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REGULAR ARTICLE

An exponential multi-reference wavefunction ansatz: connectivity analysis and application to N_2

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Abstract A connectivity analysis for the exponential multi-reference wavefunction ansatz (MRexpT) (J Chem Phys 123:84102, 2005) is carried out. Assuming a complete model space and separating interactions carrying active labels the cluster operator carrying no active labels is fully connected. The valence (active) part of the MRexpT cluster operator, however remains disconnected. Consequently, the MRexpT correlation energy scales linearly with the number of non-active electrons as single reference coupled cluster does while MRexpT additionally can treat multi reference cases. Therefore, MRexpT should be well suited to be applied to a large number of molecular applications. Its applicability to periodic systems with multi-reference unit cells however seems to be limited. An application to the triple bond breaking of the N_2 molecule is presented.

Keywords Coupled-cluster · Multi-reference · State selective · Electronic structure · MRCC

1 Introduction

The single-reference (SR) coupled-cluster (CC) methods [1–3] have proven to be the standard tool of wavefunction-based ab initio quantum chemistry. Their CCSD [4] and CCSD(T) [5] variants provide an efficient tool to carry out electronic structure calculations routinely. Despite this success SRCC methods have a limited applicability. There are many problems (near degeneracy, dissociation, excited states) which typically require an explicit multi-reference (MR) treatment. A direct application of SR-based methods becomes very inefficient for such problems due to the need to include very high body terms in the cluster operator.

Despite of many efforts the generalization of the SRCC approach to an MR model space, there is still no ultimate MRCC so far. There is a large number of MRCC approaches in the literature reflecting only the difficulty of this problem. There are two major crucial problems for any MRCC theory: (1) the ambiguity of the genealogy of the projection manifold and (2) the connectivity (size extensivity) of the equations. Both problems were solved by the state universal (SUMRCC) [6,7] and valence universal (VUMRCC) ansätze [8–12] by considering simultaneously several n-particle or $n, n-1, \ldots$particle states, respectively. However, this achievement is affected by the occurrence of intruder states or a still restricted applicability limiting the success of these approaches. Consequently, the research on MRCC methods continued.

In addition to the state universal and valence universal approaches the literature offers many different state selective approaches. Among these are the dressed configuration interaction (CI)-based ansätze of Malrieu and coworkers [13–15], SUMRCC based ansätze as [16,17] of Mukherjee and coworkers and Brillouin–Wigner-based ansätze of Pittner, Hubac and coworkers [18–20].

Another state-specific ansatz is that of Oliphant and Adamowicz [21] and Piecuch et al. [22] (single-reference formalism multi-reference coupled cluster, SRMRCC) and variants [23–26]. The former have been initially implemented by several groups [27–29]. Efficient implementations are available [30–32]. The ansatz may be interpreted as a recast of an SRCC method into an MR method by adapting the excitation manifold to span an MR space. However, this recast makes one reference special and causes symmetry broken solutions [30,33]. Recent further developments [34] try to address the symmetry issues. However, the wavefunction is

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still not fully cured of symmetry problems and the connectivity of the equations is in question.

Recently Evangelista et al. [35,36] reviewed and evaluated various MRCC ansätze for higher than singles/doubles base excitations for various model systems. However, they did not include the MRexpT ansatz [33,37] in their considerations. This has now successfully been carried out [38].

The goal of this paper is to show that at the separation of interactions containing active labels the non-active part of the MRexpT cluster operator is connected. This goes beyond the the proof of size-consistency given in [33]. It is very important for the numerical accuracy of the method for large systems. The ability of the MRexpT approach to break bonds or to describe excited states has been already given [33,37,38].

The outline of this paper is as follows: in Sect. 2, we introduce a convenient notation according to the literature. Section 3 briefly summarizes the MRexpT wavefunction ansatz and shows the shape of the wave function for a simple example explicitly. Section 4 reformulates the MRexpT equations to make them accessible to a connectivity analysis. Finally in Sect. 5, an application of the MRexpT ansatz to the dissociation of the nitrogen molecule is given and compared with MRCI and SRMRCC approaches.

2 Notation and spaces

We shall introduce the following common notational conventions [39,33]: orbitals occupied in any/a few/none of the reference determinants are called occupied (core) /active (valence)/virtual orbitals.[1] They are denoted as $\mathbb{O}$, $\mathbb{A}$, $\mathbb{V}$, respectively. Furthermore we introduce arbitrary orbitals $p, q, \ldots \in \mathbb{W} = \mathbb{O} \cup \mathbb{A} \cup \mathbb{V}$. Reference determinants are denoted by the Greek letters $|\lambda\rangle, |\mu\rangle, \ldots \in \mathbb{P}$. They are associated to the reference-specific orbital spaces $\mathbb{O}_\mu$ and $\mathbb{V}_\mu$ with $\prod_{p\in\mathbb{O}_\mu} \hat{a}_p^\dagger|\rangle = |\mu\rangle$ and $\mathbb{V}_\mu = \mathbb{W}\backslash\mathbb{O}_\mu$. It is $\mathbb{O} = \bigcap_{\mu\in\mathbb{P}} \mathbb{O}_\mu$, $\mathbb{V} = \bigcap_{\mu\in\mathbb{P}} \mathbb{V}_\mu$ and we get $\mathbb{A} = \mathbb{W}\backslash(\mathbb{O} \cup \mathbb{V})$. Based on the fermion creation and annihilation operators $\hat{a}^\dagger$ and $\hat{a}$ we define excitation operators $\hat{\tau} \in \mathbb{T}$ as $\hat{\tau} = \hat{a}_{a_1}^\dagger \ldots \hat{a}_{a_m}^\dagger \hat{a}_{i_m} \ldots \hat{a}_{i_1}$. Given two sets of orbitals $\mathbb{X}$ and $\mathbb{Y}$ we define the standard set of excitation operators

$$\mathbb{T}_m(\mathbb{X}, \mathbb{Y}) = \bigcup_{i_v\in\mathbb{X}, a_v\in\mathbb{Y}} \hat{a}_{a_1}^\dagger \ldots \hat{a}_{a_m}^\dagger \hat{a}_{i_m} \ldots \hat{a}_{i_1} \tag{1}$$

at excitation level m. If m is of no special concern it is skipped. Using Eq. (1) the cluster operators are given as $\hat{T}_\mu = \mathrm{ls}\,\mathbb{T}_\mu = \sum_{\hat{\tau}_i\in\mathbb{T}_\mu} t_i \hat{\tau}_i$.

[1] According to the original literature [12], we also use the terms "core" and "valence" as synonyms to "occupied" and "active", respectively. This should not be confused with the term "core" in the sense of "frozen" as non-correlated orbitals.

Assuming $\mathbb{P}$ to be complete (CAS space) and prohibiting excitations to other references $\mathbb{T}_\mu$ becomes

$$\mathbb{T}_\mu^{\mathrm{CAS}} = \mathbb{T}(\mathbb{O}_\mu, \mathbb{V}_\mu)\backslash\mathbb{T}(\mathbb{O}_\mu, \mathbb{A}) \tag{2}$$

and implies

$$\langle\lambda|e^{\hat{T}_\mu^{\mathrm{CAS}}}\mu\rangle = 0, \quad \forall_{\lambda\neq\mu} \tag{3}$$

since $\mathbb{T}_\mu^{\mathrm{CAS}}$ contains at least one virtual orbital from $\mathbb{V}_\mu\backslash\mathbb{A}$ which cannot be annihilated anymore later. Consequently the overlap with other $\mathbb{P}$-space determinants is zero.

Equation (3) will be crucial to eliminate E from the MRexpT equations conveniently, making the introduction of a complete active space essential.

The reference determinants $|\mu\rangle$ span the $\mathbb{P}$-space and the substituted determinants $|\alpha\rangle$ span the $\mathbb{Q}$-space with $\mathbb{P}\cap\mathbb{Q}=\emptyset$. $\mathbb{Q}$ may be more explicitly given as $\mathbb{Q}_{\mu n}$ specifying a certain reference and a certain substitution level n according to $\mathbb{Q}_{\mu,n} = \bigcup_{\hat{\tau}\in\mathbb{T}_{\mu n}} \hat{\tau}|\mu\rangle$.

3 The MRexpT ansatz

As the state universal ansatz [6] the MRexpT ansatz [33] uses a reference-specific cluster operator. The wave function ansatz reads

$$|\Psi\rangle = \sum_\mu c_\mu e^{\hat{T}_\mu}|\mu\rangle \tag{4}$$

and the cluster operators are given as

$$\hat{T}_\mu = \phi(c_\mu) \sum_{\hat{\tau}_{\mu,i}\in\mathbb{T}_\mu} t_{\hat{\tau}_{\mu,i}|\mu\rangle} \hat{\tau}_{\mu,i}. \tag{5}$$

In contrast to the state universal coupled-cluster formalism which uses an excitation and reference-based amplitude indexing ($t_{\hat{\tau}_{\mu,i}}$) Eq. (5) contains a determinant-based amplitude indexing ($t_{\hat{\tau}_{\mu,i}|\mu\rangle}$) with the sign rule $t_{-|\beta\rangle} = -t_{|\beta\rangle}$ applied. The reference phase compensation factor $\phi(z)$ is given by $\phi(z) = e^{-i\arg z}$, $z \in \mathbb{C}$, and guarantees the potential completeness of Eq. (4). One should note that this phase factor is given by the reference coefficient c_μ itself and does not introduce any new degree of freedom.

Figure 1 shows the genealogy of the excitations and determinants for a simple example. The upper and lower part (with respect to a mirror line at half height) belong to the $|ip\rangle$ and $|iq\rangle$ reference, respectively. The dotted excitations on the

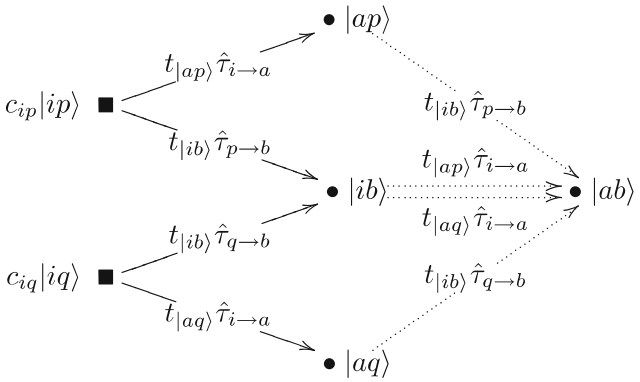

Fig. 1 Example: excitation graph of MRexpT including products (*dotted lines*)

right-hand side of Fig. 1 correspond to the second factor of possible product excitations. Applying the Eqs. (4) and (5) to the simple example given in Fig. 1 the wave function reads for $c_\mu \in \mathbb{R}$

$$|\Psi\rangle = \begin{pmatrix} c_{ip} \\ c_{iq} \\ |c_{ip}|\, t_{|ap\rangle} \\ (|c_{ip}| + |c_{iq}|)\, t_{|ib\rangle} \\ |c_{iq}|\, t_{|aq\rangle} \\ c_{ip} t_{|ap\rangle} t_{|ib\rangle} + c_{iq} t_{|aq\rangle} t_{|ib\rangle} \end{pmatrix}^{\mathrm{T}} \cdot \begin{pmatrix} |ip\rangle \\ |iq\rangle \\ |ap\rangle \\ |ib\rangle \\ |aq\rangle \\ |ab\rangle \end{pmatrix}. \tag{6}$$

We note that for product excitations in the last line the factor $\frac{1}{2!}$ of the exponential cancels with the 2! possible paths per reference to reach $|ab\rangle$ $(\hat{\tau}_{i\to a}\hat{\tau}_{p\to b} + \hat{\tau}_{p\to b}\hat{\tau}_{i\to a})$ which is in common with the usual SRCC. Furthermore we see the sign factor ϕ causing absolute values in c at the linear level.

Inserting Eq. (4) into the Schrödinger equation we get

$$\hat{H} \sum_\mu c_\mu e^{\hat{T}_\mu} |\mu\rangle = E \sum_\mu c_\mu e^{\hat{T}_\mu} |\mu\rangle. \tag{7}$$

Projecting Eq. (7) from the left onto $\langle\rho|$ we obtain a system of equations linear in the reference coefficients c_μ and non linear in the amplitudes $t_{|\alpha\rangle}$

$$\sum_\mu c_\mu \langle\rho|\hat{H} - E|e^{\hat{T}_\mu}\mu\rangle = 0, \quad \forall_{\langle\rho|}. \tag{8}$$

Additionally we fix the norm of the reference coefficients by

$$\sum_\mu |c_\mu|^2 = 1. \tag{9}$$

In case of a single reference case Eq. (9) collapses to the usual intermediate normalization of single reference-coupled cluster theory. Eqs. (8) and (9) together form a set of $\mathrm{ord}(\mathbb{P}) + \mathrm{ord}(\mathbb{Q}) + 1$ equations for the unknowns c_μ and $t_{\hat{\tau}_{\mu,i}|\mu\rangle}$ and E, respectively. Alternatively, one may separate an eigenvalue problem for the $\mathbb{P}$ space requiring a two step process.

4 Connectivity analysis

In this section, we shall analyze the connectivity properties of the MRexpT ansatz. Although the ansatz of MRexpT is conceptually very simple the explicit proof of connectivity is cumbersome. This is in line with other proofs of connectivity in the literature [6,16,17].

It should be stated that the simple occurrence of E in the Eq. (8) does not necessarily prohibit the connectivity of the equations a priori. The unlinked (not similarity transformed) form of single reference coupled cluster shares the occurrence of E in the projections. Nevertheless, under certain conditions it turns out to be connected. As usual for the fragile and subtle matter of connectivity things are a bit more involved.

Unfortunately, a direct analysis of MRexpT by means of a perturbative expansion turns out to be a rather sophisticated task since E enters the expansions and the amplitudes are coupled in a complicated way through Eq. (5). Therefore, we shall proceed as follows: First of all we recast the MRexpT equations eliminating E and continue by setting up the perturbative expansion of the cluster operator $\hat{T}_\mu$ without any further assumptions. Then we introduce the core/valence separation causing significant simplifications to the recasted MRexpT equations. Finally, these results are transferred to the perturbative expansion which will easily be seen to be connected for the core part of $\hat{T}_\mu$.

4.1 Algebraic reformulation of the MRexpT equations

Solving Eq. (8) for E we obtain

$$E = \frac{\sum_\mu c_\mu \langle\rho|\hat{H} e^{\hat{T}_\mu}\mu\rangle}{\sum_\mu c_\mu \langle\rho|e^{\hat{T}_\mu}\mu\rangle} \tag{10}$$

$$\overset{(3)}{=} \sum_\mu \frac{c_\mu}{c_\lambda} \langle\lambda|\hat{H} e^{\hat{T}_\mu}\mu\rangle \tag{11}$$

where we chose $\rho = \lambda \in \mathbb{P}$ for convenience since the sum in the denominator will collapse for this case according to Eq. (3).

Inserting Eq. (11) into Eq. (8) for $\rho = \alpha \in \mathbb{Q}$ we get

$$0 = \sum_\mu c_\mu \left[\langle \alpha | \underset{\uparrow}{\hat{H} e^{\hat{T}_\mu}} \mu\rangle - \langle \alpha | e^{\hat{T}_\mu} \mu\rangle \sum_{\mu'} \frac{c_{\mu'}}{c_\mu} \langle \mu | \hat{H} e^{\hat{T}_{\mu'}} \mu' \rangle \right] \tag{12}$$

$$= \sum_\mu c_\mu \left[\langle \alpha | e^{\hat{T}_\mu} e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle - \underbrace{\langle \alpha | e^{\hat{T}_\mu} \mu\rangle \langle \mu | \hat{H} e^{\hat{T}_\mu} \mu\rangle}_{A_\mu} \right.$$
$$\left. - \underbrace{\langle \alpha | e^{\hat{T}_\mu} \mu\rangle \sum_{\mu' \neq \mu} \frac{c_{\mu'}}{c_\mu} \langle \mu | \hat{H} e^{\hat{T}_{\mu'}} \mu' \rangle}_{B_\mu} \right] \tag{13}$$

$$= \sum_\mu c_\mu \left[\langle \alpha | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle + \sum_{i=1}^{\infty} \frac{1}{i!} \langle \alpha | \hat{T}_\mu^i \underset{\uparrow}{e^{-\hat{T}_\mu}} \hat{H} e^{\hat{T}_\mu} \mu\rangle \right.$$
$$\left. - A_\mu - B_\mu \right] \tag{14}$$

$$= \sum_\mu c_\mu \left[\langle \alpha | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle \right.$$
$$+ \underbrace{\underbrace{\sum_{i=1}^{\infty} \frac{1}{i!} \langle \alpha | \hat{T}_\mu^i \mu\rangle}_{\langle \alpha | e^{\hat{T}_\mu} \mu\rangle} \langle \mu | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle - A_\mu - B_\mu}_{0}$$
$$\left. + \underbrace{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{|\omega\rangle \in \mathbb{Q}_{\mu j}} \frac{1}{i!} \langle \alpha | \hat{T}_\mu^i \omega\rangle \langle \omega | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle}_{C_\mu} \right] \tag{15}$$

$$0 = \sum_\mu c_\mu \left[\langle \alpha | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle - B_\mu + C_\mu \right] \tag{16}$$

using the following algebraic operations:

Eq. (12)→Eq. (13): insertion of $1 = e^{\hat{T}_\mu} e^{-\hat{T}_\mu}$ at the arrow marker and splitting the sum over μ' with respect to $\mu' = \mu$ and $\mu' \neq \mu$. We introduce the shorthands $A_\mu := \langle \alpha | e^{\hat{T}_\mu} \mu\rangle \langle \mu | \hat{H} e^{\hat{T}_\mu} \mu\rangle$ and $B_\mu := \langle \alpha | e^{\hat{T}_\mu} \mu\rangle \sum_{\mu' \neq \mu} \frac{c_{\mu'}}{c_\mu} \langle \mu | \hat{H} e^{\hat{T}_{\mu'}} \mu' \rangle$.

Eq. (13)→Eq. (14): expanding the first $e^{\hat{T}_\mu}$ of Eq. (13) into a Taylor series in $\hat{T}_\mu^i$ and splitting with respect to $i = 0$ and $i > 0$.

Eq. (14)→Eq. (15): insertion of a complete basis at the arrow marker according to $1 = \sum_\omega |\omega\rangle\langle\omega| = \sum_{j=0}^{\infty} \sum_{\omega \in \mathbb{Q}_{\mu j}} |\omega\rangle\langle\omega|$ with $\mathbb{Q}_{\mu j}$ consisting of j-fold substituted determinants with respect to $|\mu\rangle$. Finally, we split the summation into the reference and the rest according to $1 = |\mu\rangle\langle\mu| + \sum_{j=1}^{\infty} \sum_{\omega \in \mathbb{Q}_{\mu j}} |\omega\rangle\langle\omega|$. We introduce the shorthand $C_\mu := \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{|\omega\rangle \in \mathbb{Q}_{\mu j}} \frac{1}{i!} \langle \alpha | \hat{T}_\mu^i \omega\rangle \langle \omega | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle$.

Eq. (15)→Eq. (16): since it is $\langle \alpha | \hat{T}_\mu^0 \mu\rangle = 0$ we may write $\sum_{i=1}^{\infty} \frac{1}{i!} \langle \alpha | \hat{T}_\mu^i \mu\rangle = \langle \alpha | e^{\hat{T}_\mu} \mu\rangle$ and as $\langle \mu | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle = \langle \mu | \hat{H} e^{\hat{T}_\mu} \mu\rangle$ the second sum in Eq. (15) cancels A_μ.

Finally, we conclude that Eq. (16) and the original MRexpT (Eq. (8)), although looking quite different, are fully equivalent since we did not make any approximations.

However, Eq. (16) is now ready to be analyzed with respect to connectivity properties by means of a perturbative analysis.

4.2 Perturbative expansion

In order to analyze the connectivity properties of $\hat{T}$ in Eq. (16) we will expand $\hat{T}$ into a perturbation series. Starting from

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{17}$$

we assume all determinants to be eigenfunctions of $\hat{H}_0$, making the representation of $\hat{H}_0$ diagonal

$$\hat{H}_0 = \sum_{p \in \mathbb{W}} \epsilon_p \hat{a}_p^\dagger \hat{a}_p \tag{18}$$

with excitation rank 0. $\hat{V}$ is a two-particle operator

$$\hat{V} = \frac{1}{4} \sum_{pqrs \in \mathbb{W}} v_{pq,rs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \tag{19}$$

and given by $\hat{V} = \hat{H} - \hat{H}_0$. Introducing the short hand notation $\epsilon_{|\alpha\rangle} = \langle \alpha | H_0 \alpha \rangle$ we split the term $\langle \alpha | e^{-\hat{T}_\mu} \hat{H} e^{\hat{T}_\mu} \mu\rangle$ of Eq. (16) into its $\hat{H}_0$ and $\hat{V}$ part:

$$0 = \sum_{\mu \in \mathbb{P}_\alpha} |c_\mu|\, t_{|\alpha\rangle} (\epsilon_{|\alpha\rangle} - \epsilon_{|\mu\rangle})$$
$$+ \sum_\mu c_\mu \left[\langle \alpha | e^{-\hat{T}_\mu} \hat{V} e^{\hat{T}_\mu} \mu\rangle - B_\mu + C_\mu \right] \tag{20}$$

introducing $\mathbb{P}_\alpha = \{\mu \in \mathbb{P} \mid \alpha \in \mathbb{Q}_\mu\}$ to simplify the $\hat{H}_0$ term of Eq. (20) as it is $\langle \alpha | e^{-\hat{T}_\mu} \hat{H}_0 e^{\hat{T}_\mu} \mu\rangle = 0$, $\forall_{\mu \notin \mathbb{P}_\alpha}$. Furthermore, we used the identity $\langle \alpha | (\hat{H}_0 + [\hat{H}_0, \hat{T}_\mu] + \cdots) \mu\rangle = t_{|\alpha\rangle} (\epsilon_{|\alpha\rangle} - \epsilon_{|\mu\rangle})$ since (1) $\langle \alpha | \hat{H}_0 \mu\rangle = 0$ as $\hat{H}_0$ does not carry an excitation and (2) it is $\langle \alpha | [\hat{H}_0, \hat{T}_\mu] \mu\rangle = t_{|\alpha\rangle} (\epsilon_{|\alpha\rangle} - \epsilon_{|\mu\rangle})$ and (3) higher commutators vanish since only one $\hat{T}_\mu$ may be connected to $\hat{H}_0$.

Solving Eq. (20) for $t_{|\alpha\rangle}$ yields:

$$t_{|\alpha\rangle} = \frac{\sum_\mu c_\mu \left[\langle\alpha|e^{-\hat{T}_\mu}\hat{V}e^{\hat{T}_\mu}\mu\rangle - B_\mu + C_\mu\right]}{\sum_{\mu\in\mathbb{P}_\alpha}|c_\mu|(\epsilon_{|\mu\rangle} - \epsilon_{|\alpha\rangle})}. \tag{21}$$

It is

$$\hat{T}_\lambda = \phi(c_\lambda)\sum_{|\alpha\rangle\in\mathbb{Q}_\lambda} t_{|\alpha\rangle}\hat{\tau}_{|\lambda\rangle\to|\alpha\rangle}. \tag{22}$$

In order to assemble $\hat{T}_\lambda$ according to Eq. (22) we append $\hat{\tau}_{|\lambda\rangle\to|\alpha\rangle}$ to Eq. (21) and sum over $|\alpha\rangle \in \mathbb{Q}_\lambda$.

$$\frac{\hat{T}_\lambda}{\phi(c_\lambda)} = \sum_{|\alpha\rangle\in\mathbb{Q}_\lambda} \frac{\sum_\mu c_\mu \left[\langle\alpha|e^{-\hat{T}_\mu}\hat{V}e^{\hat{T}_\mu}\mu\rangle - B_\mu + C_\mu\right]}{\sum_{\mu\in\mathbb{P}_\alpha}|c_\mu|(\epsilon_{|\mu\rangle} - \epsilon_{|\alpha\rangle})}\hat{\tau}_{|\lambda\rangle\to|\alpha\rangle} \tag{23}$$

Once more we conclude that in deriving Eq. (23) we made no approximation so far. However, since the term B_μ in Eq. (23) is likely to contain disconnected parts they will likewise show up in $\hat{T}$.

4.3 Core connectivity

To analyze the connectivity properties of MRexpT we decompose the full Hamiltonian and the cluster operator into their core (carrying no active orbital) and valence (carrying some active orbital) part

$$\hat{H} = \hat{H}^{\bar{\mathrm{v}}} + \hat{H}^{\mathrm{v}} \tag{24}$$

$$\hat{T} = \hat{T}^{\bar{\mathrm{v}}} + \hat{T}^{\mathrm{v}}. \tag{25}$$

The related implications on the many body spaces are discussed in the appendix. Since Eq. (24) implies the core and the valence system not to interact we may exploit the already proven size consistency of MRexpT [33] and restrict the further analysis to the core Hamiltonian. To this end we split the summation over $|\alpha\rangle \in \mathbb{Q}_\lambda$ in Eq. (23) according to Eq. (25) with respect to its core and valence parts and get

$$\hat{T}^{\bar{\mathrm{v}}}_\lambda + \hat{T}^{\mathrm{v}}_\lambda = \phi(c_\lambda)\left[\sum_{|\alpha\rangle\in\mathbb{Q}^{\bar{\mathrm{v}}}_\lambda}\frac{\cdots}{\cdots} + \sum_{|\alpha\rangle\in\mathbb{Q}^{\mathrm{v}}_\lambda}\frac{\cdots}{\cdots}\right]. \tag{26}$$

Returning to Eq. (16) in the framework of the core Hamiltonian we substitute $\hat{H}$ by $\hat{H}^{\bar{\mathrm{v}}}$. Introducing the shorthand notation $B^{\bar{\mathrm{v}}}_\mu = B_\mu|_{\hat{H}\to\hat{H}^{\bar{\mathrm{v}}}}$ and $C^{\bar{\mathrm{v}}}_\mu$ correspondingly Eq. (16) reads

$$0 = \sum_\mu c_\mu\left[\langle\alpha|e^{-\hat{T}_\mu}\hat{H}^{\bar{\mathrm{v}}}e^{\hat{T}_\mu}\mu\rangle - B^{\bar{\mathrm{v}}}_\mu + C^{\bar{\mathrm{v}}}_\mu\right]. \tag{27}$$

Now, considering Eq. (27) in projections onto $|\alpha\rangle \in \mathbb{Q}^{\bar{\mathrm{v}}}_\lambda$ only we shall achieve significant and crucial simplifications by exploitation of Eqs. (35) and (3). An analysis of the addends within the large brace of Eq. (27) while limiting the projection to $|\alpha\rangle \in \mathbb{Q}^{\bar{\mathrm{v}}}_\lambda$ yields:

- $\langle\alpha|e^{-\hat{T}_\mu}(\hat{V}^{\bar{\mathrm{v}}} + \hat{H}^{\bar{\mathrm{v}}}_0)e^{\hat{T}_\mu}\mu\rangle$: since $\hat{V}^{\bar{\mathrm{v}}}$ does not carry any valence labels while $\hat{H}^{\bar{\mathrm{v}}}_0$ does not carry any substitution at all we may apply Eq. (35) to find only the term $\mu = \lambda$ to survive as $e^{-\hat{T}_\mu}$ does not contain deexcitations.
- $B^{\bar{\mathrm{v}}}_\mu$: it is $B^{\bar{\mathrm{v}}}_\mu = \langle\alpha|e^{\hat{T}_\mu}\mu\rangle\sum_{\mu'\neq\mu}\frac{c_{\mu'}}{c_\mu}\langle\mu|\hat{H}^{\bar{\mathrm{v}}}e^{\hat{T}_{\mu'}}\mu'\rangle$. Since $\hat{H}^{\bar{\mathrm{v}}}$ does not carry any valence excitation while $e^{\hat{T}_{\mu'}}$ does not excite from one reference to another due to Eq. (3), $B^{\bar{\mathrm{v}}}_\mu$ vanishes completely.
- $C^{\bar{\mathrm{v}}}_\mu$: $\langle\alpha|\hat{T}^i_\mu\omega\rangle$ may be decomposed into $\langle\alpha|\hat{T}^i_\mu\hat{\tau}_{\mu\to\omega}\mu\rangle$. The latter vanishes for $\mu \neq \lambda$ since $\hat{T}^i_\mu$ and $\hat{\tau}_{\mu\to\omega}$ contain excitations from the same set and the compound product excitation may not contain the same active label for creators and annihilators at the same time.

Summarizing, we conclude that the sum over μ in Eq. (27) collapses to a single λ while $B^{\bar{\mathrm{v}}}_\mu$ vanishes completely:

$$0 = \langle\alpha|e^{-\hat{T}_\lambda}\hat{H}^{\bar{\mathrm{v}}}e^{\hat{T}_\lambda}\lambda\rangle + C^{\bar{\mathrm{v}}}_\lambda, \quad \forall_{\alpha\in\mathbb{Q}^{\bar{\mathrm{v}}}_\lambda} \tag{28}$$

Introducing $D_{\omega\lambda} := \langle\omega|e^{-\hat{T}_\lambda}\hat{H}^{\bar{\mathrm{v}}}e^{\hat{T}_\lambda}\lambda\rangle$ Eq. (28) becomes

$$0 = D_{\alpha\lambda} + \sum_{i,j=1}^{\infty}\sum_{|\omega\rangle\in\mathbb{Q}_{\lambda j}}\frac{1}{i!}\underbrace{\langle\alpha|\hat{T}^i_\lambda\omega\rangle D_{\omega\lambda}}_{R}, \quad \forall_{\alpha\in\mathbb{Q}^{\bar{\mathrm{v}}}_{\lambda k}}. \tag{29}$$

where we specified the substitution level k of the projecting determinants in $\mathbb{Q}^{\bar{\mathrm{v}}}_{\lambda k}$ explicitly.

Equation (29) is now completely analogous to the single reference unlinked coupled cluster case and we shall briefly analyze the conditions under which the term R vanishes: Since $\hat{T}$ is a pure excitation operator the sum over j does actually not carry on until infinity but is bounded by k decreased by the minimal excitation level of $\hat{T}$. Obviously, in analogy to the single reference unlinked-coupled cluster equations for a specific j, $D_{\omega\lambda}$ with $|\omega\rangle \in \mathbb{Q}_{\lambda j}$ reflects the j-fold amplitude projection of the linked equations. Now one may assemble consecutive projection levels recursively in the following manner: in the singles projection the term $\langle\alpha|\hat{T}^i_\lambda\omega\rangle$ vanishes due to the above mentioned summation restriction on j. Consequently the unlinked singles projection matches the linked one and is accordingly solved. At the doubles projection level the term $\langle\alpha|\hat{T}^i_\lambda\omega\rangle$ does no longer vanish. However, since $D_{\omega\lambda}$ reflects the singles projection equations (as it is $1 = j < k = 2$) which are already solved it will vanish anyway and we may proceed to higher excitation levels. Obviously, for this recursive chain to work we must not step into a projection level which is not already solved. Therefore, $\mathbb{Q}$ has to be closed with respect to deexcitations from $\mathbb{T}^\dagger$, that is $\hat{\tau}^\dagger|\alpha\rangle \in \mathbb{Q}$, $\forall_{\hat{\tau}\in\mathbb{T},|\alpha\rangle\in\mathbb{Q}}$ (cf. [40]).

Consequently, a sufficient condition for R in Eq. (29) to vanish is that $\hat{T}$ contains a consecutive sequence of excitation levels (e.g. S, SD, SDT, ...).

Reiterating the perturbative expansion Eq. (23) (assuming $R = 0$) and exploiting $|\alpha\rangle \in \mathbb{Q}_\lambda^{\overline{\nu}} \Rightarrow \mathbb{P}_\alpha = \{|\lambda\rangle\}$, collapsing the sum in the denominator we finally arrive at

$$\hat{T}_\lambda^{\overline{\nu}} = \phi(c_\lambda) \sum_{|\alpha\rangle \in \mathbb{Q}_\lambda^{\overline{\nu}}} \frac{c_\lambda \langle \alpha | e^{-\hat{T}_\lambda} \hat{V}^{\overline{\nu}} e^{\hat{T}_\lambda} \lambda \rangle}{|c_\lambda| (\epsilon_{|\lambda\rangle}^{\overline{\nu}} - \epsilon_{|\alpha\rangle}^{\overline{\nu}})} \hat{\tau}_{|\lambda\rangle \to |\alpha\rangle}$$
$$= \sum_{|\alpha\rangle \in \mathbb{Q}_\lambda^{\overline{\nu}}} \frac{\langle \alpha | e^{-\hat{T}_\lambda} \hat{V}^{\overline{\nu}} e^{\hat{T}_\lambda} \lambda \rangle}{(\epsilon_{|\lambda\rangle}^{\overline{\nu}} - \epsilon_{|\alpha\rangle}^{\overline{\nu}})} \hat{\tau}_{|\lambda\rangle \to |\alpha\rangle}. \quad (30)$$

which exactly resembles the corresponding expression of the linked form of single reference coupled cluster theory and is easily seen to be connected.

We conclude that the assumption of a complete model space and the separation of the Hamiltonian according to Eq. (24) enabled us to prove the connectivity of the core part of the cluster operator making the MRexpT ansatz scaling linearly with the number of core electrons.

To summarize the MRexpT ansatz is connected as single reference coupled cluster within the non-active part while it is size consistent (including the active part, of course) and able to dissociate bonds. However, MRexpT lacks full connectivity within the active part and therefore misses the correct scaling description of the pure valence and the core-valence interaction part. Nevertheless, if one considers the number and location of the valence electrons to be fixed and considers $N_{\text{core}} \to \infty$ the ratio core/valence becomes large making the (not correctly scaling) core-valence interaction negligible and the whole energy size extensive.

Additionally MRexpT can describe size intensive properties correctly (e.g. dissociation of a bond on a long polymer) as long as it does not require valence extensivity. It should be noted that for common molecular applications connectivity within the core part is expected to be more important than connectivity within the valence part since the number of core electrons may grow rather quickly while the number of valence electrons typically does not grow with the size of the molecule that fast. For solids containing a multi-reference unit cell, however, one may also encounter rapidly increasing valence spaces. In this case core connectivity is expected to be not sufficient.

5 Application: dissociation of N_2

Finally we report on the ground state potential energy surface of the dissociation of N_2 calculated with MRCI, SRMRCC [21,22], and MRexpT.

The natural reference space to break the triple bond is made up by the 2×3 p-electrons from the atomic nitrogen forming a CAS(6 e$^-$, $6 \times p$) space. The calculations were carried out using MOLCAS [41] with an interface [42] to generate the MO-transformed one- and two-electron integrals. Using a cc-PVDZ [43] basis we set up two different sets of CAS(6 e$^-$, $6 \times p$) space orbitals leaving the $1s$ and $2s$ orbitals inactive:

(i) $1\,^7\Sigma_u^+$ excited state orbitals (actually consisting of a single determinant)
(ii) $X\,^1\Sigma_g^+$ ground state orbitals.

In the following correlation calculations we used the same CAS space as reference space and left the $1s$ and $2s$ orbitals frozen due to implementational limitations. This set up may be considered as a worst case scenario for MRexpT since there are no inactive orbitals in the correlating calculation. Nevertheless, MRexpT performs very well completing previous studies [33,37,38] containing non-empty inactive spaces.

Table 1 and Fig. 2 show the results for MRCI, SRMRCC and MRexpT employing $^7\Sigma_u^+$ orbitals while Table 2 and Fig. 3 show the results for the $^1\Sigma_g^+$ ground state orbitals.

Discussing the results from the $^7\Sigma_u^+$ orbitals first we see from Table 1 MRCI to have a very significant NPE of 3394 μE_H. The MRCI energies become especially poor for small r. SRMRCC has an NPE of 795 μE_H which is smaller by a factor of 4 than that of MRCI. The largest errors appear near the equilibrium geometry while they become less for smaller r. However, in Fig. 2 we see the energies to drop below the zero line turning from underestimation to overestimation of the correlation energy. Although coupled cluster

Table 1 N_2, $^1\Sigma_g^+$ ground state, cc-PVDZ basis set, all p-electrons correlated, $^7\Sigma_u^+$ orbitals used, r in Bohr, FCI energies in Hartree, MRCI, SRMRCC and MRexpT energy differences with respect to FCI in micro-Hartree

r	FCI	MRCI	SRMRCC	MRexpT
1.5	−108.487 961	3,774	−97	214
1.75	−108.975 817	3,518	181	434
2	−109.118 617	3,148	528	675
2.25	−109.117 266	2,346	698	701
2.5	−109.062 128	1,800	667	591
3	−108.936 811	1,395	662	507
3.5	−108.859 925	1,101	594	435
4	−108.831 689	752	385	299
4.5	−108.824 479	534	250	174
5	−108.822 632	442	198	117
10	−108.821 243	380	178	79
20	−108.821 240	380	178	79
100	−108.821 240	380	179	79
NPE	–	3,394	795	622

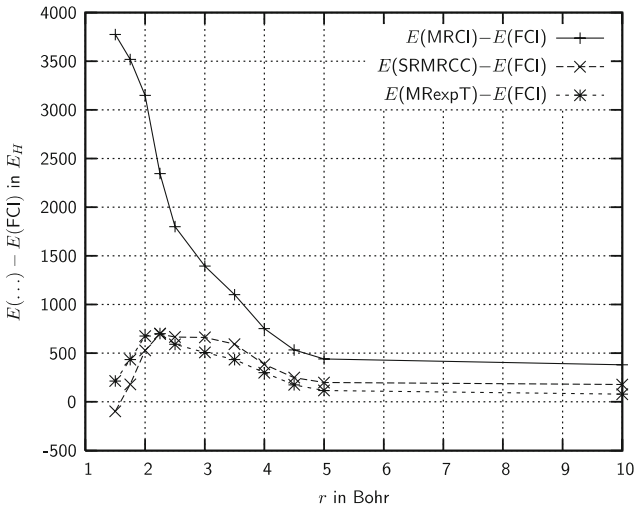

Fig. 2 N_2, $^1\Sigma_g^+$ ground state, cc-PVDZ basis set, all p-electrons correlated, $^7\Sigma_u^+$ orbitals used, r in Bohr, energy differences with respect to FCI

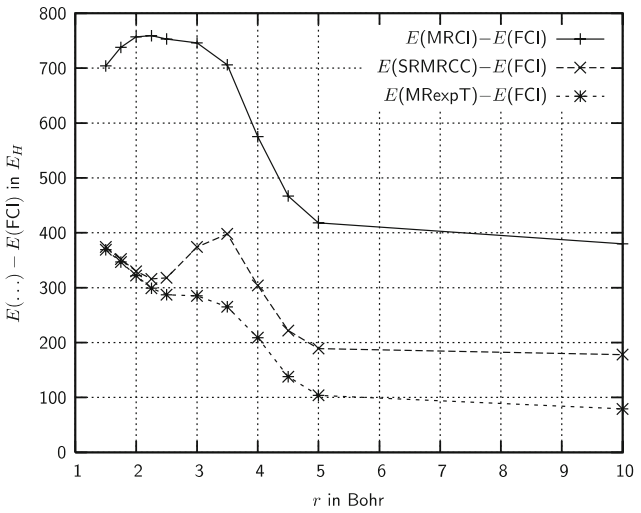

Fig. 3 N_2, $^1\Sigma_g^+$ ground state, cc-PVDZ basis set, all p-electrons correlated, $^1\Sigma_g^+$ ground state orbitals used, r in Bohr, energy differences with respect to FCI

Table 2 N_2, $^1\Sigma_g^+$ ground state, cc-PVDZ basis set, all p-electrons correlated, ground state $^1\Sigma_g^+$ orbitals used, r in Bohr, FCI energies in Hartree, MRCI, SRMRCC and MRexpT energy differences with respect to FCI in micro-Hartree

r	FCI	MRCI	SRMRCC	MRexpT
1.5	−108.505 480	704	374	369
1.75	−108.995 919	738	352	347
2	−109.141 085	757	330	322
2.25	−109.138 848	759	316	299
2.5	−109.081 766	754	318	287
3	−108.949 436	746	374	285
3.5	−108.866 194	706	398	265
4	−108.834 089	575	304	209
4.5	−108.825 390	467	222	138
5	−108.823 011	418	189	104
10	−108.821 243	380	178	79
20	−108.821 240	380	178	79
100	−108.821 240	380	179	79
NPE	–	379	220	290

in its standard projected form is of course not variational the correlation energies are usually underestimated. From our experience we know that the accuracy of the calculated energies typically decreases when dropping below the full CI energies. The MRexpT results show a similar behavior as the SRMRCC results while they perform slightly better in terms of the NPE and the maximum deviation from full CI. The NPE is 622 μE_H being about a factor of 5 smaller than those of MRCI. In Fig. 2 we see the maximum error for MRexpT to appear at smaller r leaving the correlation energy still underestimated for $r = 1.5$ Bohr.

Employing the ground state orbitals we see from Table 2 the overall errors to be much smaller for all considered methods. Now, also MRCI with an NPE of 379 μE_H performs rather accurate due to the small number of correlated electrons although the coupled cluster methods are still about a factor of two more accurate. SRMRCC has the smallest NPE of 220 μE_H (in comparison to 290 μE_H for MRexpT) while MRexpT shows throughout all considered geometries lower overall errors. Considering Fig. 3 we see MRCI and SRMRCC to have a rather significant slope around $r = 3.5$ Bohr where the orbitals rearrange to assemble the atomic system. While SRMRCC shows an artificial maximum at $r = 3.5$ Bohr the MRexpT energies are less affected by the orbital rotations and remain smooth.

6 Conclusion

A connectivity analysis of the MRexpT ansatz has been presented. Assuming a complete active space the connectivity of the core part of the cluster operator upon the separation of interactions carrying active and non-active orbital labels has been proven algebraically. This is an important and non-trivial result. It goes beyond the proof of size consistency given in [33] as size consistency is *not* sufficient for core extensivity. The accuracy of correlated calculations for a growing number of particles is insured by connectivity (that is extensivity) not by consistency.

Consequently, MRexpT preserves the connectivity of the single-reference coupled cluster ansatz within the non-active

part while it is at the same time size consistent for direct product reference spaces. However, connectivity does not hold for substitutions containing active orbitals. MRexpT is able to break bonds, describe potential energy surfaces and excited states as shown for BeH_2, CH_2, Li_2 and nH_2 in [33], H_4 and H_8 in [37], and ground state of N_2 in this work. The MRexpT results are very close to full CI and compare very well to other MRCC ansätze from the literature as shown in [38,35] and this work.

Appendix

We define pure core excitation spaces as well as their complements and corresponding excitation manifolds as

$$\mathbb{Q}_\mu^{\bar{\mathbb{v}}} = \mathbb{Q}_\mu \setminus \bigcup_{\lambda \neq \mu} \mathbb{Q}_\lambda \tag{31}$$

$$\mathbb{Q}_\mu^{\mathbb{v}} = \mathbb{Q}_\mu \cap \bigcup_{\lambda \neq \mu} \mathbb{Q}_\lambda \tag{32}$$

$$\mathbb{T}^{\bar{\mathbb{v}}} = \mathbb{T}(\mathbb{O}, \mathbb{V}) \tag{33}$$

$$\mathbb{T}_\mu^{\mathbb{v}} = \mathbb{T}_\mu \setminus \mathbb{T}^{\bar{\mathbb{v}}} \tag{34}$$

with $\mathbb{Q}_\mu^{\bar{\mathbb{v}}} \cup \mathbb{Q}_\mu^{\mathbb{v}} = \mathbb{Q}_\mu$ and $\bigcup_{\hat{\tau} \in \mathbb{T}^{\bar{\mathbb{v}}}} \hat{\tau}|\mu\rangle = \mathbb{Q}_\mu^{\bar{\mathbb{v}}}$ and $\bigcup_{\hat{\tau} \in \mathbb{T}_\mu^{\mathbb{v}}} \hat{\tau}|\mu\rangle = \mathbb{Q}_\mu^{\mathbb{v}}$ The involved many body spaces are shown in Fig. 4.

We conclude that Eq. (2) implies

$$\langle \alpha | e^{\hat{T}_\mu} \mu \rangle = 0, \quad \forall_{\alpha \in \mathbb{Q}_\lambda^{\bar{\mathbb{v}}}}, \lambda \neq \mu \tag{35}$$

which plays an important role in the proof of core extensivity. Equation (35) states that $e^{\hat{T}_\mu}$ does not contain excitations corresponding to the dashed arrow in Fig. 4. To see this we consider a $|\mu\rangle \in \mathbb{P}$ and an $|\alpha\rangle \in \mathbb{Q}_\lambda^{\bar{\mathbb{v}}}$ and $\lambda \neq \mu$. Consequently, it is $|\alpha\rangle = \ldots \hat{a}_a^\dagger \hat{a}_i \hat{a}_x^\dagger \hat{a}_y |\mu\rangle$ with $a \in \mathbb{V}_\mu$, $i \in \mathbb{O}_\mu$, and $x, y \in \mathbb{A}$. That is: we need (at least) one creator and one annihilator from $\mathbb{A}$ leading from $|\mu\rangle$ to $|\lambda\rangle$. However, Eq. (2) rules out $\hat{T}$ to contain any active creators $\Rightarrow$ Eq. (35) holds.

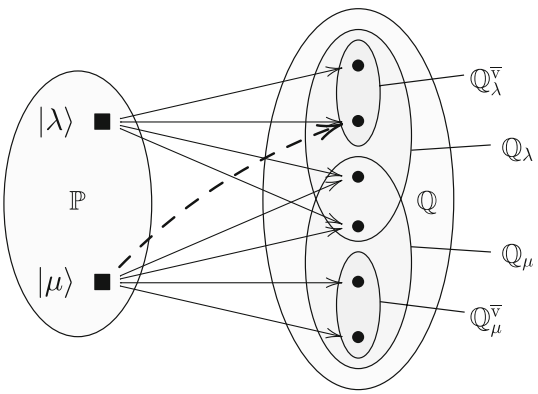

Fig. 4 Reference and excited spaces with core/valence separation

It should be remarked that validity of Eq. (35) is not strictly tied to the completeness of $\mathbb{P}$ but may be shown to hold at weaker assumptions.

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