Multireference Coupled Cluster Ansatz

Bogumil Jeziorski

▶ **To cite this version:**

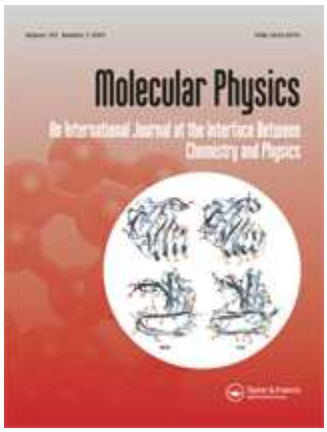
Bogumil Jeziorski. Multireference Coupled Cluster Ansatz. Molecular Physics, 2010, 108 (21-23), pp.3043-3054. 10.1080/00268976.2010.524169 . hal-00643844

HAL Id: hal-00643844
https://hal.science/hal-00643844

Submitted on 23 Nov 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Multireference Coupled Cluster Ansatz

Journal:	*Molecular Physics*
Manuscript ID:	TMPH-2010-0265.R1
Manuscript Type:	Special Issue Paper - Electrons, Molecules, Solids and Biosystems: Fifty Years of the Quantum Theory Project
Date Submitted by the Author:	09-Sep-2010
Complete List of Authors:	Jeziorski, Bogumil; University of Warsaw, Chemistry
Keywords:	coupled cluster theory, multireference cluster Ansatz

Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.

Jeziorski_TMPH-2010-0265.R1.tex
Jeziorski_TMPH-2010-0265.R1.bbl

SCHOLARONE™
Manuscripts

Multireference Coupled Cluster Ansatz

Bogumil Jeziorski

Faculty of Chemistry, University of Warsaw,

Pasteura 1, 02-093 Warsaw, Poland

(Dated: September 9, 2010)

Abstract

The origin of the multireference coupled cluster Ansatz for the wave function and the wave operator, discovered in Quantum Theory Project in 1981, is presented from the historical perspective. Various methods of obtaining the cluster amplitudes - both state-universal and state-selective are critically reviewed and further prospects of using the multireference coupled cluster Ansatz in electronic structure theory are briefly discussed.

For Peer Review Only

I. INTRODUCTION

In the late 1970's it has become clear that the coupled cluster (CC) theory, initiated in nuclear physics [1, 2] and developed after a while for quantum chemical applications [3–5], is a very promising - formally attractive and potentially accurate - computational tool for the electronic structure theory [6, 7]. For an enlightening, firsthand account of the origins of the CC theory the reader is referred to Refs. 8–11. In 1978/1979 I was visiting the Department of Physics, University of Utah, and became familiar with the coupled cluster work done in Salt Lake City by Frank Harris [12] and Henk Monkhorst [13]. I was very impressed by the mathematical beauty and power of the coupled cluster theory, and in particular by the global insight it provided into - at that time - formidably complex structure of the many-body perturbation theory (MBPT). In fact, shortly after I joined Harris's group we used the coupled cluster Ansatz to propose a simple scheme for generating an explicitly connected form of the MBPT expansion in an order-by-order fashion [14, 15]. We realized at that time that the success of the CC approach relies heavily on the availability of a single, preferably closed-shell, reference determinant Φ, providing a reasonably good approximation to the exact wave function Ψ. It was therefore clear to us that a development of an appropriate generalization of the CC method to quasidegenerate/multireference situations is important and very timely.

We were not the first to be aware of this challenge. A simple solution of the problem, that suggests itself rather naturally, appears to be possible if the determinant Φ is replaced by a multideterminantal approximation Ψ_0 to Ψ obtained, e.g., from spin-symmetry considerations, or from an MCSCF-type optimization. Thus, in the conventional CC Ansatz

$$\Psi = e^T \Phi, \tag{1}$$

the single determinant Φ may be substituted by, say, an MCSCF wave function Ψ_0, as proposed by Banerjee and Simons [16]. The problem with this solution is that the form of the cluster operator T relies strongly on the single-determinant form of Φ and on the classification of orbitals defined by Φ. Specifically, T is a linear combination of single, double, etc. excitation operators replacing a set of orbitals occupied in Φ by a set of virtual orbitals (i.e., orbitals orthogonal to all orbitals occupied in Φ). These excitation operators are usually expressed via the conventional fermion creation ($a_r^\dagger$) and annihilation (a_α) operators,

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

e.g., the two-body part of T takes the form

$$T_2 = \sum_{\alpha<\beta} \sum_{r<s} t_{rs}^{\alpha\beta}\, a_r^\dagger\, a_s^\dagger\, a_\beta\, a_\alpha, \tag{2}$$

where $t_{rs}^{\alpha\beta}$ are cluster amplitudes, but an equivalent first-quantized representation through integral ("ket-bra") operators is also possible [17], e.g.,

$$T_2 = \sum_{i<j} \hat{t}_2(ij), \tag{3}$$

$$\hat{t}_2 = \sum_{\alpha<\beta} |\tau_{\alpha\beta}\rangle\langle\phi_\alpha\phi_\beta|, \tag{4}$$

where i and j label electronic coordinates, including spin, ϕ_α, ϕ_β are spinorbitals occupied in Φ, and $\tau_{\alpha\beta}(ij)$ are pair functions expanded usually (but not always [17]) in terms products of virtual orbitals $\phi_r(i)\phi_s(j)$. Using either the first- or the second-quantized representation of T one can easily show that T is uniquely defined by Ψ and that any wave function can be represented in the form of Eq. (1). One can also show [16] that any wave function which is orthogonal neither to Φ nor to Ψ_0 can be represented as $\Psi = e^S\Psi_0$ with S uniquely defined by Ψ, but only if the excitation structure of S is the same as that of T, and is defined via equations of the form of Eqs. (2) and (3), i.e., relative to a single determinant Φ. It would be desirable, however, to define S in a way that would not be biased towards a single determinant but would treat all determinants in Ψ_0 on equal footing. Unfortunately, it appears that no construction of the Ansatz of the form $\Psi = e^S\Psi_0$ proposed so far: (i) treats all basic determinants in a symmetric way, (ii) leads to cluster amplitudes uniquely defined by Ψ, and (iii) is capable to represent the exact wave function. It should be noted however, that multireference (MR) coupled cluster methods employing the Ansatz $\Psi = e^S\Psi_0$, and biased towards a single determinant, have been proposed [18–21] and used with a considerable success in practical applications [22–26].

An entirely different, and a much more general approach was proposed by Offermann, et al [27, 28], Mukherjee et al [29]. and by Lindgren [30] (see also an early, insightful attempt by Mukherjee et al [31, 32] and subsequent Fock-space formulations [33–37]). In this approach the exponential Ansatz (most often in the so-called normal ordered form) is used to represent not a single wave function, but a wave operator mapping a manifold of simple multideterminantal functions (the model space) onto the exact solutions of the Schrödinger equation. A special feature of this Ansatz is its valence universality [29] (VU),

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

meaning that a single cluster operator applies to systems with different numbers of valence electrons. With a proper choice of the model space this valence-universal Ansatz is exact and the cluster amplitudes are uniquely defined by the FCI wave functions from several layers (sectors) of the Fock space[38]. It also turns out that only in one layer of the Fock space is the normal-ordered valence-universal Ansatz truly exponential, and in this layer it coincides with the conventional Ansatz of Eq. (1). In other layers, corresponding to systems with attached or removed electrons, the Ansatz becomes really linear [28, 38]. This has the consequence that the cluster amplitudes can be obtained by diagonalization of an appropriate matrix. In fact, the energies of ionized or excess-electron states obtained by applying the VU Ansatz [i.e., using the VU-CC or Fock-space (FS-CC) theory] turned out to be identical [39–42] with the energies of the IP-EOM-CC [43–45] and EA-EOM-CC [46–48] theories. For the excitation energies there is no equivalence with the conventional EE-EOM-CC method [49–51], but still, in view of the factual linearity of the Ansatz, the excited state wave functions of the VU-CC method can be directly obtained from diagonalization of an intermediate Hamiltonian [42, 52], or a suitable matrix representation of the Bloch equation [53]. In conclusion, from the present-day perspective the VU-CC Ansatz is not really a multireference CC Ansatz. Similarly as in the EOM-CC theory, this is a conventional single reference Ansatz for the initial state, and a linear Ansatz for the ionized, excess-electron or excited states. As shown in the next section, a genuine multireference CC Ansatz, capable of correctly describing dissociation of a chemical bond, cannot be based on a single exponential function.

II. FORMULATION OF THE MRCC ANSATZ FOR THE WAVE FUNCTION AND THE WAVE OPERATOR

The fundamental feature of the coupled cluster Ansatz of Eq. (1) is the connected nature of the cluster operator T. Physically, this means that that cluster amplitudes, e.g., a two-body one $t_{rs}^{\alpha\beta}$, vanish when the spinorbitals — ϕ_α, ϕ_β, ϕ_r, and ϕ_s in this case — are localized, and one or more of them moves away to infinity and cease to interact with the remaining ones. Equivalently, when the whole system dissociates into two localized subsystems A and B separated by a distance R, the cluster operator T becomes the sum of the cluster operators

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

T_A and T_B of the fragments:

$$\lim_{R\to\infty} T = T_A + T_B. \tag{5}$$

Eq. (5) may be viewed as a justification of the exponential Ansatz. If this equation did not hold, the exponential Ansatz would not make sense. It is instructive to see the proof of Eq. (5). We assume that when $R \to \infty$, our N-electron system separates into an N_A- and N_B-electron subsystems described by wave functions Ψ_A and Ψ_B, respectively. Each of these wave functions can be represented with its own exponential Ansatz

$$\Psi_A = e^{T_A}\,\Phi_A \qquad\qquad \Psi_B = e^{T_B}\,\Phi_B, \tag{6}$$

defined in terms of orbitals localized at A and B, respectively. The virtual and occupied orbitals on each subsystem may be assumed to have zero differential overlap in the limit $R \to \infty$. If we also assume that [54, 55]

$$\lim_{R\to\infty} \Psi(1,\ldots,N) = \mathcal{A}\,\Psi_A(1,\ldots,N_A)\,\Psi_B(N_A+1,\ldots,N), \tag{7}$$

where $\mathcal{A}$ is the N-electron antisymmetrizer normalized such that $\mathcal{A}^2 = \sqrt{N!/(N_A!N_B!)}\,\mathcal{A}$, and use Eq. (6), then we can write

$$\lim_{R\to\infty} \Psi(1,\ldots,N) = \mathcal{A}\,e^{T_A(1,\ldots,N_A)+T_B(N_A+1,\ldots,N)}\,\Phi_A(1,\ldots,N_A)\,\Phi_B(N_A+1,\ldots,N). \tag{8}$$

Since the orbitals used to define T_A and Φ_B are mutually orthogonal we can replace $T_A(1,\ldots,N_A)$ in Eq. (8) by $T_A(1,\ldots,N)$, where $T_A(1,\ldots,N)$ is the natural extension of $T_A(1,\ldots,N_A)$ to the whole N-electron Hilbert space, defined by second quantization, or by equations of the form of Eq. (3). Extending $T_B(N_A+1,\ldots,N)$ in a similar way one can write

$$\lim_{R\to\infty} \Psi(1,\ldots,N) = e^{T_A(1,\ldots,N)+T_B(1,\ldots,N)}\,\mathcal{A}\,\Phi_A(1,\ldots,N_A)\,\Phi_B(N_A+1,\ldots,N), \tag{9}$$

since now the antisymmetrizer $\mathcal{A}$ commutes with the exponential. Noting also that $\Phi \equiv \mathcal{A}\,\Phi_A(1,\ldots,N_A)\,\Phi_B(N_A+1,\ldots,N)$, we finally obtain

$$\lim_{R\to\infty} \Psi \equiv \lim_{R\to\infty} e^T\Phi = e^{T_A+T_B}\,\Phi, \tag{10}$$

where all wave function arguments $1,\ldots,N$ were suppressed for brevity reason. Eq. (10) shows that indeed $T \to T_A + T_B$ when $R \to \infty$, i.e., the validity of Eq. (5).

For Peer Review Only

The validity of the proof given above depends upon the validity of Eq. (7). This equation holds when a closed-shell system dissociates into closed-shell fragments, or in the case of dissociation of high-spin systems when the product $\Psi_A\Psi_B$ is in a pure spin state. Eq. (7) does not hold, however, when a singlet state dissociates into two doublet states, i.e., in the case of breaking the simplest chemical bond. In such a case Eq. (5) is not valid, and the exponential Ansatz is not useful at large R.

In general, when a low-spin system dissociates into high-spin ones, Eq. (7) must be modified by inserting a spin-projection operator $\hat{\Pi}$ in front of the antisymmetrizer $\mathcal{A}$. In the simplest case, when a singlet dissociates into two doublets one can easily show (by inspecting relevant spin functions) that both at the correlated or independent-particle level the spin-projection can be effected by the projection operator $\hat{\Pi} = \frac{1}{2}(1 + \hat{R}_{\pi/2})$, where the operator $\hat{R}_{\pi/2}$ rotates the spin functions α and β by 90°, i.e., performs the operation $\alpha \rightarrow \beta$, $\beta \rightarrow -\alpha$.

Substituting $\hat{\Pi}\,\mathcal{A}$ for $\mathcal{A}$ in Eq. (7), and following the reasoning presented between Eqs. (7) and (10), we find that now the asymptotic, large-R form of the wave function Ψ is

$$\lim_{R\rightarrow\infty} \Psi = \frac{1}{2}\,(1 + \hat{R}_{\pi/2})\,e^{T_A+T_B}\,\Phi = \frac{1}{2}\,e^{T}\,\Phi + \frac{1}{2}\,e^{T'}\,\Phi', \tag{11}$$

where $\Phi' = \hat{R}_{\pi/2}\,\Phi$, $T = T_A + T_B$, and $T' = \hat{R}_{\pi/2}\,T\,\hat{R}_{\pi/2}$. It should be noted that the function $2^{-1/2}(\Phi + \Phi')$ represents the conventional independent particle approximation to open-shell singlet, and that the operator T' is defined in the standard way but relative to the vacuum Φ'. Eq. (11) shows that for the dissociation to open-shell fragments a single exponential cannot be adequate, since asymptotically, at large R, the wave function does not factorize in the conventional way, given by Eq. (7). Only if we represent the wave function as a sum of exponentials, we have a chance that at large R the cluster operators will separate as $T_A + T_B$, with T_A and T_B equal or simply related to fragment's cluster operators.

Generalizing Eq. (11) to more complicated spin projections, and to even more general situations, when the asymptotics cannot be obtained by projection [56, 57], we can conjecture that a general quasidegenerate/multireference wave function can be written in the form

$$\Psi = \sum_{\mu=1}^{M} c_\mu\,e^{T^\mu}\,\Phi_\mu, \tag{12}$$

where Φ_μ, $\mu = 1, \ldots, M$ are determinants needed to obtain a correct zeroth-order approximation to Ψ, and each of the cluster operators T^μ is defined with respect to its own vacuum

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

Φ_μ. Eq. (12) is just the multireference coupled cluster Ansatz which Henk Monkhorst and myself proposed [58] during my first visit to QTP in 1981.

When Eq. (12) is formally applied to a set of quasidegenerate states, one obtains the following exponential Ansatz for the wave operator U

$$U = \sum_{\mu=1}^{M} e^{T^\mu} P_\mu, \tag{13}$$

where $P_\mu = | \Phi_\mu \rangle \langle \Phi_\mu |$ and the operators T^μ are universal for all exact states Ψ_ν in the range of U. The wave operator U is usually intermediately normalized such that $PU = P$ and $UP = U$, where

$$P = \sum_{\mu=1}^{M} P_\mu. \tag{14}$$

With this normalization, U may be viewed an the inverse of P if the domains of U and P are restricted to the manifolds spanned by the set of Ψ_ν's and Φ_μ's, respectively. One can easily show [58] that U is a non-orthogonal projector, $U^2 = U$, and that it satisfies the so-called Bloch equation [59]

$$HU = UHU, \tag{15}$$

where H is the Hamiltonian of the system. Because of the universal character of T^μ operators, the applications of Eq. (13) are usually referred to as the state-universal (SU) CC theories. Using Eq. (12), geared specifically to treat a single quantum state, leads to the state-selective (SS) MRCC methods.

The usefulness of Eq. (12), or Eq. (13), depends on the possibility of providing a proof that the amplitudes of T^μ's are connected and, in the final instance, on the quality of numerical results obtained using the Ansätze of Eqs. (12) and (13). The existence of the connectedness proof depends, in turn, on the specific method chosen to define approximate cluster amplitudes and is not guaranteed by Eqs. (12) and (13) themselves.

Since 1981 there appeared a large number of applications of Eqs. (12) and (13). The literature presenting these applications, or formal discussion of the Ansätze (12) and (13) includes now about 500 positions and is still growing. It is impossible to cite this literature here or even to acknowledge most of the significant contributions to the field of MRCC theory based on the Ansätze (12) or Eq. (13). Fortunately, there are two excellent reviews devoted specifically to this subject and the reader is referred to these reviews for bibliographical information. The 2002 review by Piecuch and Kowalski [60] is devoted to state-universal

For Peer Review Only

approaches and contains very competent presentation of theoretical developments until 2001, as well as an extensive, almost complete presentation of applications published until the same time. The very recent review by Paldus, Pittner and Čársky [61] has a broader scope. It can be recommended especially for the extensive and insightful discussion of state-selective MRCC approaches, sometimes only indirectly related to Eq. (12). In the two remaining sections of this perspective article I shall concentrate on the main features of state-universal and state-selective MRCC approaches which rely directly upon the application of Eq. (12) or Eq. (13).

III. STATE-UNIVERSAL CC THEORY

The SU-CC theory is formally simplest if one assumes that the *model space* $\mathcal{M}_0$, spanned by all determinants Φ_μ, is complete, i.e., invariant under unitary transformations of active orbitals (orbitals occupied in some but not in all Φ_μ's). In such a case the operators T^μ do not contain amplitudes with exclusively active labels. One can show that the knowledge of the operator U of the form of Eq. (13) is equivalent to the knowledge of all M full configuration interaction (FCI) solutions for the states Ψ_μ and that the cluster amplitudes defining T^μ operators can be uniquely expressed via the linear coefficients of these FCI solutions and vice versa [38, 62]. To obtain equations from which T^μ's can be directly computed, we insert Eq. (13) into Eq. (15), multiply the resulting equations from the right by $|\,\Phi_\mu\rangle$, premultiply by $\exp(-T^\mu)$ from the left and project against all excited states from the space $\mathcal{M}_0^\perp$ orthogonal to $\mathcal{M}_0$. The resulting SU-CC equation is

$$\langle\, \delta T^\mu\, \Phi_\mu \mid e^{-T^\mu} H\, e^{T^\mu} \Phi_\mu \rangle = \sum_{\nu \neq \mu}^{M} H^{\rm eff}_{\nu\mu}\, \langle\, \delta T^\mu\, \Phi_\mu \mid e^{-T^\mu} e^{T^\nu} \Phi_\nu \rangle, \tag{16}$$

where $H^{\rm eff}_{\nu\mu}$ is the effective Hamiltonian matrix [59]

$$H^{\rm eff}_{\nu\mu} = \langle\, \Phi_\nu \mid e^{-T^\mu} H e^{T^\mu}\, \Phi_\mu \rangle \tag{17}$$

and δT^μ is an arbitrary variation of T^μ, i.e., in practice, an arbitrary excitation operator contributing to T^μ. The SU-CC energies are obtained by diagonalizing the (nonsymmetric) matrix $H^{\rm eff}_{\nu\mu}$. The l.h.s. of Eq. (16) has the same form as the single-reference CC equation and is usually referred to as the direct term. The r.h.s. is referred to as the coupling term and is characteristic of the MR theory.

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

Assuming the completeness of the model space $\mathcal{M}_0$, one can prove [58] that the perturbation expansion of $H^{\rm eff}_{\nu\mu}$ and of the amplitudes of T^μ contains only connected diagrams, i.e, that the effective Hamiltonian and the cluster operators are connected objects. It should be noted that to represent the effective Hamiltonian in the explicitly connected form (17) one has to assume that

$$(T^\mu)^\dagger \, \Phi_\nu = 0. \tag{18}$$

This equation holds only if the model space $\mathcal{M}_0$ is complete.

Kucharski and Bartlett [63, 64] proposed another form of the SU-CC equation. For the complete model spaces their equation

$$\langle \, \delta T^\mu \, \Phi_\mu \mid (H - H^{\rm eff}_{\mu\mu}) \, e^{T^\mu} \Phi_\mu \rangle = \sum_{\nu \neq \mu}^{M} H^{\rm eff}_{\nu\mu} \, \langle \, \delta T^\mu \, \Phi_\mu \mid e^{T^\nu} \Phi_\nu \rangle, \tag{19}$$

is equivalent to Eq. (16). The subtraction of $H^{\rm eff}_{\mu\mu}$ from H on the l.h.s. leads to cancellation of numerous disconnected (and unlinked terms) but some disconnected ones (which, however, are linked) remain in the direct term. The coupling term in Eq. (19) is significantly simpler to code than the one in Eq. (16). For this reason the Kucharski-Bartlett form has been often used in practical applications [65–73]. Equation (19) is manifestly finite, what may not be immediately clear in the case of Eq. (16), especially when the Baker-Campbell-Hausdorff formula is used to expand the product of exponentials in terms of commutators.

In practical applications the cluster operators are expanded either in terms of spinorbital excitations, as in Eq. (2), or using the unitary group generators [74, 75] to preserve the spin symmetry of reference functions. Among early applications the former approach was adopted, e.g., in Refs. 65–69, 72, 73, 76, while the latter in Refs. 77–84. These early applications, carried out for very small model spaces and usually at the CCSD level of theory, have shown that the SU-CC method is capable of providing very accurate results, as long as no intruder states are present, in particular when reference determinants are degenerate or almost degenerate. As an example one can mention excellent results for the dissociation of the Li_2 molecule [66], for the singlet-triplet splitting in methylene [73, 83] or for the lowest singlet-singlet energy gap in methylene [81].

These early calculations have also shown [78, 80, 85], however, that the SU-CCSD equations may have unphysical solutions, that the physical solutions are hard to converge, and that a solution, which is physical in the degenerate region, may become unphysical in other

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

regions of nuclear geometries. It appears particularly troublesome that, as the homotopy theory calculations show [86], the number unphysical solutions is very large, by far larger than the number of solutions of the FCI equations or even the Bloch equation [87]. This is of course a consequence of the highly nonlinear form of the SU-CC equations. Some of the unphysical solutions may be related to the intruder states causing divergence of the multireference MBPT expansion but the number of the perturbed level crossings responsible for this divergence is smaller than the number of unphysical solutions [86]. This is certainly not a situation conducive to black-box type applications of the SU-CC theory. There is some hope, however, that the inclusion of higher than doubly-excited clusters will help to reduce the number of multiple solutions [60, 87, 88] and will alleviate problems with converging the SU-CC equations in physically relevant applications.

Clearly, the problems discussed above will get even more severe when the model space is larger, which will necessarily happen when the number of active orbitals is larger than two and the completeness of the model space is required. It is, thus, desired to relax the completeness requirement. Equation (13) is valid for incomplete, general model spaces (GMS) but, unfortunately, the connectedness proof given in Ref. 58 cannot be carried out in this case. In fact, one can show [58] that if the intermediate normalization is assumed ($PU = U$) in the GMS case, then the perturbation expansion of the effective Hamiltonian does contain some disconnected contribution, also in the case of a fully degenerate model space (in contradiction to the conjecture [89] based on diagrammatic arguments).

There are two ways to overcome this difficulty. One is to abandon the intermediate normalization and use the resulting freedom to eliminate disconnected terms. This solution was chosen by Meissner, Kucharski and Bartlett [64, 90, 91] and employed in practice by Balková et al [67]. Another approach was taken by Li and Paldus [92–97]. These authors maintain the intermediate normalization but show, both analytically and numerically [93, 94], that with a proper choice of the GMS one can obtain size-consistent (correctly dissociating) solutions of SU-CC equations. To achieve that one has to correctly handle the internal excitations (into the model space $\mathcal{M}_0$), which have to be included in the cluster operators to guarantee the convergence of the method to the FCI limit. Specifically, in the case of an GMS the cluster operators T^μ in Eq. (13) have to be replaced by the operators [58]

$$X^\mu = W^\mu + S^\mu + T^\mu, \tag{20}$$

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

where W^μ excites into $\mathcal{M}_0$, S^μ excites into states from $\mathcal{M}_0^\perp$ belonging also to the smallest complete model space $\mathcal{M}_\mathrm{c}$ containing $\mathcal{M}_0$, and T^μ excites into determinants from $\mathcal{M}_\mathrm{c}^\perp$. Similarly as before, T^μ does not contain excitations labeled by active orbitals only. The intermediate normalization $PU = P$ implies that

$$P\, e^{X^\mu}\, \Phi_\mu = \Phi_\mu, \tag{21}$$

and, consequently,

$$\langle \Phi_\nu \mid e^{W^\mu + S^\mu}\, \Phi_\mu \rangle = 0 \tag{22}$$

for $\nu \neq \mu$. After expanding the exponential and inspecting the lowest-order terms, one finds [58] that $W_1^\mu = 0$ and

$$\langle \Phi_\nu \mid W_2^\mu \Phi_\mu \rangle = -\frac{1}{2} \langle \Phi_\nu \mid S_1^\mu\, S_1^\mu \Phi_\mu \rangle \tag{23}$$

$$\langle \Phi_\nu \mid W_3^\mu \Phi_\mu \rangle = -\langle \Phi_\nu \mid S_1^\mu\, S_2^\mu + S_1^\mu\, W_2^\mu + \frac{1}{6} S_1^\mu\, S_1^\mu\, S_1^\mu \Phi_\mu \rangle. \tag{24}$$

These are the so-called C-conditions derived independently and presented in a different form by Li and Paldus [92]. These conditions show that the amplitudes of internal excitations (contained in W^μ) can be completely expressed via amplitudes of external excitations contained in the S^μ operator. It is difficult to say now which approach to incomplete model spaces is better but it appears that the intermediately normalized approach of Li and Paldus is more developed at the moment, e.g., triple excitations can be included [97, 98] in a noniterative way. It enables one to handle relatively large model spaces and yields excellent results in practical applications [96, 99], also for excited states [100, 101].

IV. STATE-SELECTIVE THEORIES

Since in majority of applications one is interested in a single quantum state, it is tempting to neglect other, possibly quasidegenerate states, and to concentrate on the chosen one, using the Ansatz of Eq. (12). One then immediately faces the difficulty that the number of free parameters in Eq. (12) is much larger than the number of FCI coefficients for a single state (even if we limit ourselves to, say, the CCSD approximation, the number of independent equations is smaller than the number of unknown amplitudes). Three solution of this problem, known as state-selective MRCC theories, have been developed thus far. These are the so-called Brillouin-Wigner (BW)[102–106] and Mukherjee (Mk)[107–111] approaches,

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

and the Hanrath method [112, 113]. In this section I shall briefly present the main features of these state-specific theories.

A. Brillouin-Wigner CC theory

The Brillouin-Wigner method is computationally simplest and is the most developed for chemical applications, see. e.g., Ref. 114–117. The original derivation was based on the wave operator theory [102–104]. However, the working BW-CC equation can be very easily derived by simple manipulations directly from Eq. (12). Assuming that the wave function Ψ of Eq. (12) is exact and satisfies the Schrödinger equation $(H - E)\Psi = 0$, we can write

$$\sum_{\mu=1}^{M} c_\mu \, (H - E) \, e^{T^\mu} \, \Phi_\mu = 0, \tag{25}$$

where E is the exact energy. Projecting Eq. (25) against model functions Φ_ν shows that, if the operators T^μ are known, the energy can be obtained by diagonalizing the effective Hamiltonian matrix

$$H^{\text{eff}}_{\nu\mu} = \langle \, \Phi_\nu \mid H e^{T^\mu} \, \Phi_\mu \rangle. \tag{26}$$

This form of $H^{\text{eff}}_{\nu\mu}$, valid also for incomplete model spaces, becomes equivalent to Eq. (17) when the model space is complete. If we now project Eq. (25) on the excited space $\mathcal{M}_0^\perp$ with the operator $Q = 1 - P$, and employ the sufficiency condition [61, 109], we find that

$$Q \, (H - E) \, e^{T^\mu} \, \Phi_\mu = 0. \tag{27}$$

In other words, the fulfillment of Eq. (27), with E being an eigenvalue of the matrix (26), guarantees that Ψ of Eq. (12) satisfies the Schrödinger equation (25). It should be stressed that the sufficiency condition cannot be applied directly to Eq. (25) (before projection with Q), because the resulting equation would not have a solution if the intermediate normalization $\langle \, \Phi_\nu \mid e^{T^\mu} \Phi_\mu \rangle = \delta_{\nu\mu}$ is enforced or would be trivially equivalent to the Schrödinger equation otherwise. Equation (27) is just the basic equation of the BW-CC theory. Further projection with the set of individual excited determinants brings this equation to the more familiar form,

$$\langle \, \delta T^\mu \, \Phi_\mu \mid (H - H^{\text{eff}}_{\mu\mu}) \, e^{T^\mu} \Phi_\mu \rangle = (E - H^{\text{eff}}_{\mu\mu}) \, \langle \, \delta T^\mu \, \Phi_\mu \mid e^{T^\mu} \Phi_\mu \rangle, \tag{28}$$

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

somewhat similar to the Kucharski-Bartlett form of the SU-CC equations. The l.h.s. of this equation contains connected and disconnected (but linked) terms. Now these disconnected terms do not cancel against the disconnected ones on the r.h.s. and, consequently, the BW-CC method is not size-consistent. One can also premultiply Eq. (27) with $\exp(-T^\mu)$ and, after some manipulation (involving the substitution of Q with $1-P$), obtain an apparently more connected form of the BW-CC equation

$$\langle\, \delta T^\mu\, \Phi_\mu \mid e^{-T^\mu} H\, e^{T^\mu} \Phi_\mu \rangle = \sum_{\nu=1}^{M} (H^{\rm eff}_{\nu\mu} - E\, \delta_{\mu\nu})\, \langle\, \delta T^\mu\, \Phi_\mu \mid e^{-T^\mu} \Phi_\nu \rangle. \tag{29}$$

The l.h.s. is now fully connected but the r.h.s. is disconnected, as it must be since for complete model spaces Eq. (29) is equivalent to Eq. (28). Approximate *a posteriori* size-consistency corrections to the BW-CC energies have been developed [105, 106, 118]. Some of these corrections [105] have turned out to give good results in practical applications [114–117]. The good accuracy achieved in recent applications of the BW-CC method was possible also due to the development of codes accounting for triple excitations [119–121]. Analytic gradients for the BW-CC method have also been developed [122].

B. Mukherjee's MkCC theory

Formally more satisfactory but computationally more demanding SS-MRCC theory was proposed by Mukherjee and collaborators [107–111]. The wave function in this method is also given by the MRCC Ansatz of Eq. (12) and the energy is obtained by diagonalizing the matrix (26). Also the derivation of equations for the cluster operators is based on Eq. (25) and on the sufficiency conditions but before these conditions are applied, one inserts the following resolution of identity in front of the μth term in Eq. (25)

$$1 = e^{T^\mu}\, P\, e^{-T^\mu} + e^{T^\mu}\, Q\, e^{-T^\mu}. \tag{30}$$

After expanding P as the sum of one-dimensional projectors $\mid \Phi_\nu\rangle\langle\Phi_\nu \mid$, one obtains

$$\sum_{\mu=1}^{M} c_\mu\, e^{T^\mu}\, Q\, e^{-T^\mu} (H - E)\, e^{T^\mu} \Phi_\mu + \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} c_\mu\, (H^{\rm eff}_{\nu\mu} - E\, \delta_{\mu\nu})\, e^{T^\mu}\, \Phi_\nu = 0, \tag{31}$$

where $H^{\rm eff}_{\nu\mu}$ is now given by Eq. (17), i.e., is in the explicitly connected form, even for incomplete model spaces. To apply the sufficiency conditions to Eq. (31), Mukherjee et

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

al changed the summation order in the second term and relabeled the summation indexes $\mu \leftrightarrow \nu$. The resulting equations, sufficient for the fulfillment of Eq. (25), are

$$c_\mu \, e^{T^\mu} \, Q \, e^{-T^\mu} (H - E) \, e^{T^\mu} \Phi_\mu + \sum_{\nu=1}^{M} c_\nu \, (H^{\rm eff}_{\mu\nu} - E \, \delta_{\mu\nu}) \, e^{T^\nu} \, \Phi_\mu = 0. \tag{32}$$

Premultiplication with $\exp(-T^\mu)$ and projections against excited states $\delta T^\mu \Phi_\mu$ leads to the conventional from of the amplitude equation in the Mukherjee's theory:

$$c_\mu \, \langle \delta T^\mu \Phi_\mu \, | \, e^{-T^\mu} \, H \, e^{T^\mu} \Phi_\mu \rangle + \sum_{\nu \neq \mu}^{M} c_\nu \, H^{\rm eff}_{\mu\nu} \, \langle \delta T^\mu \Phi_\mu \, | \, e^{-T^\mu} e^{T^\nu} \, \Phi_\mu \rangle = 0. \tag{33}$$

Equation (33) bears some similarity to the SU-CC equation (16) but there are essential formal differences. Firstly, Eq. (33) involves the combining coefficients c_μ for the state of interest, so that the process of solving it is not independent of the stage of diagonalization the effective Hamiltonian, which must be done in each iteration. Secondly, the structure of the coupling term is significantly simpler [123] because the bra and ket vectors are expressed with respect of the same vacuum. Mukherjee et al proved [107–109] that their method is size-extensive and size-consistent, when localized active orbitals are used. It is also resistant to intruder states as long as the target energy E is well separated from the energies of states evolving from $\mathcal{M}_0^\perp$. A number of applications of Mukherjee's theory have been already reported in the literature [99, 123–131], most of them carried out by Evangelista and collaborators [123, 125, 126, 128, 131], who introduced the abbreviation MkCC for this version of the MRCC theory. These applications, accounting also for triple excitations, showed that the MkCC method performs very well and usually gives better results than the SU-CC and BW-CC approaches. On should add that also the analytical gradient of the MkCC energies was also developed [129]. Very recently a study of the MkCC method, based on a new string-based [132, 133] implementation, has been presented [134]. This very informative study discusses also convergence problems which hamper the transformation of the MkCC method into an efficient black-box procedure.

One should also mention that a linked (not explicitly connected) formulation of the MkCC method is possible and has been recently presented [135]. In this formulation Eq. (32) is not premultiplied with e^{-T^μ} but is directly projected against $\delta T^\mu \Phi_\mu$. The resulting "linked" form of the MkCC equation [61, 135],

$$c_\mu \, \langle \delta T^\mu \Phi_\mu \, | \, (H - H^{\rm eff}_{\mu\mu}) \, e^{T^\mu} \Phi_\mu \rangle + \sum_{\nu=1}^{M} c_\nu \, H^{\rm eff}_{\mu\nu} \, \langle \delta T^\mu \Phi_\mu \, | \, e^{T^\nu} \, \Phi_\mu \rangle = 0, \tag{34}$$

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

is equivalent to Eq. (33) if the model space is complete. In such a case we can use Eq. (18) to substitute $1-\mid\Phi_\mu\rangle\langle\Phi_\mu\mid$ for Q in Eq. (32) and obtain the first term in Eq. (34). This term is identical with the l.h.s. of the Kucharski-Bartlett form of the BW-CC equation (28). The advantage of using Eq. (34) stems from the fact that the coupling term involves a single exponential and is easier to code. By employing Eq. (34), the MkCC codes can be obtained by a modification of the BW-CC codes.

C. Hanrath's MRexpT theory

A very original solution to the problem of the redundant amplitudes in a state-specific application of Ansatz (12) has been proposed by Hanrath [112, 113]. Generally speaking the idea of the Hanrath method, referred to by him as the MRexpT method, is to parametrize all T^μ operators with a single set of amplitudes, uniquely assigned to excited determinants rather than to excitation operators. Let us consider, for example, the case of single and double excitations out of the model space $\mathcal{M}_0$. The linear span of all determinants from $\mathcal{M}_0^\perp$, which can be obtained by replacing a single spinorbital in one of Φ_μ functions, will be denoted by $\mathcal{M}_1$. The subspace of double excitations $\mathcal{M}_2$ is defined similarly as the subspace of $\mathcal{M}_0^\perp \ominus \mathcal{M}_1$ spanned by the determinants that can be obtained by double substitutions from determinants in $\mathcal{M}_0$. The orthogonal sum $\mathcal{M}_1 \oplus \mathcal{M}_2$ is just the MRCISD excitation space. Hanrath employs Eq. (12) for the wave function and assumes that the cluster operators have the form

$$T^\mu = e^{-i\arg(c_\mu)} \sum_I^\mu t_I \hat{G}_I^\mu, \tag{35}$$

where the superscript μ at the summation sign indicates that the sum runs over those determinants Φ_I from $\mathcal{M}_1 \oplus \mathcal{M}_2$ which are singly or doubly excited relative to Φ_μ. For each I and μ, the excitation operator $\hat{G}_I^\mu$ is uniquely defined by

$$\Phi_I = \hat{G}_I^\mu \Phi_\mu. \tag{36}$$

Thus, each T^μ is a sum of all single and double excitation operators but the single set of amplitudes t_I is used to parametrize all T^μ's. The phase factor $e^{-i\arg(c_\mu)}$ in Eq. (35) was introduced to guarantee the potential completeness of the proposed wave-function Ansatz [112, 113]. The total number of coefficients c_μ and the amplitudes t_I is the same as the number of MRCI coefficients, so the redundancy problem is resolved. The c_μ coefficients

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

and the energy are obtained by diagonalizing the effective Hamiltonian (17) and the t_I coefficients by solving the MRexpT equations of the form

$$\sum_{\mu=1}^{M} c_\mu \langle \Phi_I | (H - E)\, e^{T^\mu}\, \Phi_\mu \rangle = 0, \tag{37}$$

where Φ_I are determinants spanning $\mathcal{M}_1 \oplus \mathcal{M}_2$. Hanrath has shown that the energy obtained by solving these equations is size consistent [112] and core but not "valence" [136, 137] extensive. Hanrath argues [138] that the set of active, i.e. "valence" orbitals is typically not large, so this limitation should not be too restrictive. Several applications of the Hanrath method, performed thus far small model systems [112, 139–142], indicate that the MRexpT method has a potential to be very accurate. A theoretical rationalization of a more satisfactory performance of this method, as compared to other state-selective MRCC approaches, has been given recently by Kong [143]. A drawback of the MRexpT method is that, due to the determinantal indexing, the resulting amplitude equations are extraordinarily complex and cannot be derived and solved using standard techniques developed during the last decades by the coupled cluster community. A new, efficient implementation of the general (arbitrary excitation order) coupled cluster code [144] can be expected to help to circumvent this difficulty.

V. CONCLUDING REMARKS

Despite the enormous progress made in the understanding and implementation of the MRCC Ansatz of Eq. (12), none of the proposed methods is close to routine black-box type applications. Such applications would require, e.g., an availability of analytical gradients and very little has been done in this area, both in the state-universal [122, 145–148] and state-specific [122, 129] subfields.

There are two major sources of difficulties which still need to be seriously addressed. The first one is the excessively large number of amplitudes, especially when the full extensivity of the theory is required, and the second, is the difficulty in converging the MRCC equations, resulting from their highly nonlinear structure. The MRexpT method of Hanrath [112, 139–142] and the C-conditions method of Li and Paldus [92–97] seem to offer a promising solution of the first problem. On should also point out that the incomplete model spaces and the C-conditions can also be used in the state-selective framework – in the BW-CC [119] and

For Peer Review Only

MkCC [149, 150] approaches. Another possibility was chosen by Kowalski and Piecuch [60, 151], who approximated the core-virtual bi-excited amplitudes by perturbation theory and obtained very good results with a greatly reduced number of variables in the nonlinear CC equations. In fact, this core-virtual bi-excited amplitudes are, through the first order of perturbation theory, independent of μ and one may contemplate to determine them non-perturbatively from MRCC equation assuming that they are the same for all μ's through all orders [152]. One should also mention that the number of amplitudes per considered quantum state is usually much smaller in the SU-CC applications, as compared to the applications of the SS-MRCC theories. From this perspective, the results of applying the SU-CC Ansatz in such a way that each T^{μ} includes excitation to all determinants from the MRCISD space $\mathcal{M}_1 \oplus \mathcal{M}_2$ would be very informative.

The difficulties to converge the solutions of MRCC equations may be overcome by using better convergence acceleration or equation regularization techniques [134], or by including higher excitations in T^{μ}, which should reduce the number of unphysical solutions [60, 86] hampering convergence to the physical ones. A promising way of solving these convergence difficulty, successfully applied in the context of the Fock space CC theory [42], is to use the intermediate-Hamiltonian approach to reformulate the SU-CC equations [153].

Another difficulty of the MRCC approaches relying on the Ansatz (12), is the lack of invariance to rotations of active orbitals [134, 154, 155] (this Ansatz and the resulting SU-CC, BW-CC, MkCC, and MRexpT approaches are, however, fully invariant to separate rotations of core and virtual orbitals). This lack of invariance is less severe if the $\mathcal{M}_1 \oplus \mathcal{M}_2$ space is chosen as the range of all T^{μ} operators [131], but it is to be determined how significant this lack of invariance is in practice (probably is not very significant in applications of the general model space method of Li and Paldus [92–97]).

One should also mention that is it possible to improve the results of SU-CCSD calculations by approximately accounting for higher than double excitations. This has been done using appropriate generalization [156, 157] of the method of moments [158] or by merging the SU-CC method [159] with the reduced multireference (RMR) coupled cluster approach of Li and Paldus [160, 161].

In conclusion, during the last decade we have witnessed a remarkable progress in the development of MRCC methods relying on the Ansatz (12). It is very impressive how much ingenuity and insight has been invested in this development. Although a black-box MRCC

URL: http://mc.manuscriptcentral.com/tandf/tmph

For Peer Review Only

method is not in sight, I believe that these developments have brought us much closer to the situation when the MRCC methods will be routinely used in the hands of competent theoretical chemists to solve well defined classes of multireference problems of experimental interest.

Acknowledgments

On this occasion I would like to thank Henk Monkhorst for my five enjoyable visits to QTP and for the pleasure of collaborating with him on several projects throughout the decade of 1980s. I also thank Michael Hanrath, Debashis Mukherjee, Josef Paldus, Piotr Piecuch, and Jiří Pittner for valuable comments on the manuscript.

[1] F. Coester, Nucl. Phys. **7**, 421 (1958).

[2] F. Coester and H. Kümmel, Nucl. Phys. **17**, 477 (1960).

[3] J. Čížek, J. Chem. Phys. **45**, 4256 (1966).

[4] J. Čížek and J. Paldus, Int. J. Quantum Chem. **9**, 105 (1971).

[5] J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A **5**, 50 (1972).

[6] R. J. Bartlett and G. D. Purvis III, Int. J. Quantum Chem. **14**, 561 (1978).

[7] J. Pople, R. Krishnan, and J. Schlegel, H.B. ans Binkley, Int. J. Quantum Chem. **14**, 545 (1978).

[8] H. Kümmel, Theor. Chim. Acta **80**, 81 (1991).

[9] J. Čížek, Theor. Chim. Acta **80**, 91 (1991).

[10] J. Paldus, in *Theory and Applications of Computational Chemistry: The First 40 Years. A Volume of Technical and Historical Perspectives*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, Amsterdam, 2005), p. 115.

[11] R. J. Bartlett, in *Theory and Applications of Computational Chemistry: The First 40 Years. A Volume of Technical and Historical Perspectives*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, Amsterdam, 2005), p. 1191.

[12] F. E. Harris, Int. J. Quantum Chem. Symp. **11**, 403 (1977).

[13] H. J. Monkhorst, Int. J. Quantum Chem. Symp. **11**, 421 (1977).

For Peer Review Only

[14] F. E. Harris, B. Jeziorski, and H. J. Monkhorst, Phys. Rev. A **23**, 1632 (1981).

[15] H. J. Monkhorst, B. Jeziorski, and F. E. Harris, Phys. Rev. A **23**, 1639 (1981).

[16] A. Banerjee and J. Simons, Int. J. Quantum Chem. **19**, 207 (1981).

[17] B. Jeziorski, H. J. Monkhorst, K. Szalewicz, and J. G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984).

[18] N. Oliphant and L. Adamowicz, J. Chem. Phys. **94**, 1229 (1991).

[19] P. Piecuch, N. Oliphant, and L. Adamowicz, J. Chem. Phys. **99**, 1875 (1993).

[20] L. Z. Stolarczyk, Chem. Phys. Lett. **217**, 1 (1994).

[21] J. Paldus and J. Planelles, Theor. Chim. Acta **89**, 13 (1994).

[22] P. Piecuch and L. Adamowicz, J. Chem. Phys. **102**, 898 (1995).

[23] P. Piecuch, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **110**, 6103 (1999).

[24] X. Li and J. Paldus, J. Chem. Phys. **124**, 174101 (2006).

[25] X. Li and J. Paldus, J. Chem. Phys. **129**, 054104 (2008).

[26] V. V. Ivanov, D. I. Lyakh, and L. Adamowicz, Phys. Chem. Chem. Phys. **11**, 2355 (2009).

[27] R. Offermann, W. Ey, and H. Kümmel, Nucl. Phys. A **273**, 349 (1976).

[28] R. Offermann, Nucl. Phys. A **273**, 368 (1976).

[29] D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. **33**, 955 (1977).

[30] I. Lindgren, Int. J. Quantum Chem. Symp. **12**, 33 (1978).

[31] D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Pramana **4**, 247 (1975).

[32] D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. **30**, 1861 (1975).

[33] W. Kutzelnigg, J. Chem. Phys. **77**, 3081 (1982).

[34] W. Kutzelnigg and S. Koch, J. Chem. Phys. **79**, 4315 (1983).

[35] W. Kutzelnigg, J. Chem. Phys. **80**, 822 (1984).

[36] L. Z. Stolarczyk and H. J. Monkhorst, Phys. Rev. A **32**, 725 (1985).

[37] L. Z. Stolarczyk and H. J. Monkhorst, Phys. Rev. A **32**, 743 (1985).

[38] B. Jeziorski and J. Paldus, J. Chem. Phys. **90**, 2714 (1989).

[39] D. Sinha, S. K. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, Chem. Phys. Lett. **154**, 544 (1989).

[40] L. Meissner and R. J. Bartlett, J. Chem. Phys. **94**, 6670 (1991).

[41] D. Mukhopadhyay, S. K. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, Theor. Chim. Acta **80**, 441 (1991).

For Peer Review Only

[42] L. Meissner, J. Chem. Phys. **108**, 9227 (1998).

[43] M. Nooijen and J. G. Snijders, Int. J. Quantum Chem. **48**, 15 (1992).

[44] J. F. Stanton and J. Gauss, J. Chem. Phys. **101**, 8938 (1994).

[45] M. Musiał, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **118**, 1128 (2003).

[46] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **102**, 3629 (1995).

[47] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **102**, 6735 (1995).

[48] M. Musiał and R. J. Bartlett, J. Chem. Phys. **119**, 1901 (2003).

[49] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem. Symp. **18**, 255 (1984).

[50] J. Geertsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989).

[51] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).

[52] M. Musiał and R. J. Bartlett, J. Chem. Phys. **129**, 134105 (2008).

[53] M. Musiał and R. J. Bartlett, J. Chem. Phys. **129**, 044101 (2008).

[54] R. Ahlrichs, Theor. Chim. Acta **41**, 7 (1976).

[55] B. Jeziorski and W. Kołos, in *Molecular Interactions*, edited by H. Ratajczak and W. Orville-Thomas (Wiley, New York, 1982), vol. 3, p. 1.

[56] D. Klein, Int. J. Quantum Chem. **32**, 377 (1987).

[57] T. Korona, B. Jeziorski, R. Moszyński, and G. H. F. Diercksen, Theor. Chem. Acc. **101**, 282 (1999).

[58] B. Jeziorski and H. J. Monkhorst, Phys. Rev. A **24**, 1668 (1981).

[59] J. Paldus and X. Li, Adv. Chem. Phys. **110**, 1 (1999).

[60] P. Piecuch and K. Kowalski, Int. J. Mol. Sci. **3**, 676 (2002).

[61] J. Paldus, J. Pittner, and P.Čársky, in *Recent Progress in Coupled-Cluster Methods: Theory and Applications*, edited by P. Čársky, J. Paldus, and J. Pittner (Springer, Berlin, 2010), p. 455.

[62] J. Paldus and X. Li, J. Chem. Phys. **118**, 6769 (2003).

[63] S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **95**, 8227 (1991).

[64] S. A. Kucharski and R. J. Bartlett, Int. J. Quantum Chem. Symp. **26**, 107 (1992).

[65] A. Balková, S. A. Kucharski, L. Meissner, and R. J. Bartlett, Theor. Chim. Acta **80**, 335 (1991).

[66] A. Balková, S. A. Kucharski, and R. J. Bartlett, Chem. Phys. Lett. **182**, 511 (1991).

[67] A. Balková, S. A. Kucharski, L. Meissner, and R. J. Bartlett, J. Chem. Phys. **95**, 4311 (1991).

For Peer Review Only

[68] A. Balková and R. J. Bartlett, Chem. Phys. Lett. **193**, 364 (1992).

[69] S. A. Kucharski, A. Balková, P. Szalay, and R. J. Bartlett, J. Chem. Phys. **97**, 4289 (1992).

[70] S. Berkovic and U. Kaldor, Chem. Phys. Lett. **199**, 42 (1992).

[71] S. Berkovic and U. Kaldor, J. Chem. Phys. **98**, 3090 (1993).

[72] A. Balková and R. J. Bartlett, J. Chem. Phys. **101**, 8972 (1994).

[73] A. Balková and R. J. Bartlett, J. Chem. Phys. **102**, 7116 (1995).

[74] J. Paldus and B. Jeziorski, Theor. Chim. Acta **73**, 81 (1988).

[75] B. Jeziorski, J. Paldus, and P. Jankowski, Int. J. Quantum Chem. **56**, 129 (1995).

[76] L. Meissner, K. Jankowski, and J. Wasilewski, Int. J. Quantum Chem. **34**, 535 (1988).

[77] B. Jeziorski and J. Paldus, J. Chem. Phys. **88**, 5673 (1988).

[78] J. Paldus, L. Pylypow, and B. Jeziorski, in *Many-Body Methods in Quantum Chemistry*, edited by U. Kaldor (Springer, New York, 1989), vol. 52 of *Lecture Notes in Chemistry*, p. 151.

[79] J. Paldus, P. Piecuch, B. Jeziorski, and L. Pylypow, in *Recent Progress in Many-Body Theories*, edited by T. L. Ainsworth, C. E. Campbell, B. E. Clements, and E. Krotschek (Plenum Press, New York, 1992), vol. 3, p. 287.

[80] J. Paldus, P. Piecuch, L. Pylypow, and B. Jeziorski, Phys. Rev. A **47**, 2738 (1993).

[81] P. Piecuch and J. Paldus, J. Chem. Phys. **101**, 5875 (1994).

[82] X. Li, J. Paldus, and P. Piecuch, Chem. Phys. Lett. **224**, 267 (1994).

[83] P. Piecuch, X. Li, and J. Paldus, Chem. Phys. Lett. **230**, 377 (1994).

[84] X. Li and J. Paldus, J. Chem. Phys. **101**, 8812 (1994).

[85] P. Piecuch and J. Paldus, Phys. Rev. A **49**, 3479 (1994).

[86] K. Kowalski and P. Piecuch, Phys. Rev. A **61**, 052506 (2000).

[87] K. Kowalski and P. Piecuch, Int. J. Quantum Chem. **80**, 757 (2000).

[88] P. Piecuch, R. Tobola, and J. Paldus, Chem. Phys. Lett. **210**, 243 (1993).

[89] G. Hose and U. Kaldor, J. Phys. B **12**, 3827 (1979).

[90] L. Meissner, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **91**, 6187 (1989).

[91] L. Meissner and R. J. Bartlett, J. Chem. Phys. **91**, 561 (1990).

[92] X. Li and J. Paldus, J. Chem. Phys. **119**, 5320 (2003).

[93] X. Li and J. Paldus, J. Chem. Phys. **119**, 5346 (2003).

[94] X. Li and J. Paldus, Int. J. Quantum Chem. **99**, 914 (2004).

For Peer Review Only

[95] X. Li and J. Paldus, J. Chem. Phys. **120**, 5890 (2004).

[96] X. Li and J. Paldus, Mol. Phys. **104**, 661 (2006).

[97] X. Li and J. Paldus, J. Chem. Phys. **124**, 034112 (2006).

[98] X. Li and J. Paldus, Mol. Phys. **104**, 2047 (2006).

[99] X. Li and J. Paldus, J. Chem. Phys. **131**, 114103 (2009).

[100] X. Li and J. Paldus, J. Phys. Chem. A **114**, 8591 (2010).

[101] X. Li and J. Paldus, Int. J. Quantum Chem. Symp. **000**, 0000 (2010).

[102] I. Hubač, in *New Methods in Quantum Theory*, edited by A. Tsipis, V. S. Popov, D. R. Herschbach, and J. S. Avery (Kluver, Dordrecht, 1996), p. 183.

[103] J. Mášik and I. Hubač, Adv. Quantum Chem. **31**, 75 (1999).

[104] J. Pittner, P. Nachtigall, P. Čársky, J. Mášik, and I. Hubač, J. Chem. Phys. **110**, 10275 (1999).

[105] I. Hubač, J. Pittner, and P. Čársky, J. Chem. Phys. **112**, 8779 (2000).

[106] J. Pittner, J. Chem. Phys. **118**, 10876 (2003).

[107] U. S. Mahapatra, B. Datta, B. Bandyopadhyay, and D. Mukherjee, Adv. Quantum Chem. **30**, 163 (1998).

[108] U. S. Mahapatra, B. Datta, and D. Mukherjee, Mol. Phys. **94**, 157 (1998).

[109] U. S. Mahapatra, B. Datta, and D. Mukherjee, J. Chem. Phys. **110**, 6171 (1999).

[110] U. S. Mahapatra, B. Datta, and D. Mukherjee, J. Phys. Chem. A **103**, 1822 (1999).

[111] D. Pahari, S. Chattopadhyay, S. Das, and D. Mukherjee, Chem. Phys. Lett. **381**, 223 (2003).

[112] M. Hanrath, J. Chem. Phys. **123**, 84102 (2005).

[113] M. Hanrath, Chem. Phys. Lett. **420**, 426 (2006).

[114] O. Demel, J. Pittner, P. Čársky, and I. Hubač, J. Phys. Chem. A **108**, 3125 (2004).

[115] I. S. K. Kerkines, P. Čársky, and A. Mavridis, J. Phys. Chem. A **109**, 10148 (2005).

[116] J. Brabec and J. Pittner, J. Phys. Chem. A **110**, 11765 (2006).

[117] L. Veis, P. Čársky, J. Pittner, and J. Michl, J. Phys. Chem. A **108**, 3125 (2004).

[118] J. Pittner and P. Piecuch, Mol. Phys. **107**, 1209 (2009).

[119] J. Pittner and O. Demel, J. Chem. Phys. **122**, 181101 (2005).

[120] O. Demel and J. Pittner, J. Chem. Phys. **124**, 144112 (2006).

[121] O. Demel and J. Pittner, J. Chem. Phys. **128**, 104108 (2008).

[122] J. Pittner and J. Šmydke, J. Chem. Phys. **127**, 114103 (2007).

For Peer Review Only

[123] F. A. Evangelista, W. D. Allen, and H. F. Schaefer III, J. Chem. Phys. **127**, 024102 (2007).

[124] S. Chattopadhyay:04, P. Ghosh, and U. S. Mahapatra, J. Phys. B **37**, 495 (2004).

[125] F. A. Evangelista, W. D. Allen, and H. F. Schaefer III, J. Chem. Phys. **125**, 154113 (2006).

[126] F. A. Evangelista, A. C. Simmonett, W. D. Allen, H. F. Schaefer III, and J. Gauss, J. Chem. Phys. **128**, 124104 (2008).

[127] K. Bhaskaran-Nair, O. Demel, and J. Pittner, J. Chem. Phys. **129**, 184105 (2008).

[128] F. A. Evangelista, A. C. Simmonett, H. F. Schaefer III, D. Mukherjee, and W. Allen, Phys. Chem. Chem. Phys. **11**, 4728 (2008).

[129] E. Prochnov, F. A. Evangelista, H. F. Schaefer III, W. D. Allen, and J. Gauss, J. Chem. Phys. **131**, 064109 (2009).

[130] B. K. Carpenter, J. Pittner, and L. Veis, J. Phys. Chem. A **113**, 10557 (2009).

[131] F. A. Evangelista, E. Prochnov, J. Gauss, and H. F. Schaefer III, J. Chem. Phys. **132**, 074107 (2010).

[132] M. Kallay and P. R. Surjan, J. Chem. Phys. **115**, 2945 (2001).

[133] M. Kallay, P. G. Szalay, and P. R. Surjan, J. Chem. Phys. **117**, 980 (2001).

[134] S. Das, D. Mukherjee, and M. Kallay, J. Chem. Phys. **132**, 074103 (2010).

[135] K. Bhaskaran-Nair, O. Demel, and J. Pittner, J. Chem. Phys. **132**, 154105 (2010).

[136] M. Hanrath, Theor. Chim. Acta **121**, 187 (2008).

[137] M. Hanrath, Chem. Phys. **356**, 31 (2009).

[138] A. Engels-Putzka and M. Hanrath, J. Mol. Struct. (THEOCHEM) **902**, 59 (2009).

[139] M. Hanrath, J. Chem. Phys. **128**, 154118 (2008).

[140] M. Hanrath, Mol. Phys. **106**, 1949 (2008).

[141] A. Engels-Putzka and M. Hanrath, Mol. Phys. **107**, 143 (2009).

[142] M. Hanrath and A. Engels-Putzka, Theor. Chim. Acta **122**, 197 (2009).

[143] L. Kong, Int. J. Quantum Chem. **109**, 441 (2009).

[144] M. Hanrath and A. Engels-Putzka, J. Chem. Phys. **133**, 064108 (2010).

[145] P. G. Szalay, Int. J. Quantum Chem. **55**, 151 (1994).

[146] P. G. Szalay and R. J. Bartlett, J. Chem. Phys. **101**, 4936 (1995).

[147] K. R. Shamasundar and S. Pal, J. Chem. Phys. **114**, 1981 (2001).

[148] K. R. Shamasundar and S. Pal, J. Chem. Phys. **115**, 1979 (2001).

[149] X. Li and J. Paldus, Chem. Phys. Lett. **496**, 183 (2010).

For Peer Review Only

[150] X. Li and J. Paldus, J. Chem. Phys. **000**, 0000 (2010).

[151] K. Kowalski and P. Piecuch, Chem. Phys. Lett. **334**, 89 (2001).

[152] S. Das, S. Pathak, R. Maitra, and D. Mukherjee, in *Recent Progress in Coupled-Cluster Methods: Theory and Applications*, edited by P. Čársky, J. Paldus, and J. Pittner (Springer, Berlin, 2010), p. 57.

[153] E. Eliav, A. Borschevsky, K. R. Shamasundar, S. Pal, and U. Kaldor, Int. J. Quantum Chem. **109**, 2909 (2009).

[154] L. Kong, Int. J. Quantum Chem. **110**, 2603 (2010).

[155] F. A. Evangelista and J. Gauss, J. Chem. Phys. **000**, 000 (2010).

[156] K. Kowalski and P. Piecuch, J. Mol. Struct. (THEOCHEM) **547**, 191 (2001).

[157] K. Kowalski and P. Piecuch, Mol. Phys. **102**, 2425 (2004).

[158] P. Piecuch and K. Kowalski, in *Computational Chemistry: Reviews of current Trends*, edited by J. Leszczynski (World Scientific, Singapore, 2000), p. 1.

[159] X. Li and J. Paldus, J. Chem. Phys. **119**, 5334 (2003).

[160] X. Li and J. Paldus, J. Chem. Phys. **110**, 2844 (1999).

[161] X. Li and J. Paldus, J. Chem. Phys. **113**, 9966 (2000).

For Peer Review Only