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Development and applications of a relaxation-inducing cluster expansion theory for treating strong relaxation and differential correlation effects*

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Abstract. We present in this paper a multi-reference coupled cluster (MRCC) formulation for energy differences which treats orbital relaxation and correlation effects on the same footing, by invoking a novel cluster ansatz of the valence portion of the wave operator Ω_v. Unlike in the traditional normal-ordered exponential representation of Ω_v, our new relaxation-inducing ansatz, represented symbolically as $E_r(S)$, allows contractions between the spectator lines and also certain other special contractions. By an extensive theoretical analysis, taking as an example the case of one-hole model space (the IP problem), we demonstrate that our ansatz incorporates in a manifestly spin-free form the orbital relaxation to all orders. The traditional Thouless-type of exponential transformation via one-body excitations can induce the same effect, as is done in the valence-specific or the quasi-valence-specific MRCC formalisms, but they have to be done in the spin-orbital basis – making the spin adaptation of the problem a complicated exercise. In contrast, we use a spin-free representation of the cluster operators right from start, but expand the rank of the cluster operators by involving spectator orbitals to distinguish the various spin possibilities. The combinatorial factors entering the contracted power series in $E_r(S)$ are chosen in such a way that they correspond to what we would have obtained if we had used a Thouless-like transformation to induce the orbital relaxation. Our working equations generally have only finite powers of the cluster operators S, resulting in a very compact formulation of the relaxation problem. Pilot numerical applications for the IP computations of HF and H_2O in the core, the inner valence and the outer valence regions show very good performance of the method vis-a-vis those obtained using the traditional normal ordered ansatz for Ω_v. The improvement in the core IP value is particularly impressive, although even for the valence regions there is an overall improvement of the IP values.

Key words: Multi-reference coupled cluster (MRCC) theory – Orbital relaxations in MRCC theory – MRCC theory for core holes – Relaxation-inducing cluster ansatz in MRCC theory

1 Introduction

Electron correlation plays a major role in shaping diverse structural and spectroscopic properties. Often the simple molecular orbital picture fails to provide even a qualitative understanding of the experimental results. A case in point is the breakdown of the orbital picture in describing the inner valence ionization of molecules [1–3]. In particular, to interpret the spectroscopic energy differences, one has to account for the changes in the correlation energy as well as the relaxation of orbitals accompanying excitation or ionization, which demands theories capable of providing a good description of the differential correlation and the orbital relaxation effects. For the core-hole ionization and excitation processes, orbital relaxation is very important. The so-called direct methods for computing energy differences seem somehow superior to the traditional approach of computing the total energies of the two states concerned, since in the direct methods all the common correlation terms cancel out in the energy difference, and an inherently more accurate description of the differential correlation and relaxation effects can be modelled. This is, for example, the philosophy of many of the modern methods for energy differences [1–15]. The advantage of the direct method is predicated by the use of a common set of orbitals to describe both the ground and the excited/ionized states of interest, which implies that one would require an efficient and compact treatment of the orbital relaxation effects when the situation so demands, as for example in the core-excitation and core-ionization processes, but without explicitly changing the orbitals. There is also a concomitant combined interplay of differential correlation and orbital relax-

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ation effects, both of which may be important, as for the core-hole satellites and in the inner valence region. This poses a real challenge to electronic structure theory. We propose to present and apply in this paper a coupled cluster theory for an efficient non-perturbative treatment of the relaxation and differential correlation effects via the use of a novel cluster ansatz of the wave operator. We will illustrate the basic thrust of our formulation by taking as an example the case of the one-hole problem, viz. the IP computations. A comprehensive general formulation will be given in a forthcoming article in near future.

Although the propagator-based methods have been generally successful in the inner and outer valence ionization processes, they warrant a special innovation to handle orbital relaxation effects [16–18] for core holes. The resulting methods have rather complex structures and have not been as widely used as the more traditional variants for the inner and outer valence regions. The coupled-cluster-based linear response theories [4, 7, 10, 14] and the closely related SAC-CI approach [2, 3] also have mostly considered the inner and outer valence regions. These methods also would require considerable expansion of the operator space than is traditionally invoked to give a good account of the relaxation effects accompanying core ionization (e.g., see schemes envisaged in [19] and [20]). Special care is also needed for core IPs for other approaches [21–24]. The traditional valence-universal multi-reference coupled cluster theory (VU-MRCC) [5, 11–13], for energy differences, using the valence-universal normal ordered cluster ansatz for the wave operator, treats electron correlation effects to high accuracy but fails to take complete account of the orbital relaxation effects (vide infra, Sect. 2.3). Conversely, the valence-specific MRCC (VS-MRCC) theory [25], using separate exponential representations of the components of the wave operator acting on each model determinant, treats both the correlation and the orbital relaxation effects on the same footing, since the latter is brought out via the Thouless correction involving single excitations from the model functions [26]. The VS-MRCC theory, however, is tailored to compute state energies per se, and not energy differences. The use of the Thouless-like correction can nevertheless be exploited in energy difference calculations too, as shown by Mukhopadhyay and Mukherjee [27], by formulating a coupled-cluster theory with the ansatz for the wave operator as advocated for the valence-specific theory, but extending the scope of the formalism to encompass energy differences involving states with different numbers of electrons, as in ionization. This quasi-valence-specific MRCC theory (QVS-MRCC) has been found to successfully tackle the relaxation effects. However, this method has the technical disadvantage in that the generation of a proper spin-free form of the QVS-MRCC equations is cumbersome, since the use of multiple vacua implies in general the use of non-singlet vacuum functions. This makes the cluster amplitudes dependent on spins. As a result, they have to be represented in a spin-orbital basis. In contrast, the VU-MRCC method with a fixed closed-shell vacuum renders the spin adaptation a very simple exercise. In the VU-MRCC theory, in addition to having true n-body excitation operators of rank n, there are also rank n operators which induce only $(n-m)$-fold excitations, since they involve $m \leq n$ spectator orbitals. The various direct and exchange amplitudes for these pseudo n-body operators take account of the possible different m-fold excitations that would be present in the VS- or the QVS-MRCC theories written in the spin-orbital basis.

What is obviously needed is the flexibility in the spin adaptation of the VU-MRCC approach, but to incorporate the Thouless-like correction as permitted by the QVS-MRCC formulation [27]. A preliminary formulation towards achieving this goal was initiated by Mukhopadhyay et al. [15] some years ago, using an ansatz which takes care of the relaxation effects. In this paper, we develop a different, more general and more compact formulation, using a new ansatz for the valence portion of the wave operator, Ω_v. Our relaxation-inducing theory is a major improvement over the method proposed earlier [15], which led to the emergence of diagrams with contractions between the cluster operators in a chain-like fashion. This made the resultant MRCC equations both quite lengthy and potentially non-terminating. In our formulation, we propose a new relaxation-inducing cluster expansion which allows a *finite* power series expansion of the MRCC equations. The generation of the finite power series MRCC equations warrants a careful classification of the terms into strongly and weakly connected entities. The strongly connected entities have all the cluster operators connected to the hamiltonian vertex, by at least one line other than the spectator lines. It turns out that this ansatz is the *exact equivalent* of the QVS-MRCC formulation [27] in the context of the single-vacuum-based formulation.

The relaxation-inducing cluster expansion of the wave operator for ionized/excited states we are going to introduce in this paper makes an implicit use of the Thouless type of exponential transformation [26], but invokes a different structure of the transforming operator – *in a manifestly spin-free form* in the framework of a single vacuum. Although the theory is general with respect to the number of valence (active) electrons present in the systems, for the present we will apply the theory to the single-valence core- and valence-ionization processes, using only one active orbital to illustrate the formalism. Thus although ours is an MRCC formulation, we shall currently use it with only one reference function in the model space.

The paper is organized as follows. The main theoretical ideas leading to the relaxation-inducing transformation are summarized in Sect. 2, where a multi-determinantal generalization to Thouless parametrization using a single vacuum is discussed. The algebraic correspondence of our cluster ansatz with the multi-exponential ansatz of the QVS-MRCC theory is also discussed in the same section. In Sect. 3, we generate from the Bloch equation for the energy differences a connected set of MRCC equations for the cluster amplitudes. With our choice of Ω_v, we have a chain of contractions of the cluster operators with spectator lines. We also show here that by a careful classification of the various terms in the MRCC equations into what we call the strongly and the weakly connected entities, we can

transcribe the parent set of equations containing both the strongly and the weakly connected terms in favour of another having only strongly connected entities. The latter set has only a finite power series expansion of the cluster operators. Section 4 contains the first molecular applications of the theory for the core- and the valence-ionization processes. Section 5 contains the concluding remarks.

2 Towards a relaxation-inducing cluster ansatz

2.1 Multi-determinant generalization to Thouless parametrization: pro and contra issues

Thouless [26] showed the way to handle the orbital relaxation effects without explicitly changing the orbitals via an exponential of a one-body operator acting on a determinant whose orbitals we want to relax. According to Thouless, when the exponential of a one-body operator acts on a determinant ϕ, it results in another modified determinant ϕ', non-orthogonal to ϕ, with altered orbitals, i.e.

$$\phi' = \exp(S_1)\phi \tag{1}$$

where

$$S_1 = \sum_{p\gamma} S_\gamma^p a_p^\dagger a_\gamma \tag{2}$$

The Greek labels refer to the occupied and the Latin labels refer to the unoccupied orbitals in ϕ. Though the theorem is used for a single determinant for orbital relaxation, this theorem can be generalized in a straightforward manner to transform a combination of determinants ψ to a similar combination ψ', having altered orbitals in each determinant. The multi-determinant Thouless theorem can be described as

$$\psi' = \Omega\psi \tag{3}$$

$$\Omega = \sum_\alpha \exp(S_{1\alpha})|\phi_\alpha\rangle\langle\phi_\alpha| \tag{4}$$

where

$$\psi = \sum_\alpha \phi_\alpha C_\alpha \tag{5}$$

Using Eqs. (3)–(5), we then find the actual form for ψ':

$$\begin{aligned}\psi' &= \sum_\alpha \phi'_\alpha C_\alpha \\ &= \sum_\alpha \exp(S_{1\alpha})\phi_\alpha C_\alpha\end{aligned} \tag{6}$$

$S_{1\alpha}$ involves all possible single hole-particle excitations out of ϕ_α. We also note at this stage that if we now add the higher-rank cluster operators $S_{n\alpha}$ with $n \geq 2$, then we introduce correlation effects and this coincides with the ansatz used by Jeziorski and Monkhorst (JM) [25] of the wave operator in the VS-MRCC theory. We thus see that the orbital relaxation is a built-in feature of the JM ansatz. Unfortunately, the JM ansatz has two important limitations: (1) it is traditionally used only for obtaining the state-energies per se and not in computing energy differences as the VU-MRCC does; (2) the ansatz has a simple structure only in the spin-orbital basis – its spin adaptation turns out to be pretty non-trivial [28].

The first limitation is easily remedied [27] by formulating the QVS-MRCC theory where one first determines the cluster operator T for the closed-shell ground state:

$$H\exp(T)\phi = E_0\exp(T)\phi \tag{7}$$

where ϕ is the singlet determinant of the neutral system. We can write the Bloch equation of the energy differences in terms of the transformed hamiltonian $\bar{H}$, given by

$$\bar{H} = \exp(-T)H\exp(T) - E_0 \tag{8}$$

The Bloch equation for the energy differences can then be derived using the following ansatz for Ω:

$$\Omega = \exp(T)\Omega_{\rm v} \tag{9}$$

where $\Omega_{\rm v}$ is the valence portion of the wave operator, which brings about the extra correlation and relaxation effects:

$$\Omega_{\rm v} = \sum_\alpha \exp(S_\alpha)|\phi_\alpha\rangle\langle\phi_\alpha| \tag{10}$$

If we write the exact functions of the excited or ionized states ψ_K as

$$\psi_K = \sum_{\alpha=1,N} \exp(S_\alpha)\phi_\alpha C_{\alpha K} \tag{11}$$

then the Bloch equation for the energy differences $E - E_0 \equiv \Delta E$ can be expressed as

$$\bar{H}\sum_{\alpha=1,N}\exp(S_\alpha)\phi_\alpha C_{\alpha K} = \Delta E\sum_{\alpha=1,N}\exp(S_\alpha)\phi_\alpha C_{\alpha K}, \quad \forall\alpha, K \tag{12}$$

for an N-dimensional model space. This can be equivalently written as

$$\bar{H}\Omega_{\rm v}P = \Omega_{\rm v}\bar{H}_{\rm eff}P \tag{13}$$

$$\bar{H}_{\rm eff} = P\bar{H}\Omega_{\rm v}P \tag{14}$$

The situation regarding a spin-free formulation turns out to be much more non-trivial in this formulation. We explain the basic issue here by again taking our example case of the single ionization, but considering just one determinant $\phi_\alpha = a_\alpha\phi$. The difficulty shows up even in this case. Let us assume that ϕ_α has a vacancy in the spin orbital α with up spin. If we consider the single excitations from core orbitals to particle orbitals, then we discern that an excitation $\gamma \rightarrow p$ and the spin-reversed counterpart $\bar{\gamma} \rightarrow \bar{p}$ will have different excitation amplitudes in the exact function, since they see an exchange potential contributed by the spin orbital α with up spin. As a result, we will not be able to express the amplitudes of the single excitation operators in spin-free form using the spin-free generator of the unitary group. We need two such operators, depending on spin. The situation is the same for higher-body excitations. Herein lies the principal difficulty with the JM representation, even

when the formulation is extended to handle the energy differences [27].

On the other hand, using the closed-shell determinant ϕ as the vacuum, we can get around the difficulty by invoking the spectator orbital α for the hole. So, instead of a one-body operator for single excitation in a spin-orbital basis, we use a *two-body* operator to induce the single excitation, where the other orbital scatters the hole vacancy in α to itself. Since this can be done in both the direct and the exchange modes, we will have two different amplitudes and this resolves both the spin dependence of the cluster operators and the freedom of retaining two amplitudes of the two single excitations, viz. for up and down spins. For the higher-body operators, the situation is entirely analogous. This procedure of spin adaptation is routinely used in VU-MRCC formulations (e.g. see [5]), and has also been used by us previously [15]. We want to exploit this simplification also in the framework of a relaxation-inducing formalism. This aspect is further discussed below.

2.2 A spin-free representation of the excitation operators in VU-MRCC theory

Let us assume that all the excitation operators are independent of spin. Let us introduce two single excitation two-body amplitudes $s^{p\alpha}_{\gamma\alpha}$ and $s^{p\alpha}_{\alpha\gamma}$. The former scatters the spectator orbital α in direct mode, while the latter scatters it in the exchange mode. It can be shown by straightforward verification that the action of the two-body single excitation operators involving excitations $\gamma \rightarrow p$ and $\bar{\gamma} \rightarrow \bar{p}$ can be expressed in terms of two distinct amplitudes. Thus, $s^{p\alpha}_{\gamma\alpha}\{a^\dagger_p a^\dagger_\alpha a_\alpha a_\gamma\} + s^{p\alpha}_{\alpha\gamma}\{a^\dagger_p a^\dagger_\alpha a_\gamma a_\alpha\}$ on ϕ_α will generate $[s^{p\alpha}_{\gamma\alpha} - s^{p\alpha}_{\alpha\gamma}]\phi_\alpha$,while $s^{\bar{p}\alpha}_{\bar{\gamma}\alpha}\{a^\dagger_{\bar{p}} a^\dagger_\alpha a_\alpha a_{\bar{\gamma}}\}$ will generate just $s^{\bar{p}\alpha}_{\bar{\gamma}\alpha}\phi_\alpha$. These two coefficients accompanying ϕ_α are thus effectively different. We should note here that we cannot have an exchange excitation amplitude for $\bar{\gamma} \rightarrow \bar{p}$ owing to our assumption of spin independence of the excitation amplitudes.

From the above discussions, it may appear that there exists a simple recipe by which we can transcribe the JM ansatz in a spin-free form by way of invoking spectator orbitals, and using formalisms akin to a QVS-MRCC theory. This unfortunately is not the case. The normal ordering ansatz for the wave operator traditionally used in the VU-MRCC theory does not allow *full exponential representation* of the relaxation-inducing terms. This aspect was recognized and discussed by Mukhopadhyay et al. [15] earlier, who formulated the first relaxation-inducing ansatz. To keep the continuity, we briefly discuss the limitation of the normal ordered ansatz here, taking again as an example the singly ionized state ϕ_α. It is enough that we consider the action of the wave operator on just the function ϕ_α.

The normal ordered ansatz for Ω_v will have the single excitation operators of the types $s^{p\alpha}_{\gamma\alpha}\{a^\dagger_p a^\dagger_\alpha a_\alpha a_\gamma\}$ and $s^{p\alpha}_{\alpha\gamma}\{a^\dagger_p a^\dagger_\alpha a_\gamma a_\alpha\}$, etc., appearing in the exponent of a normal ordered exponential. Each of these operators has one hole destruction operator for the orbital α. We want these operators to introduce multiple single excitations on ϕ_α in a way exactly analogous to what $\exp(S_\alpha)$ would have done in the JM ansatz in Eq. (6). The normal ordering ansatz has many advantages, but giving the full exponential expansion involving the relaxation terms is not one of them. Since no S operators can be contracted among themselves in a normal ordered exponential, the linear term of the normal ordered expansion already has one destruction operator for the hole α, the second power would have two hole destruction operators for the hole, and so on. Moreover, ϕ_α has only one hole, so that the action of the second and higher powers of S would give trivially vanishing contributions by their actions on ϕ_α. As a result, we would get just the linear term corresponding to the single excitation from ϕ_α, and not products of single excitations needed for the full orbital relaxation, as can be easily done with the JM ansatz. In the general n-valence problems, the normal ordering will cause the expansion of the normal ordered exponential to terminate at the nth power. What is obviously needed is the requirement that we want the operators in Ω_v with the spectators to contract among themselves, and to generate exactly the same combinatoric factors as an exponential would have done. Mukhopadhyay et al. [15] introduced one such ansatz in their attempt to account for the relaxation effects. However, the combinatoric factors in the various terms in the contracted operators were not conducive to generate a compact expression of the working equations. As a result, their equations were somewhat unwieldy, containing a non-terminating chain of terms with S-S contactions where many S operators were not joined to the hamiltonian vertex at all. We shall introduce a new relaxation-inducing ansatz, which facilitates a reduction of the MRCC equations to compact expressions for the working equations involving only a finite power series expansion of the cluster amplitudes. We will discuss these aspects in Sect. 3. Presently we discuss the theoretical considerations motivating such a choice.

2.3 Towards the relaxation-inducing $E_r(S)$ ansatz

As emphasized earlier, we want our relaxation-inducing ansatz to have the same physical content as a multi-exponential representation of the JM ansatz as used in the QVS-MRCC theory, but which will work within the framework of a single closed vacuum, as in the VU-MRCC theory. The ansatz will also be general in the sense that it would treat both the differential correlation and orbital relaxation on the same footing. We specialize to the singly ionized state only in this paper.

Let us classify the various operators that enter Ω_v in terms of the physical effects they induce. For the concreteness of presentation, we confine ourselves to, at most, two-body operators, though this can be easily generalized for higher-body terms. All the S operators are written in normal order with respect to the closed-shell ground state ϕ. There is only one kind of one-body operator. This excites a hole in an orbital which contains an electron, and fills in the hole present in the model function ϕ_α. Obviously it contains no spectator line, but it does involve α. We call this operator as S_1. The two-

body operators require careful classification. There are single excitation two-body operators which have spectators – either as direct spectator scattering or in an exchange mode. They induce orbital relaxations, and we will call these operators as S_{2r}. We want the operators S_1 and S_{2r} to be present in Ω_v in all powers, with combinatoric factors as in an exponential expansion. The rest of the two-body operators, to be henceforth called as S_{2c}, are genuine double excitations which introduce correlations appropriate to ionized states. We consider the single excitations first, which bring in the orbital relaxations. As emphasized earlier, the normal ordered exponential $\exp(S)$, acting on ϕ_α, will terminate the series after the first power. We replace this ansatz by another which allows contractions between the single excitations. Thus typical terms in our new ansatz for Ω_v should allow contractions of the types shown in Fig. 1. Figure 1a shows contractions between two two-body operators S_{2r} with α as the spectator orbital. For simplicity, only the direct types of spectator scatterings are shown, though in actual implementation both direct and the exchange spectator operators would be allowed to contract. Figure 1b shows a similar contraction, which involves the single excitation from S_1 with a two-body S_{2r}. Our new ansatz for Ω_v must allow chains of such contractions to be done to all powers. This then would entail the same types of terms as an exponential of one-body excitations would have allowed on ϕ_α in a JM ansatz, as in Eq. (6).

We now look carefully at the combinatorial factors that should accompany these chains of contractions. To discern these, we formally try to relate our ansatz using ϕ as the vacuum to the corresponding expression where ϕ_α is taken as the vacuum. In other words, we want to transcribe the power series expansion of S in Ω_v, written in normal order with respect to ϕ as the vacuum to one which is written with respect to ϕ_α as the vacuum. In the latter form, we want to get the exponential ansatz of JM. Thus we want to associate those factors in our contracted terms which, on transcription, will give the factors appearing in an exponential. Such a transcription changes the role of α from that of a hole in ϕ to a particle when ϕ_α is taken as the vacuum. The Wick's theorem reordering the terms with the vacuum taken as ϕ_α would generate two terms. One is the operator in normal order with respect to ϕ_α, and the other with the orbital α contracted. The first term has a destruction operator for the orbital α (remember that α is a particle in ϕ_α now!), whose action on ϕ_α would be zero. So, the non-trivial operator after the new normal ordering would be the second term, where the orbital α is contracted. This is however now a *one-body* operator. These one-body operators with α contracted are depicted in Fig. 2. For the term in Fig. 1a, we would have the non-vanishing term as a product of two such one-body operators as shown in Fig. 2a. They are, as expected, the second power of two one-body operators. They can appear in two different ways in the exponential representation in the JM ansatz, so that the exponential expansion attaches a factor $1/2!$ corresponding to the number of ways we can arrange the two vertices. Clearly, it is possible to have the contractions of the two two-body operators in Fig.1a also in two different orderings. Thus in our new ansatz, if we associate the factor $1/2!$, corresponding to the two ways the two operators in the two arrangements can be contracted, then the correct combinatorial factor will emerge when we attempt to rewrite our expansion of the powers of S written with respect to ϕ as vacuum to another with ϕ_α as vacuum. The situation is tricky and different for the term of Fig. 1b. In this case, we can join the one-body operator only from the left. A transcription of this term to another in normal order with respect to ϕ_α would generate the term of Fig. 2b. In the exponential representation it should appear in two ways: (1) the order in which it appears and (2) another in which they appear in the reversed order. We now realize that the second term cannot appear from our ansatz, since the contraction in the reversed order is not possible in Fig. 1b. However, in the exponential representation in the JM ansatz, the two operators shown in Fig. 2b commute, so we may represent the two terms as just one, appearing in the way they do in Fig. 2b, but with a factor 1 rather than the customary $1/2!$. This resolves our problem: we should attach a factor 1 to our Fig. 1b, corresponding to the number of ways we can join the two vertices. Thus our combinatorial factors in the power series representation of Ω_v are not as in an exponential: they are rather equal to the inverse of the number of ways the vertices can be contracted among themselves in the various distinct manners. If the two vertices are equivalent, then there is one distinct mode of joining, and this should be kept in mind. This analysis is quite general.

If we now include the correlation terms on top of the single excitations, we would have to allow the spectator line going to the left of a relaxation vertex to contract with any line in an operator S_c carrying the labels of the spectator. Thus, we allow contractions like the ones we have in Fig. 1a, but with the first vertex now an S_{2c}, with a line labelled other than α as it emerges to the left. Such

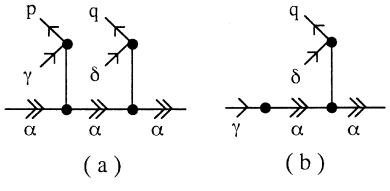

Fig. 1a, b. Connections allowed in the new ansatz $E_r(S)$ for Ω_v

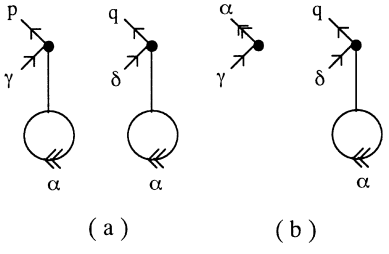

Fig. 2a,b. Transcription of the terms of Fig. 1 drawn using ϕ as the vacuum to a set using ϕ_α as the vacuum

vertices would thus be genuine double excitations S_{2c}. Since the line coming out on the left would not have the label α on it, we would not be able to contract the two vertices in the reverse order. As a result, we would attach a factor 1 for such contractions.

For more than one model functions, the situation is essentially the same. We would then have S operators with one active line entering from left of each vertex which are labelled by the active lines α, β, etc. We allow the vertices with same spectator labels to contract among themselves, and also allow those to contract from the left which have to their right a line with the same label. It is straightforward to verify that it will generate $\sum_\alpha \exp(S_\alpha)\phi_\alpha$ if we transcribe our power series for each operator with the spectator orbital labelled by α in terms of normal ordered terms taking the corresponding ϕ_α as the vacuum.

Thus we invoke the following ansatz for the relaxation inducing cluster expansion of Ω_v:

$$\Omega_v = E_r(S) \tag{15}$$

$$S = \sum_{\alpha i} S_{\alpha i} \tag{16}$$

$$E_r(S) = 1 + \sum_\alpha \left[\sum_i S_{\alpha i} + \sum_{ij} 1/f_{ij} \{\overline{S_{\alpha i} S_{\alpha j}}\} + \sum_{ijk} 1/f_{ijk} \{\overline{S_{\alpha i} S_{\alpha j} S_{\alpha k}}\} + \sum_{ijk} 1/f_{ij} \{\overline{S_{\alpha i} S_{\alpha j}} S_{\alpha k}\} \right] + \cdots \tag{17}$$

where $S_{\alpha i}$ denotes a specific operator with the spectator α. Each term in the expansion of E_r in Eq. (17) above is in normal order with respect to ϕ. The factors f_{ij}, f_{ijk}, etc., are the number of ways the associated S operators can be contracted among themselves. $E_r(S)$ can be equivalently written as a normal ordered exponential involving another cluster operator σ:

$$E_r(S) = \{\exp(\sigma)\} \tag{18}$$

$$\sigma = \sum_\alpha \left[\sum_i S_{\alpha i} + \sum_{ij} 1/f_{ij} \{\overline{S_{\alpha i} S_{\alpha j}}\} + \sum_{ijk} 1/f_{ijk} \{\overline{S_{\alpha i} S_{\alpha j} S_{\alpha k}}\} \right] + \cdots \tag{19}$$

We note here that σ is a connected operator. σ in general contains a non-terminating chain of S-S contractions in it. The only terms which terminate are those where there is a contraction from left of an S vertex with no spectator orbital, as in Fig. 1b. As a result, a straightforward use of Ω_v in terms of σ in Bloch equation will generate a non-terminating series in S. In the next section we will discuss the MRCC equations obtained from our ansatz for Ω_v. Written in terms of σ, they involve in general a chain of S-S contractions. By classifying the various terms appropriately, we would eventually generate another set where only a finite power series of S appears.

3 The emergence of Bloch equation using the $E_r(S)$ cluster ansatz

3.1 Generation of MRCC equations with non-terminating chain of terms

Adducing the same arguments as were invoked in the traditional VU-MRCC theory [5, 8], with normal ordered Ω_v [13], we find the energy and the amplitude finding equations for S from the ansatz for Ω_v in Eq. (16). Using the alternative representation, Eq. (18), for Ω_v, in the Bloch equation, Eq. (14), we have

$$\{\overline{\bar{H}\exp(\sigma)}\}_{ex} P = \{\overline{\exp(\sigma)\bar{H}_{eff}}\}_{ex} P \tag{20}$$

which are the set of equations for S. $\bar{H}_{eff}$ is given by

$$\bar{H}_{eff} = \{\overline{\bar{H}\exp(\sigma)}\}_{cl} \tag{21}$$

where "ex" and "cl" denote the excitation and the closed parts of an operator [13]. For the ionization problem, the model space P is spanned by the singly ionized functions ϕ_α.

Since we consider here only one active orbital, the relevant terms in the equations above are the ones with only one active line entering from the right for each composite. Calling the quantities $\{\overline{\bar{H}\exp(\sigma)}\}$ and $\{\overline{\exp(\sigma)\bar{H}_{eff}}\}$ as X and Y, respectively, the relevant portion of the Bloch equation can be written as

$$X^{(1)}_{ex} = Y^{(1)}_{ex} \tag{22}$$

where the superscript indicates the valence rank [13] of the composites. The effective hamiltonian matrix for computing the energy differences is obtained as

$$\bar{H}_{eff} = PXP = X^{(1)}_{cl} \tag{23}$$

Since both the operators are connected, and involve the connected entity σ, the equations are connected and our theory is size extensive. X and Y are, however, defined with respect to the composites of S in σ, and are thus non-terminating series in general of S. In contrast, if we had used the JM ansatz, as in the earlier QVS-MRCC formalism [27] for the same problem, we would have obtained the following equations for S and $\bar{H}_{eff}$:

$$\{\overline{\bar{H}\exp(S_\alpha)}\}_{\alpha(ex)} |\phi_\alpha\rangle = \sum_{\beta\neq\alpha} \{\exp(-S_\alpha)\exp(S_\beta)\}_{(ex)} |\phi_\beta\rangle [\bar{H}_{eff}]_{\beta\alpha} \tag{24}$$

$$[\bar{H}_{eff}]_{\beta\alpha} = \langle\phi_\beta| \{\overline{\bar{H}\exp(S_\alpha)}\}_\alpha |\phi_\alpha\rangle \tag{25}$$

which have a *totally different* algebraic structure. The notation $\{\cdots\}_\alpha$ denotes an operator in normal order with respect to ϕ_α. The entity on the left side of the equation contains a connected term where all S_α operators are connected to $\bar{H}$. This then has a finite power series structure since $\bar{H}$ has finite number of creation/annihilation operators in it. It has no chain-like non-terminating series. The term on the right side of the equation can in principle be non-terminating, but in practice for a truncation in the rank of S it would still be

terminating, but this has contractions among the S_α and S_β operators. Since our ansatz for Ω_v is algebraically analogous to the JM ansatz, we should be able to transcribe our equations to a form similar to Eqs. (24) and (25) above, leading to a much more compact structure of our working equations.

Achieving this is the other key innovative part of our formalism. Our intention is to transcribe these equations into another set where each X-like term has all the cluster operators connected to $\bar{H}$, thus resulting in a finite power series expansion of the cluster operators for this entity in the transcribed MRCC equations. For the Y-like operators containing $\bar{H}_{\text{eff}}$ we may have terms with a chain-like contracted series, as in the right side of Eq. (24). It turns out that this transformation demands the algebraic structure of the wave operator to be as invoked by us in this paper – the earlier ansatz proposed by Mukhopadhyay et al. [15] does not allow the sought-after transcription of the MRCC equations.

The transcription is best followed by classifying the diagrams of X and Y into strongly and weakly connected terms. A strongly connected term is one in which all the cluster operators are connected to $\bar{H}$ by at least one line other than just the spectator lines. They may, in addition, have connections among themselves. A weakly connected term, by contrast, is one in which either some cluster operators are connected in a chain-like fashion to other cluster operators but these are not directly connected to $\bar{H}$, or in which some S operators are joined to $\bar{H}$ by just the spectator lines, or both. We want to eliminate the weakly connected terms in favour of equivalent strongly connected terms, by proceeding hierarchically from the MRCC equations of lower particle ranks to those with higher particle ranks. The resulting equations are much more compact than the parent ones. In the general theory with several functions in the model space, we ultimately obtain a set of equations with only strongly connected terms of the X type, but there are generally weakly connected terms in the portion involving $\bar{H}_{\text{eff}}$. This feature of our MRCC equations is exactly analogous to the one in the multi-vacua formulation, viz. in Eq. (24). The left side of Eq. (24) is a connected series, while the right side involves commutators of S_α with S_β, and thus generally have S terms connected to other S, but not to $\bar{H}_{\text{eff}}$.

We will again illustrate the relevant manipulations using the one-valence problem as an example. Furthermore, in the case of a one-valence problem with just one model space function, the case we are explicitly considering in this paper, the transcribed Bloch equation does not even contain any weakly connected terms at all. This is again exactly analogous to what is expected from Eq. (24): when there is only one model function ϕ_α, the right side of Eq. (24) is zero.

3.2 Transcription to a strongly connected series

In what follows, it will be convenient to express the Bloch equation in terms of the two strongly connected quantities Z and W. Z is a connected composite of the external type where all the S operators are strongly connected to $\bar{H}$ from the right. W is a closed operator of similar structure. Any arbitrary diagram of X and Y variety can then be written as either a Z or a W connected weakly to various other S operators. In the chain of S operators in a given diagram, some are directly connected to $\bar{H}$. The rest are weakly connected. The S vertices which have spectator lines can be connected anywhere in the chain if the chain has spectator orbitals at both the ends. Such a chain is of the type of Fig. 1a. If the left-most weakly connected vertex has no spectator line to the left, then all the other S operators with spectator lines can be connected anywhere on the right of this left-most S. All these various terms are topologically equivalent, and give the same contribution. We keep in this case just one among all these weakly connected diagrams, and multiply it by the number of ways the S operators could have been placed in the chain. A good point of our formalism is that these topological factors are just the weights f_{ij} introduced in the definition of $E_r(S)$, and cancel the inverses stemming from $E_r(S)$. To uniquely specify which among these diagrams we wish to keep, we use the following convention: if, in the chain, there are spectator lines at both ends, then we choose only that diagram which has all the S operators with spectators placed at the extreme left end of the chain. If the chain has no spectator lines to the left of the chain, as in Fig. 1b, then we keep them *to the extreme right*. We illustrate this aspect diagrammatically by showing two topologically equivalent terms where there are spectator lines at both the ends in the set of weakly connected diagrams. Figure 3 shows two such equivalent diagrams that can be generated. We keep only the one where the weakly connected S is at the extreme *left* end of the spectator line. The topological weight 2, corresponding to the number of ways the two S operators can be joined, exactly cancels the factor $1/2$ coming from $E_r(S)$.

The resultant composite X for the one-valence problem is always of the following four forms: Z connected weakly to S_r, W connected weakly to S_r, S_r connected weakly to Z and S_r connected weakly to W. Similarly, Y can always be represented as S operators connected weakly with a W, and S operators connected

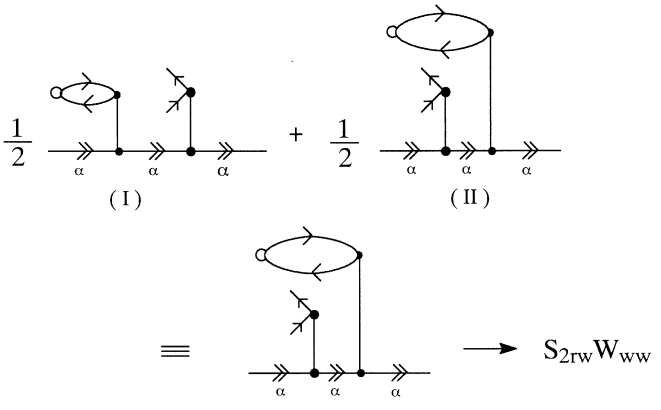

Fig. 3. Topologically equivalent diagrams and the convention of choosing one of them multiplied by a topological weight illustrated

strongly with a W. In order to represent these various terms, we introduce a subscript in the operators which indicates the type of linking: strong or weak. Every S operator has at least one active line to its right. If it has no such active line to its left with the same label, the particular S has no spectator lines, and it is enough if we indicate its linking to a Z or W by a subscript s or w indicating its strong or weak linking. Obviously, these types of S operators are either S_1 or the correlation operators S_c. Those with the spectators would generally need two subscripts to indicate its connection with other operators both to its left and to its right. This is true for all the S_r operators. The composite Z may or may not have spectator orbitals to its left. If it has this, Z is of the shape of the relaxation operators S_r, henceforth denoted as Z_r, and would need two subscripts. If it does not have a spectator line to its left, it is either of the shape of S_1, or of the S_c of the correlation type. We use the symbols Z_s and Z_w to indicate whether the active line from the left is attached directly to $\bar{H}$ or to an S, respectively. For the example of the one-valence problem, W is just a one-body closed operator.

Construction of the working equations may be made easier by working in terms of diagrams and classifying them into various blocks. We shall represent the Z and W operators as diamond shaped vertices. The lines which are directly connected to the $\bar{H}$ vertex are shown as joined to the middle portion of the diamond or a large circle, those joined to other S vertices (i.e. weak connection) are shown as connected to the diamond from below. As examples of the diagrams constituting the blocks, we show in Fig. 4 some typical diagrams of W and Z. The spin adaptation in these diagrams is quite trivial: we merely multiply each diagram by a factor of 2 for each loop.

With these notations, the equations for the one-body S can be symbolically written as

$$Z_{1s} + Z_{1w} + S_{1w}W_{ww} - S_{1s}W_{ss} - S_{1s}W_{sw} - S_{1w}W_{ww} = 0 \tag{26}$$

The third term should carefully be noted. It stems from an X where S_1 can connect weakly to an S operator in X. By our convention, we have kept the weakly connected S to the left-most part of the chain. We have already encountered a typical diagram of this structure in Fig. 3(II). This term exactly cancels a similar folded term stemming from Y, viz. the last term. Cancelling these two terms explicitly, we have

$$Z_{1s} + Z_{1w} - S_{1s}W_{ss} - S_{1s}W_{sw} = 0 \tag{27}$$

The equations for S_{2r} can be similarly written as

$$\begin{aligned} Z_{2rss} + Z_{2rsw} + Z_{2rww} + S_{2rw}W_{ww} + W_{sw}S_{2rw} \\ - S_{2rs}W_{ss} - S_{2rs}W_{sw} - S_{2rw}W_{ww} = 0 \end{aligned} \tag{28}$$

In these equations, the fourth and the last term cancel, so that we have the simplified equations

$$Z_{2rss} + Z_{2rsw} + Z_{2rww} = 0 \tag{29}$$

The equation for S_c is given by

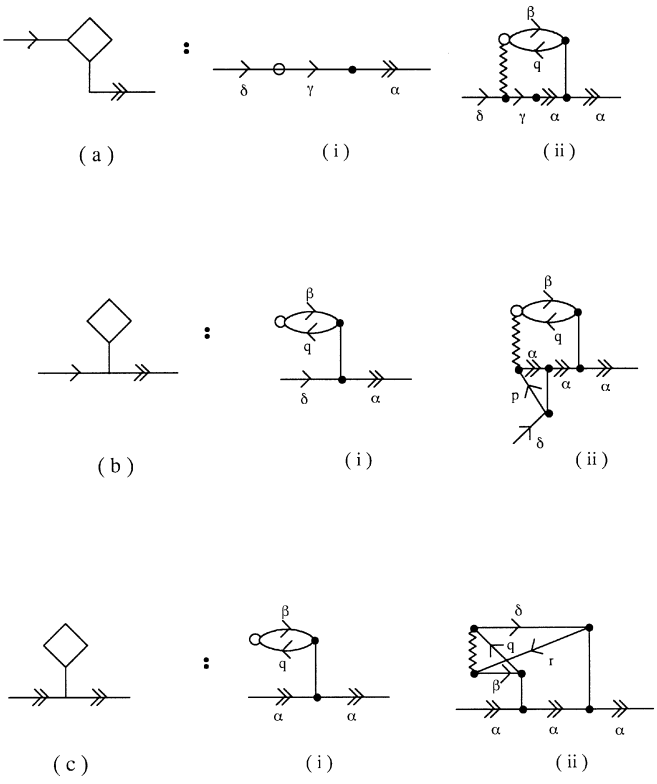

Fig. 4a–c. Typical diagrams entering the one-body blocks are shown: **a** shows the block of Z_{1sw}; **b** shows the block of Z_{1ww}; **c** shows the block of W_{ww}

$$\begin{aligned} Z_{2s} + Z_{2w} + (Z_{1s} + Z_{1w})S_{2rw} + S_{1w}Z_{2rww} \\ + S_{2cw}W_{ww} + S_{1w}S_{2rww}W_{ww} - S_{2cs}W_{ss} \\ - S_{2cs}W_{sw} - S_{1w}S_{2rws}W_{ss} - S_{1w}S_{2rws}W_{sw} \\ - S_{2cw}W_{ww} - S_{1w}S_{2rww}W_{ww} = 0 \end{aligned} \tag{30}$$

The fifth and the eleventh and also the sixth and the last terms cancel among themselves. We are still left with weakly connected terms after this cancellation. The equation for S_c now requires careful substitution from Eqs. (27) and (29) generated above to obtain a strongly connected expression. Substituting the expression of $Z_s + Z_w$ in the above equation from those in Eq. (27), the weakly connected terms all cancel and we get a strongly connected series. The resultant equation reads as

$$Z_{2s} + Z_{2w} - S_{1s}Z_{2rss} - S_{1s}Z_{2rsw} - S_{2cs}W_{ss} - S_{2cs}W_{sw} = 0 \tag{31}$$

Figure 5–7 display the equations for S operators in terms of the blocks. Figure 5(I) has an active line attached to $\bar{H}$, while Fig. 5(II) and Fig. 5(III) have active lines connected to other S operators. Similarly, Fig. 5(I′) has the active line attached to $\bar{H}$, while the line emerges from an S vertex in Fig. 5(II′).

We should mention here that we would have a similar set of equations for the exchange part of S_{2r}. Equation (27), the direct and exchange types of Eq. (29) and Eq. (31), is the principal working equation of our MRCC

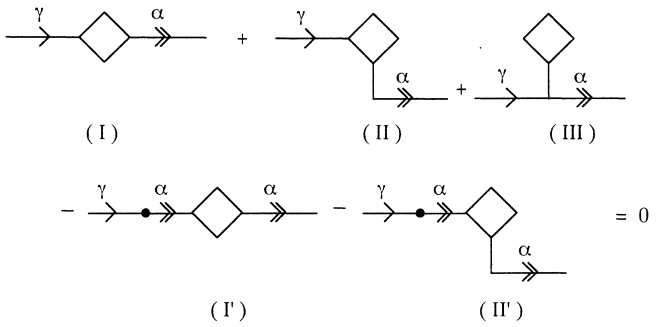

Fig. 5. Block diagrams appearing in the equation for S_1

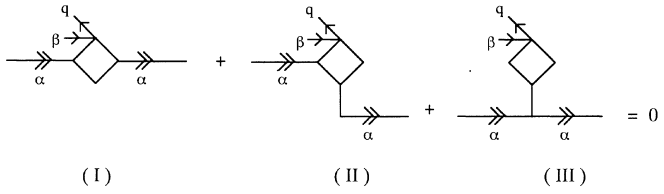

Fig. 6. Block diagrams appearing in the equation for S_{2r}

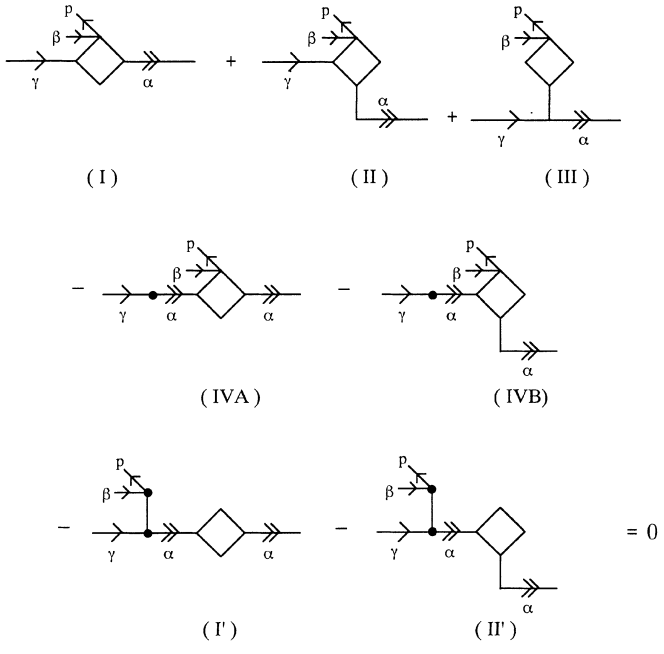

Fig. 7. Block diagrams appearing in the equation for S_{2c}

theory. Sine each block described above contains an $\bar{H}$, and several S-vertices, the MRCC equations are coupled simultaneous equations in the amplitudes of S.

The above reduction procedure generating the strongly connected terms from the weakly connected chain of expressions is quite general, and will be shown in detail in our future communications.

In our pilot applications, we have not included a set of terms which are cubic in power in the cluster amplitudes. A more detailed and complete applications of our formalism will be published in near future.

4 Computational implementations

We have applied our formalism to compute the IPs for both the core and the inner- and the outer-valence ionizations for HF and H_2O at the equilibrium geometry of the molecules. We have utilized the correlation consistent basis [29–31] in our calculations. To assess the importance of orbital relaxations, we have also computed the IPs with the standard MRCC theory using normal ordered cluster ansatz $\{\exp(S)\}$ [5] to compare with those obtained from the $E_r(S)$ method. As we have emphasized repeatedly in this paper, the $\{\exp(S)\}$ ansatz can take care of the orbital relaxation effects in only a very incomplete manner. The performance of the two methods is assessed by comparing the results with experimental IP values. Since in the present formulation we have used only one model function ϕ_α, W is just a number – rather than a matrix – and is the IP for the problem. For computing the various IPs involving the core or an inner- or an outer-valence orbital, we have taken each such orbital in turn as the active orbital α.

4.1 HF molecule

For HF, we have used the correlation-consistent basis with the contraction scheme, (4S1P)//[3SIP] for the hydrogen atom and (9S5P1D)//[5S3P1D] for the fluorine atom [29, 31]. The Hartree-Fock orbitals of the neutral HF at the equilibrium bond length of 1.7328 a.u. are used in our calculation. An excellent estimate of the extent of just the orbital relaxation for the core can be obtained by doing another restricted Hartree-Fock calculation for the core- ionized state. The ΔSCF value for core-IP is thus calculated as 693.9042 eV. A comparison with the experimental results (694.0 eV) (as quoted in [15]) indicates that orbital relaxation is the dominant effect for the core IP of HF.

The results are displayed in Table 1. The IP values from the $E_r(S)$ theory are uniformly closer to the experimental values as compared to those from the $\{\exp(S)\}$ formalism. The improvement is particularly dramatic for the core IP, although there is also a substantial improvement for the IPs computed for the valence region. Comparison between the {exp(S)} and $E_r(S)$ results indicates that the direction of changes for the core IP and the valence IPs are opposite, although both for the core IP and the valence IPs the changes brought about by the $E_r(S)$ method are always in the correct direction.

4.2 H_2O molecule

The H_2O molecule is isoelectronic with HF. We have again used the correlation-consistent basis, with the contraction scheme (5S1P)//[3S1P] for the hydrogen atom and (11S6P1D)//[5S4P1D] for the oxygen atom [30, 31]. The bond length of the O—H bond in the equilibrium geometry of H_2O of 1.80885 a.u. and the ∠HOH of 104.524° have been used for our calculations.

Table 1. Ionization potentials of HF by $E_r(S)$ and $\{\exp(S)\}$ methods

Orbital	$\{\exp(S)\}$ (eV)	$E_r(S)$ (eV)	Expt. (eV)	Koopmans' value (eV)	Ref.
1π	15.5342	15.7730	16.05	17.4381	[32]
			16.19		[33]
3σ	19.5745	19.7747	19.83	20.6624	[32]
			19.90		[33]
1σ	694.9042	694.0794	694.0	715.1606	[15]

Table 2. Ionization potentials of H_2O by $E_r(S)$ and $\{\exp(S)\}$ methods

Orbital	$\{\exp(S)\}$ (eV)	$E_r(S)$ (eV)	Expt. (eV)	Koopmans' value (eV)	Ref.
$1b_1$	12.0657	12.2980	12.61	13.6490	[34]
$3a_1$	13.9713	14.2020	14.73	15.3051	[34]
$1b_2$	18.7186	18.8818	18.55	19.3978	[34]
$1a_1$	540.5315	539.6616	539.7	559.3706	[21]

The ΔSCF value for the core IP is 539.0250 eV, which – compared to the experimental core IP of 539.7 eV – implies that this ionization also is dominated by relaxation. The results of our calculations are displayed in Table 2. The trends observed are again very similar to those observed for HF. There is again a dramatic improvement of the core IP as predicted by the $E_r(S)$ method as compared to that from the $\{\exp(S)\}$ method. Again the changes are in the opposite direction for the valence IPs compared to that for the core IP. However, the changes always bring in better correspondence with the experimental values [21, 34].

We have thus demonstrated that our pilot numerical applications illustrate the efficacy of the $E_r(S)$ method to tackle both the strong orbital relaxation and the differential correlation effects with equal facility. The improvement in the prediction of the core IP is particularly impressive, which is dominated by orbital relaxation.

5 Summarizing remarks

We have presented in this paper an MRCC formulation for energy differences which can treat the orbital relaxation effects to all orders. This is accomplished by invoking a new cluster ansatz of the valence portion of the wave operator Ω_v. Unlike in the traditional normal-ordered exponential representation of Ω_v, our new relaxation-inducing ansatz, represented symbolically as $E_r(S)$, allows contraction between the spectator lines. It also treats correlations systematically to the same degree of sophistication, which calls for certain other contractions to be allowed as well. By a detailed theoretical analysis, taking as an example the case of one-hole model spaces (the IP problem), we demonstrate that our ansatz incorporates in a manifestly spin-free form the orbital relaxation to all orders. The traditional Thouless-type of exponential transformation via one-body excitations can induce the same effect, as is done in the valence-specific or the quasi-valence-specific MRCC formalisms, but they have to be done in the spin-orbital form, making the spin adaptation a rather involved problem. In contrast, we use a spin-free representation of the cluster operators right from the start, but use spectator orbitals to distinguish the various spin possibilities. The combinatoric factors entering the contracted power series in $E_r(S)$ are chosen in such a way that they correspond to what we would have obtained had we used a Thouless-like transformation to induce the orbital relaxation. Our working equations generally have only finite powers of the cluster operators S, resulting in a very compact formulation of the relaxation problem. Pilot numerical applications for the IP computations of HF and H_2O in the core, the inner valence and the outer valence regions show very good performance of the method vis-a-vis those obtained using the traditional normal ordered ansatz for Ω_v. The improvement in the core IP value is particularly impressive, although an overall improvement is observed in the valence regions as well.

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