that can be derived by including size-extensiveness corrections into the CISDTQ equations. Clearly, size-extensiveness requires a) that corrections are included in all projection equations rather than just into the Q and the T equations and b) that higher than just quadratic correction terms have to be included.

3 Properties of size-extensive CI (ECI) methods

PHR derived the QCISD method by just including quadratic terms in the two highest CI equations, namely $\hat{T}_1\hat{T}_2$ into the S excitation equation and $\frac{1}{2}\hat{T}_2^2$ into the D excitation equation [8]. Extension of this idea to CISDT did not lead to a size-extensive method as was pointed out by Paldus and co-workers [9]. Inspection of the ECISDT Eqs. (30), (31), (32), and (43) indicates that one has to include corrections in all but the energy equation. Thus, size-extensiveness requires that the $\hat{T}_1\hat{T}_2$ term is included into the S excitation equation while PHR suggested to leave this equation uncorrected. As for the T equation of CISDT, one has to include 5 quadratic terms and one cubic term to achieve size-extensiveness.

For CISDTQ, all equations have to be extended by quadratic terms (1 for the energy, 2 for the S, 4 for the D, 6 for the T, 8 for the Q equation), but in addition cubic (1 for the S, 2 for the D, 4 for the T and 7 for the Q equation), quartic (1 for the D, 4 for the T, 4 for the Q equation) and higher corrections have to be included so that in the end the CCSDTQ equations result.

One might ask whether it is possible to drop any of the correction terms for reasons of simplification and still get a size-extensive ECI method. If this would be possible, then the derivation of the ECI methods given in Sect. 2 would be erroneous. To check this possibility, we have analyzed in Table 1 the T projection Eq. (43) of ECISDT for the case that one of the correction terms is dropped. For each of the six possible simplifications, we get a new method that is no longer size-extensive. Therefore, we conclude that the ECI methods presented in Sect. 2 *are the simplest size-extensive methods that can be directly derived from the CI methods* [17].

Table 1. Analysis of the ECISDT triple projection equation for a selective deletion of cluster operators

Term to be deleted in Eq. (43)	Disconnected terms of Eq. (43)
$\frac{1}{2}\hat{T}_1^2$	$\langle\Phi_{ijk}^{abc}\vert\hat{T}_1[\bar{H}(1+\hat{T}_2+\hat{T}_3+\frac{1}{2}\hat{T}_2^2)]_C\vert\Phi_0\rangle\neq 0$
$\hat{T}_1\hat{T}_2$	$\langle\Phi_{ijk}^{abc}\vert\hat{T}_1[\bar{H}(1+\hat{T}_1+\hat{T}_3+\frac{1}{2}\hat{T}_2^2)]_C\vert\Phi_0\rangle+\langle\Phi_{ijk}^{abc}\vert\hat{T}_1\hat{T}_2(\bar{H}\hat{T}_2)_C\vert\Phi_0\rangle$ $+\langle\Phi_{ijk}^{abc}\vert\hat{T}_2[\bar{H}(\hat{T}_2+\hat{T}_3+\hat{T}_1\hat{T}_2)]_C\vert\Phi_0\rangle\neq 0$
$\hat{T}_1\hat{T}_3$	$\langle\Phi_{ijk}^{abc}\vert\hat{T}_1[\bar{H}(1+\hat{T}_1+\hat{T}_2+\frac{1}{2}\hat{T}_2^2)]_C\vert\Phi_0\rangle\neq 0$
$\frac{1}{2}\hat{T}_2^2$	$\langle\Phi_{ijk}^{abc}\vert\hat{T}_2[\bar{H}(\hat{T}_1+\hat{T}_3+\hat{T}_1\hat{T}_2)]_C\vert\Phi_0\rangle\neq 0$
$\hat{T}_2\hat{T}_3$	$\langle\Phi_{ijk}^{abc}\vert\hat{T}_2[\bar{H}(\hat{T}_1+\hat{T}_2+\hat{T}_1\hat{T}_2)]_C\vert\Phi_0\rangle-a_{ijk}^{abc}E_{corr}^{ECISDT}\neq 0$
$\frac{1}{2}\hat{T}_1\hat{T}_2^2$	$\langle\Phi_{ijk}^{abc}\vert\hat{T}_1[\bar{H}(1+\hat{T}_1+\hat{T}_2+\hat{T}_3)]_C\vert\Phi_0\rangle$ $+\langle\Phi_{ijk}^{abc}\vert\hat{T}_2[\bar{H}(\hat{T}_1+\hat{T}_2+\hat{T}_3)]_C\vert\Phi_0\rangle-\langle\Phi_{ijk}^{abc}\vert\hat{T}_1\hat{T}_2\vert\Phi_0\rangle E_{corr}^{ECISDT}\neq 0$

As was shown in Sect. 2.4, ECISDTQ is identical with CCSDTQ. It is easy to show that this also holds for any higher method (CCSDTQP, etc.). Obviously, the ECI methods do not form a hierarchy of independent methods or, in other words, the idea of deriving from CI size-extensive methods leads in all cases, apart from CISD and CISDT, directly to the corresponding CC methods.

Although ECISDT is not a member of a series of independent methods, one might consider to test the feasibility and usefulness of such a method. In Table 2, ECISDT and CCSDT are compared with regard to their computational requirements. Clearly, ECISDT is as costly as CCSDT, even though it contains less cluster operators in the projection equations. However, all but one of the $O(M^8)$ dependent terms are included in the T equation, which hinders ECISDT to become an economically attractive alternative to CCSDT. At 5th order, ECISDT and CCSDT differ in just the ST and a part of the TQ energy contributions, which are missing in the former method (compare with Figs. 2 and 3). Accordingly, TST, TSD, TSS, and DTS contributions are not covered at 6th order, which may be problematic in

Tabe 2. Analysis of computational requirements for ECISDT and CCSDT

Eq.	Terms	Cost	ECISDT	CCSDT
S	$\hat{T}_1$	$O(N^5)$	X	X
	$\hat{T}_2$	$O(M^5)$	X	X
	$\hat{T}_3$	$O(M^6)$	X	X
	$\hat{T}_1\hat{T}_2$	$O(M^5)$		X
	$\frac{1}{2}\hat{T}_1^2$	$O(M^5)$		X
	$\frac{1}{3!}\hat{T}_1^3$	$O(M^5)$		X
D	1	$O(M^5)$	X	X
	$\hat{T}_1$	$O(M^5)$	X	X
	$\hat{T}_2$	$O(M^6)$	X	X
	$\hat{T}_3$	$O(M^7)$	X	X
	$\frac{1}{2}\hat{T}_2^2$	$O(M^6)$	X	X
	$\frac{1}{2}\hat{T}_1^2$	$O(M^5)$		X
	$\hat{T}_1\hat{T}_2$	$O(M^6)$		X
	$\hat{T}_1\hat{T}_3$	$O(M^7)$		X
	$\frac{1}{3!}\hat{T}_1^3$	$O(M^5)$		X
	$\frac{1}{2}\hat{T}_1^2\hat{T}_2$	$O(M^6)$		X
	$\frac{1}{4}\hat{T}_1^4$	$O(M^5)$		X
T	$\hat{T}_2$	$O(M^7)$	X	X
	$\hat{T}_3$	$O(M^8)$	X	X
	$\hat{T}_1\hat{T}_2$	$O(M^7)$	X	X
	$\hat{T}_1\hat{T}_3$	$O(M^8)$	X	X
	$\frac{1}{2}\hat{T}_2^2$	$O(M^7)$	X	X
	$\hat{T}_2\hat{T}_3$	$O(M^8)$	X	X
	$\frac{1}{2}\hat{T}_1\hat{T}_2^2$	$O(M^7)$	X	X
	$\frac{1}{2}\hat{T}_1^2\hat{T}_2$	$O(M^7)$		X
	$\frac{1}{2}\hat{T}_1^2\hat{T}_3$	$O(M^8)$		X
	$\frac{1}{3!}\hat{T}_1^3\hat{T}_2$	$O(M^7)$		X

those cases where the S excitations turn out to be important. Apart from this, ECISDT should lead to results that are comparable with CCSDT. Therefore, one can say that the cost-effectiveness ratio of ECISDT will be similar to that of CCSDT and, accordingly, that there will be no significant advantage in using ECISDT.

4 Derivation of a size-extensive QCISDT method

Once the ECI projection equations have been derived in their connected form, one can delete all terms but the connected linear and quadratic terms. In this way one gets from the ECISDT Eqs. (30), (33), (34), and (44) the projection equations of a size-extensive QCISDT method:

$$E_{corr}^{QCISDT} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle \tag{71}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2 | \Phi_0 \rangle_C = 0 \tag{72}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C = 0 \tag{73}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3) | \Phi_0 \rangle_C = 0. \tag{74}$$

The equations differ from the QCISDT equations of PHR in three ways: First of all, only the connected part of the quadratic correction terms is included. Secondly, quadratic correction terms $(\bar{H}\hat{T}_2\hat{T}_p)_C$ are added to all CISDT equations but the energy equation, i.e. $p = 1, 2, 3$. Finally, the linear term $\langle \Phi_{ijk}^{abc} | \bar{H}\hat{T}_1 | \Phi_0 \rangle$ has been deleted since it represents a disconnected term (see Sect. 5).

To distinguish the size-extensive method represented by Eqs. (71)–(74) from the QCISDT method suggested by PHR [8], we use the abbreviation QCISDTc where the c indicates that the projection equations contain just connected terms and, therefore, size-extensiveness is guaranteed contrary to QCI methods of PHR.

It is interesting to compare QCISDTc with both CCSDT and QCISD(T). For this purpose, we expand the QCISDTc correlation energy in terms of nth order many body perturbation theory where we use the same techniques as we have described recently [12–14]. In this way, we get Eq. (75):

$$\begin{aligned} E_{corr}^{QCISDTc} &= \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \lambda^4 E^{(4)} \\ &+ \lambda^5 (E_{SS}^{(5)} + 2E_{SD}^{(5)} + E_{DD}^{(5)} + 2E_{DQ}^{(5)} + E_{ST}^{(5)} + 2E_{DT}^{(5)} + E_{TT}^{(5)} \\ &+ E_{QQ}^{(5)}(I)) + \lambda^6 [E_{SSS}^{6} + 2E_{SSD}^{(6)} + E_{SDS}^{(6)} + 2E_{SDD}^{(6)} + 2E_{SDQ}^{(6)} + E_{DSD}^{(6)} + E_{DDD}^{(6)} \\ &+ E_{DQD}^{(6)} + 2E_{DDQ}^{(6)} + E_{DQQ}^{(6)}(I) + E_{QQD}^{(6)}(I) + E_{QDQ}^{(6)} + E_{QQQ}^{(6)}(I) \\ &+ E_{STS}^{(6)} + E_{STD}^{(6)} + E_{STQ}^{(6)}(I) + E_{QTS}^{(6)}(I) + E_{DTD}^{(6)} + E_{QTQ}^{(6)}(I) + E_{SST}^{(6)} \\ &+ 2E_{SDT}^{(6)} + E_{STT}^{(6)} + E_{DST}^{(6)} + 2E_{DDT}^{(6)} + 2E_{DTT}^{(6)} + 2E_{TDQ}^{(6)} + E_{TDT}^{(6)} \\ &+ E_{TTT}^{(6)} + E_{QPQ}^{(6)}(I) + E_{QHQ}^{(6)}(I) + E_{TPQ}^{(6)}(\mathrm{I}) + E_{QPT}^{(6)}(\mathrm{I}) \\ &+ E_{TPT}^{(6)}(\mathrm{I})] + O(\lambda^7), \end{aligned} \tag{75}$$

	QCISD(T)	$QCISDT_c$	ECISDT	CCSDT
SS	yes	yes	yes	yes
DD	yes	yes	yes	yes
TT		yes	yes	yes
QQ	(yes)	(yes)	(yes)	(yes)
SD,DS	y,y	y,y	y,y	y,y
DQ,QD	y,y	y,y	y,y	y,y
ST,TS	y,y	y,-	y,-	y,y
DT,TD	y,y	y,y	y,y	y,y
TQ,QT			(y),-	y,-

Fig. 2. Analysis of energy contributions at 5th-order many-body perturbation theory covered by QCISD(T), QCISDTc, ECISDT, and CCSDT correlation energies. Yes or y denote that the particular term is fully contained in the correlation energy while (yes) or (y) indicate that the term is only partially covered

where $E^{(n)}_{ABC\ldots}$ denotes a particular energy contribution at nth order perturbation theory and $E^{(n)}_{ABC\ldots}(I)$ indicates that this energy contribution is covered only partially. In Figs. 2 and 3, Eq. (75) is used to compare QCISD(T), ECISDT, and CCSDT with QCISDTc at 5th and 6th order utilizing results which we have obtained recently [12, 13]. According to this comparison, QCISDTc should be significantly better than QCISD(T), which we have found to suffer from an exaggeration of T effects in molecular calculations [12, 18, 19]. The latter results from the fact that TT coupling effects are totally missing for QCISD(T) at 5th and 6th order thus leading to the observed exaggeration of T effects. QCISDTc, however, covers 6 of the 11 possible TAT and TTA terms (partially or totally) and, hence, compares well with CCSDT that covers 9 of these terms [13]. Compared to CCSDT, QCISDTc lacks TS, TSA, TQ, and TQA energy contributions. This is also reflected by Eqs. (77) and (78), which give energy differences between the various methods up to 6th order.

$$
\begin{aligned}
E_{corr}^{QCISDT_c} - E_{corr}^{QCISD(T)} = {} & \lambda^{(5)}(E^{(5)}_{TT} - E^{(5)}_{TS}) + \lambda^{(6)}[E^{(6)}_{STT} + 2E^{(6)}_{DTT} + E^{(6)}_{TDT} \\
& + E^{(6)}_{TTT} + E^{(6)}_{QPQ}(I) + E^{(6)}_{TPQ}(I) + E^{(6)}_{QPT}(I) \\
& + E^{(6)}_{TPT}(I) - E^{(6)}_{DTS} - E^{(6)}_{TSS} - E^{(6)}_{TSD}] + O(\lambda^7) \qquad (77)
\end{aligned}
$$

$$
\begin{aligned}
E_{corr}^{CCSDT} - E_{corr}^{QCISDT_c} = {} & \lambda^{(5)}(E^{(5)}_{TS} + E^{(5)}_{TQ}) + \lambda^{(6)}[E^{(6)}_{DTS} + E^{(6)}_{STQ}(II) + E^{(6)}_{QTS}(II) \\
& + E^{(6)}_{DTQ} + E^{(6)}_{TSS} + E^{(6)}_{TTS} + E^{(6)}_{TSD} + E^{(6)}_{TQD} + E^{(6)}_{TST} \\
& + E^{(6)}_{TQQ}(I) + E^{(6)}_{TTQ}(I) + E^{(6)}_{TPT}(II)] + O(\lambda^7) \qquad (78)
\end{aligned}
$$

QCISDTc, contrary to CCSDT, is not able to describe a 3-electron system correctly (see Eq. (78)). However, QCISDTc should be superior to QCISD(T) and, probably, should come close to the performance of CCSDT in those cases where TS and TQ contributions are not important. On the other hand, this improvement is obtained at the cost of going from an $O(M^7)$ method, namely QCISD(T), to a $O(M^8)$ method.

	QCISD(T)	QCISDT	ECISDT	CCSDT
SSS	yes	yes	yes	yes
SSD,DSS	y,y	y,y	y,y	y,y
SDS	yes	yes	yes	yes
SDD,DDS	y,y	y,y	y,y	y,y
SDQ,QDS	y,y	y,y	y,y	y,y
DSD	yes	yes	yes	yes
DDD	yes	yes	yes	yes
DQD	yes	yes	yes	yes
DDQ,QDD	y,y	y,y	y,y	y,y
DQQ,QQD	(y),(y)	(y),(y)	(y),(y)	(y),(y)
QDQ	yes	yes	yes	yes
QQQ	(yes)	(yes)	(yes)	(yes)
STS	yes	yes	yes	yes
STD,DTS	y,y	y,-	y,-	y,y
STQ,QTS	(y),(y)	(y),(y)	y,(y)	y,y
DTD	yes	yes	yes	yes
DTQ,QTD			(y),-	y,-
QTQ	(yes)	(yes)	(yes)	(yes)
SST,TSS	y,y	y,-	y,-	y,y
SDT,TDS	y,y	y,y	y,y	y,y
STT,TTS		y,-	y,(y)	y,y
DST,TSD	y,y	y,-	y,-	y,y
DDT,TDD	y,y	y,y	y,y	y,y
DQT,TQD			-,(y)	-,y
DTT,TTD		y,y	y,y	y,y
TDQ,QDT	y,y	y,y	y,y	y,y
TQQ,QQT			(y),-	(y),-
TTQ,QTT			(y),-	y,-
TST				yes
TDT		yes	yes	yes
TQT				
TTT		yes	yes	yes
QPQ		(yes)	(yes)	(yes)
QHQ	(yes)	(yes)	(yes)	(yes)
TPQ,QPT		(y),(y)	(y),(y)	(y),(y)
TPT		(yes)	(yes)	yes

Fig. 3. Analysis of energy contributions at 6th-order many-body perturbation theory covered by QCISD(T), QCISDTc, ECISDT, and CCSDT correlation energies. Yes or y denote that the particular term is fully contained in the correlation energy while (yes) or (y) indicate that the term is only partially covered

5 A Hierarchy of size-extensive QCI methods

A size-extensive QCISDTQc method can be derived from ECISDTQ = CCSDTQ in the same way as described above for QCISDTc. Its projection equations are given by Eqs. (79)–(83):

$$E_{corr}^{QCISDTQc} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle \tag{79}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2 | \Phi_0 \rangle_C = 0 \tag{80}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C = 0 \tag{81}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_2\hat{T}_3) | \Phi_0 \rangle_C = 0 \tag{82}$$

$$\langle \Phi_{ijkl}^{abcd} | \bar{H}(\hat{T}_3 + \hat{T}_4 + \hat{T}_2\hat{T}_4) | \Phi_0 \rangle_C = 0 \tag{83}$$

Formally, the QCIc equations can be derived starting at the corresponding CI equations rather than the ECI or CC equations as done above. For this purpose, we write the projection equations of a truncated CI method that includes up to n-fold excitations as:

$$E_{corr}^{CI} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle \tag{84}$$

$$\langle \Phi_p | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n) | \Phi_0 \rangle = c_p E_{corr}^{CI} \quad (p = 1, 2, \ldots, n) \tag{85}$$

or, alternatively, as:

$$\langle \Phi_s | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_s E_{corr}^{CI} \tag{86}$$

$$\langle \Phi_d | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_d E_{corr}^{CI} \tag{87}$$

$$\left\langle \Phi_p \middle| \bar{H}\left(\sum_{i=p-2}^{min[p+2,n]} \hat{T}_i \right) \middle| \Phi_0 \right\rangle = c_p E_{corr}^{CI} \quad (n \geqslant p \geqslant 3) \tag{88}$$

where s, d, and p are S, D, and general excitation indices.

As shown in Sect. 2, it suffices to add $\hat{T}_1\hat{T}_2$ and $\frac{1}{2}\hat{T}_2^2$ to the S and D projection Eqs. (86) and (87), respectively, to eliminate all disconnected terms from these equations. For any excitation index p higher than d, there appear just two disconnected terms, namely $\langle \Phi_p | \bar{H}\hat{T}_{p-2} | \Phi_0 \rangle (= \langle ab \| ij \rangle c_{p-2})$ and $c_p E_{corr}^{CI}$ in the corresponding projection equation. Introducing $-\bar{H}\hat{T}_{p-2}$ and parts of the term $\bar{H}\hat{T}_2\hat{T}_p$, namely $(\bar{H}\hat{T}_2\hat{T}_p)_C$ and $\hat{T}_p(\bar{H}\hat{T}_2)_C$, on the left side of Eq. (88) leads to a cancellation of all disconnected terms and to the QCIc equations in their general form:

$$E_{corr}^{QCIc} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle \tag{89}$$

$$\langle \Phi_s | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) + (\bar{H}\hat{T}_1\hat{T}_2)_C | \Phi_0 \rangle = 0 \tag{90}$$

$$\langle \Phi_d | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) + \tfrac{1}{2}(\bar{H}\hat{T}_2^2)_C | \Phi_0 \rangle = 0 \tag{91}$$

$$\left\langle \Phi_p \middle| \bar{H}\left(\sum_{i=p-1}^{min[p+2,n]} \hat{T}_i \right) + (\bar{H}\hat{T}_2\hat{T}_p)_C \middle| \Phi_0 \right\rangle = 0 \quad (n \geqslant p \geqslant 3) \tag{92}$$

Clearly, these equations leads to *a hierarchy of QCI methods that are all size-extensive.*

6 Conclusions

The following conclusions can be drawn from the analysis presented in this paper.

1. The simplest size-extensive methods that can be *directly* derived from the CI projection equations are the ECI methods presented in Sect. 2. ECID is identical with CCD while ECISD is identical with QCISD thus confirming size-extensiveness for the latter method [8]. On the other hand, ECISDT differs considerably from the non-size-extensive QCISDT method reflecting the fact that size-extensiveness in general cannot be achieved by just considering quadratic correction terms in the two highest projection equations.
2. If Q and higher excitations are included into CI, then the corresponding size-extensive ECI methods become identical with the corresponding CC methods. Thus CCSDTQ, CCSDTQP (P for pentuple excitations), etc. are the simplest size-extensive methods that can be directly derived from the corresponding CI methods in the way described above.
3. Clearly, the size-extensive ECI methods do not form a hierarchy of independent CC methods and, therefore, the concept of improving CI to size-extensive CI is not a generally useful concept. The same holds for the quadratic CI approach in the sense it was originally derived [8].
4. A hierarchy of size-extensive quadratic CI methods can easily be derived if one starts from the ECI or CC projection equations in their connected form and deletes all cluster operators but those required by the original QCI concept.
5. The size-extensive QCISDTc and QCISDTQc methods thus obtained are easier to program than the corresponding CC methods. But their computational requirements are as high as those of CCSDT and CCSDTQ ($O(M^8)$ and $O(M^{10})$).
6. QCISDTc will be superior to QCISD(T) since it contains contrary to the later methods TT coupling terms at 5th and 6th order that are needed to provide a balanced description of T effects.
7. There exists a hierarchy of size-extensive QCIc methods that can be derived from the corresponding CI methods by formally adding the connected part $(\bar{H}\hat{T}_2\hat{T}_p)_C$ of the quadratic correction terms $(\bar{H}\hat{T}_2\hat{T}_p)$. Contrary to the QCI methods suggested by PHR, the QCIc equations require quadratic correction terms for all but the energy equation. In addition, they no longer contain linear terms $\langle \Phi_p|\bar{H}\hat{T}_{p-2})|\Phi_0\rangle$ since these represent disconnected terms.

Work is in progress to provide information on the usefulness of QCIc methods, in particular QCISDTc [20].

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15. We avoid the acronyms SCI or SECI since these may be confused with single excitation CI.
16. We use in this work Brandow diagrams according to the conventions described by Kucharski SA, Bartlett RJ (1986) Adv Quant Chem 18:281
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