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Multireference self-consistent size-extensive state-selective configuration interaction

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In this work, we propose a state-specific self-consistent “dressing” of the multireference configuration interaction (MRCI) space to include all single- and double-substituted determinants for the most important reference configurations. The aim of the method is to provide a size-extensive description of the dynamic electron correlation effects for states which mandate a multideterminantal reference wave function. Such states can represent electronic excited states or ground states of the molecular systems which are significantly deformed from their equilibrium structures. The proposed approach follows the concept introduced in our recently proposed quasilinear ansatz for the state-selective multireference coupled-cluster method. The purpose of the dressing procedure is to eliminate the contributions which introduce size-extensivity violating terms in the MRCI approach. © 1996 American Institute of Physics. [S0021-9606(96)03634-3]

I. INTRODUCTION

The coupled cluster (CC) method has emerged in recent years as one of the most accurate approaches to study the electronic structure of atoms and molecules. Single reference coupled cluster (SRCC) method^{1–3} has been largely successful in providing accurate values of energy^{4–7} and molecular properties^{8–18} for the nondegenerate ground states of closed shell systems as well as of high-spin open-shell systems. In such cases, the zeroth order approximation to the exact wave function can be satisfactorily described by a single determinant, which is usually the restricted Hartree–Fock (RHF) function. However, problems that are of chemical interest often correspond to more complicated situations where a few leading configurations of the full configuration interaction (FCI) space contribute almost equally to the wave function of the state of interest. (It is important to realize that a configuration composition of a state is dependent of the particular choice of the molecular orbital basis and a state which is significantly “multiconfigurational” in one basis may appear to be much less so in other basis.) The proper way to deal with such open-shell/quasidegenerate situations is to include the dominant configurations in the model/reference space and generate the exact wave function by applying a suitable wave operator on this reference space. The genuine multireference CC methods like Fock^{19–21} and Hilbert space^{22,23} versions follow such a direction and eventually arrive at an eigenvalue equation involving an effective Hamiltonian defined through the Bloch equation.

Another class of formalisms focuses on one given state at a time and introduces multireference character of the zeroth order wave function through suitable modifications in the SRCC ansatz. These are called the state-selective (SS) theories.^{24–31} The state-selective multireference coupled cluster theory (SSMRCC) of Oliphant and Adamowicz³² rep-

resents such an exercise and attempts to provide an efficient, reasonably accurate approximation to SRCC with sufficient flexibility to handle open-shell phenomena. In this method,^{32–37} the exponential cluster operator of SRCC is partitioned into internal and external parts such that the former acts on a suitably chosen single-determinant formal reference to generate a multideterminantal model space and the latter acts on this model space to generate the exact function. Both operators are exponential series of relevant cluster operators. Another SSMRCC ansatz which we recently proposed³⁸ to handle better quasidegenerate situations arising in excited states, where the cluster structure of the electron correlation effect is expected to be different from the quasidegeneracy resulting from stretching chemical bonds, has the internal part linearized but the external part still retains the exponential form. Such linearization makes the computation of the dominant internal amplitudes simpler. This point has been addressed by various authors in related ansätze before.^{25,27}

In certain cases the use of the partially linearized ansatz can be a preferred approach. One of the advantages in using this approach in size-extensive representation of the wave function, rather than a fully exponential one, is to avoid any particular assumption regarding the cluster structure through the exponentiated excitation operator. However, if a linearized ansatz is used, one needs to either consider all the configurations which can be constructed with the use of the active orbitals (the full CI expansion) or use some other means, such as size-extensive corrections to the Hamiltonian matrix in order to obtain a fully size-extensive theory. In the recently proposed method termed [(SC)²CI],^{39,40} the size extensivity was achieved through a self-consistent dressing of the diagonal elements of the CI matrix. Such an approach, which proceeds through the construction of an effective Hamiltonian matrix by including contributions from higher excitations in the diagonal element, offers some potential advantages over the conventional coupled-cluster approach.

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One such advantage is reducing the nonlinearity of the equations for the configuration amplitudes; another being that the method offers a scheme which can be easily implemented within the conventional CI method and can provide size-consistent results not only for the ground state at the equilibrium geometry but also for structures significantly distorted from the equilibrium as well as for excited states. Although, for some excited states, which are well described by single excitations from the Hartree–Fock wave function, the equation-of-motion (EOM) method based on the single-determinant coupled-cluster approach, provides very good results,⁴¹ there are states, particularly those with considerably different electronic configuration than the ground state, where a different approach is necessary. Dealing with those states requires that the effective Hamiltonian method is extended beyond the single reference case allowing for several determinants to significantly contribute to the wave function of the state of interest. This type of case requires that within the effective Hamiltonian method a multireference approach is implemented in a way similar to that done in the multireference coupled-cluster theories. The conceptual similarity between the coupled cluster method and the size-consistent configuration interaction method allows search for an extension of the single-reference (SC)²CI approach towards MR(SC)²CI approach in a similar way as such an extension has been suggested in the coupled-cluster method. Naturally, since there is a number of different proposals regarding the formulation of the MRCC scheme, with each of them offering some unique advantages, several different avenues can be explored in conjunction with a MR(SC)²CI procedure. Based on our previous experience, we would like to limit ourself here to a search for a state-selective scheme, i.e., a scheme, which can be applied to determine only one state of the system (this being either the ground or excited state) in a single calculation. As a matter of fact, the multireference (SC)²CI procedure proposed before by one of us with collaborators⁴⁰ was a state-selective approach. The reason for such a choice is the realization, that in most applications of the theory one is concerned with a single electronic state or a small subset of states. Moreover, if several states are simultaneously considered in a calculation, one either needs to compromise the accuracy of the calculation by having the states share the same orbitals and some configuration amplitudes (this may be a more reasonable assumption for some states than for the other), or perform a calculation which, in essence, would be equivalent in complexity and effort to a set of independent calculations, each aiming to determine a different state.

We also find reasonable to assume that the initial stage in our approach will be a complete active space self-consistent field (CASSCF) calculation, which will produce orbitals and the initial reference function for the state under consideration. The CASSCF method⁴² is a well established approach, which through implementation of the second-order orbital and configuration optimization procedure, has become a popular and effective method to study states with multireference character. At present, however, it seems that a satisfactory method to treat the dynamic electron correlation

effects in a size-consistent fashion is still an open problem. In particular, it seems that no satisfactory approach has yet been proposed that equivalently describes the dynamic and nondynamic electron correlation contributions and allows them to interact in a self-consistent manner.

In this work, we propose a state-selective multireference size-consistent configuration interaction approach which is derived from the state-selective multireference coupled-cluster method. Some definitions and a review of some relevant features of the coupled cluster and size-consistent CI methods, are presented in the first two sections. The proposed approach is described in the third section.

II. STATE SELECTIVE MULTIREFERENCE CC FORMALISM

In the originally introduced version of the SSMRCC method, the traditional SRCC exponential wave operator e^T is partitioned into two parts, $e^{T^{(int)}}$ and $e^{T^{(ext)}}$, such that the former acts on a suitably chosen single-determinantal formal reference function $|0\rangle$ to generate the model space $|\Phi^{(int)}\rangle$ determinants and the latter produces virtual space excitations. The formal reference determinant, $|0\rangle$, can be different for different states. Thus, the exact function is generated as

$$|\Psi\rangle = e^{T^{(ext)}}|\Phi^{(int)}\rangle = e^{T^{(ext)}}e^{T^{(int)}}|0\rangle. \quad (1)$$

Both $T^{(int)}$ and $T^{(ext)}$ are mutually commutative, hole-particle creation operators. In order to specify the orbital indices in these two operators, the one-electron function space is divided into active and inactive subspaces. The inactive space contains core and virtual orbitals which are always occupied and unoccupied, respectively, in all model space configurations. Active space orbitals are those which have different occupancies for different model space configurations $|\Phi^{(int)}\rangle$. The formal reference determinant, $|0\rangle$, chosen as the Fermi vacuum, defines the partition of the active space into two subsets namely, the active hole (occupied in $|0\rangle$) and active particle (not occupied in $|0\rangle$) spaces. Hole and particle indices in $T^{(int)}$ have fully internal (all active) labeling. For $T^{(ext)}$, the indices are either all external (inactive) or semi-internal (a mixture of internal and external labeling). In this work, we have followed the convention of indicating orbitals of different categories: core (inactive holes) **i, j, k, l**; active holes **I, J, K, L**; active particles **A, B, C, D**; and virtual (inactive particles) **a, b, c, d**. If the active or inactive character of a particular spin-orbital is irrelevant, we designate it in italics (holes ***ij,kl***; particles ***ab,cd***). With the use of the above indexing convention, the $T^{(int)}$ and $T^{(ext)}$ operators can be written in terms of particle-hole (p-h) excitation operators, $E_{i_1 i_2 \dots i_\eta}^{a_1 a_2 \dots a_\eta}$ ($|0_{i_1 i_2 \dots i_\eta}^{a_1 a_2 \dots a_\eta}\rangle = E_{i_1 i_2 \dots i_\eta}^{a_1 a_2 \dots a_\eta}|0\rangle$), in the following way:

$$T^{(int)} = \sum_{\kappa=1}^{N^{(int)}} T_{\kappa}^{(int)}, \quad (2)$$

$$T^{(ext)} = \sum_{\eta=1}^{N^{(ext)}} T_{\eta}^{(ext)}, \quad (3)$$

where

$$T_{\kappa}^{(\text{int})} = (\kappa!)^{-2} \sum_{\substack{I_1 > I_2 > \dots > I_{\kappa} \\ A_1 > A_2 > \dots > A_{\kappa}}}^{(\text{int})} t_{A_1 A_2 \dots A_{\kappa}}^{I_1 I_2 \dots I_{\kappa}} E_{I_1 I_2 \dots I_{\kappa}}^{A_1 A_2 \dots A_{\kappa}}, \quad (4)$$

$$T_{\eta}^{(\text{ext})} = (\eta!)^{-2} \sum_{\substack{i_1 > i_2 > \dots > i_{\eta} \\ a_1 > a_2 > \dots > a_{\eta}}}^{(\text{ext})} t_{a_1 a_2 \dots a_{\eta}}^{i_1 i_2 \dots i_{\eta}} E_{i_1 i_2 \dots i_{\eta}}^{a_1 a_2 \dots a_{\eta}}, \quad (5)$$

where among the $a_1 a_2 \dots a_{\eta}$ and $i_1 i_2 \dots i_{\eta}$ indices, either at least one label corresponds to a nonactive orbital, or all indices are active, but in this case the level of the external excitation is at least by one higher than the highest excitation level in $T^{(\text{int})}$. $N^{(\text{int})}$ and $N^{(\text{ext})}$ denote the highest levels of excitation possible in $T^{(\text{int})}$ and $T^{(\text{ext})}$. ($N^{(\text{ext})}$ is equal to the number of all correlated electrons.) SSMRCC expressions for determining correlation energy ΔE and amplitudes are obtained with assumption of intermediate normalization $\langle \Psi | 0 \rangle = \langle 0 | 0 \rangle = 1$ as follows:

$$\langle 0 | [H_N e^{T^{(\text{ext})}} e^{T^{(\text{int})}}]_c | 0 \rangle = \Delta E, \quad (6)$$

$$\langle \Phi^* | [H_N e^{T^{(\text{ext})}} e^{T^{(\text{int})}}]_c | 0 \rangle = 0, \quad (7)$$

where Φ^* are the virtual configurations and H_N represents the Hamiltonian in the normal order form. It is the sum of one- and two-body operators, F_N and V_N , whose matrix elements are the one- and two-electron molecular integrals. For practical use, expansions of $T^{(\text{int})}$ and $T^{(\text{ext})}$ in terms of respective k -body operators $T_{\kappa}^{(\text{int})}$ and $T_{\eta}^{(\text{ext})}$ have to be truncated. In all the applications performed up to date, internal set was restricted to include only $T_1^{(\text{int})}$ and $T_2^{(\text{int})}$ operators, while the external set contained all possible semi-internal and external, singly and doubly excited amplitudes plus those restricted semi-internal three- and four-body amplitudes, which are external single and double excitations, into the inactive orbitals from all the model space configurations generated by acting with $T^{(\text{int})}$ on the formal reference determinant, $|0\rangle$. However, it is quite possible that a higher level of the internal excitations will be required in studies of excited states. The three-body external amplitudes are restricted to carry at least one pair of active hole-particle labels and four body amplitudes should carry at least two active hole-particle pair labels. The approximate version of SSMRCC with all singles and doubles amplitudes and internal and restricted semi-internal types of triple amplitudes is called the SSMRCCSD(T) method. The version which includes internal and restricted semi-internal quadruple amplitudes is termed SSMRCCSD(TQ) method. These versions have the following Anzätze for the wave function:

$$|\Psi^{\text{SS MRCC SD}(T)}\rangle = \exp[T_1^{(\text{ext})} + T_2^{(\text{ext})} + T_3^{(abC)}] \times \exp(T_1^{(\text{int})} + T_2^{(\text{int})})|0\rangle, \quad (8)$$

$$|\Psi^{\text{SS MRCC SD}(TQ)}\rangle = \exp[T_1^{(\text{ext})} + T_2^{(\text{ext})} + T_3^{(abC)} + T_4^{(abCD)}] \exp(T_1^{(\text{int})} + T_2^{(\text{int})})|0\rangle. \quad (9)$$

It has been shown, with a number of examples, that the SSMRCCSD method based on the above wave functions

handles very well the dissociation process of single and double bonds, as well as quasidegenerate situations in some excited states where the cluster structure is similar to the situation which occurs when electrons occupying bonding orbitals get separated. In order to effectively handle a more general quasidegeneracy problem, we recently proposed the use of a linearized form for the internal operator, $e^{T^{(\text{int})}}$, while retaining our previous description for the external operator.³⁸ The resulting ansatz assumes the form

$$|\Psi\rangle = e^{T^{(\text{ext})}}(1 + C^{(\text{int})})|0\rangle. \quad (10)$$

In this case, the equations for the amplitudes are linear in terms of $C^{(\text{int})}$. In order for the ansatz represented by Eq. (10) to provide a size-extensive wave function, the internal part, $(1 + C^{(\text{int})})|0\rangle$, should include the complete set of the determinants within the manifold of configurations constructed with the use of all active orbitals. Thus, the substitution of $e^{T^{(\text{int})}}$ with $(1 + C^{(\text{int})})$ will satisfy the linked cluster theorem and preserve the size-extensivity requirement only if the full CI representation of the internal part of the wave function is assumed and no truncation is made in the $C^{(\text{int})}$ amplitude set. However, because of the exponential nature of the $T^{(\text{ext})}$ operator, the series can be truncated after including any particular level of multibody operators. For example, including one- and two-body excited operators, $T_1^{(\text{ext})}$ and $T_2^{(\text{ext})}$, is one of the possible choices. In this case the ansatz for the wave function has the following form:

$$|\Psi\rangle = e^{T_1^{(\text{ext})} + T_2^{(\text{ext})} + T_3^{(abC)} + T_4^{(abCD)} + T_5^{(abCDE)} + \dots} \times (1 + C^{(\text{int})})|0\rangle, \quad (11)$$

where the $C^{(\text{int})}$ operator comprises the following excitations:

$$C_1^A, C_{IJ}^{AB}, C_{IJK}^{ABC}, C_{IJKL}^{ABCD}, \dots, \quad (12)$$

and can be defined as

$$C^{(\text{int})} = \sum_{\kappa=1}^N C_{\kappa}^{(\text{int})}, \quad (13)$$

$$C_{\kappa}^{(\text{int})} = \sum_{\substack{I_1 > I_2 > \dots > I_{\kappa} \\ A_1 > A_2 > \dots > A_{\kappa}}}^{(\text{int})} c_{A_1 A_2 \dots A_{\kappa}}^{I_1 I_2 \dots I_{\kappa}} E_{I_1 I_2 \dots I_{\kappa}}^{A_1 A_2 \dots A_{\kappa}}. \quad (14)$$

The $T^{(\text{ext})}$ operator comprises the same types of fully external and semiexternal amplitudes as in the fully exponential ansatz. The only difference is that, since all fully internal excitations are included in $C^{(\text{int})}$, there is no need to include any higher-level fully internal excitations in $T^{(\text{ext})}$ as was done with the fully exponential ansatz, where the external excitations have to be augmented by internal triple and quadruple excitations, $T_3^{(ABC)}$ and $T_4^{(ABCD)}$, in the SSMRCCSD(T) and SSMRCCSD(TQ) levels of theory to account for connected internal single and double excitations from important single- and double-excited configurations generated by $T^{(\text{int})}$. If we assume that all the configurations generated by the action of $(1 + C^{(\text{int})})$ on $|0\rangle$ are equally important then, in principle one needs to include in $T^{(\text{ext})}$ all

fully external and semiexternal excitations which are single and double excitations from all the $(1 + C^{(\text{int})})|0\rangle$ configurations. This would necessitate, in the case when the $C^{(\text{int})}$ in a κ -body operator, including certain selected $\kappa + 1$ and $\kappa + 2$ body $T^{(\text{ext})}$ amplitudes. Although, there are certainly cases where one cannot avoid high-level connected excitations, one can always make an attempt for the state of interest to reduce the importance of higher excited configurations in the model space manifold. One way of accomplishing this, is by transforming the model space configuration expansion for the state to an expansion in terms of configurations constructed with the use of natural orbitals determined for this state. With this kind of transformation, it may be possible to reduce the active orbital set (the degree of the reduction can be different for different states) by including only those orbitals which are more significantly occupied. In consequence, one can reduce the level of the $T^{(\text{ext})}$ excitations.

The following types of amplitudes are included in the $T^{(\text{ext})}$ operator: three types of single amplitudes:

$$t_a^i, t_A^i, t_a^i, \quad (15)$$

eight types of double-excitation amplitudes:

$$t_{AB}^{IJ}, t_{AB}^{Ij}, t_{AB}^{Ij}, t_{ab}^{IJ}, t_{ab}^{ij}, t_{ab}^{Ij}, t_{ab}^{ij}, t_{ab}^{ij}, \quad (16)$$

and eight types of triple excitation amplitudes:

$$t_{ABC}^{IJK}, t_{ABC}^{IjK}, t_{ABC}^{IjK}, t_{abc}^{IJK}, t_{abc}^{ijK}, t_{abc}^{IjK}, t_{abc}^{IjK}, t_{abc}^{ijK}. \quad (17)$$

From the above, it is easy to see how to determine what types of higher level amplitudes should be included if higher level internal excitations become important. Those can be generated by adding one or more active hole-particle label pairs, (L,D), (L,M,D,E), etc., to the above triple amplitudes. The resulting eight classes of the general types of external excitation amplitudes are

$$t_{ABC\cdots D}^{IJK\cdots L}, t_{ABC\cdots D}^{IjK\cdots L}, t_{ABC\cdots D}^{IjK\cdots L}, t_{abc\cdots D}^{IJK\cdots L}, t_{abc\cdots D}^{ijK\cdots L}, t_{abc\cdots D}^{IjK\cdots L}, t_{abc\cdots D}^{IjK\cdots L}, t_{abc\cdots D}^{ijK\cdots L}. \quad (18)$$

In the following sections, we will use $\mathcal{M}^{(\text{ext})}$ to denote the manifold of excitations generated by the action of $T^{(\text{ext})}$ on $|0\rangle$. Conversely, the manifold of configurations generated by the action of $C^{(\text{int})}$ on $|0\rangle$ will be called $\mathcal{M}^{(\text{int})}$.

Finally, one can consider complete elimination of the exponential component in the wave function by replacing the external excitation part by the linearized operator:

$$|\Psi\rangle = (1 + C^{(\text{ext})})(1 + C^{(\text{int})})|0\rangle. \quad (19)$$

In order for the above ansatz to be size-consistent one needs to include the complete set of both internal and external excitations. Obviously, this would lead to the full CI wave function.

In the above discussion, one point needs to be clarified in order to avoid a contradiction between what is commonly understood as “the reference function” and the meaning of this term which we use in this work. First, in Eq. (1) we introduced a single determinantal wave function $|0\rangle$, which

we call the formal reference. Next, we introduced two new functions, $e^{T^{(\text{int})}}|0\rangle$ and $(1 + C^{(\text{int})})|0\rangle$, which are defined in the active orbital space and in the commonly used terminology would be also called reference functions. In the subsequent step, we act with $e^{T^{(\text{ext})}}$ on those reference functions to introduce the dynamic correlation effects. It is important to distinguish between the formal reference determinant, which is used to establish the partition of the orbital space into the active and nonactive subspaces and to define the Fermi vacuum, and the reference functions defined in the active configuration manifold with the internal excitation operators. According to the conventional definition, the latter are the “true” reference functions, which provide the first approximations for the state under consideration. The formal reference determinant is usually not a good representation of the state and, if a CASSCF wave function is used as the “true” reference, its choice is ambiguous since all active-space configurations are included.

III. REVIEW OF THE SINGLE-REFERENCE (SC)²CI METHOD

The (SC)²CI method starts with the conventional CI expansion of the wave function based on the selected single reference, $|0\rangle$

$$|\Psi\rangle = c_0|0\rangle + \sum_i c_i|i\rangle, \quad (20)$$

with the correlation energy being written as

$$E_c = \left(\sum_i c_i \langle 0|H|i\rangle \right) c_0^{-1}. \quad (21)$$

Since the Hamiltonian is a two-body operator, only single and double excitations with respect to $|0\rangle$ contribute to the above sum. In order to insure that the correlation energy is size extensive, the cancellation of the unlinked contributions is accomplished by “dressing” the diagonal elements of the Hamiltonian matrix to account for higher level excitations. It has been demonstrated^{39,40} that the diagonal dressing leads to adding the following quantity to each diagonal element of the Hamiltonian matrix:

$$\Delta_{ii} = \langle i|\Delta|i\rangle = \left(\sum_{D_j|i\rangle \neq 0, \notin \mathcal{M}^{(\text{int})} \cup \mathcal{M}^{(\text{ext})}} \langle 0|H|j\rangle c_j \right) c_0^{-1}, \quad (22)$$

where D_j is a single- or double-excitation operator, and $\mathcal{M}^{(\text{int})} \cup \mathcal{M}^{(\text{ext})}$ is the manifold of configurations which are included in the CI expansion (20). Naturally,

$$\Delta_{ij} = 0, \quad \text{for } i \neq j. \quad (23)$$

Due to the presence of the configuration coefficients in the dressing elements, only one state is computed in a single calculation. The procedure is iterative and it is carried until self-consistency is reached. The dressing elements account for contributions of higher excitations to whom the dressing procedure attributes coefficients which are products of the

coefficients corresponding to excitations which, when combined, produce the higher level excitations. This facilitates the size-consistent character of the method.

IV. MULTIREFERENCE (SC)²CI METHOD

The purpose of the present study is to propose a generalization of the single-reference (SC)²CI method to describe multireference cases. As we mention in the Introduction, we assume that the CASSCF calculation was performed for the state of interest and that the CASSCF wave function expressed in terms of the complete set of configurations constructed with the use of the active orbital set is determined for the state of interest. This expansion has the form

$$|\Psi\rangle = c_0|0\rangle + \sum_{i \in \mathcal{M}^{(\text{int})}} c_i|i\rangle, \quad (24)$$

where the excited determinant $|i\rangle$ can be expressed in terms of the active hole-particle generator in the following way:

$$|i\rangle = E_{I_1 I_2 \dots I_\kappa}^{A_1 A_2 \dots A_\kappa} |0\rangle. \quad (25)$$

The level of excitation in the above equation is determined by the number of active orbitals. Although a particular determinant is chosen as a formal vacuum state, thus separating the active orbitals into the active occupied ($I_1 I_2 \dots I_\kappa$) and active unoccupied subsets ($A_1 A_2 \dots A_\eta$), this does not mean that this determinant plays any special role, since the CASSCF approach assumes the full CI expansion in the active space. The formal separation of the active space into occupied and unoccupied subspaces allows us to formulate the multireference (SC)²CI method in a similar way as it was done in the SSMRCC method (see Sec. II).

The first observation which one makes regarding the multireference case is that if the CASSCF wave function provides the first approximation for the state of interest, the dynamic correlation effect will require that all single and double excitations from all CAS configurations are explicitly

represented in the wave function through appropriate connected configuration amplitudes. This requires that the multireference configuration interaction (MRCI) problem is solved with the following wave function:

$$|\Psi\rangle = (1 + C^{(\text{ext})})(1 + C^{(\text{int})})|0\rangle, \quad (26)$$

where the $C^{(\text{ext})}$ operator comprises the same excitations from $|0\rangle$ as previously included in the definition of $T^{(\text{ext})}$ in the SSMRCC theory [Eqs. (15)–(18)]:

$$C^{(\text{ext})} = \sum_{i \in \mathcal{M}^{(\text{ext})}} c_i E_i. \quad (27)$$

Obviously, the above wave function will not be size consistent if the external (fully external and semi-internal) excitations are truncated by including only single and double excitations from the CAS configurations of the type given by Eqs. (15)–(18). It is not possible to make the approach size extensive by propagating the $C^{(\text{ext})}$ operator through including it in the exponent in the way it is done with the $T^{(\text{ext})}$ operator in the SSMRCC theory, because the $C^{(\text{ext})}$ operator is not “connected” and including it in the exponent would lead to overcounting of some terms. This kind of overcounting is avoided when the $T^{(\text{ext})}$ operator is used because this operator is fully connected. Therefore, the only alternative which remains in order to make Eq. (27) size consistent is to determine the connected components in $C^{(\text{ext})}$ and then propagate only those components through including them in the exponent. Since the $C^{(\text{int})}$ and $C^{(\text{ext})}$ operators include identical sets of excitations from the formal reference determinant, $|0\rangle$, as the $T^{(\text{int})}$ and $T^{(\text{ext})}$ operators of Eq. (1) (however, in this case $T^{(\text{int})}$ cannot be terminated at some level of excitations and should include all excitations allowed in CAS), one can transform the $C^{(\text{int})}$ and $C^{(\text{ext})}$ operators to the connected $T^{(\text{int})}$ and $T^{(\text{ext})}$ operators. If we consider that all single and double excitations from the CAS determinants are allowed, then the transformation concerns the following set of configuration interaction coefficients and the coupled-cluster amplitudes:

$$\begin{aligned} & \{c_A^I, c_a^I, c_A^i, c_a^i, c_{AB}^{IJ}, c_{aB}^{IJ}, c_{AB}^{Ij}, c_{aB}^{Ij}, c_{AB}^{Ij}, c_{aB}^{Ij}, c_{AB}^{ij}, c_{aB}^{ij}, c_{AB}^{ij}, c_{aB}^{ij}, \\ & c_{ABC}^{IJK}, c_{ABC}^{IjK}, c_{ABC}^{IjK}, c_{ABC}^{IjK}, c_{ABC}^{IjK}, c_{ABC}^{IjK}, c_{ABC}^{IjK}, c_{ABC}^{IjK}, \dots, \\ & c_{ABC \dots D}^{IJK \dots L}, c_{ABC \dots D}^{IjK \dots L}, c_{ABC \dots D}^{IjK \dots L}, c_{ABC \dots D}^{IjK \dots L}, c_{ABC \dots D}^{IjK \dots L}, c_{ABC \dots D}^{IjK \dots L}, c_{ABC \dots D}^{IjK \dots L}, c_{ABC \dots D}^{IjK \dots L}\} \\ & \rightarrow \\ & \{t_A^I, t_a^I, t_A^i, t_a^i, t_{AB}^{IJ}, t_{aB}^{IJ}, t_{AB}^{Ij}, t_{aB}^{Ij}, t_{AB}^{Ij}, t_{aB}^{Ij}, t_{AB}^{ij}, t_{aB}^{ij}, t_{AB}^{ij}, t_{aB}^{ij}, \\ & t_{ABC}^{IJK}, t_{ABC}^{IjK}, t_{ABC}^{IjK}, t_{ABC}^{IjK}, t_{ABC}^{IjK}, t_{ABC}^{IjK}, t_{ABC}^{IjK}, t_{ABC}^{IjK}, \dots, \\ & t_{ABC \dots D}^{IJK \dots L}, t_{ABC \dots D}^{IjK \dots L}, t_{ABC \dots D}^{IjK \dots L}, t_{ABC \dots D}^{IjK \dots L}, t_{ABC \dots D}^{IjK \dots L}, t_{ABC \dots D}^{IjK \dots L}, t_{ABC \dots D}^{IjK \dots L}, t_{ABC \dots D}^{IjK \dots L}\}. \end{aligned} \quad (28)$$

The transformation can be performed with the use of the following known relation between the CI coefficients and the coupled-cluster amplitudes (in order to make use of this relation the CI coefficients are first renormalized by dividing all the coefficients by the coefficient of the formal reference determinant, c_0 ; the renormalized CI coefficients are denoted in the following equation as c'):

$$\begin{aligned}
t_1 &= c'_1, \\
t_2 &= c'_2 - \frac{1}{2}(c'_1)^2, \\
t_3(\text{abC}) &= c'_3(\text{abC}) - c'_1 c'_2 + \frac{1}{3}(c'_1)^3, \\
t_4(\text{abCD}) &= c'_4(\text{abCD}) - c'_1 c'_3(\text{abC}) - \frac{1}{2}(c'_1)^2 c'_2, \\
&\dots
\end{aligned} \tag{29}$$

In the set of all t 's generated with the above procedure, one can distinguish the amplitudes corresponding to the $T^{(\text{int})}$ and $T^{(\text{ext})}$ operators. In order to define the dressing of the Hamiltonian matrix elements, one needs to define the domain of configurations which do not belong to the configuration set used to diagonalize the Hamiltonian and are obtained by operating with $C^{(\text{int})}$ and $C^{(\text{ext})}$ on $|0\rangle$. This domain of configurations will be used for the dressing. The domain can be defined in terms of the configuration generators, E , as

$$\begin{aligned}
\{\mathcal{M}\} &= \text{span}\{\{e^{E_i^a + E_{ij}^{ab} + E_{ijk}^{abc} + E_{ijkl}^{abcd} + \dots + E_{ij \dots Klm}^{abcd \dots E}} |0\rangle\} \\
&\quad \setminus \{E_i^A |0\rangle, E_{ij}^{AB} |0\rangle, E_{ijk}^{ABC} |0\rangle, \dots, E_{ijkl \dots M}^{ABCD \dots D} |0\rangle\} \\
&\quad \setminus \{E_i^a |0\rangle, E_i^A |0\rangle, E_i^a |0\rangle, \\
&\quad E_{ij}^{aB} |0\rangle, E_{ij}^{AB} |0\rangle, E_{ij}^{aB} |0\rangle, E_{ij}^{aB} |0\rangle, E_{ij}^{aB} |0\rangle, E_{ij}^{aB} |0\rangle, E_{ij}^{aB} |0\rangle, E_{ij}^{aB} |0\rangle, \\
&\quad E_{ijk}^{aBC} |0\rangle, E_{ijk}^{aBC} |0\rangle, E_{ijk}^{aBC} |0\rangle, E_{ijk}^{aBC} |0\rangle, E_{ijk}^{aBC} |0\rangle, E_{ijk}^{aBC} |0\rangle, E_{ijk}^{aBC} |0\rangle, E_{ijk}^{aBC} |0\rangle, \dots\}.
\end{aligned} \tag{30}$$

In the above expression, the indices of the generators indicate which types of orbitals (nonactive or active, occupied or unoccupied) are being excited from and to in the particular generator. Summations over all orbitals belonging to the particular type is assumed. Among the configurations obtained by expanding the exponent in Eq. (30) and by acting with products of generators on $|0\rangle$ only those are included in the set \mathcal{M} , which are not more than singly and doubly excited from the configurations in the $\mathcal{M}^{(\text{int})}$ and $\mathcal{M}^{(\text{int})}$ sets. The dressing of the MRCI Hamiltonian matrix is done in a similar way as was accomplished in the single-reference theory. The dressing needs to be applied only to the matrix elements, which correspond to external and semi-internal configurations because the part of the expansion in terms of the internal configurations is size extensive due to the fact that the full CI expansion in the internal manifold is included in the wave function (26). The dressing will consist in including the interaction of the external excitations with the excitations which belong to the configuration domain \mathcal{M} . By analogy to the single-reference case, we propose the following dressing elements. Here also, only the diagonal dressing is applied:

$$\Delta_{ii} = \langle i | \Delta | i \rangle = (c_i^{-1} c_0) \sum_{j, |j\rangle \in \mathcal{M}} \langle i | H | j \rangle \langle j | e^{T^{(\text{ext})}} e^{T^{(\text{int})}} | 0 \rangle, \tag{31}$$

where the index i runs over all configurations in the $\mathcal{M}^{(\text{ext})}$ manifold, and in the summation only those excitations are

considered which belong to the \mathcal{M} space and give nonzero Hamiltonian matrix elements with the configuration $\langle i |$. It can be noticed that $\langle i | H | j \rangle \langle j | e^{T^{(\text{ext})}} e^{T^{(\text{int})}} | 0 \rangle$ terms include connected as well as disconnected dressing contributions. The unlinked terms are necessary to cancel out the unlinked part of the term $(c_i^{-1} c_0)$ leaving only that having Pauli exclusion principle violating (EPV) character. The dressing defined by Eq. (31) allows accounting for higher level excitations in the MRCI matrix. The configuration coefficients of these excitations are assumed to be equal to the products of connected coupled-cluster amplitudes. Part of the terms (the quadratic terms) resulting from expanding the exponential operators in Eq. (31) in the power series in terms of $T^{(\text{int})}$ and $T^{(\text{ext})}$ were included in the multireference self-consistent single- and double-configuration interaction theory formulation by Malrieu *et al.*⁴⁰ Since in the present approach all the expansion terms are included, we can term it ‘‘the complete exponential dressing procedure.’’ The factor $c_i^{-1} c_0$ in Eq. (22) provides the proper renormalization of the dressing term.

By expanding the exponent in Eq. (31), depending on the particular form of the configuration $\langle i | \in \mathcal{M}$, one gets a different expression of the dressing element Δ_{ii} . The coupling elements $\Lambda \equiv \langle i | H | j \rangle \langle j | e^{T^{(\text{ext})}} e^{T^{(\text{int})}} | 0 \rangle$, $|j\rangle \in \mathcal{M}$, can be written in the following symbolic form:

$$\Lambda_a^i \equiv \langle 0_a^a | H | j \rangle \langle j | [(1 + T_1 + T_2 + T_3(a' b' c')) + (\frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{6} T_1^3)] | 0 \rangle, \tag{32}$$

$$\Lambda_{ab}^{ij} \equiv \langle 0_{ab}^{ij} | H | j \rangle \langle j | [(1 + T_1 + T_2 + T_3(a' b' c')) + T_4(a' b' c' d')) + (\frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{6} T_1^3 + T_1 T_3(a' b' c')) + \frac{1}{2} T_2^2 + \frac{1}{2} T_1^2 T_2 + \frac{1}{24} T_1^4]] | 0 \rangle, \tag{33}$$

$$\Lambda_{abC}^{Ijk} \equiv \langle 0_{Ijk}^{abC} | H | j \rangle \langle j | [(T_1 + T_2 + T_3(a'b'C') + T_4(a'b'C'D') + T_5(a'b'C'D'E')) + (\frac{1}{2}T_1^2 + T_1T_2 + \frac{1}{6}T_1^3 + T_1T_3(a'b'C'D')) + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2T_2 + \frac{1}{24}T_1^4 + T_1T_4(a'b'C'D') + T_2T_3(a'b'C') + \frac{1}{2}T_1^2T_3(a'b'C') + \frac{1}{2}T_1T_2^2 + \frac{1}{6}T_1^3T_2 + \frac{1}{120}T_1^5)] | 0 \rangle, \quad (34)$$

$$\Lambda_{abCD}^{Ijkl} \equiv \langle 0_{Ijkl}^{abCD} | H | j \rangle \langle j | [(T_2 + T_3(a'b'C') + T_4(a'b'C'D') + T_5(a'b'C'D'E')) + T_6(a'b'C'D'E'F')) + (\frac{1}{2}T_1^2 + T_1T_2 + T_1T_3(a'b'C') + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2T_2 + \frac{1}{24}T_1^4 + T_1T_4(a'b'C'D') + T_2T_3(a'b'C') + \frac{1}{2}T_1^2T_3(a'b'C') + \frac{1}{2}T_1T_2^2 + \frac{1}{6}T_1^3T_2 + \frac{1}{120}T_1^5 + T_1T_5(a'b'C'D'E') + T_2T_4(a'b'C'D') + \frac{1}{2}[T_3(a'b'C')]^2 + \frac{1}{2}T_1^2T_4(a'b'C'D') + T_1T_2T_3(a'b'C') + \frac{1}{6}T_2^3 + \frac{1}{6}T_1^3T_3(a'b'C') + \frac{1}{4}T_1^2T_2^2 + \frac{1}{24}T_1^4T_2 + \frac{1}{740}T_1^6)] | 0 \rangle, \quad (35)$$

where primes are being used to distinguish between the summation indices, that appear in the many-body expansions of the triply and quadruply excited clusters and fixed spin-orbitals labels which characterize projections onto configurations belonging to the $\mathcal{M}^{(\text{ext})}$ space.

In the above equation the symbol of the type 0_{Ijk}^{abC} is used to denote the $\mathcal{M}^{(\text{ext})}$ -space determinant obtained by replacing the Ijk spin orbital labels by the abC labels in the formal reference. In each of the above equations, the part linear in terms of the CC amplitudes was separated from the nonlinear part. The projection of the linear part on the configurations from the \mathcal{M} set will give zero result, since the components of the linear part, if they are included in the expansion, can only generate determinants which belong to either the $\mathcal{M}^{(\text{int})}$ or the $\mathcal{M}^{(\text{ext})}$ set, and not to the \mathcal{M} set. A nonzero result can only result from the nonlinear part, where products of CC operators when operating on the formal vacuum can produce configurations belonging to the \mathcal{M} set. One notices, that in Eqs. (32)–(35) we indicate contribution of up to sextuple connected excitations from the formal reference determinant. Such excitations also will appear in the MRCI expansion based on the CASSCF reference if the active space consists of four or more active orbitals for four active electrons and single and double excitations from active and core orbitals are included in the wave function. However, one needs to notice that in the case of higher excitations only a very limited number of them is included due to the restriction that they cannot contain more than double excitations into the nonactive orbitals. Obviously, due to an iterative self-consistent procedure for solving for the configuration coefficients and subsequent determination of the coupled-cluster amplitudes from the CI coefficients, the electron correlation effects described by the internal excitations are allowed to interact with the correlation effects described by semi-internal and external excitations.

Diagonalization of the “dressed” Hamiltonian matrix

$$\mathbf{c}^\dagger (\mathbf{H} + \Delta) \mathbf{c} = \mathbf{E} \quad (36)$$

in the space of $\{|0\rangle, \mathcal{M}^{(\text{int})}, \mathcal{M}^{(\text{ext})}\}$ configurations gives rise to the $\{c_0, c^{(\text{int})}, c^{(\text{ext})}\}$ configuration coefficients and the energy of the state under consideration. After transformation of

the CI coefficients to the coupled-cluster amplitudes, the Hamiltonian matrix is dressed again and the procedure is repeated.

V. SUMMARY

In this work, we propose a state-specific, size-extensive expansion for the wave function, which is constructed with the use of single and double excitations out of the CASSCF reference wave function. The expansion is accomplished through a state-specific dressing of the CI Hamiltonian matrix by first selecting a leading reference determinant in the CASSCF wave function and next defining a single-reference coupled-cluster exponential orbital excitation operator based on this determinant, which expands the CASSCF reference into the nonactive space. The dressing of the Hamiltonian matrix introduces interactions of singly- and doubly-excited configurations from the CASSCF reference function with higher level excitations. In the first step of the procedure, coupled-cluster amplitudes of connected excitations are determined with the use of the CI coefficients obtained from the diagonalization of the Hamiltonian matrix. Next, the higher level excitations and their coefficients are generated with the use of the exponential operator defined using the coupled-cluster amplitudes and the corresponding configuration generators. Although, in the exponential ansatz a single determinant is used as a formal reference, the proposed method is not restricted to single-reference states, but can be also used for multireference cases in the same way as it is done in the state-selective multireference coupled-cluster scheme. Finally, the dressing Hamiltonian elements are determined with the use of the connected expansion of the interaction terms.

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¹F. Coester, Nucl. Phys. **7**, 421 (1958); F. Coester and H. Kümmel, *ibid.* **17**, 477 (1960); J. Čížek, J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **14**, 35 (1969); J. Čížek and J. Paldus, Int. J. Quantum Chem. **5**, 359 (1971); J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A **5**, 50 (1972).

- ²R.J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981); *J. Phys. Chem.* **93**, 1697 (1989).
- ³J. Paldus, *Diagrammatic Methods for Many-Fermion Systems* (University of Nijmegen, Holland, 1981); R.J. Bartlett, C.E. Dykstra, and J. Paldus, in *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, edited by C.E. Dykstra (Reidel, Dordrecht, 1984), pp. 127–159; J. Paldus, in *New Horizons of Quantum Chemistry*, edited by P.-O. Löwdin and B. Pullman (Reidel, Dordrecht, 1983), pp. 31–60. J. Paldus, in *Methods in Computational Molecular Physics*, Vol. 293, NATO Advanced Study Institute, Series B: Physics, edited by S. Wilson and G.H.F. Diercksen (Plenum, New York, 1992), pp. 99–194.
- ⁴G.D. Purvis III and R.J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982); G.W. Trucks, J. Noga, and R.J. Bartlett, *Chem. Phys. Lett.* **145**, 548 (1988); J.F. Stanton, J. Gauss, J.D. Watts, and R.J. Bartlett, *J. Chem. Phys.* **94**, 4334 (1991); J. Noga and R.J. Bartlett, *ibid.* **86**, 7041 (1987); *ibid.* **89**, 3401 (1988) (Erratum).
- ⁵G.E. Scuseria, T.J. Lee, and H.F. Schaefer III, *Chem. Phys. Lett.* **130**, 236 (1986); T.J. Lee and J.E. Rice, *ibid.* **150**, 406 (1988); G.E. Scuseria, C.L. Janssen, and H.F. Schaefer III, *J. Chem. Phys.* **89**, 7382 (1988); G.E. Scuseria and H.F. Schaefer III, *Chem. Phys. Lett.* **152**, 382 (1988).
- ⁶R.A. Chiles and C.E. Dykstra, *J. Chem. Phys.* **74**, 4544 (1981); C.E. Dykstra and J.D. Augspurger, *Chem. Phys. Lett.* **145**, 545 (1988).
- ⁷J. Noga, V. Kellö, and M. Urban, Comenius Technical Report, Comenius University, Bratislava, 1985.
- ⁸H.J. Monkhorst, *Int. J. Quantum Chem. Symp.* **11**, 421 (1977).
- ⁹T. Helgaker and P. Jørgensen in *Methods in Computational Molecular Physics*, edited by S. Wilson and G. Diercksen (Plenum, New York, 1992); P. Jørgensen and T. Helgaker, *J. Chem. Phys.* **89**, 1560 (1988); H. Koch and P. Jørgensen, *ibid.* **93**, 3333 (1990).
- ¹⁰P. Jørgensen and J. Simons, *J. Chem. Phys.* **79**, 334 (1983); R.J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, Vol. 166, NATO Advanced Study Institute, Series C: Mathematical and Physical Sciences, edited by P. Jørgensen and J. Simons (Reidel, Dordrecht, 1986), pp. 35–61.
- ¹¹L.A. Adamowicz, W.D. Laidig, and R.J. Bartlett, *Int. J. Quantum Chem. Symp.* **18**, 245 (1984).
- ¹²G. Fitzgerald, R.J. Harrison, and R.J. Bartlett, *J. Chem. Phys.* **85**, 5143 (1986).
- ¹³A.C. Scheiner, G.E. Scuseria, J.E. Rice, T.J. Lee, and H.F. Schaefer III, *J. Chem. Phys.* **87**, 5361 (1987).
- ¹⁴N. C. Handy and H.F. Schaefer III, *J. Chem. Phys.* **81**, 5031 (1984).
- ¹⁵J. Noga and M. Urban, *Theor. Chim. Acta* **73**, 291 (1988); R.J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29 (1988); M. Urban, G.H.F. Diercksen, A.J. Sadlej, and J. Noga, *Theor. Chim. Acta* **77**, 29 (1990); J.D. Watts, G.W. Trucks, and R.J. Bartlett, *Chem. Phys. Lett.* **157**, 359 (1989).
- ¹⁶E.A. Salter, G.W. Trucks, and R.J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989); E.A. Salter and R.J. Bartlett, *ibid.* **90**, 1767 (1989); H. Sekino and R.J. Bartlett, *Int. J. Quantum Chem. Symp.* **18**, 255 (1984); *J. Chem. Phys.* **84**, 2726 (1986); E. A. Salter, H. Sekino, and R. J. Bartlett, *ibid.* **87**, 502 (1987).
- ¹⁷S. Pal, *Phys. Rev. A* **33**, 2240 (1986); K. B. Ghose and S. Pal, *ibid.* **45**, 1518 (1992); S. Pal, *Phys. Rev. A* **42**, 4385 (1990); K.B. Ghose, P.G. Nair, and S. Pal, *Chem. Phys. Lett.* **211**, 15 (1993); S. Pal and K.B. Ghose, *Curr. Sci.* **63**, 667 (1992); S. Pal, *Phys. Rev. A* **34**, 2682 (1986); K.B. Ghose and S. Pal, *ibid.* **36**, 1539 (1987); S. Pal, *ibid.* **39**, 2712 (1989); N. Vaval, K.B. Ghose, and S. Pal, *J. Chem. Phys.* **101**, 4914 (1994); K.B. Ghose, *Int. J. Quantum Chem.* **53**, 275 (1995).
- ¹⁸H. Koch, H.J.Aa. Jensen, P. Jørgensen, T. Helgaker, G.E. Scuseria, and H.F. Schaefer III, *J. Chem. Phys.* **92**, 4924 (1990); R. Kobayashi, H. Koch, and P. Jørgensen, *ibid.* **101**, 4956 (1994).
- ¹⁹B. Jeziorski and J. Paldus, *J. Chem. Phys.* **90**, 2714 (1989).
- ²⁰I. Lindgren and D. Mukherjee, *Phys. Rep.* **151**, 93 (1987).
- ²¹D. Mukherjee and S. Pal, *Adv. Quantum Chem.* **20**, 291 (1989).
- ²²B. Jeziorski and H.J. Monkhorst, *Phys. Rev. A* **24**, 1668 (1981).
- ²³B. Jeziorski and J. Paldus, *J. Chem. Phys.* **88**, 5673 (1988).
- ²⁴F.E. Harris, *Int. J. Quantum Chem. Symp.* **11**, 403 (1977).
- ²⁵J. Paldus, J. Čížek, M. Saute, and A. Laforgue, *Phys. Rev. A* **17**, 805 (1978); M. Saute, J. Paldus, and J. Čížek, *Int. J. Quantum Chem.* **15**, 463 (1979).
- ²⁶H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978); **67**, 329 (1979); H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053, 4279 (1978); H. Nakatsuji, *Int. J. Quantum Chem. Symp.* **17**, 241 (1983).
- ²⁷A. Banerjee and J. Simons, *Int. J. Quantum Chem.* **19**, 207 (1981); *J. Chem. Phys.* **76**, 4548 (1982).
- ²⁸H. Baker and M.A. Robb, *Mol. Phys.* **50**, 20 (1983).
- ²⁹R. Tanaka and H. Terashima, *Chem. Phys. Lett.* **106**, 558 (1984).
- ³⁰M.R. Hoffman and J. Simons, *J. Chem. Phys.* **88**, 993 (1988).
- ³¹S.A. Kucharski and R.J. Bartlett, *Theor. Chim. Acta* **80**, 387 (1991); *J. Chem. Phys.* **97**, 4282 (1992); J. Paldus, *ibid.* **67**, 303 (1977).
- ³²N. Oliphant and L. Adamowicz, *J. Chem. Phys.* **94**, 1229 (1991); N. Oliphant and L. Adamowicz, *ibid.* **96**, 3739 (1992).
- ³³P. Piecuch, N. Oliphant, and L. Adamowicz, *J. Chem. Phys.* **99**, 1875 (1993); N. Oliphant and L. Adamowicz, *Int. Rev. Phys. Chem.* **12**, 339 (1993).
- ³⁴P. Piecuch and L. Adamowicz, *J. Chem. Phys.* **100**, 5792 (1994); *Chem. Phys. Lett.* **221**, 121 (1994).
- ³⁵N. Oliphant and L. Adamowicz, *Chem. Phys. Lett.* **190**, 13 (1992); P. Piecuch and L. Adamowicz, *J. Chem. Phys.* **100**, 5857 (1994).
- ³⁶K.B. Ghose and L. Adamowicz, *J. Chem. Phys.* **103**, 9324 (1995).
- ³⁷K.B. Ghose, P. Piecuch, and L. Adamowicz, *J. Chem. Phys.* **103**, 9331 (1995).
- ³⁸L. Adamowicz (unpublished).
- ³⁹J.-P. Daudey, J.-L. Heully, and J.-P. Malrieu, *J. Chem. Phys.* **99**, 1240 (1990).
- ⁴⁰J.-P. Malrieu, J.-P. Daudey, and R. Caballol, *J. Chem. Phys.* **101**, 8908 (1994).
- ⁴¹J. Geertsen, M. Rittby, and R.J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989); J.F. Stanton and R.J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993); D. C. Comeau and R.J. Bartlett, *Chem. Phys. Lett.* **207**, 414 (1993); R. J. Bartlett and J.F. Stanton, *Rev. Comp. Chem.* **5**, 65 (1994); M. Nooijen and R.J. Bartlett, *J. Chem. Phys.* **102**, 3629 (1995); *J. Chem. Phys.* **102**, 6735 (1995).
- ⁴²B.O. Roos, in *Lecture Notes in Quantum Chemistry*, edited by B. O. Roos (Springer, Berlin, 1992), Vol. 58, pp. 177–254.