CHEMICAL REVIEWS

REVIEW

pubs.acs.org/CR

Multireference Nature of Chemistry: The Coupled-Cluster View

Dmitry I. Lyakh,* Monika Musiał, Victor F. Lotrich, and Rodney J. Bartlett

Quantum Theory Project, University of Florida, Gainesville, Florida 32611, United States

CONTENTS

1. INTRODUCTION

> "The more accurate the calculations become the more concepts tend to vanish into thin air."
>
> Robert S. Mulliken

The coupled cluster (CC) theory has played a revolutionary role in establishing a new level of accuracy in electronic structure calculations and quantum chemical simulations. Thirty years of active development have resulted in a variety of CC methods capable of providing ~1 kcal/mol accuracy (*chemical accuracy*) in calculations of the electronic correlation energy for chemical systems with up to hundreds of correlated electrons. Reliable geometry optimization, thermochemical and spectroscopic predictions, weak interaction modeling, and other theoretical problems can be accurately treated with the existing CC machinery.

Despite the huge progress made in the field, several classes of quantum chemical problems are still awaiting a more reliable

Special Issue: 2012 Quantum Chemistry

Received: April 27, 2011
Published: December 28, 2011

ACS Publications

dx.doi.org/10.1021/cr2001417 | *Chem. Rev.* 2012, 112, 182–243

solution. Namely, we are talking about the description of electronic structure of chemical systems plagued by "*quasidegeneracy*". Quasidegeneracy exhibits itself through the presence of *several* leading components in the wave function, thus breaking the accuracy of the Hartree−Fock approach and seriously deteriorating the accuracy of those correlation models which rely on the "*single-determinant*" assumption. Unfortunately, many chemical (especially photochemical) processes fall into this category. Description of homolytic bond breaking/formation, open-shell and excited electronic states, transition-metal complexes, and transition states of chemical reactions are the examples of quasidegenerate (*multireference*, MR) problems. In such cases, conventional CC approaches (called *single-reference*, SR) often fail to provide a meaningful result, being far from the chemical accuracy. Complementary CC methods, which are supposed to extend the practical applicability of CC theory to quasidegenerate phenomena, form the *multireference CC theory* (MRCC).

Interestingly, the MRCC theory started approximately at the same time as the SRCC theory (conventional CC theory). However, even now the situation in the MRCC field is not satisfactory, since none of the MRCC methods is in a wide use (for different reasons). Nevertheless, recent advances in MRCC theory make us believe that things can be changed in a positive way. In this review, we would like to summarize and critically analyze numerous efforts put forth to solve quasidegenerate (multireference) problems with the CC theory. We hope that our critical analysis and broad vision of the problem can facilitate a "synthesis" of an ultimate MRCC route (routes) in the nearest future. This would significantly extend the domain of reliable (chemically accurate) applicability of CC theory.

The review is organized as follows. In section 2, we remind the reader of the origins of the CC theory, stressing its very important formal property called *size-extensivity*. Subsequently, we expose the reasons why the conventional SRCC theory fails in solving MR problems. Thus, we motivate the necessity of a proper MRCC extension of the CC theory. In section 3 we address the so-called "*genuine*" *Hilbert-space* MRCC methodology, including the classical *multistate* approaches based on the *effective* Hamiltonian, the "*state-specific*" formulations, and the recently advanced *internally contracted* MRCC methods (which look quite promising). In section 4, we address the so-called "*genuine*" *Fock-space* MRCC methods, which can simultaneously compute electronic states with a different number of particles (contrary to the Hilbert-space MRCC theory). We describe the classical *valence-universal* MRCC approaches (based on the *effective* Hamiltonian) as well as the formulations based on the *intermediate* Hamiltonian (which efficiently overcome the *intruder* state problem). In section 5 we proceed to *alternative* MRCC schemes, which simply adjust the SRCC formalism to MR problems (in most cases by properly extending the SRCC wave function). Such methods include the SRMRCC theory, the "*externally corrected*" approaches, the *equation-of-motion* based CC techniques, the CC *method of moments*, the *orbital optimized* CC approaches, the CC schemes inspired by the generalized-valence-bond method, and the so-called "*adaptive*" and "*semiadaptive*" CC approaches. Besides the pure CC theory, the "*dressed*" MRCI (multireference configuration interaction) approaches are also briefly discussed. Finally, in section 6 we collected numerous numerical results which are used to complement our theoretical analysis of MRCC methods. Our conclusions are given in section 7.

2. EXPONENTIAL ERA OF ELECTRON CORRELATION THEORY

2.1. Separability/Extensivity Properties and the Origins of the Coupled Cluster Theory

The electron correlation theory was given a second birth with the emergence of the *coupled cluster* (CC) theory, the most prominent many-body method for constructing correlated many-particle wave functions. The exponential form of the correlated wave operator, called the *exponential ansatz*, is the distinguishing feature of the coupled cluster theory:

$$|\Psi\rangle = e^{\hat{T}}|0\rangle \tag{2.1.1}$$

where $|\Psi\rangle$ is the N-electron CC wave function, $|0\rangle$ is an N-electron *reference* Slater determinant also called the *Fermi vacuum* (for example, the Hartree−Fock determinant), and $\hat{T}$ is an *excitation operator* which generates a manifold of *excited* determinants by promoting electrons from *occupied* orbitals of the reference determinant to the *virtual* ones.[1] Contrary to the configuration interaction (CI) theory, the excitation operator is exponentiated. The exponential representation first appeared in the paper of Hubbard,[2,3] which is viewed as the natural inverse of the *linked diagram* theorem (LDT) of Brueckner and Goldstone,[4−10] which was usually written via a logarithm. The $e^{\hat{T}}$ construct naturally provided an infinite-order summation of the linked diagrams of *many-body perturbation theory* (MBPT).[11] It was then considered in nuclear physics by Coester and Kümmel,[12,13] though no explicit equations were presented. Interestingly, an exponential representation of "correlated" functions for atoms and molecular units (not electrons) together with the concept of cumulants had been used in statistical many-body theory long before.[14] The exponential representation (cumulant-based representation of the moment-generating function) is fundamental in correlated many-particle physics, as emphasized by Kubo.[396] Nevertheless, the method began to truly prosper when the coupled cluster approach was brought into *quantum chemistry* by Čížek,[15,16] Čížek and Paldus,[17] Paldus et al.,[18] Bartlett and Purvis,[19,20] and Pople et al.[21] In this context, it is also worth mentioning the related *many-electron theory* (MET) of Sinanoğlu[22] and the method of Nesbet.[23] The next important series of developments was accomplished by Bartlett and coworkers, who introduced the full coupled-cluster singles and doubles (CCSD) method,[24] subsequently adding full triple (CCSDT)[25,26] and quadruple (CCSDTQ)[27] clusters into the excitation operator $\hat{T}$. Besides a full inclusion of all such terms, various approximate versions, either iterative, like CCSDT-n,[25,26] or noniterative, like CCSD[T],[28] were introduced. The latter approach evolved into the so-called "*gold standard*" of quantum chemistry due to two additions, one due to Ragavachari et al.[29] (see also Bartlett et al.[30]) and the other by Watts et al.[31] Together they provide all fourth-order corrections to CCSD for any choice of the reference determinant.[28−31] The further CC machinery of equal significance for chemistry was developed to enable analytical forces to be obtained for the nonvariational CC methods,[32−40] to treat excited elec tronic states with the equation-of-motion (EOM) CC extension[41−43,424] or linear response (LR) CC theory,[55,441,442] and to apply such tools to higher-order molecular properties.[44,45] Approximate methods like the symmetry-adapted-cluster (SAC) approach[46,47] together with its SAC-CI extension for excited states[47,439,440] and the coupled-electron-pair approximation

(CEPA)[48] were concurrently considered, but they either lacked the rigorous size-extensivity of CC theory or its orbital invariance properties or neglected some nonlinear terms that give CC theory its power. Consequently, since the late 1970s the *single-reference* coupled cluster (SRCC) theory, based on the ansatz in eq 2.1.1, has remarkably advanced and is widely recognized as being the most accurate *practical* tool for ab initio correlated calculations of small-to-medium-sized chemical systems not far from their equilibrium geometries.[1]

The exponential form of the CC wave operator, $e^{\hat{T}}$, is a natural consequence of satisfying a critical property of the exact wave function called *multiplicative separability*.[15−22,49,438] Indeed, the exact wave function $|AB\rangle$ of a supersystem of two (or more) *noninteracting* subsystems must be simply a product of the subsystem wave functions ($|A\rangle$, $|B\rangle$):

$$|AB\rangle = \hat{S}_{AB}|A\rangle|B\rangle = \hat{S}_{BA}|B\rangle|A\rangle, \tag{2.1.2}$$

where AB designates the supersystem consisting of two noninteracting subsystems, A and B, and $\hat{S}_{AB}/\hat{S}_{BA}$ is the "intersystem" antisymmetrizer of electron coordinates. Hereafter a "*system*" means a system of electrons moving in a certain field (created by nuclei, for example). The *product structure* of the wave function is a consequence of the *direct-sum* structure of the Hamiltonian of such a supersystem: $\hat{H} = \hat{H}_A \oplus \hat{H}_B = \hat{H}_A\hat{I}_B + \hat{I}_A\hat{H}_B$.[49] For the sake of simplicity, we omit the requirement of spin purity for the composite wave function, which in general may prevent such a direct-product separability (in such a case, a proper linear combination of degenerate direct products must be constructed). Note that *separability* of the total wave function also requires the vacuum state (reference function) to separate correctly:

$$|\rangle_{AB} = \hat{S}_{AB}|\rangle_A|\rangle_B = \hat{S}_{BA}|\rangle_B|\rangle_A \tag{2.1.3}$$

Using *second quantization*, one can rewrite eq 2.1.2 in terms of wave operators ($\hat{\Omega}$):

$$\hat{\Omega}_{AB}|\rangle_{AB} = \hat{\Omega}_A\hat{\Omega}_B|\rangle_{AB} = \hat{\Omega}_B\hat{\Omega}_A|\rangle_{AB} \tag{2.1.4}$$

where $\hat{\Omega}_A$ and $\hat{\Omega}_B$ operators commute, since they act on different degrees of freedom (difference subsystems).

It is known that the exponential wave operator $\hat{\Omega} = e^{\hat{T}}$ automatically satisfies the requirement of proper separability (disregarding spin purity for now):

$$\hat{\Omega}_{AB} = e^{\hat{T}_{AB}} = e^{\hat{T}_A + \hat{T}_B} = e^{\hat{T}_A}e^{\hat{T}_B} = e^{\hat{T}_B}e^{\hat{T}_A} \tag{2.1.5}$$

$$[\hat{T}_A, \hat{T}_B] = 0 \tag{2.1.6}$$

$$\hat{T}_{AB} = \hat{T}_A + \hat{T}_B \tag{2.1.7}$$

where an arbitrary $\hat{T}_A$ or $\hat{T}_B$ excitation operator acts only on the subsystem A or B, respectively. This also makes them commute. Such *multiplicative separability* of the wave function leads to *additive separability* of the energy, that is, the energy of a supersystem composed of noninteracting subsystems equals the sum of the subsystem energies. In our case, $E_{AB} = E_A + E_B$. Indeed, rearranging the supersystem eigenvalue problem one has

$$\begin{aligned} E_{AB}e^{\hat{T}_A + \hat{T}_B}|0\rangle &= \hat{H}_{AB}e^{\hat{T}_A + \hat{T}_B}|0\rangle \\ &= (\hat{H}_A + \hat{H}_B)e^{\hat{T}_A + \hat{T}_B}|0\rangle \\ &= e^{\hat{T}_B}\hat{H}_A e^{\hat{T}_A}|0\rangle + e^{\hat{T}_A}\hat{H}_B e^{\hat{T}_B}|0\rangle \\ &= e^{\hat{T}_B}E_A e^{\hat{T}_A}|0\rangle + e^{\hat{T}_A}E_B e^{\hat{T}_B}|0\rangle \\ &= (E_A + E_B)e^{\hat{T}_A + \hat{T}_B}|0\rangle \Longrightarrow \\ E_{AB} &= E_A + E_B \end{aligned} \tag{2.1.8}$$

In molecular electronic structure, the ability of a method to provide additively separable energies for a supersystem composed of noninteracting subsystems is called *size-consistency*.[49,338] Size-consistency is closely related to the multiplicative separability of the wave function[49] or, in general, to the *direct-product* structure of the composite Hilbert space used for a supersystem description.[397] Provided that the reference function adopts a direct-product form in the noninteracting separated limit ($|0\rangle_{AB} = |0\rangle_A \otimes |0\rangle_B$), the use of an exponential ansatz for the wave function ensures size-consistency.

In quantum chemistry, size-consistency is a highly desirable property due to the necessity of simulating chemical reactions where the reactants (at the beginning) and the products (at the end) do not interact. Consequently, the method employed must not introduce any unphysical correlations in order to obtain an accurate *potential energy surface* (PES). Standard CC methods provide a size-consistent description of chemical problems. In contrast, standard configuration interaction (CI) approaches introduce unphysical correlations and violate the requirement of size-consistency due to the "artificial" neglect of higher excitations (higher excited components of the Hilbert space with a determinantal basis) that spawns *unlinked diagrams* in the corresponding many-body equations.[50] In the CC theory, higher excitations naturally appear as products of lower excitations, canceling all unphysical (unlinked) terms. The additive separability of the CC correlation energy and the cancellation of all unlinked terms in the CC equations can be seen as an exhibition of another important formal property called *size-extensivity* (to be clarified below).

In principle, eq 2.1.8 ($E_{AB} = E_A + E_B$) provides a possibility of a simple numerical check whether the correlation energy obtained with a particular method is additively separable or not. However, in practice such a *supersystem additivity* test is not always possible, in particular because the underlying method must be equally applicable to both the supersystem and the subsystems (for example, there might be problems when the supersystem is of closed-shell type while subsystems are open shells). Also, convergence problems due to orbital degeneracy can occur when the supersystem is composed of *identical* noninteracting units (either closed-shell or open-shell).

From the brief discussion of *separability properties* of a many-body wave function, let us now proceed to *extensivity/intensivity properties* of a many-body method. While size-consistency in quantum chemistry assumes the absence of subsystem interactions (sometimes also excluding possible spin coupling) and makes sense only when a physical separation of certain units occurs, the formal property of *size-extensivity* is tightly connected to thermodynamics of general extended many-body systems. As known, all observables in thermodynamics are either *extensive* ("proportional" to the number of particles) or *intensive* ("independent" of the number of particles). Hence, it is extremely important for a particular approximate method to preserve the principal extensivity/intensivity of the observable calculated, especially when simulating large chemical systems. In this sense, the standard CC theory, as well as its perturbative approximations in the form of MBPT, are known to be *size-extensive*,[4−11,49,51,52,397] that is, the CC/MBPT *correlation energy* per particle is negative and bounded in the asymptote of an infinite number of particles being correlated in a stable extended chemical system. In contrast, the correlation energy produced by a truncated CI approach is *not* size-extensive (the CI correlation energy per particle tends to zero in the limit). Thus, ordinary CI theory violates both the separability and size-extensivity requirements which are actually related to some extent. Note that for the calculated total electronic energy, which is a sum of the *reference energy*, the *correlation energy*, and the *excitation energy*, to be "truly" size-extensive, the first two components must be individually size-extensive while the excitation energy must be size-intensive (or zero).

Despite the existence of excellent reviews on separability and extensivity properties encountered in quantum chemistry,[49−52,308] these concepts can have different meaning in other quantum sciences, due to historical reasons. In particular, in solid-state physics one is predominantly concerned with extensivity properties of a method while using the name "size-consistency". In the recent paper,[53] Hirata tried to adopt and elaborate the definitions coming from the solid-state physics such that they can be applied in molecular electronic-structure theory. Notwithstanding some interesting aspects of such a formulation, we still believe that separability and size-extensivity must be distinguished in general. Indeed, the correct description of chemical reactions (noninteracting units are involved) is as important as the correct scaling of the energy when enlarging the size of the simulated chemical system (crystals, polymers, *etc.*). In this paper, we adopt the following definitions:

Definition: A **method** is a particular formalism that can be applied to a certain class of quantum problems that represent its **domain** of use.

Definition: **Size-extensivity/size-intensivity** is a formal property of a many-body *method* that guarantees the proper scaling behavior of calculated extensive/intensive physical quantities with respect to the number of particles in the system. A real function $E(N)$ is *size-extensive* in the asymptote $N \rightarrow \infty$ if its value per particle, $E(N)/N$, stays confined in a finite real interval which does not contain zero (N is the number of particles in the system). A function $E(N)$ is *size-intensive* if the limit $\lim_{N\rightarrow\infty}E(N)$ exists.

Note that the above definitions of size-extensive/size-intensive functions apply to an arbitrary inhomogeneous chemical system.[397] For periodical systems, the finite real interval mentioned above asymptotically reduces to a point ($\lim_{N\rightarrow\infty}E(N)/N$ exists). When talking about the *size-extensivity/size-intensivity* of a method, one must explicitly state the physical quantity (function) it applies to. In particular, extensive quantities are the *total energy* of a system or the *correlation energy* of a system, while an intensive quantity is the *excitation energy*, for example.

Definition: **Size-consistency** is a property of a calculation of a system composed of a finite amount of noninteracting subsystems, such that the computed energy of the entire system equals the sum of the energies of the subsystems calculated separately with the same method.

Size-consistency applies to a description of a quantum system that requires specification of the system itself, its particular electronic state, and all the methods employed (independent particle model, correlated model, perturbative or CI corrections, etc.). Here all the details generally matter (closed- or open-shell, singlet or triplet state, RHF or UHF reference, etc.). Note that both the supersystem and the subsystems must belong to the *domain* shared by all the methods employed in the calculation. Therefore, the size-consistency check is not always possible. In general, size-extensivity and size-consistency are neither necessary nor sufficient for each other, although they are not completely independent. It is known that size-extensivity ensures the additive separability of the supersystem energy, provided that the reference function adopts a *direct-product form in the separated limit*.[49] Hence, the requirement of size-extensivity is *mandatory* when developing high-end correlated models.[53] Here we restate a sufficient condition for size-extensivity, traditionally based on the many-body diagrammatic formalism and the *linked diagram theorem*[2−10,101] (see ref 11 for a detailed explanation of many-body techniques; a critical analysis of the linked diagram theorem can be found in ref 397).

Sufficient ("many-body") condition for size-extensivity: A calculated value of a physical quantity preserves its original scaling characteristics if it can be expressed in terms of solely *linked* diagrams involving only *connected* operators.

It is also important to ensure the invariance of calculated *intensive* quantities with respect to an addition of noninteracting molecular fragments (size-consistency of calculated intensive physical quantities). By definition, a size-intensive quantity stays bounded upon increasing the number of particles in the system. If one can prove that the calculated quantity approaches some limit (or stays invariant when adding noninteracting fragments), it is size-intensive, regardless of the actual error. Being added to an extensive quantity, it cannot change the scaling, thus resulting in another extensive quantity. In contrast, size-extensive quantities are "proportional" to the number of particles in the system. Hence, their calculated values must scale properly with the number of particles (according to the above definition of a size-extensive function). Otherwise, a *progressively growing* relative error is introduced[54] such that the method becomes progressively less accurate with the system size (this happens in conventional truncated CI theory). For example, truncated CI approaches yield correlation energies that scale as a square root of the number of electrons in the system (while the exact quantity must be "proportional" to the number of electrons). Thus, in correlation energy calculations, conventional CI theory has *zero efficiency* in the limit of infinitely large systems. Here by "*efficiency*" we understand the fraction of the exact correlation energy captured by a method. Any stable deviation from size-extensivity in the limit leads to a zero efficiency of the method when calculating size-extensive quantities, like correlation energy. Hence, it is extremely important to preserve *connectivity* of the many-body formalism, ensuring the linkedness of the calculated extensive quantities in accordance with the above sufficiency condition based on the classical linked diagram theorem.

Sometimes it is also convenient to analyze the wave function of a correlated method in terms of *extensive* and *intensive* parts. Many correlated methods split the description of an electronic state into two stages. First, the *global* part of the wave function is computed, such that one captures the electron correlation effects all over the system. Second, the wave function is *locally corrected* such that the specificity of the electronic state comes into play. For instance, when describing electronic excitations (which can hardly involve the entire system if the latter is large), one is interested in correcting only the part of the wave function related to the excitation problem. An example is the equation-of-motion (EOMCC) approach,[41−43,424] where the ground state CC calculation captures the electronic correlation effects over the entire electronic system, producing an exponential wave function that "covers" the whole system. Then, a CI operator modifies only the part of the wave function that is involved in the excitation process of interest. Thus, the ground state CC calculation supplies size-extensive *core energy* and the global (*extensive*) part of the wave function, while the CI calculation yields only a size-intensive excitation energy and the corresponding "semilocal" (*intensive*) part of the wave function.[52,55] The total energy of the excited state will be size-extensive, because the addition of an intensive quantity (excitation energy) to an extensive quantity (global ground-state correlation energy + reference energy) will preserve size-extensivity. Adding new fragments to the system, which are irrelevant to the excitation process (core fragments), will result in modifying solely the extensive (exponential) part of the wave function. Hence the total energy will still be size-extensive.

Because *size-extensivity does not assume the absence of interaction*, it is hard to check it numerically. Nooijen et al. suggested the concept of *generalized extensivity*.[49] Unlike size-extensivity, the generalized extensivity allows, in principle, a numerical check,[49,398] which was the main motivation for introducing this concept. Loosely speaking, the generalized extensivity test is based on dividing the orbitals into two subsets in all possible ways, zeroing out the integrals simultaneously involving orbitals from both subsets, and checking the additive separability of the energy. Later, Hanrath suggested a simplification for the generalized extensivity test.[398] If a method fulfills the requirement of generalized extensivity, it is also size-extensive and, under additional conditions (direct-product structure of the reference state), provides a size-consistent description of the problem (guarantees additive separability of the energy for a system composed of noninteracting subsystems). Opposite statements do not hold in general, amplifying the role of size-extensivity/generalized-extensivity when developing new many-body methods. Generalized extensivity and size-extensivity also lead to *size-intensivity* when one describes intensive physical properties[49] (which are supposed to be invariant or convergent as the number of correlated particles grows). There is also a less stringent concept of *core-extensivity*.[308] The core-extensivity is typically thought of as size-extensivity with respect to the closed-shell (core) part of the problem[52] (as in the above example with the EOMCC approach). Analogously, *core-intensivity* would mean the invariance of the calculated intensive quantity with respect to an addition of noninteracting closed-shell (core) fragments.

Let us summarize all important properties shared by coupled-cluster methods:

(1) size-extensivity/size-intensivity;
(2) multiplicative separability of the wave function and size-consistency;
(3) an exponential CC wave function is defined in the entire Hilbert space (the cluster operator must include all single excitations);
(4) yet the parametrization of the wave function is compact, being represented by a tractable set of unknown cluster amplitudes;
(5) cluster amplitudes have connected topology that facilitates elaboration of efficient linear scaling CC approaches with explicit exploitation of locality of interactions;
(6) a truncated version of the CC ansatz, for instance the CCSD approach with one- and two-electron clusters ($\hat{T} = \hat{T}_1 + \hat{T}_2$), is exact not only for any two-electron system but also for any ensemble composed of noninteracting two-electron systems (this feature is drastically different from the CISD approach). Adding the $\hat{T}_3$ cluster operator leads to the exact description of any ensemble composed of noninteracting three- or/and two-electron systems, and so on.

Thus, CC methods cleverly combine the all-order-summation property of CI with the size-extensivity property of MBPT. In other words, the SRCC theory sums to all orders all the perturbative terms of the connected exponent appearing in the exponential representation of the wave operator.[2,11,51]

2.2. Asymmetric Coupled Cluster Ansatz

In SRCC theory a particular single determinant, $|0\rangle$, plays a special role in defining the *Fermi vacuum* and establishing the *excitation-rank hierarchy*, where singly excited determinants are obtained by promoting one electron from an occupied spin-orbital of the Fermi vacuum to a virtual one, doubly excited determinants are obtained by promoting two electrons from two occupied spin−orbitals to the virtual ones, and so on, as illustrated in Figure 1. All possible excited determinants serve as a many-particle basis set spanning the Hilbert space (orthonormalization is implied). In the basic CCSD approach the wave function is constructed with the following wave operator:

$$
\begin{aligned}
|\Psi^{\mathrm{CCSD}}\rangle &= \mathrm{e}^{\hat{T}_1 + \hat{T}_2}|0\rangle \\
&= \left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_1{}^2 + \hat{T}_2\hat{T}_1 + \frac{1}{3!}\hat{T}_1{}^3 \right. \\
&\quad \left. + \frac{1}{2!}\hat{T}_2{}^2 + \frac{1}{2!}\hat{T}_2\hat{T}_1{}^2 + \frac{1}{4!}\hat{T}_1{}^4 + \ldots\right)|0\rangle
\end{aligned}
\qquad (2.2.1)
$$

$$
\hat{T}_1 = \sum_{\substack{a_1\\ i_1}} t_{i_1}^{a_1}\hat{\tau}_{i_1}^{a_1}, \quad \hat{T}_2 = \frac{1}{2!2!}\sum_{\substack{a_1, a_2\\ i_1, i_2}} t_{i_1 i_2}^{a_1 a_2}\hat{\tau}_{i_1 i_2}^{a_1 a_2} \qquad (2.2.2)
$$

where $\hat{\tau}_{i_1}^{a_1} = \hat{a}_1^{+}\hat{i}_1^{-}$, $\hat{\tau}_{i_1 i_2}^{a_1 a_2} = \hat{a}_1^{+}\hat{a}_2^{+}\hat{i}_2^{-}\hat{i}_1^{-}$ are single and double elementary excitation operators expressed in second quantization, and $t_{i_1}^{a_1}$, $t_{i_1 i_2}^{a_1 a_2}$ are corresponding cluster amplitudes. The linear terms in eq 2.2.1 are called *connected clusters* ($\hat{T}_1$, $\hat{T}_2$), whereas the nonlinear terms are called *disconnected* ($\hat{T}_1\hat{T}_2$, $\hat{T}_2\hat{T}_2$, etc.). Importantly, the latter terms "propagate" through the entire Hilbert space, ensuring the size-extensivity of the method. Let us assign italic letters *i*, *j* to Fermi-vacuum *holes* (*occupied spin−orbitals*) and *a*, *b* to *particles* (*virtual spin−orbitals*). In the following, we will use a spin−orbital based representation of the corresponding tensors (amplitudes of operators), except the cases where we explicitly deal with a spin-adapted formulation.

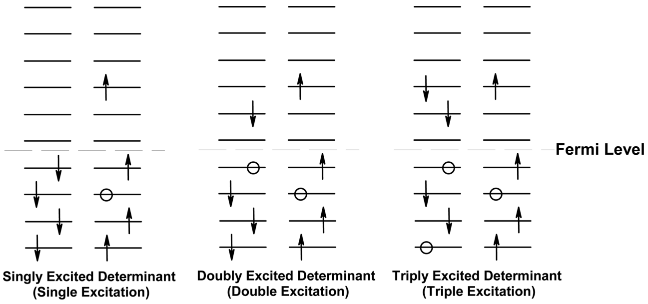


Figure 1. Excitation rank hierarchy of determinants in the hole–particle formalism.

In coupled cluster theory, a natural normalization of the wave function is the *intermediate normalization*

$$\langle 0|\Psi\rangle = 1 \tag{2.2.3}$$

Hence, the configurational weight of the reference determinant is unity (the first term in the McLauren series expansion of an exponential), other determinants *presumably having much smaller configurational coefficients* ($C^{a_1a_2\ldots}_{i_1i_2\ldots}$) expressed in terms of the products of cluster amplitudes $t^{a_1}_{i_1}$, $t^{a_1a_2}_{i_1i_2}$, etc.:

$$C^{a_1}_{i_1} = t^{a_1}_{i_1} \tag{2.2.4}$$

$$C^{a_1a_2}_{i_1i_2} = t^{a_1a_2}_{i_1i_2} + (t^{a_1}_{i_1}t^{a_2}_{i_2} - t^{a_2}_{i_1}t^{a_1}_{i_2}) = t^{a_1a_2}_{i_1i_2} + t^{a_1}_{i_1} \wedge t^{a_2}_{i_2} \tag{2.2.5}$$

$$C^{a_1a_2a_3}_{i_1i_2i_3} = t^{a_1a_2a_3}_{i_1i_2i_3} + t^{a_1a_2}_{i_1i_2} \wedge t^{a_3}_{i_3} + t^{a_1}_{i_1} \wedge t^{a_2}_{i_2} \wedge t^{a_3}_{i_3} \tag{2.2.6}$$

where $\wedge$ generates all *unique* permutations of indices modifying the sign appropriately. The expression in eq 2.2.6 would not contain triply excited clusters, $t^{a_1a_2a_3}_{i_1i_2i_3}$, in the CCSD model. The CCSD equations are formed by projections of the Schrödinger equation, premultiplied by $e^{-(\hat{T}_1+\hat{T}_2)}$, against all singly and doubly excited determinants together with the projection against the reference determinant that defines the correlation energy:

$$\forall\ \langle x| \in \{\langle 0| \cup \langle{}^{a_1}_{i_1}| \cup \langle{}^{a_1a_2}_{i_1i_2}|\} :$$
$$\langle x|e^{-(\hat{T}_1+\hat{T}_2)}\hat{H}_N e^{\hat{T}_1+\hat{T}_2} - \Delta E|0\rangle = 0 \tag{2.2.7a}$$

$$\forall\ \langle x| \in \{\langle 0| \cup \langle{}^{a_1}_{i_1}| \cup \langle{}^{a_1a_2}_{i_1i_2}|\} :$$
$$\langle x|(\hat{H}_N e^{\hat{T}_1+\hat{T}_2})_C - \Delta E|0\rangle = 0 \tag{2.2.7b}$$

where $\Delta E = \langle 0|(\hat{H}_N e^{\hat{T}_1+\hat{T}_2})_C|0\rangle$ is the correlation energy, the subscript C means that only connected terms are retained in the equations, and $\hat{H}_N = (\hat{H} - E^0)$ is the *normal-ordered* many-body Hamiltonian

$$\hat{H}_N = \sum_{p,q} f^p_q\{\hat{p}^+\hat{q}^-\} + \frac{1}{4}\sum_{\substack{p,q\\r,s}} V^{pq}_{rs}\{\hat{p}^+\hat{q}^+\hat{s}^-\hat{r}^-\} \tag{2.2.8}$$

while E^0 is the reference energy (for example, the Hartree–Fock energy), f^p_q are Fock-matrix elements, $V^{pq}_{rs} = \langle pq|\hat{r}^{-1}_{12}|rs\rangle - \langle pq|\hat{r}^{-1}_{12}|sr\rangle$ are antisymmetrized two-electron integrals, and curly brackets mean normal-ordering with respect to $|0\rangle$. Indices designated by p, q, r, s run over the entire orbital range (hole and particle). The construct $e^{-\hat{T}}\hat{H}_N e^{\hat{T}} = (\hat{H}_N e^{\hat{T}})_C$ is called the *similarity-transformed* Hamiltonian. It can be reexpressed in terms of commutators

$$\begin{aligned}\overline{\hat{H}} &\equiv e^{-\hat{T}}\hat{H}_N e^{\hat{T}}\\ &= \hat{H}_N + [\hat{H}_N, \hat{T}] + \frac{1}{2!}[[\hat{H}_N, \hat{T}], \hat{T}]\\ &\quad + \frac{1}{3!}[[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!}[[[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}], \hat{T}]\end{aligned} \tag{2.2.9}$$

where higher than 4-fold commutators cannot appear because of the *two-body* nature of the Hamiltonian and *commutativity* of all components in $\hat{T}$. Because of the above form of the similarity-transformed Hamiltonian, the SRCC theory is nonhermitian and nonvariational.[1]

Removal of the $\hat{T}_1$ operator from the CCSD ansatz yields the CCD approach. By neglecting nonlinear terms in the CC ansatz, one obtains the *linearized* coupled cluster theory. Addition of perturbative estimates for higher-rank amplitudes (mostly triples) usually improves the quality of the results. The widely used CCSD(T) method[28−31] is an approach of this kind. The existence of the SRCC *Lagrangian*

$$\tilde{E} = \langle 0|(1 + \hat{\Lambda})e^{-\hat{T}}\hat{H}_N e^{\hat{T}}|0\rangle \tag{2.2.10}$$

allows evaluation of *analytic energy gradients*. Here the $\hat{\Lambda}$ operator has the structure of the conjugated excitation operator, $\hat{T}^+$, with the same amount of amplitudes separately determined via the $\hat{\Lambda}$ equations:

$$\forall\ \hat{X},\ \hat{X}|0\rangle \in \{|{}^{a_1}_{i_1}\rangle \cup |{}^{a_1a_2}_{i_1i_2}\rangle \cup |{}^{a_1a_2\ldots}_{i_1i_2\ldots}\rangle\} :$$
$$\langle 0|(1 + \hat{\Lambda})[e^{-\hat{T}}\hat{H}_N e^{\hat{T}}, \hat{X}]|0\rangle = 0 \tag{2.2.11}$$

where $\hat{X}$ is an elementary excitation operator. Unfortunately, unlike $\hat{T}$, the $\hat{\Lambda}$ operator is *not* fully connected, which can affect (in principle) the calculation of molecular properties (via SRCC reduced density matrices).

Importantly, *practical SRCC approximations assume the dominance of the reference determinant*, $|0\rangle$, *in the exact wave function*, $|\Psi_{\text{exact}}\rangle$:

$$\forall\ \langle x|,\ \langle x|x\rangle = 1,\ \langle x|0\rangle = 0 :\ |\langle x|\Psi\rangle| \le \varepsilon,\ \langle 0|\Psi\rangle = 1 \tag{2.2.12}$$

where roughly $\varepsilon \approx 0.1-0.2$ (saying "practical" we mean CCD, CCSD, their approximate variants and perturbatively corrected analogues, like CCSD(T), that is, a variety of computationally affordable SRCC approaches whose computational cost is no higher than $\sim O(N^7)$ with respect to the total number of orbitals, N). Therefore, *having an exponential SRCC wave operator requires a selection of one special determinant (reference determinant) whose configurational coefficient is supposed to have the largest magnitude in the exact wave function. We want to emphasize that it is the* availability of such a determinant (usually the Hartree–Fock determinant) that leads to the *success* of ordinary SR approaches, in particular ordinary SRCC methods. This determinant defines a hole–particle vacuum on top of which excited determinants (excitations) can be generated by promoting electrons from occupied orbitals to the virtual ones. The possibility of a chemically accurate approximation of the exact wave function using only singly and doubly excited cluster amplitudes is only due to the ability of the mean-field approximation to capture the major part of the wave function in a single determinant. Failure to commit such a single-determinant "*compression*" will result in a poor ability of an ordinary correlated SR approach to construct the residual part of the wave function, which is *no longer "small"* in this case. Roughly speaking, *ordinary* SR methods heavily rely on reasonable mean-field independent-particle models, for example, the Hartree–Fock method or another physically motivated approach, like that due to Brueckner,[56] Kohn–Sham,[57] the first natural determinant,[58] quasi-Hartree–Fock,[324,325] etc. In this context, an attractive feature of the CC methods containing the $\hat{T}_1$ operator is their relative insensitivity to the orbital choice,[1] provided that the orbitals come from a physically reasonable independent-particle model capturing the major interactions in the considered electronic system. In more difficult cases, a *chemically accurate* (~1 kcal/mol for relative energies) representation of the exact molecular wave function requires a correlated method that either *explicitly accounts for higher excitations* or is *free from the "single-determinant assumption"*. This would be especially true for excited states, where the Hartree–Fock method (or other single-determinant models) is not generally applicable.

The SRCC exponential ansatz built upon one particular determinant is *not invariant* with respect to the choice of the reference determinant, $|0\rangle$. This becomes obvious after realizing the fact that by changing the Fermi vacuum one also changes (a) the subspace against which the Schrödinger equation is projected and (b) the nonlinear parametrization of higher excitations. The exponential parametrization of higher excitations via disconnected clusters essentially changes when proceeding from one Fermi vacuum to another. Because of the truncation of the cluster excitation operator, it is always a good idea to choose the Fermi vacuum determinant to be the *dominant* one, thus reducing the absolute values of "*nonadjustable*" disconnected higher excitations and improving the convergence properties of the CC expansion. The less the norm of the nonadjustable part of the wave function, the less the potentially harmful effect caused by its being not adjusted (not exact).

Concerning the spin/spatial symmetry of the SRCC wave function, there is also a complication when open-shell systems are considered. Contrary to CI theory, the presence of products of cluster $\hat{T}$ operators in the CC ansatz can lead to a *symmetry-contaminated* wave function because the cluster products in general can have components from different irreducible representations, even though the cluster operators themselves have a proper symmetry (closed-shell singlet states do not experience this problem). It is interesting to note that disconnected cluster products (for example, $\hat{T}_1\hat{T}_2$, $(1/2!)\hat{T}_2^2$, etc.) make CC methods size-extensive but can distort the symmetry of the wave function at the same time. In general, the inherent multiplicatively separable nature of the exponential wave function with a truncated cluster operator may lead to the inability of such a wave function to rigorously reproduce the proper symmetry of the electronic state under consideration (unless the cluster operator is complete). In other words, a set of independent variables employed in a particular truncated CC model might not be sufficient to fulfill all symmetry requirements, since the dimension of the space "occupied" by the CC wave function is much larger than the amount of independent variables (cluster amplitudes). Therefore, we have the following tradeoff: *rigorous multiplicative separability versus rigorous symmetry of the wave function*. These two merge in the limit when the cluster operator is complete. However, in practice, conventional CC theory emphasizes the multiplicative separability of the wave function and size-extensivity of the energy, whereas conventional CI theory routinely employs symmetry-adapted wave functions.

In regard to this problem, Nakatsuji suggested a *symmetry projector* applied to nonlinear terms in the SAC expansion,[46,47] filtering out all wrong-symmetry components. Originally, the solution scheme was based on the CI formalism neglecting higher-order cluster products[46] that destroys the power of CC theory. In general, the process of excluding selected (or all) nonlinear cluster products from the wave function can break the connectivity of the approach because such procedures formally introduce disconnected cluster amplitudes in the ansatz (they serve for annihilation of the corresponding wrong-symmetry disconnected excitations). Other approximations of this sort were suggested for open-shell systems by Janssen and Schaefer[59] and Neogrády et al.[60] Bartlett et al. simply employed a high-spin ROHF reference (or symmetry-broken UHF) with no further attempt at spin-projection, although the $\hat{S}^2$ expectation value of the final CC wave function was monitored.[61] Apparently, if the wave function is close enough to the exact solution, it is virtually a spin eigenfunction (unless the wave function corresponds to a degenerate eigenvalue of the electronic Hamiltonian). Szalay and Gauss suggested an adaptation scheme by explicitly specifying spin dependencies between the amplitudes.[62−64] A methodological study of the formal spin-adaptation problem was done by Nooijen and Bartlett.[65] We should also note that usually the energetic impact of spin-contamination is small, although the wave function may become qualitatively wrong in some cases.

A general *orthogonally spin-adapted* CC theory was developed by Paldus and co-workers,[66−73] based on the *unitary group* approach.[66,74−76] Indeed in the case of a spin-free Hamiltonian, $\hat{H}$, for which $[\hat{H}, \hat{S}^2] = 0$, one can employ *spin-free* excitation operators, $\hat{E}$, based upon unitary group generators such that all components transform according to a particular irreducible representation of the unitary group $U(n)$.[69−76] Such excitation operators are explicitly defined in terms of spatial molecular orbitals, thus commuting with the total spin operator: $[\hat{E}, \hat{S}^2] = 0$. Acting on a spin-free *configuration state function* (spin eigenfunction), the spin-free excitation operators ensure the proper spin-symmetry of the total CC wave function while formally preserving the exponential parametrization.[65,67−73] For closed-shell singlet electronic states built upon a closed-shell reference, the spin-adapted CC formulation is equivalent to the ordinary CC approach based upon spin–orbitals and non-spin-adapted excitation operators. In such a case, the spin-adapted scheme clearly reduces the amount of independent amplitudes by a factor of 2−3. However, for open-shell states the two approaches are no longer equivalent in general. In the presence of open-shell electrons in the reference function, the orthogonally spin-adapted CC ansatz contains *noncommuting* excitation operators, preventing the commutator series (eq 2.2.9) from its usual termination after the fourth power in $\hat{T}$.[69−73] The corresponding spin-adapted equations become extremely convoluted bringing to naught the profit from reducing the amount of variables in the ansatz. Nevertheless, such approaches allow obtaining an $\hat{S}^2$-pure solution when non-spin-adapted CC methods fail. An attempt at alleviating the problems caused by the presence of noncommuting operators in the spin-adapted exponential ansatz was undertaken by Datta and Mukherjee.[77,78] Importantly, those authors pointed out the proper exponential expansion factors (*automorphic factors*). In general, to truly make an exponential properly symmetric is quite difficult in practical implementations. Consequently, efficient computer implementations of rigorously spin-adapted open-shell CC methods are practically absent. Note that *spin-adaptation* must be clearly distinguished from *spin-integration*. The latter technical procedure has been routinely used in almost all CC/PT/CI methods, reducing their computational cost (spin-integration is just a summation over the spin coordinates in spin−orbital formulas). Spin-integration does not change the method itself and does not guarantee spin-purity of the wave function.

Concluding, we should say that the SRCC theory combined with its EOMCC extension is a rather flexible, size-extensive, and efficient tool for an accurate "black-box" account of electron correlation.[1] As one will see in the next sections, when ordinary SRCC theory fails, it is usually due to the inability of a single-determinant reference function to adequately represent the zeroth-order wave function for the problem under consideration. This encouraged the extension of the SRCC formalism to produce efficient size-extensive MRCC methods applicable to a wide class of chemically interested problems.

2.3. Failure of the Ordinary Single-Reference Coupled-Cluster Theory

It seems that in practice the deviation of the exponentially parametrized approximate SRCC wave function from the exact one is small when (i) the *problem has a single-reference character* (eq 2.2.12) and (ii) *when the leading (dominating) determinant is taken as the Fermi vacuum*. The former means that the Møller−Plesset perturbation due to the electron repulsion ($1/\hat{r}_{12}$) *can be made small* (by a proper choice of the Fermi vacuum), while the latter assures that it *is actually made small*. Most closed-shell molecular systems around their equilibrium geometries possess a single-reference character in the ground electronic state. If one partitions the Hamiltonian of such SR systems into the self-consistent-field (SCF) zeroth-order part, $\hat{H}_0$, and a perturbation, $\hat{V}$, as

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad (2.3.1)$$

$$\hat{H}_0 \equiv \sum_i \hat{f}(i) \qquad (2.3.2)$$

where $\hat{f}(i) \equiv \hat{h}(i) + \hat{u}(i)$ is a one-electron Fock operator (or other effective one-electron SCF operator containing the one-electron part of the Hamiltonian, $\hat{h}(i)$, and the mean-field term, $\hat{u}(i)$), then the perturbation operator

$$\hat{V} \equiv \frac{1}{2}\sum_{i,j}\frac{1}{\hat{r}_{ij}} - \sum_i \hat{u}(i) \qquad (2.3.3)$$

will be relatively "small" (its matrix will have a relatively small norm as compared to the unperturbed part, $\hat{H}_0$). The perturbation operator $\hat{V}$ represents the *irreducible* part of the electron repulsion not captured by the self-consistent field. The presence of this operator in the Hamiltonian is the origin of the electron correlation effects that can result in a *principal multiconfigurationality* of the wave function. When $\hat{V}$ is sufficiently "small" the wave function is dominated by a single SCF determinant, and the singly and doubly excited cluster amplitudes (or CI coefficients) adopt relatively small values. Consequently, the total weight of higher excitations (3-fold, 4-fold, etc.), represented in the CCSD model solely by nonlinear cluster products, converges quite fast, such that the deviation of higher-excited wave function components from the exact values has negligible consequences on the accuracy of the calculation. Otherwise, we have a *multireference* (MR) problem where $\hat{V}$ is *not* small enough and eq 2.2.12 does not hold. The latter means that there exist two or more leading determinants with *similar large configurational weights* (in the exact wave function):

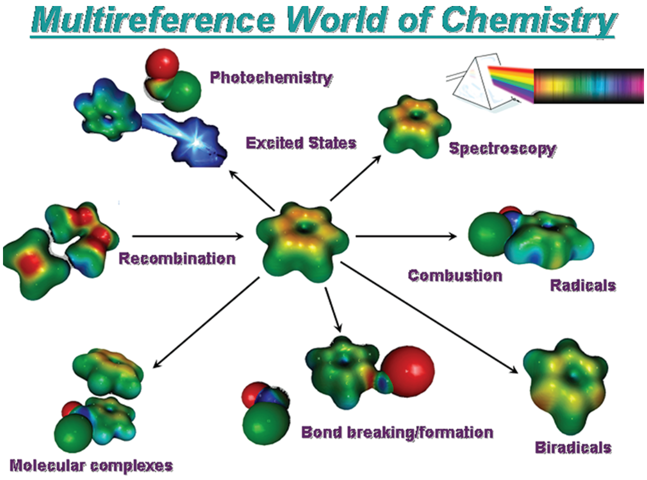


Figure 2. Multireference chemical phenomena.

$$\exists\ \langle x|,\ \langle x|x\rangle = 1,\ \langle x|0\rangle = 0:$$

$$|\langle x|\Psi\rangle| > \varepsilon, \quad \langle 0|\Psi\rangle = 1 \qquad (2.3.4)$$

where roughly $\varepsilon \approx 0.1-0.2$ (it is hard to define the exact measure of "multireference" which depends on the desired accuracy). Equation 2.3.4 formally reflects the so-called *configurational quasidegeneracy* (CQD) of the wave function. CQD is *not* a rare phenomenon and routinely emerges when describing bond breaking/formation processes (chemical reactions), transition states, excited electronic states (photochemistry, spectroscopy), radicals/biradicals (combustion chemistry, chemical kinetics), and other chemical phenomena, as illustrated in Figure 2. In all these cases, the independent-particle models (self-consistent-field methods) *fail* to provide a qualitatively correct (zeroth-order) description of the problem using a single determinant. The Møller−Plesset perturbation $\hat{V}$ (eq 2.3.3) is no longer small. Consequently, the values of the singly and doubly excited amplitudes grow. The CCSD exponential parametrization built on top of such an inadequate single-determinant reference function is *unable* to approximate higher excitations (which are no longer small in this case) with sufficient accuracy. Such inaccurate approximations of higher-excited wave function components will deteriorate the values of lower-excited components and, consequently, the correlation energy (the correlation energy is explicitly dependent on singly and doubly excited amplitudes only). Obviously, by extending the cluster operator with all triple (CCSDT), quadruple (CCSDTQ), pentuple (CCSDTQP), etc. clusters (or CI coefficients in CI methods) one will eventually account for any perturbation, curing the deficiency of the CCSD model and correcting the higher-excited components of the wave function. However, the corresponding approaches have unfavorable computational demands expressed in powers of the 1e basis set size, N, as $O(N^8)$, $O(N^{10})$, $O(N^{12})$, etc., respectively. This prevents such methods from being used in practice. For the purposes of this review, we define *practical* CC methods as those scaling *no worse* than $O(N^7)$.

We distinguish two reasons when CQD appears in the wave function. First, the exact wave function is supposed to have a proper symmetry (for example, spin and/or spatial symmetry). Depending on the desired symmetry and orbitals used, a many-body wave function may require several highly contributing determinants to be coupled in a proper spin/spatial-symmetry combination. This is what we call *static electron correlation*. It is mostly pertinent to open-shell and/or spatially degenerate electronic states, like those in transition-metal atoms, where spin-adaptation of the wave function is likely to be as important as the correlation, per se.

Another problem appears when one describes bond-breaking processes using delocalized molecular orbitals (MO), for instance canonical Hartree−Fock orbitals. In general a proper homolytic separation of interacting chemical fragments requires a *multideterminantal* zeroth-order wave function which has enough degrees of freedom to localize electrons on the separating units. This is what we call *nondynamic electron correlation*, sometimes called *left-right correlation*. Finally, the *dynamic electron correlation* is the residual correlation part mostly responsible for keeping electrons apart. Contrary to the nondynamic/static electron correlation, the effects of the dynamic electron correlation are extremely well captured by the SRCC theory.

Depending on the employed orbitals, the static and nondynamic electron correlations can mix. For example, let us consider a homonuclear single-bond breaking in the ground electronic state, involving two identical atoms and two valence orbitals. Based on the localized orbitals, the singlet-state-coupled wave function in the dissociation limit can be expanded as

$$|\Psi\rangle = (|(\text{core})\chi_1^{\alpha}\chi_2^{\beta}\rangle - |(\text{core})\chi_1^{\beta}\chi_2^{\alpha}\rangle) + \varepsilon|\Theta\rangle \qquad (2.3.5)$$

where $\chi_k^{\alpha/\beta}$ is a valence atomic α/β-spin−orbital located on atom k and $|\Theta\rangle$ is the residual part of the exact wave function whose configurational weight in the intermediate normalization is $|\varepsilon|^2$. In our case (in the dissociation limit), the value of $|\varepsilon|^2$ is supposed to be small. One can see that the exact wave function in eq 2.3.5, expressed in the intermediate normalization, includes *two* determinants with the *same* configurational weight of unity, such that they couple to a singlet electronic state (minus sign). This is a pure case of static electron correlation. Now let us pass from a localized orbital description to delocalized canonical Hartree−Fock orbitals. In the dissociation limit we will have the bonding (+) and antibonding (−) valence molecular orbitals:

$$\phi_+ = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2), \quad \phi_- = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2) \qquad (2.3.6)$$

Now in the dissociation limit the exact wave function expands as

$$|\Psi\rangle = (|(\text{core})\phi_+^{\alpha}\phi_+^{\beta}\rangle - |(\text{core})\phi_-^{\alpha}\phi_-^{\beta}\rangle) + \varepsilon|\Theta\rangle \qquad (2.3.7)$$

By substituting the molecular orbitals ϕ by the corresponding linear combinations of the atomic orbitals (eq 2.3.6) and expanding the Slater determinants, one will obtain the singlet-coupled wave function of eq 2.3.5. However, the wave function in eq 2.3.7 is a pure example of nondynamic electron correlation. Therefore, depending on the orbitals used, one may have "pure" static correlation or "pure" nondynamic correlation. In the intermediate region of the bond-breaking coordinate, there is always *mixing* between the static and nondynamic electron correlations. In the equilibrium region, where by a suitable choice of orbitals one can make a single determinant dominate in the ground-state wave function, the effects of the nondynamic/static electron correlation are usually negligible. This is a *single-reference situation* where only the dynamic electron correlation is significant. When the effects of the nondynamic/static electron correlation are non-negligible, one has a *multireference situation*.

Let us provide the basic concepts of "*multireference quantum chemistry*":

1. The presence of the nondynamic/static electron correlation is generally *unavoidable* when considering the entire potential energy surface. There exist truly multireference regions of the potential energy surface which *cannot be reduced* to a single-reference character by the aid of orbital rotations.
2. The strength of the nondynamic/static electron correlation is proportional to the *complexity* of the problem. Complexity is understood as the *minimal* amount of wave function parameters (for example, cluster amplitudes) that can *ensure* sufficient accuracy of the calculation, excluding accidental coincidence of the calculated values with the exact ones.
3. The extent of *mixing* between the nondynamic and static electron correlation depends on the *orbitals* used. Except for some special points on the potential energy surface, such mixing always includes the effect of *both*.
4. In general, one *cannot* always *reduce* the nondynamic electron correlation to the static electron correlation by the aid of orbital rotations, and vice versa.
5. While it is generally impossible to completely reduce the multireference problem to a single-reference case with the aid of orbital rotations, it is always possible to do the *opposite*, thus artificially *increasing the complexity* of the problem.

In particular, concept 4 implies that special attention must be paid to a description of the intermediate regions of bond-breaking coordinates, where the correlation problem cannot be reduced to a pure spin-coupling task. One should also note that the static electron correlation is normally attributed to the use of the determinantal basis set where different determinants must be coupled in a proper symmetric configuration. Replacing determinants by configuration state functions (CSF) implicitly removes the necessity of proper spin coupling thus restoring the single-reference nature of the problem, provided that the nondynamic electron correlation is negligible.[69−73,77,78] Although special spin-adapted CC codes for open-shells of particular types exist, we are not aware of any widely used computer implementation of the spin-adapted CC theory for electronic states of arbitrary spin symmetry.

One way or another, the presence of CQD separates a *set of leading determinants with similar large weights*. Hence, the main assumption of the ordinary SRCC theory (eq 2.2.12) is violated. Ordinary SRCC approaches construct the bra-projection space to comprise not higher than doubly excited determinants with respect to the Fermi vacuum, primarily because the electronic Hamiltonian contains at most *two-body* terms. Indeed double excitations (excited determinants) appear in the first order because they are directly coupled with the reference determinant (SRCC zeroth-order wave function) via the Hamiltonian

$$\exists \ \langle{}^{a_1a_2}_{i_1i_2}| : \quad \langle{}^{a_1a_2}_{i_1i_2}|\hat{H}_N|0\rangle \neq 0 \qquad (2.3.8)$$

Such directly coupled excitations will be called *principal excitations* (*principal excited determinants*). Using a set of independent variables (amplitudes) the projected Schrödinger equation is satisfied in the bra-space spanned by the principal excitations. The values of residual higher-rank projections (projections against $\langle{}^{a_1a_2a_3}_{i_1i_2i_3}|$, $\langle{}^{a_1a_2a_3a_4}_{i_1i_2i_3i_4}|$, etc., that is, the projections beyond those explicitly taken care of) are *believed to be small*, such that the obtained solution is supposed to be sufficiently close to the exact one (full CI). When there are *several* leading determinants with *similar large* weights (in the exact wave function) an adequate zeroth-order wave function must comprise *all* of them. Let us call these important determinants, comprising the zeroth-order wave function, the *model (reference) determinants*, and the space spanned by them the *model space* (or *reference space*). For a zeroth-order multidimensional reference function the *first-order interaction space* must include all *double* (and *single*, in general) excitations *with respect to each reference determinant*, because these excitations are directly coupled with the zeroth-order reference function (*multideterminantal* in this case) via the Hamiltonian:

$$\forall\ \mu,\ \exists\ \langle {}^{a_1a_2}_{i_1i_2}(\mu)| :\quad \langle {}^{a_1a_2}_{i_1i_2}(\mu)|\hat{H}_N|\mu\rangle \neq 0 \qquad (2.3.9)$$

where μ enumerates different reference determinants $\langle\mu|$, and $\langle {}^{a_1a_2}_{i_1i_2}(\mu)|$ is a double excitation on top of $\langle\mu|$. We will use Greek letters to specify *reference determinants*. Now it becomes clear why ordinary SRCC approaches often *fail* in multireference situations: the ordinary SRCC bra-projection space is essentially *unbalanced* because *the principal excitations from only one reference determinant are included in it*! Hence, it is *not* the deficiency of the SRCC ansatz itself. Because of the use of such an unbalanced bra-space, the weight of higher-rank residual projections (eq 2.3.9) *is no longer small*, since many of them are *involved in the first-order interaction space* with respect to a *multideterminantal* zeroth-order reference function (see eq 2.3.9):

$$\exists\ \langle x| \in \{\langle {}^{a_1a_2a_3}_{i_1i_2i_3}(0)| \cup \langle {}^{a_1a_2a_3a_4}_{i_1i_2i_3i_4}(0)| \cup \ldots\} :$$

$$|\langle x|(\hat{H}_N - \Delta E)e^{\hat{T}_1 + \hat{T}_2}|0\rangle| > \varepsilon \qquad (2.3.10)$$

where ε is some threshold dependent on the desired accuracy of the calculation, and the higher-rank excited determinants, $\{\langle {}^{a_1a_2a_3}_{i_1i_2i_3}(0)| \cup \langle {}^{a_1a_2a_3a_4}_{i_1i_2i_3i_4}(0)| \cup\ldots\}$, are actually *single* and *double* excitations from other than $|0\rangle$ reference determinants (they belong to the first-order interaction space). For those excitations that lie outside the ordinary SRCC bra-projection space but still belong to the first-order interaction space, "rigid" disconnected cluster products are *unable* to reproduce the exact configurational coefficients with a sufficient accuracy. For example, for the CCSD approach one has

$$\forall\ \langle x(0)| \in \{\langle 0| \cup \langle {}^{a_1}_{i_1}(0)| \cup \langle {}^{a_1a_2}_{i_1i_2}(0)|\} :$$

$$\langle x(0)|(\hat{H}_N - \Delta E)e^{\hat{T}_1 + \hat{T}_2}|0\rangle = 0 \qquad (2.3.11)$$

$$\forall\ \mu \neq 0,\ \exists\ \langle x(\mu)| \in \{\langle\mu| \cup \langle {}^{a_1}_{i_1}(\mu)| \cup \langle {}^{a_1a_2}_{i_1i_2}(\mu)|\} :$$

$$|\langle x(\mu)|(\hat{H}_N - \Delta E)|e^{\hat{T}_1 + \hat{T}_2}|0\rangle| > \varepsilon \qquad (2.3.12)$$

where again ε is an empirical threshold distinguishing small and significant residual values (depends on the desired accuracy of the calculation) and 0 and μ in parentheses designate reference determinants (Fermi vacua), while x enumerates excitations on top of them. Such an *unbalanced* SRCC description of MR problems often leads to *significant errors* and even *unphysical* results (qualitatively incorrect results). In particular, this happens when one is trying to describe the dissociation of the N_2 molecule with ordinary methods (Figure 3; notice how drastically inadequate ordinary methods are)[79−82] or homolytic bond breaking in other molecules[79−81] or certain open-shell or/and excited electronic states (see section 6).

To adjust the configurational coefficients from the multireference first-order interaction space, that is, to satisfy (at least to a high extent) the projected Schrödinger equation in the multireference first-order interaction space, one must properly modify the CC ansatz.

> *The essence of any multireference method is to provide a quantitatively correct description of excitations from the multireference first-order interaction space together with the reference function.*

In other words, the projected Schrödinger equation must include all important matrix elements of the Hamiltonian, that is, the matrix elements which *significantly interact* with the *multidimensional* reference function (eq 2.3.9). Once again, it must be clearly understood that *all practical ab initio methods* of molecular electronic structure theory (HF/CC/CI/PT) deal with some *approximate Hamiltonian matrices*. One should never forget that even though the underlying Hamiltonian integrals can be calculated exactly, the matrix can still be far from being complete. Hence, its eigenvalues can noticeably differ from the exact ones. However, only the *exact* eigenvalues are directly related to the experimental results. In order to *ensure* the *accuracy* of some *method* in solving some quantum *problem*, one must meet two important conditions:

(1) The Hamiltonian matrix used in the method must be *close enough* to the exact one. This can only be achieved by considering a *sufficiently large* Hilbert space (a linear space where the quantum problem is being solved).

(2) Provided that the Hamiltonian matrix is sufficiently accurate, the method must be able to approximate the eigenvectors of this matrix with a sufficient accuracy.

It is important to realize that a certain method might yield very accurate eigenvectors of the Hamiltonian matrix, but if the Hamiltonian matrix is not complete enough, the results will be far from reality. This is where the importance of full CI benchmarks comes into play.

Let us begin with an abstract multireference CC theoretical model (MRCC method). Contrary to SRCC theoretical models, an MRCC method has more flexibility. Similarly, in an MRCC theoretical model one can select the *highest excitation rank* in the wave operator (the truncation level), as well as the *level of perturbation theory*, used for estimating the values of higher-rank excitations beyond those explicitly included. However, in addition to these degrees of freedom, one can also *vary the model space* in MRCC methods, more precisely, the *dimension* and *constitution* of the model space (in SRCC theories the model space is trivially one-dimensional, allowing only a change of orbitals). In the following discussion, we will insist that *it is the multidimensional reference space that distinguishes between SRCC and MRCC theoretical models*. From our point of view this is a more appropriate definition of an MRCC method, where the main accent is put onto the use of a *multidimensional zeroth-order (reference) wave function*. Apparently all "*genuine*" MRCC methods (those based on the *effective Hamiltonian*, *intermediate Hamiltonian*, and *internally contracted* MRCC approaches) comply with this definition. However, there is also a category of CC approaches that employ the concept of a multidimensional reference space, yet are operationally based on the SRCC formalism. As we will see below, such approaches are competitive with the genuine MRCC techniques, being in some cases superior in accuracy and/or computationally less expensive. Nonetheless, all existing MRCC

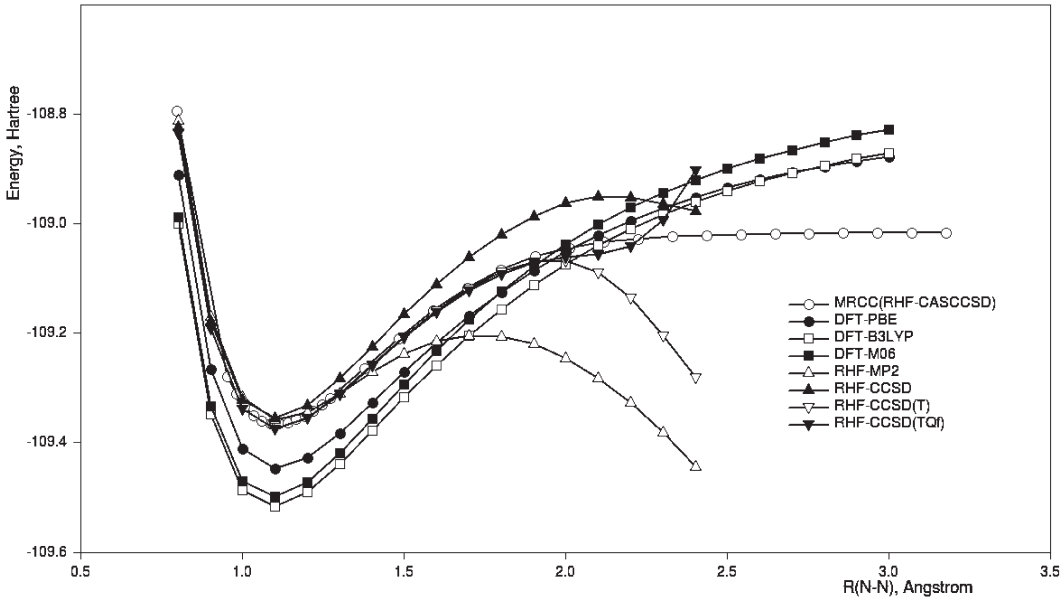


Figure 3. Dissociation of the N_2 molecule as described by DFT, MBPT, and CC methods (cc-pVTZ).

approaches are *not* free from certain methodological problems. Our broad vision of the "*multireference coupled cluster*" theory allows us to "*synthesize*" an ultimate notion of a *multireference problem*, and, perhaps, to devise an effective solution to it, using the strengths of all possible MRCC routes. This is also in line with the previous paper of one of the authors.[83]

In order to distinguish between different classes of MRCC methods, we will call *genuine* those MRCC approaches (gen-MRCC) that use nontrivial MR generalizations of an exponential operator, like that due to Jeziorski and Monkhorst,[84] the valence-universal (VU) CC ansätze,[85−87,188,444−449] or internally contracted MRCC ansätze.[77,90,188,266,317−321,334,389−391,394,395] MRCC methods that are *operationally* based upon SRCC formalism (or another alternative MRCC scheme) will be called *alternative* (alt-MRCC). We will also consider a special class of alternative CC methods, which we call *adaptive*. By construction, an adaptive CC model is generally applicable to both SR and MR problems, although it might still employ the SRCC formalism. Compared to conventional SRCC and MRCC models, the adaptive CC approaches can (in principle) provide results with an a priori set accuracy (in a given 1e basis set). However, the computational cost of such methods can widely vary, depending on the electronic system and accuracy.

From the historical point of view, MRCC approaches began to appear in electronic structure theory right after the SRCC approaches as a generalization for nontrivial open-shell electronic states.[84−89,91−100,188,190,444] The *linked diagram theorem* had been reexamined for MRCC methods (MR-LDT) [84−86,101−104,188,190,202,412,413,451,452] (an attempt to present an alternative, pure algebraic approach for connectivity analysis can be found in ref 397). The classical MR-LDT is based on the analysis of the perturbative expansion of the effective Hamiltonian, since the classical MRCC methods are based on the *effective Hamiltonian* formalism (see subsection 3.1). Depending on whether the reference state has the same number of particles as the target state, two branches of MRCC theory were initially considered: the *Hilbert-space* MRCC theory (particle number is preserved) and the *Fock-space* MRCC theory (variable particle number). Originally all eigenvalues of the effective Hamiltonian were supposed to be *exact* if the wave operator is complete (multistate theory). If this requirement is abandoned for some eigenstates or all but one eigenstate, the *intermediate Hamiltonian* and the *state-specific* gen-MRCC theories are obtained, respectively. In most cases "non-trivial" MR generalizations of the exponential (CC) wave operator introduce *non-commutative* cluster operators, leading to more complex equations as compared to SRCC (contractions between MRCC cluster operators become possible). In order to avoid such internal complexity of the gen-MRCC theory (and for some other reasons highlighted below), alternative MRCC (alt-MRCC) methods were suggested, on the basis of the advanced SRCC formalism [e.g., the single-reference-based MRCC (SRMRCC) theory, the externally corrected approaches, the method of CC moments, the pseudovariational CC methods, the orbital-optimized CC approach, the MR-modified EOMCC and SAC-CI techniques, CASSCF/GVB inspired CC schemes, etc.]. Predominantly, the alt-MRCC methods avoid coupling between different electronic states (*state-specific* calculation regime). The ideas of the Fock-space MRCC theory, namely, the use of a universal wave operator acting on the entire reference function, were recently reborn in the *internally contracted* MRCC approaches.

Despite the large effort put into the MRCC development, there have always been some complications that prohibited the MRCC theory from becoming a well-established practical approach of electronic structure theory. Nevertheless, a *proper MRCC methodology is absolutely necessary* for contemporary quantum chemistry. It would provide a reliable tool for chemically accurate simulations of a wide variety of chemical/photochemical/electrochemical phenomena, and underlying chemical transformations. To provide a framework for the following discussion, we list desiderata we have for MRCC methods. An MRCC method should

- provide *chemically accurate relative energies* (~1 kcal/mol);
- be *size-extensive/size-intensive* and *size-consistent*;
- *not exceed* $O(N^7)$ computational scaling with respect to the number of correlated orbitals, N, and allow an exploitation of *local techniques* for larger systems;

- be *invariant* to the (inactive) *occ*−*occ* and (inactive) *virt*−*virt* orbital rotations and be *invariant* (or at least *insensitive*) to the *active*−*active* orbital rotations;
- preserve the symmetry of the wave function (e.g., spin symmetry);
- provide a well-defined scheme for *specifying the reference space* (if applicable);
- naturally *reduce* to an SRCC approach when the problem is of SR character;
- provide a tractable scheme for evaluating *analytic energy gradients* and calculating *molecular properties*;
- allow a "*black-box*" logic for adjusting all parameters of the method;
- have some internal control of accuracy of a calculation.

We emphasize that without fulfilling the first requirement all other demands are irrelevant.

3. GENUINE MULTIREFERENCE COUPLED-CLUSTER THEORY IN HILBERT SPACE

3.1. Multidimensional Model Space

For the following discussion we need to establish a nomenclature. First, let us define the following projectors and associated subspaces of the Hilbert space:

- $\hat{P} = \Sigma_\mu|\mu\rangle\langle\mu|$: a projector onto the *model* space (*reference* space), P. Greek letters will enumerate reference determinants. Determinants from the model space will be also called *internal (internal excitations)*. The reference function (zeroth-order wave function) is expanded in this space.
- $\hat{P}_0 = |0\rangle\langle 0|$: a projector onto a *one-dimensional* subspace, P_0, of the model space, P. This subspace is spanned by only one *specific* reference determinant, $|0\rangle$.
- $\hat{Q} = \Sigma_x|x\rangle\langle x|$: a projector onto the *external space*, Q, which is a space spanned by the determinants formed as excitations outside the model space, such that the Schrödinger equation is projected against the *union of the model and external spaces*. x will enumerate components of the external space. In many cases, the external space is chosen to be the first-order interaction space, thus involving all single and double excitations outside the model space. However, in general, *the external space can differ from the first-order interaction space*.
- $\hat{Q}_0 = (\hat{P} + \hat{Q}) - \hat{P}_0$.
- $\hat{Q}' = \hat{I} - (\hat{P} + \hat{Q}) = \hat{I} - (\hat{P}_0 + \hat{Q}_0)$: a projector onto the *orthogonal complement space*, Q', that is, the space spanned by disconnected clusters only (cannot be reached from the model space by an action of a connected cluster operator).

The determinantal many-electron basis set is assumed to be *orthonormal*.

A zeroth-order MRCC wave function is defined solely in the model (reference) space of dimension M:

$$|\Psi_k^{(0)}\rangle = \sum_{\mu=1}^{M} C_k^\mu|\mu\rangle \tag{3.1.1}$$

where k enumerates different eigenstates of interest, $1 \le k \le L$ with $L \le M$. The full (potentially exact) MRCC wave function, $|\Psi_k\rangle$, for the kth energy eigenstate is obtained from $|\Psi_k{}^{(0)}\rangle$ by the action of some wave operator, $\hat{\Omega}$:

$$|\Psi_k\rangle = \hat{\Omega}|\Psi_k^{(0)}\rangle \tag{3.1.2}$$

In CC theory $|\Psi_k\rangle$ is expanded in the entire Hilbert space (in CI theory the orthogonal-complement space, Q', is *not* used). In many MRCC theories, the *intermediate normalization* with respect to the reference space, P, is adopted

$$\langle\Psi_k^{(0)}|\Psi_k\rangle = \langle\Psi_k^{(0)}|\hat{\Omega}|\Psi_k^{(0)}\rangle = 1 \tag{3.1.3}$$

$$\hat{P}\hat{\Omega} = \hat{P} \tag{3.1.4}$$

$$\hat{\Omega}\hat{P} = \hat{\Omega} \tag{3.1.5}$$

$$\hat{\Omega}^2 = \hat{\Omega} \tag{3.1.6}$$

that is, the wave operator $\hat{\Omega}$ *acts solely on the model space while excites only outside it* (leaving the reference function unchanged). Classical genuine MRCC approaches are mostly based on the *effective Hamiltonian* formalism, such that the *Bloch equation* [87,105,106,412] is invoked to determine the wave operator $\hat{\Omega}$:

$$\hat{H}\hat{\Omega}\hat{P} = \hat{\Omega}\hat{H}\hat{\Omega}\hat{P} \tag{3.1.7}$$

$$\hat{H}\hat{\Omega}\hat{P} = \hat{\Omega}\hat{H}^{\rm eff}\hat{P} \tag{3.1.8}$$

$$\begin{aligned} &\hat{H}^{\rm eff} \equiv \hat{P}\hat{H}\hat{\Omega}\hat{P}:\\ &\hat{H}^{\rm eff}|\Psi_k^{(0)}\rangle = E_k|\Psi_k^{(0)}\rangle, \quad 1 \le k \le L \end{aligned} \tag{3.1.9}$$

where $\hat{H}^{\rm eff}$ is the so-called *effective Hamiltonian*,[87,106] which is defined *solely within the model space* (of dimension M). All $L = M$ eigenvalues, E_k, are supposed to be *equal* to selected eigenvalues of the original Hamiltonian, $\hat{H}$, provided that the wave operator $\hat{\Omega}$ is *exact*. Having obtained the wave operator, $\hat{\Omega}$, the eigenvalue problem is *transferred* via the effective Hamiltonian from the entire Hilbert space to the model space only. Diagonalization of the effective Hamiltonian in the model space yields required electronic energies, E_k. If in eq 3.1.9 only the first $L < M$ eigenstates are supposed to be exact when the wave operator is complete, then the effective Hamiltonian formalism turns into the *intermediate Hamiltonian* formalism[116,136−138,221,233,413,414] with an ultimate case of the *state-specific* approach ($L = 1$).

The Bloch equation for the wave operator is *equivalent* to the Schrödinger equation,[87,106] being just more convenient when the effective Hamiltonian formalism is employed:

$$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle, \quad \forall\ k \tag{3.1.10}$$

$$\hat{H}\hat{\Omega}|\Psi_k^{(0)}\rangle = E_k\hat{\Omega}|\Psi_k^{(0)}\rangle, \quad \forall\ k \tag{3.1.11}$$

$$\hat{\Omega}\hat{H}\hat{\Omega}|\Psi_k^{(0)}\rangle = E_k\hat{\Omega}|\Psi_k^{(0)}\rangle, \quad \forall\ k \tag{3.1.12}$$

$$\begin{aligned} \forall\ k: \quad &\hat{H}\hat{\Omega}|\Psi_k^{(0)}\rangle = \hat{\Omega}\hat{H}\hat{\Omega}|\Psi_k^{(0)}\rangle\\ &\equiv \hat{\Omega}\hat{H}^{\rm eff}|\Psi_k^{(0)}\rangle \leftrightarrow \hat{H}\hat{\Omega}\hat{P} = \hat{\Omega}\hat{H}^{\rm eff}\hat{P} \end{aligned} \tag{3.1.13}$$

where eq 3.1.12 uses eq 3.1.6, and eq 3.1.13 is obtained by subtraction of eq 3.1.12 from eq 3.1.11. Usually the Bloch equation is resolved in the *external space* as

$$\hat{Q}\hat{H}\hat{\Omega}\hat{P} = \hat{Q}\hat{\Omega}\hat{H}\hat{\Omega}\hat{P} \tag{3.1.14}$$

or, equivalently,

$$\hat{Q}\hat{H}\hat{\Omega}\hat{P} = \hat{Q}\hat{\Omega}\hat{H}^{\rm eff}\hat{P} \tag{3.1.15}$$

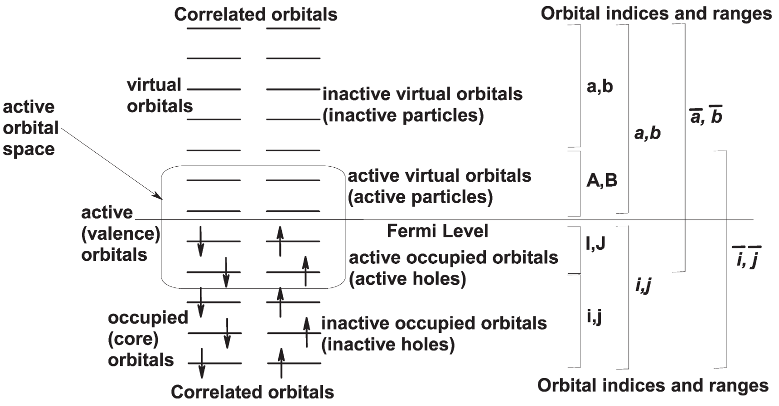


Figure 4. Active-orbital-space-based partitioning of orbitals involved in a correlated calculation.

with a subsequent diagonalization of the effective Hamiltonian:

$$\forall\ k,\ \ \forall\ \mu: \quad \sum_{\nu} (\hat{H}^{\text{eff}})^{\mu}_{\nu} C^{\nu}_{k} = E_k C^{\mu}_{k} \tag{3.1.16}$$

In the following we will highlight only the general algebraic structure of different MRCC approaches. The detailed equations can be subsequently derived using well-established diagrammatic techniques.[11]

The *multidimensional* model space *P* plays a crucial role in the MRCC theory. We distinguish the following ways for its construction:

(1) *Complete active space (m,n)* or *CAS(m,n)*: The model space is spanned by determinants obtained by *all* possible distributions of *m* electrons among *n* molecular orbitals. These electrons and molecular orbitals are called *active* (or *valence*). When the global Fermi vacuum is specified, the active holes/particles (active orbitals that are occupied/unoccupied in the global Fermi vacuum) will be designated by capital letters I_1, I_2, .../A_1, A_2, ..., respectively. The nonactive (*inactive*) holes/particles (orbitals which are occupied/unoccupied in *all* reference determinants) will be designated by small roman letters i_1, i_2, .../a_1, a_2,..., respectively. Small italic letters are still used for *general* hole/particle ranges. The CAS concept is graphically illustrated in Figure 4. Usually active orbitals constitute only a small fraction of the total orbital space used in a correlated calculation. Physically, the active (valence) orbitals are those predominantly involved in the chemical problem under consideration (for example, bonding/antibonding valence orbitals in the case of bond breaking).

(2) *Incomplete active space (m,n)* or *IAS(m,n)*: This model space is an arbitrary subspace of the CAS(*m*,*n*) model space.

(3) *General model space* or *GMS*: This model space can comprise arbitrary determinants. Any GMS model space can be viewed as some IAS(*m*,*n*) model space. For the sake of convenience, we distinguish GMS as a model space that does *not* need a division of orbitals into active and inactive.

4) *Occupation restricted multiple active spaces* or *ORMAS*: This model space is constructed by dividing active orbitals into *several* groups and imposing *specific restrictions* on the orbital occupancy in each group. In contrast to MRCI and MRPT theories, we are not aware of the use of ORMAS[387] in MRCC theory. ORMAS can also be viewed as a special variant of IAS.

In earlier works a certain class of IAS model spaces was called (initially by Lindgren) *quasicomplete* [86,95] (rarely used now).

3.2. Jeziorski–Monkhorst Ansatz and the State-Universal Multireference Coupled-Cluster Theory. The Intruder State Problem

The Jeziorski–Monkhorst (JM) MRCC ansatz[84] is the starting point of many genuine *Hilbert-space multireference* (HS-MRCC) methods in both *state-universal* (SU) and *state-specific* (SS) formulations. In HS-MRCC approaches, the target electronic states have the *same number of particles* as all the model space determinants do. The *state-universal* (SU) formulation implies a simultaneous calculation of as many electronic states as the dimension of the model space (through the full diagonalization of the effective Hamiltonian), whereas the *state-specific* (SS) formulations focus on only *one* state at a time. In principle, it is also possible to elaborate an *intermediate* Hamiltonian formulation, where only *several* relevant roots are obtained.

The JM wave operator is a natural MR extension of the SRCC exponential wave operator for a multidimensional reference space

$$\hat{\Omega} = \sum_{\mu} \mathrm{e}^{\hat{T}^{\mu}} |\mu\rangle\langle\mu| \tag{3.2.1}$$

where μ (and Greek letters in general) enumerates model space determinants. Here the cluster operators $\hat{T}^{\mu}$ are defined as regular excitation operators, but with respect to their *own Fermi vacua*, $|\mu\rangle$. The conventional singles-and-doubles (SD) truncation scheme leads to

$$\hat{\Omega} = \sum_{\mu} \mathrm{e}^{\hat{T}^{\mu}_1 + \hat{T}^{\mu}_2} |\mu\rangle\langle\mu| \tag{3.2.2}$$

$$\hat{T}^{\mu}_1 = \sum_{\substack{i_1\\ a_1}} t^{a_1}_{i_1}(\mu)\hat{\tau}^{a_1}_{i_1}(\mu),$$

$$\hat{T}^{\mu}_2 = \frac{1}{2!2!} \sum_{\substack{i_1, i_2\\ a_1, a_2}} t^{a_1 a_2}_{i_1 i_2}(\mu)\hat{\tau}^{a_1 a_2}_{i_1 i_2}(\mu) \tag{3.2.3}$$

where all the quantities (holes and particles) correspond to their specific Fermi vacua, $|\mu\rangle$. In such a *multivacuum* approach, the cluster operators corresponding to different vacua do *not* commute:

$$[\hat{T}^{\mu}_{k}, \hat{T}^{\nu}_{l}] \neq 0, \quad \mu \neq \nu \tag{3.2.4}$$

The external space used for solving the Bloch equation (or, equivalently, the Schrödinger equation) is spanned by determinants that can be reached from the model space by an action of at least one connected $\hat{T}^{\mu}$ operator ($\hat{T}^{\mu}$ acting on one of the reference determinants). Projections of the Bloch equation (on the left) against all determinants from the *external* space yield a system of *nonlinear* equations used to determine the unknown cluster amplitudes of the JM wave operator[84] (amplitudes of all $\hat{T}^{\mu}$ operators):

$$\forall\ k, \quad \forall\ \langle x| \in Q: \quad \langle x|\hat{H}(\sum_{\nu} e^{\hat{T}^{\nu}}|\nu\rangle\langle\nu|)(\sum_{\mu} C^{\mu}_{k}|\mu\rangle)$$

$$= \langle x|(\sum_{\nu} e^{\hat{T}^{\nu}}|\nu\rangle\langle\nu|)\hat{H}^{\text{eff}}(\sum_{\mu} C^{\mu}_{k}|\mu\rangle) \tag{3.2.5}$$

where $(\Sigma_{\mu} C_{k}{}^{\mu}|\mu\rangle) \equiv |\Psi_{k}{}^{(0)}\rangle$ is the zeroth-order wave function (reference function) of the kth electronic state

$$|\Psi_{k}\rangle = \left(\sum_{\nu} e^{\hat{T}^{\nu}}|\nu\rangle\langle\nu|\right)|\Psi^{(0)}_{k}\rangle = \sum_{\nu} C^{\nu}_{k} e^{\hat{T}^{\nu}}|\nu\rangle \tag{3.2.6}$$

All M eigenstates (M is the dimension of the model space) must be determined simultaneously, because otherwise the number of amplitude equations is less than the number of unknown amplitudes.[84] This happens because different determinants from the external space can be generated in *multiple* ways (in general), by different connected operators $\hat{T}^{\mu}$ acting on their own reference determinants, $|\mu\rangle$. In other words, different $\hat{T}^{\mu}|\mu\rangle$ vectors overlap. This is schematically illustrated in Figure 5. If $\hat{Q}^{\mu}$ is a projector associated with the space spanned by all determinants which can be reached by the excitation operator $\hat{T}^{\mu}$ acting on $|\mu\rangle$, then one can formally write

$$\exists\ \nu \neq \mu: \quad \hat{Q}^{\mu} - \hat{Q}^{\nu} \neq 0 \tag{3.2.7}$$

In the full CI *limit*, when all cluster operators $\hat{T}^{\mu}$ are *complete* (include all possible excitations with respect to their own Fermi vacua), the JM ansatz contains M times more amplitudes than the dimension of the *complete* external space (since the JM wave operator describes M electronic states simultaneously).

The set of equations in eq 3.2.5 constitutes the basis of the *state-universal* (SU) MRCC approach[84] suggested by Jeziorski and Monkhorst. Originally, the SU-MRCC method employed the CAS model space. In order to keep the intermediate normalization (eq 3.1.3) and avoid additional redundancy in the wave function, all $\hat{T}^{\mu}$ operators are prohibited from producing excitations solely within the CAS model space. Hence, the wave operator $\hat{\Omega}$ *always excites outside the reference space* when acting on *any* reference determinant, thus preserving the intermediate normalization. A detailed configurational analysis of the SU-MRCC ansatz can be found in ref 107.

eq 3.2.5 can be further transformed as

$$\forall\ k, \quad \forall\ \langle x| \in Q: \quad \sum_{\mu} C^{\mu}_{k}\langle x|\hat{H}e^{\hat{T}^{\mu}}|\mu\rangle$$

$$= \sum_{\mu} C^{\mu}_{k} \sum_{\nu} \langle x|e^{\hat{T}^{\nu}}|\nu\rangle \hat{H}^{\text{eff}}_{\nu\mu} \tag{3.2.8}$$

$$\hat{H}^{\text{eff}}_{\nu\mu} \equiv \langle\nu|\hat{H}^{\text{eff}}|\mu\rangle \tag{3.2.9}$$

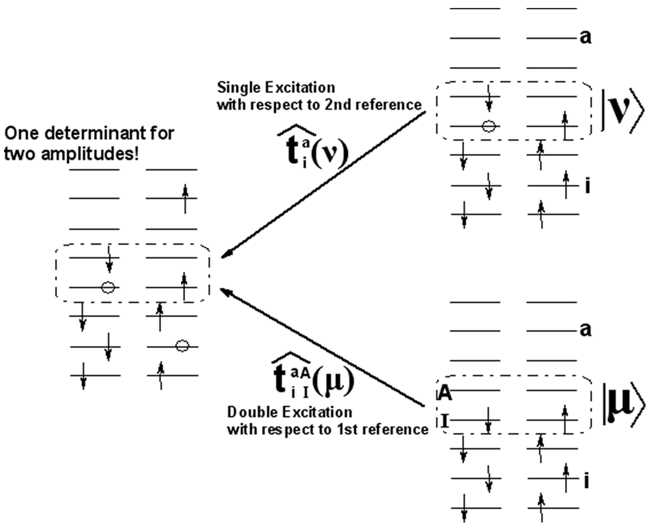


Figure 5. Illustration of the redundancy of the Jeziorski−Monkhorst ansatz.

Since range(k) = range(μ) = [1,M], one may equate each individual term in the left sum of eq 3.2.8 to the corresponding term in the right sum:

$$\forall\ \mu, \quad \forall\ \langle x| \in Q^{\mu}: \quad \langle x|\hat{H}e^{\hat{T}^{\mu}}|\mu\rangle = \sum_{\nu} \langle x|e^{\hat{T}^{\nu}}|\nu\rangle \hat{H}^{\text{eff}}_{\nu\mu} \tag{3.2.10}$$

Thus, the number of equations is equal to the number of unknown cluster amplitudes (all M eigenstates are simultaneously determined). In practice, for each μ a subset of equations is formed via projections against all single, double, etc. excitations (depending on the level of the SU-MRCC approach) with respect to the corresponding reference determinant $|\mu\rangle$:

$$\forall\ \mu, \quad \forall\ \langle x(\mu)| \in \{\langle^{a_1}_{i_1}(\mu)| \cup \langle^{a_1 a_2}_{i_1 i_2}(\mu)| \cup ...\}$$

$$: \quad \langle x(\mu)|\hat{H}e^{\hat{T}^{\mu}}|\mu\rangle = \sum_{\nu} \langle x|e^{\hat{T}^{\nu}}|\nu\rangle \hat{H}^{\text{eff}}_{\nu\mu} \tag{3.2.11}$$

where each equation has an associated unknown cluster amplitude from the set $\{\forall\ \mu, t^{a_1}_{i_1}(\mu), t^{a_1 a_2}_{i_1 i_2}(\mu),...\}$. Having obtained the amplitudes of the JM wave operator, one can rebuild the effective Hamiltonian (eq 3.2.9) and diagonalize it as in eq 3.1.16 (the eigenvalues are the electronic energies). Subsequently, the new matrix elements $\hat{H}^{\text{eff}}_{\nu\mu}$ will affect the amplitude equations (eq 3.2.11), which are to be resolved again. The entire two-step procedure is repeated until convergence. Depending on the highest excitation rank in $\hat{T}^{\mu}$, one has SU-MRCCSD,[84,93,94,433] SU-MRCCSDT,[108] etc. models.

Alternatively, in order to exhibit the *connected* nature of equations (eq 3.2.11), one can premultiply both sides by $e^{-\hat{T}^{\mu}}$:

$$\forall\ \mu, \quad \forall\ \langle x(\mu)| \in \{\langle^{a_1}_{i_1}(\mu)| \cup \langle^{a_1 a_2}_{i_1 i_2}(\mu)| \cup ...\}:$$

$$\langle x(\mu)|e^{-\hat{T}^{\mu}}\hat{H}e^{\hat{T}^{\mu}}|\mu\rangle = \sum_{\nu} \langle x|e^{-\hat{T}^{\mu}}e^{\hat{T}^{\nu}}|\nu\rangle \hat{H}^{\text{eff}}_{\nu\mu} \tag{3.2.12}$$

Equations 3.2.11 and 3.2.12 are equivalent because the $e^{-\hat{T}^{\mu}}$ operator is a pure *de-excitation* operator when acting on the left. Hence, it does not change the bra-projection manifold, except introducing the model space determinants in it. However, projections against the model space determinants are trivially satisfied in the SU-MRCC approach:

$$\forall\ \langle\mu| \in P,\ \langle\lambda| \in P: \quad \langle\lambda|\hat{H}\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle = \sum_{\nu} \langle\lambda|\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle \hat{H}^{\mathrm{eff}}_{\nu\mu} \tag{3.2.13}$$

Taking into account the intermediate normalization one has

$$\forall\ \langle\mu| \in P,\ \langle\lambda| \in P: \quad \langle\lambda|\hat{H}\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle = \hat{H}^{\mathrm{eff}}_{\lambda\mu} \tag{3.2.14}$$

$$\forall\ \langle\mu| \in P, \quad \langle\lambda| \in P: \quad \langle\lambda|\hat{H}\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle = \langle\lambda|\hat{H}\left(\sum_{\nu} \mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle\langle\nu|\right)|\mu\rangle = \langle\lambda|\hat{H}\hat{\Omega}|\mu\rangle \equiv \hat{H}^{\mathrm{eff}}_{\lambda\mu} \tag{3.2.15}$$

proving that eq 3.2.13 is automatically fulfilled.

The left-hand side of eq 3.2.12 is manifestly connected if $\hat{T}^{\mu}$ operators are connected

$$\langle x(\mu)|\mathrm{e}^{-\hat{T}^{\mu}}\hat{H}\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle = \langle x(\mu)|(\hat{H}\mathrm{e}^{\hat{T}^{\mu}})_{C}|\mu\rangle \tag{3.2.16}$$

where $\mathrm{e}^{-\hat{T}^{\mu}}\hat{H}\mathrm{e}^{\hat{T}^{\mu}}$ is the similarity-transformed Hamiltonian of SRCC theory. In order for the right-hand side of eq 3.2.12 (called the *coupling term*) to be connected, the effective Hamiltonian $\hat{H}^{\mathrm{eff}}$ must be connected. This is true for the CAS-SU-MRCC method:[84]

$$\begin{aligned}\forall\ \mu, \quad \forall\ \lambda: \quad H^{\mathrm{eff}}_{\lambda\mu} &= \langle\lambda|\hat{H}\hat{\Omega}|\mu\rangle \\ &= \langle\lambda|\hat{H}\left(\sum_{\nu} \mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle\langle\nu|\right)|\mu\rangle = \langle\lambda|\hat{H}\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle \\ &= \langle\lambda|\mathrm{e}^{-\hat{T}^{\mu}}\hat{H}\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle = \langle\lambda|(\hat{H}\mathrm{e}^{\hat{T}^{\mu}})_{C}|\mu\rangle\end{aligned} \tag{3.2.17}$$

where we used the fact that $\hat{T}^{\mu}$ operators are *not* allowed to produce excitations solely within the model space (intermediate normalization condition for the CAS model space). The connectedness of the effective Hamiltonian guarantees the connectedness of the entire coupling term, since all nonzero components of the *coupling factor* $\langle x|\mathrm{e}^{-\hat{T}^{\mu}}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle$ involve active orbitals, which distinguish $|\mu\rangle$ and $|\nu\rangle$ [the matrix element $H^{\mathrm{eff}}_{\nu\mu} \equiv \langle\nu|(\hat{H}\mathrm{e}^{\hat{T}^{\mu}})_{C}|\mu\rangle$ is explicitly dependent on these active orbitals, thus getting connected to the coupling factor $\langle x|\mathrm{e}^{-\hat{T}^{\mu}}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle$].[84] Therefore, eq 3.2.12 is manifestly connected (if a CAS model space is used), preserving the connectedness of all cluster operators $\hat{T}^{\mu}$. Because the CAS model space involves all possible excitations within the active orbitals (CASFCI space), a diagonalization of the connected effective Hamiltonian, $\hat{H}^{\mathrm{eff}}$, in such a space simultaneously provides *size-extensive* energies for M electronic states, where M is the dimension of the CAS model space. However, in a GMS model space the fact that the effective Hamiltonian is connected is not sufficient for obtaining rigorously size-extensive energies because disconnected terms can appear during the diagonalization of the effective Hamiltonian.[95]

The CAS-SU-MRCC method can be *spin-adapted*,[69−73,77,78,109] although the complexity of the resulting approach is extreme. The *perturbatively corrected* CAS-SU-MRCCSD(T) method[110] has been suggested, where perturbative estimates of *triply* excited clusters are used to improve the energies. A *linear-response* approach has been built on top of the SU-MRCC theory to investigate *molecular properties*.[111,112] A general theoretical framework for evaluating MRCC *analytic energy gradients*, in particular for the CAS-SU-MRCC approach, has also been formulated,[113,114] albeit we are not aware of any commonly accessible computer implementation of it.

Nevertheless, all the above-mentioned developments have limited applicability because of an inherent problem of the CAS-SU-MRCC approach. The CAS model space together with the intermediate normalization makes the CAS-SU-MRCC method size-extensive, but at the same time it leads to a severe problem called the *intruder state* problem (see refs 115−120 and also references therein). The essence of the problem can be briefly explained as follows. When all cluster amplitudes in all $\hat{T}^{\mu}$ operators are zero, the eigenvalues of the effective Hamiltonian $\hat{H}^{\mathrm{eff}}$ are obtained by a diagonalization of the bare electronic Hamiltonian $\hat{H}$ in the model space, yielding its zeroth-order spectrum. In the presence of the dynamic electron correlation, one can expand the cluster amplitudes of all $\hat{T}^{\mu}$ as a power series with respect to the perturbation parameter. Thus, one can perturbatively construct a wave function in the entire Hilbert space. The eigenvalues of the effective Hamiltonian $\hat{H}^{\mathrm{eff}}$ also become functions of the perturbation parameter. The larger the CAS model space, the greater the chance that the perturbation will bring together different eigenvalues or even interchange their order. This does not constitute a problem within the model space, but this does create *severe* convergence problems when some low lying *external* (intruder) roots (from the first-order interaction space) approach the highest model-space root. In such a case the Bloch equation can hardly be converged (some cluster amplitudes grow large), leaving the entire correlation problem unsolved. In fact, MRCC methods are usually designed for treating bond-breaking processes and open-shell/excited states that require a sufficiently large active space for capturing the nondynamic/static electron correlations. At the same time, in such calculations the Hamiltonian eigenvalues are often close to each other, especially higher roots from the model space and the subsequent low-lying external roots. This certainly leads to a very high chance of encountering the intruder state problem when using the CAS-SU-MRCC method. Roughly speaking, the CAS-SU-MRCC method is formally well-suited for the problems where it cannot be practically used due to the loss of convergence. Soon after the appearance of the Jeziorski−Monkhorst ansatz a partial solution was given by Laidig and Bartlett, who introduced a decoupled linearized MR-LCCM method,[88] one of the first MRCC methods that exploits the state-specific paradigm (only one state at a time is calculated).

Yet another essential problem is that the CAS-SU-MRCC method is often less accurate when calculating SR electronic states. This seems to be a common drawback of several MRCC methods based on the JM ansatz. The reason will be highlighted below after discussing other genuine HS-MRCC methods. Apart from the major HS-MRCC developments presented below, let us mention an interesting HS-MRCC approach suggested by Hoffmann and Khait, based on the unitary MRCC ansatz and hermitian effective Hamiltonian.[411] The method is free of the intruder state problem and is claimed to properly reduce to the SRCC theory.

3.3. Incomplete-Active-Space and General-Model-Space State-Universal Coupled-Cluster Theories

The intruder state problem stimulated a search of variations of the SU-MRCC method which would be free from severe convergence problems. A logical approximation would be to maximally *shrink* the size of the model space, removing all determinants of low importance (together with the corresponding electronic states), such that there would be a sufficient "*buffer*" between the model space roots and the external roots of the Hamiltonian. Indeed, SU-MRCC approaches which use *incomplete active spaces* or *general model spaces* (IAS-SU-MRCC/GMS-SU-MRCC) have been suggested.[95−99,121,122] By using an IAS/GMS model space, one focuses on a simultaneous calculation of some *low-lying* Hamiltonian roots from the *parental CAS model space*, preserving a sufficient separation from higher roots. Such a practical solution often circumvents the intruder state problem, but being applied straightforwardly, it introduces disconnected contributions into equations and leads to a loss of the rigorous size-extensivity of the method.[49] Indeed, operationally both IAS and GMS are formed by excluding some selected determinants from the *parental CAS model space* and moving them into the *external* space. Hence, the dimension of the model space is reduced (as compared to CAS) while the corresponding cluster amplitudes (for determinants released from the model space) must be added to the wave operator in order to keep the MRCC ansatz potentially exact in the limit. The products of these newly introduced clusters, in general, can produce excited determinants from the model space

$$\exists\ |\nu\rangle \neq |\mu\rangle : \quad \langle\nu|\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle \neq 0 \tag{3.3.1}$$

violating the intermediate normalization. Consequently, the effective Hamiltonian inherits *disconnected* contributions due to the presence of the following disconnected products: (a) $\langle\nu|\hat{H}|\lambda\rangle\langle\lambda|\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle \neq 0$ and (b) $\langle\nu|\hat{H}|x\rangle\langle x|\mathrm{e}^{\hat{T}^{\mu}}|\mu\rangle \neq 0$ (where $|x\rangle$ designates a determinant from the external space that originally was present in the parental CAS model space; $|x\rangle$ is obtained from $|\mu\rangle$ by substituting some *active* orbitals present in $|\mu\rangle$ with other *active* orbitals). The presence of the above disconnected products *violates* the connectivity and rigorous size-extensivity of the method.

Two major routes to preserve the size-extensivity of the SU-MRCC approach while using IAS or GMS model spaces have been suggested. The first route goes back to the papers of Mukherjee and co-workers[98,399] and Meissner et al.[95,96] In order to restore rigorous size-extensivity the intermediate normalization of the MRCC wave function should be abandoned,[85,98,399] thus introducing a nontrivial overlap matrix

$$\exists\ S_{\mu\nu} \equiv \langle\mu|\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle \neq \delta_{\mu\nu} \tag{3.3.2}$$

and redefining the effective Hamiltonian matrix

$$H^{\mathrm{eff}}_{\mu\nu} = \sum_{\lambda} S_{\mu\lambda}{}^{-1}\langle\lambda|\hat{H}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle \tag{3.3.3}$$

A cluster operator $\hat{T}^{\mu}$ is extended by adding *internal* amplitudes in it (amplitudes containing solely active indices). These amplitudes are used to *nullify* all disconnected products in the effective Hamiltonian (a and b, shown above). The amount of these additional internal amplitudes coincides with the number of distinct disconnected products. Thus, the corresponding IAS-SU-MRCC equations are still well-defined. Such cancellation of all disconnected products restores the connectedness of the effective Hamiltonian and the rigorous size-extensivity of the IAS/GMS-SU-MRCC method. Connectivity of the IAS-SU-MRCC equations was first proven for a special class of IAS model spaces[95] (still keeping $\hat{T}^{\mu}$ cluster operators external with respect to the entire model space), followed by a proof for a general IAS model space[96,98,99] (where the intermediate normalization is completely abandoned). The resulting GMS-SU-MRCC method of Meissner/Mukherjee is *rigorously size-extensive* and *satisfies the generalized extensivity test.* However, it is believed that the additional cluster components required for restoring the connectivity of the equations may deteriorate the accuracy of the approach.[49] Also, as was pointed out by Berkovic and Kaldor, the IAS-SU-MRCC approach can lead to degeneracy breaking, where degenerate energy levels artificially split.[123,124] Nevertheless, the IAS-SU-MRCC methods were successfully tested in some model studies,[97,99] although they have not been implemented in any production-level code. No scheme for evaluating analytic gradients of the IAS/GMS-SU-MRCC energy was reported so far, albeit the corresponding techniques exist for the CAS-SU-MRCC approach.[113,114]

Another route was picked by Paldus and Li, who also augmented the JM ansatz with additional cluster amplitudes in order to cancel undesired internal excitations produced by the original JM wave operator in the GMS model space.[121,122] However, Paldus and Li tried to preserve the intermediate normalization in their GMS-SU-MRCC approach. The corresponding GMS-MRCC ansatz can be expressed as

$$\begin{aligned}|\Psi_k\rangle &= \Big(\sum_{\nu} \mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle\langle\nu|\Big)|\Psi_k^{(0)}\rangle\\ &= \sum_{\nu} C_k^{\nu}\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle = \sum_{\nu} C_k^{\nu}\mathrm{e}^{\hat{G}^{\nu}+\hat{T}^{\nu}}|\nu\rangle\end{aligned} \tag{3.3.4}$$

where $\hat{G}^{\nu}$ is an additional excitation operator acting solely within the model space

$$\hat{P}\hat{G}^{\nu}|\nu\rangle \neq 0, \quad \hat{Q}\hat{G}^{\nu}|\nu\rangle = 0 \tag{3.3.5}$$

As we have pointed out, the standard JM wave operator (eq 3.2.1), in general, produces *internal excitations* (reference space components) when applied with a GMS/IAS model space (eq 3.3.1). Because cluster operators $\hat{T}^{\nu}$ are not allowed to excite within the model space, these internal excitations are generated by products of the cluster operators, leading to a loss of connectivity of the equations. With the aid of the additional cluster operators $\hat{G}^{\nu}$, one can cancel undesired internal excitations produced by the wave operator:

$$\forall\ \nu,\ \ \forall\ \mu : \quad \langle\mu|\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle = \delta_{\mu\nu} \tag{3.3.6}$$

thus restoring the intermediate normalization metrics. The amplitudes of $\hat{G}^{\nu}$ are defined to be negatives of the coefficients of the reference determinants produced by internal disconnected excitations, such that each construct $\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle$ does *not* produce internal excitations (excitations within the model space). These additional conditions defining $\hat{G}^{\nu}$ are called the *C-conditions* (connectivity conditions), since they are intended to make the GMS-SU-MRCC equations connected and the electronic energies (rigorously) size-extensive. However, Nooijen et al.[49] conjectured that the GMS-SU-MRCC scheme of Paldus and Li still contains disconnected contributions. Following their arguments one can formally write

$$\begin{aligned}H^{\mathrm{eff}}_{\mu\nu} &= \langle\mu|\hat{H}\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}|\nu\rangle\\ &= \langle\mu|\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}(\mathrm{e}^{-\hat{T}^{\nu}}\mathrm{e}^{-\hat{G}^{\nu}}\hat{H}\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}})|\nu\rangle\\ &= \langle\mu|\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}(\hat{H}\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}})_C|\nu\rangle\end{aligned} \tag{3.3.7}$$

Thus, for a certain class of GMS model spaces the effective Hamiltonian $H^{\mathrm{eff}}_{\mu\nu}$ will still contain disconnected products where $(\hat{H}\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}})_C$ and $\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}$ are *not* connected. In other words, in general the $\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}}$ operator can "excite" the vector $(\hat{H}\mathrm{e}^{\hat{G}^{\nu}}\mathrm{e}^{\hat{T}^{\nu}})_C|\nu\rangle$ back to a particular reference determinant via *disconnected* clusters. Indeed, one can check that the C-conditions cancel only the disconnected contributions of type a, $\langle\nu|\hat{H}|\lambda\rangle\langle\lambda|e^{\hat{T}^\mu}|\mu\rangle$, while the disconnected contributions of type b, $\langle\nu|\hat{H}|x\rangle\langle x|e^{\hat{T}^\mu}|\mu\rangle \neq 0$, are kept in the effective Hamiltonian. However, even though these contributions do violate the generalized extensivity, the GMS-SU-MRCC approach of Li and Paldus is still *core-extensive*[397] and *size-consistent*.[49]

Moreover, the GMS-SU-MRCC method based on the *C*-conditions was thoroughly tested on model systems as well as on some small molecules, where it succeeded to provide accurate energies for the ground and excited MR electronic states.[125−128,407] A *perturbative triples correction* has been devised for the GMS-SU-MRCC approach of Li and Paldus.[129] In practical calculations one should be careful in selecting the reference determinants. This is crucial for both the accuracy and the elimination of the intruder state problem. Unfortunately, an unambiguous procedure for this purpose does not exist, although the authors suggested a potentially useful technique based on the configurational analysis of the CISD wave function.[128] Similarly to the IAS/GMS-SU-MRCC method of Meissner/Mukherjee, we are not aware of any implemented scheme for evaluating analytic energy gradients for the GMS-SU-MRCC approach of Li and Paldus. Otherwise this would significantly extend the applicability of the method in the studies of PES of the ground and excited MR electronic states.

Notwithstanding the two major GMS-SU-MRCC schemes described above, there also exist more approximate IAS-SU-MRCC methods, for example, the *two-determinantal state-specific* MRCCSD method (TD-MRCCSD or, better, 2D-MRCCSD),[110,130] which can be used for calculating open-shell singlet excited states where the model space consists of only two degenerate determinants. Such MR problems can be reduced to two separate SR problems. Because of this simplification, analytic energy gradients are available for the 2D-MRCCSD method.[113]

3.4. State-Specific Formulations of the Genuine Multireference Coupled-Cluster Theory: Sufficiency Conditions

Yet another route to overcome the intruder state problem while employing the JM ansatz was discovered. As we have mentioned above, Laidig and Bartlett attempted to cure the drawback of the SU-MRCC approach by linearizing and decoupling the equations,[88] thus formally introducing a *state-specific* HS-MRCC theory. Later Hubač with co-workers[131−133] and Mukherjee with co-workers[134,135] introduced two different variants of the *state-specific* (SS) formulation of the HS-MRCC approach based on the JM ansatz. Contrary to *multistate* approaches, *state-specific* methods focus on only *one* electronic state at a time. Usually such a single-root separation circumvents the intruder state problem. A state-specific formulation can be viewed as a particular case of the *intermediate Hamiltonian* technique, where only the first few roots are supposed to be exact in the limit while other roots serve for "*buffering*" and getting rid of the intruder states by shifting them away.[116] This will be described in more detail in section 4 when discussing the Fock-space methods, where the intermediate Hamiltonian technique[136−138] has been very fruitful for a long time. A pilot application of the intermediate Hamiltonian technique to the HS-MRCC approach was recently reported by Eliav et al.[139] In this subsection we will focus on the state-specific formulation, where only one root is supposed to be exact in the limit (the electronic state of interest). All other roots are just byproducts of the calculation, serving to maintain a sufficient separation of the root of interest.

As we have pointed out, the exact JM ansatz[84] (with *complete* cluster operators) involves *M* times more variables than the dimension of the external space, *M* being the dimension of the model space. In the SU-MRCC formalism, this redundancy is naturally resolved by a simultaneous consideration of *M* electronic states. However, the state-specific formulation considers only *one* state at a time, thus introducing to the *redundancy problem* (the number of equations is less than the number of unknown cluster amplitudes). In general, the redundancy problem is resolved via appropriate *sufficiency conditions,* which make the number of equations equal to the number of variables.[131−135,140] In the next discussion, we will abandon the classical way of deriving state-specific HS-MRCC equations. Instead, we will follow the elegant *grouping approach* introduced by Kong[141] (which also covers the classical derivation). The approach is based on different grouping of the terms obtained from the projected Schrödinger equation, leading to four different HS-MRCC theories: SS *Brillouin−Wigner* (BW) MRCC,[131−133,140] multistate SU-MRCC,[84] SS *Mukherjee*-MRCC,[134,135,142−144] and the so-called H2E2-MRCC variant.[141] The latter approach is closely related (though not equivalent) to the *single-root* sr-MRCC method[135,400,401] of Mahapatra et al. Following the work of Hanrath,[145] this unified way of deriving genuine HS-MRCC methods (based on the JM ansatz) will also exhibit their serious drawback (which leads to less accurate description of SR cases, in particular). Note that the SU-MRCC method discussed above can also be derived in this way. Another interesting (but less general) unified view on different HS-MRCC theories and their interrelationship was demonstrated by Pittner.[140]

In accordance with the grouping approach,[141] one starts from the Schrödinger equation with a wave function based upon the JM ansatz (eq 3.2.6)

$$\sum_\mu (\hat{H} - E_k) C_k^\mu e^{\hat{T}^\mu} |\mu\rangle = 0 \tag{3.4.1}$$

where E_k is the energy of the *k*th electronic state. Projecting eq 3.4.1 against the reference determinants as well as the determinants from the external space, *two* sets of equations can be obtained:

$$\forall\ \langle\nu| \in P: \qquad \sum_\mu \langle\nu|(\hat{H} - E_k) C_k^\mu e^{\hat{T}^\mu} |\mu\rangle = 0 \tag{3.4.2}$$

$$\forall\ \langle x| \in Q: \qquad \sum_\mu \langle x|(\hat{H} - E_k) C_k^\mu e^{\hat{T}^\mu} |\mu\rangle = 0 \tag{3.4.3}$$

where *P* is the *reference* (*model*) space while *Q* is the *external* space (see subsection 3.1). The CAS model space and the *intermediate normalization* are assumed

$$\forall\ \mu,\ \ \forall\ \nu: \qquad \langle\nu|e^{\hat{T}^\mu}|\mu\rangle = \delta_{\nu\mu} \tag{3.4.4}$$

where $\delta_{\nu\mu}$ is the Kronecker delta. The first set of equations (eq 3.4.2) together with eq 3.4.4 leads to the already known eigenvalue problem for the effective Hamiltonian, $\hat{H}^{\text{eff}}$

$$\forall\ k,\ \ \forall\ \nu: \qquad \sum_\mu C_k^\mu \langle\nu|\hat{H}e^{\hat{T}^\mu}|\mu\rangle = E_k \sum_\mu C_k^\mu \delta_{\nu\mu} \tag{3.4.5}$$

$$\forall\ k,\ \ \forall\ \nu: \qquad \sum_\mu C_k^\mu H_{\nu\mu}^{\text{eff}} = E_k C_k^\nu \tag{3.4.6}$$

where the effective Hamiltonian is defined as before:

$$H^{\text{eff}}_{\nu\mu} = \langle\nu|\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle = \langle\nu|\mathrm{e}^{-\hat{T}^\mu}\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle = \langle\nu|(\hat{H}\mathrm{e}^{\hat{T}^\mu})_C|\mu\rangle \tag{3.4.7}$$

Equation 3.4.7 assumes the CAS intermediate normalization condition ($\hat{T}^\mu$ operators always excite outside the model space). A diagonalization of the effective Hamiltonian yields required electronic energies (from which only one root might be relevant). However, in order to compute the effective Hamiltonian, $\hat{H}^{\text{eff}}$, one must solve eq 3.4.3, which can be rewritten as

$$\forall\ k, \quad \forall\ \langle x| \in Q: \quad \sum_\mu C^\mu_k\langle x|\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle = \sum_\mu E_k C^\mu_k\langle x|\mathrm{e}^{\hat{T}^\mu}|\mu\rangle \tag{3.4.8}$$

Now each side of eq 3.4.8 can be reexpressed at least in two different ways leading to

left-hand side

1. $\Sigma_\mu C^\mu_k\langle x|\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle$;
2. $\Sigma_\mu(C^\mu_k\langle x|\mathrm{e}^{\hat{T}^\mu}\hat{Q}\mathrm{e}^{-\hat{T}^\mu}\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle + \Sigma_\nu C^\nu_k\langle x|\mathrm{e}^{\hat{T}^\nu}|\mu\rangle H^{\text{eff}}_{\mu\nu})$ (the *resolution of identity* was inserted, $\mathrm{e}^{\hat{T}^\mu}\hat{I}\mathrm{e}^{-\hat{T}^\mu} = \mathrm{e}^{\hat{T}^\mu}\hat{P}\mathrm{e}^{-\hat{T}^\mu} + \mathrm{e}^{\hat{T}^\mu}\hat{Q}\mathrm{e}^{-\hat{T}^\mu}$, assuming completeness of $P \oplus Q$; in the second term the summation indices, μ and ν, were replaced, $\mu \leftrightarrow \nu$);

right-hand side

1. $\Sigma_\mu E_k C^\mu_k\langle x|\mathrm{e}^{\hat{T}^\mu}|\mu\rangle$;
2. $\Sigma_\mu C^\mu_k\Sigma_\nu\langle x|\mathrm{e}^{\hat{T}^\nu}|\nu\rangle H^{\text{eff}}_{\nu\mu}$ (eq 3.4.6 and *renaming* of summation indices, $\mu \leftrightarrow \nu$).

Correspondingly, four different combinations lead to four different gen-HS-MRCC theories. Because of the *redundancy problem,* when equating each variant of the *left-hand side (lhs)* to each variant of the *right-hand side (rhs)*, the outer sums are split such that each component in the lhs outer sum is to be equal to the corresponding component in the rhs outer sum. Hence, we end up with

(1) The state-specific Brillouin–Wigner HS-MRCC method (BW-MRCC):

$$\forall\ \mu, \ \forall\ \langle x| \in Q^\mu: \quad \langle x|\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle = E_k\langle x|\mathrm{e}^{\hat{T}^\mu}|\mu\rangle \tag{3.4.9}$$

(2) The multistate SU-MRCC method (linked form):

$$\forall\ \mu, \ \forall\ \langle x| \in Q^\mu: \quad \langle x|\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle = \sum_\nu \langle x|\mathrm{e}^{\hat{T}^\nu}|\nu\rangle H^{\text{eff}}_{\nu\mu} \tag{3.4.10}$$

(3) The state-specific Mukherjee HS-MRCC method (Mk-MRCC) (linked form):

$$\forall\,\mu, \forall\,\langle x| \in Q^\mu: \quad \langle x|\mathrm{e}^{\hat{T}^\mu}\hat{Q}\mathrm{e}^{-\hat{T}^\mu}\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle C^\mu_k + \sum_\nu \langle x|\mathrm{e}^{\hat{T}^\nu}|\mu\rangle H^{\text{eff}}_{\mu\nu}C^\nu_k = E_k\langle x|\mathrm{e}^{\hat{T}^\mu}|\mu\rangle C^\mu_k \tag{3.4.11}$$

(4) The state-specific H2E2-MRCC method:

$$\forall\,\mu, \forall\,\langle x| \in Q^\mu: \quad \langle x|\mathrm{e}^{\hat{T}^\mu}\hat{Q}\mathrm{e}^{-\hat{T}^\mu}\hat{H}\mathrm{e}^{\hat{T}^\mu}|\mu\rangle C^\mu_k + \sum_\nu \langle x|\mathrm{e}^{\hat{T}^\nu}|\mu\rangle H^{\text{eff}}_{\mu\nu}C^\nu_k = C^\mu_k\sum_\nu \langle x|\mathrm{e}^{\hat{T}^\nu}|\nu\rangle H^{\text{eff}}_{\nu\mu} \tag{3.4.12}$$

In all the equations Q^μ designates an excitation subspace of the external space, Q, which consists of singles, doubles, etc. (up to the highest excitation rank in the cluster operator $\hat{T}^\mu$) that can be reached by an action of $\hat{T}^\mu$ on $|\mu\rangle$. Hence, the number of equations is always *equal* to the number of unknown cluster amplitudes, because each μth subset of cluster amplitudes ($\hat{T}^\mu$) is determined from the corresponding μth subset of projected equations, where each equation is associated with a particular cluster amplitude. Note that the working equations of state-specific HS-MRCC approaches explicitly depend on the eigenstate of interest (via index k). This also requires a *self-consistent* procedure in order to solve the equations.

Equations 3.4.9–3.4.12 are obtained by direct projections against determinants from the external subspace. In order to transform the equations to the canonical form and exhibit *connectivity* of eqs 3.4.10 and 3.4.11, one can replace direct projections by their analogs premultiplied with $\mathrm{e}^{-\hat{T}^\mu}$:

$$\langle x(\mu)| \rightarrow \langle x(\mu)|\mathrm{e}^{-\hat{T}^\mu}, \quad \forall\ \mu, \ \forall\ x(\mu) \tag{3.4.13}$$

Usually such a transformation leads to an *equivalent* set of equations when the projection space is *closed* under de-excitations. In our case, this transformation extends the original projection space, Q^μ, to include the model space determinants (determinants from P):

$$\exists\ \mu, \ \exists\ \{\langle x| \in Q^\mu, \ |\nu\rangle \in P\}: \quad \langle x|\mathrm{e}^{-\hat{T}^\mu}|\nu\rangle \neq 0 \tag{3.4.14}$$

Thus, we can apply this transformation only to those HS-MRCC methods for which the working equations (eqs 3.4.9–3.4.12) are also satisfied in the reference space, P. Inserting $\langle\lambda| \in P$ instead of $\langle x| \in Q^\mu$, one obtains the following restrictions:

(1) BW-MRCC (very restrictive condition):

$$H^{\text{eff}}_{\lambda\mu} = E_k\delta_{\lambda\mu} \tag{3.4.15}$$

(2) SU-MRCC (trivial):

$$H^{\text{eff}}_{\lambda\mu} = H^{\text{eff}}_{\lambda\mu} \tag{3.4.16}$$

(3) Mk-MRCC (trivial):

$$\sum_\mu H^{\text{eff}}_{\lambda\mu}C^\mu_k = E_k C^\lambda_k \tag{3.4.17}$$

(4) H2E2-MRCC (restrictive; satisfied in the limit of an *infinite* number of electrons):

$$\begin{cases} \mu = \lambda: & \sum_\nu H^{\text{eff}}_{\lambda\nu}C^\nu_k = H_{\lambda\lambda}C^\lambda_k = E_k C^\lambda_k \\ \mu \neq \lambda: & H^{\text{eff}}_{\lambda\mu} = 0 \end{cases}$$
$$\Longrightarrow \text{diagonal} \quad H^{\text{eff}}_{\lambda\mu} \tag{3.4.18}$$

One can see that the BW-MRCC approach cannot satisfy eq 3.4.15. Indeed, it requires the effective Hamiltonian to be essentially a scalar, with all diagonal elements equal to the energy of the calculated electronic state, E_k. Hence, one cannot apply $\langle x(\mu)| \rightarrow \langle x(\mu)|\mathrm{e}^{-\hat{T}^\mu}$ transformation in the BW-MRCC theory, unless the effective Hamiltonian and all reference determinants are *exactly degenerate*. In this case, one can formally transform eq 3.4.9 to

$$\forall \mu,\ \forall \left\langle x \right| \in Q^\mu : \left\langle x \middle| \mathrm{e}^{-\hat{T}^\mu} \hat{H} \mathrm{e}^{\hat{T}^\mu} \middle| \mu \right\rangle = 0$$
$$\forall\ \mu : E_k = \left\langle \mu \middle| \mathrm{e}^{-\hat{T}^\mu} \hat{H} \mathrm{e}^{\hat{T}^\mu} \middle| \mu \right\rangle \qquad (3.4.19)$$

eq 3.4.19 is simply a set of SRCC equations, that is, there is *no coupling term* at all. In general, BW-MRCC equations (eq 3.4.9) are *coupled through the energy* of the calculated electronic state that makes them *unlinked* and the BW-MRCC method *not size-extensive*. Approximate *size-extensivity correction* schemes have been suggested and quite successfully tested on model systems.[140,146−149] The *full-triples* as well as approximate and *perturbative-triples* (T) versions of the BW-MRCC theory have been reported.[150−152] The relative simplicity of the BW-MRCC equations has made *analytic energy gradients* readily available.[114] Nevertheless, the *unlinked* nature of the BW-MRCC equations makes the method noticeably less competitive, especially when proceeding to larger chemical systems.

In the case of the H2E2-MRCC approach, in order for the $\langle x(\mu)| \rightarrow \langle x(\mu)|\mathrm{e}^{-\hat{T}^\mu}$ transformation to be legitimate, the effective Hamiltonian must be *diagonal*. Thus, in general we cannot formulate a manifestly connected version of the H2E2-MRCC approach. However, a manifestly connected version can be postulated by using appropriate sufficiency conditions. The resulting SS-HS-MRCC approach is called sr-MRCC ("sr" stands for "*single-root*").[135,400,401] The manifestly connected sr-MRCC equations are given below. Remarkably, the two HS-MRCC approaches (H2E2-MRCC and sr-MRCC) become virtually *equivalent* when the number of electrons in the system is sufficiently large.[397] This happens because only *diagonal* elements of the effective Hamiltonian are supposed to grow *linearly* with the number of electrons in the system (the off-diagonal elements should stay bounded[397]). Hence, at some point, the effective Hamiltonian will become sufficiently *diagonal-dominated*, such that the results of both the H2E2-MRCC and sr-MRCC methods will virtually coincide.

Let us summarize the corresponding *connected* equations wherever possible:

(1) Brillouin−Wigner MRCC method (BW-MRCC): *not applicable*.

(2) SU-MRCC method (connected form):

$$\forall\ \mu,\ \ \forall\ \langle x| \in Q^\mu :$$
$$\langle x|\mathrm{e}^{-\hat{T}^\mu} \hat{H} \mathrm{e}^{\hat{T}^\mu}|\mu\rangle = \sum_\nu \langle x|\mathrm{e}^{-\hat{T}^\mu} \mathrm{e}^{\hat{T}^\nu}|\nu\rangle H^{\mathrm{eff}}_{\nu\mu} \qquad (3.4.20)$$

(3) Mukherjee MRCC method (Mk-MRCC) (connected form):

$$\forall\ \mu,\ \ \forall\ \langle x| \in Q^\mu :$$
$$\langle x|\mathrm{e}^{-\hat{T}^\mu} \hat{H} \mathrm{e}^{\hat{T}^\mu}|\mu\rangle C^\mu_k + \sum_\nu \langle x|\mathrm{e}^{-\hat{T}^\mu} \mathrm{e}^{\hat{T}^\nu}|\mu\rangle H^{\mathrm{eff}}_{\mu\nu} C^\nu_k$$
$$= 0 \qquad (3.4.21)$$

(4) sr-MRCC method (or H2E2-MRCC method with a diagonal $H^{\mathrm{eff}}_{\nu\mu}$):

$$\forall\ \mu,\ \forall\ \langle x| \in Q^\mu :$$
$$\langle x|\mathrm{e}^{-\hat{T}^\mu} \hat{H} \mathrm{e}^{\hat{T}^\mu}|\mu\rangle C^\mu_k + \sum_\nu \langle x|\mathrm{e}^{-\hat{T}^\mu} \mathrm{e}^{\hat{T}^\nu}|\mu\rangle H^{\mathrm{eff}}_{\mu\nu} C^\nu_k$$
$$= C^\mu_k \sum_\nu \langle x|\mathrm{e}^{-\hat{T}^\mu} \mathrm{e}^{\hat{T}^\nu}|\nu\rangle H^{\mathrm{eff}}_{\nu\mu} \qquad (3.4.22)$$

It was shown that both *coupling factors*, $\langle x|\mathrm{e}^{-\hat{T}^\mu}\mathrm{e}^{\hat{T}^\nu}|\nu\rangle$ and $\langle x|\mathrm{e}^{-\hat{T}^\mu}\mathrm{e}^{\hat{T}^\nu}|\mu\rangle$, are connected with the effective Hamiltonian (via common active indices), and the entire *coupling terms* are *connected* if the CAS model space is used.[84,134,135] Hence, the amplitude equations for all three CAS-HS-MRCC theories (SU-MRCC, Mk-MRCC, and sr-MRCC) are manifestly *connected*, keeping the methods rigorously *size-extensive*. The methods also provide a *size-consistent* description of MR problems when the orbitals are localized on noninteracting fragments.

A generalization of the Mk-MRCC and sr-MRCC methods for IAS/GMS model spaces can be achieved either via abandoning the intermediate normalization[443] or via the use of the *C*-conditions,[408] in an analogous way as in the GMS-SU-MRCC approach (bearing in mind that the latter route is only *core-extensive*).

Due to recent extensive works of Evangelista et al.,[108,153−156] Pittner and co-workers,[402,403] and Mukherjee with collaborators,[157,404−406] the Mk-MRCC method was thoroughly studied (both theoretically and practically). Both Mk-MRCCSD[134,135] and Mk-MRCCSDT[154,404] approaches as well as their approximate variants[154,405,406] have been explored. Two *perturbatively* corrected Mk-MRCCSD(T) schemes were suggested by Evangelista et al.[156] and Pittner and co-workers.[158,406] A simplification of the coupling term was elaborated under the name the *uncoupled* SS-Mk-MRCC approach.[402,405,406] A rigorously *spin-adapted* Mk-MRCC approach has been formulated by Datta and Mukherjee.[403] A general theory of *analytic gradients* based on the Lagrangian technique[113] is available for the Mk-MRCC approach.[155] Techniques for calculating *molecular properties* were also suggested.[142−144] However, in practice most of the Mk-MRCC calculations were limited to a small CAS(2,2) model space (the analytic energy gradients are still available only for the CAS(2,2)-Mk-MRCCSD approach).

A recent *general-order* implementation of the Mk-MRCC approach reported by Das et al.[157] exhibited *significant errors* produced by the Mk-MRCCSD approach for larger CAS model spaces when *delocalized* orbitals were used. Also, *convergence problems* were encountered when employing the Mk-MRCC scheme, especially for SR electronic states (where many reference determinants lose their configurational weight)[157] and for *excited* electronic states.[128] Although the reference determinants are treated on the *same footing*, the Mk-MRCC method (as well as SU-MRCC, BW-MRCC, sr-MRCC, and H2E2-MRCC) *lacks any invariance* with respect to *active orbital rotations*.[159,388] Actually, the Mk-MRCCSD approach is rather *sensitive* to the choice of active orbitals, where a poor choice can lead to a *noticeable accuracy loss*[157,159] (despite having the reference space formally unchanged). All these disturbing features point to the necessity of an essential further improvement of the Mk-MRCC scheme. Quite surprisingly, an approximate version of the Mk-MRCCSD method in the form of the MR-CEPA approach[160] produced noticeably better results,[157,160] although most likely this can be attributed to some accidental *error compensation* (fortunately or unfortunately, this phenomenon occurs quite often in quantum chemistry).

3.5. The "Proper Residual" Problem and the MRexpT Multireference Coupled-Cluster Method

It is believed that the above-mentioned deficiencies of the Mk-MRCCSD approach mostly come from the so-called "*proper residual*" problem, as first pointed out by Hanrath[145] and later Kong.[141] Actually, this problem is shared by all aforementioned HS-MRCC methods based on the JM ansatz. It turns out that the above routes of resolving the redundancy problem (*sufficiency conditions*) have a necessary consequence of having *numerous residual components* of the projected Schrödinger equation that are *not equal to zero* (Schrödinger is not satisfied). Indeed, eqs 3.4.9−3.4.12, which resolve the redundancy problem and define four different HS-MRCC approaches, are solved in the bra-space, Q^μ, consisting of all singles, doubles, etc. excitations, up to the maximal excitation rank present in the cluster operator $\hat{T}^\mu$ *with respect to the reference determinant* $|\mu\rangle$. But Q^μ is only a *subspace* of the external space Q, which is the *union* of all Q^μ:

$$Q^\mu \subset Q, \quad \forall \ \mu \tag{3.5.1}$$

$$Q = \cup_\mu Q^\mu \tag{3.5.2}$$

Consequently, the basic projected Schrödinger equation (eq 3.4.3) is rigorously satisfied *only* in the subspace formed by an *intersection* of all Q^μ:

$$\forall \ \langle x| \in \cap_\mu Q^\mu : \quad \sum_\mu C_k^\mu \langle x|(\hat{H} - E_k)\mathrm{e}^{\hat{T}^\mu}|\mu\rangle = 0 \tag{3.5.3}$$

$$\exists \ \langle x| \in Q \setminus \cap_\mu Q^\mu : \quad \sum_\mu C_k^\mu \langle x|(\hat{H} - E_k)\mathrm{e}^{\hat{T}^\mu}|\mu\rangle \neq 0 \tag{3.5.4}$$

We will adopt the name "*proper residual condition*" given to eq 3.5.3 in ref 141. Now we should stress that the dimension of the union-space $Q = \cup_\mu Q^\mu$ *increases (roughly) linearly* with the dimension of the model space, whereas the intersection-space $Q_\mathrm{I} = \cap_\mu Q^\mu$ *very soon becomes empty*! Indeed, all aforementioned HS-MRCC approaches with cluster operators restricted to singles and doubles have *an empty "proper residual" subspace*,

$$Q_\mathrm{I} = \cap_\mu Q^\mu \tag{3.5.5}$$

when the model space involves a pair of reference determinants, one of which is higher than 3-fold excited with respect to the other. For example, if a moderate-size CAS(4,4) model space is employed in any of the above HS-MRCCSD approaches (such a model space is used to dissociate the H_2O molecule), the "proper residual" subspace is empty. In such cases the Schrödinger equation is not satisfied at all (none of its external projections is satisfied). This explains why the most successful applications of the Mk-MRCCSD method were limited to the CAS(2,2) model space and why one observes a poor behavior of the method when describing multiple-bond breaking processes (where the model space is CAS(4,4) or larger; see section 6). Let us note again that the "proper residual" problem equally applies to all aforementioned MRCC approaches: BW-MRCC, CAS-SU-MRCC, IAS-SU-MRCC, GMS-SU-MRCC, Mk-MRCC, sr-MRCC, and H2E2-MRCC.

In order to restore a nonempty "*proper residual*" subspace, one must add *higher-excited* cluster operators into the JM ansatz (*triples* at least). Apparently the method will rapidly become impractical. Moreover, the majority of triple and higher excitations lie *outside* the first-order interaction space when the Hamiltonian contains no higher than two-body terms. Another possibility for a rigorous alleviation of the "proper residual" problem is to employ the SRMRCC ideology[161−168] (see subsection 5.1) and *symmetrize* each subspace Q^μ built on top of each reference determinant $|\mu\rangle$, such that $\forall \ \mu$: $Q^\mu = Q$.[159,428] However, the computational cost of the resulting method is high.

The above considerations have led to a radically different route of resolving the redundancy problem introduced by Hanrath.[145] In his MRexpT method,[145] the redundancy problem is resolved in a natural way by eliminating redundant cluster amplitudes. This is done by *reindexing* the cluster amplitudes and *uniquely* associating them with the corresponding projection-space determinants, regardless of the reference determinant (an amplitude is marked with indices of the determinant it corresponds to). Thus, originally distinct cluster amplitudes, which are associated with the same excited determinant but defined with respect to different reference determinants, are grouped together. In order to keep the wave function potentially exact, special *phase factors*, $\phi(z) = \mathrm{e}^{-i \arg z}$, must be included in the MRexpT ansatz:

$$|\Psi_k\rangle = \sum_\mu C_k^\mu \exp\left(\phi(C_k^\mu) \sum_{\hat{\tau}_i(\mu) \in \hat{T}^\mu} t_{\hat{\tau}_i(\mu)|\mu\rangle} \hat{\tau}_i(\mu)\right)|\mu\rangle \tag{3.5.6}$$

where $\hat{\tau}_i(\mu)$ is an elementary excitation operator (it creates an excited determinant $\hat{\tau}_i(\mu)|\mu\rangle$ whose indices are used to mark the associated amplitude $t_{\hat{\tau}_i(\mu)|\mu\rangle}$). The MRexpT working equations are obtained by projecting the Schrödinger equation with the above wave function against the *union* of the model, P, and external, Q, spaces:

$$\forall \ \langle\nu| \in P :$$

$$\langle\nu| \sum_\mu C_k^\mu (\hat{H} - E_k) \exp\left(\phi(C_k^\mu) \sum_{\hat{\tau}_i(\mu) \in \hat{T}^\mu} t_{\hat{\tau}_i(\mu)|\mu\rangle} \hat{\tau}_i(\mu)\right)|\mu\rangle = 0 \tag{3.5.7}$$

$$\forall \ \langle x| \in Q :$$

$$\langle x| \sum_\mu C_k^\mu (\hat{H} - E_k) \exp\left(\phi(C_k^\mu) \sum_{\hat{\tau}_i(\mu) \in \hat{T}^\mu} t_{\hat{\tau}_i(\mu)|\mu\rangle} \hat{\tau}_i(\mu)\right)|\mu\rangle = 0 \tag{3.5.8}$$

The MRexpT equations are *state-specific* (explicitly dependent on the calculated state via the index k). In the MRexpT method, the model space, P, is CAS, leading to the standard intermediate normalization of the wave function. The MRexpT method is free of intruder states, potentially *exact* in the limit, provides a *size-consistent* description of the problem, and *it does satisfy the projected Schrödinger equation* in the union of the model and external spaces (as it should). The latter property resulted in highly *accurate* results demonstrated in model calculations of MR ground and excited electronic states.[145,169−172] Remarkably the approach gives an accurate description of SR cases as well. Unfortunately, the method is *not* rigorously size-extensive for valence electrons, being only *core-extensive*.[145,172] From the practical point of view, the operational scaling of the MRexpT approach with *singles* and *doubles* is still $O(N^6)$, although the prefactor can be large (it rapidly grows with the size of the active space).

3.6. Multideterminantal Vacuum States and Internally Contracted Multireference Coupled-Cluster Approaches

Despite treating all reference determinants on the same footing, all above HS-MRCC approaches are *not invariant* with respect to linear transformations in the active orbital space (*active-orbital rotations*).[159,388] This problem seems to have significant numerical consequences for the Mk-MRCCSD method[157,159] and, presumably, for other HS-MRCCSD approaches suffering from the "*proper residual*" problem (addition of triples provides a remedy, but it is computationally expensive). However, for those HS-MRCCSD methods that satisfy the projected Schrödinger equation, it is hard to believe that active-orbital rotations can lead to significant discrepancies. Moreover, the requirement of invariance with respect to active-orbital rotations does *not* make sense for the GMS-SU-MRCC approach, where the active orbitals are *not* a necessary construct. Nevertheless, it is esthetically (and often practically) attractive to have active-orbital invariance in an HS-MRCC method.

The lack of the active-orbital invariance in HS-MRCC methods, in particular, in the Mk-MRCC approach, was originally attributed to the "proper residual" problem.[309] However, Evangelista and Gauss[159] numerically and Kong[388] theoretically proved that there is a fundamental *inability* of the JM ansatz to comply with the property of active-orbital invariance. The reason is that each cluster operator $\hat{T}^{\mu}$ is still assigned its *own vacuum*, $|\mu\rangle$. In order to abandon such an individual assignment of cluster operators, Evangelista and Gauss later implemented the *internally contracted* ic-MRCC approach,[389] following the ideas of Mukherjee and co-workers.[391] Even earlier Chan and co-workers suggested an internally contracted MRCC approach based on the canonical transformation of the Hamiltonian (CT).[317−321] Contrary to other HS-MRCC schemes, in the internally contracted MRCC methods a *single* cluster operator creates excitations on top of a *multideterminantal vacuum state* treated as a *whole* (before we had several *distinct* vacua with their own cluster operators). Development of such an approach had become feasible due to the existence of the *extended* and *generalized* Wick's theorems which (in particular) prescribe normal ordering for *multideterminantal* vacuum states.[392−394] For the sake of convenience, let us "violate" the chronological order and describe the most recent ic-MRCC development first (the method is quite promising).

In the ic-MRCC method,[389] the *reference function* is generated in the usual way, as a linear combination of determinants obtained by all possible distributions of active electrons among the active orbitals (CAS reference):

$$|\Psi^{(0)}\rangle = \sum_{\mu} C^{\mu}|\mu\rangle = \sum_{\mu} C^{\mu}\hat{\mu}^{+}|\text{core}\rangle \qquad (3.6.1)$$

where $|\text{core}\rangle$ is the *core vacuum* with all active orbitals empty, and $\hat{\mu}^{+}$ is a string of *active creators*, which generate the reference determinant $|\mu\rangle$ by acting on the core vacuum. Since the internally contracted MRCC methods are *state-specific*, we omit the state index. In the ic-MRCC cluster ansatz

$$|\Psi\rangle = \mathrm{e}^{\hat{T}}|\Psi^{(0)}\rangle = \mathrm{e}^{\hat{T}}\sum_{\mu} C^{\mu}|\mu\rangle = \mathrm{e}^{\hat{T}}\sum_{\mu} C^{\mu}\hat{\mu}^{+}|\text{core}\rangle \qquad (3.6.2)$$

the cluster operator has the following structure:

$$\hat{T} = \sum_{m=1}^{M}\hat{T}_m = \sum_{m=1}^{M}\left(\frac{1}{m!m!}\sum_{\substack{\bar{a}_1\ldots\bar{a}_m\\ \bar{i}_1\ldots\bar{i}_m}} T^{\bar{a}_1\ldots\bar{a}_m}_{\bar{i}_1\ldots\bar{i}_m}\hat{\bar{a}}^{+}_1\ldots\hat{\bar{a}}^{+}_m\hat{\bar{\mathrm{i}}}^{-}_m\ldots\hat{\bar{\mathrm{i}}}^{-}_1\right) \qquad (3.6.3)$$

where $\hat{T}_m \equiv 1/(m!m!)\sum_{\substack{\bar{a}_1\ldots\bar{a}_m\\ \bar{i}_1\ldots\bar{i}_m}} T^{\bar{a}_1\ldots\bar{a}_m}_{\bar{i}_1\ldots\bar{i}_m}\hat{\bar{a}}^{+}_1\ldots\hat{\bar{a}}^{+}_m\hat{\bar{\mathrm{i}}}^{-}_m\ldots\hat{\bar{\mathrm{i}}}^{-}_1$, $\bar{i}_k$ indices run over the *union* of the core and active orbital ranges, $\bar{a}_k$ indices run over the *union* of the virtual and active orbital ranges (see Figure 4), and M defines the truncation level in the cluster operator. The cluster amplitudes containing solely active indices are permanently set to *zero*. Because of the overlap of covariant and contravariant indices, the corresponding cluster excitation operators do *not* commute. Such a structure of the cluster operator is also pertinent to the Fock-space MRCC theory (section 4). Actually, a *universal cluster operator* first appeared within the Fock-space framework, represented by works of Mukherjee and co-workers,[102,188,190] Lindgren,[86,87] and Lindgren and Mukherjee,[85] whereas the size-extensivity of the ic-MRCC approach as well as the resolution of linear dependencies (see below) were first studied by Mahapatra et al.[391]

The "preliminary" ic-MRCC amplitude and energy equations read as

$$\langle\Psi^{(0)}|\hat{X}^{+}_{k}\mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}|\Psi^{(0)}\rangle = 0, \qquad \forall\ k \qquad (3.6.4)$$

$$E = \langle\Psi^{(0)}|\mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}|\Psi^{(0)}\rangle \qquad (3.6.5)$$

where $\langle\Psi^{(0)}|\hat{X}^{+}_{k}$ is some linear combination of determinants from the external space, Q, created by a certain elementary excitation operator, $\hat{X}^{+}_{k}$, acting on the *multideterminantal* reference, $\langle\Psi^{(0)}|$. The manifold of excitation operators $\{\hat{X}^{+}_{k}, \forall\ k\}$ generates the bra-space conjugated to the ket-space generated by $\hat{T}$ acting on $|\Psi^{(0)}\rangle$. Despite some formal similarity to the SRCC equations, there are two principal differences:

- The ic-MRCC ansatz is *overdetermined* (overparameterized): the amount of cluster amplitudes (or, equivalently, the amount of distinct $\hat{X}_k^+$) exceeds the dimension of the space generated by the components of $\hat{T}$ acting on $|\Psi^{(0)}\rangle$ (or $\{\hat{X}_k^+, \forall\, k\}$ acting on $\langle\Psi^{(0)}|$).
- The commutator expansion of $e^{-\hat{T}}\hat{H}e^{\hat{T}}$ generally involves *higher* than 4-fold commutators due to the *noncommutativity* of the excitation operators that constitute $\hat{T}$. If M is the highest excitation rank in a truncated ic-MRCC cluster ansatz (eq 3.6.3), then up to $(4 + 2M)$-fold commutators appear in amplitude equations.[90] The energy expression in eq 3.6.5 includes up to *4-fold* commutators. In order for such terminations to happen, the $\hat{T}$ operator is *not allowed* to excite within the model (reference) space.

The first problem can be resolved via the *singular value decomposition* (SVD) of the *metric* matrix[389,391]

$$S_{kl} = \langle\Psi^{(0)}|\hat{X}_k^+\hat{X}_l|\Psi^{(0)}\rangle \tag{3.6.6}$$

Then a *linear independent* set of amplitude (residual) equations is formed by taking proper linear independent combinations of the original residuals given by eq 3.6.4. The original amplitude vector (vector of unknowns) is transformed (reduced) accordingly. However, technically, all original residuals have to be evaluated and all original cluster amplitudes are in use. Note that the metric matrix depends on the model space components, C^μ, of the wave function. Very recently Hanauer and Köhn recognized that linear dependencies can be removed in *multiple* ways.[90] Interestingly, they have concluded that only one way leads to an ic-MRCC approach which provides a *size-consistent* description of quantum chemical problems (called by the authors ic-MRCC-D). Other variants generally violate size-consistency due to the presence of specific *spectator* amplitudes [cluster amplitudes containing the same (active) index in both covariant and contravariant rows] which turned out to be disconnected.[90]

The second problem (the presence of higher-rank commutators) leads to rather *complex formulas* as compared to an analogous SRCC approximation (many more diagrams; diagrams contain more operators). Nevertheless, the use of an automated formula generator has confirmed the $O(N^6)$ computational scaling of the ic-MRCCSD approach,[90] although the prefactor is significantly larger than in the SRCC case. Moreover, the prefactor rapidly grows with the size of the active orbital space defining the CAS model space. As a practical solution, one can neglect some higher-rank commutators.[90,389] Provided that the reference function is a good zeroth-order approximation to the exact wave function, the cluster amplitudes should be relatively small, thus justifying a truncation of the commutator series.

In the ic-MRCC method the reference coefficients, C^μ, can be iteratively relaxed by solving the eigenvalue problem in the reference space, P:

$$\sum_{\nu} \langle\mu|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\nu\rangle C^\nu = EC^\mu, \qquad \forall\ \mu \tag{3.6.7}$$

However, by modifying the model space components of the wave function, one also changes the metrics in eq 3.6.6, such that a new linear transformation of the residuals is required. By using proper iterative schemes, both ground and excited electronic states are accessible. Moreover, one can write a *Lagrangian* for the ic-MRCC approach, making *analytic energy gradients* available (in principle).[90] Preliminary tests have shown the ability of the method to provide *accurate* potential energy surfaces for small molecules.[90,389] The ic-MRCCSD energies are of the same (high) quality as those produced by the MRexpT-SD[145,169−172] and CASCCSD[82,168,246−253] methods. At the same time, the amount of variables in the ic-MRCCSD method does not grow so fast with the size of the CAS model space (a big advantage of the internally contracted ansätze). However, the energy produced by internally contracted MRCCSD approaches can noticeably depend on the SVD threshold used for eliminating linear dependencies (for example, when describing the N_2 molecule dissociation[90]). This is a potential source of PES discontinuities. Besides, the ic-MRCC approach does not account for the reference-specific orbital relaxation.

In the context of a methodological development of CC theories based on *noncommutative* cluster expansions, we should mention the important works of Mukherjee and coworkers[77,390] where the authors stress the necessity of redefining the factors in a noncommuting exponential expansion, such that each distinct excitation appears only *once* in the cluster expansion. The corresponding combinatoric factors are known as *automorphic factors*. The redefined noncommutative exponential was used by the authors within the valence-universal framework under the name the *combinatoric open-shell coupled cluster theory*.[77,390]

As we have already mentioned, prior to the ic-MRCC approach, other variants of the internally contracted HS-MRCC theory had been suggested. Chan and co-workers[317−321] elaborated the *canonical transformation* (CT) CC theory, which relies on the reference function $|\Psi^{(0)}\rangle$ constructed with either CASSCF or DMRG methods (only the corresponding density matrices are really needed). Importantly, the use of DMRG reference functions noticeably extends the maximal size of the active space that can be employed for the zeroth-order description of the MR problem. Subsequently, the dynamic electron correlation is captured with a *unitary* exponential wave operator:

$$|\Psi\rangle = e^{\hat{T} - \hat{T}^+}|\Psi^{(0)}\rangle \tag{3.6.8}$$

Because of the unitary form, the expansion of the *canonically* transformed Hamiltonian

$$e^{-(\hat{T} - \hat{T}^+)}\hat{H}e^{\hat{T} - \hat{T}^+} = \hat{H} + [\hat{H}, \hat{T} - \hat{T}^+] + \frac{1}{2!}[[\hat{H}, \hat{T} - \hat{T}^+], \hat{T} - \hat{T}^+] + \ldots \tag{3.6.9}$$

does *not* terminate naturally (each commutator has a higher excitation rank than the operators involved in it). The CT-CC theory exploits the *density cumulant decomposition* technique[450,453] for approximating higher−rank density matrices[317] (density matrices naturally appear in internally contracted CC theories[392−394]). The reference function can further be *relaxed* by making stationary the expectation value of the canonically transformed Hamiltonian, $\langle\Psi^{(0)}|e^{-(\hat{T}-\hat{T}^+)}\hat{H}e^{(\hat{T}-\hat{T}^+)}|\Psi^{(0)}\rangle$ (with respect to the reference space coefficients defining $|\Psi^{(0)}\rangle$). The CT-CC theory is invariant to active-orbital rotations. If the cluster operator is truncated at the level of singles-and-doubles, the computational scaling of the resulting approach is $O(N^6)$, though the leading term is o^1v^5, where o/v is the amount of occupied/virtual orbitals, respectively. As an internally contracted MRCC scheme the CT-CC method also requires an elimination of certain linear dependencies when solving the amplitude equations (with the aid of the overlap matrix). In general, this can lead to convergence problems and discontinuities of potential energy surfaces.[90,321] In order to improve the convergence properties, the *strongly contracted* CT-CC theory was recently introduced.[321] The CT-CC methods were tested in several MR calculations, and certain results are encouraging.[317−321]

From a formal point of view, the SS-MRCC approach of Banerjee and Simons[91] and the SS-EOMCC/pIC-MRCC methods of Nooijen and co-workers[333,334,395] also employ a single cluster operator acting on a *multideterminantal* reference function. However, the principal distinction of these HS-MRCC methods is the use of *commutative* excitation operators in the cluster ansatz (covariant and contravariant index ranges do not overlap in amplitude tensors). Banerjee and Simons[91] suggested a *state-specific* MRCC ansatz of the form

$$|\Psi\rangle = \mathrm{e}^{\hat{T}}\hat{C}|0\rangle = \mathrm{e}^{\hat{T}}|\Psi^{(0)}\rangle \tag{3.6.10}$$

where

$$|\Psi^{(0)}\rangle \equiv \hat{C}|0\rangle = \sum_{\mu} C^{\mu}\hat{\mu}^{+}|0\rangle = \sum_{\mu} C^{\mu}|\mu\rangle \tag{3.6.11}$$

is the CAS reference function (initially taken from a CASSCF calculation). Here $|0\rangle$ is the *core* determinant containing only *core-orbitals* (the orbitals which are occupied in *all* reference determinants), while $\hat{\mu}^{+}$ contains solely active-particle creators, generating the reference determinant $|\mu\rangle$ from the core vacuum $|0\rangle$. The cluster operator $\hat{T}$ is usually truncated at the *singles-and-doubles* level. The peculiarity of the approach of Banerjee and Simons is that the cluster operator correlates only active electrons by exciting them to inactive virtual orbitals:

$$\hat{T}_k = \frac{1}{k!k!} \sum_{\substack{\mathrm{a}_1\ldots\mathrm{a}_k \\ I_1\ldots I_k}} t^{\mathrm{a}_1\ldots\mathrm{a}_k}_{I_1\ldots I_k}\hat{\tau}^{\mathrm{a}_1\ldots\mathrm{a}_k}_{I_1\ldots I_k} \tag{3.6.12}$$

where each index from $I_1...I_k$ designates an *active* hole (an active orbital which is occupied in some but not all reference determinants). Thus, *all active orbitals* are *holes* (there is no active particles), while *inactive virtuals* constitute the *particle* range. The exponential operator $\mathrm{e}^{\hat{T}}$ acts on the entire reference vector $\Sigma_{\mu}C^{\mu}|\mu\rangle$. The cluster amplitudes are determined by solving the internally contracted residual equations:

$$\forall\ x: \quad \langle\Psi^{(0)}|\hat{\tau}^{+}_{x}\mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}|\Psi^{(0)}\rangle = 0 \tag{3.6.13}$$

where x runs through all components of the cluster operator $\hat{T}$, while different vectors $\langle\Psi^{(0)}|\hat{\tau}^{+}_{x}$ are not orthogonal again. The model space components, C^{μ}, can be either iteratively adjusted or fixed at the CASSCF values.[91]

Contrary to other internally contracted MRCC methods, the MRCC ansatz of Banerjee and Simons is never complete, since it does not include the *core-active* excitations (active orbitals are not included in the particle range). These excitations are also called *semi-internal* and they are quite important in practice. Besides some earlier attempts at improvement,[240,241] a real resurrection of the MRCC approach of Banerjee and Simons occurred due to the works of Nooijen and co-workers,[333,334,395] who employed the EOMCC method for a (partial) inclusion of semi-internal excitations. Their *state-specific* (SS) MR-EOMCC method,[333,334] which later evolved into the *partially internally contracted* MRCC approach[395] (pIC-MRCC), is based on the following ansatz:

$$\begin{aligned} |\Psi\rangle &= \mathrm{e}^{\hat{T}}\hat{R}|\Psi^{(0)}\rangle = \mathrm{e}^{\hat{T}}\hat{R}|\sum_{\mu} C^{\mu}|\mu\rangle \\ &= \mathrm{e}^{\hat{T}}(\sum_{\mu} C^{\mu}|\mu\rangle + \sum_{\mu,l} C^{\mu}\hat{R}^{l}_{\mu}|\mu\rangle) \end{aligned} \tag{3.6.14}$$

where $|\Psi^{(0)}\rangle \equiv \Sigma_{\mu}C^{\mu}\hat{\mu}^{-}|0\rangle = \Sigma_{\mu}C^{\mu}|\mu\rangle$ is a *multidimensional* reference vector generated from the core vacuum, $|0\rangle$, in which all active orbitals are occupied ($\hat{\mu}^{-}$ annihilates excessive active electrons, creating the reference determinant $|\mu\rangle$; alternatively, one can start from the core vacuum where all active orbitals are empty and then create $|\mu\rangle$ with $\hat{\mu}^{+}$). A set of operators $\hat{R}^{l}_{\mu}$ generates excitations absent in the cluster operator. The cluster operator is truncated at the level of *singles and doubles*, $\hat{T} = \hat{T}_1 + \hat{T}_2$, where

$$\hat{T}_k = \frac{1}{k!k!} \sum_{\substack{\mathrm{a}_1\ldots\mathrm{a}_k \\ \bar{i}_1\ldots\bar{i}_k}} t^{\mathrm{a}_1\ldots\mathrm{a}_k}_{\bar{i}_1\ldots\bar{i}_k}\hat{\tau}^{\mathrm{a}_1\ldots\mathrm{a}_k}_{\bar{i}_1\ldots\bar{i}_k} \tag{3.6.15}$$

where $\hat{\tau}^{\mathrm{a}_1\ldots\mathrm{a}_k}_{\bar{i}_1\ldots\bar{i}_k}$ are *spin-free* unitary generators. Similarly to the ansatz of Banerjee and Simons, all active orbitals are included into the hole range, $\bar{i}_m$, together with inactive occupied orbitals. Inactive virtuals constitute the particle range, a_m. The *state-specific* cluster amplitudes are determined by solving a spin-adapted version of eq 3.6.13. Provided that the reference function, $|\Psi^{(0)}\rangle$, is a spin eigenfunction, the SS-MR-EOMCC/pIC-MRCC wave function is automatically *spin-adapted*. As we already know, the internally contracted residual equations can suffer from near-*singularities*, requiring a procedure for removing linearly dependent components. Again the use of discarding thresholds can lead to PES discontinuities. To alleviate this problem, the perturbative estimates of discarded amplitudes can be used.[334] Alternatively, a solution procedure based on the *many-body residuals* of the similarity-transformed Hamiltonian is free from near-singularities.[395]

Having determined the cluster operator, one proceeds with a similarity-transformation of the Hamiltonian, $\bar{\hat{H}} = \mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}$, accompanied by a subsequent diagonalization in the MRCIS space (reference space + all singles from each reference CSF):

$$\forall\ l: \quad \bar{\hat{H}}^{(k)}|R_l\rangle = E_l|R_l\rangle \tag{3.6.16}$$

where the vector $|R_l\rangle$ is expanded in the MRCIS space, and the superscript (k) means that the similarity-transformed Hamiltonian is constructed with the cluster amplitudes computed for the kth electronic state (all other eigenstates appear as byproducts). Importantly, $|R_l\rangle$ contains *semi-internal* excitations initially absent in $\mathrm{e}^{\hat{T}}|\Psi^{(0)}\rangle$, which, in particular, allow the reference-specific *orbital relaxation* (absent in the ic-MRCC method, for example). In order to include all important semi-internal excitations, the authors declared all holes as *active*, which can result in a quite large MRCIS diagonalization. In practice, the SS-MR-EOMCC/pIC-MRCC approach has several approximations intended to decrease its computational cost.[334,395]

The SS-MR-EOMCC/pIC-MRCC method of Nooijen and co-workers was shown to provide quite accurate results for several MR problems.[333,334,395] Formally, the method can be applied to any ground or excited state in a state-specific manner. Due to the use of a single cluster operator, larger active spaces can be considered, although in the current version the MRCIS diagonalization space can grow quite fast. The approach is invariant to active orbital rotations, because all active orbitals are holes in $\hat{T}$, while MRCIS preserves the invariance due to its linear structure. However, because of the MRCIS diagonalization step, the SS-MR-EOMCC/pIC-MRCC method violates generalized extensivity, being only *core-extensive*.

Another somewhat related formalism, called the *block-correlated* CC approach (BCCC), was suggested by Fang and Li.[266−268] The peculiarity of their scheme is that the entire CAS model space is considered as a single block that can be in several different states, each state corresponding to a particular distribution of N_0 active electrons among active orbitals. N_0 ranges from 0 to the maximal amount of electrons that fits the active orbital space. In other words, this multiorbital block can be in any state from the complete Fock space built on the active orbitals only. Inactive orbitals are treated conventionally (one orbital per block). The presence of such a multiorbital block changes the hierarchy of cluster operators. The BCCC ansatz can be formally represented as

$$|\Psi\rangle = e^{\hat{T}_1^B + \hat{T}_2^B + \hat{T}_3^B + \hat{T}_4^B + \cdots}|0\rangle \tag{3.6.17}$$

where $\hat{T}_k^B$ is a cluster operator defined with respect to blocks (not individual orbitals), and $|0\rangle$ is the lowest-energy CASSCF determinant. A truncation of the cluster operator on $\hat{T}_4^B$ leads to the BCCC4 approach. The BCCC4 approach scales as $O(N^6)$, where N is the total number of orbitals. When the multiorbital block reduces to a single orbital (SR case, one-dimensional model space) the BCCC4 method turns into the regular CCSD approach. The BCCC4 method with a *CAS(2,2)* model space is *invariant* with respect to separate unitary transformations within the inactive-occupied/active/inactive-virtual orbital spaces. The BCCC4 approach was successfully tested on some model systems.[266−268] However, in order to describe multiple-bond breaking processes or other "*strong*" MR phenomena, one needs to either extend the active space together with the cluster operator (computationally expensive) or to introduce multiple active spaces.

3.7. Conclusions: Genuine Hilbert-Space Multireference Coupled-Cluster Theory

The genuine HS-MRCC theory has been significantly advanced over the last period of time. Several essential problems pertinent to classical formulations ("proper residual", amplitude redundancy, intruder states, etc.) were revealed, thoroughly analyzed, and mostly alleviated. A brief summary characterizing each HS-MRCC scheme (implying their computationally tractable approximations) is given in Table 1. Having efficiently implemented such MRCC methods as ic-MRCCSD, pIC-MRCCSD, MRexpT-SD, GMS-SU-MRCCSD, and Mk-MRCCSD, one can already resolve certain *complex* quantum-chemical problems[410] severely plagued by *quasidegeneracy*. Of course, neither MRCC approach is ideal (nor is SRCC) and further improvements are desirable. We want to emphasize that the pessimism toward MRCC techniques has been mostly caused by the complexity of MRCC theory. However, it should be realized that in general *complex problems unavoidably require complex methods*. At the same time, complex methods need an *efficient* and *user-friendly* computer implementation in order to be used by a wide chemical community.

Unfortunately almost all MR methods (MRCC, MRCI, and MRPT) require a *manual selection* of the *model space* for the problem of interest. Even a more fundamental problem stems from the fact that the model space can *change* along the PES. The reference determinants important in one region of the PES can become low-contributing in another region. In particular, most MR approaches do not automatically reduce to SR approaches in SR regions of a PES because of the necessity of keeping the reference space consistent along the *entire* PES. However, to maintain all ever-required determinants in the model space can be *expensive computationally*, or plagued by the *intruder* state problem. On the other hand, modifying the model space in accord with the dynamically changing character of the PES will necessarily introduce *discontinuities* to the calculated energy. This is a fundamental problem of MR approaches that can hardly be resolved within the classical "theoretical model chemistry" scheme.

4. GENUINE MULTIREFERENCE COUPLED-CLUSTER THEORY IN FOCK SPACE

4.1. The Valence-Universal Wave Operator: Subsystem Embedding Conditions

Historically, the *Fock-space multireference coupled-cluster* (FS-MRCC) approaches were among the first attempts to treat *open-shell* electronic states,[85−87,102,188−191] mostly focusing on an appropriate account of the *static* electron correlation (fully degenerate MR problems). Similarly to the HS-MRCC formalism, the FS-MRCC theory also uses a *multidimensional* model space in which the zeroth-order reference wave function is constructed. In a similar fashion, the target wave functions are obtained by the action of a wave operator that is determined by solving the Bloch equation (eq 3.1.7). However, contrary to the HS-MRCC methods based on the JM ansatz, the FS-MRCC theory is based on the so-called *valence-universal* (VU) exponential ansatz, pioneered in the works of Mukherjee and co-workers.[102,188,189] Such an ansatz is composed of a *single* exponential operator capable of generating wave functions with a different number of electrons (or quasi-particles) when acting on appropriate reference functions. Notwithstanding some early forms of the VU-MRCC wave operator,[188,189,192] now all practical FS-MRCC schemes are based on the *normal-ordered valence-universal* wave operator, $\hat{\Omega} = \{e^{\hat{S}}\}$, introduced by Lindgren:[87]

$$|\Psi_k\rangle = \{e^{\hat{S}}\}|\Phi_k\rangle \tag{4.1.1}$$

where the curly brackets {} mean *normal-ordering* of all terms with respect to a certain *unique Fermi vacuum*, $|0\rangle$, and $|\Phi_k\rangle$ is the reference function for the kth eigenstate, $|\Psi_k\rangle$, of the normal-ordered (with respect to $|0\rangle$) Hamiltonian expressed in the second-quantized form by eq 2.2.8 (different eigenstates may correspond to different amounts of particles). Similar schemes were also investigated by Offerman et al.[193] and Ey[194] in the field of nuclear physics.

In contrast to the Hilbert-space MRCC theory, FS-MRCC approaches operate in the *Fock space*, **F**, which is a union of Hilbert spaces, $\mathbf{H}(N)$, with a different number of particles, N:

$$\mathbf{F} = \cup_N \mathbf{H}(N) \tag{4.1.2}$$

Therefore, in FS-MRCC theory one can simultaneously access electronic states with a different number of electrons (or *quasiparticles* in the hole−particle formalism): the ground state

Table 1. A Summary for HS-MRCC Methods

method	size-extensivity/ size-consistency	proper residual	convergence
BW-MRCC	no/no	no	OK
CAS-SU-MRCC	yes/yes	no	often poor
IAS/GMS-SU-MRCC (Paldus, Li)	core-extensive/yes	no	OK (with a proper IAS/GMS)
IAS/GMS-SU-MRCC (Meissner/Mukherjee)	yes/yes	no	OK (with a proper IAS/GMS)
Mk-MRCC	yes/yes	no	OK; poor for SR and excited states
sr-MRCC	yes/yes	no	OK; poor for SR and excited states
SS-H2E2-MRCC	asymptotic size-extensivity/yes	no	unknown
MRexpT	core-extensive/yes	yes	OK
CTCC	yes/yes	approx.	OK; sometimes poor
ic-MRCC	yes/not always	yes	OK; sometimes poor
pIC-MRCC	core-extensive/not always	yes	OK

(based on $|0\rangle$), ionized/electron-attached states ($-1/+1$ particle or, equivalently, $+1$ quasiparticle), excited states ($+2/+4/...$ quasiparticles), mixed states, etc.[85,86,449] The corresponding wave functions are still constructed with the *same* valence-universal wave operator, which can be either a pure exponential,[188] $\hat{\Omega} = e^{\hat{S}}$, or normal-ordered exponential,[87] $\hat{\Omega} = \{e^{\hat{S}}\}$, the latter being more compact and convenient in practice. Such flexibility makes FS-MRCC theory very attractive for quantum chemistry.

Formally, FS-MRCC approaches tackle MR problems in a different way, as compared to HS-MRCC methods. In the following we will restrict ourselves to the FS-MRCC theory based on the *hole–particle* formalism (for more general FS-MRCC formalism, we refer the reader to the works of Stolarczyk and Monkhorst[444−449]). First of all, there is a *special (usually closed-shell) determinant*, $|0\rangle$, that defines the *global Fermi vacuum* which is universal for all operators involved in the theory, regardless of the calculated electronic state. In FS-MRCC theory, the model space is constructed using active orbitals, but in a more general way than in HS-MRCC theory. Namely, the number of active electrons can *vary*; i.e., the reference function, $|\Phi_k\rangle$, can contain different amounts of active electrons, depending on the calculated state. The orbital space partitioning together with orbital labeling is shown in Figure 4. The cluster excitation operator $\hat{S}$ can be represented as

$$\hat{S} = \hat{S}_1 + \hat{S}_2 + ... + \hat{S}_n \tag{4.1.3}$$

$$\hat{S}_m = \frac{1}{m!m!} \sum_{\substack{\bar{a}_1...\bar{a}_m \\ \bar{i}_1...\bar{i}_m}} S^{\bar{a}_1...\bar{a}_m}_{\bar{i}_1...\bar{i}_m} \hat{\tau}^{\bar{a}_1...\bar{a}_m}_{\bar{i}_1...\bar{i}_m} \tag{4.1.4}$$

where $\hat{\tau}^{\bar{a}_1...\bar{a}_m}_{\bar{i}_1...\bar{i}_m} \equiv \{\hat{\bar{a}}^+_1...\hat{\bar{a}}^+_m \hat{\bar{i}}^-_m...\hat{\bar{i}}^-_1\}$ is an elementary normal-ordered excitation operator, $S^{\bar{a}_1...\bar{a}_m}_{\bar{i}_1...\bar{i}_m}$ is the corresponding cluster amplitude, and the *summation excludes index combinations where all indices are active* (no internal excitations/amplitudes). One can notice a close resemblance with eq 3.6.3 (the internally contracted HS-MRCC methodology is actually based on the arguments of FS-MRCC theory). The indices $\bar{i}_1...\bar{i}_m$ run over the combined [*inactive_occupied+active*] range, whereas $\bar{a}_1...\bar{a}_m$ run over the combined [*active+inactive_virtual*] range, as illustrated in Figure 4. Hence, operators $\hat{S}_m$ have a *mixed excitation/de-excitation* nature and do *not commute* with each other (active holes/particles can be both created and annihilated, causing possible contractions between the cluster operators). The first FS-MRCC methods explicitly dealt with a *noncommutative* algebra, facing the necessity of valence universality in order to resolve redundancies.[102,188,189] However, very soon the advantages of the *normal-ordered* VU-MRCC formulation (with the exponential given by eq 4.1.1) became clear.[85−87]

In practical calculations the excitation operator $\hat{S}$ in eq 4.1.3 is truncated, usually at the singles and doubles level (FS-MRCCSD).[195] For the following analysis it is convenient to split the summation in eq 4.1.4, which defines the cluster operator $\hat{S}_m$, into subsummations by separating hole/particle subranges in each index range. The derived summations define more specific operators that differ in the amount of *quasiparticle (hole/particle) annihilators* in $\hat{\tau}^{\bar{a}_1...\bar{a}_m}_{\bar{i}_1...\bar{i}_m} \equiv \{\hat{\bar{a}}^+_1...\hat{\bar{a}}^+_m \hat{\bar{i}}^-_m...\hat{\bar{i}}^-_1\}$:

$$\hat{S}_m = \hat{S}^{(0,0)}_m + \hat{S}^{(0,1)}_m + \hat{S}^{(1,0)}_m + \hat{S}^{(1,1)}_m + ... + \hat{S}^{(m,m-1)}_m + \hat{S}^{(m-1,m)}_m \tag{4.1.5}$$

where $\hat{S}^{(k,l)}_m$ means that the rank of the operator is $2m$ and it has k active-particle annihilators, $\hat{A}^-$, and l active-hole annihilators, $\hat{I}^+$, with respect to the *hole-particle vacuum,* $|0\rangle$. Note that there is no $\hat{S}^{(m,m)}_m$ operator because it would have carried solely active indices. The (k,l) pair specifies the so-called *sector of the Fock space*, $(k + l)$ being the *valence rank* of the corresponding $\hat{S}^{(k,l)}_m$ operator.[449] Each sector (k,l) of the Fock space is a Hilbert space associated with $(k + l)$ quasiparticles or the corresponding amount of real particles [see eq 4.1.2; the number of electrons is equal to $(N_0 + k - l)$, where N_0 is the number of electrons in the Fermi vacuum]. Thus, each sector of the Fock space is an *invariant* subspace of the *quasiparticle number operator.*[449] However, all wave functions are still obtained with the same *valence-universal* wave operator: $|\Psi^{(k,l)}_n\rangle = \{e^{\hat{S}}\}|\Phi^{(k,l)}_n\rangle$, $\forall$ k, l, n. Contrary to SRCC methods, in FS-MRCC theory there is no 1−1 correspondence between the excitation rank of the cluster operator $\hat{S}^{(k,l)}_m$ and the excitation rank of the determinants generated by it, since the latter rank depends on the reference determinant the $\hat{S}^{(k,l)}_m$ operator acts on.

In FS-MRCC theory, the model space and the external space also inherit the *sector structure*:

$$P = P^{(0,0)} \oplus P^{(0,1)} \oplus P^{(1,0)} \oplus P^{(1,1)} + ... \tag{4.1.6}$$

$$Q = Q^{(0,0)} \oplus Q^{(0,1)} \oplus Q^{(1,0)} \oplus Q^{(1,1)} + ... \tag{4.1.7}$$

Associated projectors will have operator hats on top:

$$\hat{P}^{(0,0)} = |0\rangle\langle 0| \tag{4.1.8}$$

$$\hat{P}^{(0,1)} = \sum_{I} |{}_{I}\rangle\langle{}_{I}|, \quad |{}_{I}\rangle = \hat{I}^{-}|0\rangle \tag{4.1.9}$$

$$\hat{P}^{(1,0)} = \sum_{A} |{}^{A}\rangle\langle{}^{A}|, \quad |{}^{A}\rangle = \hat{A}^{+}|0\rangle \tag{4.1.10}$$

$$\hat{P}^{(1,1)} = \sum_{I,A} |{}^{A}_{I}\rangle\langle{}^{A}_{I}|, \quad |{}^{A}_{I}\rangle = \hat{A}^{+}\hat{I}^{-}|0\rangle \tag{4.1.11}$$

etc., and

$$\hat{Q}^{(0,0)} = \sum_{m} \hat{Q}^{(0,0)}_{m}, \quad \hat{Q}^{(0,0)}_{m} = \sum_{\substack{a_1 < \ldots < a_m \\ i_1 < \ldots < i_m}} |{}^{a_1 \ldots a_m}_{i_1 \ldots i_m}\rangle\langle{}^{a_1 \ldots a_m}_{i_1 \ldots i_m}| \tag{4.1.12}$$

$$\hat{Q}^{(0,1)} = \sum_{m} \hat{Q}^{(0,1)}_{m}, \quad \hat{Q}^{(0,1)}_{m} = \sum_{\substack{a_1 < \ldots < a_{m-1} \\ i_1 < \ldots < i_m}} |{}^{a_1 \ldots a_{m-1}}_{i_1 \ldots i_m}\rangle\langle{}^{a_1 \ldots a_{m-1}}_{i_1 \ldots i_m}| \tag{4.1.13}$$

$$\hat{Q}^{(1,0)} = \sum_{m} \hat{Q}^{(1,0)}_{m}, \quad \hat{Q}^{(1,0)}_{m} = \sum_{\substack{a_1 < \ldots < a_m \\ i_1 < \ldots < i_{m-1}}} |{}^{a_1 \ldots a_m}_{i_1 \ldots i_{m-1}}\rangle\langle{}^{a_1 \ldots a_m}_{i_1 \ldots i_{m-1}}| \tag{4.1.14}$$

$$\hat{Q}^{(1,1)} = \sum_{m} \hat{Q}^{(1,1)}_{m}, \quad \hat{Q}^{(1,1)}_{m} = \sum_{\substack{a_1 < \ldots < a_{m-1} \\ i_1 < \ldots < i_{m-1}}} |{}^{a_1 \ldots a_{m-1}}_{i_1 \ldots i_{m-1}}\rangle\langle{}^{a_1 \ldots a_{m-1}}_{i_1 \ldots i_{m-1}}| \tag{4.1.15}$$

etc. Summations in eqs 4.1.12−4.1.15 *exclude internal excitations*, while the model space projectors in eqs 4.1.8−4.1.11 are fully based on *internal excitations/removals/attachments*. Thus, $\hat{P}$ and $\hat{Q}$ projectors are mutually exclusive (the model space and the external space are orthogonal). Each $|\Phi_n^{(k,l)}\rangle$ is expanded in $P^{(k,l)}$.

Therefore, in FS-MRCC theory we have a *hierarchical* structure of operators, induced by the *direct sum decomposition* of the Fock space (eq 4.1.2). From the above definitions it follows that

$$\hat{S}^{(m,n)}\hat{P}^{(k,l)} = 0, \quad \text{if} \quad m > k \quad \text{or} \quad n > l \tag{4.1.16}$$

This rule also applies to products of $\hat{S}^{(m,n)}$:

$$\hat{R}^{(m,n)}\hat{P}^{(k,l)} = 0, \quad \text{if} \quad m > k \quad \text{or} \quad n > l \tag{4.1.17}$$

where $\hat{R}^{(m,n)} \equiv S^{(i,j)}S^{(m-i,n-j)}$ (or any other product containing an arbitrary amount of operators). In this sense particle/hole sector pointers are *additive*. Due to the above conditions many terms in the expansion $\{e^{\hat{S}}\}\hat{P}^{(k,l)}$ will be *identically zero.*

Similarly to HS-MRCC theory, the FS-MRCC amplitude equations are derived from the Bloch equation (subsection 3.1), which is *consecutively resolved in each sector of the Fock space* [in a nondescending order of $(k + l)$, starting from (0,0)]:

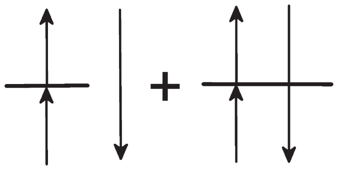
$$\forall \ (k,l): \quad \hat{Q}^{(k,l)}\hat{H}\{e^{\hat{S}}\}\hat{P}^{(k,l)} = \hat{Q}^{(k,l)}\{e^{\hat{S}}\}\hat{H}^{\text{eff}}\hat{P}^{(k,l)} \tag{4.1.18}$$

$$\hat{H}^{\text{eff}} = \hat{P}^{(k,l)}\hat{H}\{e^{\hat{S}}\}\hat{P}^{(k,l)} \tag{4.1.19}$$

A diagonalization of the *effective Hamiltonian*, $\hat{H}^{\text{eff}}$, in the model space of each sector ($P^{(k,l)}$) yields the required electronic energies and reference wave functions corresponding to that sector. The target wave functions can be obtained from the reference wave functions, $|\Phi_n^{(k,l)}\rangle$, by the action of the *valence-universal* wave operator: $\{e^{\hat{S}}\}|\Phi_n^{(k,l)}\rangle$ (the target wave functions are *not* necessarily exact in the limit). Equation 4.1.18 for each subsequent $(k + l)$ implies the existence of solutions (amplitudes) for all preceding values of $(k + l)$, starting from (0,0). In such a *hierarchical* way the number of amplitude equations in each sector is *equal* to the number of unknown cluster amplitudes in that sector. The necessity of a hierarchical equation solver is dictated by the presence of amplitudes from lower sectors in the amplitude equations for higher sectors. For example, the following matrix element appears in the (1,1) sector:

$$\langle{}^{\mathrm{a}}_{I}|\hat{S}|{}^{A}_{I}\rangle = S^{\mathrm{a}}_{A} + S^{I\mathrm{a}}_{IA} \tag{4.1.20}$$

meaning that a particular excited determinant $\langle{}^{\mathrm{a}}_{I}|$ from the external space $Q^{(1,1)}$ can be reached in multiple (two) ways: (1) $|{}^{\mathrm{a}}_{I}\rangle = \hat{\mathrm{a}}^{+}\hat{A}^{-}|{}^{A}_{I}\rangle$ with the amplitude S^{a}_{A} of $\hat{S}_1^{(1,0)}$, and (2) $|{}^{\mathrm{a}}_{I}\rangle = \hat{\mathrm{a}}^{+}\hat{I}^{-}\hat{I}^{+}\hat{A}^{-}|{}^{A}_{I}\rangle$ with the amplitude $S^{I\mathrm{a}}_{IA}$ of $S_2^{(1,1)}$, where $|{}^{A}_{I}\rangle$ is a reference determinant from the model space $P^{(1,1)}$. Diagrammatically the matrix element in eq 4.1.20 can be expressed as



(4.1.21)

The isolated single line in the first diagram is called a *spectator line*. The cluster amplitudes containing the same index in both covariant and contravariant rows are called *spectator amplitudes.* Due to the presence of spectators, the FS-MRCC amplitude equations in each subsequent sector (k,l) involve amplitudes from *lower* sectors (i,j): $i \leq k$, $j \leq l$. The *hierarchical* solution scheme is called the *subsystem embedding conditions* (SEC).[85,86,190] In a more general case, one can also employ the FS-MRCC framework of Stolarczyk and Monkhorst,[444−449] which is based on a systematic *decoupling* of the Fock-space eigenvalue problem via consecutive *similarity transformations* of the original second-quantized Hamiltonian.

In practice, one starts by choosing a certain Fermi vacuum, $|0\rangle$, which is usually a nondegenerate *closed-shell* determinant. This determinant serves as a reference function for the (0,0)-sector eigenproblem. The (0,0)-sector amplitude equations are simply the conventional SRCC equations with a truncated cluster operator $\hat{T} \equiv \hat{S}^{(0,0)}$. Hence *it is important that the Fermi-vacuum determinant,* $|0\rangle$, *is the only leading determinant in the (0,0)-sector wave function* (unless $\hat{T}$ is sufficiently complete). Thus, $|0\rangle$ can be either a closed-shell or a high-spin open-shell determinant.[195] It is convenient to rewrite the Bloch equation (eqs 4.1.18 and 4.1.19) by separating the $\hat{S}^{(0,0)}$ operator as

$$\hat{S} = \tilde{\hat{S}} + \hat{S}^{(0,0)} = \tilde{\hat{S}} + \hat{T} \qquad (4.1.22)$$

thus obtaining

$$\begin{aligned} \forall\ (k,l):\quad & \hat{Q}^{(k,l)}(\mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}})\{\mathrm{e}^{\tilde{\hat{S}}}\}\hat{P}^{(k,l)} \\ &= \hat{Q}^{(k,l)}\{\mathrm{e}^{\tilde{\hat{S}}}\}\hat{P}^{(k,l)}\hat{H}\{\mathrm{e}^{\hat{S}}\}\hat{P}^{(k,l)} \end{aligned} \qquad (4.1.23)$$

eq 4.1.23 was premultiplied with $\mathrm{e}^{-\hat{T}}$ ($\hat{T} \equiv \hat{S}^{(0,0)}$). A factorization of $\mathrm{e}^{\hat{T}}$ is possible because $\hat{T}$ does not contain quasiparticle annihilators and the wave operator, $\{\mathrm{e}^{\hat{S}}\}$, is normal-ordered. Recognizing the connected *similarity-transformed Hamiltonian* of SRCC theory, $\overline{\hat{H}} \equiv \mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}$, one can finally write down the FS-MRCC equations as

$$\forall\ (k,l):\quad \hat{Q}^{(k,l)}\overline{\hat{H}}\{\mathrm{e}^{\tilde{\hat{S}}}\}\hat{P}^{(k,l)} = \hat{Q}^{(k,l)}\{\mathrm{e}^{\tilde{\hat{S}}}\}\hat{H}^{\mathrm{eff}}\hat{P}^{(k,l)} \qquad (4.1.24)$$

$$\hat{H}^{\mathrm{eff}} = \hat{P}^{(k,l)}\hat{H}\{\mathrm{e}^{\hat{S}}\}\hat{P}^{(k,l)} \qquad (4.1.25)$$

where one should not forget that $\hat{H}^{\mathrm{eff}}$ is different in different sectors (we omitted the sector pointer). Equation 4.1.24 serves for determining cluster amplitudes of $\hat{S}_m^{(k,l)}$ (for all m included in the VU-MRCC ansatz). Because of eq 4.1.16, the construct $\{\mathrm{e}^{\tilde{\hat{S}}}\}\ \hat{P}^{(k,l)}$ terminates quite fast and the lhs of eq 4.1.24 is *linear* in unknown cluster amplitudes (amplitudes of $\hat{S}_m^{(k,l)}, \forall\ m$) whereas the rhs is *not* ($\hat{H}^{\mathrm{eff}}$ depends on the unknown cluster amplitudes).

Even though the above equations are not manifestly connected, it can be shown that all *disconnected terms cancel*,[85−87,308] such that one can equivalently use a *connected* form of the FS-MRCC equations (connected form of eq 4.1.24). Thus, the above FS-MRCC theory is *size-extensive* for total energies and *size-intensive* for energy differences. Also the FS-MRCC equations are *invariant* with respect to the active-orbital rotations which do not change the Fermi vacuum (do not mix holes and particles of the Fermi vacuum).[198] Indeed, the cluster operator $\hat{S}$ is invariant to active-orbital rotations by construction (eq 4.1.4).

From the chemical point of view, each sector of the Fock space corresponds to a certain type of electronic state.[85,86,196,215,449] The type of electronic state is determined by the reference wave function, $|\Phi_n^{(k,l)}\rangle$, which is supposed to dominate in the complete (target) quasiparticle wave function (the reference function should *qualitatively* describe the corresponding quasiparticle state). Therefore, the (0,1) sector corresponds to *ionized* electronic states (one-hole states), (1,0) sector to *electron-attached* states (one-particle states), (1,1) sector to *singly excited* states (one-particle−one-hole states), (0,2) sector to *doubly ionized* states (two-hole states), (2,0) to *doubly electron-attached* states (two-particle states), (1,2) sector to *singly excited ionized states* (one-particle−two-hole "shake-up" spectra),[197] (2,1) sector to *singly excited electron-attached* states (two-particle−one-hole states), (2,2) sector to *doubly excited* states (two-particle−two-hole states), and so on. Formally, the FS-MRCC theory is ideally suited for *spectroscopy*. However, one needs to pass quite a long way to obtain excited states dominated by double excitations (with respect to $|0\rangle$).

Let us more carefully analyze the normal-ordered FS-MRCC ansatz[198]

$$|\Psi_n^{(k,l)}\rangle = \mathrm{e}^{\hat{T}}\{\mathrm{e}^{\tilde{\hat{S}}}\}|\Phi_n^{(k,l)}\rangle \qquad (4.1.26)$$

where n enumerates eigenstates in the (k,l) sector. A separation of the SRCC exponential operator, $\mathrm{e}^{\hat{T}}$, from the genuine FS-MRCC part, $\{\mathrm{e}^{\tilde{\hat{S}}}\}$, is more "fundamental" than just being convenient. The cluster operator $\hat{T}$ is a "pure" excitation operator, whereas $\tilde{\hat{S}}$ is always a mixed de-excitation/excitation operator, that is, all components of $\tilde{\hat{S}}$ always contain *quasiparticle annihilators* (hole/particle annihilators) which are shifted to the right due to normal-ordering. Hence,

$$\tilde{\hat{S}}|0\rangle = 0 \qquad (4.1.27)$$

For example, the cluster operator $\hat{S}_m^{(i,j)}$ acting on the reference function $|\Phi_n^{(k,l)}\rangle \in P^{(k,l)}$ ($i \le k$, $j \le l$) first *de-excites/annihilates* certain active quasiparticles [if $i = k$ and $j = l$, all quasiparticles in $|\Phi_n^{(k,l)}\rangle$ are annihilated, returning to the Fermi-vacuum state, $|0\rangle$] and then builds up an *excitation* to the external space, Q. In accordance with eqs 4.1.16 and 4.1.17, the expansion $\{\mathrm{e}^{\hat{S}}\}|\Phi_n^{(k,l)}\rangle$ terminates quite quickly [all products of $\hat{S}_m^{(i,j)}$ with "combined" sectors exceeding (k,l) produce zeros]. For instance, in the (1,1) sector, a truncated cluster operator $\tilde{\hat{S}} = \tilde{\hat{S}}_1 + \tilde{\hat{S}}_2$ leads to

$$\begin{aligned} \{\mathrm{e}^{\tilde{\hat{S}}}\}|\Phi_n^{(1,1)}\rangle = {}& |\Phi_n^{(1,1)}\rangle + \{\hat{S}_1^{(0,1)} + \hat{S}_2^{(0,1)}\}|\Phi_n^{(1,1)}\rangle \\ & + \{\hat{S}_1^{(1,0)} + \hat{S}_2^{(1,0)}\}|\Phi_n^{(1,1)}\rangle + \{\hat{S}_1^{(1,0)}\hat{S}_1^{(0,1)} \\ & + \hat{S}_1^{(1,0)}\hat{S}_2^{(0,1)} + \hat{S}_2^{(1,0)}\hat{S}_1^{(0,1)} + \hat{S}_2^{(1,0)}\hat{S}_2^{(0,1)} \\ & + \hat{S}_2^{(1,1)}\}|\Phi_n^{(1,1)}\rangle \end{aligned} \qquad (4.1.28)$$

One can see that the expansion is rather short (as compared to $\mathrm{e}^{\hat{T}}|0\rangle$, for example). Taking into account the structure of the reference function in $P^{(1,1)}$

$$|\Phi_n^{(1,1)}\rangle = \sum_{I,A} C_I^A|_I^A\rangle \qquad (4.1.29)$$

one can classify excitations in eq 4.1.28. The first term on the rhs is the reference function itself, $|\Phi_n^{(1,1)}\rangle$. The second term augments the reference function as

$$\begin{aligned} & \{\hat{S}_1^{(0,1)} + \hat{S}_2^{(0,1)}\}|\Phi_n^{(1,1)}\rangle \\ & = \sum_{i_1,I_1} S_{i_1}^{I_1}\Big(\sum_{A_1} C_{I_1}^{A_1}\Big)|_{i_1}^{A_1}\rangle + \frac{1}{2!}\sum_{\substack{i_1,i_2,\\ a_1,I_1}} S_{i_1i_2}^{I_1a_1}\Big(\sum_{A_1} C_{I_1}^{A_1}\Big)|_{i_1i_2}^{A_1a_1}\rangle \\ & = \sum_{i_1,A_1} R_{i_1}^{A_1}|_{i_1}^{A_1}\rangle + \frac{1}{2!}\sum_{\substack{i_1,i_2,\\ a_1,A_1}} R_{i_1i_2}^{A_1a_1}|_{i_1i_2}^{A_1a_1}\rangle \end{aligned} \qquad (4.1.30)$$

where $R_{i_1}^{A_1} = \Sigma_{I_1} S_{i_1}^{I_1} C_{I_1}^{A_1}$, $R_{i_1i_2}^{A_1a_1} = \Sigma_{I_1} S_{i_1i_2}^{I_1a_1} C_{I_1}^{A_1}$. Analogously, the third term gives

$$\{\hat{S}_1^{(1,0)} + \hat{S}_2^{(1,0)}\}|\Phi_n^{(1,1)}\rangle = \sum_{I_1,a_1} R_{I_1}^{a_1}|_{I_1}^{a_1}\rangle + \frac{1}{2!}\sum_{\substack{i_1,I_1,\\ a_1,a_2}} R_{I_1i_1}^{a_1a_2}|_{I_1i_1}^{a_1a_2}\rangle \qquad (4.1.31)$$

where $R^{a_1}_{I_1} = \Sigma_{A_1} S^{a_1}_{A_1} C^{A_1}_{I_1}$, $R^{a_1 a_2}_{I_1 i_1} = \Sigma_{A_1} S^{a_1 a_2}_{A_1 i_1} C^{A_1}_{I_1}$. Finally, the fourth term gives

$$\{\hat{S}_1^{(1,0)}\hat{S}_1^{(0,1)} + \hat{S}_1^{(1,0)}\hat{S}_2^{(0,1)} + \hat{S}_2^{(1,0)}\hat{S}_1^{(0,1)} + \hat{S}_2^{(1,0)}\hat{S}_2^{(0,1)} + \hat{S}_2^{(1,1)}\}|\Phi_n^{(1,1)}\rangle = \sum_{\substack{i_1,\\ a_1}} R^{a_1}_{i_1}\left|{}^{a_1}_{i_1}\right\rangle + \frac{1}{2!2!}\sum_{\substack{i_1, i_2,\\ a_1, a_2}} R^{a_1 a_2}_{i_1 i_2}\left|{}^{a_1 a_2}_{i_1 i_2}\right\rangle + \frac{1}{3!3!}\sum_{\substack{i_1, i_2, i_3,\\ a_1, a_2, a_3}} R^{a_1 a_2 a_3}_{i_1 i_2 i_3}\left|{}^{a_1 a_2 a_3}_{i_1 i_2 i_3}\right\rangle \tag{4.1.32}$$

where $R^{a_1}_{i_1}$, $R^{a_1 a_2}_{i_1 i_2}$, and $R^{a_1 a_2 a_3}_{i_1 i_2 i_3}$ coefficients can be derived analogously. Note that S amplitudes carrying only active indices are always zero. Thus, $\{e^{\hat{S}}\}|\Phi_n^{(1,1)}\rangle$ is simply a linear combination of singly, doubly, and triply excited determinants with respect to $|0\rangle$ (excluding $|0\rangle$ itself). A very detailed analysis of the FS-MRCC ansatz can be found in ref 198.

Therefore, the genuine FS-MRCC part, $\{e^{\hat{S}}\}|\Phi_n^{(k,l)}\rangle$, is (in some sense) *"pseudoexponential"*. In practice (due to eqs 4.1.16 and 4.1.17) it terminates much sooner than reaching the maximum possible excitation rank (number of electrons). The true exponential part comes from the SRCC exponential, $e^{\hat{T}}$, because any product of $\hat{T}$ still belongs to the (0,0) sector. Alternatively, one can start from the SRCC *similarity-transformed Hamiltonian* $\hat{\bar{H}} \equiv e^{-\hat{T}}\hat{H}e^{\hat{T}} = (\hat{H}e^{\hat{T}})_C$ (instead of the bare Hamiltonian $\hat{H}$) and hierarchically solve the FS-MRCC equations in higher sectors (k,l), $k + l > 0$. In such a way, the FS-MRCC problem splits into two stages: (1) obtaining the SRCC exponential $e^{\hat{T}}$, which describes the *dynamic* electron correlation over the entire electronic system, and (2) hierarchically solving the pseudoexponential FS-MRCC equations with the similarity-transformed Hamiltonian, $\hat{\bar{H}}$. In the second step, one accounts for the *nondynamic/static* electron correlation peculiar to the state of interest (in a given sector of the Fock space). Again one can notice that similarity-transformations of the Hamiltonian *decouple* the original eigenvalue problem (at least approximately) into subproblems.[449] When the cluster operator is *complete*, such decoupling is *exact*. However, regardless of the truncation of the cluster operator, the similarity-transformed Hamiltonian preserves the original (exact) set of eigenvalues. At the same time, the corresponding eigenvectors are *not* automatically exact. Because of decoupling, in each sector only the relevant part of the wave function is determined, i.e., the part corresponding to a given sector (particular number of quasiparticles). However, the exact (full CI) electronic wave function can have components in different quasiparticle sectors. For example, the wave function of a singly excited electronic state in general can contain the Fermi-vacuum determinant. However, in the SEC-FS-MRCC approach each particular sector of the quasiparticle Fock space is decoupled from the lower sectors. Consequently, any FS-MRCC wave function in the (1,1) sector cannot contain the Fermi-vacuum determinant since the latter belongs to the (0,0) sector. Note that this peculiarity holds even if the cluster operator is complete. Hence, in order to determine the entire wave function, additional conditions must be imposed.

There is also a methodological subtlety related to the numerical check of *additive separability* of FS-MRCC energies (as well as HS-MRCC). Suppose we are concerned with singly excited electronic states, thus working in the (1,1) sector. We want to numerically check whether a simultaneous FS-MRCC description of two *noninteracting* singly excited states (simultaneous excitations) gives us a sum of the energies obtained by separate FS-MRCC calculations of each of those states. We can accomplish a separate calculation of each singly excited state by specifying the (1,1)-sector model space and employing the (1,1)-sector VU-MRCC wave operator. However, in order to calculate the *supersystem* we must proceed to the (2,2) sector, because two simultaneous single excitations produce a *double excitation*. Consequently, the (2,2)-sector model space for the supersystem must be a *direct product* of the (1,1)-sector model spaces used in the subsystem calculations. Also the valence-universal wave operator must be extended to the (2,2) sector, that is, we also need (0,2), (2,0), (1,2), and (2,1) sectors to be considered prior to the final (2,2)-sector calculation. Following these arguments, one realizes that a simultaneous supercalculation of *three* noninteracting systems would require the (3,3) sector, *four* noninteracting systems would require the (4,4) sector, and so on. In other words, the level of the theoretical model becomes dependent on the amount of noninteracting systems considered. This is different from what one has in SRCC theory, where the model space is trivially *one-dimensional*, such that any *direct product* of one-dimensional model spaces is also *one-dimensional*. In contrast, a *multidimensional* model space requires a method to be properly extended when simultaneously calculating *noninteracting open-shell fragments*, such that the model space for the supersystem is a direct product of the subsystem model spaces while the wave operator is modified accordingly. This equally applies to both the *Fock-space* and *Hilbert-space* MRCC theories. The only exception from this rule is an addition of SR *closed-shell* noninteracting fragments, i.e., molecular fragments described by a SR wave function built upon a *single determinant* (*one-dimensional model space*). Apparently, the addition of noninteracting closed-shell SR fragments will not change the dimensionality of the original MR model space, since the corresponding direct-product space has the same dimension.

Fortunately, the hierarchical structure of the SEC-based FS-MRCC theory ensures that the current-sector space has a proper *direct-product* form with respect to the lower sectors of the Fock space. Hence, SEC-FS-MRCC methods can provide a *size-consistent* description of such phenomena as *charge-transfer* excitations, where the excitation energy [for example, in the (1,1) sector] in the separated limit equals the sum of the ionization [(0,1) sector] and electron-attachment [(1,0) sector] energies. This is because the corresponding composite (1,1)-sector linear space is a direct product of the (0,1)- and (1,0)-sector spaces. Thus, the SEC-FS-MRCC theory has an additional property of maintaining size-consistency between different sectors of the Fock space. Apart from a general *size-consistency* test (like that described above), the *generalized-extensivity* test[49,398] is always applicable in FS-MRCC and HS-MRCC theories.

For the sake of completeness, we should add that the basic FS-MRCCSD method has been extended to include *triply* excited clusters, either fully[203,204] or approximately.[205,206] Kaldor and coworkers[204,207] succeeded to access $(0,n)/(n,0)$ sectors where $0 \leq n \leq 6$, and also (1,2)/(2,1) sectors.[197] Several schemes for calculating *molecular properties* within the FS-MRCC framework have been suggested.[208−211,459,460] The FS-MRCC theory was also employed in studies of *electron scattering*.[212] A *relativistic* variant of the FS-MRCC approach is available.[213,214]

4.2. Intermediate Hamiltonian Fock-Space Multireference Coupled-Cluster Approach

Despite the attractive generality of the FS-MRCC theory, in practical calculations it severely suffers from the same *intruder state* problem[215] that made impractical the CAS-SU-MRCC approach. Insufficient separation of the model-space roots from the external-space roots (from the first-order interaction space) causes severe *convergence problems*, making the CAS-FS-MRCC approach inapplicable to most chemical problems. Consequently, similarly to the HS-MRCC theory, the FS-MRCC theory has been extended to incomplete and general model spaces (IAS/GMS-FS-MRCC) that helped to partially overcome the intruder state problem.[98,199,200,202,216−218,451] Despite some other attempts to restore convergence,[219,220] a real resurrection of the FS-MRCC formalism occurred due to the appearance of the so-called *intermediate Hamiltonian* (IH) technique.[116]

The intermediate Hamiltonian technique was introduced by Malrieu,[116] who originally applied it to circumvent the intruder state problem in the MR formulation of perturbation theory. The technique was adopted for the FS-MRCC theory by Mukherjee and co-workers,[136,413] by Koch,[414] by Meissner,[137,221] and later by Kaldor and co-workers.[138,233] The scheme of Meissner has been extensively developed in the works of Musiał and Bartlett.[222−227] All formulations are called IH-FS-MRCC, although we will mainly focus on the IH-FS-MRCC approach of Meissner because of its elegant theoretical structure based on similarity-transformations. Nevertheless, other schemes will also be discussed.

In general the so-called *intermediate space* is a special "*buffer*" space, namely, a *subspace of the external space* that is "energetically" close to the model space. However, in Meissner's IH-FS-MRCC scheme[137] the intermediate space is spanned by *all* excited determinants, which can be reached from the model space by an action of the current−sector cluster operator, $\hat{S}^{(k,l)}$, thus coinciding with the *external* space. In such a case the dimension of the intermediate space in each sector is equal to the number of unknown cluster amplitudes defining the unknown cluster operator $\hat{S}^{(k,l)}$. In general, one can distinguish *four* spaces in the IH-FS-MRCC theory:

1. *model* (main) space P_M with a projector $\hat{P}_M = \Sigma_\mu|\mu\rangle\langle\mu|$;
2. *intermediate* space P_I with a projector $\hat{P}_I = \Sigma_x|x\rangle\langle x|$ (determinants from the intermediate space will be designated as $|x\rangle$, as former external-space determinants;
3. *residual external* space Q with a projector $\hat{Q} = \Sigma_y|y\rangle\langle y|$ ($|y\rangle$ designates the remaining external-space determinants *not* included in the intermediate space);
4. the *orthogonal-complement* space Q' with a projector $\hat{Q}' = \hat{I} - (\hat{P}_M + \hat{P}_I + \hat{Q}) = \Sigma_z|z\rangle\langle z|$. This space cannot be directly reached by the action of the cluster operator $\hat{S}^{(k,l)}$ on the reference function, $|\Phi_n^{(k,l)}\rangle$ (P_I and Q can).

Thus, the original *external* space splits into the *intermediate* space and the *residual external* space (which can become empty). The *resolution of identity* in a particular sector of the Fock space reads as

$$\hat{I}^{(k,l)} = \hat{P}_M^{(k,l)} + \hat{P}_I^{(k,l)} + \hat{Q}^{(k,l)} + \hat{Q}'^{(k,l)} \tag{4.2.1}$$

The main goal of the IH-FS-MRCC scheme of Meissner is to reformulate the standard iterative FS-MRCC equation solver (based on the effective Hamiltonian) to a more robust linear-algebraic procedure such as a *matrix diagonalization* (while keeping the results unchanged). The peculiarity of the approach of Meissner is the use of the entire external space as the intermediate space. Meissner's scheme can be elegantly formulated[137] via the similarity transformations of the original many-body Hamiltonian. The first similarity-transformation reads as

$$\tilde{\hat{H}} = e^{-\hat{X}}(e^{-\hat{T}}\hat{H}e^{\hat{T}})e^{\hat{X}} = e^{-\hat{X}}\overline{\hat{H}}e^{\hat{X}} \tag{4.2.2}$$

where $\hat{T}$ is the SRCC cluster operator obtained in the (0,0) sector and

$$\hat{X} = \{e^{\tilde{\hat{S}}} - 1\}\hat{P}_M^{(k,l)} \tag{4.2.3}$$

It follows that $\hat{X}$ is *nilpotent*:

$$\hat{X}^2 = 0 \tag{4.2.4}$$

that leads to

$$\tilde{\hat{H}} = (1 - \hat{X})e^{-\hat{T}}\hat{H}e^{\hat{T}}(1 + \hat{X}) = (1 - \hat{X})\overline{\hat{H}}(1 + \hat{X}) \tag{4.2.5}$$

where $\overline{\hat{H}} \equiv e^{-\hat{T}}\hat{H}e^{\hat{T}}$. One can partition the $\tilde{\hat{H}}$ matrix as

$$\tilde{\hat{H}} = \begin{bmatrix} \hat{P}_M\overline{\hat{H}}(1+\hat{X})\hat{P}_M & \hat{P}_M\overline{\hat{H}}(\hat{P}_I + \hat{Q}') \\ (\hat{P}_I + \hat{Q}')(1 - \hat{X})\overline{\hat{H}}(1+\hat{X})\hat{P}_M & (\hat{P}_I + \hat{Q}')(1 - \hat{X})\overline{\hat{H}}(\hat{P}_I + \hat{Q}') \end{bmatrix} \tag{4.2.6}$$

where the explicit sector numeration was omitted, implicitly assuming the current (k,l) sector. In the limit of the *complete* cluster operator $\hat{Q}' = 0$ and $\hat{I}^{(k,l)} = \hat{P}_M^{(k,l)} + \hat{P}_I^{(k,l)}$. Now the SEC-FS-MRCC equations given by eq 4.1.24 are equivalent to nullifying the *left-bottom block* of the partitioned $\tilde{\hat{H}}$:

$$\hat{P}_I(1 - \hat{X})\overline{\hat{H}}(1 + \hat{X})\hat{P}_M = 0 \tag{4.2.7}$$

giving

$$\begin{aligned} \hat{P}_I\overline{\hat{H}}(1 + \hat{X})\hat{P}_M &= \hat{P}_I\hat{X}\hat{P}_M\overline{\hat{H}}(1 + \hat{X})\hat{P}_M \\ &= \hat{P}_I(1 + \hat{X})\hat{P}_M\overline{\hat{H}}(1 + \hat{X})\hat{P}_M \end{aligned} \tag{4.2.8}$$

$$\hat{P}_I\overline{\hat{H}}(1 + \hat{X})\hat{P}_M = \hat{P}_I(1 + \hat{X})\hat{H}^{\text{eff}}\hat{P}_M \tag{4.2.9}$$

where $\hat{H}^{\text{eff}} = \hat{P}_M\overline{\hat{H}}(1 + \hat{X})\hat{P}_M = \hat{P}_M\overline{\hat{H}}\{e^{\tilde{\hat{S}}}\}\hat{P}_M$. Because the $\hat{P}_I\tilde{\hat{H}}\hat{P}_M$ block is made zero, the model-space eigenvalue problem is decoupled:

$$\tilde{\hat{H}}|\Phi_n^{(k,l)}\rangle = \hat{P}_M^{(k,l)}\overline{\hat{H}}(1 + \hat{X})|\Phi_n^{(k,l)}\rangle = E_n|\Phi_n^{(k,l)}\rangle \tag{4.2.10}$$

where n enumerates different eigenstates in the (k,l) sector. If the cluster operator is *complete*, then the obtained eigenvalues are *exact*. In practice, a truncation of the cluster operator leads to $\hat{Q}' \neq 0$, meaning that only the subblock $\hat{P}_I\tilde{\hat{H}}\hat{P}_M$ of the $(\hat{P}_I + \hat{Q}')\tilde{\hat{H}}\hat{P}_M$ block is rigorously zero. The presence of the nonzero $\hat{Q}'\tilde{\hat{H}}\hat{P}_M$ block leads to *approximate* eigenvalues.

Nevertheless, we still have *two* separate problems expressed by eq 4.2.9 and eq 4.2.10. In order to derive the final "*one-shot*" IH-FS-MRCC procedure, we need to perform a *second similarity transformation,* which changes only the upper off-diagonal block in eq 4.2.6. Let us define the following operators

$$\hat{Z} = \hat{P}_I\hat{X} \tag{4.2.11}$$

$$\hat{Y} = \hat{Q}'\hat{X} \tag{4.2.12}$$

such that

$$\hat{X} = \hat{Y} + \hat{Z} \tag{4.2.13}$$

$$(1 + \hat{X}) = (1 + \hat{Y})(1 + \hat{Z}) \tag{4.2.14}$$

$$(1 - \hat{X}) = (1 - \hat{Z})(1 - \hat{Y}) \tag{4.2.15}$$

where $\hat{Y}\hat{Z} = \hat{Z}\hat{Y} = \hat{Y}\hat{Y} = \hat{Z}\hat{Z} = 0$ (see eq 4.2.4). Equation 4.2.5 can be rewritten as

$$\tilde{\hat{H}} = (1 - \hat{X})\overline{\hat{H}}(1 + \hat{X}) = (1 - \hat{Z})(1 - \hat{Y})\overline{\hat{H}}(1 + \hat{Y})(1 + \hat{Z}) \tag{4.2.16}$$

In Meissner's IH-FS-MRCC approach, the doubly similarity-transformed Hamiltonian

$$\begin{aligned}\tilde{\tilde{\hat{H}}} &= (\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})(1 - \hat{Y})\overline{\hat{H}}(1 + \hat{Y})(\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}}) \\ &= (\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})\overline{\hat{H}}(1 + \hat{Y})(\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})\end{aligned} \tag{4.2.17}$$

is called the *intermediate Hamiltonian* (IH).[137] Within a union of the model and intermediate spaces, the intermediate Hamiltonian is related to $\tilde{\hat{H}}$ (eq 4.2.16) via a similarity transformation:

$$\begin{aligned}&\mathrm{e}^{-\hat{Z}}\tilde{\tilde{\hat{H}}}\mathrm{e}^{\hat{Z}} \\ &= (\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})(1 - \hat{Z})(1 - \hat{Y})\overline{\hat{H}}(1 + \hat{Y})(1 + \hat{Z})(\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}}) \\ &= (\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})(1 - \hat{X})\overline{\hat{H}}(1 + \hat{X})(\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}}) \equiv \tilde{\hat{H}}\end{aligned} \tag{4.2.18}$$

thus possessing the same eigenvalue spectrum. A diagonalization of the intermediate Hamiltonian (eq 4.2.17) directly yields the required energy eigenvalues. A subset of the eigenvalues corresponding to the model space coincides with the eigenvalue spectrum of the effective Hamiltonian of the standard FS-MRCC theory.

The intermediate Hamiltonian can be expanded as

$$\tilde{\tilde{\hat{H}}} = (\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})\overline{\hat{H}}(\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}}) + (\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})\overline{\hat{H}}\hat{Y}\hat{P}_{\mathrm{M}} \tag{4.2.19}$$

where the first term on the rhs is simply the *similarity-transformed Hamiltonian* of the SRCC theory, while the second term is the so-called "*dressing*".[137,221] The dressing operator $\hat{Y}$ contains all the terms of the $\{\mathrm{e}^{\tilde{\hat{S}}}\}$ expansion that produce excitations out of the intermediate space when acting on the model space determinants. It is important to note that in each sector of the Fock space the dressing term is always built from the amplitudes coming from the lower sectors. For example, there is no dressing in the (0,1) and (1,0) sectors, such that the SEC-FS-MRCC theory in these sectors is equivalent to the corresponding IP/EA-EOMCC theory.[228] In the (1,1) sector with a truncated cluster operator $\hat{S}^{(1,1)} = \hat{S}_2^{(1,1)}$ one has[221]

$$\begin{aligned}\hat{Y}\hat{P}_{\mathrm{M}}^{(1,1)} = \{&\hat{S}_2^{(1,0)} + \hat{S}_2^{(0,1)} + \hat{S}_1^{(1,0)}\hat{S}_2^{(0,1)} \\ &+ \hat{S}_1^{(0,1)}\hat{S}_2^{(1,0)} + \hat{S}_2^{(0,1)}\hat{S}_2^{(1,0)}\}\hat{P}_{\mathrm{M}}^{(1,1)}\end{aligned} \tag{4.2.20}$$

whereas the $\hat{Z}$ operator gives

$$\begin{aligned}\hat{Z}\hat{P}_{\mathrm{M}}^{(1,1)} = \{&\hat{S}_1^{(1,0)} + \hat{S}_1^{(0,1)} + \hat{S}_1^{(1,0)}\hat{S}_1^{(0,1)} \\ &+ \hat{S}_2^{(1,1)}\}\hat{P}_{\mathrm{M}}^{(1,1)}\end{aligned} \tag{4.2.21}$$

It should be noted that the intermediate Hamiltonian, being expressed diagrammatically, contains *disconnected* terms. However, all these disconnected contributions *exactly cancel* during the CI-like diagonalization of $\tilde{\tilde{\hat{H}}}$, thus preserving rigorous *size-extensivity* of the IH-FS-MRCC method[137] (obviously if the IH-FS-MRCC eigenvalue spectrum is the same as the original FS-MRCC eigenvalue spectrum, the size-extensivity of these roots is preserved automatically).

Although only the model-space roots are guaranteed to be exact in the limit, the above IH-FS-MRCC theory does not explicitly distinguish the model space when diagonalizing the intermediate Hamiltonian. However, the model space is exposed when constructing the dressing term, $(\hat{P}_{\mathrm{M}} + \hat{P}_{\mathrm{I}})\overline{\hat{H}}\hat{Y}\hat{P}_{\mathrm{M}}$. First of all, the *required eigenvectors must have the largest components in the model space*. Besides, CI eigenvectors obtained from the lower sectors of the Fock space must be reexpressed in terms of *cluster amplitudes*, which will be subsequently used for constructing the dressing term in higher sectors of the Fock space. Note that all model-space roots are required. The necessary formulas are based on dividing the space into the model space and the external space, partitioning the Hamiltonian matrix accordingly, and considering the block eigenvalue problem[227]

$$\mathbf{H}_{\mathrm{PP}} + \mathbf{H}_{\mathrm{PQ}}\mathbf{S} = \mathbf{H}^{\mathrm{eff}} \tag{4.2.22}$$

$$\mathbf{H}_{\mathrm{QP}} + \mathbf{H}_{\mathrm{QQ}}\mathbf{S} - \mathbf{S}\mathbf{H}^{\mathrm{eff}} = \mathbf{0} \tag{4.2.23}$$

where

$$\mathbf{S} = \mathbf{C}_{\mathrm{Q}}\mathbf{C}_{\mathrm{P}}^{-1} \tag{4.2.24}$$

$$\mathbf{H}^{\mathrm{eff}} = \mathbf{C}_{\mathrm{P}}\mathbf{E}\mathbf{C}_{\mathrm{P}}^{-1} \tag{4.2.25}$$

assuming that $\mathbf{C}_{\mathrm{P}}$ is an invertible matrix that contains all model-space eigenvector components, whereas $\mathbf{C}_{\mathrm{P}} \oplus \mathbf{C}_{\mathrm{Q}}$ specifies the complete eigenvectors of $\mathbf{H}$ obtained by the diagonalization of $\tilde{\tilde{\hat{H}}}$.

Equations 4.2.22−4.2.25 are also useful in analyzing *interconnections* between the IH-FS-MRCC theory and the *equation-of-motion* CC approach (EOMCC).[227,235−239] Musiał and Bartlett suggested an alternative way of calculating the *dressing* term of the intermediate Hamiltonian, presenting some advantages during the conversion of CI coefficients to FS-MRCC cluster amplitudes.[227] Indeed, as one could see from eq 4.2.19, the intermediate Hamiltonian is just the EOMCC Hamiltonian plus the *dressing* term. The latter serves for restoring additional *size-consistency* when describing chemical phenomena involving different sectors of the Fock space. A close relation to the EOMCC approach might be useful in devising a scheme for calculating analytic energy gradients within the IH-FS-MRCC theory (still unavailable).

The above IH-FS-MRCC formulation of Meissner is not unique. Other IH-FS-MRCC approaches have been presented by Mukherjee and co-workers[136,413] and Kaldor and co-workers.[138,233] The two approaches are similar, originating from the *quasidegenerate perturbation theory*.[412] These IH-FS-MRCC methods are more pragmatic in the sense that the intermediate space is chosen to be a subspace of the original external space, which is sufficient to separate the model-space roots from the external roots. Thus, in practical implementations (with a truncated cluster operator) one deals with all four spaces, P_{M}, P_{I}, Q, and Q'. Usually the union $P_{\mathrm{M}} \oplus P_{\mathrm{I}}$ is of

CAS type (in order to achieve rigorous size-extensivity). Both IH-FS-MRCC formulations exploit the *shifted Bloch equation*, where the shift is used to make all relevant energy denominators large enough, thus stabilizing convergence. The basic shifted Bloch equation in Mukherjee's IH-FS-MRCC scheme is[136]

$$\hat{Q}[(\hat{H}_0 + \hat{W}_0), \{e^{\hat{S}}\}](\hat{P}_M + \hat{P}_I) + \hat{Q}\hat{V}\{e^{\hat{S}}\}(\hat{P}_M + \hat{P}_I) = \hat{Q}\{e^{\hat{S}}\}\hat{V}\{e^{\hat{S}}\}(\hat{P}_M + \hat{P}_I) \qquad (4.2.26)$$

$$\tilde{\tilde{\hat{H}}} \equiv (\hat{P}_M + \hat{P}_I)\hat{V}\{e^{\hat{S}}\}(\hat{P}_M + \hat{P}_I) \qquad (4.2.27)$$

where a conventional PT partitioning of the Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{V}$, is used, and $\hat{W}_0$ is the *shift operator* defined exclusively in the intermediate space, P_I. The idea is to introduce suitable $Q \leftarrow P_I$ transition components of $\{e^{\hat{S}}\}$ such that possible quasi-degeneracy between the P_I- and Q-space functions is avoided via suitable shifts.[136] Provided that $P_M \oplus P_I$ is large enough, the model space, P_M, is automatically well-separated from Q, since $P_M \subset P_M \oplus P_I$ and $(P_M \cup P_I) \cap Q = \varnothing$. The formalism is rigorously *size-extensive/size-intensive* if $\hat{W}_0$ is additively separable.

An alternative "*buffered*" IH-FS-MRCC scheme was suggested by Kaldor and co-workers.[138,233] Again the union $P_M \oplus P_I$ is supposed to be of CAS type and a nonempty Q space serves to account for the dynamic electron correlation. The basic shifted Bloch equation is

$$\hat{Q}((E - \hat{H})\{e^{\hat{R}}\})_C(\hat{P}_M + \hat{P}_I) = \hat{Q}(\{e^{\hat{S}}\}(E - \hat{H})\{e^{\hat{R}}\})_C(\hat{P}_M + \hat{P}_I) \qquad (4.2.28)$$

where *two* normal-ordered CC wave operators are used, $\{e^{\hat{S}}\}$ and $\{e^{\hat{R}}\}$, while the cluster operators $\hat{S}$ and $\hat{R}$ are related. E is an arbitrary *shift parameter*. Analogously, the $Q \leftarrow P_I$ transition components of $\{e^{\hat{R}}\}$ serve for separating the $(P_M \oplus P_I)$ and Q spaces.[138,233] Upon fulfilling, the criterion

$$\hat{Q}\hat{S}\hat{P}_M \approx \hat{Q}\hat{R}\hat{P}_M \qquad (4.2.29)$$

confirms that the intermediate space is adequate. This IH-FS-MRCC formalism is also *size-extensive* due to connectivity of the equations. In practical versions the results are slightly dependent on the value of the shift parameter, E.[138]

Kaldor and co-workers also formulated a relativistic variant of the IH-FS-MRCC method.[229] The method has been extensively employed in highly accurate studies of heavy atoms[229−233] and even in a model study of quantum dots.[234] Importantly, Landau et al. suggested a *mixed-sector* variant of the IH-FS-MRCC method (MIH-FS-MRCC), where flexibility in constructing the model space is enhanced by *mixing different sectors* of the Fock space.[201] This brings *relaxation* to the lower sectors of the Fock space and adds absent components to the higher-sector wave functions, thus improving the description of the corresponding electronic states.

4.3. Conclusions: Genuine Fock-Space Multireference Coupled-Cluster Theory

Due to its flexibility the Fock-space MRCC theory is very attractive for spectroscopy, enabling simultaneous consideration of several electronic states of different character (ionized, electron-attached, excited, shake-ups, etc.). The intermediate Hamiltonian formulation of the FS-MRCC theory has resolved the intruder state problem, making possible its practical use. The IH-FS-MRCC approach is rigorously size-extensive/size-intensive and provides a size-consistent description of a wide variety of MR chemical problems. The theory also provides a framework for formulating additional size-consistency corrections to the EOMCC scheme.[235−239] Another important aspect is that the FS-MRCC theory is also applicable to certain problems encountered in atomic and nuclear physics. As we have pointed out, a relativistic variant of the IH-FS-MRCC theory is already available. It was shown to yield highly accurate results in studies of heavy atoms.

Unfortunately, the FS-MRCC method and its intermediate Hamiltonian formulations are far from being "black-box" in use, especially in higher sectors of the Fock space. In order to proceed to a certain higher sector, one must obtain all relevant Hamiltonian roots in all preceding lower sectors that might be expensive from the computational point of view. Also for higher sectors the *orbital relaxation* effects will soon become significant, since the orbitals obtained in the (0,0) sector become progressively less optimal in higher sectors. Another noticeable drawback is an incompleteness of SEC-FS-MRCC wave functions in higher sectors. For this case a proper "completing" technique should be developed. Also schemes for evaluating analytic energy gradients, transition moments, and molecular properties are highly desirable. Besides, the FS-MRCC/IH-FS-MRCC equations rapidly become very complicated (in higher sectors), such that a symbolic algebra tool is required to derive, factorize, and code them. The IH-FS-MRCC approach is still awaiting a robust and efficient computer implementation, which would allow its practical use for chemically interesting problems.

5. ALTERNATIVE MULTIREFERENCE COUPLED-CLUSTER METHODS

5.1. The Complete-Active-Space State-Specific Multireference Coupled-Cluster Approach Based on the Single-Reference Formalism

SRCC formalism has always been more attractive than the *genuine* MRCC theory because of the *conceptual simplicity* and efficient *black-box* implementations of the former. A possibility of describing MR phenomena, yet staying within the SRCC formalism, stimulated extensive studies in this direction. A straightforward addition of *higher excited clusters* into the SRCC ansatz will finally solve *any* MR problem, because the corresponding SRCC wave function is *exact* in the limit. However, the computational cost of such methods (CCSDT, CCSDTQ, etc.) very quickly becomes *prohibitive* (o^3v^5, o^4v^6, etc.), unless some localized approximations are employed (for a reasonable accuracy, a linear-scaling regime can be achieved, in principle). Even with contemporary computational resources, a full-triples CCSDT calculation is affordable only for small molecular systems. Twice increasing the system size (both the number of electrons and the number of virtual orbitals) leads to a 2^{3+5} = 256 times more expensive calculation! From the other side, triples, quadruples, etc. do not constitute the first-order interaction space with respect to a particular reference determinant (they are not directly coupled with that determinant via the Hamiltonian). It looks unreasonable to explicitly include *all* triples, quadruples, etc. clusters in the CC ansatz. As we already know, MRCC methods introduce the concept of a *multidimensional model space* which defines

1. *the minimal space* (spanned by reference determinants) that is required for constructing an adequate zeroth-order wave function in order to provide a *qualitatively correct* description of the correlated problem and
2. *the first-order interaction space* which comprises all *single* and *double* excitations with respect to *each* reference determinant. The first-order interaction space implies a set of independent variables (cluster amplitudes, for example) required for an *accurate* representation of the wave function in this space, such that *quantitatively correct* results can be obtained (to a reasonable accuracy). The amount of unknown variables does not have to be equal to the dimension of the first-order interaction space (it just must be sufficient for an accurate representation of the wave function in this space).

Because the dimension of the model space is usually quite small and the complete first-order interaction space includes only singles and doubles with respect to each reference determinant, the amount of variables involved in an MRCC theoretical model is roughly M times greater than the corresponding amount used in the conventional CCSD approach (M is the dimension of the model space). It turns out that one can employ the concept of a multidimensional model space, yet operationally staying within SRCC formalism. We call such methods *alternative* MRCC approaches (alt-MRCC), contrary to the *genuine* MRCC methods (gen-MRCC). Most alt-MRCC approaches are *state-specific*, describing one electronic state at a time. In such a way all the attractive features of the SRCC theory are preserved while the underlying wave function is constructed following the MRCC route (by introducing a *multidimensional* reference space with the corresponding first-order interaction space).

A very general state-specific alt-MRCC framework is based on the CC ansatz originally suggested by Oliphant and Adamowicz.[161,162] Summarizing numerous developments since then,[163−168,242−253,434,435] we will refer to all relevant alt-MRCC approaches based on the SRCC formalism as the *SRMRCC theory*. The general form of the SRMRCC ansatz[168] is

$$|\Psi\rangle = \mathrm{e}^{\hat{T}^{\mathrm{ext}}}(1 + \hat{C}^{\mathrm{int}})|0\rangle \tag{5.1.1}$$

where $|0\rangle$ is a particular determinant from a multidimensional reference space. By acting on $|0\rangle$ the $(1+\hat{C}^{\mathrm{int}})$ operator generates the complete *multidimensional reference function* (by *internal* excitations in the reference space)

$$|\Psi^{(0)}\rangle \equiv (1 + \hat{C}^{\mathrm{int}})|0\rangle = |0\rangle + \sum_{\mu \neq 0} C^{\mu}|\mu\rangle \tag{5.1.2}$$

Originally SRMRCC methods employed a CAS model space,[161,162] leading to a *fully exponential* form of the CAS-SRMRCC ansatz

$$|\Psi\rangle = \mathrm{e}^{\hat{T}^{\mathrm{ext}}}\mathrm{e}^{\hat{T}^{\mathrm{int}}}|0\rangle \tag{5.1.3}$$

where

$$\mathrm{e}^{\hat{T}^{\mathrm{int}}}|0\rangle = (1 + \hat{C}^{\mathrm{int}}_{\mathrm{CAS}})|0\rangle \tag{5.1.4}$$

The use of IAS/GMS model spaces in SRMRCC theory is discussed in the next subsection. As usual, the CAS model space is supposed to be adequate for a *qualitative description* of the MR problem under consideration. It is expected to capture the major *nondynamic/static* electron correlation effects. The *internal* cluster operator $\hat{T}^{\mathrm{int}}$ as well as any product of $\hat{T}^{\mathrm{int}}$ generates excitations solely within the active space (*internal* excitations):

$$\hat{T}^{\mathrm{int}}_{k} = \frac{1}{k!k!}\sum_{\substack{A_1\ldots A_k\\ I_1\ldots I_k}} t^{A_1\ldots A_k}_{I_1\ldots I_k}\hat{\tau}^{A_1\ldots A_k}_{I_1\ldots I_k} \tag{5.1.5}$$

The standard orbital partitioning is used (Figure 4). The CAS cluster operator $\hat{T}^{\mathrm{int}}$ is complete in the active orbital space (contains all possible internal excitations).

As one can see, the SRMRCC ansatz in eq 5.1.1 is built on top of one particular reference determinant $|0\rangle$, which is called the *formal reference determinant*, or simply the *formal reference*. The formal reference determinant $|0\rangle$ specifies the *global Fermi vacuum* such that *all reference determinants as well as all other determinants are defined as excitations with respect to this formal reference determinant.*[161,162] The entire wave function obeys the *intermediate normalization* with respect to the formal reference determinant:

$$\langle 0|\Psi\rangle = \langle 0|\mathrm{e}^{\hat{T}^{\mathrm{ext}}}(1 + \hat{C}^{\mathrm{int}})|0\rangle = 1 \tag{5.1.6}$$

The remaining *external* cluster operator $\hat{T}^{\mathrm{ext}}$ generates *external* excitations (excitations out of the model space) which are supposed to provide an adequate description of the *dynamic* electron correlation. In principle, one can define $\hat{T}^{\mathrm{ext}}$ quite arbitrarily ($\hat{C}^{\mathrm{int}}$ also), resulting in different variants of the SRMRCC theory. However, the most natural (physically motivated) choice is to include *all single and double external excitations with respect to each reference determinant*, thus explicitly accounting for the entire MR first-order interaction space. This *canonical* CAS-SRMRCC approximation, advocated by Ivanov and Adamowicz, is called the complete-active-space coupled-cluster method with singles and doubles, CASCCSD.[168] It was shown to be highly *accurate* in resolving MR problems.[82,168,246−253]

Operationally, $\hat{T}^{\mathrm{ext}}$ involves *selected higher excited clusters* (triples, quadruples, etc. with respect to $|0\rangle$). For example, in the CASCCSD approach, one includes all single and double excitations with respect to each reference determinant, but all of them are redefined as excitations with respect to $|0\rangle$:

$$|\Psi\rangle = e^{\hat{T}^{\mathrm{ext}}_1 + \hat{T}^{\mathrm{ext}}_2 + \tilde{\hat{T}}^{\mathrm{ext}}_3 + \tilde{\hat{T}}^{\mathrm{ext}}_4 + \ldots + \tilde{\hat{T}}^{\mathrm{ext}}_{M+2}} \times (1 + \hat{C}^{\mathrm{int}}_1 + \ldots + \hat{C}^{\mathrm{int}}_M)|0\rangle \tag{5.1.7}$$

where M is the highest excitation rank of a reference determinant (with respect to $|0\rangle$) and the tilde means that only *selected* external clusters of this excitation rank are included. Because the CASCCSD ansatz includes all single and double excitations with respect to each reference determinant, it automatically comprises all important *semi-internal* excitations. The corresponding restricted $\tilde{\hat{T}}^{\mathrm{ext}}_k$ operators are defined as

$$\forall\ k \geq 3: \quad \tilde{\hat{T}}^{\mathrm{ext}}_{k} = \sum_{\substack{A_1 < \ldots < A_{k-2} < a_1 < a_2\\ i_1 < i_2 < I_1 < \ldots < I_{k-2}}} t^{A_1\ldots A_{k-2}a_1a_2}_{i_1i_2I_1\ldots I_{k-2}}\hat{\tau}^{A_1\ldots A_{k-2}a_1a_2}_{i_1i_2I_1\ldots I_{k-2}} \tag{5.1.8}$$

where components without *inactive* indices are excluded. In SRMRCC theory, all cluster operators *commute*. Besides the canonical CASCCSD approach, simplified variants have been suggested with a more restricted $\hat{T}^{\mathrm{ext}}$ operator.[242−245,260]

SRMRCC cluster amplitudes can be obtained by solving restricted general-order SRCC equations[168,245,434]

$$\forall\ \langle x| \in (P \cup Q \setminus P_0): \quad \langle x|(\hat{H}\mathrm{e}^{\hat{T}_1 + \hat{T}_2 + \tilde{\tilde{\hat{T}}}_3 + \ldots + \tilde{\tilde{\hat{T}}}_L})_C|0\rangle = 0 \tag{5.1.9}$$

while the *energy* is computed as

$$E = \langle 0|(\hat{H}\mathrm{e}^{\hat{T}_1 + \hat{T}_2 + \tilde{\tilde{\hat{T}}}_3 + \ldots + \tilde{\tilde{\hat{T}}}_L})_C|0\rangle = \langle 0|(\hat{H}\mathrm{e}^{\hat{T}_1 + \hat{T}_2})_C|0\rangle \tag{5.1.10}$$

where $\hat{H}$ does not contain higher than two-body terms, and $\hat{T}_k = \hat{T}_k^{\mathrm{int}} + \hat{T}_k^{\mathrm{ext}}$. The SRMRCC equations are *connected* and the resulting method is *size-extensive*. Moreover, the projected Schrödinger equation is satisfied.

Taking advantage of the SRCC based formulation, one can immediately write down the SRMRCC *Lagrangian*:

$$\tilde{E} = \langle 0|(1 + \hat{\Lambda}^{\mathrm{int}} + \hat{\Lambda}^{\mathrm{ext}})\mathrm{e}^{-\hat{T}^{\mathrm{int}}}\mathrm{e}^{-\hat{T}^{\mathrm{ext}}}\hat{H}\mathrm{e}^{\hat{T}^{\mathrm{ext}}}\mathrm{e}^{\hat{T}^{\mathrm{int}}}|0\rangle \tag{5.1.11}$$

where $\hat{\Lambda}^{\mathrm{int}}$ and $\hat{\Lambda}^{\mathrm{ext}}$ operators have the same meaning as in the standard SRCC theory [254,255] (their structure in analogous to $(\hat{T}^{\mathrm{int}})^+$ and $(\hat{T}^{\mathrm{ext}})^+$, respectively). Having determined $\hat{\Lambda}^{\mathrm{int}}$ and $\hat{\Lambda}^{\mathrm{ext}}$, any *energy derivative* can be computed as

$$\frac{\partial \tilde{E}}{\partial \chi} = \langle 0|(1 + \hat{\Lambda}^{\mathrm{int}} + \hat{\Lambda}^{\mathrm{ext}})\mathrm{e}^{-\hat{T}^{\mathrm{int}}}\mathrm{e}^{-\hat{T}^{\mathrm{ext}}}\frac{\partial \hat{H}}{\partial \chi}\mathrm{e}^{\hat{T}^{\mathrm{ext}}}\mathrm{e}^{\hat{T}^{\mathrm{int}}}|0\rangle \tag{5.1.12}$$

The theory of *analytic first* and *second derivatives* has been developed for SRCC/SRMRCC approaches with an *arbitrary* excitation operator.[254,255]

The presence of higher excited clusters in the SRMRCC ansatz makes the working equations rather complex, sometimes involving thousands of distinct diagrams. As a remedy, several *automated schemes* have been suggested.[168,245,256−259,377] It can be shown that regardless of the highest excitation rank in the cluster operator the CASCCSD approach still scales as $O(N^6)$, provided that the active-space dimension does not grow with the number of particles in the system. However, the prefactor in this dependence can grow quite fast with the active space size.

The major formal drawback of the SRMRCC theory is *the lack of invariance with respect to the choice of the formal reference determinant.*[145,245,247] Thus, reference determinants are *not* treated on an equal footing. The SRMRCC ansatz is *symmetry-broken* in this sense. In practice, one should always pick the *leading determinant* (or one of them) as the formal reference, ensuring the fastest convergence of the exponential expansion. A wrong choice of the formal reference determinant would amplify the weight of higher excited clusters and, more dangerously, the configurational weight of disconnected cluster products. This can severely affect the accuracy of the SRMRCC approach, introduce discontinuities to the calculated PES, or even cause convergence problems. In practice, if the exact wave function is dominated by a *nondegenerate* determinant, the SRMRCC ansatz built on top of this determinant does not have noticeable problems with symmetry contaminations (provided that the model space is adequate and the external space contains the major part of the first-order interaction space). However, if the leading determinant is *degenerate*, it can introduce a noticeable symmetry distortion into the wave function[247] when taken as the formal reference. In order to alleviate this problem, Lyakh et al. suggested the *symmetry-corrected* CASCCSD approach called XCASCCSD[247] (X stands for "eXtended"). In this approach, the projection space is reduced by forming *proper linear combinations of symmetric excitations*. The authors implemented such a procedure for the case when the exact wave function is dominated by a *pair* of degenerate determinants (either spin-momentum degenerate, like open-shell singlet/triplet states, or spatial-momentum degenerate). The XCASCCSD approach was shown to significantly reduce the symmetry contamination of the original CASCCSD ansatz built upon a degenerate determinant, while preserving the high accuracy of the energy obtained.[247] However, in general, the XCASCCSD scheme introduces disconnected cluster amplitudes, thus violating size-extensivity.

CAS-SRMRCC methods (as MRCC approaches) require specification of the model space by selecting *active orbitals*. Hence they are less suitable for a black-box implementation. In order to alleviate this deficiency, a semiautomated active-orbital selection scheme was suggested.[82] A performance of seminatural orbitals was studied by Köhn and Olsen.[435]

A *general-order linear-response* technique for treating excited electronic states has been developed on top of the general-order SRMRCC approach.[261] There are also several other implementations of the active-space-based EOMCC scheme available.[262−264,417−419] Besides restricting the cluster operator to contain only selected higher excitations, all these approaches (in a similar way) restrict the linear EOM CI operator, which generates excited state vectors.

In the context of SRMRCC theory, it is interesting to note that Nakatsuji also suggested a MR variant of his SR *symmetry-adapted-cluster* (SAC) theory, called MR-SAC or MEG4 (the fourth variant of the mixed exponentially generated wave function ansatz).[92] Conceptually, the MR-SAC method is close to the SRMRCC approach. As the SRMRCC theory extends the applicability of the SRCC theory to MR cases, yet staying within the SRCC formalism, the MR-SAC approach extends the applicability of the SAC method in the same manner. However, the MR-SAC method has some special features because of which it can be classified as a *semiadaptive approach*. The so-called *adaptive* methods will be highlighted at the end of this section.

5.2. Other Single-Reference-Based Multireference Coupled-Cluster Approaches

Despite all the attractive features of the CASCCSD method, its computational cost can still be too high when employing large active spaces. Li and Paldus suggested a simplified version where they replaced the CAS model space by the GMS model space and *linearized* the CASCCSD equations for higher-than-double projections:[265]

$$\forall\ \langle x| = \langle x|(\hat{Q}_1 + \hat{Q}_2): \quad \langle x|(H\mathrm{e}^{\hat{T}_1 + \hat{T}_2 + \tilde{\tilde{\hat{T}}}_3 + \ldots + \tilde{\tilde{\hat{T}}}_L})_C|0\rangle = 0 \tag{5.2.1}$$

$$\forall\ \langle x| = \langle x|\hat{Q}_k,\ \ k \geq 3: \quad \langle x|[\hat{H}, \hat{T}_1 + \hat{T}_2 + \tilde{\tilde{\hat{T}}}_3 + \ldots + \tilde{\tilde{\hat{T}}}_L]|0\rangle = 0 \tag{5.2.2}$$

where $\hat{Q}_k$ is a projector associated with k-fold excited determinants (with respect to $|0\rangle$) and L is the maximal excitation rank in the cluster operator. The cluster operator $(\hat{T}_1 + \hat{T}_2 + \tilde{\tilde{\hat{T}}}_3 + \ldots + \tilde{\tilde{\hat{T}}}_L)$ is constructed to include all single and double excitations with respect to the GMS model space. The method is called plMR-CCSD, where "pl" stands for "*partially-linearized*".[265] The plMR-CCSD approach has been augmented with *perturbative corrections*.[265] Because of the partial linearization of equations, the corresponding approach is less computationally demanding.

An alternative SRMRCC formalism that partially includes 3- and 4-fold excited clusters was suggested by Xu et al.[269] The approach can be viewed as a restricted CCSDTQ method where the restrictions on the cluster operators are based on the concept of an electron pair. The resulting method scales as $O(N^7)$. It can be used in calculations of ground electronic states possessing a moderate MR character, for example, for single-bond breaking processes.[269] However, a later development of Li and co-workers seems to be more promising.[270] The approach, called CCSD(T)-h, combines the active-space-based selection of higher excited clusters (as in the CASCCSD scheme truncated at triples, or, equivalently, CCSDt[167]) with the perturbative triples (T) correction.[270] After obtaining the CCSDt wave function, the values of other triply excited amplitudes are estimated using the perturbation theory in the form of the (T) correction. Although the correlation scheme itself is not radically new, in ref 270 the authors suggested an original automated procedure for *selecting active orbitals*. The procedure is based on the use of the *corresponding* UHF orbitals,[271,272] where each α UHF orbital is assigned a unique β counterpart. Then the orbital overlaps can be used to estimate the importance of an orbital in the ground-state MR process under consideration. This gives a possibility to select the most important orbitals automatically. Unfortunately, this active-orbital selection scheme cannot be generally applied to excited-state problems.

Another interesting approach is based on a complete removal of the *static* electron correlation by means of a rigorous *spin-adaptation* of the CC wave function. Following the classical works of Paldus and co-workers,[69−73] one can formulate a spin-free SR/MR CC theory operating in the space of *configuration state functions* (CSF)[69−73,77,78] ($\hat{S}^2$ eigenfunctions). Thus, an artifact of the necessity of proper *spin-coupling* of determinants is completely removed. For example, a multireference open-shell singlet state becomes single-reference when the CC wave function is expanded in terms of CSF. However, the price paid is the extreme complexity of the corresponding spin-adapted equations and their explicit dependence on the symmetry of the state being calculated. The complications come from the appearance of *noncommuting spin-free excitation operators* in the exponential. So far, only doublet and low-spin singlet/triplet electronic states have been considered,[69−73,77,78] for which an automated formula/code generator was written.[69−73]

For the sake of completeness, we will briefly mention other nonstandard SRCC approaches that attempt to include the effects of higher excitations but do not normally use the model space concept (purely SRCC formulation). A particular route being pursued for a long time is based on systematic (noniterative) *perturbative corrections* to the original SRCC approach (e.g. to CCSD). There are numerous so-called *renormalized* (R-CC) and *completely renormalized* (CR-CC) approaches available.[262,273,415,416,420] The original renormalization procedure was based on the following disconnected energy functional:

$$F(\Psi) = \frac{\langle\Psi|\hat{H}e^{\hat{T}}|0\rangle}{\langle\Psi|e^{\hat{T}}|0\rangle} = E_{\mathrm{CC}} + \frac{\langle\Psi|\hat{Q}'\hat{H}e^{\hat{T}}|0\rangle}{\langle\Psi|e^{\hat{T}}|0\rangle} = E_{\mathrm{CC}} + \delta_{\mathrm{CC}} \qquad (5.2.3)$$

where $\langle\Psi|$ is the exact wave function (unknown in practice), while E_{CC} and $e^{\hat{T}}$ correspond to a certain conventional SRCC approach "suffering" from MR effects, and δ_{CC} is the *energy correction* sought. In practice, $\langle\Psi|$ is approximated using *perturbation theory* or imported from an MRCI calculation.[274] The projections against components of the orthogonal-complement space (in the enumerator) are sometimes called the CC *moments* (they represent residuals from the subspace where the Schrödinger equation has not been satisfied due to the use of a truncated CC ansatz). An approximate account of these residual components forms the basis of the so-called *method of moments*[274,421] (MMCC), which extends the applicability of the underlying SRCC/EOMCC methods to moderate-character MR problems. The original R-CC and CR-CC approaches were *not* size-extensive due to the use of the disconnected energy functional (eq 5.2.3). Subsequently, in order to restore size-extensivity, the asymmetric CC energy functional[275] was employed

$$F(\Psi) = \langle 0|(1 + \hat{\Lambda})((\hat{P}_0 + \hat{Q}_0) + \hat{Q}')(\hat{H}e^{\hat{T}})_C|0\rangle = E_{\mathrm{CC}} + \delta_{\mathrm{CC}} \qquad (5.2.4)$$

where the exact bra-eigenvector is represented as $\langle 0|(1 + \hat{\Lambda})$.[276,277,422] Obviously, the latter is approximated in practice.

The method of moments (a quite general route for perturbative corrections) was also incorporated with different EOMCC approaches[263,278,417−419,423] (for treating excited states). Since the MMCC methods are derived in the spirit of perturbative corrections (as the CCSD(T) approach), there is no self-consistency brought into the formalism (the MMCC corrections are noniterative). Such approaches work satisfactory when the MR perturbation is relatively small, for example, when describing moderate MR phenomena like single-bond breaking.[273,274,276] But they often fail to provide a quantitative (or even qualitative) description of severe MR problems like multiple-bond breaking[416] or doubly excited states.[372] An exception is the *externally corrected* MMCC methods, where the description of the nondynamic/static electron correlation comes from the MRCI method (infinite-order approach).[274,421] Another efficient route is to combine the MMCC technique with the SRMRCC theory. The MMCC scheme has been also applied to certain *genuine* MRCC methods, yielding noniterative energy corrections in a similar fashion.[274]

Even earlier the CC functional was utilized in deriving the ΛCCSD(T) method, which is also based on the perturbative-triples correction.[280,430,431] In practice, ΛCCSD(T) is a more robust analog of the CCSD(T) approach for moderate MR problems.[280−282,430] Because of its *quasivariational* nature, the method can be useful in describing single-bond-breaking processes. Importantly, the ΛCCSD(T) method is rigorously *size-extensive* and has proper orbital invariance properties. Note that the R-CCSD(T), CR-CCSD(T), and ΛCCSD(T) approaches involve a noniterative computational step scaling as $O(N^7)$.

A *doubly exponential* energy functional

$$E_{\mathrm{ECC}} = \langle 0|e^{\hat{S}^+}e^{-\hat{T}}\hat{H}e^{\hat{T}}e^{-\hat{S}^+}|0\rangle \qquad (5.2.5)$$

was employed to derive the so-called *extended* CC approach (ECC),[275,283−286] which partially alleviates the deficiency of ordinary SRCC methods in describing bond-breaking processes. Importantly, the ECC approach yields a fully connected two-density cumulant[454] (while conventional SRCC theory does not). Unfortunately, ECC methods are relatively computationally expensive.

A systematic study of the *variational* and *quasivariational* SRCC approaches based on the hermitian energy functional

$$E = \frac{\langle 0|e^{\hat{T}^+}\hat{H}e^{\hat{T}}|0\rangle}{\langle 0|e^{\hat{T}^+}e^{\hat{T}}|0\rangle} = \langle 0|(e^{\hat{T}^+}\hat{H}e^{\hat{T}})_C|0\rangle \qquad (5.2.6)$$

was undertaken by Szalay et al.[287] Unfortunately, the corresponding equations either involve *nonterminating* series or still require *both* left-hand and right-hand solutions. Thus, only *perturbative approximations* were feasible in practice. Recently, Evangelista implemented and thoroughly studied the *extended*, *unitary*, and *variational* CC theories of general order,[409] with a conclusion that the improvement over the conventional SRCC theory is not worth the effort. The XCC approach was also applied in calculations of molecular properties.[455,456]

A CC method accompanied by a simultaneous *optimization* of *valence* orbitals is available under the name the *valence-orbital-optimized* (VOO-CC) approach.[288,289] The orbital optimization partially alleviates shortcomings of ordinary SRCC methods in MR situations. The VOO-CC energy functional is made stationary with respect to cluster amplitudes, Λ-coefficients, and *valence orbitals* as well. Note that, in general, the orbital-optimized CC theory might not be exact in the limit.[436] The VOO-CC scheme has been extended for *excited states* via the EOMCC approach.[290] In practice, the corresponding methods can provide a reasonable description of moderate-character MR problems.

The arguments of the *generalized valence-bond* (GVB) theory were used in deriving the so-called *imperfect-paring* and *perfect-pairing* approximations to the CASSCF method,[291,292] where only certain types of amplitudes are kept in the CAS exponential ansatz, thus reducing the cost of the method and allowing the use of larger active spaces. A promising exponential-like expansion is also used in the GVB-CC method of Head-Gordon and coworkers:[432]

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{K<L} t_{KL}|\Psi_{KL}\rangle + \frac{1}{2!}\sum_{\substack{K<L,\\ M<N}} t_{KL}t_{MN}|\Psi_{KL,MN}\rangle + \ldots \qquad (5.2.7)$$

where $|\Psi_0\rangle$ is an antisymmetrized product of singlet orbital pairs, $|\Psi_{KL}\rangle$ is obtained from $|\Psi_0\rangle$ by "re-coupling" two orbital pairs, K and L, while t_{KL} is the corresponding amplitude. The approach efficiently treats the effects of the nondynamic/static electron correlation. In principle, it can "break" any chemical bond properly. However, in order to deliver "chemical accuracy", the corresponding ansätze must be augmented with some treatment of the *dynamic* electron correlation.[291−295]

5.3. Externally Corrected Multireference Coupled-Cluster Methods

Upon analyzing all preceding methods, one could notice that the exponential SRCC ansatz is ideally suited for accounting for the *dynamic* electron correlation, while the *nondynamic/static* electron correlation effects require CI-like schemes to be devised on top of the CC theory. It is known that the MRCI method is robust and quite efficient in solving true MR problems (of small size). However, MRCI needs a proper account of the dynamic electron correlation, especially when considering larger molecular systems (size-extensivity corrections). Having realized this, Li and Paldus suggested several so-called *externally corrected* (EC) approaches[296−305] where the wave function consists of *two* parts: the *fixed* part imported from a CI calculation and the dynamic *exponential* CC part adjusted in the presence of the fixed CI part. Thus, the fixed CI part *corrects* the values of cluster amplitudes in the CC ansatz. The most successful variant is called the *reduced multireference coupled cluster* method with singles and doubles (RMR-CCSD).[296−301] The RMR-CCSD ansatz can be represented as

$$|\Psi\rangle = e^{\hat{T}_1 + \hat{T}_2 + \tilde{\hat{T}}_3 + \tilde{\hat{T}}_4}|0\rangle \qquad (5.3.1)$$

where $\tilde{\hat{T}}_3$ and $\tilde{\hat{T}}_4$ operators are *fixed* cluster operators imported from an MRCI calculation. The amplitudes of these operators are obtained from the MRCI eigenvector by a well-known CI−CC conversion procedure (see eqs 2.2.4−2.2.6). Hence, the only variable quantities in the RMR-CCSD ansatz are *singly* and *doubly* excited cluster amplitudes defining $\hat{T}_1$ and $\hat{T}_2$.

The RMR-CCSD approach was successfully applied in many MR studies.[127,296−301,306,307,309,310,429] However, it has a formal drawback: the approach is neither size-extensive nor provides a size-consistent description of the problem (like MRCI).[397] Despite the fully exponential form of the RMR-CCSD ansatz and connectedness of the residual equations, the imported $\tilde{\hat{T}}_3$ and $\tilde{\hat{T}}_4$ operators contain *disconnected* contributions if they come from a truncated CI calculation. Nevertheless, one can expect that the size-extensivity error of the RMR-CCSD method will be smaller than that of MRCI. Another disadvantage is that the method may have problems when applied to excited states of the same symmetry as the ground state. In such a case, a collapse to the ground state can occur because the singly and doubly excited amplitudes are *not* restricted in any way. The dimension of the MRCI vector (required in the RMR-CCSD method) as well as the amount of imported cluster amplitudes can be reduced by using the *perturbatively selected* CI scheme (PSCI),[311] as has been done for many years in CI technology.

An analogous RMR modification has been applied to the GMS-SU-MRCCSD method of Li and Paldus. In a similar way the SU-MRCCSD ansatz is augmented with *higher excited clusters*, $\tilde{\hat{T}}_3^{\mu}$ and $\tilde{\hat{T}}_4^{\mu}$, imported from a multistate MRCI calculation:[312]

$$\forall\ k: \quad |\Psi_k\rangle = \sum_{\mu} C_k^{\mu} e^{\hat{T}_1^{\mu} + \hat{T}_2^{\mu} + \tilde{\hat{T}}_3^{\mu} + \tilde{\hat{T}}_4^{\mu}}|\mu\rangle \qquad (5.3.2)$$

The presence of higher excited clusters was shown to improve the energies in calculations of small systems.[312] However, the resulting (N,M)-CCSD approach is also *not* size-extensive ($\tilde{\hat{T}}_3^{\mu}$ and $\tilde{\hat{T}}_4^{\mu}$ operators contain *disconnected* contributions if they come from an MRCI calculation).

A more pragmatic point of view is exploited in the "*tailored*" CCSD approach (TCCSD) suggested by Kinoshita et al.[313] This state-specific approach is also based on the SRMRCC fully exponential ansatz given by eq 5.1.3. In contrast to other externally corrected methods, the TCCSD approach insists on a *proper structure of the multidimensional reference function*

$$|\Psi^{(0)}\rangle = \sum_{\mu} C^{\mu}|\mu\rangle = e^{\hat{T}^{\text{int}}}|0\rangle \qquad (5.3.3)$$

obtained in a "small" full CI (or full CC) calculation in the CAS model space:

$$\hat{P}\hat{H}e^{\hat{T}^{\text{int}}}|0\rangle = E^{(0)}e^{\hat{T}^{\text{int}}}|0\rangle \qquad (5.3.4)$$

The singly and doubly excited *internal* cluster amplitudes (or even all cluster amplitudes of $\hat{T}^{\text{int}}$ from eq 5.3.4) are inserted into the CCSD ansatz and kept "*frozen*" during the CCSD projections in the Q space:

$$\forall\ \langle x| = \langle x|\hat{Q}:\quad \langle x|e^{-\hat{T}^{\text{ext}}}(e^{-\hat{T}^{\text{int}}}\hat{H}e^{\hat{T}^{\text{int}}})e^{\hat{T}^{\text{ext}}}|0\rangle = 0 \tag{5.3.5}$$

$$E = \langle 0|e^{-\hat{T}^{\text{ext}}}(e^{-\hat{T}^{\text{int}}}\hat{H}e^{\hat{T}^{\text{int}}})e^{\hat{T}^{\text{ext}}}|0\rangle \tag{5.3.6}$$

In such a way, the $\hat{T}^{\text{ext}}$ cluster operator is determined (it is mostly responsible for the dynamic electron correlation).

The TCCSD approach provides an *inexpensive size-extensive* way for "probing" MR problems with a reasonable accuracy. In contrast to the RMR-CCSD method, it can access the ground and excited states of the same symmetry because a *fixed* reference vector prevents collapsing into another electronic state (actually the reference vector determines which state is being calculated). The error of the TCCSD approach mostly comes from the *lack of relaxation* in the reference space. This also makes the method rather sensitive to the *orbital choice* and the *active space* used.[313,314] In order to partially alleviate this problem, the TCCSD approach has been augmented with the perturbative-triples (T) energy correction, TCCSD(T).[315] Another possible variant of bringing the relaxation into the TCCSD reference vector is to use a *double active space* strategy, as suggested in the *enhanced* TCCSD approach (eTCCSD).[316] In general, the TCCSD wave function, like any SRMRCC wave function,[247] can be noticeably *symmetry-contaminated* when an *open-shell* determinant is taken as the Fermi vacuum, $|0\rangle$ (even though the TCCSD energy might have a reasonable value).

5.4. Equation-of-Motion Coupled-Cluster Methods for Multireference Problems

The ideas of the Hilbert-space and Fock-space MRCC theories can be combined within the EOMCC scheme[41−43] suitable for MR problems.[322,323,326−334,395] From the MR point of view, the EOM extension (CI vector) introduces the required MR part of the wave function on top of the SRCC exponential:

$$\hat{H}\hat{R}_k\, e^{\hat{T}}|0\rangle = E_k\hat{R}_k e^{\hat{T}}|0\rangle \tag{5.4.1}$$

where $e^{\hat{T}}$ (acting on $|0\rangle$) generates the global (*extensive*) part of the wave function, while a CI-like EOM operator $\hat{R}_k$ provides a "*semilocal*" correction to the kth eigenstate (*intensive* part).[52,397] Thus, $e^{\hat{T}}$ mostly describes the (ground-state) *dynamic* electron correlation, whereas $\hat{R}_k$ is supposed to bring the *state-specific relaxation* and describe the *nondynamic/static* electron correlation. In such a way, the EOMCC approach is usually applied to excited/ionized/electron-attached electronic states. The flexibility of the EOM $\hat{R}_k$ operator allows accessing different sectors of the Fock space with a different number of particles (or quasiparticles) than in the ground-state problem, resembling the FS-MRCC theory.[227,235] The $\hat{R}_k$ operator is determined by solving the EOM eigenvalue problem[41−43]

$$[e^{-\hat{T}}\hat{H}e^{\hat{T}}, \hat{R}_k]|0\rangle = \omega_k\hat{R}_k|0\rangle \tag{5.4.2}$$

where $\omega_k = E_k - E_0$, E_0 is the ground state CC energy, and $\hat{R}_k$ commutes with $\hat{T}$. E_0 is *size-extensive*, while ω_k is *size-intensive*, keeping the target energy E_k *size-extensive* (more precisely, core-extensive).[52,53,397]

Utilizing the Fock-space strategy, the EOMCC approach can also be used for calculating MR *ground* states. For example, homolytic breaking of a *single* chemical bond typically leads to *two open-shell fragments*, each containing one open-shell electron. Adding (or removing) two electrons to such a system (one electron to each fragment) makes both fragments *closed-shell*. The corresponding *closed-shell determinant* can be taken as the Fermi vacuum and an SRCC calculation (e.g., CCSD) can be performed, supplying the *global* exponential part of the wave function, $e^{\hat{T}}|0\rangle$. Then the CI-like operator

$$\hat{R}^{(0,2)} = \frac{1}{2!}\sum_{i,j}\hat{R}_{ij} + \frac{1}{3!}\sum_{i,j,k,a}\hat{R}^{a}_{ijk} + \ldots \tag{5.4.3}$$

takes care of restoring the *proper number of electrons*, bringing some *relaxation* to the wave function and accounting for the *nondynamic/static* electron correlation (conventional orbital partitioning is given in Figure 4). $\hat{R}^{(0,2)}$ is determined by solving the EOM eigenvalue problem in eq 5.4.2, thus also determining the target state energy $E_k = E_0 + \omega_k$. Figure 6 demonstrates how the $\hat{R}_{ij}$ operator (first term in eq 5.4.3) generates the *CAS(2,2)* reference space for the MR problem. One can see that all needed N-electron reference determinants appear from the (N+2)-electron vacuum by removing appropriate pairs of electrons. Remarkably, in such a way all reference determinants are treated on the same footing. The MR-EOMCC scheme in which two electrons are removed from the (N+2)-electron vector is called the MR-DI-CC method ("DI" stands for "double ionization").[322] Analogously, one can start from an ($N - 2$)-electron closed-shell vacuum and *add* two electrons, leading to the MR-DA-CC method ("DA" stands for "double attachment").

A proper generalization to larger active spaces would require more electrons to be added/removed, leading to the MR-MI/MA-CC theory ("M" stands for "multiple").[322] Using the Fock-space terminology, one can explicitly specify the sector of $\hat{R}$ as $\hat{R}^{(k,l)}$

$k \le l$:

$$\hat{R}^{(k,l)} = \sum_{n \ge l}\ \sum_{\substack{a_1 < \ldots < a_k < \ldots < a_{n-l+k}\\ i_1 < \ldots < i_l < \ldots < i_n}} R^{a_1\ldots a_k\ldots a_{n-l+k}}_{i_1\ldots i_l\ldots i_n}\hat{\tau}^{a_1\ldots a_k\ldots a_{n-l+k}}_{i_1\ldots i_l\ldots i_n} \tag{5.4.4}$$

$k > l$:

$$\hat{R}^{(k,l)} = \sum_{n \ge k}\ \sum_{\substack{a_1 < \ldots < a_k < \ldots < a_n\\ i_1 < \ldots < i_l < \ldots < i_{n-k+l}}} R^{a_1\ldots a_k\ldots a_n}_{i_1\ldots i_l\ldots i_{n-k+l}}\hat{\tau}^{a_1\ldots a_k\ldots a_n}_{i_1\ldots i_l\ldots i_{n-k+l}} \tag{5.4.5}$$

where $\hat{\tau}$ is an elementary removal/addition/excitation operator, and $R^{a_1\ldots a_m}_{i_1\ldots i_n}$ are the CI coefficients being sought. Usually the MR-MI/MA-CC excitation operator, $\hat{R}^{(k,l)}$, is truncated after the first two terms (in each sector).

Being a diagonalization-based theory, the MR-MI/MA-CC approach does not suffer from the intruder state problem. The wave function is automatically a *spin eigenfunction* if the Fermi vacuum is a *nondegenerate closed-shell* determinant (and the CC/EOM projection space is appropriate). *Analytic energy gradients* can be evaluated using conventional techniques.[424] The reference determinants are treated on the same footing. Moreover, since all "active" orbitals are either holes or particles of the ground-state Fermi vacuum, the approach is *invariant* to active-orbital rotations (active-orbital rotations form a subgroup of either hole or particle rotations). Importantly, the MR-MI/MA-CC approach naturally reduces to the corresponding SRCC theory when the problem is of SR character. As in any EOMCC scheme, a sufficient *transferability of the dynamic electron*

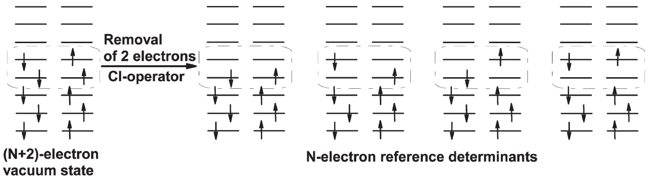


Figure 6. Generation of the multideterminantal reference function in the DI-MR-EOMCC method. Active orbitals and electrons are highlighted.

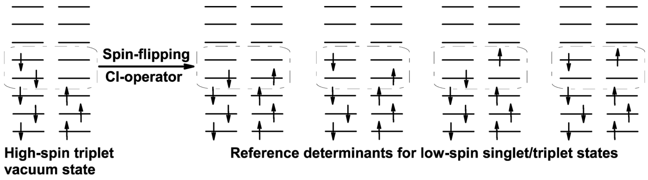


Figure 7. Generation of the multideterminantal reference function in the spin-flip EOMCC method. Active orbitals and electrons are highlighted.

correlation from the $(N+M)$-electron problem to the N-electron problem is assumed (which is not always true though).

In practice, the above formulation of the MR-MI-CC method has difficulties if the electronic system becomes *unstable* after adding additional electrons. In such cases, the ground state $(N+M)$-electron wave function may have potentially "unbounded" components. The problem can be partially alleviated by a proper choice of orbitals.[322−325] At the same time, the MR-MA-CC method does not experience this problem, but it might be more sensitive to the orbital choice (needs proper low-lying virtuals). Also, MR-MA-CC is more computationally expensive than analogous MR-MI-CC (the virtual orbital range usually noticeably exceeds the occupied orbital range). The other complication is that higher-sector MR-MI/MA-CC approaches have unfavorable computational scaling, unless some active-space-based restrictions are imposed on the corresponding tensors.

A conceptually similar way of approaching MR problems with the EOMCC scheme is used in the *spin-flip* EOMCC method (SF-EOMCC).[326−332] Here in order to describe a MR electronic state one starts from the appropriate *high-spin determinant* in which all *open-shell* electrons are given the *same* spin. Such a vacuum is utilized in the SRCC calculation (ROHF or UHF), producing the global $e^{\hat{T}}$ operator. For example, if one wants to describe an open-shell singlet electronic state dominated by two degenerate determinants, then the Fermi vacuum is a high-spin triplet obtained by a spin-inversion of one of the open-shell electrons (see Figure 7). The corresponding high-spin open-shell electronic state is assumed to be of SR character. After the SRCC calculation, the EOM operator $\hat{R}$ produces excitations that change the spin quantum number back, thus describing the *nondynamic/static* electron correlation. The formal machinery does not differ from other EOMCC schemes. Again, the idea is to find an electronic state of SR character that is believed to be able to provide a reasonable description of the *dynamic* electron correlation for the MR state of interest. This description is *imported* by adopting the corresponding exponential cluster operator. Finally, the nondynamic/static electron correlation problem is resolved via a CI-like wave operator, which also captures the state-specific part of the dynamic electron correlation (and orbital relaxation). In general, the final SF-EOMCC wave function is *not* a spin eigenfunction. The SF-EOMCC theory was successfully employed in many chemically interesting MR studies,[326−332] although its generalization to larger active spaces is plagued with the same problems as described above.

In the context of the EOMCC formalism, we should also mention the *similarity-transformed* EOMCC (STEOM-CC) [237−239,425−427,458] and the EOM-CCx[236] methods, whose *separability properties* are correct (contrary to EOMCC) when describing *nonlocal* excitations (size-consistent description). Both methods are "mixtures" of the EOMCC approach and the FS-MRCC theory in lower sectors of the quasiparticle Fock space. The original EOM Hamiltonian $\bar{\hat{H}} \equiv e^{-\hat{T}}\hat{H}e^{\hat{T}}$ is *dressed* via FS-MRCC cluster amplitudes obtained from the (0,1) and (1,0) sectors of the Fock space. In the STEOM-CC scheme, the second similarity transformation, $\hat{G} \equiv \{e^{\hat{S}(0,1)+\hat{S}(1,0)}\}^{-1}e^{-\hat{T}}\hat{H}e^{\hat{T}}\{e^{\hat{S}(0,1)+\hat{S}(1,0)}\}$, also serves for partial *decoupling* of spaces corresponding to different excitation ranks (singles, doubles, etc.), thus reducing the intermediate space to a particular excitation rank (the computational cost is also decreased). The use of the FS-MRCC dressing extends the size-consistency domain of the STEOM-CC and EOM-CCx methods to *charge-transfer* (CT) single excitations, because the necessary amplitudes are imported from the corresponding lower sectors of the Fock space, thus ensuring a proper separability in the (1,1) sector (similarly to the FS-(1,1)-MRCC approach). Formally, conventional EOMCC schemes do not always provide a size-consistent description of MR problems, since the composite space used in the MR problem does not automatically adopt a *direct-product* structure with respect to lower sectors. The use of the hierarchical structure of the FS-MRCC ansatz provides a remedy in such cases. Importantly, the STEOM-CC method was extended to deal with excited states dominated by *double* excitations.[238] Such MR electronic states are poorly described by standard EOMCC methods. *Analytic energy gradients* are available for the STEOM-CC approach.[427]

5.5. Universal Adaptive and Semiadaptive Coupled-Cluster Approaches

Until now we have considered the methods of "*theoretical model chemistry*", which are designed to fulfill a series of *formal* requirements besides the main requirement of giving *quantitative accuracy*. Unfortunately, the latter requirement is often disregarded in favor of satisfying some formal methodological properties. At the early stage of electron correlation theory, the lack of computational power forced the correlated models to be rather compact in terms of the number of independent variables used. Perturbatively selected CI schemes,[335,336] natural orbital-based expansions,[337] and spin-adapted approaches gained the maximal profit from existing computers. As the computer power increased, the formal properties of correlated models attracted more and more attention, resulting in the era of "*theoretical model chemistries*".[51,338] During this fruitful period, the coupled cluster theory and its many-body perturbative approximations became the most prominent paradigms used in the electron correlation calculations. A set of formal requirements exposed to a theoretical model included size-extensivity, size-consistency, exactness for two electrons, proper orbital invariance, variational structure and hermiticity, modest computational demands, etc. However, it turns out that such an ideal method can hardly exist in practice because of the mutually exclusive nature of some of the above requirements. Moreover, they leave the *actual accuracy* of the method generally *unpredictable*. As a result, the "model chemistry" market now contains plenty of different methods, each of which is suited for its particular set of correlated problems.

Unfortunately, in most cases the *method* and the *problem* are considered *separately*. A typical correlated method is constructed using CI/PT/CC machinery, the *reference/external space* concept, and the *excitation rank* hierarchy. Once the method is constructed, only a *few* parameters can be adjusted in order to get the "best" description of a particular electron correlation problem (simplicity has always been convenient for users). However (because of some formal requirements), such theoretical models are often *not* sufficiently flexible for obtaining the most *compact* description of the considered problem with *quantitatively correct* results. In general, one set of method parameters can lead to an *incomplete* correlated model such that the description of the problem is *inadequate*, whereas another set of method parameters can lead to a *redundant* model, where the price paid for the adequate solution is *too high* (computationally expensive). For example, the CCSD method may fail in many situations, while the CCSDT method is too expensive computationally, and the necessity of an inclusion of *all triples* is primarily dictated by the definition of the method and the requirement of rigorous *occ*—*occ*, *virt*—*virt* orbital invariances. Moreover, usually one does *not* have any reliable *accuracy estimates* for the results obtained. The results are produced with "*zero liability*" (as notified in many quantum-chemical packages). In some sense, most existing correlated methods are "*static*", meaning that they cannot *adjust to the correlated problem* by themselves. There is *no* internal "*truth criterion*" in such a theoretical model that could guarantee *convergence to the right answer* (at least with certain confidence). Instead, the user is fully responsible for finding a correct method for the problem under consideration (often the search is completely based on intuition and availability). Even if the method is classified as a "*black box*", its application to an electronic-structure problem is still far from being so. Therefore, there is an apparent need in "*universal*" approaches suited for any correlated problem from a sufficiently *wide class* of them. For example, a method well suited for both SR and MR correlated problems is highly demanded. More precisely, a *universal method must be able to adjust to the considered correlated problem such that the number of independent variables used is as compact as minimally required for obtaining quantitative results* (with a reasonable accuracy). We will call such a property the "*adaptivity*" of a method. We will also abandon the term *universal* and call such methods *adaptive*, thus more precisely reflecting their nature. In order to be adaptive, a method should have an *internal convergence criterion* controlling the expansion of the set of independent variables. Thus, we define

> *An* ***adaptive method*** *for electronic structure calculations is a theoretical model that is able to vary the set of independent variables allowing convergence to the full CI limit (or even the exact result) with reasonable accuracy in a computationally tractable way.*

A "*computationally tractable way*" means some *modest polynomial dependence* with respect to the number of electrons, potentially allowing a *linear-scaling* regime when proceeding to sufficiently *large* systems (obviously only the relative accuracy can be maintained in this way). Ideally, the adaptivity should be applied to both the *electronic correlation* account and the *basis set incompleteness* problem. Leaving aside the latter problem, which recently gained noticeable attention as well,[339−342] we will highlight some adaptive and semiadaptive methods where the adaptivity is used to efficiently capture MR electron correlation effects (adaptive methods are still at the early stage of development). Contrary to the fully adaptive methods, in a *semiadaptive method* the selection of an *accuracy-sufficient* set of independent variables is done by the user (not by the method itself).

In principle, the "*dynamic nature*" of an adaptive method should allow an *automatic fine adjustment to the problem under consideration*. However, at the same time, a rigorous fulfillment of some formal properties might be violated, although these formal properties should still hold to a desired accuracy. It is important to realize that only the extent of violation of formal properties really matters in practice. An adaptive method converges to the full CI solution by definition (to some reasonable accuracy). Hence, the corresponding wave function is exact (correct) to some precision defined a priori by a user.

We believe it is time to separate a class of approaches that share the concept of adaptivity one way or another (in particular, adaptive CC methods). The "ancient" *perturbatively selected* CI approaches employ a perturbation-theory-based screening procedure for constructing the CI configurational space.[335] This scheme was used by Nakatsuji, who introduced a class of semiadaptive methods based on the SAC/SAC-CI theory, in particular in the form of SAC-CI-general-R method [343−346] and *exponentially generated* CI (EGCI) approaches.[347,348] The idea behind these methods is a *selective* inclusion of *higher* CI excitations, based on the values of singly and doubly excited CI coefficients and a set of *predefined* thresholds. One should note that higher excitations are included in the CI form, albeit this CI vector is formally generated using disconnected products from the exponential expansion. For example, in the SAC-CI-general-R method the singly and doubly excited cluster amplitudes (S_1 and S_2) of the SAC ansatz [46,47]

$$\hat{O}e^{\hat{S}_1 + \hat{S}_2}|0\rangle \tag{5.5.1}$$

are selected *perturbatively* ($\hat{O}$ is a formal symmetry-projector). Then the similarity-transformed Hamiltonian

$$e^{-\hat{S}_1 - \hat{S}_2}\hat{H}e^{\hat{S}_1 + \hat{S}_2} \tag{5.5.2}$$

is used in a CI diagonalization within the space of singles and doubles, thus obtaining R_1 and R_2 sets of CI coefficients (for the states of interest). Finally, the CI space is augmented by those higher excitations that are estimated to be important, on the basis of the cluster decomposition in terms of R_1 and R_2. This selection scheme is called *exponentially generated* CI (EGCI).[347] Because the thresholds are selected manually, we classify this method as semiadaptive.

Another semiadaptive approach of Nakatsuji is more relevant to MR problems. The approach is called the *mixed exponentially generated* SAC (MEG4/EX-MEG4-SAC, where "EX" stands for "excited") or, equivalently, the MR-SAC method.[92,348] The corresponding wave function can be represented as

$$|\Psi\rangle = \hat{R}e^{\hat{S}_1 + \hat{S}_2}\hat{C}|0\rangle \tag{5.5.3}$$

where $\hat{R}$ and $\hat{C}$ operators are arbitrary-rank CI operators. Both $\hat{R}$ and $\hat{C}$ are constructed using the EGCI algorithm described above. The $\hat{C}$ operator is responsible for the *nondynamic/static* electron correlation (it creates the reference part of the wave function) while $e^{\hat{S}_1+\hat{S}_2}$ takes care of the *dynamic* electron correlation. $\hat{R}$ "lifts up" the ground state vector $\mathrm{e}^{\hat{S}_1+\hat{S}_2}\hat{C}|0\rangle$ to a particular excited state (like in the SAC-CI or EOMCC schemes). For the ground electronic state, $\hat{R} = \hat{1}$. For SR problems, $\hat{C} = \hat{1}$. Construction of $\hat{R}$ and $\hat{C}$ is regulated by predefined thresholds. The semiadaptive MEG4/EX-MEG4 ansatz is quite flexible and was successfully employed in solving some SR/MR problems.[92] Compared to the SRMRCC theory, it has the advantage of *not* using the *active-orbital-space* concept. However, strictly speaking, both SAC-CI-general-R and MEG4/EX-MEG4 methods are not rigorously size-extensive.

A fully adaptive CI approach was suggested by Nakatsuji and Ehara. The method is called *iterative* CI with *general singles and doubles* (ICI-GSD).[349] The ICI-GSD wave function

$$|\Psi\rangle = \left(\prod_n (1 + \hat{T}^{(n)})\right)|0\rangle \tag{5.5.4}$$

is constructed by iteratively applying the GSD operator $\hat{T}^{(n)}$ until the equations

$$\langle\Psi|(\hat{H} - E)\hat{p}^{+}\hat{r}^{-}|\Psi\rangle = 0, \ \forall\ p, r \tag{5.5.5}$$

$$\langle\Psi|(\hat{H} - E)\hat{p}^{+}\hat{q}^{+}\hat{s}^{-}\hat{r}^{-}|\Psi\rangle = 0, \ \forall\ p, q, r, s \tag{5.5.6}$$

are satisfied. These equations are equivalent to the Schrödinger equation, reflecting the one- and two-body nature of the electronic Hamiltonian.[350]

Another branch of adaptive CI approaches is connected with the Monte-Carlo (MC) implementation (MCCI).[351] In the MCCI approach, the initial CI space is iteratively extended by randomly driven augmentation with single and double excitations, until the convergence is reached. After each diagonalization, configurations with small weights are discarded. Other possibly adaptive Monte-Carlo CI/CC developments have been suggested by Alavi et al.[352−354] and Thom.[457] In the context of adaptive methods, the density matrix renormalization group (DMRG) approach also allows a *systematic* convergence to the full CI result.[355−358]

Recently, a straightforward fully adaptive MR approach based on the "pure" CC formalism was suggested by Lyakh and Bartlett.[359] The @CC method ("@" stands for "*adaptive theory*") fully exploits the advantages of CC theory. The method is *state-specific* and is formally based on the arbitrary-excitation-rank SRCC ansatz

$$|\Psi\rangle = \mathrm{e}^{\hat{T}(\varepsilon)}|0\rangle \tag{5.5.7}$$

where the cluster operator $\hat{T}(\varepsilon)$ is *adaptive*

$$\hat{T}(\varepsilon) = \sum_{X:\ \zeta(X) > \varepsilon} t_X \hat{\tau}_X \tag{5.5.8}$$

where ε is a formal threshold discriminating the cluster amplitudes t_X included in the @CC ansatz ($\zeta(X) > \varepsilon$) from those not included ($\zeta(X) \leq \varepsilon$). $0 \leq \zeta(X) \leq 1$ is the *discriminatory function* (*importance selection function*, ISF) whose exact form is *unknown*, but reasonable approximations are possible, for example, the *fully multiplicative approximation*:

$$\forall\ X \equiv {}^{a_1 a_2 \ldots a_n}_{i_1 i_2 \ldots i_m}: \quad \zeta(X) = \prod_{k=1}^{m} \vartheta(i_k) \prod_{k=1}^{n} \vartheta(a_k) \tag{5.5.9}$$

where $\vartheta(i_k)$ and $\vartheta(a_k)$ are *individual* orbital contributions (importance).[359] Importantly, the @CC approach does *not* employ active orbitals in any form (thus no selection is needed).

The @CC equations are based on the arbitrary-rank SRCC equations:

$$\begin{aligned} &\forall\ X,\ \zeta(X) > \varepsilon: \quad \langle X|\mathrm{e}^{-\hat{T}(\varepsilon)}\hat{H}_N \mathrm{e}^{\hat{T}(\varepsilon)}|0\rangle = 0, \\ &E(\varepsilon) = \langle 0|\mathrm{e}^{-\hat{T}(\varepsilon)}\hat{H}_N \mathrm{e}^{\hat{T}(\varepsilon)}|0\rangle \end{aligned} \tag{5.5.10}$$

where *new* cluster amplitudes are automatically introduced into the @CC cluster operator, $\hat{T}(\varepsilon)$, upon decreasing ε, until the convergence of the energy, $E(\varepsilon)$, is observed (the convergence is *not* monotonic though):

$$\lim_{\varepsilon \to 0} E(\varepsilon) = E_{\mathrm{fullCI}} \tag{5.5.11}$$

Note that eq 5.5.11 does not assume exactness of the ISF.

Formally, the @CC approach has obvious advantages. The CC ansatz converges *much faster* to the full CI solution than an analogous CI expansion. The @CC method is rigorously *size-extensive*. The @CC ansatz is *exact in the limit* for *any* electronic state. Thus, both the ground and excited electronic states of any (SR or MR) character can be considered in a state-specific manner (to improve convergence, the reference determinant $|0\rangle$ must be one of the dominating determinants). In the case of excited states of the same symmetry as the ground state, special care must be taken in order to provide a good initial guess for the @CC calculation. Moreover, topological properties of cluster amplitudes can be efficiently exploited when devising linear-scaling implementations. Actually, Auer and Nooijen suggested the dynamically screened CCSD approach[437] (also called adaptive, ACCSD), where the adaptivity refers to a selective inclusion of singles and doubles, avoiding the amplitudes that involve weakly interacting orbitals due to their spatial locality. An interesting idea would be to combine the two types of adaptivity in a single CC approach.

A pilot implementation of the @CC method showed some encouraging results.[359] However, in order to draw more definitive conclusions, a more robust form of the ISF, as well as an efficient computer implementation of the @CC approach, is required. Unfortunately, the computational cost of the @CC method widely varies, depending on the electronic system and accuracy desired. Also, special care must be taken when evaluating analytic energy gradients, since the ε threshold formally introduces discontinuities.

5.6. Size-Extensivity Corrections to the Multireference Configuration-Interaction Approach

Although this review is dedicated to MRCC theory, we cannot omit the *size-consistent multireference* CI approach of Malrieu and co-workers [SC-MRCI, MR(SC)^{2}CI][173−175] because this approach is closely related to the HS-MRCC theory while utilizing an efficient *intermediate Hamiltonian* (IH) technique[116] in a *state-specific* manner. Here we will briefly discuss the possibility of iterative size-extensivity corrections to the MRCI approach.

It turns out that one can make a general CI approach size-extensive by introducing the so-called *dressing of the Hamiltonian*,[176−179] which cancels out unlinked and disconnected contributions contained in the original CI equations (at least approximately). From the linear-algebraic point of view, such a *dressing* restores a proper (linear) scaling of the norm of the Hamiltonian matrix. For the sake of simplicity let us consider a state-specific variant of the MR(SC)^{2}CI approach.

The exact wave function can be represented as

$$|\Psi\rangle = \sum_{\mu} C^{\mu}|\mu\rangle + \sum_{x} C^{x}|x\rangle + \sum_{y} C^{y}|y\rangle \qquad (5.6.1)$$

where $|\mu\rangle$ belongs to the *model* space P, $|x\rangle$ belongs to the *external* space Q, and $|y\rangle$ belongs to the *orthogonal-complement* space Q'. Suppose the external space includes all single and double excitations with respect to the model space (excluding the model space itself). Then the $(P \oplus Q)$ part of the CI eigenvalue problem is

$$\forall\ \langle\mu| \in P: \quad \sum_{\nu} H^{\mu}_{\nu} C^{\nu} + \sum_{x} H^{\mu}_{x} C^{x} - EC^{\mu} = 0 \qquad (5.6.2)$$

$$\forall\ \langle z| \in Q: \quad \sum_{\nu} H^{z}_{\nu} C^{\nu} + \sum_{x} H^{z}_{x} C^{x} + \sum_{y} H^{z}_{y} C^{y} - EC^{z} = 0 \qquad (5.6.3)$$

where $H^{[index]}_{[index]}$ refers to matrix elements of the Hamiltonian and E is an energy eigenvalue. Now the problem reads: "*Assuming that C^{y} coefficients can be approximated as functions of C^{μ}, C^{x}, and E, how can one redefine the eigenvalue problem solely within the* $(P \oplus Q)$ *space?*". In order to treat all reference determinants, $|\mu\rangle$, on an equal footing one can always write

$$C^{y} = \sum_{\mu} C^{y}_{\mu} \qquad (5.6.4)$$

Consequently, eq 5.6.3 can be rewritten as

$$\forall\ \langle z| \in Q: \quad \sum_{\nu}\left(\left(H^{z}_{\nu} + (C^{\nu})^{-1}\sum_{y} H^{z}_{y} C^{y}_{\nu}\right) C^{\nu}\right) + \sum_{x} H^{z}_{x} C^{x} - EC^{z} = 0 \qquad (5.6.5)$$

Introducing the so-called *dressing* matrix

$$\Delta^{z}_{\nu} = (C^{\nu})^{-1}\sum_{y} H^{z}_{y} C^{y}_{\nu} \qquad (5.6.6)$$

one can reformulate the eigenvalue problem as

$$\forall\ \langle z| \in Q: \quad \sum_{\nu} \tilde{H}^{z}_{\nu} C^{\nu} + \sum_{x} \tilde{H}^{z}_{x} C^{x} - EC^{z} = 0 \qquad (5.6.7)$$

where the matrix

$$\tilde{\hat{H}} \equiv \hat{H} + \hat{\Delta} \qquad (5.6.8)$$

is called the *dressed Hamiltonian*. Note that the $\tilde{\hat{H}}$ matrix is defined solely in the $(P \oplus Q)$ space, but its eigenvector is a $(P \oplus Q)$-projection of the exact Hamiltonian eigenvector, provided that the *dressing* $\hat{\Delta}$ is exact:

$$(\hat{P} + \hat{Q})\tilde{\hat{H}}(\hat{P} + \hat{Q})|\Psi\rangle = (\hat{P} + \hat{Q})E|\Psi\rangle \qquad (5.6.9)$$

In practice, the *dressing* matrix $\hat{\Delta}(C^{\mu},C^{x},E)$ is only *approximate*, leading to approximate eigenvalues and eigenvectors. In order to expand C^{y}_{ν} coefficients and define $\hat{\Delta}(C^{\mu},C^{x},E)$, one can employ the perturbation theory or the coupled cluster framework.[173−178] In the latter case, C^{y}_{ν} coefficients are approximated as products of external and model space coefficients. For example,

$$C^{y}_{\nu} \approx \sum_{(x_1,x_2)\rightarrow y} C^{x_1}C^{x_2}C^{\nu} \qquad (5.6.10)$$

where the sum runs over all external excitation pairs (x_1,x_2) producing $|y\rangle \in Q'$ when acting on the reference determinant $|\nu\rangle$. Such disconnected dressing has the same effect as disconnected cluster products in CC theory, ensuring that the norm of the Hamiltonian matrix scales linearly with the number of electrons. Appropriately built dressing restores the *size-extensivity* of the MRCI approach. At the same time its *variational nature is lost*.

Because the dressing $\hat{\Delta}(C^{\mu},C^{x},E)$ depends on the eigenvector coefficients, the MR(SC)^{2}CI method is *state-specific*, while an *iterative* procedure is required to repeatedly resolve the eigenvalue problem in the $(P \oplus Q)$ space and reconstruct the dressing $\hat{\Delta}(C^{\mu},C^{x},E)$:

$$\begin{aligned}\hat{\Delta}^{(0)} &:= 0 \rightarrow (\hat{P} + \hat{Q})\hat{H}(\hat{P} + \hat{Q})|\Psi\rangle \\ &= E^{(0)}(\hat{P} + \hat{Q})|\Psi\rangle \rightarrow \hat{\Delta}^{(1)} \\ &\rightarrow (\hat{P} + \hat{Q})\tilde{\hat{H}}^{(1)}(\hat{P} + \hat{Q})|\Psi\rangle \\ &= E^{(1)}(\hat{P} + \hat{Q})|\Psi\rangle \rightarrow \hat{\Delta}^{(2)} \rightarrow \ldots\end{aligned} \qquad (5.6.11)$$

Alternatively, instead of rescaling the Hamiltonian matrix elements, one can apply an analogous procedure to the *metric* matrix and consider a *generalized eigenvalue* problem.[179] In the latter case, one explicitly modifies the norm in the Hilbert space, such that the Hamiltonian matrix yields eigenvalues that scale correctly with the number of electrons in the system. *Dressing* techniques present a quite general way of restoring (at least approximately) size-extensivity of an arbitrary CI approach together with its ability to provide a size-consistent description of certain quantum problems. It also allows reformulating the nonlinear iterative CC equations as a diagonalization of the dressed Hamiltonian. Numerically, diagonalization is a more stable procedure than solving highly nonlinear equations.

The MR(SC)^{2}CI method was successfully tested on some model systems,[173−175] although we are not aware of any production-level computer implementation of the approach. Also *no analytic schemes* for evaluating *energy gradients* are available for the approach.[50] Later, a pseudofunctional analog of the MR(SC)^{2}CI approach, which simplifies the evaluation of *analytic energy gradients*, was formulated.[179]

Besides the MR(SC)^{2}CI method, there are well-known *multireference averaged quadratic* CC (MR-AQCC) [180,181] and *multireference averaged coupled-pair functional* CC (MR-ACPF)[182,183] approaches, both being modifications of the MRCI method with *approximate size-extensivity corrections* constructed via averaging of correlation energy contributions. These two similar schemes can also be formulated as an eigenvalue problem for a dressed Hamiltonian (diagonal dressing is used).[50,184] Hence they can be equally applied to both ground and excited electronic states (via a state-specific dressing). In practice, the MR-AQCC method gives remarkably *accurate* results in MR situations and is usually preferred over the MR-ACPF, although the only formal difference is the value of a special scalar parameter G in the underlying energy functional:[184]

$$E = \frac{\langle \sum_{i} C_i\Phi_i|\hat{H}|\sum_{i} C_i\Phi_i\rangle}{\sum_{i\,\in\,P} |C_i|^2 + G\sum_{i\,\notin\,P} |C_i|^2} \qquad (5.6.12)$$

The existence of such a functional makes *analytic energy gradients* readily available using the standard MRCI machinery.[50,187]

We should note that these size-extensivity/size-consistency corrected MRCI approaches belong to the class of MR-CEPA methods,[88,160,179,185,186] that is, a group of MR methods that *eliminate unlinked terms* from the MRCI equations (either exactly or approximately). MR-CEPA methods can be viewed as an intermediate approximation between MRCI and MRCC, even though some of them originate from genuine MRCC approaches.[88,160] A comprehensive review of the MRCI/MR-CEPA methods can be found in ref 187.

5.7. Conclusions: Alternative Multireference Coupled-Cluster Methods

Taking into account all above arguments we can conclude that alt-MRCC methods are (at least) competitive with gen-MRCC approaches. Being conceptually simpler, the SRCC-based MRCC methods inherit all the effort put into SRCC theory, such as analytic gradients, molecular properties, efficient computational schemes, etc. The CASCCSD, RMR-CCSD/RMR-CCSD(T), TCCSD/TCCSD(T) methods and the MR-EOMCC schemes are able to provide quantitative description of many MR problems for which certain genuine MRCCSD approaches fail (and vice versa).

Particular attention should be paid to development of adaptive CC formulations (not necessarily @CC) which have an internal *accuracy-control mechanism*, thus converging to the "*right answer*" up to a predefined precision (at least they should provide some reasonable confidence in the result obtained). In principle, an adaptive approach provides a seamless connection between SR and MR regions of the PES for any electronic state, although some additional "*surface-smoothing*" algorithms might be required. Importantly, adaptive methods do not require selection of active orbitals.

Therefore, we do believe that alt-MRCC methods have all perspectives for being a reliable practical tool for solving MR (and SR) correlated problems. They should in no way be neglected when discussing practical solutions to MR chemical problems. One potential drawback of alt-MRCC methods is connected with the corresponding ansätze not being rigorously symmetric with respect to reference determinants (except MR-EOMCC schemes). However, in practice these contaminations are often small. The main drawback of several genuine HS-MRCC formulations, namely, the inability to satisfy the projected Schrödinger equation, is far more severe than the symmetry breaking in the SRMRCC ansatz. Nevertheless, in general, alt-MRCC approaches cannot replace gen-MRCC methods, which might be more advantageous in certain MR situations, especially when correct symmetry of the wave function is crucial (for example, in highly open-shell systems, like transition-metal complexes).

6. NUMERICAL ILLUSTRATIONS

In order to illustrate numerical performance of different MRCC approaches, we have collected numerous results obtained in calculations of systems exhibiting MR character in some (or all) regions of the PES. In each case, the PES numerically represents a particular *chemical transformation*, such as bond-breaking, isomerization, configurational changes, etc. Both ground- and excited-state PES's are considered here. Since all shown molecular systems are quite small, we can use (for the sake of compactness) the following two integral PES characteristics, the *nonparallelism error (NPE)*[360] and the *maximal absolute deviation (MAD)*. NPE characterizes the extent of *nonparallelism* of the calculated PES as compared to the "pseudoexact" (full CI) one

$$\mathrm{NPE} = |\Delta E_{\max} - \Delta E_{\min}| \tag{6.1}$$

where $\Delta E_{\max} = \max_i(E_i - E_i^{\mathrm{FCI}})$, $\Delta E_{\min} = \min_i(E_i - E_i^{\mathrm{FCI}})$, E_i is the electronic energy calculated with a particular method, E_i^{FCI} is the corresponding full CI energy, and i runs over all calculated points of the PES. Correspondingly, MAD shows the *maximal absolute error* along the PES

$$\mathrm{MAD} = \max_i(|E_i - E_i^{\mathrm{FCI}}|) \tag{6.2}$$

Although the number of calculated points can vary greatly, these two integral PES characteristics provide a good estimate of accuracy as long as at least one point is computed in *each distinct region* of a PES.

Besides the classical problem of *bond breaking*, we demonstrate numerical results obtained for other *multireference* phenomena, such as *excited states* and *electronic excitation processes*, description of *biradicals*, *highly symmetric* systems and *transition state* models, reactions of *isomerization*, etc. The charts shown below summarize the results of numerous works already referenced throughout the review. The acronyms of the methods employed can be found in the list of acronyms. Certain calculations were performed by us using the ACESIII[385] and GAMESS[386] software.

Generally the same chart can involve results obtained in different basis sets. Therefore, the main purpose of this section is to show a *semiquantitative picture* of performance of different MRCC methods, mostly focusing on severe failures of particular MRCC/SRCC methods in certain cases. For the sake of clarity, we define *three ranges of energy accuracy* of a method (predominantly for NPE):

(1) ≈1−3 kcal/mol or, equivalently, ≈1−5 mH: *acceptable*.
(2) ≈3−6 kcal/mol or, equivalently, ≈5−10 mH: *conditionally acceptable*.
(3) >6 kcal/mol or, equivalently, >10 mH: *unacceptable* (for MR methods).

Strictly speaking, the three categories of accuracy apply to *relative energies* calculated with a particular method. The *absolute error* of a size-extensive method should grow roughly *linearly* with the number of electrons in the system, whereas the *relative error* should stay bounded (this is why size-extensivity is important). Nevertheless, since all the systems shown are rather small, the absolute error will also be provided for the sake of completeness. For larger molecular systems (and solids) one should use the ratio MAD/ΔE instead of MAD, where ΔE is the correlation energy.

Our assessment of the quality of different MRCC methods is mostly based on comparisons with the full CI results, although experimental values are also considered wherever it is appropriate. We would like to emphasize that, in general, the only unambiguous comparison is the one based on full CI (the *exact solution* of the Schrödinger equation in a given one-electron basis set). It is known that both the *electron correlation problem* and the *basis set incompleteness problem* are essential in providing *accurate* results. Nonetheless, the two problems are quite distinguished from each other. Indeed, the former problem is connected with delivering a sufficiently accurate expansion of the *correlated wave function* in a given (finite) Hilbert space, whereas the latter problem deals with a *systematic enlargement* of the size of that Hilbert space. Only a simultaneous solution of both problems can lead to results that can be compared with the experimental values. It is methodologically illogical (and even harmful) to assess the quality of a particular correlated method by comparing its results with experiment while neglecting the incompleteness of the basis set. Newly developed sophisticated electronic-structure methods are often computationally demanding and cannot employ the same quality basis sets as the existing less accurate approximations. An unambiguous assessment of their quality can be done by using the "*pseudoexact*" full CI results (or other sufficiently accurate solutions of the Schrödinger eigenvalue problem). It should be realized that, except for some pathological cases, if a method can construct an *accurate* wave function in a modest (but not small!) 1e basis set, it is rather likely that it will converge to the "*exact answer*" upon increasing the size of the basis set. This is the very essence of ab initio quantum chemistry. Therefore, whenever it was possible, we used the full CI results, whereas the experimental values provided an alternative when full CI was unavailable (larger basis sets).

In the following, we do not provide the results obtained with adaptive approaches, which by definition converge to the full CI solution to a desired precision. The only possible theoretical measure would be the amount of variables used to obtain a given accuracy.[359] However, this issue has not been thoroughly studied yet.

Below, along with the MRCC results, we also provide the results obtained with ordinary SRCC methods in order to stress how *badly inaccurate* they can be when a *multireference* problem is considered (leaving aside even less accurate electronic structure methods, like MP2, CISD, DFT, etc.). This proves the point that *a robust practical MRCC theory is a highly desirable and necessary tool for contemporary quantum chemistry* (rather than just being a subject of purely theoretical interest).

6.1. Transition State Models and Isomerization Reactions: H_4, H_8, BeH_2, Cyclobutadiene Automerization, Pyridyne Biradicals

A proper description of transition states of chemical reactions is the key ingredient of successful predictions in chemical kinetics. Although many transition states are still single-reference by nature, there are numerous examples where the transition state possesses higher symmetry, leading to the *configurational quasidegeneracy* in the wave function (states of MR character). Another peculiarity of transition state wave functions is a *strong coupling* between the dynamic and nondynamic electron correlations, where a sufficiently complete account of both is mandatory. Historically, in MRCC theory transition states were modeled by considering the following model molecular systems.

The first system consists of two H_2 molecules (H_4 model[361]) as shown in Figure 8. The simulated chemical transformation is based on varying the angle θ. In the limit of $\theta = 0°$ the system possesses D_{4h} symmetry, causing significant quasidegeneracy effects (strong nondynamic electron correlation). Moving away from that point decreases the degree of quasidegeneracy in the system, reducing the character of the ground state back to the SR case. In the MR region the wave function is dominated by two determinants that can be generated with the CAS(2,2) model space.

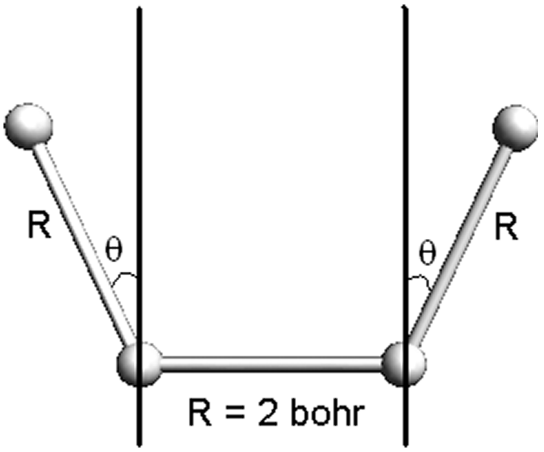


Figure 8. H_4 model system (two hydrogen molecules).

The H_4 model system was extensively employed in many MR studies. Figure 9 summarizes the NPE's produced by different methods in calculation of the PES corresponding to the variation of the angle θ. As one can see, most methods (MRCC as well as advanced SRCC) perform well for this transformation, reducing the original CCSD NPE back to the chemical accuracy range. There are three observations to be discussed. First, inclusion of perturbative triples (T) on top of the pl-MRCCSD method worsens its NPE. As we will see, this often happens when SR perturbation theory is employed in MR problems. Apparently, the Møller−Plesset perturbation is no longer small in such cases (for example, HOMO and LUMO MOs can become (quasi) degenerate). Second, a relatively high NPE of the SU-MRCCSD approach originates in the SR region of the PES (larger values of θ), as one can see from Table 2. As we pointed out in section 3, the genuine multireference SU-MRCCSD, Mk-MRCCSD, and BW-MRCCSD approaches poorly satisfy the projected Schrödinger equation that often results in noticeable errors in SR regions of PES's (also convergence problems can occur). Finally, one can observe a systematically decreasing NPE in the series: TCCSD, TCCSD(T), eTCCSD. For the SRCC-based TCCSD method the (T) correction delivers a more complete account of the dynamic electron correlation, whereas the eTCCSD approach explicitly introduces partial relaxation in the reference space (accounts for coupling between the nondynamic and dynamic electron correlations).

Figure 10 shows the next analogous model system also consisting of four hydrogen atoms, called P4.[361] However, in this case the parameter α (transformation coordinate) regulates the symmetry of the system by shifting two opposite hydrogen molecules toward/away from each other. PES NPE values produced by different methods are shown in Figure 11. The most interesting observation here is the behavior of the a posteriori extensivity-corrected BW-MRCCSD approach. Instead of improving the original (quite good) NPE of the BW-MRCCSD approach, it drastically amplifies its value, making it even worse than the CCSD result.

A more complicated case is the H_8 model molecular system.[362] As shown in Figure 12, it consists of four H_2 molecules located in an *octagonal* configuration. The parameter α is used for symmetrically separating the left and right H_2 molecules, thus reducing the symmetry from D_{8h} to D_{2h}. Again $\alpha = 0$ (D_{8h}) leads to configurational degeneracy and severe nondynamic electron correlation effects (MR point). By increasing the value of α one reduces the nondynamic electron correlation effects. In the MR region of the PES the wave function is dominated by two

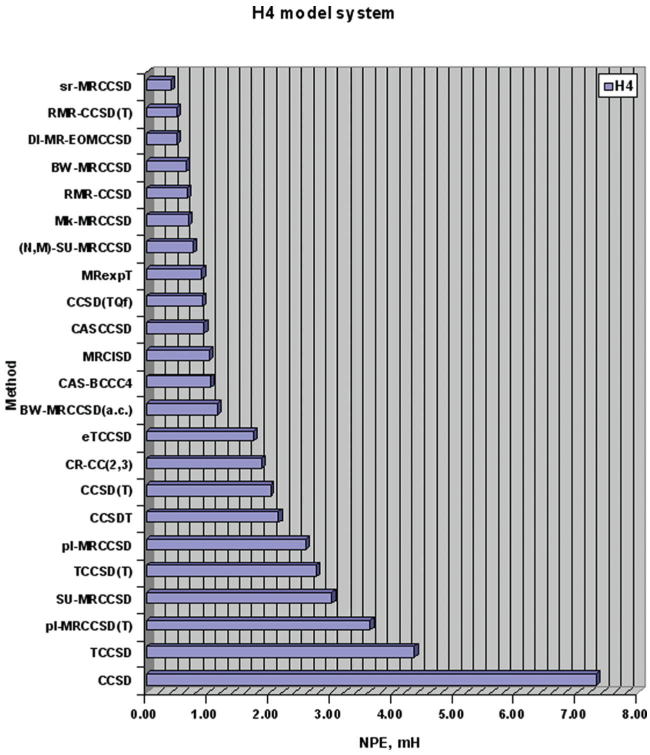


Figure 9. H_4 model system: PES nonparallelism errors (NPE) in mH.

Table 2. Errors of Different Methods (in mH) with Respect to Full CI for a Series of Geometries of the H_4 Molecule (DZP basis set)[a].

geometry parameter, θ	CCSD[b]	CAS(2,2)CCSD[b,d]	MRexpT[b]	SU-MRCCSD[c]
0	5.39	1.10/1.10	1.10	−0.69
0.05	1.25	0.67/0.89	0.73	−0.08
0.2	0.75	0.41/0.53	0.44	−1.19
0.5	0.74	0.40/0.50	0.41	−2.38
NPE	4.65	0.71/0.64	0.68	2.29

[a] $\theta = 0$ leads to the appearance of configurational degeneracy in the wavefunction (multireference state). [b] Reference 169. [c] Reference 93. [d] Two possible formal reference determinants.

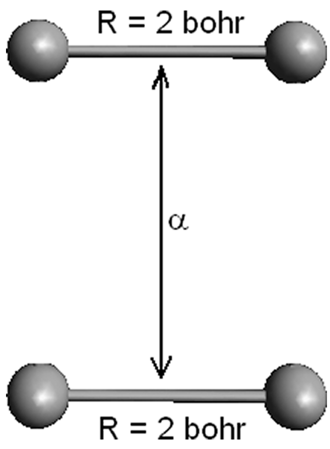


Figure 10. P4 model system (two hydrogen molecules).

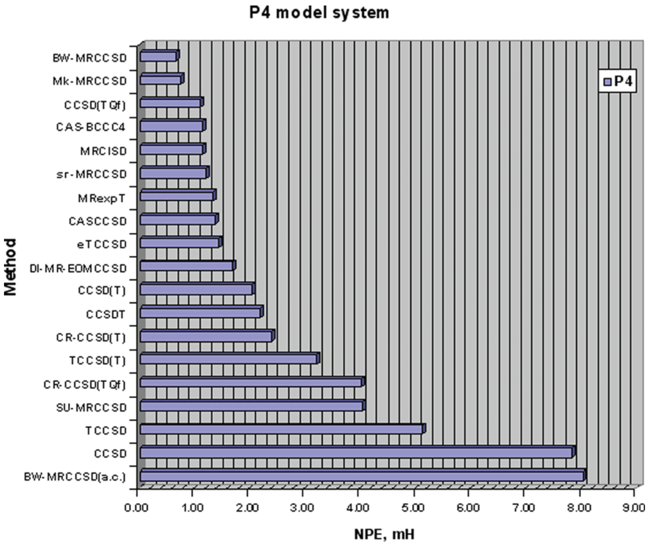


Figure 11. P4 model system (two hydrogen molecules): PES nonparallelism errors (NPE) in mH.

determinants which can be generated within the CAS(2,2) model space. However, for relatively small values of α there are other determinants that noticeably contribute to the wave function. This introduces even stronger nondynamic−dynamic correlation coupling as compared to the case of H_4. The extent of such coupling can be illustrated by comparing the NPE of the TCCSD (unrelaxed) and eTCCSD (partially relaxed) methods, as can be seen from Figure 13 (still the chemical accuracy is barely achieved). Among other results, one can notice a "uselessness" of a direct inclusion of connected triples (CCSDT) within the ordinary SRCC formalism. This happens because the first-order interaction space for the CAS(2,2) reference space involves selected triple and *quadruple* excitations. Disregarding quadruples makes the full inclusion of connected triples rather useless here. In contrast, MRCC approaches restore the balance between triples and quadruples, resulting in acceptable values of NPE. Again, the errors of the genuine MRCC methods (SU-MRCCSD, Mk-MRCCSD, BW-MRCCSD) tend to originate in the SR region of the PES.

Besides, one can notice the lack of systematic improvement when proceeding from the perturbative inclusion of triples in CCSD(T) to the perturbative inclusion of triples and factorized quadruples in CCSD(TQ_f). The completely renormalized analogues, CR-CCSD(T) and CR-CCSD(TQ_f), show even worse NPE's than the original approaches. In true MR cases, the large Møller−Plesset perturbation leads to a poor convergence of the SR-based low-order perturbation series. It is interesting to analyze a surprisingly good behavior of the CCSD(T) method. The error of ordinary SRCC approaches originates around the MR point $\alpha = 0$. Going away from that point, all ordinary SRCC methods produce quite accurate results. Table 3 explicitly shows the errors produced by different methods for the H_8 model system with $\alpha = 0$. One can see that the errors of the CCSD (≈+9.9 mH) and CCSDT (≈−8.3 mH) methods are similar but have an *opposite sign*. The CCSD(T) approach adds the leading-order effects of triple excitations on top of the CCSD approach, thus almost precisely passing half way

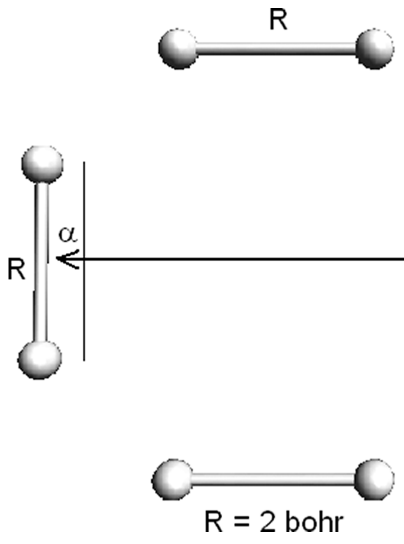


Figure 12. H_8 model system (four hydrogen molecules).

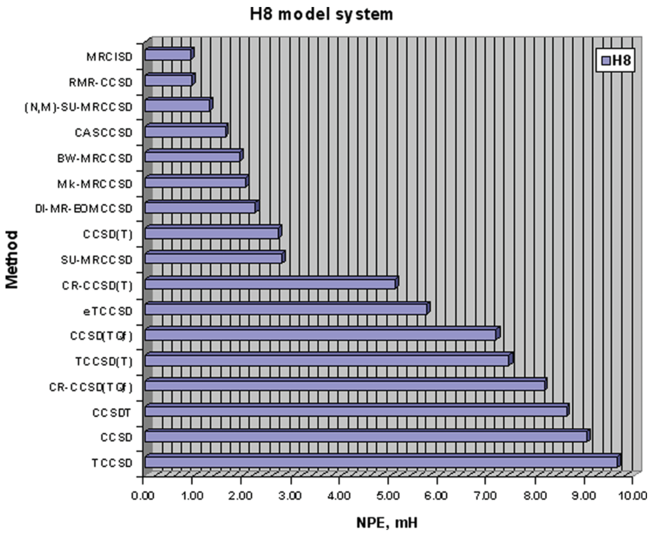


Figure 13. H_8 model system: PES nonparallelism errors (NPE) in mH.

from one inaccurate value to another one. As a result, one has a surprisingly small error of the CCSD(T) method in the highly multireference point of PES. This explains why sometimes ordinary SRCC methods work in MR problems (a similar situation can be observed in the DFT world). From our point of view, such random error cancellations cannot be considered as a reliable way when designing new chemically accurate methods. We believe that only the approaches pursuing the route of systematic convergence to the "*right answer*" can ensure high-accuracy ab initio predictions.

Table 3. H_8 Model System, cc-pVDZ Basis Set, Geometry $\alpha = 0$[a]

method	error, mH
CCSD	9.90
CCSDT	−8.31
CCSD(T)	2.95
CCSD(TQ_f)	7.39
CR-CCSD(T)[b]	5.38
CR-CCSD(TQ_f)[b]	8.44
TCCSD	11.40
TCCSD(T)	8.36
eTCCSD	−3.85
MR-DI-EOMCCSD	9.76
CAS(2,2)CCSD	2.14

[a] Errors produced by different methods with respect to full CI. [b] Calculated with GAMESS.[386,262,273,277,279]

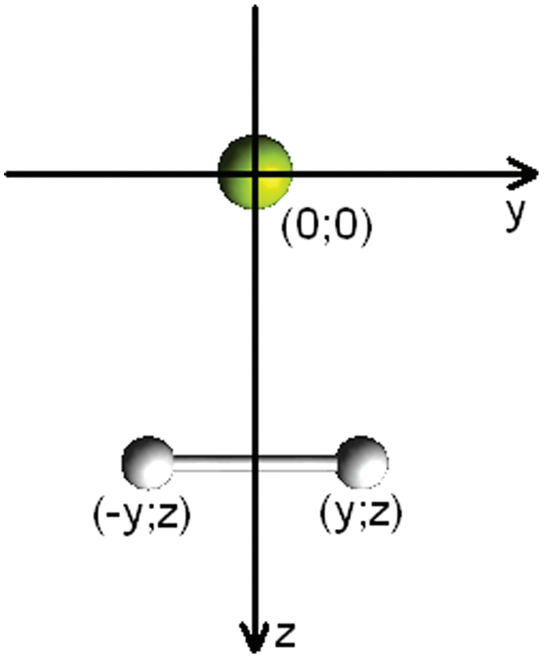


Figure 14. BeH_2 model system: an insertion of the Be atom into the H_2 molecule.

The next model system considered here is $Be\cdots H_2$,[363] shown in Figure 14. The model represents an insertion of the Be atom into the H_2 molecule. The transformation coordinate connects the noninteracting subsystems (Be + H_2) with the linear equilibrium state (H−Be−H). The transition state of this chemical transformation has a pronounced MR character. We adopt a simplified linear-dependent reaction path that relates y and z Cartesian coordinates such that the minimum and the transition state PES points fit the dependency exactly: $y(z) = \pm(2.54 - 0.46z)$ (ref 108). Another distinguishing feature of this example is a change of the character of the dominating determinant in the wave function along the PES. There are two leading determinants in the wave function, each of which dominates in a certain region of the PES while both are quasidegenerate around the transition-state geometry. As we mentioned in section 5 this leads to discontinuities in the calculated PES when using SRCC-based MRCC methods, for example, the CASCCSD approach. Fortunately, in the regions where such a change takes place, the CASCCSD energy discontinuity does not exceed the usual error of the method (however, taking a wrong reference determinant in other regions can lead to significant errors). Figure 15 illustrates the results. MRCC methods employ the CAS(2,2) reference space which contains the two leading determinants. As shown, all MRCC methods except SU-MRCCSD and L-CTSD/CASSCF(2,2)NOS (linearized canonical transformation theory,

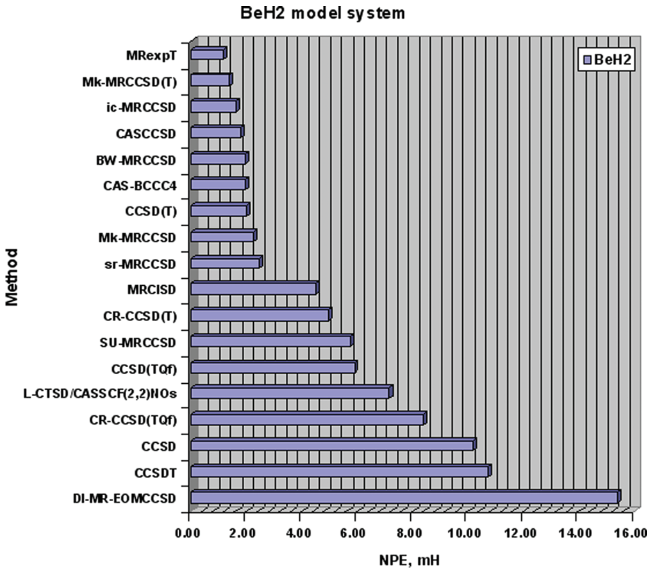


Figure 15. BeH_2 model system: PES nonparallelism errors (NPE) in mH.

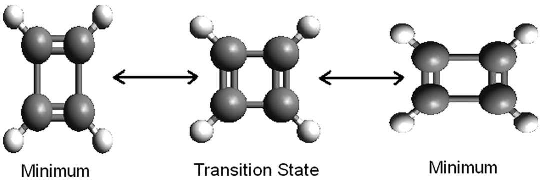


Figure 16. The automerization of the cyclobutadiene molecule.

Table 4. Barrier Height for the Automerization of Cyclobutadiene

method[a]	barrier height, kcal/mol cc-pVDZ	barrier height, kcal/mol cc-pVTZ
CCSD[b]	21.0	23.2
CCSD(T)[b]	15.8	18.3
CR-CCSD(T)[b]	18.3	–
Λ-CCSD(T)[b]	16.8	19.2
TCCSD[b]	9.4	12.9
TCCSD(T)[b]	4.6	7.0
SU-MRCCSD[c]	7.0	8.7
Mk-MRCCSD[c]	7.8	9.6
BW-MRCCSD(i.c.)[d]	6.2	7.4
RMR-CCSD[c]	10.4	13.0
SU-MRCCSD(T)[c]	4.8	5.9
Mk-MRCCSD(T)[d]	7.8	8.9
BW-MRCCSD(T)(i.c.)[d]	5.7	6.8
RMR-CCSD(T)[c]	7.2	9.5
MR-AQCCSD[e]	7.3	8.4
2D-MRCCSD(T)[f]	6.6 (DZP basis set)	–
MR-DI-EOMCCSD[b]	8.3	10.7
SS-EOM-CCSD[+2][g]	8.3	9.5
Experiment[h]	1.6 – 10.0	

[a] Geometry optimization (method/basis) does not necessarily correspond to the final correlated level. [b] Reference 315. [c] Reference 127. [d] Reference 158. [e] Reference 365. [f] Reference 110. [g] Reference 333. [h] Reference 366.

see section 3) yield satisfactory NPE. Note the harmful effect of the direct inclusion of all connected triples (CCSDT) as compared to doubles only (CCSD). Surprisingly, the perturbative inclusion of all triples again produces a quite accurate NPE in this case. Similarly to the previous examples, the BeH_2 system has a pronounced coupling between the nondynamic and dynamic electron correlations, where both require a sufficiently accurate account of higher excitations.

As one could notice, for all above systems, the MRCISD approach yields rather small NPE, reflecting a good parallelism of the MRCISD PES with respect to the full CI one. However, the MAD of the MRCISD PES (not shown) is noticeably higher than its NPE. For small molecular systems (as one will see from numerous examples below), the MRCISD method is capable of providing chemically accurate NPE, but the lack of a sufficiently complete account of the dynamic correlation results in rather large absolute errors of the calculated energies. And, of course, the MRCISD method is *not* size-extensive, although the calculated system has to be sufficiently large to exhibit this deficiency (actually the size-extensivity error already becomes significant for moderate-size systems[397]). MRCISD-based approaches with size-extensivity corrections, such as MR-AQCC and MR-ACPF, significantly improve the description of the dynamic electron correlation, thus decreasing the value of MAD and correcting the size-extensivity error. For small systems the NPE of CC methods usually correlates with MAD. A large value of either of them points out the inadequacy of the CC method in describing the problem under consideration. Apparently for larger electronic systems MAD becomes rather useless (since it grows roughly linearly with the number of particles) whereas NPE is expected to stay bounded for adequate methods (as a difference between two error values). At the same time, MAD divided by the actual correlation energy (i.e. the relative energy error) will still be a proper measure of accuracy.

A classical example of the MR transition state emerges when describing the automerization of cyclobutadiene, schematically shown in Figure 16. The corresponding PES contains two degenerate minima (D_{2h} geometries) related through the transition state which has D_{4h} spatial symmetry. Such a high symmetry leads to degeneracy of molecular orbitals (or quasi-degeneracy when a symmetry-broken Hartree–Fock solution is employed). Consequently, a configurational quasi-degeneracy plagues the wave function of the transition state, complicating its accurate description with ordinary SRCC methods. The leading determinants can be generated with the CAS(2,2) reference space built on the HOMO and LUMO MOs. The automerization of cyclobutadiene was extensively studied using a series of different MRCC methods.[110,127,158,333,364,365] Table 4 summarizes the results of calculation of the automerization energy barrier. Unfortunately, the full CI results are unavailable for the basis sets given. It is believed that the experimental value is within the range 1.6–10 kcal/mol.[366] Hence a *semiquantitative* assessment of the performance of different methods is still possible. Again the table clearly demonstrates the failure of ordinary SRCC approaches. At the same time, almost all MRCC methods provide reasonable values of the barrier height.

Another MR example is the isomerization of pyridyne.[156] There are two isomers (monocyclic and bicyclic forms) of this biradical (Figure 17) whose relative energies are close.

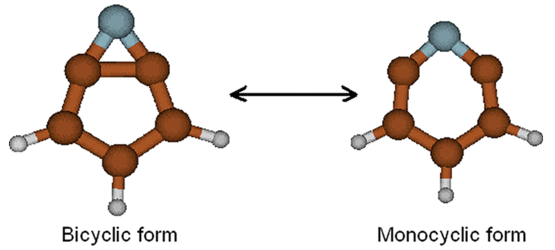


Figure 17. Bicyclic and monocyclic forms of the pyridyne biradical.

Table 5. Energy Difference between the Monocyclic and Bicyclic Forms of 2,6-Pyridyne Calculated in the cc-pCVTZ Basis Set

method	E(monocyclic) − E(bicyclic), kcal/mol
CCSD[a]	3.6
CCSD(T)[a]	−5.5
TCCSD	−6.78
TCCSD(T)	−8.96
Mk-MRCCSD[a]	−3.6
Mk-MRCCSD(T)[a]	−8.8

[a] Reference 156.

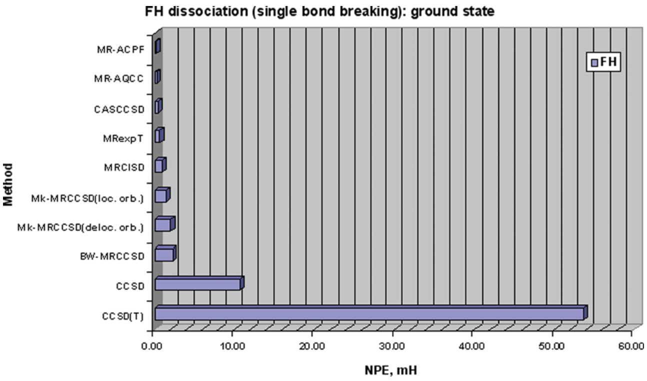


Figure 18. FH molecule dissociation: PES nonparallelism errors (NPE) in mH (part I).

The bicyclic form of the pyridyne biradical possesses a moderate MR character. The corresponding dominating determinants can be generated using the CAS(2,2) reference space which involves the HOMO and LUMO MOs. As one can see from Table 5, the CCSD approach yields a wrong sign for the relative energy between the two isomers! Both TCCSD and CCSD(T) methods predict a correct energetic order, whereas the TCCSD(T) value closely correlates with that of the Mk-MRCCSD(T) approach (for the price of a CCSD(T) calculation).

6.2. Chemical Bond Breaking Problem: F−H, F−F, H−O−H, H−N−H, CH_3, N≡N

The essential step of most chemical reactions is breaking/formation of chemical bonds, which is often connected with significant effects of the nondynamic/static electron correlation, as discussed in section 2. In particular, this is true when the bond is being broken such that two open-shell fragments appear. In order to assess the performance of different MRCC methods, we studied several di/triatomic molecules with chemical bonds of different order (single/double/triple). The severity of the problem essentially increases with the bond order. Two ultimate cases, the problem of triple-bond breaking in the N_2 molecule and the problem of C_2 bond breaking, are also shown further.

The FH molecule is used to simulate single-bond breaking. The corresponding one-dimensional PES is just the dissociation curve (energy as a function of the internuclear distance, R). Breaking a single bond in the ground electronic state typically involves two valence molecular orbitals. In the case of FH they are 3σ bonding and 4σ antibonding MOs. The multidimensional CAS(2,2) reference space, built on these orbitals, generally includes four determinants. This reference space was used in MR approaches shown.

Figures 18 and 19 show NPE's obtained for the FH PES calculated with different methods. As one can see, all MR methods yield small values of NPE, demonstrating only moderate MR character of the problem. The Mk-MRCCSD approach was employed using both localized (loc orb.) and delocalized (deloc orb.) orbitals.[157] Here, the difference between the two is not significant. However, as one will see in the next examples, the use of delocalized orbitals in the Mk-MRCCSD approach can lead to a significant error, while it is still believed that the localized orbitals can improve the results (in practice the Mk-MRCCSD-(loc orb.) approach suffers from convergence problems[157]). This is also a consequence of the "proper residual" problem (see subsection 3.5) that amplifies the lack of the active-orbital invariance in the Mk-MRCCSD method. It also severely affects the accuracy and applicability of the SU-MRCCSD and BW-MRCCSD approaches. Such sensitivity of the Mk-MRCCSD method to the orbital choice is particularly disturbing due to the fact that usually CC methods are relatively insensitive to the orbitals used ($\hat{T}_1$ cluster operator is supposed to handle moderate orbital relaxation). The "gold standard" of quantum chemistry, the CCSD(T) approach, as well as its more advanced successor CCSD(TQ$_f$), tend to be inadequate in describing chemical bond breaking in FH due to the use of the SR perturbation theory. Such perturbatively corrected SRCC approaches can handle only the equilibrium and intermediate regions of the bond-breaking coordinate, while completely failing in the dissociation limit. As we have already mentioned, the corresponding SR perturbation is no longer small when proceeding to the dissociation region. Consequently, only the MR versions of perturbation theory can still be used (for example, the CASPT2 approach where the perturbation is properly redefined, taking into account the multidimensional nature of the zeroth-order wave function). In the case of a single-bond breaking the completely renormalized (CR) corrections[273] seem to be rather efficient when applied to the CCSD(T) and CCSD(TQ$_f$) approaches. The ΛCCSD(T) approach also significantly reduces the NPE of CCSD(T), though the corresponding value is still high in this case.[281,282] Besides, let us note a "zero effect" of the perturbative triples correction (T) applied to the pl-MRCCSD method.

Similarly, Figure 20 illustrates the performance of different methods in calculating the PES corresponding to single-bond breaking in the F_2 molecule. The reference space employed in MR methods is also of CAS(2,2) type, where the highest bonding σ_g and the lowest antibonding σ_u MOs are taken as active. The results are quite similar to those obtained for FH, except for the pl-MRCCSD/pl-MRCCSD(T) methods, which in this case fall out of the chemical accuracy range.

A significantly more complicated case to describe is the symmetric dissociation of the H_2O molecule in its ground state.

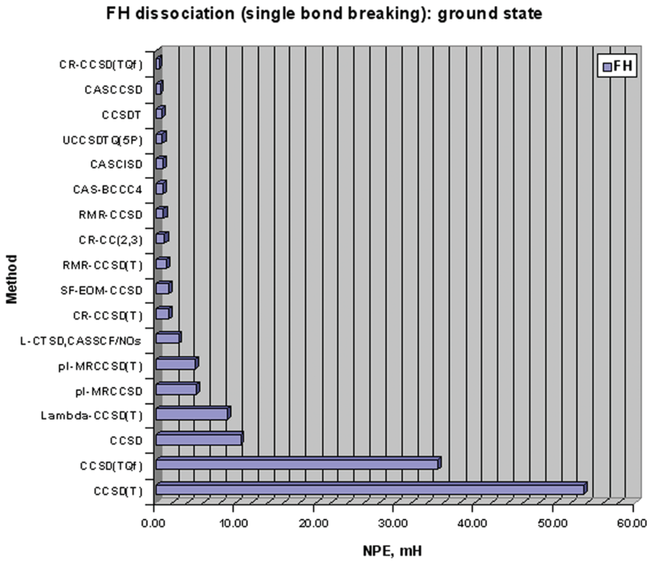


Figure 19. FH molecule dissociation: PES nonparallelism errors (NPE) in mH (part II).

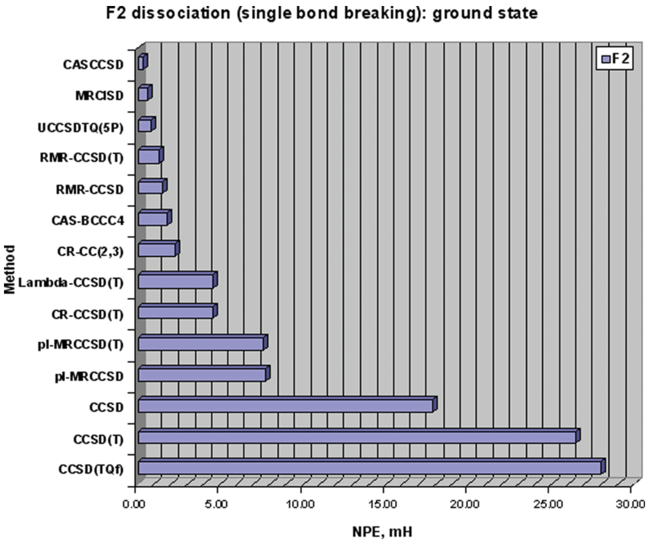


Figure 20. F_2 molecule dissociation: PES nonparallelism errors (NPE) in mH.

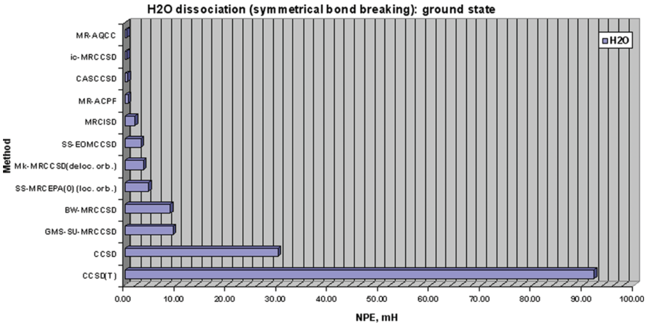


Figure 21. H_2O molecule dissociation (symmetrical bond breaking): PES nonparallelism errors (NPE) in mH (part I).

Having the angle fixed, both O−H bonds are being simultaneously stretched, leading to a one-dimensional PES. Because two single bonds are broken simultaneously, the minimal (physical) reference space is of CAS(4,4) type, involving four active MOs and four active electrons. All possible distributions of the active electrons on the active orbitals form the multidimensional reference space. Figures 21 and 22 illustrate the results of the PES simulation using different MR and SR methods. As one can see, ordinary SRCC methods drastically fail in this situation. Completely renormalized (CR) corrections are no longer able to restore the chemical accuracy of an ordinary SRCC method. 2SF-EOMCCSD stands for the double spin-flip EOMCCSD.[331] We should note that reasonable NPE values of some SRCC methods mostly originate from ignoring the dissociation limit, thus considering only moderate multireference regions of the PES. The inclusion of the dissociation limit into consideration would worsen their results. Certain genuine MRCC methods also fail to provide chemical accuracy in this case. For example, the BW-MRCCSD and GMS-SU-MRCCSD approaches yield only conditionally acceptable NPE. Two variants of the SRMRCC theory, namely the pl-MRCCSD and pl-MRCCSD(T) approaches, yield unacceptable results, the (T) correction playing against the method again. The MRCISD method itself and especially its successors (MR-ACPF, MR-AQCC, RMR-CCSD) still stand the test as well as the CASCCSD method.

A similar bond-breaking model is the symmetric dissociation of the NH_2 radical in its $^2B_1$ ground state.[157,367,368] As one can see from Figure 23, all shown MR methods, except BW-MRCCSD, provide a chemically accurate PES for this model. Remarkably, all MR methods employ the CAS(7,6) reference space involving all valence electrons.

The next logical step is to examine a simultaneous breaking of three single bonds. The CH_3 radical in its $^2B_1$ ground state represents such a model.[157,368,369] The full valence CAS(7,7) multidimensional reference space was used by MR methods. Again, according to Figure 24, all MR methods, except BW-MRCCSD, give satisfactory results.

Regarding the last two systems (NH_2 and CH_3), we should note that the corresponding CAS active spaces comprise all valence electrons, such that the addition of external singles and doubles results in a full correlation of the occupied orbital space (the actual error comes from an incomplete inclusion of virtual-orbital combinations when constructing the MRCC ansatz). Nevertheless, because of the "proper residual" problem, the Mk-MRCCSD/BW-MRCCSD methods still exhibit noticeable NPE errors.

Finally Figures 25 and 26 demonstrate the results obtained for a very difficult problem of triple bond breaking in the ground state of the N_2 molecule. The physical reference space is CAS(6,6), involving six active electrons distributed among six active MOs: $3\sigma_g$, $1\pi_u^x$, $1\pi_u^y$, $1\pi_g^x$, $1\pi_g^y$, $3\sigma_u$. Taking into account the scale of the NPE diagrams, one can see that the Mk-MRCCSD and BW-MRCCSD methods are unable to provide even conditionally acceptable accuracy. We should note that the corresponding NPE values might be underestimated for some methods, because the range of internuclear separations involved was often limited to 4.2 bohr at most.[157] The most severe MR region of the triple bond dissociation, (4.2,∞) bohr, was actually ignored in many calculations. However, as one can see from Figure 26, certain electronic-structure methods yield absolutely unphysical results, even without inclusion of the most difficult part of the PES. We should also note that the dramatic failure of particular SRCC approaches originate in the

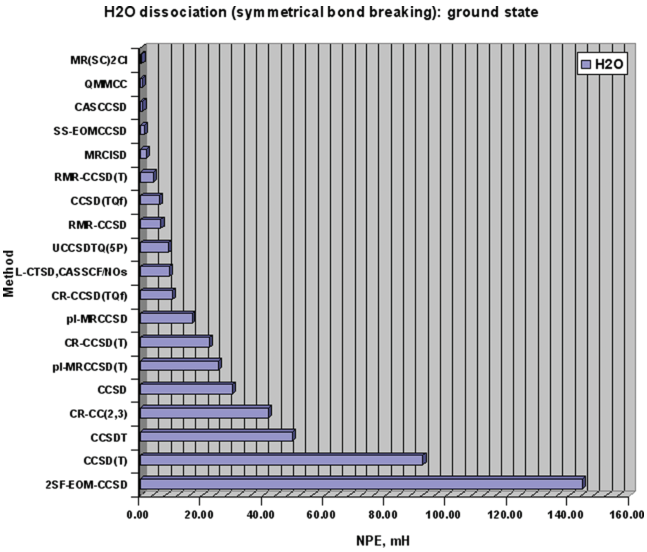


Figure 22. H_2O molecule dissociation (symmetrical bond breaking): PES nonparallelism errors (NPE) in mH (part II).

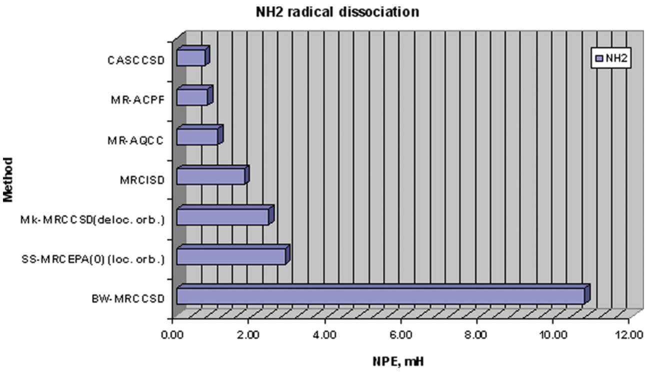


Figure 23. NH_2 dissociation: PES nonparallelism errors (NPE) in mH.

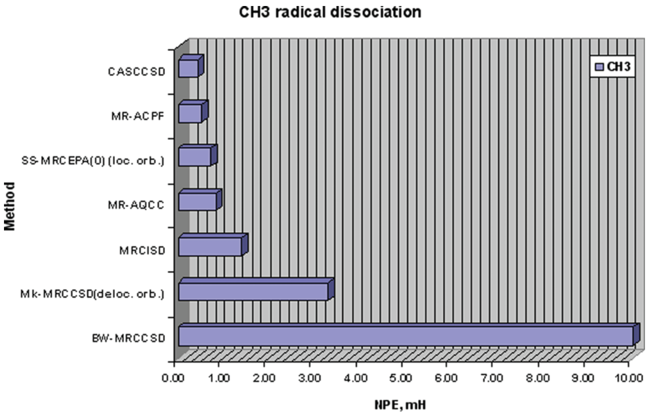


Figure 24. CH_3 dissociation: PES nonparallelism errors (NPE) in mH.

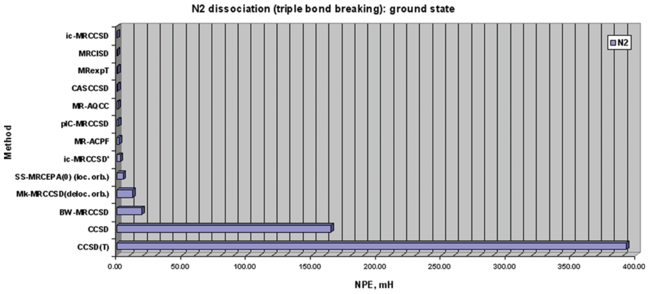


Figure 25. N_2 molecule dissociation (triple bond breaking): PES nonparallelism errors (NPE) in mH (part I).

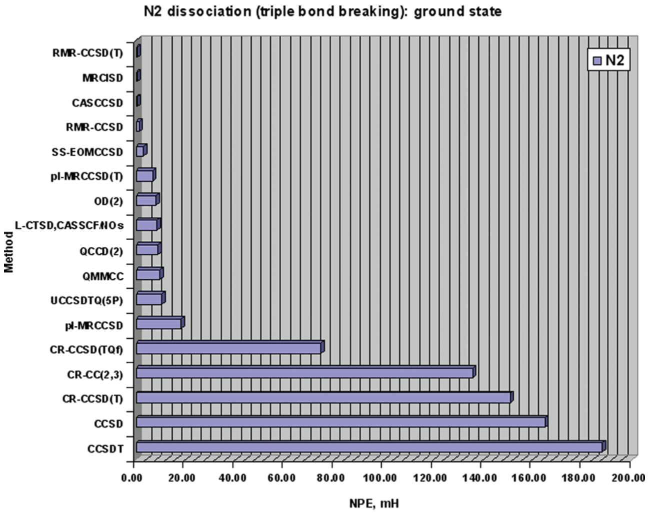


Figure 26. N_2 molecule dissociation (triple bond breaking): PES nonparallelism errors (NPE) in mH (part II).

use of the RHF reference function. For larger internuclear separations, it is difficult to obtain a stable RHF solution. The use of a symmetry-broken UHF reference noticeably reduces the error,[358] yet being far from chemical accuracy.

Overall, even the underestimated NPE values demonstrate how inadequate the SRCC/MRCC methods can be in describing triple-bond breaking. Particular attention should be paid to the failure of the RHF-CCSDT approach, which does not improve the unphysical RHF-CCSD results at all. This observation confirms the fact that the full inclusion of triple excitations is not only expensive from the computational point of view but is also inefficient in severe multireference situations. The nature of most MR problems requires an adequate representation of *selected* higher excitations (multireference first-order interaction space), either via their direct inclusion or via some genuine MR technique. However, the latter should be free of the "proper residual" problem, which otherwise can severely deteriorate the accuracy of the approach.

At the same time, the group of approximately size-extensive MRCISD-based approaches (MR-ACPF, MR-AQCC, RMR-CCSD), the SRCC-based CASCCSD method, and the SS-EOMCCSD approach all give small NPE values for this severe MR problem. Moreover, their NPE values are calculated for the entire range of N—N bond elongations. In particular, this presents a numerical proof that SRCC theory can be properly modified to effectively capture strong nondynamic/static electron correlations. An accurate NPE is also produced by the ic-MRCCSD method. The two versions given differ in the value of a threshold used in the underlying SVD decomposition.[90] In this case, a noticeable difference is observed.

Table 6. Equilibrium Geometrical Parameters and First Three Vibrational Frequencies of the Ozone Molecule (cc-pVTZ basis set)[a]

method	O−O distance, Å	O−O−O angle	$\omega_1(a_1)$, cm^{-1}	$\omega_2(a_2)$, cm^{-1}	$\omega_3(b_2)$, cm^{-1}
CCSD[b]	1.250(−0.022)	117.6(0.8)	1278(143)	763(47)	1266(177)
CCSD(T)[c]	1.275(0.003)	116.9(0.1)	1153(18)	716(0)	1054(−35)
CCSD(TQ$_f$)[h]	1.277(0.005)	116.8(0.0)	1144(9)	714(−2)	1094(5)
Mk-MRCCSD[b]	1.266(−0.006)	116.3(−0.5)	1180(45)	739(23)	1289(200)
Mk-MRCCSD(T)[f]	1.2897(0.018)	116.1(−0.7)	1081(−54)	694(−22)	1212(123)
BW-MRCCSD[b]	1.2604(−0.012)	116.6(−0.2)	1218(83)	748(32)	1331(242)
apBW-MRCCSD[b]	1.2726(0.0006)	115.8(−1.0)	1133(−2)	730(14)	1313(224)
TCCSD[d]	1.274(0.002)	116.7(−0.1)	1137(2)	718(2)	1098(9)
SF-OD/(DZP)[g]	1.289(0.017)	116.0(−0.8)	1165(30)	709(−7)	1144(55)
ic-MRCCSD[i]	1.266 (−0.006)	116.6(−0.2)	1184(49)	738(22)	1243(154)
experiment[e]	1.272	116.8	1135	716	1089

[a] Errors of the calculated quantities are given in parentheses. [b] Reference 153. [c] Reference 370. [d] Reference 314. [e] References 380, 381. [f] Reference 156. [g] Reference 327. [h] Reference 371. [i] Reference 90.

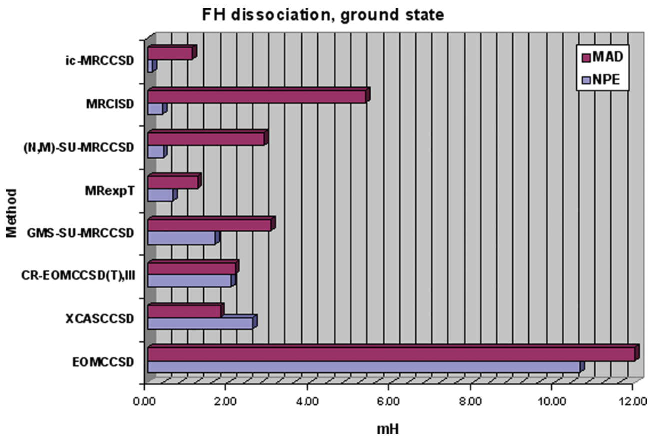


Figure 27. PES quality characteristics for the FH molecule dissociation in the X$^1\Sigma$ state.

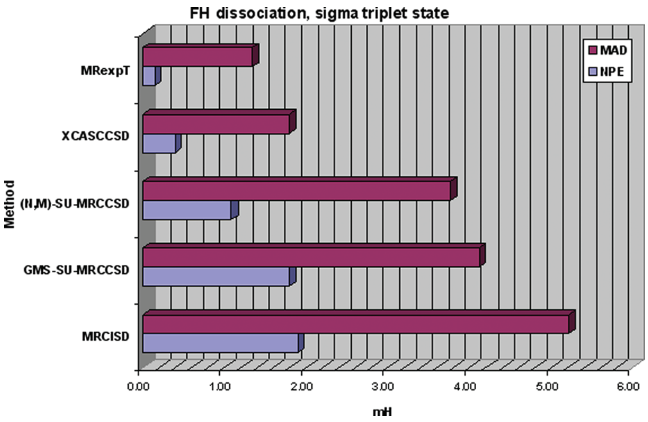


Figure 28. PES quality characteristics for the FH molecule dissociation in the excited $^3\Sigma$ state.

One more remark should be made about the stability of the Hartree−Fock solution when describing chemical bond breaking processes. Usually correlated methods are built on top of RHF solutions. However, it often happens that it is difficult to obtain the minimum RHF solution when MR effects are strong. This is a consequence of the fact that in MR situations a qualitatively correct zeroth-order wave function cannot be represented as a single determinant. In such cases a proper zeroth-order wave function should be constructed using the multiconfigurational SCF approach, MCSCF. Another alternative is to use a symmetry-broken UHF solution as a starting point. In the latter case serious symmetry contaminations can occur in the wave function. Keeping an unstable RHF solution as the reference function can introduce additional errors. For example, in the case of the N_2 molecule dissociation it is hard to obtain the minimum RHF solution after some point ($R_{N-N} \approx 4$ bohr), although this fact is almost always ignored in the literature. Fortunately, sufficiently sophisticated CC methods are relatively insensitive to the Fermi-vacuum choice, provided that it has some physical sense. However, this is not the case for SR-CI and SR-PT theories. Consequently, an attempt to utilize the SR-PT theory in order to improve an SRCC approach may lead to a complete failure. In other words, any MR problem by definition necessarily requires a *multidimensional* zeroth-order wave function (reference function). Then a proper theoretical model should be acquired in order to ensure a *balanced and sufficiently accurate* description of excitations from the *multireference first-order interaction space*. Neglecting these two postulates of MR theory can cause undesirable consequences and a failure of the method. One can still try to use a symmetry-broken UHF solution, which reduces the interelectronic-interaction perturbation by breaking the symmetry of the zeroth-order wave function. It is known that UHF-based SRCC methods usually yield superior correlation energies as compared to the RHF-based SRCC approaches.[358] However, this is only a partial solution, since one cannot guarantee that the corresponding Møller−Plesset perturbation is indeed made sufficiently small by using the UHF reference determinant, or any other physically motivated reference determinant, such as Brueckner, Natural, Kohn−Sham, etc.

In order to demonstrate the applicability of the Fock-space methodology in the description of chemical bond breaking, we show several potential energy curves in Figures 38, 39, 47, and 48. One can see that both the genuine IH-FS-(0,2)-MRCC/FS-(2,0)-MRCC method and the MR-DI/DA-CC approach provide a reasonable description of single-bond breaking for all

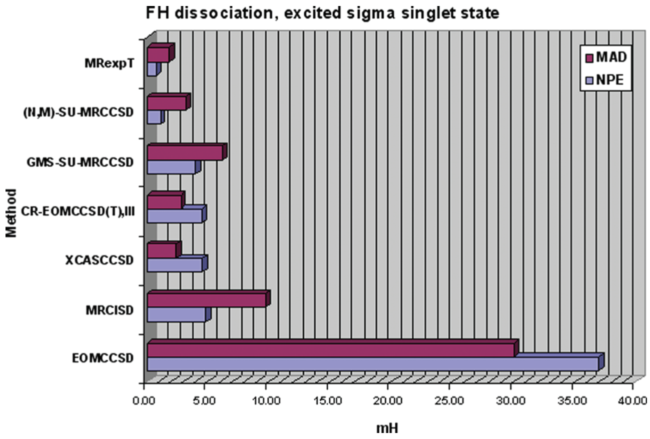


Figure 29. PES quality characteristics for the FH molecule dissociation in the excited $^1\Sigma$ state.

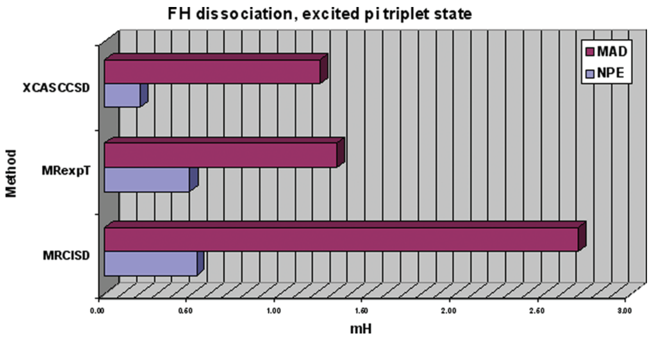


Figure 30. PES quality characteristics for the FH molecule dissociation in the excited $^3\Pi$ state.

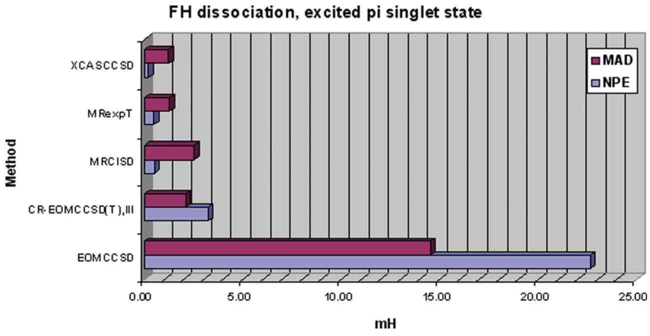


Figure 31. PES quality characteristics for the FH molecule dissociation in the excited $^1\Pi$ state.

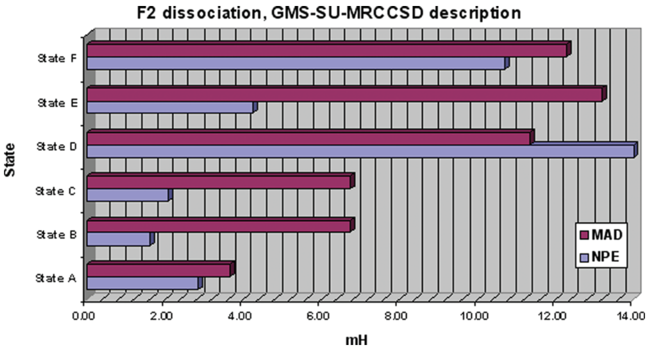


Figure 32. GMS-SU-MRCCSD description of the F_2 dissociation in five electronic states: (A) $X^1\Sigma_g^+$; (B) $1^1\Delta_g$, (C) $2^1\Sigma_g^+$, (D) $3^1\Sigma_g^+$, (E) $2^1\Delta_g$, and (F) $4^1\Sigma_g^+$ (data taken from ref 126).

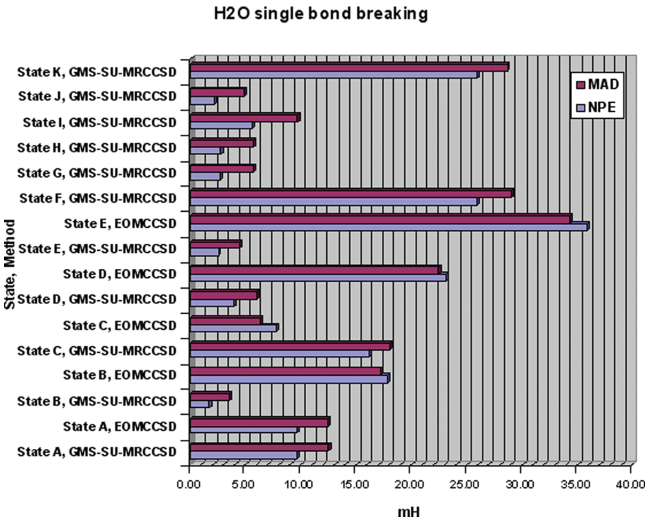


Figure 33. PES characteristics for single bond breaking in the H_2O molecule for 11 electronic states: (A) X^1A', (B) $1^1A''$, (C) $2^1A''$, (D) $1^1A'$, (E) $2^1A'$, (F) $3^1A'$, (G) $1^3A'$, (H) $2^3A'$, (I) $3^3A'$, (J) $1^3A''$, and (K) $2^3A''$ (data taken from ref 310).

molecules shown (F_2, Na_2, C_2H_6, N_2H_4). Note that the methods properly "reduce" to the SRCC theory in SR regions of the PES's.

In the context of accurate PES calculations, let us also provide a classical example of prediction of vibrational frequencies of the ozone molecule. The ground state of the O_3 molecule possesses a noticeable MR character, even around the equilibrium geometry, causing problems in accurate reproduction of the b_2 vibrational mode.[314,370] Table 6 illustrates the results obtained with different SRCC/MRCC methods (predominantly in the cc-pVTZ basis set) as compared to the experimental values (hoping that cc-pVTZ is sufficient for that). Bearing in mind the size of the basis set, two observations can be made. First, the accuracy of all shown genuine MRCC methods for the b_2 vibrational mode is comparable or even worse than the CCSD(T) value. Second, the perturbative (T) correction is essential for the Mk-MRCCSD method in order to reproduce the experimental value to a good precision. The actual convergence of the Mk-MRCCSD(T) results with the basis set size can be found in the original paper.[156] A particularly good value of the b_2 vibrational mode is supplied by the TCCSD method based on the CASSCF reference, whereas the use of RHF orbitals leads to noticeably worse results.[314]

6.3. Chemical Bond Breaking in Excited States: FH, C_2, F_2, and H_2O Molecules

An even more complicated problem is connected with bond breaking in excited electronic states. The complications come from a higher degree of "*multiconfigurationality*" of excited-state wave functions, the absence of a general single-determinant reference function for excited states, and a possibility of interstate crossings and avoided crossings, which can significantly change the character of the electronic state and the

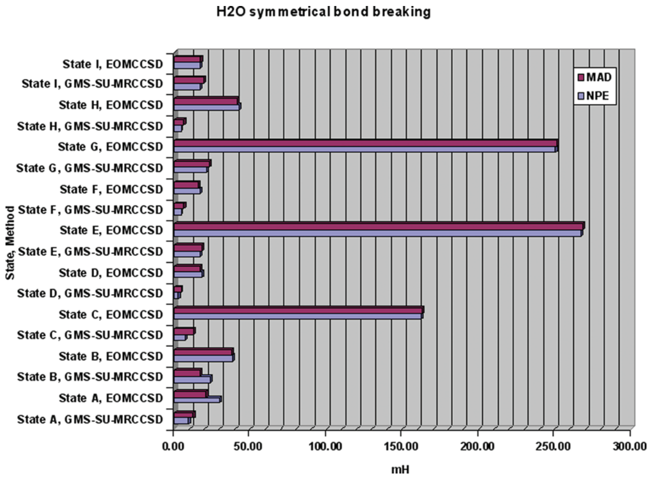


Figure 34. PES characteristics for symmetrical bond breaking in the H_2O molecule for nine electronic states: (A) X^1A', (B) 1^1A_1, (C) 2^1A_1, (D) 1^1A_2, (E) 2^1A_2, (F) 1^1B_1, (G) 2^1B_1, (H) 1^1B_2, and (I) 2^1B_2 (data taken from ref 310).

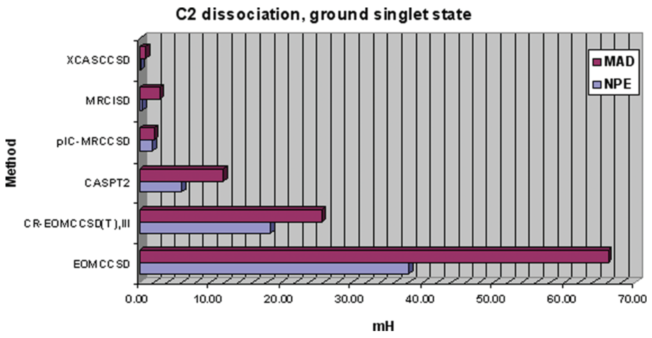


Figure 35. PES quality characteristics for the C_2 molecule dissociation in the ground $^1\Sigma_g^+$ state.

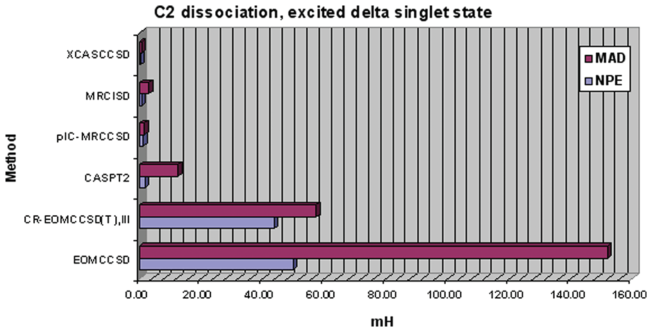


Figure 36. PES quality characteristics for the C_2 molecule dissociation in the excited $B^1\Delta_g$ state.

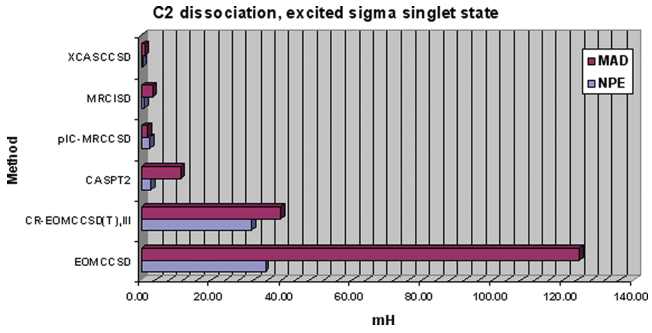


Figure 37. PES quality characteristics for the C_2 molecule dissociation in the excited $B^1\Sigma_g^+$ state.

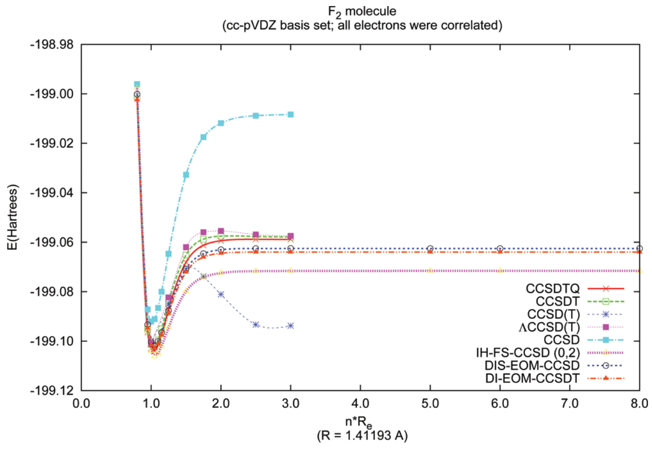


Figure 38. Dissociation of the F_2 molecule (cc-pVDZ basis set). Reprinted with permission from ref 376. Copyright 2011 American Institute of Physics.

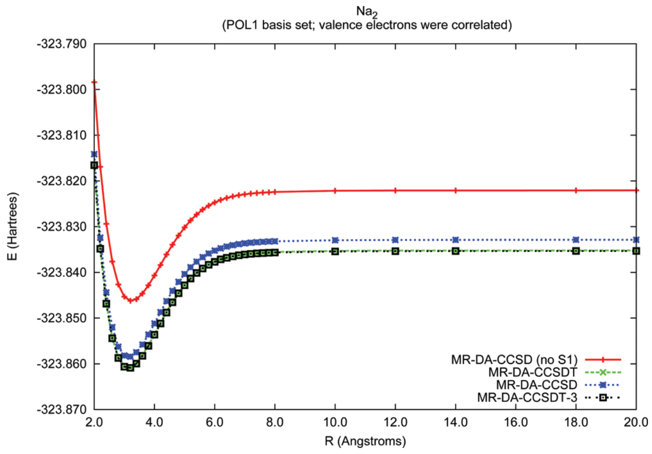


Figure 39. Dissociation of the Na_2 molecule (POL1 basis set).

corresponding wave function. Moreover, there is a common problem in describing higher excited states with *multistate* approaches (SU-MRCC, FS-MRCC, EOMCC). This problem stems from the necessity of using the same orbitals for all the states being simultaneously calculated. Usually the corresponding orbital set is obtained from the ground-state calculation, for example, by solving the Hartree–Fock equations. These orbitals are well-suited for a quite compact representation of the ground-state wave function, but there is no guarantee that they will lead to a similar compact representation of higher excited states. Actually, it can be shown that Hartree–Fock orbitals are progressively less optimal when proceeding to higher excited states (due to orthogonality of electronic states). Hence, an accurate calculation of higher excited states would require higher and higher

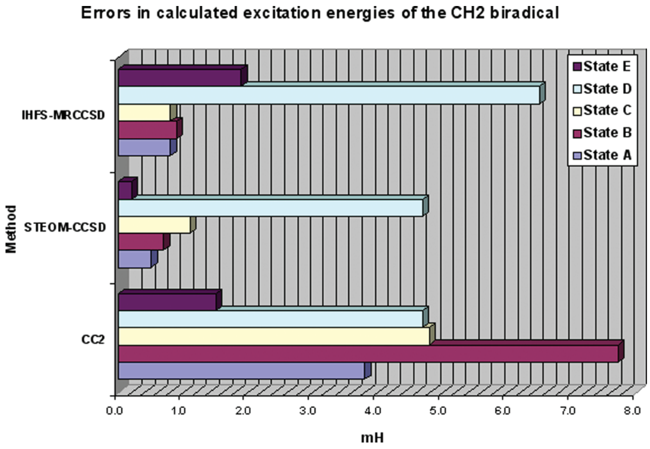


Figure 40. Absolute errors of calculated excitation energies for five electronic states of the CH_2 biradical: (A) 3^1A_1, (B) 4^1A_1, (C) 1^1B_1, (D) 1^1B_2, and (E) 1^1A_2.

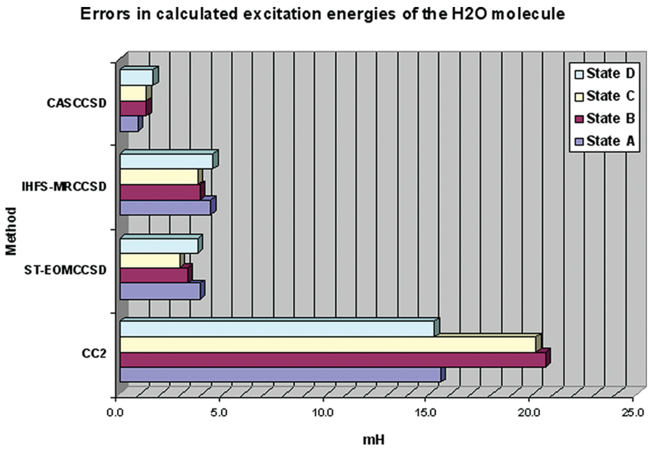


Figure 41. Absolute errors of calculated excitation energies for four electronic states of the H_2O molecule: (A) 2^1A_1, (B) 1^1B_1, (C) 1^1A_2, and (D) 1^1B_2.

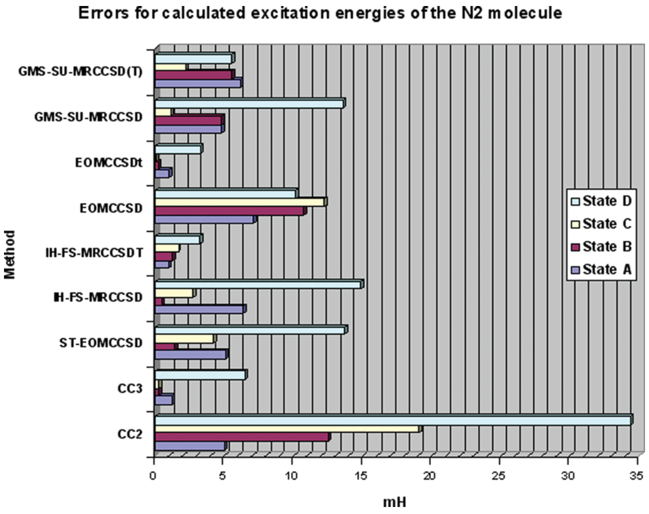


Figure 42. Absolute errors of calculated excitation energies for four electronic states of the N_2 molecule: (A) $^1\Pi_g$, (B) $^1\Sigma_u^-$, (C) $^1\Delta_u$, and (D) $^1\Pi_u$.

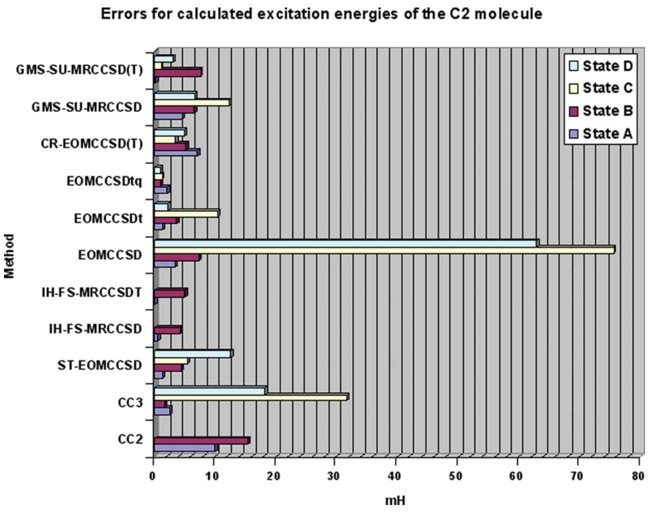


Figure 43. Absolute errors of calculated excitation energies for four electronic states of the C_2 molecule: (A) $^1\Pi_u$, (B) $^1\Sigma_u^+$, (C) $^1\Delta_g$, and (D) $^1\Pi_g$.

excited determinants to be present in the correlation ansatz, unless some proper orbital relaxation technique is built in. In multistate SR methods (like EOMCC) higher excitations (triples and higher) are necessary because there is no proper "exponential" orbital-relaxation operator for excited states. In multistate MR methods (like SU-MRCC) an increase of the reference space is needed. Consequently, both cases lead to a significant increase of computational demands of the method. In other words, staying within the same level of sophistication, the multistate approaches yield progressively less accurate results for the electronic states for which the orbitals were not optimized. Although all electronic states are formally treated on the same footing, the accuracy will noticeably depend on the state. Thus, relative energy differences (essential in chemistry) will suffer. On the other hand, extending the correlated ansatz to the "worst" state would lead to "overdescribing" the "easier" states and wasting computational resources. For example, in multistate MR methods the reference space must be sufficiently large in order to describe the "most difficult" electronic state, regardless of the character of other states. These complications make state-specific methods generally more advantageous in terms of the ratio accuracy/demands. Using a state-specific description of a certain electronic state one can adjust everything, including the orbitals, for that particular state, thus achieving a compact representation of the corresponding wave function. However, the price paid is the difficulty of calculation of matrix elements between different states (among other problems).

For our model studies, we demonstrate the results that summarize the performance of different CC methods in calculations of excited state PES's for several molecules (full excited-state PES calculations are quite rare in the literature). The first five plots (Figures 27, 28, 29, 30, and 31) illustrate the performance of different methods in calculating PES's for five electronic states of the FH molecule: (A) $X^1\Sigma$, (B) $1^3\Sigma$, (C) $2^1\Sigma$, (D) $1^3\Pi$, and (E) $1^1\Pi$. Here we provide both the MAD and NPE values. The XCASCCSD approach is a symmetry-corrected variant of the CASCCSD method,[247] the (*N*,*M*)-SU-MRCCSD approach is a multistate version of the RMR-CCSD

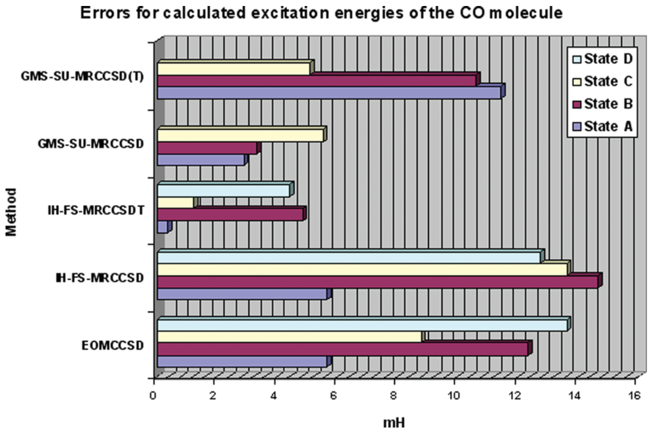


Figure 44. Absolute errors of calculated excitation energies for four electronic states of the CO molecule: (A) $^1\Pi$, (B) $^1\Sigma^-$, (C) $^1\Delta$, and (D) $^1\Sigma^+$.

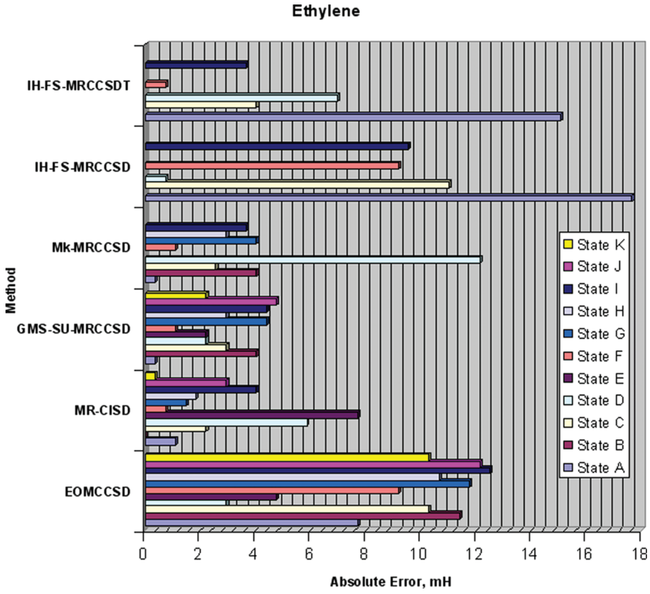


Figure 45. Absolute errors of calculated excitation energies for 11 electronic states of the ethylene molecule: (A) 1^1A_g, (B) 2^1A_g, (C) 1^1B_{1g}, (D) 1^1B_{1u}, (E) 2^1B_{1u}, (F) 1^1B_{2g}, (G) 1^1B_{2u}, (H) 2^1B_{2u}, (I) 1^1B_{3u}, (J) 2^1B_{3u}, and (K) 3^1B_{3u}.

Table 7. Singlet−Triplet Energy Splitting for Three Isomers of Benzyne (in kcal/mol).

method	*o*-benzyne	*m*-benzyne	*p*-benzyne
Mk-MRCCSD/cc-pVDZ[a]	35.1	18.7	4.5
SF-CCSD/cc-pVTZ[b]	36.4	18	3.4
SF-CCSD(dT)/cc-pVTZ[b]	37.3	20.6	4
ic-MRCCSD[e]	33.740	17.415	3.534
experiment	37.7 ± 0.7[c]	21.0 ± 0.3[d]	3.8 ± 0.3[d]
	37.5 ± 0.3[d]		2.1 ± 0.4[d]

[a] Reference 153. [b] Reference 382. [c] Reference 383. [d] Reference 384. [e] Reference 90.

method built on top of the GMS-SU-MRCCSD approach.[312] The CR-EOMCCSD(T)-III approach[372] is a completely

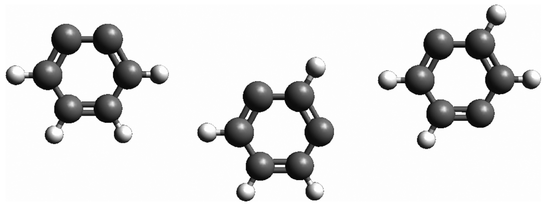


Figure 46. *o*-Benzyne, *m*-benzyne, and *p*-benzyne biradicals.

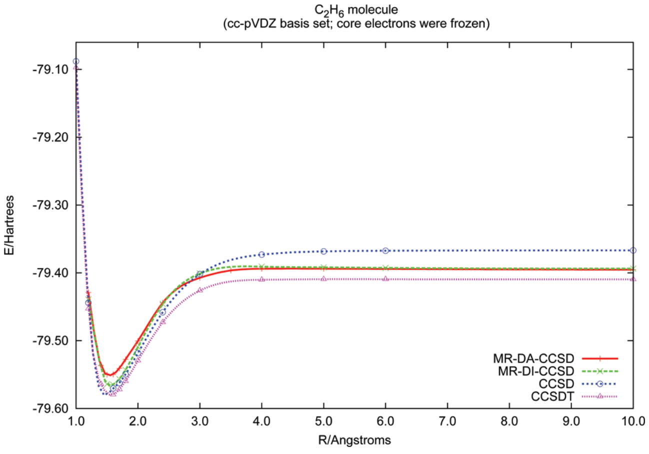


Figure 47. Dissociation of the ethane molecule (cc-pVDZ basis set).

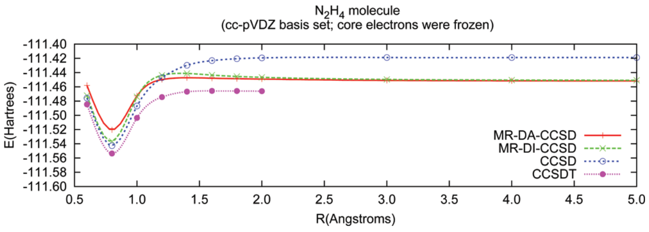


Figure 48. Dissociation of the hydrazine molecule (cc-pVDZ basis set).

renormalized analogue of the CCSD(T)/EOMCCSD(T) method for the ground/excited states, respectively. For the XCASCCSD[247] and MRexpT[171] methods the reference space is CAS(2,2), involving $\{3\sigma,4\sigma\}$ MOs for the Σ states and $\{1\pi,4\sigma\}$ MOs for the Π states. Similarly to the previous examples, the MRCISD (CASCISD) approach is capable of providing chemically accurate NPE, but the MAD is relatively high. SR-CCSD/EOMCCSD fails to provide even conditionally acceptable results because the space of SR singles and doubles used for excited states is not sufficient. For the FH molecule the CR and (T) corrections restore the accuracy of the SR-CCSD/EOMCCSD method. For all five states the MRexpT approach and SRCC-based XCASCCSD method provide chemically accurate values of the NPE/MAD. While the NPE of the GMS-SU-MRCCSD is satisfactory, the MAD value is relatively large.

Figures 32− 34 demonstrate the performance of the GMS-SU-MRCCSD method in calculations of excited state PES's for the F_2[126] and H_2O molecules.[310] In the latter case, both the single-bond breaking and the symmetric bond breaking processes are considered. From Figure 32 one can see a progressively deteriorating behavior of the method when proceeding to higher excited states. As discussed above, one possible reason is that the GMS reference space used is sufficient for lower excited states while being too restrictive for the higher ones. For single-bond breaking in the H_2O molecule the GMS-SU-MRCCSD method is noticeably superior to the SR-EOMCCSD approach, although both approaches give a significant MAD error (see Figure 33). Here we want to emphasize that the deficiency of the EOMCCSD method originates not in the EOM scheme itself, but rather in the insufficient external space used for expanding the excited-state vectors. As mentioned above, higher and higher excitations need to be added into the EOM CI operator when proceeding to higher electronic states. However, again, a direct inclusion of all triples is computationally expensive and not always necessary in practice. Usually only *selected* triple (and higher) excitations, namely, the excitations from the mutlireference first-order interaction space, are required for providing a quantitative description of the MR problem. The corresponding active-space-restricted EOMCC approaches (EOMCCSDt, EOMCCSDtq, ...)[262−264] are suitable for that. The transition from the EOMCCSD CI operator to the EOMCCSDtq... CI operator is equivalent to the transition from the CISD excitation manifold to the MRCISD excitation manifold (where all excitations are defined with respect to the same Fermi-vacuum determinant used in the ground-state CC calculation). The MRCISD excitation space includes all determinants from the first-order interaction space, ensuring the correct description of the nondynamic/static electron correlation.

Figure 34 illustrates similar results obtained for symmetric bond breaking in the H_2O molecule for several excited states. The incompleteness of the SR singles-and-doubles excitation manifold is more pronounced here, as one can notice large errors produced by the ordinary EOMCCSD approach. We should note that similar methods, like CC2,[373,374] are also likely to fail in such MR situations due to the incompleteness of the excitation manifold.

As the ground-state triple-bond dissociation in the N_2 molecule constitutes one of the hardest ground-state MR problems, the dissociation of the C_2 molecule in any of the lowest $B^1\Delta_g$ or $B^1\Sigma_g^+$ electronic states presents a challenging excited-state MR problem, where both nondynamic and static electron correlations are strong. Both excited states possess doubly excited character with respect to the ground state $X^1\Sigma_g^+$, which is highly "multireference" by itself, even around the equilibrium geometry.[375] The severity of the problem can be seen from the failure of SRCC methods, as shown in Figures 35−37. The CR correction,[372] which was efficient in the case of the FH molecule, is not able to capture such strong nondynamic/static correlations appearing along the PES of C−C bond dissociation. At the same time, the SRCC-based XCASCCSD approach and the pIC-MRCC method yield chemically accurate results for both the NPE and MAD. The minimally required multidimensional CAS reference space is rather large, being of the CAS(6,7) type.

6.4. Excitation Energy Calculations: CH_2, H_2O, N_2, C_2, CO, $H_2C{=}CH_2$, and Benzynes

The calculation of potential energy surfaces has been mostly a prerogative of the Hilbert-space MRCC and SRMRCC approaches. Albeit the FS-MRCC and EOMCC schemes can also be applied in calculations of the entire PES[376] (see Figures 38, 39, 47, and 48), they have been mostly employed in studying excitation spectra of molecules. A particular reason is that the FS-MRCC approach may need rather high sectors of the Fock space. However, the corresponding higher-sector FS-MRCC equations are rather complex and require significant effort put in an implementation of the method. For example, single-bond breaking usually requires two active electrons, double-bond breaking needs four active electrons, and triple-bond breaking needs six active electrons, etc. The corresponding FS-MRCC approaches would require an explicit consideration of the two-valence sector, four-valence sector, six-valence sector, etc. (see subsection 4.1). While the two-valence sector is readily accessible, the higher-sector FS-MRCC methods are still theoretically challenging. Nevertheless, the implementation of the corresponding methods can be accomplished via the use of automated symbolic algebra tools that have been significantly advanced during the last years.[168,256−259,377−379] A conceptually similar but easier way is offered by the MI/MA-MR-EOMCC scheme, which was recently shown to be quite efficient in describing certain MR phenomena, for example, twisting of the ethylene molecule[322] (see also Figures 38, 39, 47, and 48).

Here we will restrict ourselves to showing the performance of the IH-FS-MRCC and EOMCC methods, as well as other SRCC and MRCC approaches, in *excitation energy* calculations. Figures 40, 41, 42, 43, 44, and 45 demonstrate the results obtained with different methods for several electronically excited states of the CH_2 biradical, H_2O, N_2, C_2, CO, and ethylene molecules, respectively. The general observation is that the $O(N^6)$-scaling MRCC methods (either genuine or alternative) are noticeably more accurate in excitation energy calculations than ordinary SRCC models (EOMCCSD, CC2), although the STEOMCCSD method [237−239] demonstrates similarly good results. One should note that because of the hierarchical structure the IH-FS-MRCCSD approach (see section 4) constructs the excited-state vectors in the space of single excitations only, although both singles and doubles are used in the ground-state computation. The IH-FS-MRCCSDT method uses singles and doubles for excited states but introduces triples for the ground state. Consequently, a more appropriate scheme would mix the two methods and employ the singles-and-doubles space in both the ground- and excited-state calculations. Note that all the methods shown, except those involving full triples, have comparable computational scaling, although MRCC approaches normally have larger prefactors in the computational scaling dependency. Along with all above numerical examples, SRCC-based MRCC methods, such as CASCCSD, EOMCCSDt, and EOMCCSDtq, in most cases yield very accurate results, often of superior quality than the genuine MRCC methods (at the same level of approximation). Figure 45 is based on the data taken from ref 128. That methodologically important paper exhibited serious convergence problems experienced by the Mk-MRCCSD method in excited-state calculations. Nevertheless, as shown in Table 7, the Mk-MRCCSD approach provides quite accurate values for the singlet−triplet energy splitting in three isomers of the benzyne biradical. The ground state of all three isomers (shown in Figure 46) possesses a noticeable MR character requiring a proper MR method.

7. TO MULTIREFERENCE OR *NOT* TO MULTIREFERENCE?

The above numerical results confirm our premise that SRCC theory should not be excluded from consideration when developing reliable MRCC methods. Despite using the SRCC formalism, the corresponding alt-MRCC approaches still exploit (sometimes implicitly) the concept of a *multidimensional* reference state that provides a proper zeroth-order description of a *multireference* problem. The symmetry contamination that can plague alt-MRCC wave functions is usually quite small, whereas in adaptive/semiadaptive CC approaches it is also controllable (in principle). On the other hand, the recently developed gen-MRCC methods, especially the MRexpT, ic-MRCCSD, and pIC-MRCCSD approaches, provide remarkably accurate results for the most difficult MR problems. Thus, we believe that a fruitful "*synthesis*" of gen-MRCC and alt-MRCC theories is possible.

It is often argued that the use of a multidimensional reference space within the SRCC formalism is undesirable, because the theory loses black-box character. It is definitely true that many MRCC theories (either genuine or alternative) do require some logic to select the reference space (the active orbital space for CAS/IAS models). However, in general, it is arguable what black box should mean for an electronic structure method. If black box means that a method is a "*push a button*" procedure that generally leads to *unpredictable* results in terms of accuracy, then the current SRCC theory is purely black box (as well as the widely used SR-PT, SR-CI, and DFT theories). However, if one adopts a more intelligent definition where black box means

> *An internal logic, sufficiently sophisticated to adjust all parameters of the method in order to obtain a reasonable accuracy of the calculation,*

then the overwhelming amount of SRCC approaches, each of which works in certain cases and can *drastically* fail in other, is something that can hardly be called black box. Indeed, for a user to decide which black box SRCC method to choose (from tens of possible variants) is something equivalently complicated as the selection of the reference space in multireference theories. Unfortunately, the former does *not* guarantee a quantitative solution of the problem.

From the mathematical point of view, one cannot neglect the fact that in multireference situations the wave function cannot be adequately approximated by a single mean-field determinant. Hence, in order to create a truly *black-box* ab initio MRCC method, it is mandatory to develop a proper logic which would be capable of selecting an adequate zeroth-order wave function (reference function) in an *automated* and *unambiguous* manner. The multireference nature of the zeroth-order wave function must always be accounted for, either explicitly or implicitly. At the same time, a fixed structure of the model space can lead to "redundant" reference functions when the multireference character is lost (the problem of "*smooth*" reduction of MRCC to SRCC). Indeed, in practice some of the reference determinants may lose their impact in some regions of the PES (in SR regions of the PES) while the CAS reference function often contains low contributing determinants from the beginning. Hence, the reference function can involve determinants whose contribution to the wave function is comparable or even lower than that of some determinants from the external space (first-order interaction space).

A shared trait of gen-MRCC methods and some alt-MRCC methods is a significant complexity of the underlying equations (both represent *high-end* electronic structure theory). This fact stimulated a development of *automated symbolic algebra* tools. Even though the current MRCC theory mostly exists in "experimental" software, we feel that the power of contemporary computers has approached a critical point where such sophisticated methods can start to be routinely applied in solving important problems of quantum chemistry (relatively small for now), proving that these theories are not just mathematical constructs usually applied to model systems only. It should be realized that a reliable MRCC methodology is mandatory to extend the applicability of CC theory to *quasidegenerate* (multireference) problems, preserving the *chemical accuracy* of calculations the CC theory is famous for. It is known that more approximate models (SR-PT, DFT, etc.) are generally unable to deliver chemical accuracy, especially for multireference problems (however, a lower accuracy level allows an application to much larger electronic systems). Now the existing computer power makes possible a promotion of *chemical accuracy* to moderate-size systems of any character, single- or multireference. The development of accurate MRCC theories would also be helpful for calibrating less accurate methods.

Apart from the theoretical advances, there are two main challenges to be accomplished:

1. Development of a *massively parallel* framework for implementing MRCC and other *higher-order* CC methods.
2. Development of an *advanced black-box logic* that would adjust the method to the problem of interest, ensuring a reasonable accuracy of calculation.

Successful accomplishment of these tasks would significantly extend our *quantitative* understanding of quantum chemical processes, opening a new era of quantum chemistry.

AUTHOR INFORMATION

Corresponding Author

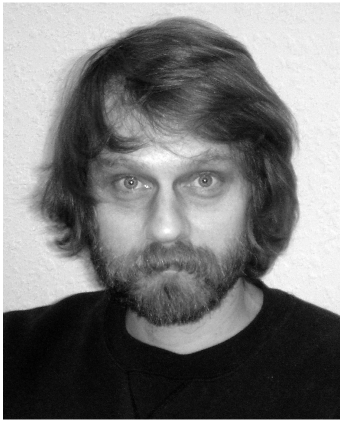
*Phone: 352-392-6714. E-mail: quant4me@gmail.com.

BIOGRAPHIES

Dmitry I. Lyakh graduated from the Karazin Kharkiv National University (Kharkiv, Ukraine) with a Ph.D. in physical chemistry (quantum chemistry and cheminformatics) in 2009. His Ph.D. thesis was devoted to a systematic study of the effects of higher-rank excitations in coupled-cluster theory and their necessity for a quantitative account of the electron correlation in molecular systems plagued with quasidegeneracy. An indistinguishable part of his research is development of automated symbolic algebra tools capable of generating, factorizing, and coding the underlying mathematical equations. In 2009, he joined the research group of

Prof. Rodney J. Bartlett in the "cradle" of quantum chemistry, the Quantum Theory Project at the University of Florida. The main research goal is development of a reliable multireference extension of coupled-cluster theory with an emphasis on adaptivity and possibility of a linear scaling parallel implementation. E-mail: liakh@qtp.ufl.edu and quant4me@gmail.com.

Monika Musiał graduated with a M.S. in theoretical chemistry from the University of Silesia in Katowice, Poland. She received her Ph.D. in 2002 for the work on the development of new coupled-cluster models including high-rank cluster operators. She spent several years at the Quantum Theory Project (University of Florida), working as a postdoctoral associate in the research group of Prof. Rodney J. Bartlett. She pursued several research projects focused on the development of new coupled-cluster models designed to describe excited and ionized electronic states within the equation-of-motion coupled-cluster (EOMCC) theory. However, her main field of research is the multireference coupled-cluster theory and its application to the studies of excited states of open- and closed-shell molecules. Currently, she is an Associate Professor of the Institute of Chemistry at the University of Silesia (Katowice, Poland). E-mail: musial@qtp.ufl.edu.



Victor Lotrich obtained his Ph.D. in physics from the University of Delaware in 1997 for his work on three-body effects in symmetry-adapted perturbation theory (SAPT). He then worked with Dr. Marcel Nooijen at Princeton University, in particular on automatic formulae/code generation for many-body methods. After a short stay at the University of Nijmegen (group of Prof. Ad van der Avoird), he moved to the University of Florida, where he is currently heavily involved in the massively parallel implementations of quantum chemical codes (ACESIII software), most notably coupled-cluster methods. E-mail: lotrich@qtp.ufl.edu.

Rod Bartlett obtained a B.S. from Millsaps College in 1966 (Double Major, Chemistry and Mathematics). In 1971 he received his Ph.D. in Quantum Chemistry from the University of Florida. He was then an NSF Postdoctoral Fellow at Aarhus University, Denmark, and then at Johns Hopkins University. After seven years at Battelle Memorial Institute at PNNL and in Columbus, Ohio, he returned to the University of Florida as Professor of Chemistry and Physics in 1981. He became the Graduate Research Professor in the Quantum Theory Project in 1987. Rod Bartlett is responsible for the development of coupled cluster theory for whole range of problems in molecular spectra and structure, emphasizing the fundamental principle of correct scaling with size (size-extensivity) as the rationale for many-body methods. Today, CC theory has become the most prominent tool in high-level contemporary molecular electronic structure and in spectroscopy. Rod Bartlett is the recipient of the American Chemical Society award in Theoretical Chemistry, 2007, the Schrödinger Medal of the World Association of Theoretical and Computational Chemists, 2008, the Boys-Rahman Award of the Royal Chemical Society, 2009, the ACS Southern Chemist Award, 2010, and the ACS Florida Award, 2000. His H-index is 88 and he is listed on http://isihighlycited.com. E-mail: bartlett@qtp.ufl.edu.

ACKNOWLEDGMENT

The authors sincerely acknowledge the support provided by the Air Force Office for Scientific Research (AFOSR), in particular, under the STTR Phase I (grant #AF09-BT40). The authors also thank Dr. Ajith Perera for certain numerical results. Valuable comments provided by Dr. Marcel Nooijen and constructive criticism from unknown referees are greatly appreciated. D.I.L. would like to acknowledge his teacher, Dr. Vladimir V. Ivanov.

LIST OF ACRONYMS

@CC	adaptive coupled cluster (method)
alt-MRCC	alternative MRCC theory (theory)
2D	two-determinantal (prefix)
BCCC	block-correlated multireference CC approach (method)
BW	Brillouin−Wigner (prefix)
CAS	complete-active space (prefix)
CASCCSD	single-reference based multireference CC approach with a CAS reference (method)
CC	coupled cluster (theory)
CCD	coupled cluster with doubles (method)

CCSD	coupled cluster with singles and doubles (method)
CCSDT	coupled cluster with singles, doubles, and triples (method)
CCSDTQ	coupled cluster with singles, doubles, triples, and quadruples (method)
CEPA	coupled-electron-pair approximation (method)
CR	completely renormalized (prefix)
CI	configuration interaction (theory)
CISD	configuration interaction with singles and doubles (method)
CQD	configurational quasidegeneracy (phenomenon)
DA	double (electron) attachment (prefix)
DI	double ionization (prefix)
EA	electron attachment (prefix)
eTCCSD	enhanced TCCSD (method)
EOM	equation-of-motion (method)
EPV	exclusion principle violation (physical concept)
FS	Fock space (prefix)
full CI/FCI	full configuration interaction (method)
gen-MRCC	genuine MRCC theory (theory)
GMS	general-model space (prefix)
GVB	generalized valence bond (method, prefix)
HOMO	highest occupied molecular orbital (chemical concept)
HS	Hilbert space (prefix)
IAS	incomplete-active space (prefix)
ic/IC	internally contracted (prefix)
ic-MRCC	Internally contracted MRCC (method)
IH	intermediate-Hamiltonian (prefix)
IMS	incomplete-model space (prefix)
IP	ionization potential (prefix)
JM	Jeziorski−Monkhorst (prefix)
LDT	linked diagram theorem (theorem)
LUMO	lowest unoccupied molecular orbital (chemical concept)
Λ-CC	Λ-based CC (method)
MA	multiple (electron) attachment (prefix)
MAD	maximal absolute deviation (quantity)
MBPT	many-body perturbation theory (theory)
MC	multiconfigurational (prefix)
Mk	Mukherjee (prefix)
mH	milihartree (atomic unit of energy)
MI	multiple ionization (prefix)
MMCC	method-of-moments in coupled cluster (theory)
MO	molecular orbital (1e spatial function)
MR	multireference (prefix)
MRCC	multireference coupled cluster (theory)
MR-ACPF	MR averaged coupled-pair functional (method)
MR-AQCC	MR averaged quadratic coupled cluster (method)
MR-FCPF	MR full coupled-pair functional (method)
MR(SC)^{2}CI	multireference size-consistent self-consistent CI approach (method)
(N,M)-CCSD	reduced multireference analogue of SU-MRCCSD (method)
NPE	nonparallelism error (quantity)
occ	occupied orbital (chemical concept)
OD	obital-optimized CC with doubles (method)
PES	potential energy surface (physical concept)
pIC-MRCC	partially internally contracted MRCC (method)
pl	partially linearized (prefix)
PT	perturbation theory (theory)
QMMCC	quasivariational MMCC (method)
RHF	restricted Hartree−Fock (method)
ROHF	restricted open-shell Hartree−Fock (method)
RMR	reduced multireference (prefix)
SAC	symmetry-adapted-cluster (method)
SAC-CI	symmetry-adapted-cluster configuration interaction (method)
SAC-CI-general-*R*	symmetry-adapted-cluster configuration interaction with semiadaptive *R* operator (method)
SCF	self-consistent field (method)
SF/2SF	spin-flip/double-spin-flip (prefix)
SR	single-reference (prefix)
SRMRCC	single-reference based multireference CC approach (method)
sr-MRCC	single-root multireference CC approach (method)
SS	state-specific (prefix)
STEOM	similarity-transformed EOM (method)
SU	state-universal (prefix)
SVD	singular value decomposition (method)
TCCSD	tailored CCSD (method)
(T)	perturbative triples correction (suffix)
(TQ$_f$)	perturbative triples and factorized quadruples correction (suffix)
UGA	unitary group approach (method)
UHF	unrestricted Hartree−Fock (method)
virt	virtual orbital (chemical concept)
VOO	valence-orbital optimized (prefix)
VU	valence-universal (prefix)

REFERENCES

(1) Bartlett, R. J.; Musiał, M. *Rev. Mod. Phys.* **2007**, *79*, 291.
(2) Hubbard, J. *Proc. R. Soc. London A* **1957**, *240*, 539.
(3) Hubbard, J. *Proc. R. Soc. London A* **1958**, *243*, 336.
(4) Goldstone, J. *Proc. R. Soc. London A* **1957**, *239*, 267.
(5) Hugenholtz, N. M. *Physica* **1957**, *23*, 481.
(6) Primas, H. *Helv. Phys. Acta* **1961**, *34*, 331.
(7) Yaris, R.; Musher, J. I. *J. Chem. Phys.* **1964**, *41*, 1701.
(8) Yaris, R. *J. Chem. Phys.* **1964**, *41*, 2419.
(9) Paldus, J.; Čížek, J. *Adv. Quantum Chem.* **1975**, *9*, 105.
(10) Manne, R. *Int. J. Quantum Chem.* **1977**, *Y-11*, 175.
(11) Shavitt I.; Bartlett R. J. *Many-Body Methods in Chemistry and Physics*; Cambridge University Press: Cambridge, 2009. ISBN: 9780521818322.
(12) Coester, F. *Nucl. Phys.* **1958**, *1*, 421.
(13) Coester, F.; Kümmel, H. *Nucl. Phys.* **1960**, *17*, 477.
(14) Ursell, H. D. *Proc. Cambridge Philos. Soc.* **1927**, *23*, 685.
(15) Čížek, J. *J. Chem. Phys.* **1966**, *45*, 4256.
(16) Čížek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.
(17) Čížek, J.; Paldus, J. *Int. J. Quantum Chem.* **1971**, *5*, 359.
(18) Paldus, J.; Čížek, J.; Shavitt, I. *Phys. Rev. A* **1972**, *5*, 50.
(19) Bartlett, R. J.; Purvis, G. D., III *Int. J. Quantum Chem.* **1978**, *14*, 561.
(20) Bartlett, R. J.; Purvis, G. D., III *Phys. Scr.* **1980**, *21*, 225.

(21) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *S14*, 545.
(22) Sinanoğlu, O. *J. Chem. Phys.* **1962**, *36*, 706.
(23) Nesbet, R. K. *Adv. Chem. Phys.* **1969**, *14*, 1.
(24) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
(25) Lee, Y. S.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *81*, 5906.
(26) Noga, J.; Bartlett, R. J.; Urban, M. *Chem. Phys. Lett.* **1987**, *134*, 126.
(27) Kucharski, S. A.; Bartlett, R. J. *Theor. Chim. Acta* **1991**, *80*, 387.
(28) Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, *83*, 4041.
(29) Ragavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
(30) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.
(31) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.
(32) Adamowicz, L.; Laidig, W. D.; Bartlett, R. J. *Int. J. Quantum Chem.* **1984**, *18*, 245.
(33) Scuseria, G. E.; Sheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F., III *J. Chem. Phys.* **1987**, *86*, 2881.
(34) Salter, E. A.; Trucks, G. W.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 1752.
(35) Salter, E. A.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 1767.
(36) Gauss, J.; Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 2623.
(37) Koch, H.; Jensen, H.J.Aa.; Jørgensen, P.; Helgaker, T.; Scuseria, G. E.; Schaefer, H. F., III *J. Chem. Phys.* **1990**, *92*, 4924.
(38) Koch, H.; Jørgensen, P. *J. Chem. Phys.* **1990**, *93*, 3333.
(39) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029.
(40) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1995**, *103*, 8931.
(41) Rowe, D. J. *Rev. Mod. Phys.* **1968**, *40*, 153.
(42) Sekino, H.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1984**, *18*, 255.
(43) Geertsen, J.; Rittby, M.; Bartlett, R. J. *Chem. Phys. Lett.* **1989**, *164*, 57.
(44) Bartlett, R. J. In *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jørgensen, P., Simons, J., Eds.; Reidel: Dordrecht, 1986; Vol. 35.
(45) Perera, A. J.; Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *100*, 1425.
(46) Nakatsuji, H.; Hirao, K. *J. Chem. Phys.* **1978**, *68*, 2053.
(47) Nakatsuji, H. *Chem. Phys. Lett.* **1979**, *67*, 329.
(48) Meyer, W. *Theor. Chim. Acta* **1974**, *35*, 277.
(49) Nooijen, M.; Shamasundar, K. R.; Mukherjee, D. *Mol. Phys.* **2005**, *103*, 2277.
(50) Szalay, P. G. Configuration Interaction: Corrections for Size-Consistency. In *Encyclopedia of Computational Chemistry*; Wiley: New York, 2005. DOI: 10.1002/0470845015.cn0066.
(51) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.
(52) Mukhopadhyay, D.; Mukhopadhyay, S.; Chaudhuri, R.; Mukherjee, D. *Theor. Chim. Acta* **1991**, *80*, 441.
(53) Hirata, S. *Theor. Chem. Acc.* **2011**, *129*, 727.
(54) Kutzelnigg, W. *Theor. Chim. Acta* **1991**, *80*, 349.
(55) Koch, H.; Jensen, H. J. Aa.; Jørgensen, P.; Helgaker, T. *J. Chem. Phys.* **1990**, *93*, 3345.
(56) Brueckner, K. A. *Phys. Rev.* **1955**, *97*, 1353.
(57) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
(58) Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1474.
(59) Janssen, C. L.; Schaefer, H. F., III *Theor. Chim. Acta.* **1991**, *79*, 1.
(60) Neogrády, P.; Urban, M.; Hubac, I. *J. Chem. Phys.* **1994**, *100*, 3706.
(61) Bartlett, R. J. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific Publishing, 1995; Part II, pp 1047−1131.
(62) Szalay, P. G.; Gauss, J. *J. Chem. Phys.* **1997**, *107*, 9028.
(63) Szalay, P. G.; Gauss, J. *J. Chem. Phys.* **2000**, *112*, 4027.
(64) Heckert, M.; Heun, O.; Gauss, J.; Szalay, P. G. *J. Chem. Phys.* **2006**, *124*, 124105.
(65) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1996**, *104*, 2652.
(66) Adams, B. G.; Paldus, J. *Phys. Rev. A* **1979**, *20*, 1.
(67) Piecuch, P.; Paldus, J. *Int. J. Quantum Chem.* **1989**, *36*, 429.
(68) Jeziorski, B.; Paldus, J.; Jankowski, P. *Int. J. Quantum Chem.* **1995**, *56*, 129.
(69) Li, X.; Paldus, J. *J. Chem. Phys.* **1994**, *101*, 8812.
(70) Li, X.; Paldus, J. *J. Chem. Phys.* **1995**, *102*, 2013.
(71) Li, X.; Paldus, J. *J. Chem. Phys.* **1995**, *102*, 8059.
(72) Li, X.; Paldus, J. *J. Chem. Phys.* **1995**, *102*, 8897.
(73) Li, X.; Paldus, J. *Int. J. Quantum Chem.* **1998**, *70*, 65.
(74) Paldus, J.; Sarma, C. R. *J. Chem. Phys.* **1985**, *83*, 5135.
(75) Paldus, J. *J. Chem. Phys.* **1974**, *61*, 5321.
(76) Paldus, J. *Phys. Rev. A* **1976**, *14*, 1620.
(77) Datta, D.; Mukherjee, D. *Int. J. Quantum Chem.* **2008**, *108*, 2211.
(78) Datta, D.; Mukherjee, D. *J. Chem. Phys.* **2009**, *131*, 044124.
(79) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; Kucharski, S. A. In *Low-Lying Potential Energy Surfaces*; ACS Symposium Series 828; Hoffmann, M. R., Dyall, K. G., Eds.; American Chemical Society: Washington, DC, 2002.
(80) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2005**, *122*, 224102.
(81) Paldus, J.; Li, X. *Adv. Chem. Phys.* **1999**, *110*, 1.
(82) Lyakh, D. I.; Ivanov, V. V.; Adamowicz, L. *Mol. Phys.* **2007**, *105*, 1335.
(83) Bartlett, R. J. *Int. J. Mol. Sci.* **2002**, *3*, 579.
(84) Jeziorski, B.; Monkhorst, H. *J. Phys. Rev. A* **1981**, *24*, 1668.
(85) Lindgren, I.; Mukherjee, D. *Phys. Rep.* **1987**, *151*, 93.
(86) Lindgren, I. *Phys. Scr.* **1985**, *32*, 291.
(87) Lindgren, I. *Int. J. Quantum Chem. Symp.* **1978**, *12*, 33.
(88) Laidig, W. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1984**, *104*, 424.
(89) Laidig, W. D.; Saxe, P.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 887.
(90) Hanauer, M.; Köhn, A. *J. Chem. Phys.* **2011**, *134*, 204111.
(91) Banerjee, A.; Simons, J. *J. Chem. Phys.* **1982**, *76*, 4548.
(92) Nakatsuji, H. *J. Chem. Phys.* **1985**, *83*, 713.
(93) Balkova, A.; Kucharski, S. A.; Meissner, L.; Bartlett, R. J. *Theor. Chim. Acta* **1991**, *80*, 335.
(94) Kucharski, S. A.; Balkova, A.; Szalay, P. G.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 4289.
(95) Meissner, L.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *91*, 6187.
(96) Meissner, L.; Bartlett, R. J. *J. Chem. Phys.* **1990**, *92*, 561.
(97) Balkova, A.; Kucharski, S. A.; Meissner, L.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 4311.
(98) Mukhopadhyay, D., Jr.; Mukherjee, D. *Chem. Phys. Lett.* **1989**, *163*, 171.
(99) Mukhopadhyay, D., Jr.; Mukherjee, D. *Chem. Phys. Lett.* **1991**, *177*, 441.
(100) Paldus, J.; Piecuch, P.; Pylypow, L.; Jeziorski, B. *Phys. Rev. A* **1993**, *47*, 2738.
(101) Brandow, B. H. *Rev. Mod. Phys.* **1967**, *39*, 771.
(102) Mukherjee, D.; Moitra, R. K.; Mukhopadhyay, A. *Mol. Phys.* **1975**, *30*, 1861.
(103) Hose, G.; Kaldor, U. *J. Phys. B* **1979**, *12*, 3827.
(104) Kirtman, B. *J. Chem. Phys.* **1981**, *75*, 798.
(105) Bloch, C.; Horowitz *J. Nucl. Phys.* **1958**, *8*, 91.
(106) Durand, P. *Phys. Rev. A* **1983**, *28*, 3184.
(107) Paldus, J.; Li, X. *J. Chem. Phys.* **2003**, *118*, 6769.
(108) Evangelista, F. A.; Allen, W. D.; Schaefer, H. F., III *J. Chem. Phys.* **2006**, *125*, 154113.
(109) Piecuch, P.; Paldus, J. *Theor. Chim. Acta* **1992**, *83*, 69.
(110) Balkova, A.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 8972.
(111) Pal, S. *Phys. Rev. A* **1989**, *39*, 39.
(112) Shamasundar, K. R.; Pal, S. *J. Chem. Phys.* **2001**, *114*, 1981.
(113) Szalay, P. G. *Int. J. Quantum Chem.* **1995**, *55*, 151.
(114) Pittner, J.; Šmydke, J. *J. Chem. Phys.* **2007**, *127*, 114103.

(115) Schucan, T. H.; Weidenmüller, H. A. *Ann. Phys.* **1972**, *73*, 108.

(116) Malrieu, J.-P.; Durand, P.; Daudey, J.-P. *J. Phys. A: Math. Gen.* **1985**, *18*, 809.

(117) Kaldor, U. *Phys. Rev. A* **1988**, *38*, 6013.

(118) Jankowski, K.; Malinowski, P. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 1287.

(119) Paldus, J.; Li, X. *Collect. Czech. Chem. Commun.* **2004**, *69*, 90.

(120) Zarrabian, S.; Laidig, W. D.; Bartlett, R. J. *Phys. Rev. A* **1990**, *41*, 4711.

(121) Li, X.; Paldus, J. *J. Chem. Phys.* **2003**, *119*, 5320.

(122) Paldus, J.; Li, X.; Petraco, N. D. K. *J. Math. Chem.* **2004**, *35*, 215.

(123) Berkovic, S.; Kaldor, U. *Chem. Phys. Lett.* **1992**, *199*, 42.

(124) Berkovic, S.; Kaldor, U. *J. Chem. Phys.* **1993**, *98*, 3090.

(125) Li, X.; Paldus, J. *J. Chem. Phys.* **2003**, *119*, 5346.

(126) Li, X.; Paldus, J. *J. Chem. Phys.* **2004**, *120*, 5890.

(127) Li, X.; Paldus, J. *J. Chem. Phys.* **2009**, *131*, 114103.

(128) Li, X.; Paldus, J. *J. Chem. Phys.* **2010**, *133*, 184106.

(129) Li, X.; Paldus, J. *J. Chem. Phys.* **2006**, *124*, 034112.

(130) Balkova, A.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *193*, 364.

(131) Hubač, I.; Neogrády, P. *Phys. Rev. A* **1994**, *50*, 4558.

(132) Mášik, J.; Hubač, I. *Collect. Czech. Chem. Commun.* **1997**, *62*, 829.

(133) Mášik, J.; Hubač, I.; Mach, P. *J. Chem. Phys.* **1998**, *108*, 6571.

(134) Mahapatra, U. S.; Datta, B.; Mukherjee, D. *Mol. Phys.* **1998**, *94*, 157.

(135) Mahapatra, U. S.; Datta, B.; Mukherjee, D. *J. Chem. Phys.* **1999**, *110*, 6171.

(136) Mukhopadhyay, D.; Datta, B.; Mukherjee, D. *Chem. Phys. Lett.* **1992**, *197*, 236.

(137) Meissner, L. *Chem. Phys. Lett.* **1996**, *255*, 244.

(138) Landau, A.; Eliav, E.; Kaldor, U. *Chem. Phys. Lett.* **1999**, *313*, 399.

(139) Eliav, E.; Borschevsky, A.; Shamasundar, K. R.; Pal, S.; Kaldor, U. *Int. J. Quantum Chem.* **2009**, *109*, 2909.

(140) Pittner, J. *J. Chem. Phys.* **2003**, *118*, 10876.

(141) Kong, L. *Int. J. Quantum Chem.* **2008**, *109*, 441.

(142) Chattopadhyay, S.; Mahapatra, U. S.; Mukherjee, D. *J. Chem. Phys.* **1999**, *111*, 3820.

(143) Chattopadhyay, S.; Mahapatra, U. S.; Mukherjee, D. *J. Chem. Phys.* **2000**, *112*, 7939.

(144) Chattopadhyay, S.; Ghosh, P.; Mahapatra, U. S. *Phys. B* **2004**, *37*, 495.

(145) Hanrath, M. *J. Chem. Phys.* **2005**, *123*, 084102.

(146) Pittner, J.; Demel, O.; Čársky, P.; Hubač, I. *Int. J. Mol. Sci.* **2002**, *2*, 281.

(147) Hubač, I.; Wilson, S. *J. Phys. B* **2000**, *33*, 365.

(148) Hubač, I.; Pittner, J.; Čársky, P. *J. Chem. Phys.* **2000**, *112*, 8779.

(149) Pittner, J.; Šmydke, J.; Čársky, P.; Hubač, I. *J. Mol. Struct.: THEOCHEM* **2001**, *547*, 239.

(150) Demel, O.; Pittner, J. *J. Chem. Phys.* **2006**, *124*, 144112.

(151) Pittner, J.; Demel, O. *J. Chem. Phys.* **2005**, *122*, 181101.

(152) Demel, O.; Pittner, J. *J. Chem. Phys.* **2008**, *128*, 104108.

(153) Evangelista, F. A.; Allen, W. D.; Schaefer, H. F., III *J. Chem. Phys.* **2007**, *127*, 024102.

(154) Evangelista, F. A.; Simmonett, A. C.; Allen, W. D.; Schaefer, H. F., III; Gauss, J. *J. Chem. Phys.* **2008**, *128*, 124104.

(155) Prochnow, E.; Evangelista, F. A.; Schaefer, H. F., III; Allen, W. D.; Gauss, J. *J. Chem. Phys.* **2009**, *131*, 064109.

(156) Evangelista, F. A.; Prochnow, E.; Gauss, J.; Schaefer, H. F., III *J. Chem. Phys.* **2010**, *132*, 074107.

(157) Das, S.; Mukherjee, D.; Kallay, M. *J. Chem. Phys.* **2010**, *132*, 074103.

(158) Bhaskaran-Nair, K.; Demel, O.; Pittner, J. *J. Chem. Phys.* **2008**, *129*, 184105.

(159) Evangelista, F. A.; Gauss, J. *J. Chem. Phys.* **2010**, *133*, 044101.

(160) Chattopadhyay, S.; Pahari, D.; Mukherjee, D.; Mahapatra, U. S. *J. Chem. Phys.* **2004**, *120*, 5968.

(161) Oliphant, N.; Adamowicz, L. *J. Chem. Phys.* **1991**, *94*, 1229.

(162) Oliphant, N.; Adamowicz, L. *J. Chem. Phys.* **1992**, *96*, 3739.

(163) Piecuch, P.; Oliphant, N.; Adamowicz, L. *J. Chem. Phys.* **1993**, *99*, 1875.

(164) Piecuch, P.; Adamowicz, L. *J. Chem. Phys.* **1994**, *100*, 5792.

(165) Piecuch, P.; Adamowicz, L. *J. Chem. Phys.* **1995**, *102*, 898.

(166) Alexandrov, V.; Piecuch, P.; Adamowicz, L. *J. Chem. Phys.* **1995**, *102*, 3301.

(167) Piecuch, P.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1999**, *110*, 6103.

(168) Lyakh, D.I.; Ivanov, V. V.; Adamowicz, L. *J. Chem. Phys.* **2005**, *122*, 024108.

(169) Hanrath, M. *Chem. Phys. Lett.* **2006**, *420*, 426.

(170) Hanrath, M. *J. Chem. Phys.* **2008**, *128*, 154118.

(171) Engels-Putzka, A.; Hanrath, M. *J. Mol. Struct.: THEOCHEM* **2009**, *902*, 59.

(172) Hanrath, M. *Theor. Chem. Acc.* **2008**, *121*, 187.

(173) Malrieu, J.-P.; Daudey, J.-P.; Caballol, R. *J. Chem. Phys.* **1994**, *101*, 8908.

(174) Meller, J.; Malrieu, J.-P.; Caballol, R. *J. Chem. Phys.* **1996**, *104*, 4068.

(175) Adamowicz, L.; Malrieu, J.-P. *J. Chem. Phys.* **1996**, *105*, 9240.

(176) Daudey, J.-P.; Heully, J.-L.; Malrieu, J.-P. *J. Chem. Phys.* **1993**, *99*, 1240.

(177) Malrieu, J.-P.; Nebot-Gil, I.; Sanchez-Marin, J. *J. Chem. Phys.* **1994**, *100*, 1440.

(178) Nebot-Gil, I.; Sanchez-Marin, J.; Malrieu, J.-P.; Heully, J. L.; Maynau, D. *J. Chem. Phys.* **1995**, *103*, 2576.

(179) Meller, J.; Malrieu, J.-P.; Heully, J.-L. *Mol. Phys.* **2003**, *101*, 2029.

(180) Szalay, P. G.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *214*, 481.

(181) Szalay, P. G.; Bartlett, R. J. *J. Chem. Phys.* **1995**, *103*, 3600.

(182) Gdanitz, R. J.; Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413.

(183) Gdanitz, R. J. *Int. J. Quantum Chem.* **2001**, *85*, 281.

(184) Szalay, P. G. *Chem. Phys.* **2008**, *349*, 121.

(185) Ruttink, P. J. A.; Van Lenthe, J. H.; Zwaans, R.; Groenenboom, G. C. *J. Chem. Phys.* **1991**, *94*, 7212.

(186) Fulde, P.; Stoll, H. *J. Chem. Phys.* **1992**, *97*, 4185.

(187) Szalay, P. G.; Müller, T.; Gidofalvi, G.; Lischka, H.; Shepard, R. Multiconfiguration self-consistent field and multireference configuration interaction methods and applications. Submitted to *Chem. Rev.*

(188) Mukherjee, D.; Moitra, R. K.; Mukhopadhyay, A. *Mol. Phys.* **1977**, *33*, 955.

(189) Mukhopadhyay, A.; Moitra, R. K.; Mukherjee, D. *J. Phys. B: At. Mol. Phys.* **1979**, *12*, 1.

(190) Haque, M. A.; Mukherjee, D. *J. Chem. Phys.* **1984**, *80*, 5058.

(191) Haque, A.; Kaldor, U. *Chem. Phys. Lett.* **1985**, *117*, 347.

(192) Reitz, H.; Kutzelnigg, W. *Chem. Phys. Lett.* **1979**, *66*, 111.

(193) Offerman, R.; Ey, W.; Kümmel, H. *Nucl. Phys. A* **1976**, *273*, 349.

(194) Ey, W. *Nucl. Phys. A* **1978**, *296*, 189.

(195) Stanton, J. F.; Bartlett, R. J.; Magnus, C.; Rittby, L. *J. Chem. Phys.* **1992**, *97*, 5560.

(196) Rittby, C. M. L.; Bartlett, R. J. *Theor. Chim. Acta.* **1991**, *80*, 469.

(197) Hughes, S. R.; Kaldor, U. *Phys. Rev. A* **1993**, *47*, 4705.

(198) Jeziorski, B.; Paldus, J. *J. Chem. Phys.* **1989**, *90*, 2714.

(199) Pal, S.; Rittby, M.; Bartlett, R. J.; Sinha, D.; Mukherjee, D. *J. Chem. Phys.* **1988**, *88*, 4357.

(200) Pal, S.; Rittby, M.; Bartlett, R. J.; Sinha, D.; Mukherjee, D. *Chem. Phys. Lett.* **1987**, *137*, 273.

(201) Landau, A.; Eliav, E.; Ishikawa, Ya.; Kaldor, U. *J. Chem. Phys.* **2004**, *121*, 6634.

(202) Mukherjee, D. *Chem. Phys. Lett.* **1986**, *125*, 207.

(203) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2004**, *121*, 1670.

(204) Hughes, S. R.; Kaldor, U. *Chem. Phys. Lett.* **1993**, *204*, 339.

(205) Vaval, N.; Pal, S.; Mukherjee, D. *Theor. Chem. Acc.* **1998**, *99*, 100.

(206) Haque, A.; Kaldor, U. *Chem. Phys. Lett.* **1985**, *120*, 261.

(207) Hughes, S. R.; Kaldor, U. *Chem. Phys. Lett.* **1992**, *194*, 99.

(208) Ajitha, D.; Vaval, N.; Pal, S. *J. Chem. Phys.* **1999**, *110*, 2316.

(209) Ajitha, D.; Pal, S. *J. Chem. Phys.* **1999**, *111*, 3832.

(210) Shamasundar, K. R.; Asokan, S.; Pal, S. *J. Chem. Phys.* **2004**, *120*, 6381.

(211) Bag, A.; Manohar, P. U.; Vaval, N.; Pal, S. *J. Chem. Phys.* **2009**, *131*, 024102.

(212) Sajeev, Y.; Santra, R.; Pal, S. *J. Chem. Phys.* **2005**, *122*, 234320.

(213) Eliav, E.; Kaldor, U.; Hess, B. A. *J. Chem. Phys.* **1998**, *108*, 3409.

(214) Visscher, L.; Eliav, E.; Kaldor, U. *J. Chem. Phys.* **2001**, *115*, 9720.

(215) Kaldor, U. *Theor. Chim. Acta* **1991**, *80*, 427.

(216) Ben-Shlomo, S.; Kaldor, U. *J. Chem. Phys.* **1988**, *89*, 956.

(217) Bera, N.; Ghosh, S.; Mukherjee, D.; Chattopadhyay, S. *J. Phys. Chem A* **2005**, *109*, 11462.

(218) Sinha, D.; Mukhopadhyay, S. K.; Chaudhuri, R.; Mukherjee, D. *Chem. Phys. Lett.* **1989**, *154*, 544.

(219) Jankowski, K.; Malinowski, P. *J. Phys. B* **1994**, *27*, 1287.

(220) Chattopadhyay, S.; Mitra, A.; Sinha, D. *J. Chem. Phys.* **2006**, *125*, 244111.

(221) Meissner, L. *J. Chem. Phys.* **1998**, *108*, 9227.

(222) Musiał, M.; Meissner, L.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **2005**, *122*, 224110.

(223) Musiał, M.; Bartlett, R. J. *Chem. Phys. Lett.* **2008**, *457*, 267.

(224) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2008**, *129*, 044101.

(225) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2008**, *129*, 244111.

(226) Musiał, M. *Chem. Phys. Lett.* **2009**, *470*, 358.

(227) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2008**, *129*, 134105.

(228) Musiał, M.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **2003**, *118*, 1128.

(229) Figgen, D.; Wedig, A.; Stoll, H.; Dolg, M.; Eliav, E.; Kaldor, U. *J. Chem. Phys.* **2008**, *128*, 024106.

(230) Landau, A.; Eliav, E.; Ishikawa, Ya.; Kaldor, U. *J. Chem. Phys.* **2001**, *115*, 6862.

(231) Eliav, E.; Vilkas, M. J.; Ishikawa, Ya.; Kaldor, U. *J. Chem. Phys.* **2005**, *122*, 224113.

(232) Pershina, V.; Borschevsky, A.; Eliav, E.; Kaldor, U. *J. Chem. Phys.* **2008**, *128*, 024707.

(233) Landau, A.; Eliav, E.; Ishikawa, Ya.; Kaldor, U. *J. Chem. Phys.* **2000**, *113*, 9905.

(234) Yakobi, H.; Eliav, E.; Kaldor, U. *J. Chem. Phys.* **2011**, *134*, 054503.

(235) Meissner, L.; Bartlett, R. J. *J. Chem. Phys.* **1995**, *102*, 7490.

(236) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2011**, *134*, 034106.

(237) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *107*, 6812.

(238) Nooijen, M.; Lotrich, V. *J. Chem. Phys.* **2000**, *113*, 494.

(239) Tobita, M.; Perera, S. A.; Musiał, M.; Bartlett, R. J.; Nooijen, M.; Lee, J. S. *J. Chem. Phys.* **2003**, *119*, 10713.

(240) Hoffmann, M. R.; Simons, J. *J. Chem. Phys.* **1988**, *88*, 993.

(241) Hoffmann, M. R.; Simons, J. *Chem. Phys. Lett.* **1987**, *142*, 451.

(242) Ivanov, V. V.; Adamowicz, L. *J. Chem. Phys.* **2000**, *112*, 9258.

(243) Adamowicz, L.; Malrieu, J.-P.; Ivanov, V. V. *J. Chem. Phys.* **2000**, *112*, 10075.

(244) Ivanov, V. V.; Adamowicz, L. *J. Chem. Phys.* **2000**, *113*, 8503.

(245) Kallay, M.; Szalay, P. G.; Surjan, P. R. *J. Chem. Phys.* **2002**, *117*, 980.

(246) Ivanov, V. V.; Adamowicz, L.; Lyakh, D. I. *J. Chem. Phys.* **2006**, *124*, 184302.

(247) Lyakh, D. I.; Ivanov, V. V.; Adamowicz, L. *J. Chem. Phys.* **2008**, *128*, 074101.

(248) Ivanov, V. V.; Lyakh, D. I.; Adamowicz, L. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2355.

(249) Ivanov, V. V.; Adamowicz, L.; Lyakh, D. I. *Collect. Czech. Chem. Commun.* **2005**, *70*, 1017.

(250) Lyakh, D. I.; Ivanov, V. V.; Adamowicz, L. *Theor. Chem. Acc.* **2006**, *116*, 427.

(251) Ivanov, V. V.; Adamowicz, L.; Lyakh, D. I. *Int. J. Quantum Chem.* **2006**, *106*, 2875.

(252) Ivanov, V. V.; Adamowicz, L.; Lyakh, D. I. *J. Mol. Struct.: THEOCHEM* **2006**, *768*, 97.

(253) Klimenko, T. A.; Ivanov, V. V.; Lyakh, D. I.; Adamowicz, L. *Chem. Phys. Lett.* **2010**, *493*, 173.

(254) Kallay, M.; Gauss, J.; Szalay, P. G. *J. Chem. Phys.* **2003**, *119*, 2991.

(255) Kallay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 6841.

(256) Kallay, M.; Surjan, P. R. *J. Chem. Phys.* **2001**, *115*, 2945.

(257) Ivanov, V. V.; Lyakh, D. I. *Kharkiv University Bulletin: Chemical Issue* **2002**, *549*, 15 (in Russian; ISSN 2220-637X).

(258) Hanrath, M.; Engels-Putzka, A. *J. Chem. Phys.* **2010**, *133*, 064108.

(259) Engels-Putzka, A.; Hanrath, M. *J. Chem. Phys.* **2011**, *134*, 124106.

(260) Stolarczyk, L. Z. *Chem. Phys. Lett.* **1994**, *217*, 1.

(261) Kallay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *121*, 9257.

(262) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 8490.

(263) Ohtsuka, Y.; Piecuch, P.; Gour, J. R.; Ehara, M.; Nakatsuji, H. *J. Chem. Phys.* **2007**, *126*, 164111.

(264) Fan, P.-D.; Kamiya, M.; Hirata, S. *J. Chem. Theory Comput.* **2007**, *3*, 1036.

(265) Li, X.; Paldus, J. *J. Chem. Phys.* **2008**, *128*, 144118.

(266) Fang, T.; Li, Sh. *J. Chem. Phys.* **2007**, *127*, 204108.

(267) Fang, T.; Shen, J.; Li, Sh. *J. Chem. Phys.* **2008**, *128*, 224107.

(268) Shen, J.; Fang, T.; Li, Sh.; Jiang, Y. *J. Phys. Chem. A* **2008**, *112*, 12518.

(269) Xu, E.; Shen, J.; Kou, Zh.; Li, Sh. *J. Chem. Phys.* **2010**, *132*, 134110.

(270) Shen, J.; Xu, E.; Kou, Zh.; Li, Sh. *J. Chem. Phys.* **2010**, *132*, 114115.

(271) Amos, A. T.; Hall, G. G. *Proc. R. Soc. London A* **1961**, *263*, 483.

(272) King, H. F.; Stanton, R. E.; Kim, H.; Wyatt, R. E.; Parr, R. G. *J. Chem. Phys.* **1967**, *47*, 1936.

(273) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; McGuire, M. J. *Int. Rev. Phys. Chem.* **2002**, *21*, 527.

(274) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; Fan, P.-D.; Lodriguito, M.; McGuire, M. J.; Kucharski, S. A.; Kus, T.; Musiał, M. *Theor. Chem. Acc.* **2004**, *112*, 349.

(275) Arponen, J. S. *Ann. Phys.* **1983**, *151*, 311.

(276) Piecuch, P.; Włoch, M. *J. Chem. Phys.* **2005**, *123*, 224105.

(277) Ge, Y.; Gordon, M. S.; Piecuch, P. *J. Chem. Phys.* **2007**, *127*, 174106.

(278) Kowalski, K.; Krishnamoorthy, S.; Villa, O.; Hammond, J. R.; Govind, N. *J. Chem. Phys.* **2010**, *132*, 154103.

(279) Kowalski, K.; Piecuch, P. *J. Mol. Struct.: THEOCHEM* **2001**, *547*, 191.

(280) Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1998**, *108*, 5243.

(281) Taube, A. G.; Bartlett, R. J. *J. Chem. Phys.* **2008**, *128*, 044110.

(282) Taube, A. G.; Bartlett, R. J. *J. Chem. Phys.* **2008**, *128*, 044111.

(283) Arponen, J. S.; Bishop, R. F.; Pajanne, E. *Phys. Rev. A* **1987**, *36*, 2519.

(284) Van Voorhis, T.; Head-Gordon, M. *Chem. Phys. Lett.* **2000**, *330*, 585.

(285) Gwaltney, S. R.; Byrd, E. F. C.; Van Voorhis, T.; Head-Gordon, M. *Chem. Phys. Lett.* **2002**, *353*, 359.

(286) Fan, P.-D.; Kowalski, K.; Piecuch, P. *Mol. Phys.* **2005**, *103*, 2191.

(287) Szalay, P. G.; Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1995**, *103*, 281.

(288) Krylov, A. I.; Sherrill, C. D.; Byrd, E. F. C.; Head-Gordon, M. *J. Chem. Phys.* **1998**, *109*, 10669.

(289) Van Voorhis, T.; Head-Gordon, M. *J. Chem. Phys.* **2000**, *113*, 8873.

(290) Krylov, A. I.; Sherrill, C. D.; Head-Gordon, M. *J. Chem. Phys.* **2000**, *113*, 6509.

(291) Parkhill, J. A.; Head-Gordon, M. *J. Chem. Phys.* **2010**, *133*, 024103.

(292) Parkhill, J. A.; Head-Gordon, M. *J. Chem. Phys.* **2010**, *133*, 124102.

(293) Van Voorhis, T.; Head-Gordon, M. *Chem. Phys. Lett.* **2000**, *317*, 575.

(294) Van Voorhis, T.; Head-Gordon, M. *J. Chem. Phys.* **2001**, *115*, 7814.

(295) Van Voorhis, T.; Head-Gordon, M. *J. Chem. Phys.* **2002**, *117*, 9190.

(296) Li, X.; Paldus, J. *J. Chem. Phys.* **1997**, *107*, 6257.

(297) Li, X.; Paldus, J. *J. Chem. Phys.* **1998**, *108*, 637.

(298) Li, X.; Paldus, J. *Chem. Phys. Lett.* **1998**, *286*, 145.

(299) Li, X.; Paldus, J. *Mol. Phys.* **2000**, *98*, 1185.

(300) Li, X.; Paldus, J. *J. Chem. Phys.* **2000**, *113*, 9966.

(301) Li, X.; Paldus, J. *J. Chem. Phys.* **2006**, *124*, 174101.

(302) Li, X.; Peris, G.; Planelles, J.; Rajadall, F.; Paldus, J. *J. Chem. Phys.* **1997**, *107*, 90.

(303) Planelles, J.; Peris, G.; Paldus, J. *Int. J. Quantum Chem.* **2000**, *77*, 693.

(304) Paldus, J.; Li, X. *Collect. Czech. Chem. Commun.* **2003**, *68*, 554.

(305) Peris, G.; Planelles, J.; Paldus, J. *Int. J. Quantum Chem.* **1997**, *62*, 137.

(306) Li, X.; Paldus, J. *J. Chem. Phys.* **2008**, *129*, 054104.

(307) Li, X.; Paldus, J. *J. Theor. Comput. Chem.* **2008**, *7*, 805.

(308) Mukherjee, D.; Pal, S. *Adv. Quantum Chem.* **1989**, *20*, 291.

(309) Li, X.; Paldus, J. *J. Chem. Phys.* **2010**, *132*, 114103.

(310) Li, X.; Paldus, J. *J. Chem. Phys.* **2010**, *133*, 024102.

(311) Peris, G.; Planelles, J.; Malrieu, J.-P.; Paldus, J. *J. Chem. Phys.* **1999**, *110*, 11708.

(312) Li, X.; Paldus, J. *J. Chem. Phys.* **2003**, *119*, 5334.

(313) Kinoshita, T.; Hino, O.; Bartlett, R. J. *J. Chem. Phys.* **2005**, *123*, 074106.

(314) Hino, O.; Kinoshita, T.; Chan, G. K.-L.; Bartlett, R. J. *J. Chem. Phys.* **2006**, *124*, 114311.

(315) Lyakh, D. I.; Lotrich, V. F.; Bartlett, R. J. *Chem. Phys. Lett.* **2011**, *501*, 166.

(316) Lyakh, D. I.; Bartlett, R. J. Enhanced 'tailored' CCSD approach for scanning potential energy surfaces in ground and excited electronic states. Manuscript in preparation.

(317) Yanai, T.; Chan, G. K.-L. *J. Chem. Phys.* **2006**, *124*, 194106.

(318) Yanai, T.; Chan, G. K.-L. *J. Chem. Phys.* **2007**, *127*, 104107.

(319) Neuscamman, E.; Yanai, T.; Chan, G. K.-L. *J. Chem. Phys.* **2009**, *130*, 124102.

(320) Yanai, T.; Kurashige, Y.; Neuscamman, E.; Chan, G. K.-L. *J. Chem. Phys.* **2010**, *132*, 024105.

(321) Neuscamman, E.; Yanai, T.; Chan, G. K.-L. *J. Chem. Phys.* **2010**, *132*, 024106.

(322) Musiał, M.; Perera, A.; Bartlett, R. J. *J. Chem. Phys.* **2011**, *134*, 114108.

(323) Musiał, M.; Perera, S. A.; Bartlett, R. J. Calculation of potential energy curves with the MR-DI-CC method. Manuscript in preparation.

(324) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033.

(325) Stanton, J. F.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 5554.

(326) Krylov, A. I. *Chem. Phys. Lett.* **2001**, *338*, 375.

(327) Krylov, A. I.; Sherrill, C. D. *J. Chem. Phys.* **2002**, *116*, 3194.

(328) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2003**, *118*, 6874.

(329) Levchenko, S. V.; Krylov, A. I. *J. Chem. Phys.* **2004**, *120*, 175.

(330) Levchenko, S. V.; Wang, T.; Krylov, A. I. *J. Chem. Phys.* **2005**, *122*, 224106.

(331) Casanova, D.; Slipchenko, L. V.; Krylov, A. I.; Head-Gordon, M. *J. Chem. Phys.* **2009**, *130*, 044103.

(332) Krylov, A. I. *Annu. Rev. Phys. Chem.* **2008**, *59*, 433.

(333) Demel, O.; Shamasundar, K. R.; Kong, L.; Nooijen, M. *J. Phys. Chem. A* **2008**, *112*, 11895.

(334) Kong, L.; Shamasundar, K. R.; Demel, O.; Nooijen, M. *J. Chem. Phys.* **2009**, *130*, 114101.

(335) Buenker, R. J.; Peyerimhoff, S. D.; Butscher, W. *Mol. Phys.* **1978**, *35*, 771.

(336) Hanrath, M.; Engels, B. *Chem. Phys.* **1997**, *225*, 197.

(337) Bender, C. F.; Davidson, E. R. *Phys. Rev.* **1969**, *183*, 23.

(338) Pople, J. A. *Rev. Mod. Phys.* **1999**, *71*, 1267.

(339) Harrison, R. J.; Fann, G. I.; Yanai, T.; Gan, Z.; Beylkin, G. *J. Chem. Phys.* **2004**, *121*, 11587.

(340) Fann, G. I.; Harrison, R. J.; Beylkin, G.; Jia, J.; Hartman-Baker, R.; Shelton, W. A.; Sugiki, S. *J. Phys.: Conf. Ser.* **2007**, *78*, 012018.

(341) Pipek, J.; Nagy, S. *J. Chem. Phys.* **2005**, *123*, 144107.

(342) Bischoff, F. A.; Valeev, E. F. *J. Chem. Phys.* **2011**, *134*, 104104.

(343) Nakatsuji, H. *Chem. Phys. Lett.* **1991**, *177*, 331.

(344) Nakatsuji, H. *J. Chem. Phys.* **1991**, *94*, 6716.

(345) Ohtsuka, Y.; Hasegawa, J.; Nakatsuji, H. *Chem. Phys.* **2007**, *332*, 262.

(346) Ishida, M.; Toyota, K.; Ehara, M.; Frisch, M. J.; Nakatsuji, H. *J. Chem. Phys.* **2004**, *120*, 2593.

(347) Nakatsuji, H. *J. Chem. Phys.* **1985**, *83*, 5743.

(348) Nakatsuji, H. *J. Chem. Phys.* **1991**, *95*, 4296.

(349) Nakatsuji, H.; Ehara, M. *J. Chem. Phys.* **2005**, *122*, 194108.

(350) Nakatsuji, H. *J. Chem. Phys.* **2000**, *113*, 2949.

(351) Győrffy, W.; Bartlett, R. J.; Greer, J. *J. Chem. Phys.* **2008**, *129*, 064103.

(352) Booth, G. H.; Thom, A. J. W.; Alavi, A. *J. Chem. Phys.* **2009**, *131*, 054106.

(353) Cleland, D.; Booth, G. H.; Alavi, A. *J. Chem. Phys.* **2010**, *132*, 041103.

(354) Booth, G. H.; Alavi, A. *J. Chem. Phys.* **2010**, *132*, 174104.

(355) Chan, G. K.-L.; Head-Gordon, M. *J. Chem. Phys.* **2002**, *116*, 4462.

(356) Dorando, J. J.; Hachmann, J.; Chan, G. K.-L. *J. Chem. Phys.* **2007**, *127*, 084109.

(357) Zgid, D.; Nooijen, M. *J. Chem. Phys.* **2008**, *128*, 014107.

(358) Chan, G.K.-L.; Kallay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *121*, 6110.

(359) Lyakh, D. I.; Bartlett, R. J. *J. Chem. Phys.* **2010**, *133*, 244112.

(360) Li, X.; Paldus, J. *J. Chem. Phys.* **1995**, *103*, 1024.

(361) Jankowski, K.; Paldus, J. *Int. J. Quantum Chem.* **1980**, *18*, 1243.

(362) Meissner, L.; Jankowski, K.; Wasilewski, J. *Int. J. Quantum Chem.* **1988**, *34*, 535.

(363) Purvis, G. D.; Shepard, R.; Brown, F. B.; Bartlett, R. J. *Int. J. Quantum Chem.* **1983**, *23*, 835.

(364) Čársky, P.; Bartlett, R. J.; Fitzgerald, G.; Noga, J.; Špirko, V. *J. Chem. Phys.* **1988**, *89*, 3008.

(365) Eckert-Maksic, M.; Vazdar, M.; Barbatti, M.; Lischka, H.; Maksic, Z. B. *J. Chem. Phys.* **2006**, *125*, 064310.

(366) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 6473.

(367) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Taylor, P. R.; Handy, N. C.; Knowles, P. J. *J. Chem. Phys.* **1986**, *85*, 1469.

(368) Mahapatra, U. S.; Chattopadhyay, S.; Chaudhuri, R. K. *J. Chem. Phys.* **2009**, *130*, 014101.

(369) Bauschlicher, C. W.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 5600.

(370) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1998**, *108*, 2511.

(371) Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1999**, *110*, 8233.

(372) Sherrill, C. D.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 124104.

(373) Christiansen, O.; Koch, H.; Jørgensen, P. *Chem. Phys. Lett.* **1995**, *243*, 409.

(374) Christiansen, O.; Koch, H.; Jørgensen, P. *J. Chem. Phys.* **1995**, *103*, 7249.

(375) Abrams, M. L.; Sherrill, C. D. *J. Chem. Phys.* **2004**, *121*, 9211.

(376) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2011**, *135*, 044121.

(377) Hirata, S. *J. Phys. Chem. A* **2003**, *107*, 9887.

(378) Shiozaki, T.; Kamiya, M.; Hirata, S.; Valeev, E. F. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3358.

(379) Lyakh, D. I.; Bartlett, R. J. Proceedings of the 50th Sanibel Symposium, St. Simon's Island, GA, Feb 24−Mar 2, 2010.

(380) Barbe, A.; Secroun, C.; Jouve, P. *J. Mol. Spectrosc.* **1974**, *49*, 171.

(381) Tanaka, T.; Morino, Y. *J. Mol. Spectrosc.* **1970**, *33*, 538.

(382) Manohar, P. U.; Krylov, A. I. *J. Chem. Phys.* **2008**, *129*, 194105.

(383) Leopold, D. G.; Miller, A. E. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1379.

(384) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279.

(385) Lotrich, V.; Flocke, N.; Ponton, M.; Yau, A.; Perera, A.; Deumens, E.; Bartlett, R. J. *J. Chem. Phys.* **2008**, *128*, 194104.

(386) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(387) Ivanic, J. *J. Chem. Phys.* **2003**, *119*, 9364.

(388) Kong, L. *Int. J. Quantum Chem.* **2010**, *110*, 2603.

(389) Evangelista, F. A.; Gauss, J. *J. Chem. Phys.* **2011**, *134*, 114102.

(390) Jana, D.; Datta, D.; Mukherjee, D. *Chem. Phys.* **2006**, *329*, 290.

(391) Mahapatra, U. S.; Datta, B.; Bandyopadhyay, D.; Mukherjee, D. *Adv. Quantum Chem.* **1998**, *30*, 163.

(392) Mukherjee, D. *Chem. Phys. Lett.* **1997**, *274*, 561.

(393) Kutzelnigg, W.; Mukherjee, D. *J. Chem. Phys.* **1997**, *107*, 432.

(394) Kong, L.; Nooijen, M.; Mukherjee, D. *J. Chem. Phys.* **2010**, *132*, 234107.

(395) Datta, D.; Kong, L.; Nooijen, M. *J. Chem. Phys.* **2011**, *134*, 214116.

(396) Kubo, R. *J. Phys. Soc. Jpn.* **1962**, *17*, 1100.

(397) Lyakh, D. I.; Bartlett, R. J. "Size-extensivity in molecular electronic structure: An algebraic formulation in the ε-approximation" was submitted to *Mol. Phys*. After revision, the manuscript will be split into two parts: "Algebraic connectivity analysis in molecular electronic structure theory, parts I/II".

(398) Hanrath, M. *Chem. Phys.* **2009**, *356*, 31.

(399) Chaudhuri, R.; Sinha, D.; Mukherjee, D. *Chem. Phys. Lett.* **1989**, *163*, 165.

(400) Mahapatra, U. S.; Chattopadhyay, S. *J. Chem. Phys.* **2010**, *133*, 074102.

(401) Mahapatra, U. S.; Chattopadhyay, S. *J. Chem. Phys.* **2011**, *134*, 044113.

(402) Das, S.; Datta, D.; Maitra, R.; Mukherjee, D. *Chem. Phys.* **2008**, *349*, 115.

(403) Datta, D.; Mukherjee, D. *J. Chem. Phys.* **2011**, *134*, 054122.

(404) Bhaskaran-Nair, K.; Demel, O.; Pittner, J. *J. Chem. Phys.* **2010**, *132*, 154105.

(405) Demel, O.; Bhaskaran-Nair, K.; Pittner, J. *J. Chem. Phys.* **2010**, *133*, 134106.

(406) Bhaskaran-Nair, K.; Demel, O.; Šmydke, J.; Pittner, J. *J. Chem. Phys.* **2011**, *134*, 154106.

(407) Li, X; Paldus, J. *J. Chem. Phys.* **2011**, *134*, 214118.

(408) Li, X; Paldus, J. *Chem. Phys. Lett.* **2010**, *496*, 183.

(409) Evangelista, F. A. *J. Chem. Phys.* **2011**, *134*, 224102.

(410) Schreiner, P. R.; Reisenauer, H. P.; Ley, D.; Gerbig, D.; Wu, C.-H.; Allen, W. D. *Science* **2011**, *332*, 1300.

(411) Hoffmann, M. R.; Khait, Yu.G. *Chem. Phys. Lett.* **1999**, *311*, 372.

(412) Lindgren, I. *J. Phys. B: At. Mol. Phys.* **1974**, *7*, 2441.

(413) Mukherjee, D. *Int. J. Quantum Chem. Symp.* **1986**, *30* (S20), 409.

(414) Koch, S. *Theor. Chim. Acta* **1991**, *81*, 169.

(415) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 18.

(416) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 5644.

(417) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2001**, *115*, 643.

(418) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2001**, *115*, 2966.

(419) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2002**, *116*, 7411.

(420) McGuire, M. J.; Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2002**, *117*, 3617.

(421) Pimienta, I. S. O.; Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2003**, *119*, 2951.

(422) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 074107.

(423) Włoch, M.; Gour, J. R.; Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 214107.

(424) Stanton, J. F. *J. Chem. Phys.* **1993**, *99*, 8840.

(425) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *106*, 6441.

(426) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *106*, 6449.

(427) Gwaltney, S. R.; Bartlett, R. J.; Nooijen, M. *J. Chem. Phys.* **1999**, *111*, 58.

(428) Das, S.; Kallay, M.; Mukherjee, D. *J. Chem. Phys.* **2010**, *133*, 234110.

(429) Li, X.; Paldus, J. *J. Chem. Phys.* **2011**, *134*, 074301.

(430) Crawford, T. D.; Stanton, J. F. *Int. J. Quantum Chem.* **1998**, *70*, 601.

(431) Stanton, J. F. *Chem. Phys. Lett.* **1997**, *281*, 130.

(432) Small, D. W.; Head-Gordon, M. *J. Chem. Phys.* **2009**, *130*, 084103.

(433) Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 8227.

(434) Olsen, J. *J. Chem. Phys.* **2000**, *113*, 7140.

(435) Köhn, A.; Olsen, J. *J. Chem. Phys.* **2006**, *125*, 174110.

(436) Köhn, A.; Olsen, J. *J. Chem. Phys.* **2005**, *122*, 084116.

(437) Auer, A. A.; Nooijen, M. *J. Chem. Phys.* **2006**, *125*, 024104.

(438) Primas, H. *Modern Quantum Chemistry: Istanbul Lectures*; Šinanoğlu, O., Ed.; Academic Press: New York, 1965.

(439) Nakatsuji, H. *Chem. Phys. Lett.* **1978**, *59*, 362.

(440) Nakatsuji, H. *Chem. Phys. Lett.* **1979**, *67*, 334.

(441) Monkhorst, H. *Int. J. Quantum Chem. Symp.* **1977**, *11*, 421.

(442) Mukherjee, D.; Mukherjee, P. K. *Chem. Phys.* **1979**, *39*, 325.

(443) Pahari, D.; Chattopadhyay, S.; Das, S.; Mukherjee, D. *Chem. Phys. Lett.* **2003**, *381*, 223.

(444) Stolarczyk, L. Z.; Monkhorst, H. *J. Int. J. Quantum Chem. Symp.* **1984**, *18*, 267.

(445) Stolarczyk, L. Z.; Monkhorst, H. *J. Phys. Rev. A* **1985**, *32*, 725.

(446) Stolarczyk, L. Z.; Monkhorst, H. *J. Phys. Rev. A* **1985**, *32*, 743.

(447) Stolarczyk, L. Z.; Monkhorst, H. *J. Phys. Rev. A* **1988**, *37*, 1908.

(448) Stolarczyk, L. Z.; Monkhorst, H. *J. Phys. Rev. A* **1988**, *37*, 1926.

(449) Stolarczyk, L. Z.; Monkhorst, H. *J. Mol. Phys.* **2010**, *108*, 3067.

(450) Harris, F. E. *Int. J. Quantum Chem.* **2002**, *90*, 105.

(451) Kutzelnigg, W.; Mukherjee, D.; Koch, S. *J. Chem. Phys.* **1987**, *87*, 5902.

(452) Mukherjee, D.; Kutzelnigg, W.; Koch, S. *J. Chem. Phys.* **1987**, *87*, 5911.

(453) Kutzelnigg, W.; Mukherjee, D. *J. Chem. Phys.* **1999**, *110*, 2800.

(454) Korona, T. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5698.

(455) Korona, T.; Jeziorski, B. *J. Chem. Phys.* **2006**, *125*, 184109.

(456) Korona, T. *Theor. Chem. Acc.* **2011**, *129*, 15.

(457) Thom, A. J. W. *Phys. Rev. Lett.* **2010**, *105*, 263004.

(458) Nooijen, M. *Spectrochim. Acta A* **1999**, *55*, 539.

(459) Barysz, M; Rittby, M.; Bartlett, R. *J. Chem. Phys. Lett.* **1992**, *193*, 373.

(460) Barysz, M. *Theor. Chim. Acta* **1995**, *90*, 257.