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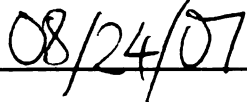
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SINGLE-REFERENCE COUPLED-CLUSTER METHODS
EMPLOYING MULTI-REFERENCE PERTURBATION THEORY

By

Maricris D. Lodriguito

A DISSERTATION

Submitted to
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ABSTRACT

SINGLE-REFERENCE COUPLED-CLUSTER METHODS EMPLOYING MULTIREFERENCE PERTURBATION THEORY

By

Maricris D. Lodriguito

A new class of noniterative coupled cluster (CC) methods, which improve the results of standard CC and equation-of-motion (EOM) CC calculations for ground and excited-state potential energy surfaces along bond breaking coordinates and for excited states dominated by two-electron transitions, is explored. The proposed approaches combine the method of moments of coupled-cluster equations (MMCC), in which the *a posteriori* corrections due to higher-order correlations are added to standard CC/EOMCC energies, with the multi-reference many-body perturbation theory (MRMBPT), which provides information about the most essential nondynamical and dynamical correlation effects that are relevant to electronic quasi-degeneracies. The newly developed variant of the MMCC theory, termed MRMBPT-corrected MMCC (MMCC/PT), is formulated using diagrammatic methods. The performance of the basic MMCC/PT approximations, in which inexpensive corrections due to triples (MMCC(2,3)/PT) or triples and quadruples (MMCC(2,4)/PT) are added to ground- and excited-state energies obtained with the CC/EOMCC singles and doubles (CCSD/EOMCCSD) approach, is illustrated by the results of benchmark calculations including bond breaking in HF, H₂O, and F₂, and excited states of CH⁺. Test calculations reveal that the MMCC(2,3)/PT and MMCC(2,4)/PT approaches provide an accurate description of bond breaking and excited states dominated by doubles, eliminating the failures of the conventional CC/EOMCC methods at larger

internuclear distances and for excited states dominated by two-electron transitions without invoking expensive steps of high-order CC/EOMCC methods. The efficient, general-purpose, highly vectorized implementations of the triply and quadruply excited moments of the CCSD/EOMCCSD equations, relevant to the MMCC(2,3)/PT and MMCC(2,4)/PT approaches, are discussed and the details of the algorithm are also presented.

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1 Introduction

Not long after the discovery of Schrödinger's equation¹ in 1926, one of the pioneers of quantum mechanics, Dirac, made a widely publicized statement that "the underlying physical laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble".² Because of this statement, chemists at that time were skeptical about the prospects of quantum theory as a way to study molecular properties. However, what has not been publicized as broadly, in the same paper Dirac also wrote that "it therefore becomes desirable that the approximate practical methods should be developed, which can lead to an explanation of the main features of complex atomic system without too much computation".² Inspired by this less known remark and despite the early reluctance of the chemical community, the field of quantum chemistry has undergone revolutionary advances brought about in part by the advent of computers and in part by much improved understanding of many-electron systems, particularly in recent four decades. The tremendous improvements in accuracy and predictive power of electronic structure methods and significant advances in the fundamental understanding of many-electron wavefunctions, which continues to improve every year, have paved the way to widespread applicability of quantum-chemical methods in solving increasingly complex chemical problems surpassing what was originally expected in late 1920's by a wide margin. Furthermore, because of its rigorous and predictive nature, quantum chemistry has become a powerful, important tool not only for theorists

but also for experimentalists, while inspiring similar developments in computational nuclear physics, biochemistry, molecular biology, and materials science, among others.

Nowadays, highly accurate *ab initio* (meaning from “first principles”) quantum mechanical calculations for small and medium size molecular systems, with up to 20-30 light atoms, a few transition metal atoms and about 100 explicitly correlated electrons, are routine. Theoretical calculations of the energetics and other molecular properties of smaller molecules can often rival those obtained experimentally.

The above successes of quantum chemistry do not mean that there are no open or challenging problems in modern electronic structure theory. Indeed, it is well known and as further elaborated on below, the key to a successful description of chemical systems is an accurate assessment of many-electron correlation effects. Electrons in molecules move in a complicated, highly correlated fashion and one cannot describe molecular properties by using a simple mean-field description which ignores electron correlation effects, particularly in cases involving bond breaking and excited electronic states. The least expensive ways of accurately accounting for electron correlation effects have computational steps that typically scale as $\mathcal{N}^6 - \mathcal{N}^7$ with the system size $\mathcal{N}$ and this limits the applicability of correlated methods to systems with about 100 correlated electrons (defined as electrons outside the frozen core). Thus, one of the challenges of modern quantum chemistry is to go to systems with hundreds or thousands of correlated electrons and basis functions. Another challenge is an accurate treatment of bond breaking (reaction pathways) and excited states, particularly those dominated by many-electron transitions, i.e. problems where a traditional description in which one starts from a single Slater determinant and builds the electronic wave-

functions on top of a single determinant through particle-hole excitations, and which works for non-degenerate states of closed-shell molecules, is no longer adequate. This thesis work addresses the latter challenge.

Considering the nature of this thesis research, which focuses on the development of accurate new methods to describe many-electron correlation effects in cases involving bond breaking and excited states, in this chapter, we outline some of the most popular electron correlation methods developed over the recent years. We begin by describing the exact solution to the Schrödinger equation in a basis set. Then, we present the various wavefunction-based approximations to solving electronic Schrödinger equation including correlation, presenting the advantages and disadvantages of each approach in terms of accuracy of the predicted energies and the computational cost requirements.

The conceptually most straightforward method of obtaining the exact solution to the electronic Schrödinger equation, within a given one-electron basis set, is the full configuration interaction (full CI) approach, which solves the Hamiltonian eigenvalue problem by including all possible Slater determinants (antisymmetrized products of one-electron wavefunctions, i.e. spin-orbitals) of the appropriate symmetry which can be formed from the given one-electron basis set. Examples of full CI calculations at a few representative geometries along potential energy curves of small, few electron molecules can be found in Refs. 3–7. Advances in algorithms and computer hardware have made it feasible to obtain full CI potential energy curves^{8–27} for several few-electron systems. There has been interest in implementing parallel full CI algorithms on massive parallel architectures and clusters.^{28–32} The largest full CI calculation

performed to date has been reported by Gan and co-workers for the C_2 molecule using the aug-cc-pVTZ basis set without the augmented diffuse d and f functions, which required about 65 billion Slater determinants.³³ This impressive calculation has only been made possible by employing highly efficient parallel and vector full CI implementation as well as the dedicated availability of massive supercomputing resources.

Indeed, there is a major problem with full CI. The factorial growth of the required number of determinants that defines the dimension of the Hamiltonian eigenvalue problem with the number of electrons and basis functions makes full CI calculations feasible only for small molecules, with up to ~ 10 correlated electrons and with modest basis sets. This critical drawback can be illustrated by the following example: a small system with six correlated electrons and 100 orbitals in a basis requires $\sim 10^9$ configuration state functions (spin-adapted combinations of Slater determinants). An increase of the system size to 12 correlated electrons employing 100 orbitals in a basis set already would require $\sim 10^{17}$ configuration state functions. This is beyond the capabilities of present-day computers, and is likely to remain so in many years to come. Hence, there is a need for alternative, affordable, approximate and yet accurate approaches in order to study the majority of chemical problems of interest. Nevertheless, the full CI method, providing exact solutions in a basis set, is invaluable in benchmarking approximate quantum chemical methods, helping the development work, including the development work described in this thesis.

The simplest approach to solving the electronic Schrödinger equation is the Hartree–Fock (H–F) approach which approximates the electronic wavefunction by a single

Slater determinant. The H-F method is a mean field theory;³⁴⁻³⁷ motion of an electron in a molecule is defined by the effective one-electron Hamiltonian (Fock operator) which describes the average field (Coulomb and exchange terms) created by the remaining electrons in the system. The H-F theory can account for about 99% of the total electronic energy. Unfortunately, it is the remaining 1% that is very important in describing chemical phenomena, such as the breaking of chemical bonds, electronic excitations in molecules, response and spectroscopic molecular properties, weak intermolecular interactions, etc. Such situations cannot be properly accounted for by H-F theory because of the neglect of the many-electron correlation effects in the theory. This necessitates going beyond the H-F theory and using more sophisticated and computationally more demanding techniques, to reach a reasonable description of molecular systems. In other words, an accurate description of molecular systems requires a precise determination of many-electron correlation effects.

At this point, it is worth introducing the term "correlation energy" which is formally defined as the difference between the exact energy, defined in this work as the full CI energy, and the corresponding H-F energy, calculated in the same basis set. The true correlation energy would require a calculation in the infinite basis set. The infinite basis set limit can be approached by performing a sequence of calculations with basis sets of increasing size. In the development work, one does not have to study the infinite basis set limit to learn about the performance of new methods. The performance of new methods in finite basis set calculations and comparisons with full CI in the same basis sets are enough to make judgements about the usefulness of the newly proposed approaches.

There are two types of electron correlation: dynamical and nondynamical (static). Dynamical correlations can be regarded as short-range correlations due to electrons instantaneously avoiding each other, particularly when they come close to each other. On the other hand, nondynamical correlations can be treated as long-range correlations which arise from the multiconfigurational character of the systems having quasi(near)-degenerate states, as in the case of electrons constituting an electron pair, which are separated during the bond breaking process, biradicals, and the majority of excited states. A well-balanced account of both dynamical and nondynamical electron correlation is important to obtain a uniformly accurate description of reactants, products, reaction intermediates, and transition states as well as the precise description of electronic excitations in molecules.

There has been tremendous progress in the development of electron correlation methods in the recent history. Here, we primarily focus on the wavefunction-based approaches which can be divided into three main categories: (1) configuration interaction (CI) approaches;^{38–41} (2) many-body perturbation theory (MBPT);^{42–46} and (3) coupled-cluster (CC) methods.^{47–51} The electron correlation methods can also be classified as single-reference and multi-reference methods. Single-reference electron-correlation methods, from the name itself, are defined by building a correlated wavefunction through electronic excitations out of a single Slater determinant (e.g., a H-F determinant). Multi-reference (MR) methods, on the other hand, utilize the multi-determinantal reference wavefunction to build the desired correlated electronic state or states. The single-reference based methods are presented first.

Of all single-reference methods, the CI approach is conceptually (but not compu-

tationally) the simplest. The CI wavefunctions are represented as linear combinations of Slater determinants obtained by promoting or exciting electrons from occupied to unoccupied orbitals, and the corresponding expansion coefficients are obtained variationally by diagonalizing the Hamiltonian matrix. One of the advantages of CI methods is the ease of access to excited states and molecular properties other than energy, which can be calculated as expectation values or transition matrix elements involving the relevant CI states, and the fact that CI energies are always the upper bounds to the corresponding exact energies. The disadvantages of CI methods include enormous computer costs, if one is aiming at high accuracy, and lack of size extensivity of the truncated CI approaches, which basically means that the resulting energy of a system does not scale correctly with the system size and a loss of accuracy occurs as the system becomes bigger. The basic CI technique, designated as CISD, which includes all singly- and doubly-excited configurations from a H-F reference, typically recovers $\sim 90\%$ of the correlation energy for small, few electron problem, as long as the H-F determinant dominates the wavefunction.⁵² By including all triple and quadruple excitations from the reference (CISDTQ), it is possible to recover nearly all of the remaining $\sim 10\%$.⁵² Furthermore, while the CISD method is inaccurate for excited states and for systems away from the equilibrium geometry, the CISDTQ wavefunction recovers almost all of the correlation energy, even in those challenging situations, as long as the number of correlated electrons is not too large,⁵³ since CISDTQ, as any other truncated CI approach, is not size extensive. The CISDTQ method is a high accuracy approach for smaller molecular problems, but, unfortunately, the cost associated with a CISDTQ computation is usually prohibitively expensive due to the

large numbers of triply and quadruply excited determinants. The CPU operational count associated with a single iteration of the CISDTQ calculation is $n_o^4 n_u^6$, where $n_o(n_u)$ is the number of occupied (unoccupied) orbitals in a basis set that are included in correlated calculations. This is more or less equivalent to the $\mathcal{N}^{10}$ scaling of the CPU time with the system size $\mathcal{N}$.

The second type of approach to the many-electron correlation problem, referred to as MBPT, uses the Rayleigh-Schrödinger or some other perturbation theory to describe correlation effects. The MBPT methods offer the following advantages: (i) unlike the truncated CI approaches, the MBPT formulations based on Rayleigh-Schrödinger perturbation theory provide size extensive results, i.e. no loss of accuracy occurs as the system size increases, (ii) low-order MBPT methods are inexpensive while offering reliable information about the most essential correlation effects. However, MBPT methods are non-variational and the MBPT series do not always converge, particularly when bond breaking is examined. Furthermore, standard MBPT methods do not apply to excited states, although one can address this problem by switching to multi-reference MBPT schemes as mentioned below.

The simplest and most economical MBPT method for including electron correlation is the second-order Møller-Plesset (or many-body) perturbation theory (MP2)⁴² which typically accounts for $\sim 80\%$ of the correlation energy when the H-F reference determinant dominates the wavefunction. Although, this will generally not take us to chemical accuracy, several molecular properties, including geometries and vibrational frequencies, are reasonably well described by MP2. In general, MP2 energy calculation requires noniterative steps that scale as $n_o^2 n_u^2$. Essentially, one can af-

ford such calculations for any system for which one can afford the H-F calculation (systems with hundreds of correlated electrons). The extension of MP2 to the fourth-order (MP4)⁵⁴ improves the electron correlation description and accounts for about 95-98% of the correlation energy in non-degenerate closed-shell cases, while requiring noniterative steps that scale as $n_o^3 n_v^4$. The higher-order MP5 and MP6⁵⁵⁻⁵⁸ theories have been pursued as well in spite of the vast increase in the number of terms involved. It is reasonable to infer that going to higher orders of MBPT should give more accurate results. However, in the work of Olsen *et al.*,⁵⁹ the authors found out that going to higher-order MBPT for many-electron systems in extended basis sets did not guarantee convergence, even for cases of trivial wavefunctions dominated by a single-reference determinant which are generally assumed to produce convergent MBPT series.^{60,61} The MBPT expansions are always strongly divergent in cases involving bond breaking, as shown, for example, by Piecuch *et al.*⁶²

The third type of wavefunction-based electron correlation methods is coupled-cluster (CC) theory, which is based on the exponential ansatz for the ground-state wavefunction, allowing CC approaches to describe high-order correlation effects at the low level approximation by generating the higher-order excitations in the wavefunctions as products of low-order excitations. Of all approaches to the many-electron correlation problem, the single-reference CC⁴⁷⁻⁵¹ methods, in which the H-F wavefunction is usually chosen as the reference state, are generally considered as the best compromise between high accuracy and relatively low computer cost. Another notable characteristic of CC theory is its ability to preserve size extensivity at any level of truncation. These and other attractive features of the CC theory have inspired

and continue to inspire significant research work on developing high accuracy methods which can be used as general-purpose tools by experts and non-experts (see Refs. 21, 25, 26, 54, 63–70 for selected reviews) and this thesis research is a contribution to this area.

In the above description, we have focused on single-reference theories, which implicitly assume that a single Slater determinant (e.g., a H-F determinant) dominates the electronic wavefunction so that one can recover the remaining part of the wavefunction through excitations of electrons to unoccupied spin-orbitals. Because of this underlying assumption, single-reference methods have the applicability which is essentially limited to non-degenerate ground states of closed- and simple open-shell molecules near the equilibrium geometries. However, large part of the chemistry research deals with chemical reactions, where bonds are stretched or broken, and processes involving excited electronic states, which cannot be described by conventional single-reference methods, since the corresponding wavefunctions have a significant multideterminantal character. In particular, there have been a great deal of interest in extending single-reference CC methods to quasi-degenerate situations, such as molecular bond dissociation and excited states dominated by two- and other many-electron transitions, which are very challenging because of the large nondynamical electron correlation effects that traditional single-reference theories cannot capture.^{63,66,67,71–73} The basic ground state CC approach with singles and doubles (CCSD)^{74–76} is accurate in describing closed-shell systems and dynamical correlation effects with relatively low computer costs that scale as $n_o^2 n_u^4$, but fails in describing bond breaking because it neglects the higher-than-pair (e.g., triply and quadruply

excited or T_3 and T_4) clusters. The CCSDT^{77,78} and CCSDTQ^{79–82} methods, which incorporate T_3 or T_3 and T_4 clusters, respectively, are capable of giving an accurate description for certain classes of systems with electronic quasi-degeneracies, in spite of their single-reference character, since they describe correlation effects to very high orders, often compensating for the inadequacies of single-reference description, but the computer costs of the CCSDT and CCSDTQ calculations are extremely high, limiting their applicability to small molecular problems with 2–3 light atoms. In particular, the CCSDT and CCSDTQ methods require iterative steps that scale as $n_o^3 n_u^5$ and $n_o^4 n_u^6$, respectively, which make them applicable to systems with up to ~ 10 correlated electrons.

To considerably reduce the computational costs of the CCSDT, CCSDTQ, and other high-order CC schemes, several CC approaches, in which the effects of higher-than-doubly excited clusters is approximately included have been developed. One of the most popular CC methods in this category is the CCSD(T)⁸³ approach in which the connected triply excited (T_3) clusters are incorporated in a computationally efficient manner through noniterative corrections to CCSD energy derived using arguments that originate from MBPT. The CCSD(T) method and its CCSD[T] analog^{84,85} are currently available in the majority of popular quantum chemistry software packages, enabling highly accurate *ab initio* calculations of useful molecular properties by experts as well as non-experts. However, while the CCSD[T] and CCSD(T) methods improve the description of molecular properties in the region of equilibrium geometry, they completely fail when chemical bonds are stretched or broken.^{18–27,62,67–70,86–100} The inclusion of noniterative quadruples (T_4 clusters) using the arguments originating

from MBPT, which leads to CCSD(TQ_f) and CCSDT(Q_f) methods¹⁰¹ and their various modifications, further improves the results in the equilibrium region but cannot help when the configurational quasi-degeneracy sets in.^{18,19,21,23,25,26,68,70,88–90,92,94,96}

Similar remarks about the performance and failures of single-reference CC methods can be made when extending the discussion to excited states calculations. The most natural extensions of the single-reference CC formalism to excited states are the linear-response CC theory^{102–107} and the closely related equation-of-motion (EOM) CC^{108–112} and symmetry-adapted cluster configuration interaction (SAC-CI) approaches.^{113–117} The basic linear response CCSD^{106,107} and EOMCCSD^{109–111} approximations, which are characterized by the manageable computational steps that scale as $n_o^2 n_u^4$ or $\mathcal{N}^6$ with the system size and the analogous SAC-CISD method provide reliable information about excited states dominated by one-electron transitions. Unfortunately, the linear response CCSD and EOMCCSD methods cannot describe excited states having significant double excitation components and excited-state potential energy surfaces along bond breaking coordinates^{10,21–26,69,97,98,118–128}.

High-order EOMCC methods including higher-than-double excitations, such as the recently implemented full EOMCCSDT (EOMCC singles, doubles, and triples)^{24,125,129} and EOMCCSDTQ (EOMCC singles, doubles, triples, and quadruples)^{128,130} approaches, provide an excellent description of excited states dominated by doubles^{24,125,128} as well as excited-state potential energy surfaces,²⁴ but large costs of the EOMCCSDT and EOMCCSDTQ calculations, which are defined by the iterative steps that scale as $\mathcal{N}^8$ and $\mathcal{N}^{10}$ with the system size, respectively,

limit their applicability to small molecules with 2–3 light atoms and relatively small basis sets. For this reason, a number of approximate and less expensive ways of incorporating triple or triple and quadruple excitations in the EOMCC and linear response CC formalisms have been developed in order to make these methods applicable to a wider range of molecular sizes. Among those are the noniterative EOMCCSDT- n approaches and their noniterative EOMCCSD(T), EOMCCSD($\tilde{T}$), and EOMCCSD(T') counterparts,^{118,119} and the analogous linear-response CC methods such as CC3^{10,121–123} and CCSDR(3),^{10,123} which use elements of MBPT to estimate triples effects. All of these methods are characterized by the relatively inexpensive $\mathcal{N}^7$ steps of the $n_o^3 n_u^4$ type and all of them improve the EOMCCSD/linear response CCSD results for excited states dominated by two-electron transitions, but there are many cases where the results of EOMCCSDT- n , EOMCCSD(T), CC3, and similar calculations are far from satisfactory or poor. This can be illustrated by the large 0.4–0.5 and 0.9 eV errors in the description of the lowest $^1\Pi_g$ and $^1\Delta_g$ states of the C₂ molecule, respectively, by the EOMCCSDT-1 and CC3 approaches¹⁰ or the failure of the CC3 and CCSDR(3) methods to provide accurate information about excited-state potential energy surfaces along bond breaking coordinates¹² (see also Ref. 22 for an additional analysis).

The above problems encountered in single-reference CC/EOMCC calculations in various cases of electronic quasi-degeneracy clearly indicate that a traditional single-reference description is not sufficient and that more flexible models are needed. The conventional wisdom is to turn to multi-reference approaches, in which instead of using a single-determinantal reference state, one selects a certain number of refer-

ence determinants to construct the appropriate zero-order wavefunction(s) adjusted to the type of bond breaking or excited states of interest. The less intuitive and yet potentially very useful is an idea of improved single-reference methods, which completely or largely rely on a single-determinantal reference state, while being capable of describing at least some of the most frequent cases of electronic quasi-degeneracies. We first overview the traditional multi-reference methods, which we classify as multi-reference CI (MRCI), multi-reference MBPT (MRMBPT), and multi-reference CC (MRCC) approaches.

In CI, the multi-reference formulation is typically accomplished by adopting a more sophisticated zeroth-order reference in the form of a multiconfiguration self-consistent field (MCSCF) wavefunction instead of using a single H-F determinant. The basic MRCISD approach (abbreviated here as MRCI) involves single and double excitations out of all reference determinants. The most popular MRCI schemes using complete active space self-consistent field (CASSCF) reference wavefunctions (CASSCF is a variant of MCSCF obtained by a distribution of a number of active electrons among a number of active orbitals in all possible ways) provide potential energy surfaces which are closely parallel to full CI surfaces, at least for small molecules. Because of this, the MRCI methods are among the most useful benchmark techniques of quantum chemistry^{52,131,132} particularly in cases where full CI results are not available, and among the most popular approaches to calculation of potential energy surfaces of smaller molecular system. One of the biggest advantages of MRCI techniques, in addition to high accuracy in calculations of potential energy surfaces, is their ability to describe ground and excited states, near-degeneracy effects, and all kinds of open-

shell systems. The fundamental drawback of the MRCI methods, their lack of size extensivity, can be addressed through either the *a posteriori* Davidson-type energy corrections^{133–138} or the *a priori* refinements through suitable Hamiltonian dressing techniques, such as the MR-average coupled pair functional (MR-ACPF)¹³⁹ and MR-average quadratic coupled cluster (MR-AQCC).^{140,141} Neither of these propositions is ideal, but benchmark calculations show that at least the main problems related to inextensivity of MRCI can be addressed in this manner (see, e.g., Ref. 142). Several other approximate extensive modifications of MRCI have been developed.^{143–145}

In addition to inextensivity, the main challenge for the MRCI methods is the fact that the lengths of the corresponding CI wavefunction expansions and the related computational effort rapidly increase with the system and basis set sizes. Although several clever ideas, such as the use of the configuration selection thresholds, combined with the extrapolation techniques,¹³⁸ and internal contractions of configuration state functions^{146,147} have been developed to reduce the costs of MRCI calculations, all MRCI methods are generally costly in all aspects of computing resources.¹⁴⁸ Even with the substantial progress in terms of algorithms, efficient implementation, and parallelization (cf. e.g., Refs. 146–154), practically all applications of MRCI remain limited to relatively small molecular systems. In addition, the existing MRCI approaches are significantly more complex than other computational chemistry methods due to several choices that the user have to make to run the MRCI calculations in a proper manner. This makes MRCI approaches popular among experts, but much less popular among non-experts.

A cost effective alternative to MRCI is represented by methods based on the

multi-reference extension of MBPT. Historically, the general MRMBPT formalisms for quasi-degenerate and open-shell states have been formulated in the late 1960's¹⁵⁵ and early 1970's,¹⁵⁶ but much of the development work geared toward practical computational schemes has been done in the last two decades. Two general categories of MRMBPT methods are distinguished in the literature: the "perturb then diagonalize" and the "diagonalize then perturb" approaches.^{157,158} The "perturb then diagonalize" approaches involve deriving the effective Hamiltonian in the multiconfigurational reference space, which in the case of the most popular second-order MRMBPT schemes is truncated at first-order terms, and then obtaining the final energies as eigenvalues of this operator.^{155,158–162} The most popular second-order "diagonalize then perturb" methods use the first-order contributions to the Schrödinger equation to define the perturbed wavefunctions, and then use the second-order equation to get the energy. Various methods, particularly of the latter family, differ from one another in the choice of the zeroth-order Hamiltonian, and other details of the algorithms used in the computer implementation.^{163–187} Among the most popular and widely used variants of MRMBPT are the complete active space second-order perturbation theory (CASPT2),^{163,164} the multi-reference Moller-Plesset perturbation theory (MRMP),¹⁶⁵ and the multi-configurational quasi-degenerate perturbation theory (MC-QDPT).¹⁷⁴

A general difficulty of MRMBPT is the choice of the zeroth-order Hamiltonian, which is much less straightforward than in the single-reference case. Another difficulty concerns the choice of reference determinants. Usually, CASSCF wavefunctions are chosen as reference functions for MRMBPT considerations. However, CASSCF often generates too many configurations, and the size of the active space can easily outgrow

the capacity of the present technology, causing tremendous difficulty in obtaining converged results, which strongly vary with the number of active electrons and orbitals and the number of roots included in the calculations.^{187–189} In addition, at least some MRMBPT methods suffer from lack of size extensivity¹⁹⁰ and intruder state problems leading to divergent behavior.^{191–193} Among the most promising approaches to eliminate intruders, while retaining manifest size extensivity, are state-specific MRMBPT methods that start with a multideterminantal reference space but target one state at a time. The state-specific MRMBPT method advocated by Mukherjee *et al.*¹⁷⁷ seems particularly promising, showing smooth performance in and around the region of intruders and reasonable accuracy.

Overall, in spite of the aforementioned problems the MRMBPT methods have been successfully applied to many chemical and spectroscopic problems and have established themselves as efficient techniques for treating nondynamical and leading dynamical correlations.^{183,185} Compared to MRCI and genuine MRCC methods discussed below, the second-order MRMBPT approaches are much more practical. The low-order MRMBPT approaches have a drawback that they are not as accurate as MRCI or CC methods in describing dynamical correlation, but this can be taken care of by combining the low-order MRMBPT theory with the CC theory, as demonstrated in this thesis research through the MRMBPT-inspired corrections to CC energies.

The last type of multi-reference methods are the multi-reference coupled-cluster (MRCC) approaches. The existing MRCC approaches can be classified into three basic categories: the Fock-space (FS) or the valence-universal approaches,^{71,72,194–196} Hilbert-space (HS) or the state-universal methods,^{73,197–205} and the state-specific or

state-selective (SS) approaches, such as, for example, those described in Refs. 206 and 207, or SSMRCC methods based on the wavefunction ansatz described in Refs. 82 and 208, which we nowadays referred to as the active-space CC methods.^{24,99,100,123,124,209–211}

The FSMRCC theories employ a single valence universal exponential wave operator to generate ground and excited states of a given system and its ions obtained by removing active electrons one by one. Thus, they are very good for valence systems around closed-shells and differential properties, such as ionization energies and electron affinities. The HSMRCC theories are based on the ansatz of Jeziorski and Monkhorst, which employs different cluster operators for different reference determinants, are particularly well suited for electronic quasi-degeneracies due to several interacting states. Both the FSMRCC and HSMRCC approaches are multiroot procedures. This should be contrasted by SSMRCC theories, which treat one electronic state at a time. We will return to the SSMRCC methods when we discuss active-space CC approaches. With an exception to active-space methods,^{24,82,99,100,123,124,208–211} the MRCC approaches are greatly limited so far and no general purpose codes have been developed due to recurring issues such as computational complexity, intruder-state problems,²¹² and difficulties with retaining size extensivity in incomplete model space considerations (cf. e.g., Refs. 213–216 for recent progress in this area). This implies that it may be more worthwhile to focus on methods that rely, at least in part, on a single-reference formalism. In general, single-reference methods are much easier to implement and use than genuine MRCC approaches. Thus, it is useful to develop new classes of single-reference CC methods that eliminate the failures of standard CC/EOMCC approximation in the bond breaking region and for excited states hav-

Table 1: The quality of the overall description of the dynamical and nondynamical electron correlation effects by selected wavefunction methods of quantum chemistry.

Method	Type of Electron Correlations	
	Dynamical	Nondynamical
MBPT(2), MP2	low-order	poor
CCSD(T), CCSD(TQ), ...	excellent	poor
MRMBPT	low-order	excellent
MRCI	excellent*	excellent*
MRCC	excellent	excellent

* MRCI is not size extensive, so there is a loss of accuracy as the system becomes larger

ing a manifestly multiconfigurational character, without involving the complexities of the FSMRCC and HSMRCC considerations.

As shown in Table 1, MRCI and MRCC are the only methods that offer an excellent treatment of both dynamical and nondynamical correlation effects. As described earlier, these methods are computationally very expensive and very difficult to use which greatly limits their applicability. Thus, we need alternative approaches which are more practical than MRCI and MRCC and which are capable of balancing dynamical and nondynamical correlations, particularly in studies of bond breaking and excited states having a significant configuration mixing.

One can think of two general ways of developing such approaches, at least within the CC formalism. The first way is to improve the existing single-reference CC methods such that they can describe at least the selected classes of bond breaking and excited states in a purely “black-box” fashion, i.e. without using any elements of multi-

reference calculation. A few ideas of this type have been proposed in recent years, including the non-iterative single-reference CC methods based on the partitioning of the similarity-transformed Hamiltonian,^{95,217–222} spin-flip CC approaches,^{223–225} and renormalized CC methods.^{18,19,21,22,25,26,68–70,87,96,98,226–228} The latter approaches are particularly successful. They are based on the idea of correcting the CC (e.g., CCSD) or EOMCC (e.g., EOMCCSD) energies for the effects of higher-order clusters (e.g., triples) using expressions for the leading terms toward full CI obtained using the formalism of the moments of CC equations.^{18,19,21,22,25,26,68–70,87,96,98,126,127,226–229} Renormalized CC methods are particularly useful in calculations of single bond breaking, reaction pathways involving biradicals, and excited states dominated by two-electron transitions.^{18,19,21,22,25,26,68–70,87,95,96,98,187,188,226–236}

Renormalized CC methods are very successful, enabling accurate, inexpensive “black-box” CC calculations for some of the most frequent multi-reference situations but there are quasi-degeneracy problems that cannot be handled in this manner. A good example is provided by the excited states in a highly degenerate Be_3 system, where one cannot obtain all excited states due to difficulties with converging the underlying CCSD and EOMCCSD equations in some cases.^{237,238} In such cases and in more general cases of electronic quasi-degeneracies, where pure “black-box” single-reference solutions do not work, it may be useful to look for alternative approaches that mix single- and multi-reference concepts with a single mathematical theory. One of the best and most successful examples of such theory is provided by the active-space CC and EOMCC methods,^{24,27,82,86,88,99,100,124,125,208–211,237–241} which can be viewed as the state-selective MRCC approaches exploiting a single-reference

CC formalism.^{27,82,86,208,239–241} These methods use active orbitals, which are normally exploited to define reference determinants in a multi-reference calculation, to select the dominant three-body and other higher-than-two-body clusters and excitation amplitudes within a standard single-reference CC or EOMCC formalism. As a result, they offer a tremendous amount of flexibility, since one can always improve the results by employing the active space. At the same time, they have a well-defined relationship with higher-order single-reference CC or EOMCC methods. For example, the active-space CC/EOMCC approach with up to triple excitations (CCSDt/EOMCCSDt) becomes equivalent to full CCSDT/EOMCCSDT theory when all orbitals are active. On the other hand, as demonstrated in numerous calculations by the inventors of this method (Piecuch, Adamowicz, and co-workers), and others who adopted active space approaches (Bartlett, Head-Gordon, Gauss, Olsen, Krylov, Sherrill, Hirata, and others), it is sufficient to use small numbers of active orbitals in active space CC/EOMCC calculations to obtain extremely accurate results for bond breaking and multi-determinantal excited states. In particular, the active space EOMCC methods lead to the virtually perfect description of the excited states of the aforementioned Be₃ system, where other methods fail.^{237,238}

Active space CC/EOMCC methods mix single- and multi-reference CC concepts, but one can go even one step further and mix CC and non-CC concepts, so that the advantages of different kinds of electronic structure theory are utilized to the utmost. One of the most successful methods in this broad category is the idea of the externally corrected single-reference CC methods^{242–250} in which the T_3 and T_4 cluster components, instead of being calculated by solving CCSDTQ or the expen-

sive CC equations, are obtained by a cluster analysis of the wavefunctions provided by some external non-CC source such as the projected unrestricted Hartree-Fock (PUHF),^{242,247} valence bond (VB),^{243,244} MCSCF or CASSCF,^{245–247,249} and MRCI²⁵⁰ wavefunctions.

The MRCI-corrected CC methods, which define the so-called reduced MRCC approaches, are particularly impressive, since the MRCI method itself is already very accurate in applications involving potential energy surfaces along bond breaking coordinates and by reading T_3 and T_4 clusters extracted from MRCI calculations and solving the resulting T_3 and T_4 -corrected CCSD equations one obtains the virtually perfect description of both dynamical and nondynamical correlations. The only problem of reduced MRCC methods is the fact that they are currently limited to lowest-energy electronic states of a given symmetry. Moreover, the MRCI calculation needed to estimate T_3 and T_4 clusters for the subsequent CCSD calculations can be quite expensive.

There is however, a major lesson on the success of the reduced MRCC approach in that it is very useful to mix multi-reference theory, which can be used to provide information about the nondynamical and leading dynamical correlation effects, with single-reference CC theory, which gives the information about the remaining correlations. The success of the reduced MRCC method has inspired the development of the CI (MRCI)-corrected approaches exploiting the aforementioned formalism of the method of moments of CC equations (MMCC).^{21,25,26,87,126,127,251} (see, also, Refs. 252–254) As already mentioned, the MMCC formalism enables one to determine the mathematical structure of terms which, when added to CC or EOMCC (e.g.,

CCSD or EOMCCD) energies, give, in the exact limit, the exact full CI energies. One can use the MMCC theory to design the “black-box” renormalized CC approximation, which we mentioned earlier, or to develop the externally corrected MMCC methods, such as the (MR)CI-corrected MMCC schemes, in which one uses selected components of the (MR)CI wavefunctions to design the MMCC corrections due to higher-order correlation effects on top of CCSD or EOMCCSD. The major advantage of the (MR)CI-corrected MMCC schemes is their applicability to ground and excited states, not just to lowest-energy states of a given symmetry, and high accuracy that in some cases is even better than the results of reduced MRCC calculations.^{252–254} The (MR)CI-corrected MMCC methods work extremely well for single, double, or even triple bond breaking and all kinds of excited states,^{21,25,26,87,126,127,252–254} but they still require additional CI calculations to generate trial wavefunctions that enter the MMCC corrections to CCSD or EOMCCSD energies. Although the main idea of the CI-corrected MMCC methods is straightforward, the CI-corrected MMCC calculations can be quite expensive if the CI calculations used in designing the MMCC corrections use larger active orbital spaces. Undoubtedly, it would be most desirable to examine if one could use another, less expensive, multi-reference method to generate the wavefunctions that enter the MMCC corrections, while retaining the high accuracy of the CI-corrected MMCC calculations.

In this dissertation, we examine the possibility of replacing the relatively expensive (MR)CI-like wavefunctions in the CI-corrected (MMCC/CI) schemes by the wavefunctions obtained in the MRMBPT calculations. As described earlier, the low-order MRMBPT methods are known to provide a reasonable description of non-

dynamical and leading dynamical correlation effects in the presence of electronic quasi-degeneracies (cf., e.g., Refs. 159, 162–165, 167, 171, 173, 174, 177, 183, 184, 187, 255–259). At the same time, the computer costs of the low-order MRMBPT (e.g., second-order) calculations are very small compared to the analogous MRCI calculations. By combining the wavefunctions obtained in the low-order MRMBPT calculations, which provide a reasonable description of electronic quasi-degeneracies, with the MMCC formalism, in which these MRMBPT wavefunctions are used to design the MMCC corrections to single-reference CC or EOMCC energies, we obtain a new class of the MRMBPT-corrected MMCC methods, referred to here and elsewhere in this thesis as the MMCC/PT approaches.^{69,97,98} Just like the MMCC/CI methods, which combine the CC and CI concepts, the MMCC/PT approaches proposed, developed, implemented, and benchmarked in this work can be viewed as the externally corrected MMCC methods. All externally corrected MMCC methods are similar, in the overall philosophy, to the externally corrected CC methods pioneered by Paldus and collaborators, in which the CC and non-CC concepts are combined together to improve the CC results in the presence of electronic quasi-degeneracies. We demonstrate in this work that by combining the single-reference CC and EOMCC methods with the low-order MRMBPT-like wavefunctions via noniterative MMCC/PT corrections to CC or EOMCC energies, we can considerably improve the results of the standard CC and EOMCC calculations in the bond breaking region and for excited states dominated by two-electron transitions, while keeping the computer costs at the low level. Thus, the MRMBPT-corrected MMCC methods provide an inexpensive alternative to other CC/EOMCC and MMCC schemes, and reduced MRCC approach

of Li and Paldus, which in the long-term may facilitate highly accurate calculations of reaction pathways and electronic excitations in larger molecular systems.

The rest of this document is organized as follows:

In Chapter 2, we summarize the main objectives of this work.

In Chapter 3, we describe the mathematical details relevant in the understanding and carrying out this research study. We outline, in particular, the single-reference CC theory for ground states and its extension to excited states via the EOMCC formalism. We also introduce the basic elements of the MMCC theory, in which our MMCC/PT work is based. The existing MMCC approaches, such as the CI-corrected methods and the selected renormalized and completely renormalized CC methods, and basic concepts of the MRMBPT methods are described in Chapter 3 as well.

In Chapter 4, we describe the details of the new MRMBPT-corrected MMCC (MMCC/PT) methods. One of the key parts of the chapter is the diagrammatic formulation and factorization of the key components of the MMCC/PT equations, called method of moments of CC/EOMCC equations, which leads to the highly efficient computer implementation of the MMCC/PT and other MMCC methods.

In Chapter 5, we present some of the benchmark calculations to illustrate the performance of the MMCC/PT approximations developed in this work.

Lastly, in Chapter 6, we present a summary and future perspectives of this work.

2 Project Objectives

The main objective of this dissertation is to combine the low-order multi-reference many-body perturbation theory (MRMBPT) with coupled-cluster (CC) and equation-of-motion CC (EOMCC) methodologies via the method of moments of CC (MMCC) equations. The specific objectives of this work are:

- A. to formulate the low-order MRMBPT approximation that can be used in the MRMBPT-corrected MMCC (MMCC/PT) formalism.
- B. to formulate the MMCC/PT approach using diagrammatic methods.
- C. to efficiently implement the leading MMCC/PT approximations, termed MMCC(2,3)/PT and MMCC(2,4)/PT, using the idea of diagram factorization and recursively generated intermediates.
- D. to benchmark the proposed MMCC/PT approaches in calculations of ground and excited states of selected molecular systems, for which the exact, full CI data can be generated.

3 Theory

In this chapter, an overview of single-reference coupled-cluster (CC) theory and its extension to excited states via the equation-of-motion (EOM) CC theory is presented. The method of moments of CC (MMCC) equations is introduced and the existing MMCC approximations, namely, the CI-corrected MMCC methods as well as the selected renormalized- and completely-renormalized CC methods are discussed.

3.1 An Overview of Coupled-Cluster (CC) Theory

3.1.1 Ground-State Formalism

The single-reference CC theory is based on the exponential ansatz for the ground-state wavefunction,

$$|\Psi_0\rangle = |\Psi_0^{(\text{CC})}\rangle \equiv e^T |\Phi\rangle, \quad (1)$$

where T is a particle-hole excitation operator referred to as the cluster operator and $|\Phi\rangle$ is the reference determinant (usually, the Hartree-Fock determinant). In the exact CC theory, T is a sum of all many-body cluster components that one can write for a given N -electron system,

$$T = \sum_{n=1}^N T_n, \quad (2)$$

where the n -body cluster component T_n is defined in a usual way as

$$T_n = \left(\frac{1}{n!}\right)^2 t_{a_1 \dots a_n}^{i_1 \dots i_n} a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1}, \quad (3)$$

with $t_{a_1 \dots a_n}^{i_1 \dots i_n}$ representing the corresponding antisymmetrized cluster amplitudes, $i_1 \dots i_n (a_1 \dots a_n)$ referring to the single-particle states (spin-orbitals) occupied (unoccupied) in the reference determinant, and a^p (a_p) designating the standard creation (annihilation) operators associated with the orthonormal spin-orbitals $|p\rangle$. Here and elsewhere in this dissertation, the Einstein summation convention over repeated upper and lower indices is employed, so that the summation symbols corresponding to the unrestricted summations over occupied and/or unoccupied spin-orbitals are omitted.

In all standard CC approximations, the many-body expansion for the cluster operator T is truncated at a given excitation level $m_A < N$ (usually $m_A \ll N$). The general form of the truncated cluster operator defining a standard CC approximation A , characterized by the excitation level m_A , is

$$T^{(A)} = \sum_{n=1}^{m_A} T_n. \quad (4)$$

An example of the standard CC approximation is the CCSD method. In this case, $m_A = 2$ and the cluster operator T is approximated by

$$T^{(\text{CCSD})} = T_1 + T_2, \quad (5)$$

where

$$T_1 = t_a^i a^a a_i \quad (6)$$

and

$$T_2 = \frac{1}{4} t_{ab}^{ij} a^a a^b a_j a_i \quad (7)$$

are the singly and doubly excited cluster components, and t_a^i and t_{ab}^{ij} are the corresponding singly and doubly excited cluster amplitudes. In accordance with our general notation, $i, j \dots (a, b \dots)$ are the occupied (unoccupied) spin-orbitals in the reference determinant $|\Phi\rangle$.

In all conventional CC approximations, the cluster amplitudes $t_{a_1 \dots a_n}^{i_1 \dots i_n}$ are determined by solving a coupled system of energy-independent non-linear algebraic equations of the form:

$$\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \bar{H}^{(A)} | \Phi \rangle = 0, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad (8)$$

where $n = 1, \dots, m_A$,

$$\bar{H}^{(A)} = e^{-T^{(A)}} H e^{T^{(A)}} = (H e^{T^{(A)}})_C \quad (9)$$

is the similarity-transformed Hamiltonian of the CC/EOMCC theory, subscript C designates the connected part of the corresponding operator expression, and $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle \equiv a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} |\Phi\rangle$ are the n -tuply excited determinants relative to reference $|\Phi\rangle$. In particular, the standard CCSD equations for the singly and doubly excited cluster amplitudes t_a^i and t_{ab}^{ij} , defining T_1 and T_2 , respectively, can be written as

$$\langle \Phi_i^a | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad (10)$$

$$\langle \Phi_{ij}^{ab} | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad i < j, \quad a < b, \quad (11)$$

where

$$\bar{H}^{(\text{CCSD})} = e^{-T^{(\text{CCSD})}} H e^{T^{(\text{CCSD})}} = (H e^{T^{(\text{CCSD})}})_C \quad (12)$$

is the similarity-transformed Hamiltonian of the CCSD/EOMCCSD approach. The explicit and computationally efficient form of $\bar{H}^{(\text{CCSD})}$ and other equations used in the CC calculations, in terms of one- and two-body matrix elements of the Hamiltonian in the normal-ordered form, $f_p^q \equiv \langle p|f|q \rangle$ and $v_{pq}^{rs} \equiv \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$, respectively, where f is the Fock operator and v is the operator representing the electron-electron interaction energy, and cluster amplitudes $t_{a_1 \dots a_n}^{i_1 \dots i_n}$ or, in the CCSD ($m_A = 2$) case, t_a^i and t_{ab}^{ij} , can be derived by applying the powerful diagrammatic techniques of many-body theory²⁶⁰ combined with technique of diagram factorization, which yields highly vectorized computer codes.^{79,91,226} The algebraic and diagrammatic structure of $\bar{H}^{\text{CCSD}}$ is presented in detail in Appendix B and the factorized forms of $\bar{H}^{\text{CCSD}}$ is shown in Appendix C. The introduction to diagrammatic methods used in this work is given in Appendix A.

Unlike the CI approaches, which are variational in nature, the CC energy is obtained by projecting the connected cluster form of the Schrödinger equation on the reference configuration $|\Phi\rangle$. In other words, once the system of equations, Eq. (8), is solved for $T^{(A)}$ or $t_{a_1 \dots a_n}^{i_1 \dots i_n}$ (or in the CCSD case, Eqs. (10) and (11) are solved for T_1 and T_2 or t_a^i and t_{ab}^{ij}), the CC energy corresponding to approximation A, characterized by the excitation level m_A , is calculated using the equation

$$E_0^{(A)} = \langle \Phi | \bar{H}^{(A)} | \Phi \rangle \equiv \langle \Phi | \bar{H}_{\text{closed}}^{(A)} | \Phi \rangle, \quad (13)$$

where $\bar{H}_{\text{closed}}^{(A)}$ is a “closed” part of $\bar{H}^{(A)}$, which is represented by those diagrams contributing to $\bar{H}^{(A)}$ that have no external (uncontracted) Fermion lines (as opposed to the “open” part of $\bar{H}^{(A)}$ which is represented by the diagrams having external or uncontracted Fermion lines).

3.1.2 Extension to Excited States via the Equation-of-Motion Formalism (EOMCC)

The ground-state CC theory has a natural extension to excited electronic states $|\Psi_\mu\rangle$ via the EOMCC formalism, in which we write

$$|\Psi_\mu\rangle = |\Psi_\mu^{(\text{CC})}\rangle \equiv R_\mu e^T |\Phi\rangle, \quad (14)$$

where T is obtained in the ground-state CC calculations and R_μ is a linear particle-hole excitation operator, similar to T , obtained by diagonalizing the similarity-transformed Hamiltonian $\bar{H} = e^{-T} H e^T$ in the space of excited determinants $|\Phi_{a_1 \dots a_n}^{i_1 \dots i_n}\rangle$ that typically correspond to excitations included in T .

In the following, we use a notation where $\mu = 0$ refers to the ground states while $\mu > 0$ designates excited states. Thus, the excitation operator R_μ is defined as a unit operator for $\mu = 0$, that is, $r_0(\mu = 0) = 1$ and $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu = 0) = 0$ for $n \geq 1$, where $r_0(\mu)$ is a coefficient defining the zero-body of R_μ and $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$ are the excitation amplitudes defining the n -body components of R_μ when $n > 1$ (see discussion below). In this way, the EOMCC ansatz, Eq. (14), reduces to the ground-state CC ansatz, Eq. (1), when $\mu = 0$.

In the exact EOMCC theory, the cluster operator T and the excitation operators R_μ are sums of all relevant many-body components that can be written for a given N -electron systems. As in the ground-state case, the standard EOMCC approximations are obtained by truncating the many-body expansion for the operator R_μ at a given excitation level $m_A < N$, which typically is the same as the excitation level used to define the truncated form of T . In general, when T is approximated by $T^{(A)}$, Eq. (4), the corresponding excitation operator R_μ defining the EOMCC method A is approximated by

$$R_\mu^{(A)} = R_{\mu,0}^{(A)} + R_{\mu,\text{open}}^{(A)}, \quad (15)$$

where

$$R_{\mu,0} = r_0(\mu) \mathbf{1}, \quad (16)$$

and the “open” part of $R_\mu^{(A)}$ is defined as

$$R_{\mu,\text{open}}^{(A)} = \sum_{n=1}^{m_A} R_{\mu,n}, \quad (17)$$

with

$$R_{\mu,n} = \left(\frac{1}{n!} \right)^2 r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu) a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} \quad (18)$$

representing the n -body component of $R_\mu^{(A)}$. For instance, in the EOMCCSD theory, which is a basic EOMCC approximation where m_A is set at 2, the excitation operator $R_\mu^{(\text{CCSD})}$ is approximated by

$$R_\mu^{(\text{CCSD})} = R_{\mu,0} + R_{\mu,1} + R_{\mu,2}, \quad (19)$$

where $R_{\mu,0}$ is given by Eq. (16) and

$$R_{\mu,1} = r_a^i(\mu) a^a a_i \quad (20)$$

and

$$R_{\mu,2} = \frac{1}{4} r_{ab}^{ij}(\mu) a^a a^b a_j a_i \quad (21)$$

are the one- and two-body components of $R_{\mu}^{(\text{CCSD})}$, with $r_a^i(\mu)$ and $r_{ab}^{ij}(\mu)$ representing the corresponding excitation amplitudes (1 in Eq. (16) is a unit operator).

The excitation amplitudes $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$ defining the excitation operator $R_{\mu, \text{open}}^{(A)}$, Eq. (15), are obtained by solving the eigenvalue problem involving the similarity-transformed Hamiltonian $\bar{H}^{(A)}$ in the space spanned by the excited determinants $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ with $n = 1, \dots, m_A$, i.e.

$$\begin{aligned} \langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | (\bar{H}_{\text{open}}^{(A)} R_{\mu, \text{open}}^{(A)})_C | \Phi \rangle &= \omega_{\mu}^{(A)} r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu), \\ i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \end{aligned} \quad (22)$$

where

$$\bar{H}_{\text{open}}^{(A)} = \bar{H}^{(A)} - \bar{H}_{\text{closed}}^{(A)} = \bar{H}^{(A)} - E_0^{(A)} \mathbf{1} \quad (23)$$

is the “open” part of $\bar{H}^{(A)}$, represented by the diagrams of $\bar{H}^{(A)}$ that have external Fermion lines, and

$$\omega_{\mu}^{(A)} = E_{\mu}^{(A)} - E_0^{(A)} \quad (24)$$

is the vertical excitation energy obtained with the EOMCC method A . In particular,

the $r_a^i(\mu)$, and $r_{ab}^{ij}(\mu)$ amplitudes of the EOMCCSD theory and the corresponding excitation energies $\omega_\mu^{(\text{CCSD})}$ are obtained by diagonalizing the similarity-transformed Hamiltonian $\bar{H}^{(\text{CCSD})}$, Eq. (12), in the space of singly and doubly excited determinants, $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$, respectively. Equation (22) alone does not provide information about the coefficient $r_0(\mu)$ at the reference determinant $|\Phi\rangle$ in the corresponding EOMCC excited-state wavefunction $R_\mu^{(A)} e^{T^{(A)}} |\Phi\rangle$. This coefficient is determined *a posteriori* using the equation

$$r_0(\mu) = \langle \Phi | (\bar{H}_{\text{open}}^{(A)} R_{\mu, \text{open}}^{(A)})_C | \Phi \rangle / \omega_\mu^{(A)}, \quad (25)$$

once the excitation amplitudes $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$ defining $R_{\mu, \text{open}}^{(A)}$ are determined (Eq. (25) is valid for $\mu > 0$, meaning excited states only; for $\mu = 0$, $r_0(\mu = 0) = 1$, as explained above).

3.2 Method of Moments of CC Equations (MMCC)

3.2.1 An Overview of the Exact MMCC Formalism

We are now equipped with the basic elements of the CC/EOMCC theory which are necessary to explain the noniterative MMCC approaches to ground and excited electronic states. In this section, we focus on the exact MMCC formalism.

As described in Section 3.1, the standard CC and EOMCC equations are obtained by projecting $\bar{H}^{(A)} |\Phi\rangle$ and $\bar{H}^{(A)} R_\mu^{(A)} |\Phi\rangle$ on the excited determinants $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ with $n = 1, \dots, m_A$ that correspond to the particle-hole excitations included in the cluster operator $T^{(A)}$ and linear excitation operator $R_\mu^{(A)}$. The corresponding ground-state

CC energy is obtained by projecting $\bar{H}^{(A)}|\Phi\rangle$ on the reference determinant $|\Phi\rangle$. It is, therefore, quite natural to expect that in order to correct the results of the standard CC/EOMCC calculations employing the cluster and excitation operators truncated at m_A -body terms, the projections of $\bar{H}^{(A)}|\Phi\rangle$ and $\bar{H}^{(A)}R_\mu^{(A)}|\Phi\rangle$ on the excited determinants $|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle$ with $n > m_A$, which span the orthogonal complement to the subspace of the N -electron Hilbert space spanned by the reference determinant $|\Phi\rangle$ and the excited determinants $|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle$ with $n = 1, \dots, m_A$, have to be considered. These projections, which are the essence of the MMCC formalism, designated by $\mathfrak{M}_{\mu, a_1\dots a_n}^{i_1\dots i_n}(m_A)$, define the generalized moments of the CC/EOMCC equations corresponding to method A .

The original single-reference MMCC theory,^{18,19,21,22,25,26,68–70,87,98} which is particularly useful in this work, is based on a simple idea that the exact, full CI, energies of the electronic states μ , E_μ , can be recovered by adding the state-selective, non-iterative energy corrections

$$\begin{aligned}\delta_\mu^{(A)} &\equiv E_\mu - E_\mu^{(A)} \\ &= \sum_{n=m_A+1}^N \sum_{k=m_A+1}^n \langle \Psi_\mu | C_{n-k}(m_A) M_{\mu,k}(m_A) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle\end{aligned}\quad (26)$$

to the ground ($\mu = 0$) and excited ($\mu > 0$) states energies $E_\mu^{(A)}$ obtained in the standard CC/EOMCC calculations, such as CCSD/EOMCCSD, etc., which we continue to designate by letter A . The alternative formulations of the MMCC theory including the generalized MMCC formalism which applies to non-standard CC methods,^{26,94} the numerator-denominator-connected MMCC expansions,⁹⁶ the multi-reference ex-

tensions of MMCC,^{73,229,261} and the most recent biorthogonal MMCC formalism which leads to rigorously size extensive renormalized CC methods,^{226–228} are of no use for the MRMBPT-corrected MMCC methods and are not discussed here. The $R_\mu^{(A)}$ and $T^{(A)}$ operators entering Eq. (26) are the truncated linear excitation and cluster operators used in the underlying CC and EOMCC calculations, respectively, and in the exact theory $|\Psi_\mu\rangle$ are the full CI states. The

$$C_{n-k}(m_A) = (e^{T^{(A)}})_{n-k} \quad (27)$$

quantity is the $(n - k)$ -body component of the wave operator $e^{T^{(A)}}$ operator, defining the CC method A , which is trivial to determine. The zero-body term, $C_0(m_A)$, equals 1; the one-body term, $C_1(m_A)$, equals T_1 ; the two-body term, $C_2(m_A)$, equals $T_2 + \frac{1}{2}T_1^2$ if $m_A \geq 2$; the three-body term $C_3(m_A)$ equals $T_1T_2 + \frac{1}{6}T_1^3$ if $m_A = 2$ and $T_3 + T_1T_2 + \frac{1}{6}T_1^3$ if $m_A \geq 3$, etc. The

$$M_{\mu,k}(m_A) = \left(\frac{1}{k!}\right)^2 \mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(m_A) a^{a_1} \dots a^{a_k} a_{i_k} \dots a_{i_1} \quad (28)$$

operator in Eq. (26) is the particle-hole excitation operator defined through the aforementioned generalized moments of the CC/EOMCC equations of method A ,

$$\mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(m_A) = \langle \Phi_{i_1\dots i_k}^{a_1\dots a_k} | (\bar{H}^{(A)} R_\mu^{(A)}) | \Phi \rangle, \quad (29)$$

which represent the projections of the CC/EOMCC equations of method A on the

excited determinants $|\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}\rangle$ with $k > m_A$ that are normally disregarded in the standard CC/EOMCC calculations. Consistent with our notation in which $R_{\mu=0}^{(A)} = 1$, Eq. (29) includes the ground-state ($\mu = 0$) case as well. In this case, moments $\mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$ reduce to the generalized moments of the ground-state CC equations, $\mathfrak{M}_{0, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$, defining approximation A , i.e.

$$\mathfrak{M}_{0, a_1 \dots a_k}^{i_1 \dots i_k}(m_A) \equiv \mathfrak{M}_{a_1 \dots a_k}^{i_1 \dots i_k}(m_A) = \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | \bar{H}^{(A)} | \Phi \rangle. \quad (30)$$

As demonstrated, for example, in Refs. 22, 25, 26, 126, 127, the generalized moments of the CC/EOMCC equations can be calculated using the following expression:

$$\begin{aligned} \mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A) &= \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | (\bar{H}_{\text{open}}^{(A)} R_{\mu, \text{open}}^{(A)})_C | \Phi \rangle \\ &+ \sum_{p=m_A+1}^{k-1} \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | (\bar{H}_p^{(A)} R_{\mu, k-p}^{(A)})_{DC} | \Phi \rangle \\ &+ r_0(\mu) \mathfrak{M}_{0, a_1 \dots a_k}^{i_1 \dots i_k}(m_A), \end{aligned} \quad (31)$$

where $r_0(\mu)$ is the coefficient at the reference determinant $|\Phi\rangle$ in the many-body expansion of $R_{\mu}^{(A)}|\Phi\rangle$, defined by Eq. (25), subscripts “open,” C , and DC refer to open (i.e. having external lines), connected, and disconnected parts of a given operator expression, O_j represents the j -body component of operator O , and $\mathfrak{M}_{0, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$ are the generalized moments of the ground-state CC equations defined by Eq. (30).

In particular, if the goal is to recover the full CI energies E_{μ} by correcting the CCSD/EOMCCSD energies $E_{\mu}^{(\text{CCSD})}$ (the $m_A = 2$ case), then the following *a posteriori*-

ori corrections $\delta_\mu^{(\text{CCSD})}$,

$$\delta_\mu^{(\text{CCSD})} = \sum_{n=3}^N \sum_{k=3}^n \langle \Psi_\mu | C_{n-k}(2) M_{\mu,k}(2) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle. \quad (32)$$

have to be added to $E_\mu^{(\text{CCSD})}$ energies. Here, the generalized moments $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(2)$ of the CCSD/EOMCCSD equations corresponding to projections of these equations on triply, quadruply, etc., excited determinants, i.e.

$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | (\bar{H}^{(\text{CCSD})} R_\mu^{(\text{CCSD})}) | \Phi \rangle, \quad (33)$$

$$\mathfrak{M}_{\mu,abcd}^{ijkl}(2) = \langle \Phi_{ijkl}^{abcd} | (\bar{H}^{(\text{CCSD})} R_\mu^{(\text{CCSD})}) | \Phi \rangle, \quad (34)$$

etc., should be evaluated. Again, $\bar{H}^{(\text{CCSD})}$ is the similiary-transformed Hamiltonian of the CCSD method defined by Eq. (12) and $R_\mu^{(\text{CCSD})}$ is the EOMCCSD excitation operator described in Eq. (19).

Equation (26) defines the exact MMCC formalism for ground and excited states. This equation can formally be derived by considering the asymmetric energy expression,

$$\Lambda[\Psi] = \langle \Psi | (H - E_\mu^{(A)}) R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle / \langle \Psi | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle, \quad (35)$$

referred to as the MMCC functional, which was introduced for the first time in the original MMCC papers by Kowalski and Piecuch in Ref. 18 for the ground-state case and Ref. 126 for the excited-state generalization. This expression satisfies the

property

$$\Lambda[\Psi_\mu] = E_\mu - E_\mu^{(A)}, \quad (36)$$

where E_μ is the exact, full CI, energy, if $|\Psi_\mu\rangle$ is a full CI state. The details of the derivation of Eq. (26) using functional $\Lambda[\Psi]$, Eq. (35), can be found in Refs. 18 and 126 (see, also, Ref. 25).

To this point we have focused the discussion on the exact forms of the MMCC energy expansions, Eqs. (26 and (32)). However, in order to develop practical MMCC methods based on these equations, the following two issues must be addressed. First, the exact MMCC corrections $\delta_\mu^{(A)}$, Eq. (26), or $\delta_\mu^{(\text{CCSD})}$, Eq. (32), are represented by complete many-body expansions including the N -body contributions, where N is the number of electrons in a system, corresponding to all many-body components of the wavefunctions $|\Psi_\mu\rangle$ that enter Eqs. (26) and (32) (cf. the summations over n in Eqs. (26) and (32)). In order to use Eqs. (26) or (32) in practical calculations, the many-body expansions for $\delta_\mu^{(A)}$ or $\delta_\mu^{(\text{CCSD})}$, must be truncated at some, preferably low, excitation level $m_B > m_A$. This leads to the MMCC(m_A, m_B) schemes.^{18,19,21,22,25,26,68–70,87,88} The second issue that has to be addressed is the fact that the wavefunctions $|\Psi_\mu\rangle$ entering the exact Eqs. (26) and (32) are the full CI states, which are not normally available. To resolve this dilemma, wavefunctions $|\Psi_\mu\rangle$ must be approximated in some way. Depending on the form of $|\Psi_\mu\rangle$, we can distinguish between externally corrected MMCC methods where $|\Psi_\mu\rangle$ is obtained in the non-CC (e.g., CI) calculations, and renormalized CC approaches, in which the form of $|\Psi_\mu\rangle$ is determined using CC arguments. The CI-corrected MMCC(2,3) and

MMCC(2,4) approaches, which are the basic CI-corrected MMCC approximations, and the CR-CCSD(T)/CR-EOMCCSD(T) methods, which are examples of renormalized CC/EOMCC approaches, are described in Section 3.3. The theoretical details of the new variant of the MMCC theory, the MRMBPT-corrected MMCC method, abbreviated as MMCC/PT, which is based on the idea of approximating $|\Psi_\mu\rangle$ by the relatively inexpensive, low-order, MRMBPT-like expansions, and which is explored in this dissertation, is presented in Chapter 4 and its performance is tested in Chapter 5. First, however, we discuss formal considerations that lead to all MMCC(m_A, m_B) truncations.

3.2.2 An Overview of the Approximate MMCC Approaches:

The MMCC(m_A, m_B) Truncation

The main goal of all approximate MMCC calculations, including the CI-corrected MMCC approaches and the renormalized and completely-renormalized methods presented in this section as well as the MRMBPT-corrected MMCC methods, which are developed for this dissertation and discussed in Chapters 4 and 5, is to approximate the exact corrections $\delta_\mu^{(A)}$, Eq. (26), such that the resulting energies, defined as

$$E_\mu^{(\text{MMCC})} = E_\mu^{(A)} + \delta_\mu^{(A)}, \quad (37)$$

are close to the corresponding full CI energies E_μ . A systematic hierarchy of approximations that allows us to achieve this goal and that are called MMCC(m_A, m_B) schemes is described below.

All MMCC(m_A, m_B) schemes are obtained by assuming that the CI expansions of the ground- and excited-state wavefunctions $|\Psi_\mu\rangle$ entering Eq. (26) do not contain higher-than- m_B -tuply excited components relative to the reference $|\Phi\rangle$, where $m_A < m_B < N$. This requirement reduces the summation over n in Eq. (26) to $\sum_{n=m_A+1}^{m_B}$. The resulting MMCC(m_A, m_B) energies, $E_\mu^{(\text{MMCC})}(m_A, m_B)$, can be given the following form:

$$E_\mu^{(\text{MMCC})}(m_A, m_B) = E_\mu^{(A)} + \delta_\mu(m_A, m_B), \quad (38)$$

where $E_\mu^{(A)}$ is the energy of the μ -th electronic state, obtained with some standard CC/EOMCC method A , and

$$\delta_\mu(m_A, m_B) = \sum_{n=m_A+1}^{m_B} \sum_{k=m_A+1}^n \langle \Psi_\mu | C_{n-k}(m_A) M_{\mu,k}(m_A) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle \quad (39)$$

is the relevant MMCC correction to $E_\mu^{(A)}$.

We restrict our discussion to the MMCC(m_A, m_B) schemes with $m_A = 2$, which enables us to correct the results of the CCSD or EOMCCSD calculations. In this category, two schemes are particularly useful, namely, MMCC(2,3) and MMCC(2,4). These schemes can be used to correct the results of the CCSD/EOMCCSD calculations for the effects of triple (the MMCC(2,3) case) or triple and quadruple excitations (the MMCC(2,4) case). The MMCC(2,3) and MMCC(2,4) energy expressions are as follows:

$$E_\mu^{(\text{MMCC})}(2, 3) = E_\mu^{(\text{CCSD})} + \langle \Psi_\mu | M_{\mu,3}(2) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle, \quad (40)$$

$$E_{\mu}^{(\text{MMCC})}(2,4) = E_{\mu}^{(\text{CCSD})} + \langle \Psi_{\mu} | M_{\mu,3}(2) + [M_{\mu,4}(2) + T_1 M_{\mu,3}(2)] | \Phi \rangle / \langle \Psi_{\mu} | R_{\mu}^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle, \quad (41)$$

where $E_{\mu}^{(\text{CCSD})}$ is the CCSD ($\mu = 0$) or EOMCCSD ($\mu > 0$) energy, $T^{(\text{CCSD})}$ is the cluster operator obtained in the CCSD calculations (cf. Eq. (5)), $R_{\mu}^{(\text{CCSD})}$ is the corresponding EOMCCSD excitation operator (cf. Eq. (19); when $\mu = 0$, $R_{\mu}^{(\text{CCSD})} = 1$), and $M_{\mu,3}(2)$ and $M_{\mu,4}(2)$ are defined as

$$M_{\mu,3}(2) = \frac{1}{36} \mathfrak{M}_{\mu,abc}^{ijk}(2) a^a a^b a^c a_k a_j a_i, \quad (42)$$

and

$$M_{\mu,4}(2) = \frac{1}{576} \mathfrak{M}_{\mu,abcd}^{ijkl}(2) a^a a^b a^c a^d a_l a_k a_j a_i, \quad (43)$$

with $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ representing the triply and quadruply excited moments of the CCSD/EOMCCSD equations, respectively.

The explicit expression for the triply excited moment $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, entering the MMCC(2,3) and MMCC(2,4) approximations discussed in Sections 3.3 and 4.2 and corresponding to the projections of the CCSD/EOMCCSD equations on the triply excited determinants $|\Phi_{ijk}^{abc}\rangle$, in terms of the many-body components of the CCSD/EOMCCSD similarity-transformed Hamiltonian $\bar{H}^{(\text{CCSD})}$, Eq. (12), and operator $R_{\mu}^{(\text{CCSD})}$, Eq. (19), is

$$\begin{aligned} \mathfrak{M}_{\mu,abc}^{ijk}(2) = & \langle \Phi_{ijk}^{abc} | (\bar{H}_2^{(\text{CCSD})} R_{\mu,2})_C | \Phi \rangle + \langle \Phi_{ijk}^{abc} | [\bar{H}_3^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2})]_C | \Phi \rangle \\ & + \langle \Phi_{ijk}^{abc} | (\bar{H}_4^{(\text{CCSD})} R_{\mu,1})_C | \Phi \rangle + r_0(\mu) \mathfrak{M}_{0,abc}^{ijk}(2), \end{aligned} \quad (44)$$

where the ground-state moment $\mathfrak{M}_{0,abc}^{ijk}(2)$, obtained by projecting the CCSD equations on triply excited determinants, is given by

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | [H_N(T_2 + T_1 T_2 + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2 T_2 + \frac{1}{2}T_1 T_2^2 + \frac{1}{6}T_1^3 T_2)]_C | \Phi \rangle. \quad (45)$$

The analogous expression for the quadruply excited moments $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, entering the MMCC(2,4) approximation, has the form

$$\begin{aligned} \mathfrak{M}_{\mu,abcd}^{ijkl}(2) = & \langle \Phi_{ijkl}^{abcd} | (\bar{H}_3^{(\text{CCSD})} R_{\mu,2})_C | \Phi \rangle + \langle \Phi_{ijkl}^{abcd} | [\bar{H}_4^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2})]_C | \Phi \rangle \\ & + \langle \Phi_{ijkl}^{abcd} | (\bar{H}_3^{(\text{CCSD})} R_{\mu,1})_{DC} | \Phi \rangle + r_0(\mu) \mathfrak{M}_{0,abcd}^{ijkl}(2), \end{aligned} \quad (46)$$

where the ground-state moment $\mathfrak{M}_{0,abcd}^{ijkl}(2)$, obtained by projecting the CCSD equations on quadruply excited determinants, is expressed as

$$\mathfrak{M}_{0,abcd}^{ijkl}(2) = \langle \Phi_{ijkl}^{abcd} | [V_N(\frac{1}{2}T_2^2 + \frac{1}{2}T_1 T_2^2 + \frac{1}{6}T_2^3 + \frac{1}{4}T_1^2 T_2^2)]_C | \Phi \rangle. \quad (47)$$

The operators $\bar{H}_p^{(\text{CCSD})}$ in Eqs. (44) and (46) represent the p -body components of $\bar{H}^{(\text{CCSD})}$ and $H_N = H - \langle \Phi | H | \Phi \rangle$ is the Hamiltonian in the normal-ordered form. The diagrammatic techniques of many-body theory greatly facilitate the derivation of the explicit expressions for $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$. The diagrams and algebraic expressions representing the triply and quadruply excited moments of the CCSD/EOMCCSD equations, in terms of molecular integrals f_p^q and v_{pq}^{rs} and cluster and excitation amplitudes t_a^i , t_{ab}^{ij} , r_i^a , and r_{ij}^{ab} , are shown in Section 4.3 and

Appendix B. The fully factorized expressions for $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, which can be used in the efficient implementations of all MMCC(2,3) and MMCC(2,4) approximations, including the CI-corrected MMCC methods and the renormalized and completely-renormalized CC approaches discussed in Section 3.3 as well as the MRMBPT-corrected MMCC methods developed for this dissertation, are described in Section 4.4.

3.3 The Existing MMCC(m_A, m_B) Approximations

Depending on the form of $|\Psi_\mu\rangle$ in the MMCC energy equations, the existing MMCC(m_A, m_B) methods that have been developed prior to this thesis work fall into one of the following two categories: (i) the CI-corrected MMCC(m_A, m_B) schemes and (ii) the renormalized and completely renormalized CC methods for the ground-state problem, and their excited-state completely renormalized EOMCC extensions. We begin with the CI-corrected MMCC approaches.

3.3.1 The CI-corrected MMCC(2,3) and MMCC(2,4) Methods

In the CI-corrected MMCC(2,3) and MMCC(2,4) calculations, the wavefunctions $|\Psi_\mu\rangle$ in Eq. (40) and (41) are replaced with the wavefunctions obtained in the active-space CISDt^{21,87,126,127,251} and CISDtq^{127,251} calculations, respectively, as shown below:

$$E_\mu^{(\text{MMCC/CI})}(2,3) = E_\mu^{(\text{CCSD})} + \langle \Psi_\mu^{(\text{CISDt})} | M_{\mu,3}(2) | \Phi \rangle / \langle \Psi_\mu^{(\text{CISDt})} | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle, \quad (48)$$

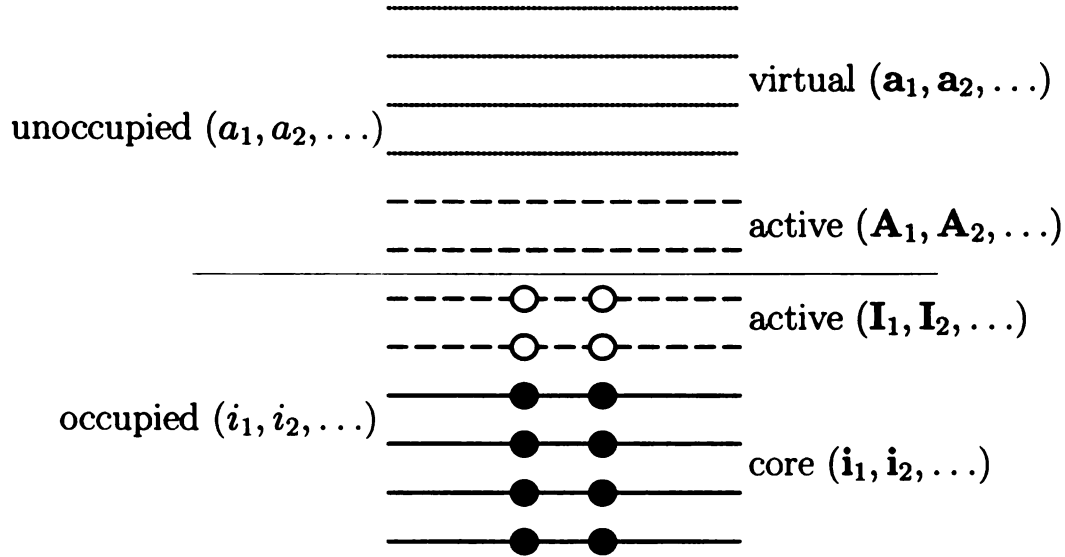


Figure 1: The orbital classification used in the active-space CI, MRMBPT, and the CI- and MRMBPT-corrected MMCC methods, such as MMCC(2,3)/CI, MMCC(2,4)/CI, MMCC(2,3)/PT, and MMCC(2,4)/PT. Core, active, and virtual orbitals are represented by solid, dashed, and dotted lines, respectively. Full and open circles represent core and active electrons of the reference determinant $|\Phi\rangle$ (the closed-shell reference determinant $|\Phi\rangle$ is assumed).

$$\begin{aligned}
E_{\mu}^{(\text{MMCC/CI})}(2,4) &= E_{\mu}^{(\text{CCSD})} + \langle \Psi_{\mu}^{(\text{CISDtq})} | M_{\mu,3}(2) + [M_{\mu,4}(2) + T_1 M_{\mu,3}(2)] | \Phi \rangle \\
&\quad / \langle \Psi_{\mu}^{(\text{CISDtq})} | R_{\mu}^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle.
\end{aligned} \tag{49}$$

In order to define the relevant CISDt and CISDtq wavefunctions, $|\Psi^{(\text{CISDt})}\rangle$ and $|\Psi^{(\text{CISDtq})}\rangle$, respectively, we follow the philosophy of multi-reference calculations, i.e., we first divide the available spin-orbitals into four groups (see Figure 1) of core spin-orbitals ($\mathbf{i}_1, \mathbf{i}_2, \dots$ or $\mathbf{i}, \mathbf{j}, \dots$), active spin-orbitals occupied in reference $|\Phi\rangle$ ($\mathbf{I}_1, \mathbf{I}_2, \dots$ or $\mathbf{I}, \mathbf{J}, \dots$), active spin-orbitals unoccupied in reference $|\Phi\rangle$ ($\mathbf{A}_1, \mathbf{A}_2, \dots$ or $\mathbf{A}, \mathbf{B}, \dots$), and virtual spin-orbitals ($\mathbf{a}_1, \mathbf{a}_2, \dots$ or $\mathbf{a}, \mathbf{b}, \dots$). The choice of active spin-

orbitals (typically, a few highest-energy occupied spin-orbitals and a few lowest-energy unoccupied spin-orbitals) is dictated by the dominant orbital excitations in the ground and excited states that we would like to calculate. A few examples of reasonable choices of active orbitals in calculations involving bond breaking and excited states are discussed in Chapter 5. Once the active orbitals are selected, the CISDt and CISDtq wavefunctions are defined as follows:

$$|\Psi_{\mu}^{(\text{CISDt})}\rangle = (C_{\mu,0} + C_{\mu,1} + C_{\mu,2} + c_{\mu,3})|\Phi\rangle, \quad (50)$$

$$|\Psi_{\mu}^{(\text{CISDtq})}\rangle = (C_{\mu,0} + C_{\mu,1} + C_{\mu,2} + c_{\mu,3} + c_{\mu,4})|\Phi\rangle, \quad (51)$$

where

$$C_{\mu,0} = c_0(\mu) \mathbf{1}, \quad (52)$$

$$C_{\mu,1} = c_a^i(\mu) a^a a_i = \sum_{i,a} c_a^i(\mu) a^a a_i, \quad (53)$$

and

$$C_{\mu,2} = \frac{1}{4} c_{ab}^{ij}(\mu) a^a a^b a_j a_i = \sum_{i<j, a<b} c_{ab}^{ij}(\mu) a^a a^b a_j a_i \quad (54)$$

are the usual reference, singly, and doubly excited contributions, respectively, to $|\Psi_{\mu}^{(\text{CISDt})}\rangle$ and $|\Psi_{\mu}^{(\text{CISDtq})}\rangle$, and

$$c_{\mu,3} = \sum_{i<j<\mathbf{K}, \mathbf{A}<b<c} c_{\mathbf{A}bc}^{ij\mathbf{K}}(\mu) a^{\mathbf{A}} a^b a^c a_{\mathbf{K}} a_j a_i, \quad (55)$$

$$c_{\mu,4} = \sum_{i<j<\mathbf{K}<\mathbf{L}, \mathbf{A}<\mathbf{B}<c<d} c_{\mathbf{A}\mathbf{B}cd}^{ij\mathbf{KL}}(\mu) a^{\mathbf{A}} a^{\mathbf{B}} a^c a^d a_{\mathbf{L}} a_{\mathbf{K}} a_j a_i. \quad (56)$$

Thus, in the CISDt approach, used in the CI-corrected MMCC(2,3) calculations (cf Eq. (48)), the wavefunctions $|\Psi_\mu\rangle$ are constructed by including all singles and doubles from $|\Phi\rangle$ and a relatively small set of internal and semi-internal triples containing at least one active occupied and one active unoccupied spin-orbital indices defined by Eq. (55). For the CISDtq approach, used for the CI-corrected MMCC(2,4) approach, an additional relatively small set of quadruples containing at least two active occupied and at least two active unoccupied spin-orbital indices is also required. The CI coefficients defining the CISDt and CISDtq wavefunctions are determined variationally, as in all CI calculations.

One of the main advantages of the CI-corrected MMCC schemes, including the MMCC(2,3)/CI and MMCC(2,4)/CI methods, is a very good control of the quality of wavefunctions $|\Psi_\mu\rangle$ used to construct the noniterative corrections $\delta_\mu(m_A, m_B)$, which is accomplished through the judicious choice of active orbitals that can always be adjusted to the type of bond-breaking or excited excited states of interest. Another advantage of the CI-corrected MMCC methods is their relatively low computer cost compared to many other approaches, which is a consequence of the fact that it is usually sufficient to use very small active orbital spaces to obtain excellent results.^{21,25,26,87,126,127,251} If N_o (N_u) is the number of active orbitals occupied (unoccupied) in $|\Phi\rangle$, the most expensive steps of the CISDt and CISDtq methods scale as $N_o N_u n_o^2 n_u^4$ and $N_o^2 N_u^2 n_o^2 n_u^4$, respectively, which are considerable savings in the computer effort compared to the $n_o^3 n_u^5$ and $n_o^4 n_u^6$ scalings of the parent CISDT (CI singles, doubles, and triples) and CISDTQ (CI singles, doubles, triples, and quadruples), respectively. Furthermore, the numbers of triples and quadruples considered in the

CISDt and CISDtq calculations are $\sim N_o N_u n_o^2 n_u^2$ and $\sim N_o^2 N_u^2 n_o^2 n_u^2$, respectively, which is significantly less than the numbers of all triples and quadruples if the number of active orbitals is small. For instance, the number of triples used in the CISDt-corrected MMCC(2,3) calculations is usually very small (no more than $\sim 30\%$ of all triples, in many cases even less than that). Additionally, the CPU times required to construct the relevant $\delta_\mu(2,3)$ corrections are often on the order of the CPU time of a single CCSD/EOMCCSD iteration. Similar remarks apply to the CISDtq-corrected MMCC(2,4) calculations.

Thus, the CI-corrected MMCC methods can be regarded as useful approaches to accurate calculations of ground- and excited-state potential energy surfaces. One may contemplate, however, an idea of reducing the costs of the CISDt-corrected MMCC(2,3) and CISDtq-corrected MMCC(2,4) calculations even further by replacing the CISDt or CISDtq wavefunctions in the MMCC(2,3) and MMCC(2,4) expressions by the wavefunctions obtained with low-order MRMBPT approaches, as presented in Chapter 4.

In the next subsection, we describe an alternative to externally corrected MMCC schemes using nothing else but the cluster and excitation operators obtained in the CC/EOMCC calculations instead of non-CC wavefunctions to define the relevant wavefunction $|\Psi_\mu\rangle$.

3.3.2 The Renormalized and Completely Renormalized CC Methods for Ground and Excited States

An interesting alternative to the CI-corrected MMCC methods, discussed in Section 3.3.1, is offered by the renormalized (R) and completely renormalized (CR) CC/EOMCC methods which can be considered as purely single-reference, “black-box” methods based on the $\text{MMCC}(m_A, m_B)$ approximations.

Let us begin with the ground-state R-CC and CR-CC methods. The R-CCSD(T) and CR-CCSD(T) methods are examples of the $\text{MMCC}(2,3)$ schemes, whereas the R-CCSD(TQ) and CR-CCSD(TQ) approaches are examples of the $\text{MMCC}(2,4)$ approximations. The energy formula defining CR-CCSD(T) method is

$$E_0^{(\text{CR-CCSD(T)})} = E_0^{(\text{CCSD})} + \langle \Psi_0^{(\text{CCSD(T)})} | M_{0,3}(2) | \Phi \rangle / \langle \Psi_0^{(\text{CCSD(T)})} | e^{T^{(\text{CCSD})}} | \Phi \rangle. \quad (57)$$

Here, again, $T^{(\text{CCSD})}$ refers to the cluster operators obtained in the CCSD calculations and $M_{0,3}(2)$ is given by Eq. (42) using the generalized moments $\mathfrak{M}_{0,abc}^{ijk}(2)$ defined by Eq. (44). The $|\Psi_0^{(\text{CCSD(T)})}\rangle$ wavefunction, entering Eq. (57), is a simple MBPT-like expression

$$|\Psi_0^{(\text{CCSD(T)})}\rangle = [1 + T_1 + T_2 + R_0^{(3)}(V_N T_2)_C + R_0^{(3)} V_N T_1] |\Phi\rangle \quad (58)$$

with $R_0^{(3)}$ representing the three-body component of the MBPT reduced resolvent and V_N designating the two-body part of the Hamiltonian in the normal-ordered form. The R-CCSD(T) approach is obtained by replacing the $\mathfrak{M}_{0,abc}^{ijk}(2)$ moments by their

lowest-order estimates, i.e. $\langle \Phi_{ijk}^{abc} | (V_N T_2)_C | \Phi \rangle$. The R-CCSD(T) approach reduces to standard CCSD(T) method when the $\langle \Psi^{(\text{CCSD(T)})} | e^{T^{(\text{CCSD})}} | \Phi \rangle$ denominator in the R-CCSD(T) energy formula is replaced by 1.

The idea of renormalizing the CCSD(T) approach can also be extended to the CCSD(TQ) method. Two variants of the CR-CCSD(TQ) approach, which are labeled “a” and “b”, are mentioned here. The CR-CCSD(TQ) energy formulas can be given in the following form:^{18,19,87,88,90}

$$E_0^{(\text{CR-CCSD(TQ),x})} = E_0^{(\text{CCSD})} + \langle \Psi_0^{(\text{CCSD(TQ),x})} | [M_{0,3}(2) + T_1 M_{0,3}(2) + M_{0,4}(2)] | \Phi \rangle / \langle \Psi_0^{(\text{CCSD(TQ),x})} | e^{T^{(\text{CCSD})}} | \Phi \rangle \quad (\text{x} = \text{a}, \text{b}), \quad (59)$$

where

$$|\Psi_0^{(\text{CCSD(TQ),a})}\rangle = |\Psi_0^{(\text{CCSD(T)})}\rangle + \frac{1}{2} T_2 T_2^{(1)} |\Phi\rangle \quad (60)$$

and

$$|\Psi_0^{(\text{CCSD(TQ),b})}\rangle = |\Psi_0^{(\text{CCSD(T)})}\rangle + \frac{1}{2} T_2^2 |\Phi\rangle, \quad (61)$$

with $T_2^{(1)}$ representing the first-order MBPT estimate of T_2 . The $M_{0,3}(2)$ operator is defined by Eq. (42) and $M_{0,4}(2)$ is defined by Eq. (43). The R-CCSD(TQ) methods are obtained by dropping the $T_1 M_{0,3}(2)$ term in Eq. (59) and by replacing the $\mathfrak{M}_{0,abc}^{ijk}(2)$ and $\mathfrak{M}_{0,abcd}^{ijkl}(2)$ moments that enter the definitions of $M_{0,3}(2)$ and $M_{0,4}(2)$, respectively, by their lowest-order estimates. As in the case of the R-CCSD(T) method, one can obtain the standard CCSD(TQ) approaches by replacing the overlap denominator $\langle \Psi_0^{(\text{CCSD(TQ),x})} | e^{T^{(\text{CCSD})}} | \Phi \rangle$ in the R-CCSD(TQ) energy expression by 1.

The standard CCSD(T) and CCSD(TQ) approaches and their (C)R-CCSD(T) and (C)R-CCSD(TQ) counterparts have nearly identical computer costs. For example, the costs of the conventional CCSD(T) calculations are $n_o^2 n_u^4$ in the iterative CCSD steps and $n_o^3 n_u^4$ in the noniterative steps defining the triples correction while the CR-CCSD(T) approach scales as $n_o^2 n_u^4$ in the iterative CCSD steps and $2n_o^3 n_u^4$ in the noniterative triples correction part. Similar remarks apply to other R-CC and CR-CC methods. In particular, the CR-CCSD(TQ),x approaches have computational steps that scale as $n_o^2 n_u^4$ in the CCSD part, $2n_o^3 n_u^4$ in the triples correction parts, and $2n_o^2 n_u^5$ in parts that deal with the quadruples corrections. This should be compared to the costs of conventional CCSD(TQ) calculations which are very similar, namely, $n_o^2 n_u^4$ in the CCSD steps, $n_o^3 n_u^4$ in the (T) part, and $n_o^2 n_u^5$ in the (Q) parts. As already mentioned, the renormalized CC methods, such as CR-CCSD(T) or its recently formulated size extensive extension (not discussed here), termed CR-CC(2,3),^{70,227,228} are particularly useful in studies of reaction pathways involving single bond breaking and biradicals.^{18,20–26,68–70,95,98,187,188,227,228,230–236} They remove failures of conventional CCSD(T), CCSD(TQ), and similar approximations without making the calculations more complex or considerably more expensive.

The idea of renormalizing conventional CC methods via the MMCC formalism can be extended to excited states. For example, in the CR-EOMCCSD(T) approach^{22,25,26,226} which is an example of the excited-state MMCC(2,3) schemes, the energies of ground and excited states E_μ are calculated as follows:

$$E_\mu^{(\text{CR-EOMCCSD(T)})} = E_\mu^{(\text{CCSD})} + \langle \Psi_\mu^{(\text{CR-EOMCCSD(T)})} | M_{\mu,3}(2) | \Phi \rangle /$$

$$\langle \Psi_{\mu}^{(\text{CR-EOMCCSD(T)})} | R_{\mu}^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle. \quad (62)$$

Depending on the specific form of the wavefunction $|\Psi_{\mu}^{(\text{CR-EOMCCSD(T)})}\rangle$ in Eq. (62), several variants of the CR-EOMCCSD(T) approach can be considered. Here, only one variant called ID (the CR-EOMCCSD(T),ID method), which represents one of the most complete versions of the CR-EOMCCSD(T) approach and which usually provides the most accurate description of excited states compared to other variants, is presented. The CR-EOMCCSD(T) wavefunction entering Eq. (62) is defined in this case as

$$\begin{aligned} |\Psi_{\mu}^{(\text{CR-EOMCCSD(T)})}\rangle &= \bar{P}(R_{\mu,0} + R_{\mu,1} + R_{\mu,2} + \tilde{R}_{\mu,3})e^{T^{(\text{CCSD})}}|\Phi\rangle \\ &= \{R_{\mu,0} + (R_{\mu,1} + R_{\mu,0}T_1) \\ &\quad + [R_{\mu,2} + R_{\mu,1}T_1 + R_{\mu,0}(T_2 + \tfrac{1}{2}T_1^2)] \\ &\quad + [\tilde{R}_{\mu,3} + R_{\mu,2}T_1 + R_{\mu,1}(T_2 + \tfrac{1}{2}T_1^2) \\ &\quad + R_{\mu,0}(T_1T_2 + \tfrac{1}{6}T_1^3)]\}|\Phi\rangle, \end{aligned} \quad (63)$$

where $\bar{P}$ is a projection operator on the subspace spanned by the reference $|\Phi\rangle$ and all singly, doubly, and triply excited determinants. The triple excitation operator $\tilde{R}_{\mu,3}$, entering Eq. (63), is calculated as

$$\tilde{R}_{\mu,3} = \frac{1}{36} \tilde{r}_{abc}^{ijk}(\mu) a^a a^b a^c a_k a_j a_i, \quad (64)$$

where

$$\tilde{r}_{abc}^{ijk}(\mu) = \mathfrak{M}_{\mu,abc}^{ijk}(2)/D_{\mu,abc}^{ijk} \quad (65)$$

are the approximate values of the triple excitation amplitudes $r_{abc}^{ijk}(\mu)$ resulting from the analysis of the full EOMCCSDT eigenvalue problem.²² As implied by Eq. (65), the approximate amplitudes $\tilde{r}_{abc}^{ijk}(\mu)$ are calculated using exactly the same set of triply excited moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ of the CCSD/EOMCCSD equations that enters the MMCC(2,3) energy expression, Eq. (40). This greatly facilitates the computer coding effort, since one can reuse the moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, which are needed to construct the triples correction of CR-EOMCCSD(T) anyway, to determine the $\tilde{r}_{abc}^{ijk}(\mu)$ amplitudes. The $D_{\mu,abc}^{ijk}$ quantities that enter Eq. (65) represent the perturbative denominators for triple excitations, which are defined as follows:

$$\begin{aligned} D_{\mu,abc}^{ijk} &= E_{\mu}^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \\ &= \omega_{\mu}^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}_1^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \\ &\quad - \langle \Phi_{ijk}^{abc} | \bar{H}_2^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \\ &\quad - \langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle, \end{aligned} \quad (66)$$

where $\bar{H}_p^{(\text{CCSD})}$, $p = 1 - 3$, are the one-, two-, and three-body components of the CCSD/EOMCCSD similarity-transformed Hamiltonian $\bar{H}^{(\text{CCSD})}$, respectively, and $\omega_{\mu}^{(\text{CCSD})}$ is the EOMCCSD vertical excitation energy.

One of the main advantages of the renormalized and completely renormalized methods is the fact these methods are as easy to use as the standard “black-box”

approaches of the CCSD(T) type while considerably improving the description of the bond breaking region and excited states without the need to define active orbitals or other elements of multi-reference theory. However, as mentioned earlier, there are cases, where the degree of quasi-degeneracy is so big that one has to use elements of multi-reference theory within the MMCC formalism. The CI-corrected MMCC methods are one possible way of incorporating multi-reference concepts into the MMCC considerations. The MRMBPT-corrected MMCC methods developed in this work represent another way. Brief information about the basic elements of MRMBPT is presented next.

3.4 The Basic Elements of Multi-Reference Many-Body Perturbation Theory (MRMBPT)

All genuine multireference theories involve two fundamental concepts, namely, that of the model or reference space $\mathcal{M}_0$ and that of the wave operator U . The model space $\mathcal{M}_0$,

$$\mathcal{M}_0 = \{|\Phi_p\rangle\}_{p=1}^M, \quad (67)$$

is spanned by M determinants or configuration state functions $|\Phi_p\rangle$ ($p = 1, \dots, M$) that provide a reasonable zero-order description of the target space

$$\mathcal{M} = \{|\Psi_\mu\rangle\}_{\mu=0}^{M-1}, \quad (68)$$

spanned by M quasi-degenerate eigenstates $|\Psi_\mu\rangle$ ($\mu = 0, 1, \dots, M-1$) of the electronic Hamiltonian H ,

$$H|\Psi_\mu\rangle = E_\mu|\Psi_\mu\rangle. \quad (69)$$

In order to define the reference configurations $|\Phi_p\rangle$, the employed molecular orbital basis set is partitioned into core, active, and virtual orbitals in a similar manner as in Figure 1. The core orbitals are occupied and the virtual ones are unoccupied in all reference configurations. The references $|\Phi_p\rangle$ differ in the occupancies of active orbitals. All possible distributions of active electrons among the active orbitals result in a complete model or active space (CAS). The use of CAS is essential to obtain size extensive results in the MRMBPT calculations, if the “perturb then diagonalize” MRMBPT method, summarized below, is considered.

The wave operator $U: \mathcal{M}_0 \rightarrow \mathcal{M}$ is defined as a one-to-one mapping between $\mathcal{M}_0$ and $\mathcal{M}$ that satisfies the intermediate normalization condition,

$$PU = P, \quad (70)$$

and the relation determining its kernel, i.e.,

$$UQ = 0. \quad (71)$$

Here, P and Q are the projection operators onto, respectively, model space $\mathcal{M}_0$ and

its orthogonal complement $\mathcal{M}_0^\perp$ in the N -electron Hilbert space,

$$P = \sum_{p=1}^M P^{(p)}, \quad P^{(p)} = |\Phi_p\rangle\langle\Phi_p|, \quad (72)$$

$$Q = 1 - P. \quad (73)$$

Based on Eqs. (70)-(73), although, unlike P and Q , the wave operator U is not Hermitian, $U \neq U^\dagger$.

The MRMBPT wavefunctions $|\Psi_\mu\rangle$ are calculated using the formula,

$$|\Psi_\mu\rangle = \sum_{p=1}^M c_{p\mu} |\Phi_p\rangle + \sum_{n=1}^{\infty} \left(\sum_{p=1}^M c_{p\mu} U^{(n)} |\Phi_p\rangle \right), \quad (74)$$

where $U^{(1)}$, $U^{(2)}$, etc. represent perturbative corrections to the wave operator U (expressed in terms of excited configurations from $\mathcal{M}_0^\perp$, i.e., other than $|\Phi_p\rangle$, $p=1,\dots,M$).

These corrections describe dynamical correlation effects.

The coefficients $c_{p\mu}$, which describe the nondynamical correlation effects, define the zero-order states belonging to $\mathcal{M}_0$,

$$|\Psi_\mu^{(0)}\rangle = \sum_{p=1}^M c_{p\mu} |\Phi_p\rangle. \quad (75)$$

In the “perturb then diagonalize” MRMBPT methods that follow the ideas described in Ref. 155, these coefficients and the corresponding energies E_μ of the ground and excited states $|\Psi_\mu\rangle$, $\mu = 0, 1, \dots, M-1$, are obtained by diagonalizing the effective

Hamiltonian,

$$H^{\text{eff}} = PHUP = PHP + \sum_{n=1}^{\infty} PHU^{(n)}P, \quad (76)$$

in the model space $\mathcal{M}_0$,

$$H^{\text{eff}}|\Psi_{\mu}^{(0)}\rangle = E_{\mu}|\Psi_{\mu}^{(0)}\rangle. \quad (77)$$

In the practical implementations of such MRMBPT theories, the wave operator U is truncated at some, preferably low, perturbation theory order n . When U is truncated at the first-order term $U^{(1)}$, i.e., $U = P + U^{(1)}$, the second-order MRMBPT function (MRMBPT(2)) is obtained; second-order since the resulting energies E_{μ} are correct through second order).

One can considerably simplify the above considerations, which are based on the generalized Bloch formalism,²⁶² in which the wave operator U is determined by solving the multiroot generalized Bloch equation²⁶² $HU = UHU$ (in the case of MRMBPT, using perturbation theory), by formulating the “diagonalize then perturb” MRMBPT methods. In those methods, one continues to use Eq. (75) to determine the zero-order states, but the coefficients $c_{p\mu}$ of the zero-order states are obtained by diagonalizing the bare Hamiltonian H rather than the effective Hamiltonian H^{eff} . Perturbative corrections to the zero-order energies $E^{(0)}$ are calculated *a posteriori* in a state-selective manner without using the multiroot generalized Bloch formalism. As mentioned in the Introduction, several methods, including the popular CASPT2 and MC-QDPT approaches, are in this category. The MRMBPT approach used to define the MRMBPT-corrected MMCC schemes discussed in detail in the next chapter (Section 4.1) belongs to the category of the “diagonalize then perturb” methods as

well.

4 The MMCC Methods Employing Multi-Reference Many-Body Perturbation Theory (MMCC/PT)

In this chapter, the new variant of the MMCC theory, referred to as the MRMBPT-corrected MMCC or, for brevity, MMCC/PT, in which the full CI wavefunctions $|\Psi_\mu\rangle$ in Eqs. (26) or (39) are approximated by the wavefunctions obtained from the low-order MRMBPT calculations, is described. The approximate MRMBPT wavefunctions used in the MMCC(m_A, m_B)/PT approaches implemented in this work are discussed. Moreover, the diagrammatic formulation of the resulting MMCC(2,3)/PT and MMCC(2,4)/PT schemes are presented. The details of the algorithm that enables one to achieve a high degree of code vectorization for the generalized moments of CC equations defining the MMCC methods are described as well.

4.1 The Multi-Reference Many-Body Perturbation Theory Wavefunctions Used in the MMCC/PT Approaches

As in all multi-reference considerations and in analogy to the CISDt and CISDtq methods discussed in Section 3.3.1, in order to define the computationally simple form of the low-order MRMBPT wavefunctions $|\Psi_\mu^{(\text{MRMBPT})}\rangle$ for the MRMBPT-corrected MMCC calculations, we begin by partitioning the molecular orbital basis set into four groups as shown in Figure 1: core spin-orbitals ($i_1, i_2, \dots$ or $i, j, \dots$), active spin-orbitals occupied in reference $|\Phi\rangle$ ($I_1, I_2, \dots$ or $I, J, \dots$), active spin-orbitals unoccupied in reference $|\Phi\rangle$ ($A_1, A_2, \dots$ or $A, B, \dots$), and virtual spin-orbitals ($a_1,$

$\mathbf{a}_2, \dots$ or $\mathbf{a}, \mathbf{b}, \dots$). As in the CI-corrected MMCC schemes, reference $|\Phi\rangle$ is one of the many reference determinants that we choose as a Fermi vacuum for the CC/EOMCC and MMCC calculations. By distributing active electrons among active spin-orbitals in all possible ways, we generate a certain number (designated here by M) of reference determinants $|\Phi_p\rangle$ (including, of course, $|\Phi\rangle$), which span the complete model space or P -space $\mathcal{M}_0$. Then, we define the zeroth-order wavefunctions of the ground and excited states $|\bar{\Psi}_\mu^{(P)}\rangle$ of interest as linear combinations of the reference configurations $|\Phi_p\rangle$,

$$|\bar{\Psi}_\mu^{(P)}\rangle = \sum_{p=1}^M \bar{c}_{p\mu} |\Phi_p\rangle, \quad (78)$$

where the coefficients $\bar{c}_{p\mu}$ and the corresponding zeroth-order eigenvalues $\bar{E}_\mu$ are obtained by diagonalizing the Hamiltonian H in the model space $\mathcal{M}_0$.

Once the model space $\mathcal{M}_0$ is defined, we introduce the Q -space which in the MMCC/PT method pursued here is a subspace of the orthogonal complement $\mathcal{M}_0^\perp$ spanned by all singly and doubly excited determinants with respect to each reference $|\Phi_p\rangle$ ($p = 1, \dots, M$), as is done, for example, in the MRCISD calculations. After eliminating the repetitions in the list of Q -space configurations, the resulting MRMBPT wavefunctions $|\Psi_\mu^{(\text{MRMBPT})}\rangle$, which will eventually be used to design the MMCC/PT (e.g. MMCC(2,3)/PT and MMCC(2,4)/PT) energy corrections, are then defined as the linear combinations of the P -space and Q -space contributions,

$$|\Psi_\mu^{(\text{MRMBPT})}\rangle = \sum_{p=1}^M c_{p\mu} |\Phi_p\rangle + \sum_{q=M+1}^R c_{q\mu} |\Phi_q\rangle, \quad (79)$$

where $|\Phi_p\rangle$ ($p = 1, \dots, M$) are the reference determinants and $|\Phi_q\rangle$ ($q = M+1, \dots, R$) are the Q -space determinants, as expressed above. In principle, we could use any of the existing low-order MRMBPT methods to determine the approximate values of the coefficients $c_{p\mu}$ and $c_{q\mu}$ that enter Eq. (79) and perform the corresponding MMCC(m_A, m_B)/PT calculations. In the simplified MRMBPT model used in the present implementation of the MMCC(2,3)/PT method^{69,97,98} as well as the MMCC(2,4)/PT scheme, we evaluate the relevant coefficients $c_{p\mu}$ ($p = 1, \dots, M$) and $c_{q\mu}$ ($q = M+1, \dots, R$) in Eq. (79) by applying the Löwdin-style partitioning technique^{263,264} to the Hamiltonian matrix in the space spanned by the P -space and Q -space determinants $|\Phi_p\rangle$ and $|\Phi_q\rangle$, respectively. Thus, if $\mathbf{C}_{P\mu}$ and $\mathbf{C}_{Q\mu}$ are the column vectors of coefficients $c_{p\mu}$ with $p = 1, \dots, M$ and $c_{q\mu}$ with $q = M+1, \dots, R$, respectively, and if $\mathbf{H}_{PP}$, $\mathbf{H}_{PQ}$, $\mathbf{H}_{QP}$, and $\mathbf{H}_{QQ}$ are the corresponding PP , PQ , QP , and QQ blocks of the Hamiltonian, we can write the Hamiltonian eigenvalue problem for the wavefunctions $|\Psi_\mu^{(\text{MRMBPT})}\rangle$, Eq. (79), in the following manner:

$$\begin{pmatrix} \mathbf{H}_{PP} & \mathbf{H}_{PQ} \\ \mathbf{H}_{QP} & \mathbf{H}_{QQ} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{P\mu} \\ \mathbf{C}_{Q\mu} \end{pmatrix} = E_\mu \begin{pmatrix} \mathbf{C}_{P\mu} \\ \mathbf{C}_{Q\mu} \end{pmatrix}. \quad (80)$$

In other words, we obtain

$$\mathbf{H}_{PP}\mathbf{C}_{P\mu} + \mathbf{H}_{PQ}\mathbf{C}_{Q\mu} = E_\mu\mathbf{C}_{P\mu}, \quad (81)$$

$$\mathbf{H}_{QP}\mathbf{C}_{P\mu} + \mathbf{H}_{QQ}\mathbf{C}_{Q\mu} = E_\mu\mathbf{C}_{Q\mu}. \quad (82)$$

If we approximate the QQ block of the Hamiltonian matrix entering Eq. (80), $\mathbf{H}_{QQ}$, by the diagonal matrix elements $\langle \Phi_q | H | \Phi_q \rangle$, we can write

$$\mathbf{C}_{Q\mu} \approx (E_\mu \mathbf{1} - \mathbf{D}_Q)^{-1} \mathbf{H}_{QP} \mathbf{C}_{P\mu}, \quad (83)$$

or, more explicitly,

$$c_{q\mu} \approx \sum_{p=1}^M (E_\mu - \langle \Phi_q | H | \Phi_q \rangle)^{-1} \langle \Phi_q | H | \Phi_p \rangle c_{p\mu}, \quad (q = M+1, \dots, R), \quad (84)$$

where $\mathbf{D}_Q$ in Eq. (83) is the diagonal part of $\mathbf{H}_{QQ}$. In practice, we obtain the working equation for the approximate values of the coefficients $c_{q\mu}$ ($q = M+1, \dots, R$) by replacing the energies E_μ and coefficients $c_{p\mu}$ ($p = 1, \dots, M$) in Eq. (84) by the zero-order energies $\bar{E}_\mu$ and coefficients $\bar{c}_{p\mu}$, respectively, resulting from the diagonalization of the Hamiltonian in the model space $\mathcal{M}_0$ (diagonalization of $\mathbf{H}_{PP}$; cf. Eq. (78)).

We use the resulting approximate values of the coefficients $c_{q\mu}$,

$$\bar{c}_{q\mu} = \sum_{p=1}^M (\bar{E}_\mu - \langle \Phi_q | H | \Phi_q \rangle)^{-1} \langle \Phi_q | H | \Phi_p \rangle \bar{c}_{p\mu}, \quad (q = M+1, \dots, R), \quad (85)$$

along with the coefficients $\bar{c}_{p\mu}$ obtained by diagonalizing $\mathbf{H}_{PP}$, to define the perturbed states of the MRMBPT theory exploited in this thesis work, which are defined as

$$|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle = \sum_{p=1}^M \bar{c}_{p\mu} |\Phi_p\rangle + \sum_{q=M+1}^R \bar{c}_{q\mu} |\Phi_q\rangle. \quad (86)$$

The wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86), are used instead of the exact $|\Psi_\mu\rangle$ states

in the MMCC(m_A, m_B) energy expressions, Eqs. (38) and (39), to define the family of the MMCC(m_A, m_B)/PT approximations.

The above perturbative procedure based on the partitioning of the Hamiltonian into the P -space and Q -space contributions equivalent to the MRCISD problem has an advantage that we only have to consider the QP matrix elements of the Hamiltonian (the $\langle \Phi_q | H | \Phi_p \rangle$ matrix elements) and the diagonal $\langle \Phi_q | H | \Phi_q \rangle$ matrix elements in the process of defining $|\bar{\Psi}_\mu\rangle$. Another advantage of this procedure is the fact that the zero-order states are obtained by simply diagonalizing the Hamiltonian in $\mathcal{M}_0$ to obtain the relevant coefficients $\bar{c}_{p\mu}$.

We have developed computer codes for the MRMBPT model defined by Eqs. (78), (85), and (86). In the actual construction of the MRMBPT wavefunctions $|\bar{\Psi}_\mu\rangle$, we use a complete model space obtained by all possible distributions of active electrons among active orbitals allowed by the spin and spatial symmetries. As discussed earlier, we limit ourselves to the Q spaces corresponding to the MRCISD problem. Because of the fact that we are mainly interested in the MMCC(2,3) and MMCC(2,4) approximations and to further simplify our MRMBPT calculations, we decided to consider only those Q -space configurations that are at most quadruply excited with respect to the reference determinant $|\Phi\rangle$ used in the CCSD/EOMCCSD and subsequent MMCC(2,3) and MMCC(2,4) calculations. Furthermore, the allowed singly excited Q -space configurations from $\mathcal{M}_0$ to $\mathcal{M}_0^\perp$ are:

- a. core $\longrightarrow$ active
- b. core $\longrightarrow$ virtual
- c. active $\longrightarrow$ virtual

and for all cases the allowed excitations are of the $\alpha \rightarrow \alpha$ and $\beta \rightarrow \beta$ types, since we are interested in the $S_z = 0$ states (in practice, singlet states) obtained out of the restricted Hartree-Fock (RHF) reference. Similarly, the doubly excited Q -space configurations from $\mathcal{M}_0$ to $\mathcal{M}_0^\perp$ can be divided into the following eight categories:

- a. core, core $\longrightarrow$ active, active
- b. core, core $\longrightarrow$ active, virtual
- c. core, core $\longrightarrow$ virtual, virtual
- d. core, active $\longrightarrow$ active, active
- e. core, active $\longrightarrow$ active, virtual
- f. core, active $\longrightarrow$ virtual, virtual
- g. active, active $\longrightarrow$ active, virtual
- h. active, active $\longrightarrow$ virtual, virtual

Again, due to the conservation of spin, the allowed Q -space double excitations are $\alpha\alpha \rightarrow \alpha\alpha$, $\beta\beta \rightarrow \beta\beta$, $\alpha\beta \rightarrow \alpha\beta$, $\alpha\beta \rightarrow \beta\alpha$, $\beta\alpha \rightarrow \beta\alpha$, and $\beta\alpha \rightarrow \alpha\beta$, if the RHF determinant is used as reference $|\Phi\rangle$.

We have implemented the simplified MRMBPT scheme described above and tested its usefulness in the MMCC calculations by examining its performance in several benchmark calculations discussed in Chapter 5. The relevant MRMBPT-corrected MMCC(2,3) and MMCC(2,4) approaches are discussed next.

4.2 The MRMBPT-corrected MMCC(2,3) and MMCC(2,4)

Approaches: MMCC(2,3)/PT and MMCC(2,4)/PT

As already mentioned, in this dissertation we focus on the basic MMCC(2,3)/PT and MMCC(2,4)/PT approaches in which the CCSD/EOMCCSD energies are corrected for the leading triples or triples and quadruples effects via corrections $\delta_\mu(2,3)$ and $\delta_\mu(2,4)$, respectively, calculated with the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86). In order to use the multi-reference wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ in the single-reference MMCC formalism, first we have to rewrite the $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ states in the form of CI expansions relative to the reference determinant $|\Phi\rangle$ used in the CC/EOMCC and MMCC calculations, as shown below:

$$|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle = (\bar{C}_{\mu,0} + \bar{C}_{\mu,1} + \bar{C}_{\mu,2} + \bar{C}_{\mu,3} + \bar{C}_{\mu,4} + \dots)|\Phi\rangle, \quad (87)$$

where

$$\bar{C}_{\mu,0} = \bar{c}_0(\mu) \mathbf{1}, \quad (88)$$

$$\bar{C}_{\mu,1} = \bar{c}_a^i(\mu) a^a a_i = \sum_{i,a} \bar{c}_a^i(\mu) a^a a_i, \quad (89)$$

$$\bar{C}_{\mu,2} = \frac{1}{4} \bar{c}_{ab}^{ij}(\mu) a^a a^b a_j a_i = \sum_{i<j, a<b} \bar{c}_{ab}^{ij}(\mu) a^a a^b a_j a_i, \quad (90)$$

$$\bar{C}_{\mu,3} = \frac{1}{36} \bar{c}_{abc}^{ijk}(\mu) a^a a^b a^c a_k a_j a_i = \sum_{i<j<k, a<b<c} \bar{c}_{abc}^{ijk}(\mu) a^a a^b a^c a_k a_j a_i, \quad (91)$$

and

$$\bar{C}_{\mu,4} = \frac{1}{576} \bar{c}_{abcd}^{ijkl}(\mu) a^a a^b a^c a^d a_i a_k a_j a_i = \sum_{i < j < k < l, a < b < c < d} \bar{c}_{abcd}^{ijkl}(\mu) a^a a^b a^c a^d a_i a_k a_j a_i \quad (92)$$

are the corresponding particle-hole excitation operators relative to $|\Phi\rangle$ defining the reference, singly, doubly, triply, and quadruply excited contributions to $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, respectively. In the specific case of the MMCC(2,3)/PT and MMCC(2,4)/PT approximations explored in this work, we further simplify the wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, in Eq. (87), by truncating the CI expansions for the $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ at the triply excited determinants (the $\bar{C}_{\mu,3}|\Phi\rangle$ term) in the MMCC(2,3)/PT case and at the quadruply excited determinants (the $\bar{C}_{\mu,4}|\Phi\rangle$ term) in the MMCC(2,4)/PT case. The final energy expressions for the MMCC(2,3)/PT and MMCC(2,4)/PT energies, obtained by replacing $|\Psi_\mu\rangle$ in Eqs. (40) and (41) by $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (87), truncated at the triply (the MMCC(2,3) case) or triply and quadruply (the MMCC(2,4) case) excited determinants, respectively, relative to $|\Phi\rangle$, are

$$E_\mu^{(\text{MMCC/PT})}(2,3) = E_\mu^{(\text{CCSD})} + \sum_{i < j < k, a < b < c} [\bar{c}_{abc}^{ijk}(\mu)]^* \mathfrak{M}_{\mu,abc}^{ijk}(2) / \bar{D}_\mu, \quad (93)$$

and

$$\begin{aligned} E_\mu^{(\text{MMCC/PT})}(2,4) &= E_\mu^{(\text{CCSD})} + \sum_{i < j < k, a < b < c} [\bar{c}_{abc}^{ijk}(\mu)]^* \mathfrak{M}_{\mu,abc}^{ijk}(2) \\ &\quad + \sum_{i < j < k < l, a < b < c < d} [\bar{c}_{abcd}^{ijkl}(\mu)]^* (\mathfrak{M}_{\mu,abcd}^{ijkl}(2) \\ &\quad + \mathcal{A}_{abc/d} \mathfrak{M}_{\mu,abc}^{ijk}(2) t_d^l) / \bar{D}_\mu, \end{aligned} \quad (94)$$

respectively, where the triply excited moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ are defined by Eqs. (44) and (45) and the quadruply excited moments $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ are defined by Eqs. (46) and (47). The $\mathcal{A}_{abc/d}$ partial antisymmetrizer is defined as

$$\mathcal{A}_{abc/d} = 1 - (ad) - (bd) - (cd), \quad (95)$$

where (pq) is a usual transposition of indices p and q , and

$$\begin{aligned} \bar{D}_\mu &\equiv \langle \bar{\Psi}_\mu^{(\text{MRMBPT})} | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle \\ &= \bar{\Delta}_{\mu,0} + \bar{\Delta}_{\mu,1} + \bar{\Delta}_{\mu,2} + \bar{\Delta}_{\mu,3} + \bar{\Delta}_{\mu,4} + \dots \end{aligned} \quad (96)$$

is the overlap denominator $\langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle$ entering Eq. (40), written for the wavefunction $|\Psi_\mu\rangle = |\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (87), truncated at triples for MMCC(2,3)/PT and at quadruples for MMCC(2,4)/PT. The $\bar{\Delta}_{\mu,0}$, $\bar{\Delta}_{\mu,1}$, $\bar{\Delta}_{\mu,2}$, $\bar{\Delta}_{\mu,3}$, and $\bar{\Delta}_{\mu,4}$ contributions to the denominator $\bar{D}_\mu$, Eq. (96), are calculated as

$$\bar{\Delta}_{\mu,0} = [\bar{c}_0(\mu)]^* r_0(\mu), \quad (97)$$

$$\bar{\Delta}_{\mu,1} = \sum_{i,a} [\bar{c}_a^i(\mu)]^* \beta_a^i(\mu), \quad (98)$$

$$\bar{\Delta}_{\mu,2} = \sum_{i<j,a<b} [\bar{c}_{ab}^{ij}(\mu)]^* \beta_{ab}^{ij}(\mu), \quad (99)$$

$$\bar{\Delta}_{\mu,3} = \sum_{i<j<k,a<b<c} [\bar{c}_{abc}^{ijk}(\mu)]^* \beta_{abc}^{ijk}(\mu), \quad (100)$$

and

$$\bar{\Delta}_{\mu,4} = \sum_{i < j < k < l, a < b < c < d} [\bar{c}_{abcd}^{ijkl}(\mu)]^* \beta_{abcd}^{ijkl}(\mu), \quad (101)$$

where $\bar{c}_0(\mu)$, $\bar{c}_a^i(\mu)$, $\bar{c}_{ab}^{ij}(\mu)$, $\bar{c}_{abc}^{ijk}(\mu)$, and $\bar{c}_{abcd}^{ijkl}(\mu)$ are the CI coefficients obtained by rewriting the MRMBPT wavefunction, $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86), in the single-reference CI form of Eq. (87), and $r_0(\mu)$,

$$\beta_a^i(\mu) = \langle \Phi_i^a | (R_{\mu,1} + R_{\mu,0}T_1) | \Phi \rangle, \quad (102)$$

$$\beta_{ab}^{ij}(\mu) = \langle \Phi_{ij}^{ab} | [R_{\mu,2} + R_{\mu,1}T_1 + R_{\mu,0}(T_2 + \frac{1}{2}T_1^2)] | \Phi \rangle, \quad (103)$$

$$\beta_{abc}^{ijk}(\mu) = \langle \Phi_{ijk}^{abc} | [R_{\mu,2}T_1 + R_{\mu,1}(T_2 + \frac{1}{2}T_1^2) + R_{\mu,0}(T_1T_2 + \frac{1}{6}T_1^3)] | \Phi \rangle, \quad (104)$$

and

$$\begin{aligned} \beta_{abcd}^{ijkl}(\mu) = & \langle \Phi_{ijkl}^{abcd} | [R_{\mu,2}(T_2 + \frac{1}{2}T_1^2) + R_{\mu,1}(T_1T_2 + \frac{1}{6}T_1^3) \\ & + R_{\mu,0}(\frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{24}T_1^4)] | \Phi \rangle \end{aligned} \quad (105)$$

are the coefficients at the reference determinant $|\Phi\rangle$ and singly, doubly, triply, and quadruply excited determinants, $|\Phi_i^a\rangle$, $|\Phi_{ij}^{ab}\rangle$, $|\Phi_{ijk}^{abc}\rangle$, and $|\Phi_{ijkl}^{abcd}\rangle$, respectively, in the CI expansion of the CCSD/EOMCCSD wavefunction $R_\mu^{(\text{CCSD})}e^{T^{(\text{CCSD})}}|\Phi\rangle$, which can be easily determined using the CCSD/EOMCCSD cluster and excitation amplitudes t_a^i , t_{ab}^{ij} , $r_0(\mu)$, $r_a^i(\mu)$, and $r_{ab}^{ij}(\mu)$.

Although the summations over $i < j < k$, $a < b < c$ in Eqs. (93) and (100) and over $i < j < k < l$, $a < b < c < d$ in Eqs. (94) and (101) have the form of

the complete summations over triples and quadruples, respectively, in reality the wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86), contain only small subsets of all triples and quadruples, once we rewrite each $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ in the form of the single-reference CI expansion, Eq. (87). This is a consequence of using active orbitals in designing the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, which limit the triple and quadruple excitations relative to the reference $|\Phi\rangle$ to a small class of triple and quadruple excitations that carry a certain number of active spin-orbital indices. Although the actual number of triples and quadruples in the $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ wavefunctions depends on the dimension of the active space used in the MRMBPT calculations, one usually needs a small portion of all triples and quadruples in the MMCC(2,3)/PT and MMCC(2,4)/PT considerations. As a result of using active orbitals in the MMCC(2,3)/PT and MMCC(2,4)/PT methods, we only need a small subset of all triexcited coefficients $\beta_{abc}^{ijk}(\mu)$, Eq. (104), and similarly a small subset of triply excited moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, Eqs. (44) and (45), which match the nonzero coefficients $\bar{c}_{abc}^{ijk}(\mu)$, to calculate the MMCC(2,3)/PT energy, Eq. (93). Similarly, for the MMCC(2,4)/PT approach, one only needs a small subset of all quadruply excited coefficients $\beta_{abcd}^{ijkl}(\mu)$, Eq. (105), and a similarly small subset of all quadruply excited moments $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, Eqs. (46) and (47), which match the nonzero coefficients $\bar{c}_{abcd}^{ijkl}(\mu)$, in the MMCC(2,4)/PT energy expression, Eq. (94).

One of the main advantages of the MRMBPT-corrected MMCC schemes, such as MMCC(2,3)/PT and MMCC(2,4)/PT, is their low computer cost, compared to the already relatively inexpensive CI-corrected MMCC methods described in Section 3.3.1. As in the case of the CI-corrected MMCC approaches, such as MMCC(2,3)/CI

and MMCC(2,4)/CI, in the MMCC(2,3)/PT and MMCC(2,4)/PT methods we have a very good control of accuracy through active orbitals defining model space $\mathcal{M}_0$, which can always be adjusted to the excited states or the bond breaking problem of interest, but unlike in the MMCC/CI schemes, we do not have to solve the iterative CISDt and CISDtq equations to generate the wavefunctions $|\Psi_\mu^{(\text{MRMBPT})}\rangle$ that enter the corrections $\delta_\mu(m_A, m_B)$ of the MRMBPT-corrected MMCC theories. We calculate the relevant CI-like coefficients, such as $\bar{c}_0(\mu)$, $\bar{c}_a^i(\mu)$, $\bar{c}_{ab}^{ij}(\mu)$, $\bar{c}_{abc}^{ijk}(\mu)$, and $\bar{c}_{abcd}^{ijkl}(\mu)$, by simply converting the expressions that define the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86), into the single-reference CI form defined by Eq. (87). Thus, the main computer effort for MMCC(2,3)/PT approach goes into the calculations of a small subset of triexcited moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, leading to the significant reduction of the $n_o^3 n_u^4$ steps that are normally needed to calculate all moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$. Likewise, the main computer effort for MMCC(2,4)/PT approach goes into the calculations of a small subset of quadruply excited moments $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$. Very little effort is needed to determine the wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ and the corresponding coefficients $\bar{c}_0(\mu)$, $\bar{c}_a^i(\mu)$, $\bar{c}_{ab}^{ij}(\mu)$, $\bar{c}_{abc}^{ijk}(\mu)$, and $\bar{c}_{abcd}^{ijkl}(\mu)$.

At this point, the remaining issue that we have to address before calculating the MMCC(2,3)/PT and MMCC(2,4)/PT energies is how to obtain the explicit algebraic expressions for the triply and quadruply excited moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$. It turns out that the best way to handle these quantities is through the use of the diagrammatic methods of the many-body theory which are described in the subsequent section.

4.3 Diagrammatic Formulation and Factorization of the Triply and Quadruply Moments of the CCSD Equations

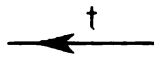
In this section, the diagrammatic derivation of the explicit equations for the triply and quadruply excited moments of the CCSD/EOMCCSD equations, $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, respectively, is presented. The procedure of diagram factorization, which is deemed necessary to obtain highly efficient computer code, is discussed as well.

Historically, the use of diagrams originated in quantum field theory using the time-dependent formalism. However, the time-independent formulation is sufficient in the development of quantum chemical and other many-body methods that rely on the time-independent Schrödinger equation. Diagrams are a graphical representation of Wick's theorem, which is a basic theorem for the algebraic manipulations involving operators in the second-quantized form. They carry information about interesting physics (e.g., connected vs. disconnected clusters), while providing powerful tool to derive and organize numerous mathematical expressions that almost any accurate many-body theory generates.

The entire discussion of diagrammatic methods described in this dissertation focuses on the time-independent formulation. It is important to note that the sequence in which the operators act (i.e. right to left in the bracket notation) is relevant; this is indicated in the diagram by means of a so-called formal time axis as shown below:



Thus if we want to represent the operator product $V_N T_1$ diagrammatically, we begin with a diagrammatic representation of T_1 at the bottom, followed by a diagram representing the operator V_N drawn above the T_1 diagram. This bottom-top convention is the convention we will be using throughout this dissertation. Another common convention, which was pioneered by Čížek and Paldus, is to place the formal time axis for the operator ordering horizontally, from right to left,



corresponding to the way we normally write a sequence of operators acting on a function. The difference between the two arrangements is the 90° rotation of the diagrams.

The standard procedure for deriving the explicit algebraic expressions for $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, Eqs. (44) and (46), in terms of the individual cluster and linear excitation amplitudes as well as one- and two-body integrals defining the Hamiltonian, is to represent the formulas, as given by Eqs. (44) and (46), in a diagrammatic form, obtain the so-called resulting diagrams by contractions of fermion lines representing the relevant creation and annihilation operators that enter the second-quantized forms of the operators, and apply the diagrammatic rules to convert the resulting diagrams back into algebraic language. Figure 2 shows the basic diagrams used to derive the equations for the generalized moments of the CCSD/EOMCCSD equations. An overview of the diagrammatic methods of many-body theory, describing the basic elements of the diagrammatic language used here, is presented in Appendix A. The diagrammatic and algebraic structure of the one-, two-, three-, and four-body components of the CCSD similarity-transformed Hamiltonian $\bar{H}^{(\text{CCSD})}$, which are the

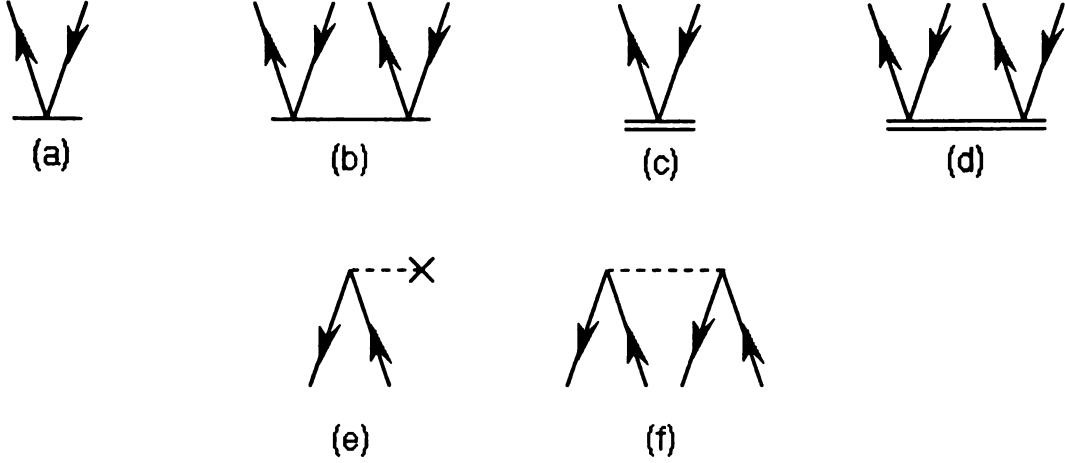


Figure 2: Diagrammatic representation of (a) T_1 as defined by Eq. (6); (b) T_2 as defined by Eq. (7); (c) $R_{\mu,1}$ as defined by Eq. (20); (d) $R_{\mu,2}$ as defined by Eq. (21); (e) $F_N = f_q^p N[a^p a_q]$, and (f) $V_N = \frac{1}{4} v_{pq}^{rs} N[a^p a^q a_s a_r]$, where F_N and V_N are the one- and two-body components of the Hamiltonian in the normal-ordered form (H_N) and $N[\dots]$ stands for the normal product of the operators.

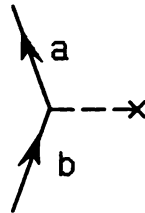
key elements for all CCSD-based methods, are shown in Appendix B.

We use the Hugenholtz (and Brandow) diagrams to derive the explicit many-body expressions for all terms that correspond to the triply and quadruply moments of the CCSD/EOMCCSD equations, $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, respectively. Other representations, such as that of Goldstone, could be used as well, but Hugenholtz diagrams are best whenever we rely on the second-quantized operators using antisymmetrized matrix elements, as is the case here. There are several methods of obtaining all resulting diagrams. The usual approach, which is followed here, is to first draw all elementary and then resulting Hugenholtz skeletons. The arrows are subsequently added in all distinct ways to produce all the distinct resulting diagrams. In the case of expressions for the generalized moments of CCSD equations, where we have to project $(H_N e^{T^{(\text{CCSD})}})_C |\Phi\rangle$ on the excited determinants $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$, we do not draw

the diagram representing the bra state $\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} |$. Instead, we draw all permissible resulting diagrams for $(H_N e^{T(\text{CCSD})})_C |\Phi\rangle$ with n incoming and n outgoing external fermion lines labeled by fixed indices $i_1, \dots, i_n$ and $a_1, \dots, a_n$, corresponding to the determinant $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ on which we project. Similar applies to moments of EOMCCSD equations. This greatly facilitates the process of drawing the resulting diagrams and makes the resulting diagrams less complicated.

To interpret the diagram algebraically, we conform to the following rules:

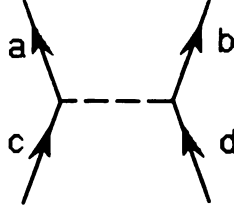
- a. Each upgoing external line is labeled with a “particle” (unoccupied) spin-orbital label $a, b, c, d, \dots$ and each downgoing external line with a “hole” (i.e. occupied) spin-orbital label $i, j, k, l, \dots$. External lines should always be labeled in canonical sequence as $a, i; b, j; c, k$; etc. The internal hole lines are labeled with $m, n, \dots$, whereas the internal particle lines are labeled with $e, f, \dots$.
- b. The one-body vertex representing the one-body component $F_N = f_p^q N[a^p a_q]$ of H_N carries the numerical value of the Fock matrix element $\langle p|f|q\rangle = f_p^q$, where p is an outgoing line and q is an incoming line. For instance,



carries a value of matrix element f_a^b .

- c. The two-body vertex representing the two-body component $V_N = \frac{1}{4} v_{pq}^{rs} N[a^p a^q a_s a_r]$ of H_N carries the numerical value of the antisymmetrized interaction matrix el-

ement $v_{pq}^{rs} = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$ where p and q are the outgoing lines and r and s are the incoming lines. For example,



carries a value of $v_{ab}^{cd} = \langle ab|v|cd \rangle - \langle ab|v|dc \rangle$. In general, $v_{pq}^{rs} = -v_{pq}^{sr} = -v_{qp}^{rs} = v_{qp}^{sr}$.

- d. The one- and two-body vertices representing the T_1 and T_2 cluster operators and the linear excitation vertices representing $R_{\mu,1}$ and $R_{\mu,2}$, i.e.,



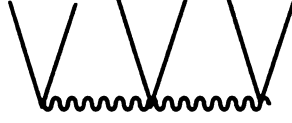
carry the numerical values of the t_a^i , t_{ab}^{ij} , $r_a^i(\mu)$, and $r_{ab}^{ij}(\mu)$ amplitudes, respectively. The two-body amplitudes are antisymmetric so that, for example, $t_{ab}^{ij} = -t_{ab}^{ji} = -t_{ba}^{ij} = t_{ba}^{ji}$ (similar applies to $r_{ab}^{ij}(\mu)$).

- e. All the spin-orbitals label are summed over “internal” lines, which are obtained by contracting external lines of F_N , V_N , T_1 , T_2 , $R_{\mu,1}$, and $R_{\mu,2}$.
- f. The sign of the diagram is obtained from $(-1)^{l+h}$ where l is the number of loops and h is the number of internal hole lines.

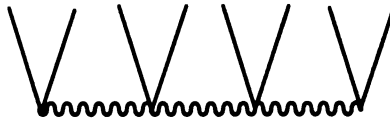
- g. The combinatorial weight factor of the connected diagram is specified by $(\frac{1}{2})^m$, where m is the number of pairs of “equivalent” lines. A pair of equivalent lines is defined as being two lines originating at the same vertex and ending at another, but also same vertex, and going in the same direction. This weight rule is specific to a Hugenholtz representation and lines that carry fixed labels (such as those defining the $\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} |$ bra states on which we project) are always regarded as non-equivalent.
- h. To maintain the full antisymmetry of a final expression for a quantity, such as moment $\mathfrak{M}_{\mu, a_1, \dots, a_n}^{i_1, \dots, i_n}(m_A)$, which is antisymmetric with respect to permutation of indices $i_1, \dots, i_n$ and $a_1, \dots, a_n$, the algebraic expression for each diagram should be preceded by a suitable complete or partial antisymmetrization operator, permuting the external lines in all distinct ways.

The procedure outlined above (cf, also, Appendix A) can be greatly simplified if we realize that the generalized moments of CCSD/EOMCCSD equations, such as $\mathfrak{M}_{\mu, abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu, abcd}^{ijkl}(2)$, are defined in terms of $\bar{H}^{(\text{CCSD})}$. As shown in Appendix B, various many-body components of $\bar{H}^{(\text{CCSD})}$ contain several diagrams of the $(F_N e^{T_1+T_2})_C$ and $(V_N e^{T_1+T_2})_C$ types, which are part of more complex diagrams representing $\mathfrak{M}_{\mu, abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu, abcd}^{ijkl}(2)$. By treating many-body component of $\bar{H}^{(\text{CCSD})}$ as more basic diagrams, which we represent by effective vertices with wavy lines, we can express moments $\mathfrak{M}_{\mu, abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu, abcd}^{ijkl}(2)$ in terms of matrix elements $\bar{h}_p^q$, $\bar{h}_{pq}^{rs}$, $\bar{h}_{pqr}^{stu}$, etc. that define one-body, two-body, three-body, etc., components of the $\bar{H}^{(\text{CCSD})}$. In this way, instead of drawing large numbers of resulting diagrams corresponding to the

original definitions of $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ in terms of F_N , V_N , T_1 , T_2 , $R_{\mu,1}$, and $R_{\mu,2}$, Eqs. (44)-(47), we can draw the relatively small number of diagrams in terms of the precomputed matrix elements of $\bar{H}^{(\text{CCSD})}$, which serve as natural intermediates (cf. Appendix B). All of the diagrams representing $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, obtained in this way, are shown in Figure 3. Note that all of the diagrams in Figure 3 have six external lines corresponding to the projections of triply excited determinant $|\Phi_{ijk}^{abc}\rangle$. The diagram



that shows up as the last term in Figure 3 is the ground-state moment $\mathfrak{M}_{0,abc}^{ijk}(2)$ defined in Eq. (45). The fact that we can represent the entire ground-state moment $\mathfrak{M}_{0,abc}^{ijk}(2)$ in this compact way is a consequence of the fact that $\mathfrak{M}_{0,abc}^{ijk}(2)$ can be regarded as one of the three-body components of $\bar{H}^{(\text{CCSD})}$; the complete set of diagrams corresponding to $\mathfrak{M}_{0,abc}^{ijk}(2)$ is shown in Figure 24 in Appendix B. The squared dot, $\square$, at $\mathfrak{M}_{0,abc}^{ijk}(2)$ in Figure 3 represents the constant $r_0(\mu)$. For the quadruply excited moments $\mathfrak{M}_{0,abcd}^{ijkl}(2)$, Eq. (46), all of the resulting diagrams should have eight external lines extending to the top and corresponding to the projection onto the quadruply excited determinant $|\Phi_{ijkl}^{abcd}\rangle$. We can see this in Figure 4, where all diagrams representing $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ are presented. Again, in analogy to $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, the diagram



that shows up as the last term in Figure 4 corresponds to the ground-state moment

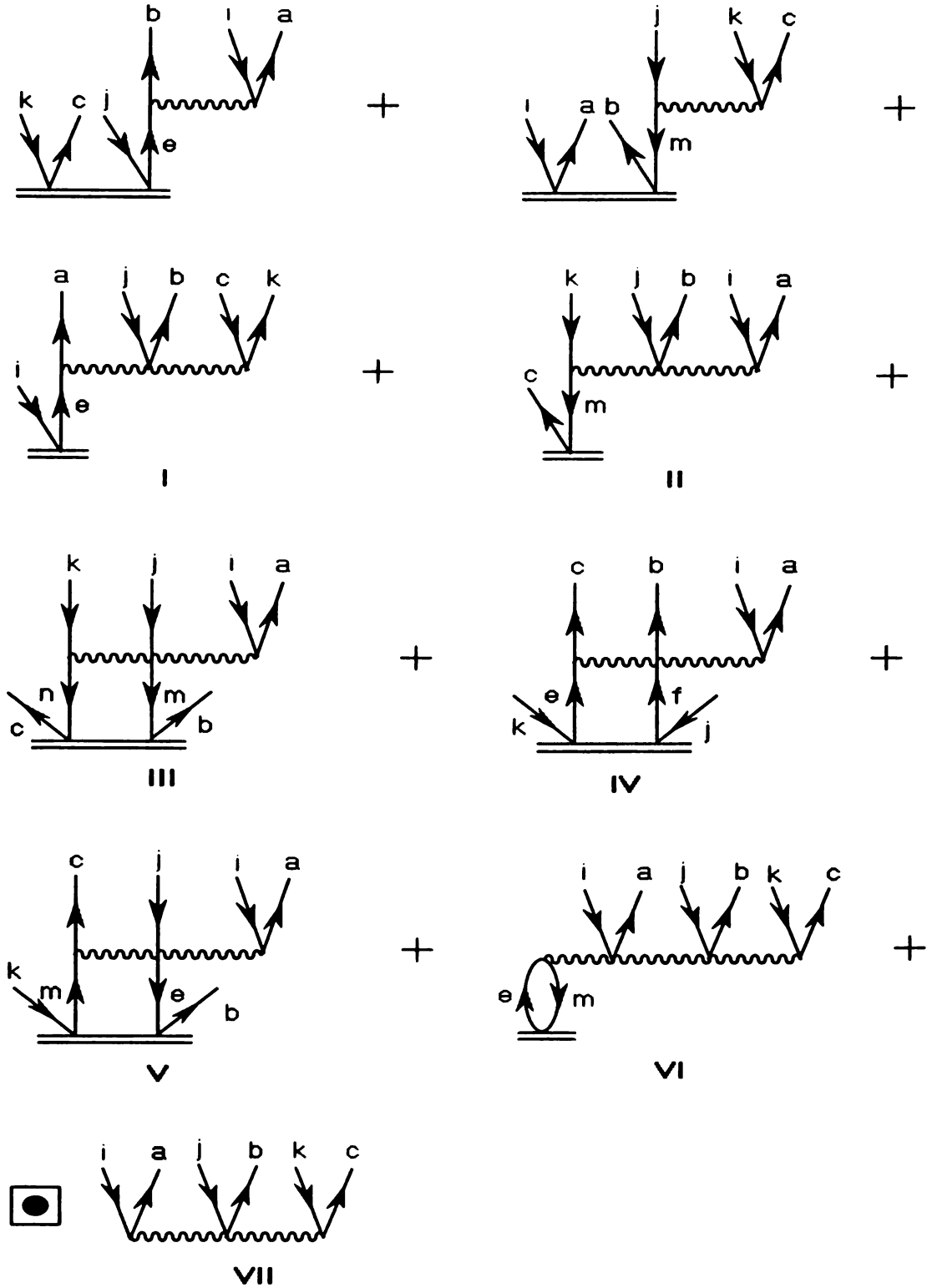


Figure 3: Diagrammatic representation of $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ using the Brandow forms of the relevant Hugenholtz diagrams. Vertices with wavy lines correspond to many-body components of $\bar{H}^{(\text{CCSD})}$. $\square$ in the last term represents $r_0(\mu)$.

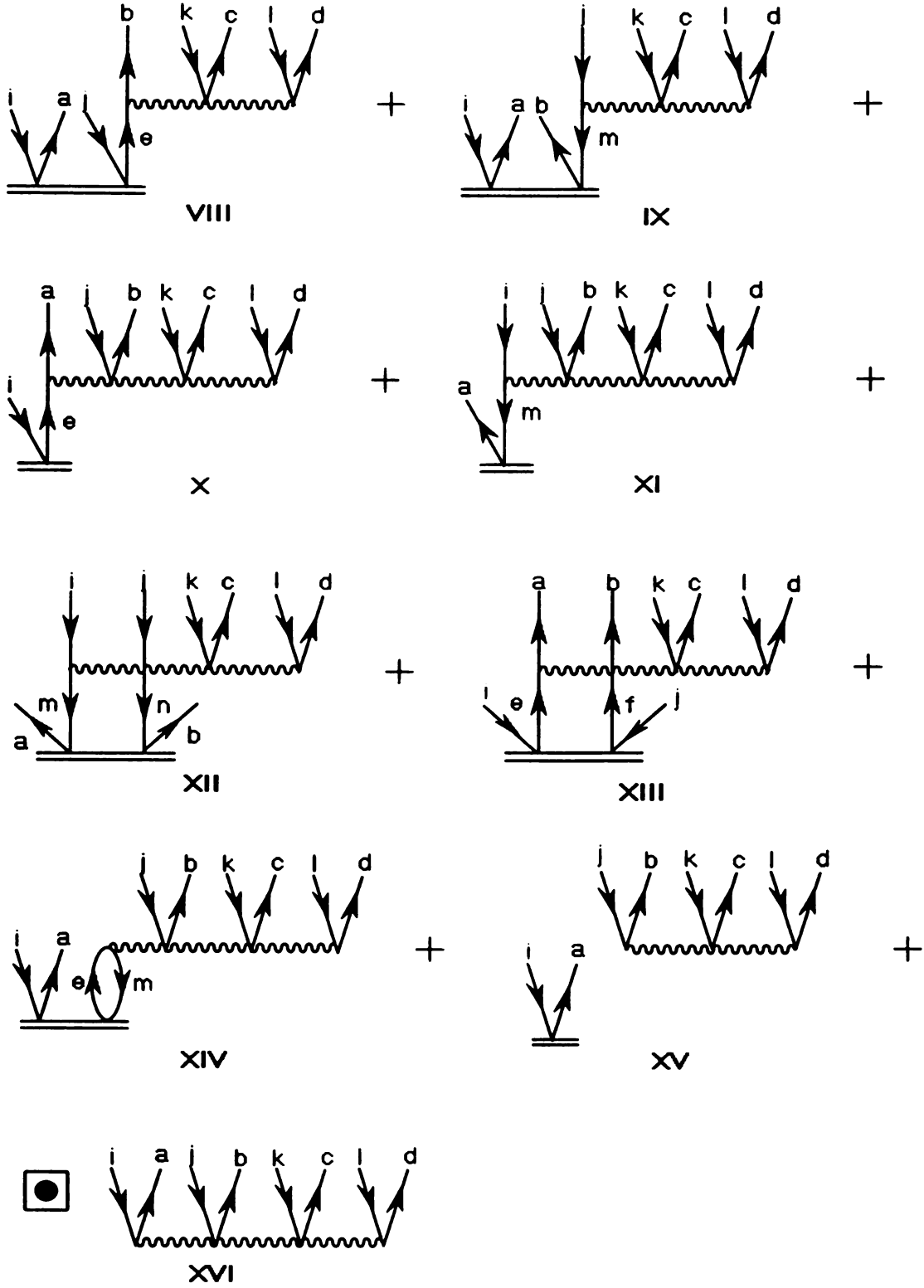
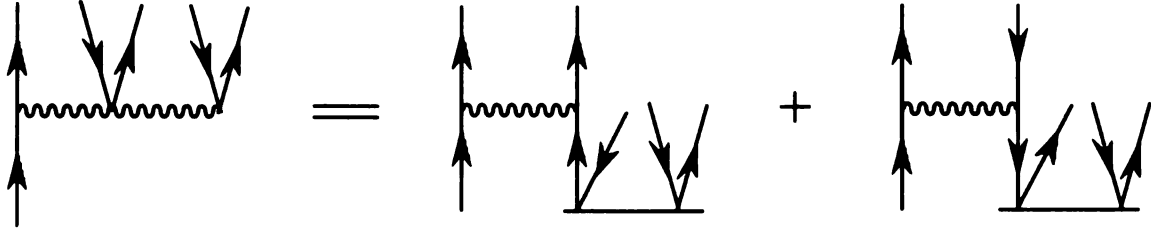


Figure 4: Diagrammatic representation of $\mathcal{M}_{\mu,abcd}^{ijkl}(2)$ using the Brandow forms of the relevant Hugenholtz diagrams. As in Figure 3, vertices with wavy lines corresponds to many-body components of $\bar{H}^{(\text{CCSD})}$ and $\square$ represents $r_0(\mu)$.

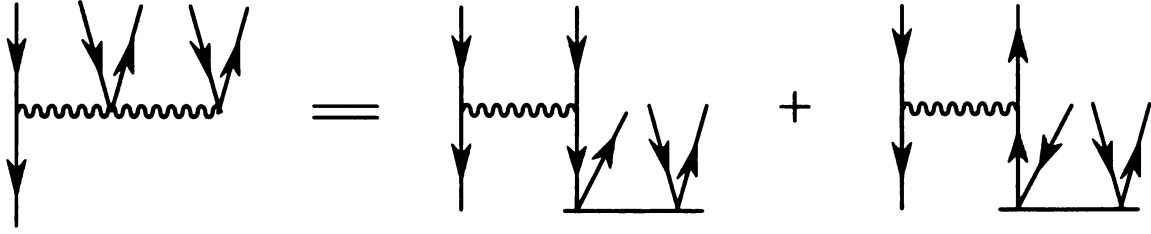
$\mathfrak{M}_{0,abcd}^{ijkl}(2)$ defined by in Eq. (47), which can also be regarded as one of the four-body components of $\bar{H}^{(\text{CCSD})}$; the complete set of diagrams corresponding to $\mathfrak{M}_{0,abcd}^{ijkl}(2)$ is shown in Figure 25 in Appendix B. Again, the squared dot, $\boxdot$, represents the coefficient $r_0(\mu)$. All of the diagrams that represent the two-, three-, and four-body components of $\bar{H}^{(\text{CCSD})}$, which enter $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, including the ground-state triply and quadruply moments of the CCSD equations described above, are given in in Appendix B (see Figures 20-25). The diagrams representing the one-body components of $\bar{H}^{(\text{CCSD})}$ do not show up in Figures 3 and 4 directly, but do show up indirectly as intermediates when the diagram factorization discussed in Section 4.4, which leads to efficient computer codes, is fully carried out (see, also, Appendix C).

Diagrams shown in Figures 3 and 4, with two-, three-, and four-body components of $\bar{H}^{(\text{CCSD})}$ represented diagrammatically in Figures 20-25, provide correct algebraic expressions for moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, but these expressions, if coded term by term, do not yield efficient computer programs. In order to reduce the number of CPU operations that are requested to calculate $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ in the most efficient manner, one has to factorize the $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ diagrams shown in Figures 3 and 4, that relate $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ to the expensive three- and four-body components of $\bar{H}^{(\text{CCSD})}$, shown in Figures 20-25. The main ideas behind diagram factorization that lead to considerable reduction in the number of CPU operations characterizing the resulting many-body expressions are explained in Appendix C. We illustrate the key steps that lead to the factorized, computationally efficient form of $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ in Figures 5-8.

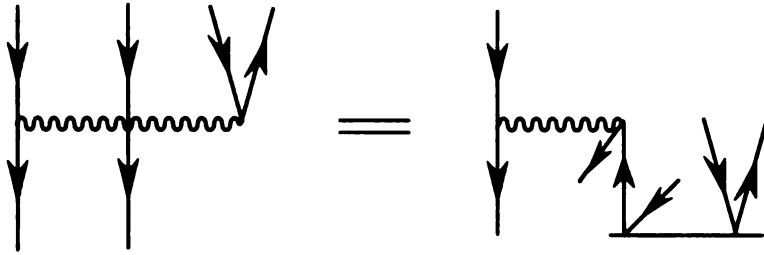
In the initial step, shown in Figure 5, we rewrite the expensive three-body matrix



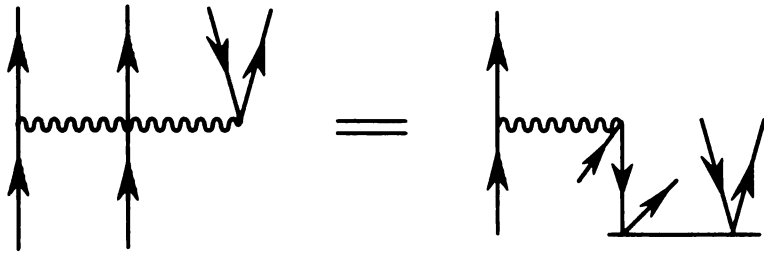
(a)



(b)



(c)



(d)

Figure 5: Factorized forms of the three-body components of $\bar{H}^{(\text{CCSD})}$ required in the derivation of $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, expressed as products of two-body matrix elements of $\bar{H}^{(\text{CCSD})}$ and T_2 cluster amplitudes.

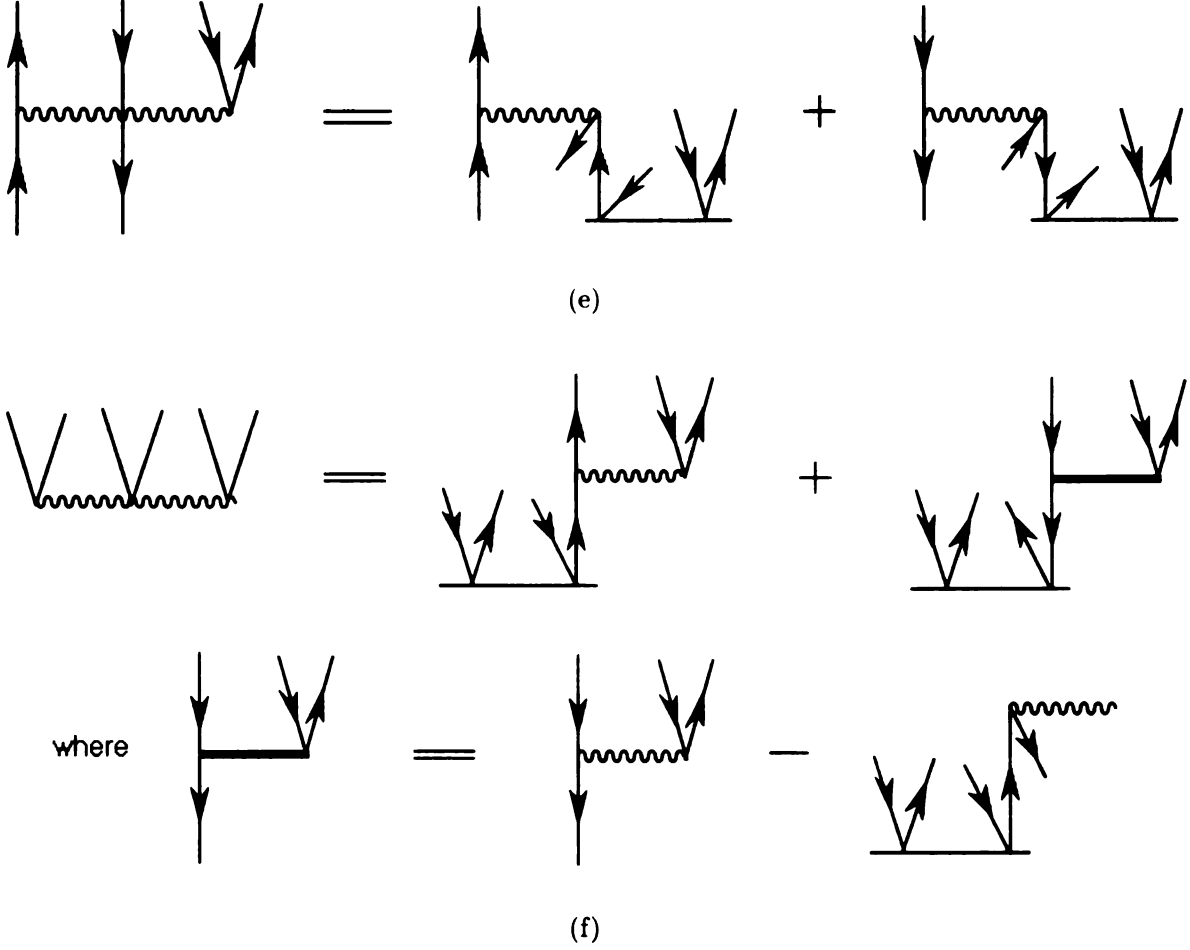


Figure 5: continued.

elements of $\bar{H}^{(\text{CCSD})}$ that enter the $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ diagrams shown in Figure 3 (see diagrams I-V in Figure 3) as tensor products of two-body matrix elements of $\bar{H}^{(\text{CCSD})}$ and T_2 cluster amplitudes. We also rewrite diagram VI of Figure 3, which uses a four-body component or $\bar{H}^{(\text{CCSD})}$, in a more explicit form in terms of V_N , T_2 , and $R_{\mu,1}$. As results of these operations, the original diagrams shown in Figure 3 acquire a new form shown in Figure 6. The first two diagrams in Figure 6 are in their final, computationally efficient, form. However, diagrams IA-VI are no longer linear in T or R_{μ} and represent multiple tensor products that need to be factorized further

by bringing them to a linearized (vectorized) form and reusing one- and two-body matrix elements of $\bar{H}^{(\text{CCSD})}$, which are easy to generate, as much as possible. This is accomplished in Figure 7 in three steps shown in Figure 7 (a), (b), and (c) where we first factor out T_2 vertices (Figure 7 (a) and (b)) and then group terms that have a similar overall structure to define the final set of intermediates linear in $R_{\mu,1}$ and $R_{\mu,2}$ and shown in Figure 7 (c). As a result of all these operation, all of the diagrams in Figure 3 or 6 acquire a compact, computationally, efficient form shown in Figure 8.

A similar procedure can be performed for the original diagrams representing $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ shown in Figure 4. Again, by replacing the three-body matrix elements of $\bar{H}^{(\text{CCSD})}$ that enter diagrams in Figure 4 (diagrams VIII and IX) by their factorized analogs shown in Figure 5 and by replacing the four-body $\bar{H}^{(\text{CCSD})}$ vertices in the diagrams in Figure 4 (diagrams X–XVI) by their factorized analogs shown in Figure 9, we obtain the set of diagram representing $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ shown in Figure 10. The factorization of non-linear diagrams in Figure 10 by factoring out common terms, grouping diagram that have a similar struture, and reusing recursively generated one- and two-body matrix elements of $\bar{H}^{(\text{CCSD})}$ and other intermediates gives the final, computationally efficient and compact form of $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ shown in Figure 11.

Figures 8 and 11 show the most compact, fully factorized, diagrammatic forms of $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, that yield the highly efficient computer codes that are characterized by the $n_o^3 n_u^4$ steps in the $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $n_o^4 n_u^5$ steps in the $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ case. Figures 12-14 show the diagrams representing all recursively generated intermediates

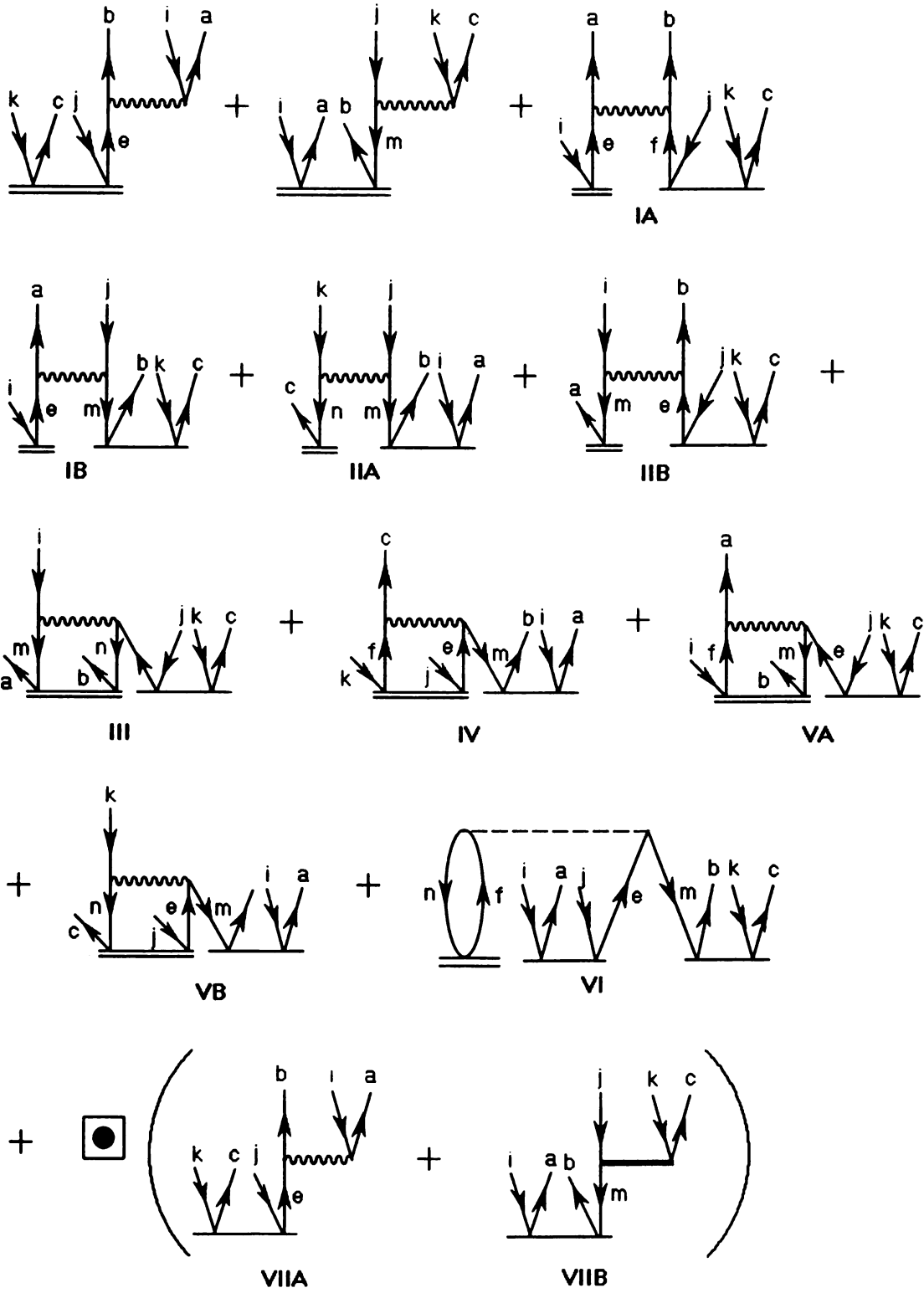


Figure 6: Diagrammatic representation of $\mathcal{M}_{\mu,abc}^{ijk}(2)$ obtained by substituting the three-body components of $\bar{H}^{(\text{CCSD})}$ in Figure 3 entering diagrams I-V by their factorized analogs shown in Figure 5 and by expressing the four-body component of $\bar{H}^{(\text{CCSD})}$ that defines diagram VI in terms of V_N , T_2 , and $R_{\mu,1}$.

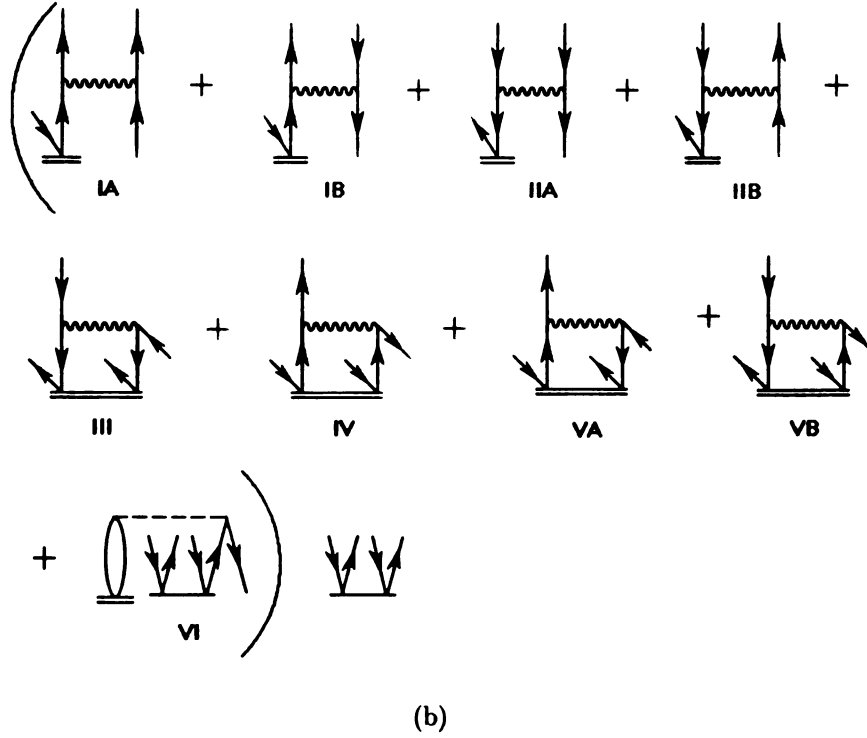
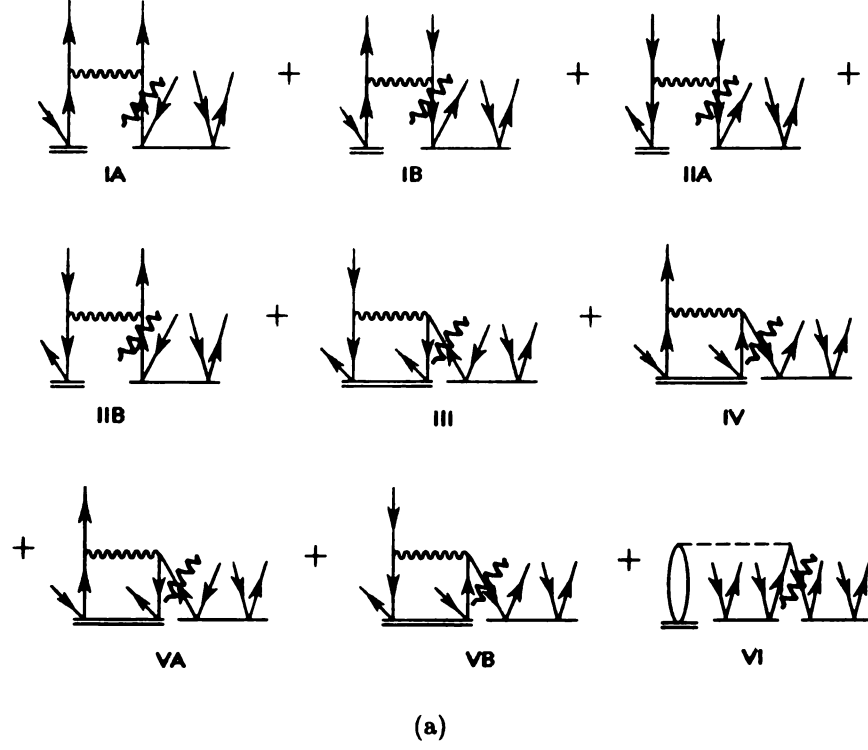


Figure 7: Process of diagram factorization for the nonlinear terms in $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ shown in Figure 6 (diagrams IA-VI). (a) and (b) The T_2 vertex is factored out. (c) Diagrams in parenthesis in (b) that have a similar structure are grouped together to define two intermediate vertices that are linear in $R_{\mu,1}$ and $R_{\mu,2}$.

(c)

Figure 7: continued.

that are needed to calculate $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ using diagrams shown in Figure 8 and 11. The explicit algebraic expressions for the intermediates shown in Figures 12-14 are given in Table 2. The final algebraic expressions for $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ used in this work and the remaining details of the computer implementation of the MMCC(2,3)/PT and MMCC(2,4)/PT methods are discussed next.

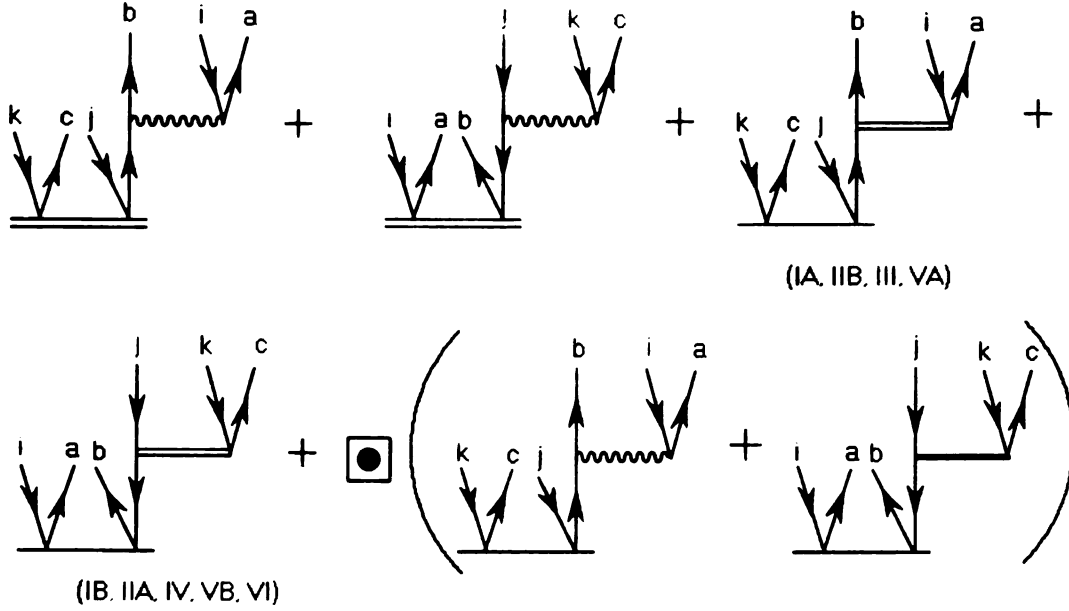
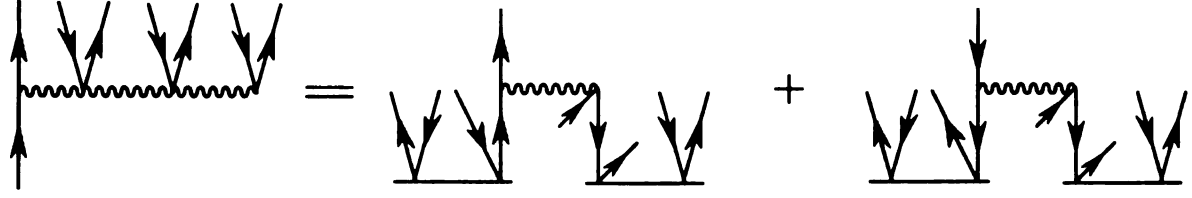


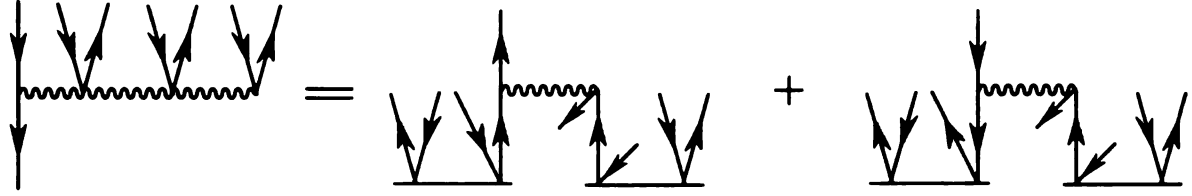
Figure 8: Final factorized form of $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ The two-body vertices marked with “=” are defined in Figure 7 (c).

4.4 Final Equations for $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ and the Remaining Details of the Implementation of the MMCC(2,3)/PT and MMCC(2,4)/PT Approaches

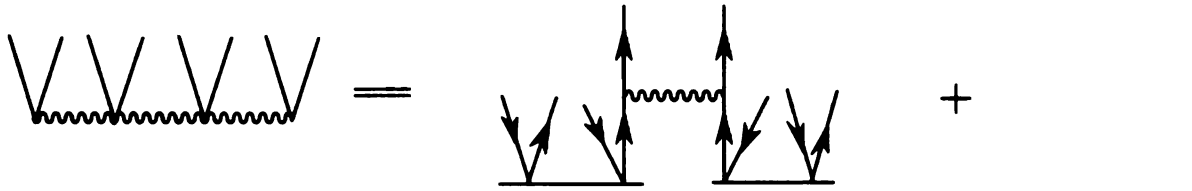
The final, fully factorized expression for the triply excited moments of the CCSD/EOMCCSD equations $\mathfrak{M}_{\mu,abc}^{ijk}(2)$, in terms of the amplitudes defining the CCSD/EOMCCSD cluster and excitation operators, T_1 , T_2 , $R_{\mu,0}$, $R_{\mu,1}$, and $R_{\mu,2}$, and molecular integrals f_p^q and v_{pq}^{rs} , obtained from the diagrams shown in Figure 8, which can be used in the highly efficient, vectorized, computer implementations of all MMCC(2,3) approximations, including the externally corrected MMCC(2,3) and MMCC(2,4) schemes, such as the MMCC(2,3)/PT and MMCC(2,4)/PT approaches pursued to this work, and their CI-corrected MMCC and renormalized CC/EOMCC



(a)

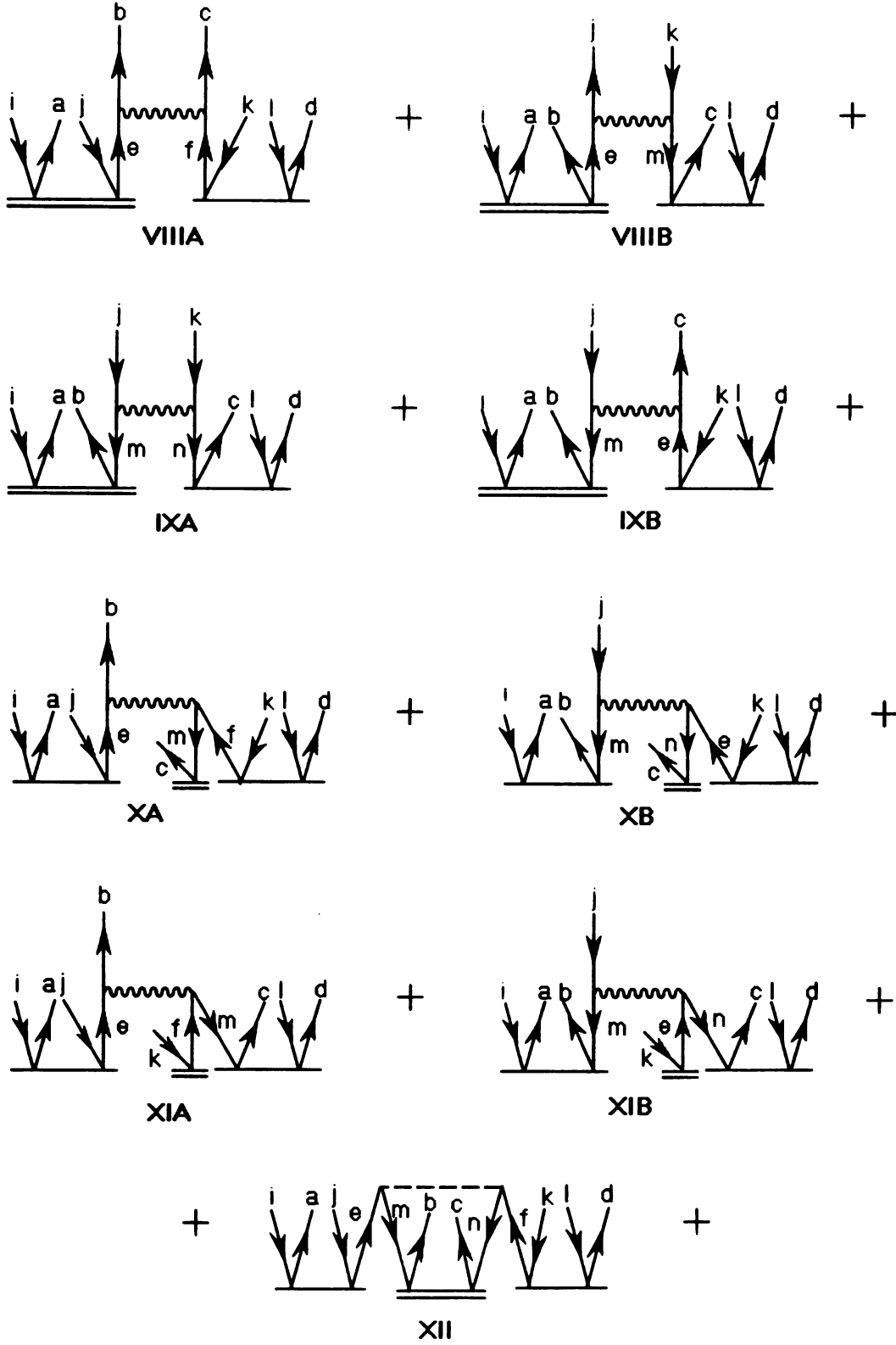


(b)

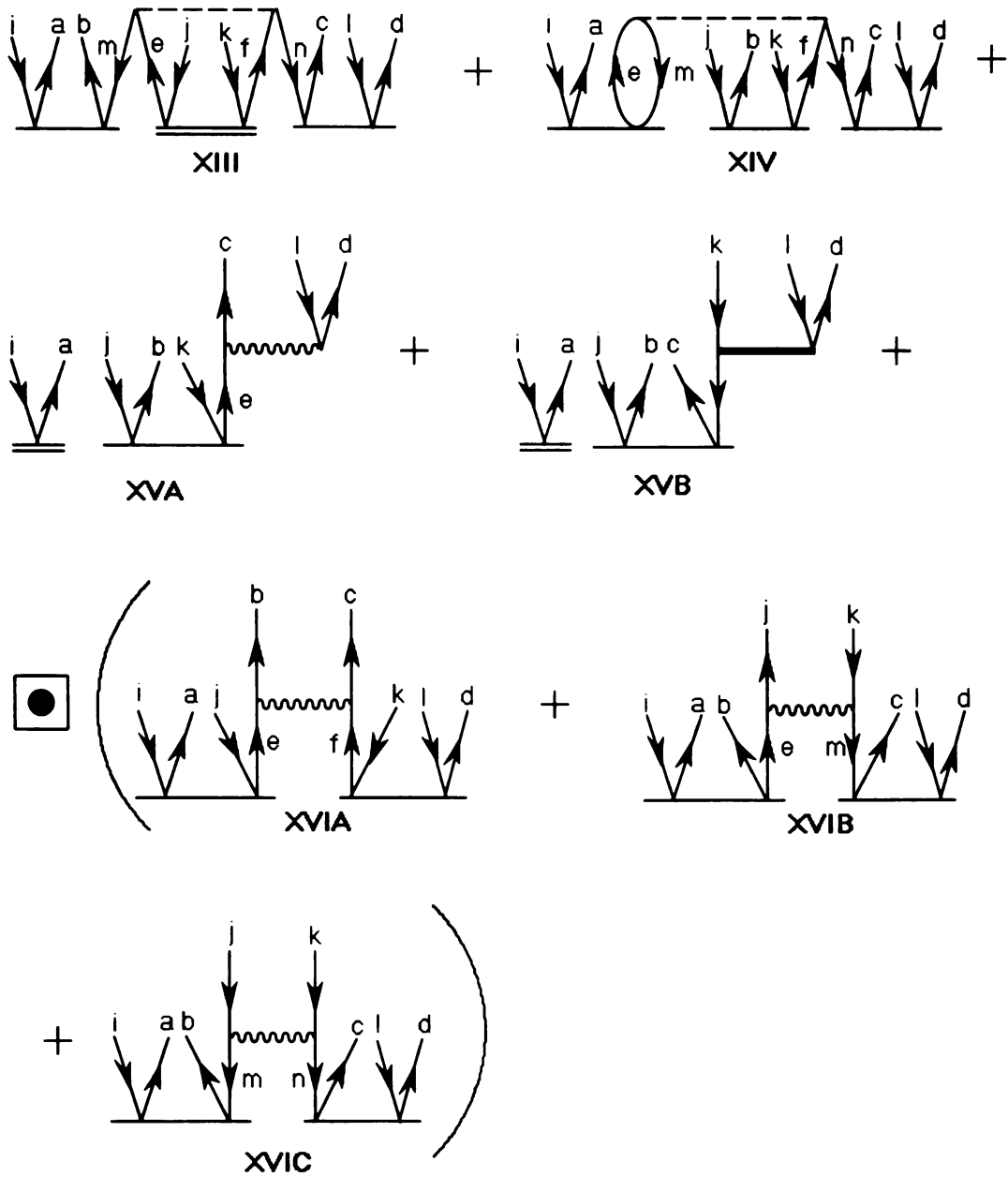


(c)

Figure 9: Factorized forms of the four-body components of $\bar{H}^{(\text{CCSD})}$ required in the derivation of $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, expressed as products of two-body matrix elements of $\bar{H}^{(\text{CCSD})}$ and T_2 cluster amplitudes.



(a)
Figure 10: Diagrammatic representation of $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ obtained by substituting the three- and four-body components of $\bar{H}^{(\text{CCSD})}$ in Figure 4 by their factorized analogs shown in Figures 5 and 9.



(b)

Figure 10: continued.

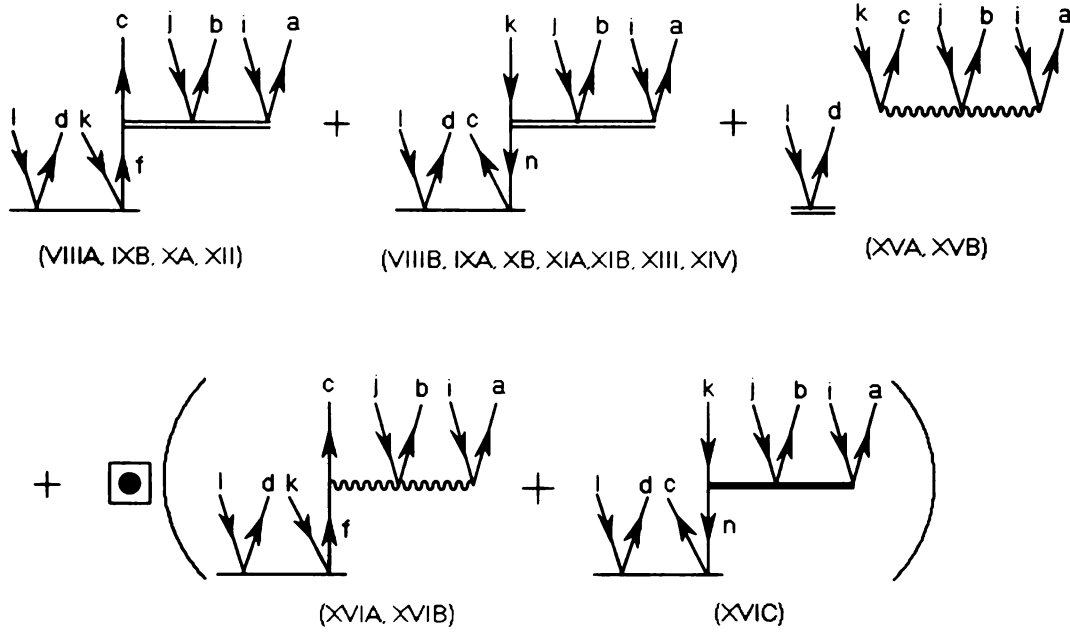


Figure 11: Final factorized form of $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$.

analog, can be given the following compact form:

$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \mathcal{A}_{abc} \mathfrak{T}_{\mu,abc}^{ijk}(2) \quad (106)$$

where

$$\begin{aligned} \mathfrak{T}_{\mu,abc}^{ijk}(2) = & \mathcal{A}^{i/jk} \left[\left(\frac{1}{2} \bar{h}_{ab}^{ie} r_{ec}^{jk} - \frac{1}{2} \bar{h}_{mc}^{jk} r_{ab}^{im} - \frac{1}{2} I_{mc}^{jk} t_{ab}^{im} + I_{ab}^{ie} t_{ec}^{jk} \right) \right. \\ & \left. + \frac{1}{2} r_0(\mu) (\bar{h}_{ab}^{ie} t_{ec}^{jk} - I_{mc}^{jk} t_{ab}^{im}) \right]. \end{aligned} \quad (107)$$

For simplicity, we dropped the symbol μ in the amplitudes $r_{ec}^{jk}(\mu)$, $r_{ab}^{im}(\mu)$, and $r_0(\mu)$ entering Eq. (107). The final, fully factorized and computationally highly efficient expression for the quadruply excited moments of the CCSD/EOMCCSD equations

$$\text{Diagram (a)} = \text{Diagram 1} + \text{Diagram 2}$$

(a) $\bar{h}_i^a$

$$\text{Diagram (b)} = \text{Diagram 1}$$

(b) I_i^a

$$\text{Diagram (c)} = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4}$$

(c) $\bar{h}_a^b$

$$\text{Diagram (d)} = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4}$$

(d) $\bar{h}_i^j$

Figure 12: One-body matrix elements of $\bar{H}^{(\text{CCSD})}$ and other one-body intermediates needed to construct $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$.

(a) $\bar{h}_{ai}^{bc}$

(b) $\bar{h}_{ij}^{ka}$

(c) $\bar{h}_{ab}^{cd}$

(d) $\bar{h}_{ij}^{kl}$

Figure 13: Two-body matrix elements of $\bar{H}^{(\text{CCSD})}$ and other two-body intermediates needed to construct $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$.

(e) v_{jb}^{ia}

(f) $\bar{h}_{jb}^{ia}$

(g) $\bar{h}_{ab}^{ic}$

Figure 13: continued.

Diagram (h) shows the expansion of a Feynman diagram. The left side is a diagram with two vertical lines labeled j and i , and two external lines labeled k and a meeting at a vertex connected by a wavy line. The right side is a sum of seven diagrams: 1) a diagram with a horizontal dashed line; 2) a diagram with a horizontal solid line and a loop involving lines k , j , e , and i ; 3) a diagram with a horizontal dashed line and a loop involving lines a , k , j , and e ; 4) a diagram with a horizontal dashed line and a loop involving lines a , k , j , and e ; 5) a diagram with a horizontal solid line and a loop involving lines a , k , j , and e ; 6) a diagram with a horizontal solid line and a loop involving lines a , k , j , and e ; 7) a diagram with a horizontal solid line and a loop involving lines a , k , j , and e .

(h) $\bar{h}_{ia}^{jk}$

Diagram (i) shows the expansion of a Feynman diagram. The left side is a diagram with two vertical lines labeled j and i , and two external lines labeled k and a meeting at a vertex connected by a horizontal solid line. The right side is a sum of five diagrams: 1) a diagram with a horizontal wavy line; 2) a diagram with a horizontal wavy line and a loop involving lines k , j , e , and i ; 3) a diagram with a horizontal wavy line and a loop involving lines a , k , j , and e ; 4) a diagram with a horizontal wavy line and a loop involving lines a , k , j , and e ; 5) a diagram with a horizontal wavy line and a loop involving lines a , k , j , and e .

(i) I_{ia}^{jk}

Diagram (j) shows the expansion of a Feynman diagram. The left side is a diagram with two vertical lines labeled j and i , and two external lines labeled k and a meeting at a vertex connected by a horizontal solid line. The right side is a difference of two diagrams: 1) a diagram with a horizontal wavy line; 2) a diagram with a horizontal wavy line and a loop involving lines k , a , j , and e .

(j) $I'_{ia}{}^{jk}$

Figure 13: continued.

(k) I_{ab}^{ic}

(l) I_{ab}^{cd}

(m) I_{kl}^{ij}

(n) I_{jb}^{ia}

Figure 13: continued.

(a) I_{abc}^{ijd}

(b) I_{abl}^{ijk}

(c) $\mathfrak{M}_{0,abc}^{ijk}(2)$

(d) I_{abc}^{ijd}

Figure 14: Three-body intermediates needed to construct $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$.

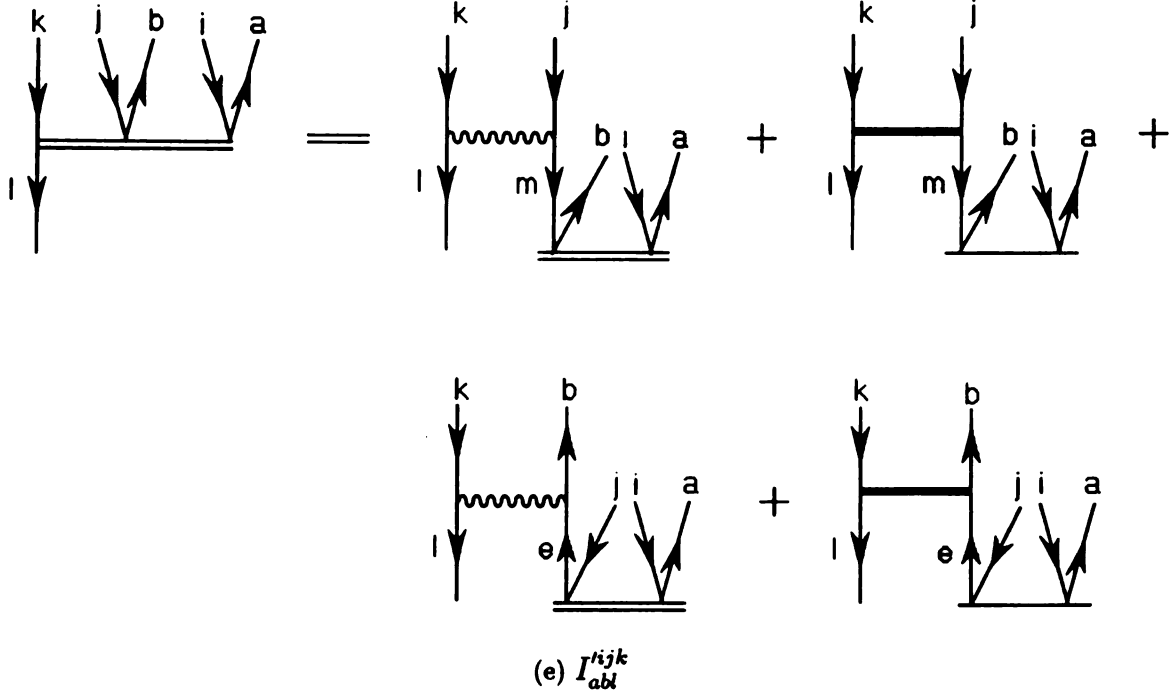


Figure 14: continued.

$\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, obtained from the diagrams shown in Figure 11, can be written as

$$\mathfrak{M}_{\mu,abcd}^{ijkl}(2) = \mathcal{A}_{abcd} \mathfrak{T}_{\mu,abcd}^{ijkl}(2), \quad (108)$$

where

$$\begin{aligned} \mathfrak{T}_{\mu,abcd}^{ijkl}(2) &= \mathcal{A}^{ij/kl} I_{abc}^{ijf} t_{fd}^{kl} - \mathcal{A}^{ijk/l} I_{abn}^{ijk} t_{cd}^{nl} + \frac{1}{6} \mathcal{A}^{ijk/l} \mathfrak{M}_{0,abc}^{ijk}(2) r_d^l \\ &+ \frac{1}{2} r_0(\mu) (\mathcal{A}^{ij/kl} I_{abc}^{ijf} t_{fd}^{kl} - \mathcal{A}^{ijk/l} I_{abn}^{ijk} t_{cd}^{nl}). \end{aligned} \quad (109)$$

with $\mathfrak{M}_{0,abc}^{ijk}(2)$ representing the ground-state triexcited moments of CCSD (see Table 2). The antisymmetrizers $\mathcal{A}_{pq}$, $\mathcal{A}_{pqr}$, $\mathcal{A}_{pq/r}$, $\mathcal{A}_{pqr/s}$, $\mathcal{A}_{pq/rs}$, $\mathcal{A}_{pq/r/s}$, $\mathcal{A}_{pqrs}$, etc. which

enter Eqs. (106)-(109) directly or through the matrix elements of $\bar{H}^{(\text{CCSD})}$, and other intermediates that are needed to construct Eqs. (107) and (109) and that are listed in Table 2, are defined in a usual way,

$$\mathcal{A}_{pq} \equiv \mathcal{A}^{pq} = 1_{pq} - (pq), \quad (110)$$

$$\mathcal{A}_{pqr} \equiv \mathcal{A}^{pqr} = 1_{pqr} - (pq) - (pr) - (qr) + (pqr) + (prq), \quad (111)$$

$$\mathcal{A}_{p/qr} \equiv \mathcal{A}^{p/qr} \equiv \mathcal{A}_{qr/p} \equiv \mathcal{A}^{qr/p} = 1_{pqr} - (pq) - (pr), \quad (112)$$

$$\mathcal{A}_{pqr/s} \equiv \mathcal{A}^{pqr/s} \equiv \mathcal{A}_{s/pqr} \equiv \mathcal{A}^{s/pqr} = 1_{pqrs} - (ps) - (qs) - (rs), \quad (113)$$

$$\mathcal{A}_{pq/rs} \equiv \mathcal{A}^{pq/rs} = 1_{pqrs} - (pr) - (ps) - (qr) - (qs) + (pr)(qs), \quad (114)$$

$$\begin{aligned} \mathcal{A}_{pq/r/s} &\equiv \mathcal{A}^{pq/r/s} \equiv \mathcal{A}_{r/pq/s} \equiv \mathcal{A}^{r/pq/s} \equiv \mathcal{A}_{r/s/pq} \equiv \mathcal{A}^{r/s/pq} \\ &= 1_{pqrs} - (pr) - (ps) - (qr) - (qs) + (pr)(qs) - (rs) \\ &\quad + (prs) + (psr) + (qrs) + (qsr) - (pqrs) \\ &= \mathcal{A}_{pq/rs} \mathcal{A}_{rs}, \end{aligned} \quad (115)$$

$$\begin{aligned} \mathcal{A}_{pqr/s} \equiv \mathcal{A}^{pqr/s} &= 1_{pqrs} - (pq) - (pr) - (ps) - (qr) - (qs) - (rs) + (qrs) \\ &\quad + (qsr) + (pqr) + (pqs) + (prq) + (prs) + (psq) \\ &\quad + (psr) + (pq)(rs) + (pr)(qs) + (ps)(qr) - (pqrs) \\ &\quad - (pqsr) - (prsq) - (prqs) - (psrq) - (psqr), \end{aligned} \quad (116)$$

with (pq) , (pqr) and $(pqrs)$ representing the cyclic permutations of two, three, and four spin-orbital indices, respectively. As mentioned in the previous section, the explicit spin-orbital expressions for one- and two-body matrix elements of $\bar{H}^{\text{CCSD}}$, $\bar{h}_p^q$ and $\bar{h}_{pq}^{rs}$, respectively, and other recursively generated intermediates entering Eqs. (107) and (109), in terms of cluster amplitudes t_a^i and t_{ab}^{ij} , excitation amplitudes $r_a^i \equiv r_a^i(\mu)$ and $r_{ab}^{ij} \equiv r_{ab}^{ij}(\mu)$, and molecular integrals f_p^q and v_{pq}^{rs} , are given in Table 2.

By using the idea of recursively generated intermediates and by reusing, as much as possible, the one and two-body matrix elements of $\bar{H}^{(\text{CCSD})}$, which are generated in the CCSD/EOMCCSD calculations that precede the calculations of moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, we achieve a very high degree of code vectorization, while avoiding the explicit construction and storing of the most expensive three- and four-body matrix elements of $\bar{H}^{(\text{CCSD})}$. Since all of the expressions defining $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ and the corresponding recursively generated intermediates are binary tensor (matrix) products, one can very effectively calculate $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ and the required intermediates with fast matrix multiplication routines available in the BLAS library.

Once the CCSD/EOMCCSD equations are solved for t_a^i , t_{ab}^{ij} , $r_0(\mu)$, $r_a^i(\mu)$ and $r_{ab}^{ij}(\mu)$, and the relevant moments $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$ and the corresponding coefficients $\bar{c}_a^i(\mu)$, $\bar{c}_{ab}^{ij}(\mu)$, $\bar{c}_{abc}^{ijk}(\mu)$, $\bar{c}_{abcd}^{ijkl}(\mu)$, $\beta_a^i(\mu)$, $\beta_{ab}^{ij}(\mu)$, $\beta_{abc}^{ijk}(\mu)$, and $\beta_{abcd}^{ijkl}(\mu)$ are determined using Eqs. (106)-(109), MRMBPT wavefunctions, $|\Psi_\mu^{(\text{MRMBPT})}\rangle$, and Eqs. (102)-(105), we construct the overlap denominators $\bar{D}_\mu$, as in Eqs. (96)-(101), and, finally, the energy corrections due to triples or triples and quadruples defining the MMCC(2,3)/PT and MMCC(2,4)/PT methods, using Eqs. (93) and (94). Our MMCC(2,3)/PT and MMCC(2,4)/PT computer programs are interfaced with the

RHF and integral transformation and sorting routines available in the GAMESS package.²⁶⁵

Table 2: Explicit algebraic expressions for one- and two-body matrix elements of $\bar{H}^{\text{CCSD}}$ (designated by $\bar{h}$) and other intermediates (designated by I or ϑ), shown in Figures 12-14, used to construct the triply and quadruply excited moments of the CCSD/EOMCCSD equations, $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, respectively.

	Expression ^a	Figure
$\bar{h}_i^a$	$f_i^a + t_e^m v_{im}^{ae}$	12 (a)
I_i^a	$r_e^m v_{im}^{ae}$	12 (b)
$\bar{h}_a^b$	$f_a^b + t_e^m v_{am}^{be} - \frac{1}{2} t_{ea}^{mn} v_{mn}^{eb} - t_a^n \bar{h}_n^b$	12 (c)
$\bar{h}_i^j$	$f_i^j + t_e^m v_{im}^{je} + \frac{1}{2} t_{ef}^{mj} v_{mi}^{ef} + t_e^j \bar{h}_i^e$	12 (d)
$\bar{h}_{ai}^{bc}$	$v_{ai}^{bc} - t_a^m v_{mi}^{bc}$	13 (a)
$\bar{h}_{ij}^{ka}$	$v_{ij}^{ka} + t_e^k v_{ij}^{ea}$	13 (b)
$\bar{h}_{ab}^{cd}$	$v_{ab}^{cd} + \frac{1}{2} t_{ab}^{mn} v_{mn}^{cd} - t_b^m \bar{h}_{am}^{cd} + t_a^m v_{bm}^{cd}$	13 (c)
$\bar{h}_{ij}^{kl}$	$v_{ij}^{kl} + \frac{1}{2} t_{ef}^{kl} v_{ij}^{ef} + t_e^l h_{ij}^{ke} - t_e^k v_{ij}^{le}$	13 (d)
ϑ_{jb}^{ia}	$v_{jb}^{ia} + t_e^i v_{jb}^{ae}$	13 (e)
$\bar{h}_{jb}^{ia}$	$\vartheta_{jb}^{ia} + t_{eb}^{mi} v_{jm}^{ae} - t_b^m \bar{h}_{jm}^{ia}$	13 (f)
$\bar{h}_{ab}^{ic}$	$v_{ab}^{ic} - t_{ab}^{im} \bar{h}_m^c + t_e^i v_{ab}^{ec} + t_b^m \vartheta_{ma}^{ic} - t_a^m \bar{h}_{mb}^{ic} + \frac{1}{2} t_{ab}^{nm} \bar{h}_{nm}^{ic} + t_{ae}^{im} \bar{h}_{mb}^{ec} - t_{eb}^{mi} v_{am}^{ce}$	13 (g)
$\bar{h}_{ia}^{jk}$	$v_{ia}^{jk} + t_{ea}^{jk} \bar{h}_i^e + t_e^j v_{ia}^{ek} + \frac{1}{2} t_{ef}^{jk} v_{ia}^{ef} + t_e^k \vartheta_{ai}^{ej} - t_a^m \bar{h}_{im}^{jk} + \mathcal{A}^{jk} t_{ea}^{mk} \bar{h}_{im}^{je}$	13 (h)
I_{ia}^{jk}	$\mathcal{A}^{jk} \bar{h}_{ia}^{je} r_e^k - \bar{h}_{im}^{jk} r_a^m + t_{ea}^{jk} I_i^e + \frac{1}{2} \bar{h}_{ia}^{ef} r_{ef}^{jk} - \mathcal{A}^{jk} \bar{h}_{im}^{ek} r_{ea}^{jm}$	13 (i)
$I'_{ia}{}^{jk}$	$\bar{h}_{ia}^{jk} - t_{ea}^{jk} \bar{h}_i^e$	13 (j)
I_{ab}^{ic}	$\frac{1}{2} \bar{h}_{ab}^{ec} r_e^i - \bar{h}_{mb}^{ic} r_a^m + \frac{1}{4} \bar{h}_{mn}^{ic} r_{ab}^{mn} - \bar{h}_{am}^{ec} r_{eb}^{im}$	13 (k)
I_{ab}^{cd}	$\frac{1}{4} v_{mn}^{cd} r_{ab}^{mn} - \bar{h}_{am}^{cd} r_b^m$	13 (l)
I_{kl}^{ij}	$\frac{1}{4} v_{kl}^{ef} r_{ef}^{ij} + \frac{1}{2} \mathcal{A}^{ij} \bar{h}_{kl}^{ie} r_e^j$	13 (m)
I_{jb}^{ia}	$-v_{mj}^{ae} r_{eb}^{im} + \bar{h}_{bj}^{ae} r_e^i - \bar{h}_{jm}^{ia} r_b^m$	13 (n)
I_{abc}^{ijd}	$\frac{1}{4} t_{ae}^{ij} \bar{h}_{bc}^{ed} - \frac{1}{2} \mathcal{A}^{ij} t_{ab}^{im} \bar{h}_{mc}^{jd}$	14 (a)
I_{abl}^{ijk}	$\frac{1}{2} \mathcal{A}^{i/jk} \bar{h}_{ml}^{jk} t_{ab}^{im}$	14 (b)
$\mathfrak{M}_{0,abc}^{ijk}(2)$	$\frac{1}{2} \mathcal{A}_{abc} \mathcal{A}^{i/jk} (\bar{h}_{ab}^{ie} t_{ec}^{jk} - I_{mc}^{jk} t_{ab}^{im})$	14 (c)
$I_{abc}^{i jd}$	$\frac{1}{2} \bar{h}_{bc}^{ed} r_{ae}^{ij} - \frac{1}{2} \mathcal{A}^{ij} \bar{h}_{mc}^{jd} r_{ab}^{im} + \frac{1}{2} t_{ae}^{ij} I_{bc}^{ed}$	14 (d)
I_{abl}^{ijk}	$\mathcal{A}^{i/jk} (\frac{1}{2} \bar{h}_{ml}^{jk} r_{ab}^{im} - \frac{1}{2} I_{ml}^{jk} t_{ab}^{im}) + \mathcal{A}^{ij/k} (\bar{h}_{bl}^{ek} r_{ae}^{ij} + I_{bl}^{ek} t_{ae}^{ij})$	14 (e)

^a Summation over repeated upper and lower indices is assumed; $f_p^q = \langle p|f|q \rangle$ and $v_{pq}^{rs} = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$ are the one- and two-electron integrals in a molecular spin-orbital basis $\{p\}$ corresponding to the Fock operator (f) and the two-body part of the Hamiltonian (v).

5 Numerical Examples

We illustrate the performance of the MRMBPT-corrected MMCC approaches developed in this work by discussing the results of the benchmark MMCC(2,3)/PT and MMCC(2,4)/PT calculations for the single bond breaking in the HF and F₂ molecules, the simultaneous dissociation of both O–H bonds in the H₂O molecule, and the valence excited states of the CH⁺ ion. We focus on a comparison of the MMCC(2,3)/PT and MMCC(2,4)/PT results with a few other ways of incorporating the triple and quadruple excitations in the CC and EOMCC formalisms, and the exact, full CI data also obtained with GAMESS.

5.1 Bond Breaking in HF

In order to test the ability of the MRMBPT-corrected MMCC approaches to improve the poor description of bond breaking by the standard CCSD and CCSD(T) methods, we applied the MMCC(2,3)/PT approach to the potential energy curve of HF. We used a double zeta (DZ) basis set,²⁶⁶ for which the exact, full CI energies²⁷ and several other useful results, including, for example, the full CCSDT energies²⁷ and their standard and completely renormalized CCSD(T) analogs,¹⁸ are available. We also compare the MMCC(2,3)/PT results with the results of the CI-corrected MMCC(2,3) (MMCC(2,3)/CI) calculations,²⁵¹ which provide yet another way of correcting the CCSD energies for the most essential effects due to triple excitations. We focus on the triples methods because generally triply excited clusters along with the singly and doubly excited clusters are sufficient to obtain a virtually exact description

of single bond breaking. In all calculations reported in this work, we used the ground-state RHF determinant as a reference $|\Phi\rangle$. The active space employed in the CI- and MRMBPT-corrected MMCC methods consisted of three highest-energy occupied orbitals, 3σ , 1π , and 2π , and the lowest-energy unoccupied orbital 4σ that correlate with valence shells of the H and F atoms. This is a natural choice of active space for the description of bond breaking in HF, since for larger internuclear separations $R_{\text{H-F}}$ the full CI wavefunction of HF is dominated by the ground-state RHF configuration,

$$|\Phi\rangle = |(1\sigma)^2(2\sigma)^2(1\pi)^2(2\pi)^2(3\sigma)^2|, \quad (117)$$

the doubly excited configuration,

$$|\Phi'\rangle = |(1\sigma)^2(2\sigma)^2(1\pi)^2(2\pi)^2(4\sigma)^2|, \quad (118)$$

corresponding to the $(3\sigma)^2 \rightarrow (4\sigma)^2$ excitation, and the $(3\sigma) \rightarrow (4\sigma)$ singly excited configuration.

The results of our MMCC(2,3)/PT calculations for the potential energy curve of HF are shown in Table 3. In this particular case, there is a 1.634 millihartree difference between the CCSD and full CI energies at the equilibrium geometry, $R_{\text{H-F}} = R_e$, which increases to 12.291 millihartree at $R_{\text{H-F}} = 5R_e$ (for most practical purposes, $R_{\text{H-F}} = 5R_e$ can be regarded as a dissociation limit). As in other cases of single bond breaking, the large differences between the CCSD and full CI energies at larger values of $R_{\text{H-F}}$ are primarily caused by the absence of the connected T_3 clusters in the CCSD

Table 3: A comparison of the CC and MMCC ground-state energies with the corresponding full CI results obtained for a few geometries of the HF molecule with a DZ basis set. The full CI total energies are given in hartree. The remaining energies are reported in millihartree relative to the corresponding full CI energy values. The non-parallelity errors (NPE), in millihartree, relative to the full CI results are given as well.

Method	R_e^a	$2R_e$	$3R_e$	$5R_e$	NPE
Full CI ^b	-100.160300	-100.021733	-99.985281	-99.983293	
CCSD	1.634	6.047	11.596	12.291	10.657
CCSDT ^b	0.173	0.855	0.957	0.431	0.784
CCSD(T) ^c	0.325	0.038	-24.480	-53.183	53.508
CR-CCSD(T) ^c	0.500	2.031	2.100	1.650	1.600
MMCC(2,3)/CI ^{d,e}	1.195	2.708	3.669	3.255	2.474
MMCC(2,3)/PT ^e	1.544	1.116	0.025	-0.889	2.433

^a $R_e = 1.7328$ bohr is the equilibrium value of the internuclear H-F distance.

^b From Ref. 27.

^c From Ref. 18.

^d From Ref. 251.

^e The active space consisted of the 3σ , 1π , 2π , and 4σ orbitals.

wavefunction. Indeed, the full CCSDT method, which includes T_3 clusters, reduces large errors in the CCSD results, relative to full CI, to as little as 0.173 millihartree at $R_{\text{H-F}} = R_e$ and 0.431 millihartree at $R_{\text{H-F}} = 5R_e$.

The full CCSDT approach works, but, CCSDT is a rather impractical method. Unfortunately, the much more practical CCSD(T) approach completely fails at large internuclear separations $R_{\text{H-F}}$. Indeed, the small, 0.325 millihartree, error in the results of the CCSD(T) calculations at $R_{\text{H-F}} = R_e$ increases (in absolute value) to 24.480 millihartree at $R_{\text{H-F}} = 3R_e$ and 53.183 millihartree at $R_{\text{H-F}} = 5R_e$ (cf. Table 3). As shown, for example, in Refs. 18, 21, 25–27, 87, the CCSD(T) potential energy curve lies significantly below the full CI curve at larger internuclear separations and

is characterized by an unphysical hump in the region of intermediate $R_{\text{H-F}}$ values.

The CR-CCSD(T) approach, which is one of the “black-box” variants of the MMCC theory, considerably improves the results of the CCSD(T) calculations, eliminating the unphysical hump on the CCSD(T) curve and reducing the 53.183 millihartree error in the CCSD(T) results at $R_{\text{H-F}} = 5R_e$ to 1.650 millihartree.^{18,25,26,87} The errors in the CR-CCSD(T) energies, relative to full CI, do not exceed 2.1 millihartree over the entire range of $R_{\text{H-F}}$ values. The CI-corrected MMCC(2,3) approach, employing the 3σ , 1π , 2π , and 4σ orbitals as active orbitals, provides similar improvements^{25,26,87,251} (see Table 3).

As shown in Table 3, the MMCC(2,3)/PT calculations employing the same set of 3σ , 1π , 2π , and 4σ active orbitals as used in the more expensive MMCC(2,3)/CI calculations reported, for example, in Ref. 251, provide the results which are better in the $R_{\text{H-F}} > R_e$ region than the already very good results of the CR-CCSD(T) and MMCC(2,3)/CI calculations. In particular, the MMCC(2,3)/PT approach reduces the large errors in the CCSD(T) results at $R_{\text{H-F}} = 3R_e$ and $R_{\text{H-F}} = 5R_e$ to small errors that do not exceed 1 millihartree. The signed errors in the MMCC(2,3)/PT results vary between 1.544 millihartree at $R_{\text{H-F}} = R_e$ and -0.889 millihartree at $R_{\text{H-F}} = 5R_e$. The overall qualities of the MMCC(2,3)/PT and MMCC(2,3)/CI results, as measured by the corresponding NPE values, are quite similar. Indeed the NPE values characterizing the MMCC(2,3)/PT and MMCC(2,3)/CI calculations are 2.433 and 2.474 millihartree, respectively. An obvious issue that may need further attention is the the quality of the MMCC(2,3)/PT energy at $R_{\text{H-F}} = R_e$, which is only slightly better than that obtained with CCSD. This is related to the fact that we use the

ground-state RHF orbitals and a small active space which is designed to describe the most essential nondynamical correlation effects in the region of larger H-F distances. The suitable orbital optimization scheme would have to be developed to improve the results of the MMCC(2,3)/PT calculations at $R_{\text{H-F}} = R_e$. One possibility could be to use CASSCF orbitals.

5.2 Bond Breaking in F_2

We now turn to the more challenging case of single bond breaking in F_2 . The results for the F_2 molecule, as described by the cc-pVDZ basis set,²⁶⁷ are shown in Table 4. Again, the ground-state RHF determinant was used as a reference. In the post-RHF calculations, the lowest two orbitals were kept frozen. The active space used in the MRMBPT-corrected MMCC calculation consisted of the five highest-energy occupied orbitals, $3\sigma_g$, $1\pi_u$, $2\pi_u$, $1\pi_g$, and $2\pi_g$, as well as the lowest-energy unoccupied orbital, $3\sigma_u$. No CI-corrected MMCC and full CI calculations were performed for this system, so we have to rely on the full CCSDT energies, reported in Ref. 88, to assess the performance of the MMCC(2,3)/PT approach.

In this case, the CCSDT energies can serve as the reference values, since it is well known that the full CCSDT approach provides an excellent description of a single σ -bond breaking (the previously discussed case of the HF molecule was an illustration of this statement). As one can see, the CCSD approach provides very poor results at all values of the F-F distance $R_{\text{F-F}}$, even at the equilibrium geometry R_e , where the difference between the CCSD and CCSDT energies is already 9.485 millihartree.

Table 4: A comparison of various CC ground-state energies obtained for a few geometries of the F_2 molecule with a cc-pVDZ basis set. In all post-RHF calculations, the lowest two orbitals were kept frozen. The Cartesian components of d orbitals were used. The CCSDT total energies are given in hartree. The remaining energies are reported in millihartree relative to the corresponding CCSDT energies. The non-parallelity errors (NPE), in millihartree, relative to the full CCSDT results are given as well.

Method	$0.75R_e$	R_e^a	$1.25R_e$	$1.5R_e$	$1.75R_e$	$2R_e$	$3R_e$	$5R_e$	NPE
CCSDT ^b	-198.92214	-199.10280	-199.08527	-199.06588	-199.05943	-199.05820	-199.05851	-199.05857	
CCSD	4.504	9.485	19.917	32.424	41.184	45.638	49.425	49.816	45.312
CCSD(T) ^b	0.102	0.248	-0.503	-5.711	-15.133	-23.596	-35.700	-39.348	39.596
CR-CCSD(T) ^b	0.709	1.799	4.482	7.408	8.636	8.660	7.460	6.350	7.951
MMCC(2,3)/PT ^c	3.899	3.725	2.920	3.254	4.044	4.601	5.283	5.618	2.698

^a $R_e = 2.66816$ bohr is the equilibrium value of the internuclear F-F distance.

^b From Ref. 88.

^c The active space included the $3\sigma_g$, $1\pi_u$, $2\pi_u$, $1\pi_g$, $2\pi_g$, and $3\sigma_u$ orbitals.

The CCSD results become even worse for larger values of $R_{\text{F-F}}$. In fact, even the relatively small stretches of the F-F bond, such as $R_{\text{F-F}} = 1.5R_e$, lead to very large, > 30 millihartree errors in the CCSD energies relative to full CCSDT. The failure of the CCSD approach illustrates the important role played by the triply excited clusters in describing the F_2 molecule. The CCSD(T) method is very successful at describing the effects due to triply excited clusters at the equilibrium geometry, reducing the large error in the CCSD result relative to full CCSDT to 0.248 millihartree but, unfortunately, the CCSD(T) approach completely fails at larger F-F distances, where the unsigned errors in the CCSD(T) energies become as large as 39.348 millihartree at $R_{\text{F-F}} = 5R_e$.

The MRMBPT-corrected MMCC theory, explored in this dissertation, dramatically improve the CCSD and CCSD(T) results. As shown in Table 4, the MMCC(2,3)/PT method employing the small active space described above reduces the 9.485 millihartree error in the CCSD energy relative to CCSDT at $R_{\text{F-F}} = R_e$ to 3.725 millihartree. In contrast to CCSD(T), the MMCC(2,3)/PT method remain accurate in the bond breaking region. It is capable of producing the results of nearly CCSDT quality along the entire potential energy curve of F_2 from $R_{\text{F-F}} = 0.75R_e$ to $R_{\text{F-F}} = 5R_e$. The largest error relative to CCSDT characterizing the MMCC(2,3)/PT calculations along the whole curve is 5.618 millihartree. Even more striking is the fact that the NPE value characterizing the MMCC(2,3)/PT energies (calculated relative to the full CCSDT results) is only 2.698 millihartree, demonstrating the ability of the relatively inexpensive MMCC(2,3)/PT approach to produce potential energy curves that accurately mimic the full CCSDT potential curve. The MMCC(2,3)/PT methods

seem to perform better in this regard than the CR-CCSD(T) which work reasonably well at larger F-F separations, but are characterized by somewhat larger NPE values. Only the recently developed size extensive modification of CR-CCSD(T), termed CRCC(2,3), shows the NPE error similar to that observed in the MMCC(2,3)/PT calculations.⁹⁸

5.3 Double Dissociation in H₂O

5.3.1 The DZ basis set

Similar improvements in the relatively poor CCSD and CCSD(T) results are observed when the MMCC(2,3)/PT approach is applied to the simultaneous dissociation of both O–H bonds in H₂O. As explained in Ref. 86 (cf., also, Ref. 251), in this case, a reasonable choice of active orbitals, which is needed to obtain a fairly uniform description of the equilibrium and bond breaking regions, is provided by the $1b_1$, $3a_1$, $1b_2$, $4a_1$, $2b_1$, and $2b_2$ orbitals. We used these orbitals to determine the MRMBPT-like wavefunctions that enter the MMCC/PT corrections to CCSD energies. Since double bond dissociations are characterized by significant quadruple effects, in addition to large effects due to triples, we also performed the MMCC(2,4)/PT calculations to explore the effects of quadruples. The simultaneous stretching or breaking of both O–H bonds in water provides us with an example of a situation, where both T_3 and their T_4 counterparts are sizable and difficult to describe with the approximate CCSDT and CCSDTQ approaches.

As shown in Table 5, the MMCC(2,3)/PT method employing a small set of the

Table 5: A comparison of the CC and MMCC ground-state energies with the corresponding full CI results obtained for the equilibrium and two displaced geometries of the H₂O molecule with the DZ basis set. The full CI total energies are given in hartree. The remaining energies are reported in millihartree relative to the corresponding full CI energy values.

Method	R_e^a	$1.5R_e^b$	$2R_e^b$
Full CI	-76.157866 ^a	-76.014521 ^b	-75.905247 ^b
CCSD	1.790	5.590	9.333
CCSDT ^c	0.434	1.473	-2.211
CCSD(T) ^d	0.574	1.465	-7.699
CR-CCSD(T) ^d	0.738	2.534	1.830
MMCC(2,3)/CI ^{e,f}	0.811	2.407	1.631
MMCC(2,3)/PT ^f	1.265	2.174	0.335
CCSDTQ ^g	0.015	0.141	0.108
CCSD(TQ _f) ^d	0.166	0.094	-5.914
CR-CCSD(TQ) _a ^{d,h}	0.195	0.905	1.461
CR-CCSD(TQ) _b ⁱ	0.195	0.836	2.853
MMCC(2,4)/CI ^{e,f}	0.501	0.942	2.416
MMCC(2,4)/PT ^f	1.069	0.380	-1.815

^a The equilibrium geometry and full CI result from Ref. 268.

^b The geometry and full CI result from Ref. 53.

^c From Ref. 77.

^d From Ref. 18.

^e From Ref. 251.

^f The active space consisted of the $1b_1$, $3a_1$, $1b_2$, $4a_1$, $2b_1$, and $2b_2$ orbitals.

^g From Ref. 80.

^h The “a” variant of the completely renormalized CCSD(TQ) method. The results are from Ref. 25.

ⁱ The “b” variant of the completely renormalized CCSD(TQ) method. The results are from Ref. 25.

$1b_1$, $3a_1$, $1b_2$, $4a_1$, $2b_1$, and $2b_2$ active orbitals reduces the 9.333 and 7.699 millihartree unsigned errors in the CCSD and CCSD(T) results at $R_{\text{O-H}} = 2R_e$ ($R_{\text{O-H}}$ is the O–H distance and R_e is the equilibrium value of $R_{\text{O-H}}$) to 0.335 millihartree. The overall description of the simultaneous stretching of both O–H bonds in H_2O by the MMCC(2,3)/PT approach, which produces the relatively small errors that do not exceed 2.2 millihartree in the entire $R_{\text{O-H}} = R_e - 2R_e$ region, is very good. The CR-CCSD(T) and MMCC(2,3)/CI methods (the active orbital space used in the MMCC(2,3)/CI calculations, which were originally reported in Ref. 251, was the same as that used in the present MMCC(2,3)/PT calculations) provide similar results. We also examined the effect of quadruples on the MMCC/PT results by considering higher-order MMCC corrections to CCSD energies employing the selected triples and quadruples contributions relative to the RHF determinant $|\Phi\rangle$ that originate from the low-order MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86). The MMCC(2,4)/PT method reduces the error of MMCC(2,3)/PT at $R_{\text{O-H}} = 1.5R_e$ further from 2.174 to 0.380 millihartree. However, the MMCC(2,4)/PT overestimates the ground-state energies of the H_2O molecule at $R_{\text{O-H}} = 2R_e$ by 1.815 millihartree. We believe this is due to the simplified version of the MRMBPT theory used in this work. Clearly, it is encouraging to observe that the inexpensive MMCC calculations, in which the simple MRMBPT-like wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86), truncated at triple excitations relative to the RHF determinant $|\Phi\rangle$, are inserted into the MMCC(2,3) energy corrections, provide a much better overall description of bond breaking in H_2O than the standard CCSD and CCSD(T) approaches.

Table 6: A comparison of various CC ground-state energies obtained for the H₂O molecule, as described by the cc-pVDZ basis set, at the equilibrium geometry and several non-equilibrium geometries obtained by stretching the O–H bonds, while keeping the H–O–H angle fixed. The spherical components of the d orbitals were used. In all post-RHF calculations, all electrons were correlated. The full CI total energies are given in hartree. The remaining energies are reported in millihartree relative to the corresponding full CI energies.

Method	R_e^a	$1.5R_e$	$2R_e$	$2.5R_e$	$3R_e$
Full CI ^b	−76.241860	−76.072348	−75.951665	−75.917991	−75.911946
CCSD	3.744	10.043	22.032	20.307	10.849
CCSDT ^b	0.493	1.423	−1.405	−24.752	−40.126
CCSD(T) ^b	0.658	1.631	−3.820	−42.564	−90.512
CR-CCSD(T) ^c	1.025	3.355	7.252	−2.270	−15.040
MMCC(2,3)/PT ^d	2.780	3.329	4.251	−7.607	−21.456

^a The equilibrium value of the O–H distance R_e equals 1.84345 bohr and the H–O–H bond angle is fixed at 110.6°. For further details of the equilibrium and non-equilibrium geometries used in this work, see Ref. 9.

^b From Ref. 9.

^c From Ref. 95.

^d The active space consisted of the $1b_1$, $1b_2$, $3a_1$, $4a_1$, $2b_2$, $5a_1$, and $3b_2$ orbitals.

5.3.2 The cc-pVDZ basis set

To explore the effect of basis set as well as to examine the performance of MRMBPT-corrected MMCC theory in a somewhat more complete scan of the potential energy surface of the doubly dissociating H₂O molecule, we tested our methods on the H₂O system as described by the cc-pVDZ basis set.

Though the CCSDT method provides an excellent description of the equilibrium region, producing an error relative to full CI of only 0.493 millihartree at $R_{O-H} = R_e$, it completely fails at larger O–H separations ($R_{O-H} > 2R_e$), where the errors in the CCSDT energies grow up to 40.126 millihartree at $R_{O-H} = 3R_e$. These results show

that even the full inclusion of T_3 clusters is not sufficient to guarantee the proper description of the double dissociation of water if we go to very large stretches of both O–H bonds. As both O–H bonds in H_2O are simultaneously stretched, the effects of triples as well as quadruples (T_4 clusters) become very important due to a significant increase of a multi-reference character of the ground-state electronic wavefunction. The MMCC(2,3)/PT approach provides a very good description of the O–H stretches up to $R_{\text{O-H}} = 2R_e$, reducing the 10.043 and 22.032 millihartree errors in the CCSD results at $R_{\text{O-H}} = 1.5R_e$ and $R_{\text{O-H}} = 2R_e$, respectively, to 3.329 and 4.251 millihartree. The errors in the MMCC(2,3)/PT results increase as we enter the $R_{\text{O-H}} > 2R_e$ region, where quadruples (neglected in the MMCC(2,3)/PT calculations) become important, but it is more it is also interesting to compare the errors relative to full CI produced by the MMCC(2,3)/PT approach with the errors produced by the full CCSDT method. As one can see in Table 6, the use of the MRMBPT-like wavefunction in determining the ground-state triples correction $\delta_0(2,3)$ of the MMCC(2,3)/PT approach seems to reduce the degree of the failure of the CCSDT method in the $R_{\text{O-H}} > 2R_e$ region.

5.4 Excited States of CH^+

One of the main advantages of the MMCC/PT formalism is that we can study ground as well as excited states. In principle, for a given M -dimensional model space $\mathcal{M}_0$, we can calculate up to M different MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eqs. (86) or (87), which represent the approximate forms of ground and excited states $|\Psi_\mu\rangle$ that enter the MMCC (e.g., MMCC(2,3)) corrections to CC and EOMCC (e.g., CCSD

and EOMCCSD) energies. If we have an *a priori* knowledge about the dominant orbital excitations that define the excited states of interest (and the leading EOMCCSD amplitudes r_a^i and r_{ab}^{ij} may help us in this regard), we can use the corresponding orbitals as active orbitals for the MRMBPT and subsequent MMCC/PT calculations. There is, of course, an issue of matching the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86) or (87), with the corresponding EOMCC states $R_\mu^{(A)}e^{T^{(A)}}|\Phi\rangle$ (in the case of the MMCC(2,3)/PT calculations, the EOMCCSD states $R_\mu^{(\text{CCSD})}e^{T^{(\text{CCSD})}}|\Phi\rangle$), so that we read the correct wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ into the MMCC corrections $\delta_\mu^{(A)}$, but this issue can be resolved by constructing, for example, the overlaps of all zero-order states $|\bar{\Psi}_\mu^{(P)}\rangle$, Eq. (78), obtained by diagonalizing the Hamiltonian in the model space $\mathcal{M}_0$, with all EOMCC states $R_\mu^{(A)}e^{T^{(A)}}|\Phi\rangle$ of interest. In most cases, only one specific zero-order state $|\bar{\Psi}_\mu^{(P)}\rangle$ gives a large overlap with a given EOMCC state $R_\mu^{(A)}e^{T^{(A)}}|\Phi\rangle$. If there are two or more states $|\bar{\Psi}_\mu^{(P)}\rangle$ that form similar overlaps with a given EOMCC state $R_\mu^{(A)}e^{T^{(A)}}|\Phi\rangle$, we can calculate the more complete MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86) or (87), that correspond to these zero-order states $|\bar{\Psi}_\mu^{(P)}\rangle$ and search for the $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ state that gives the maximum overlap with a given EOMCC state $R_\mu^{(A)}e^{T^{(A)}}|\Phi\rangle$. The resulting overlap enters the MMCC correction $\delta_\mu^{(A)}$ anyway (see, e.g., the overlap denominator $\langle \bar{\Psi}_\mu^{(\text{MRMBPT})} | R_\mu^{(A)}e^{T^{(A)}}|\Phi \rangle$ in Eq. (26)), and we can see now that the same denominator serves as a very important diagnostic for matching the EOMCC states $R_\mu^{(A)}e^{T^{(A)}}|\Phi\rangle$ and the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ for the purpose of determining the corresponding energy corrections $\delta_\mu^{(A)}$. In the specific case of the MMCC(2,3)/PT approach tested in this

Table 7: A comparison of various CC and MMCC vertical excitation energies of the CH^+ ion, as described by the $[\text{5s3p1d/3s1p}]$ basis set, at the equilibrium geometry R_e and two stretched geometries, $1.5R_e$ and $2R_e$, with the corresponding full CI results. The full CI values are the excitation energies. All other values are the deviations from the full CI results. The n 1Y energy is the vertical excitation energy from the ground state (X $^1\Sigma^+ \equiv 1$ $^1\Sigma^+$) to the n -th singlet state of symmetry Y . All energies are in eV. The equilibrium bond length R_e in CH^+ is 2.13713 bohr.

State	Full CI ^a	EOMCCSD	CC3 ^b	EOMCCSDT ^c	CR-EOMCCSD(T) ^d	MMCC				
						(2,3)/CI ^{e,f}	(2,4)/CI ^{e,f}	(2,3)/PT ^f	(2,4)/PT ^f	
$R_{\text{C-H}} = R_e$										
2 $^1\Sigma^+$	8.549	0.560	0.230	0.074	0.117	0.084	0.023	0.102	0.033	
3 $^1\Sigma^+$	13.525	0.055	0.016	0.001	0.011	0.000	-0.001	0.051	0.054	
1 $^1\Pi$	3.230	0.031	0.012	-0.003	0.007	0.007	0.010	0.015	0.017	
2 $^1\Pi$	14.127	0.327	0.219	0.060	0.113	0.105	0.037	-0.176	-0.211	
1 $^1\Delta$	6.964	0.924	0.318	0.040	0.027	0.051	0.031	0.090	0.050	
$R_{\text{C-H}} = 1.5R_e$										
2 $^1\Sigma^+$	6.954	0.668		0.055	0.105	0.072	0.020	0.102	-0.008	
3 $^1\Sigma^+$	9.344	0.124		0.023	0.011	0.005	0.004	-0.053	-0.024	
1 $^1\Pi$	1.718	0.109		0.001	0.031	0.024	0.018	0.083	0.080	
2 $^1\Pi$	8.202	0.564		0.059	0.065	0.059	-0.006	-0.022	-0.053	
1 $^1\Delta$	5.847	1.114		0.069	0.004	0.065	0.025	0.085	0.004	
$R_{\text{C-H}} = 2R_e$										
2 $^1\Sigma^+$	5.353	0.299		-0.032	0.093	0.074	0.013	-0.079	0.037	
3 $^1\Sigma^+$	6.681	0.532		0.126	0.084	0.048	0.016	-0.021	-0.045	
1 $^1\Pi$	0.566	0.234		0.002	0.061	0.045	0.021	0.133	0.115	
2 $^1\Pi$	5.363	0.467		0.026	0.018	-0.007	-0.004	-0.123	0.097	
1 $^1\Delta$	4.964	1.178		0.103	-0.009	0.079	0.029	0.005	-0.074	

^a The full CI results for R_e were taken from Ref. 269 and the full CI results for $1.5R_e$ and $2.0R_e$ were taken from Ref. 13.

^b From Ref. 122.

^c From Ref. 24.

^d The ID variant of the CR-EOMCCSD(T) theory. From Ref. 22.

^e From Ref. 127.

^f The active space consisting of the 3σ , $1\pi_x \equiv 1\pi$, $1\pi_y \equiv 1\pi$, and 4σ orbitals.

work, we matched the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$ with the EOMCCSD states $R_\mu^{(\text{CCSD})}e^{T^{(\text{CCSD})}}|\Phi\rangle$ by analyzing first the overlaps of the zero-order states $|\bar{\Psi}_\mu^{(P)}\rangle$, Eq. (78), with the EOMCCSD wavefunctions of interest. If this was not sufficient for determining the matching pairs of the MRMBPT and EOMCCSD states, we calculated the complete overlap denominators $\langle\bar{\Psi}_\mu^{(\text{MRMBPT})}|R_\mu^{(\text{CCSD})}e^{T^{(\text{CCSD})}}|\Phi\rangle$, which we need to determine the MMCC(2,3)/PT corrections to EOMCCSD energies anyway (see the denominators $\bar{D}_\mu$ in Eqs. (93) and (96)).

We illustrate the performance of the MRMBPT-corrected MMCC theory in excited-state calculations by analyzing the results of benchmark MMCC(2,3)/PT and MMCC(2,4)/PT calculations for the valence excited states of the CH^+ ion (see Table 7). We compare the MMCC(2,3)/PT and MMCC(2,4)/PT results for a few low-lying excited states of CH^+ of the $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ symmetries, obtained with the $[5s3p1d/3s1p]$ basis set described in Ref. 269 and the ground-state RHF orbitals, with the results of the corresponding full CI calculations reported in Refs. 13, 269. Along with the MMCC/PT and full CI data, we show the EOMCCSD and full EOM-CCSDT results (the latter ones obtained in Ref. 24) and the results obtained with the perturbative triples response CC3 model.¹²² In addition to the equilibrium geometry $R_{\text{C-H}} = R_e$ ($R_{\text{C-H}}$ is the C–H separation and R_e is the equilibrium value of $R_{\text{C-H}}$), we consider two stretched geometries of CH^+ , so that we can see how good the MMCC/PT theory can be in calculations of excited-state potential energy curves along bond breaking coordinates. We also compare the MMCC/PT results with the results of the MMCC/CI calculations reported in Refs. 126, 127. In calculating the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eq. (86), that enter the MMCC(2,3)/PT and

MMCC(2,4)/PT energy formulas, Eqs. (93) and (94), we used the same set of active orbitals as used in the previously reported MMCC(2,3)/CI and MMCC(2,4)/CI calculations.^{126,127} Thus, the active space employed in the calculations for CH^+ consisted of the highest-energy occupied orbital, 3σ , and the three lowest-energy unoccupied orbitals, $1\pi_x \equiv 1\pi$, $1\pi_y \equiv 2\pi$, and 4σ . This choice of active space reflects the nature of orbital excitations defining the valence excited states of CH^+ shown in Table 7 and the nature of the bond breaking in this system. (see Refs. 124–126 for details). Finally, we compare the results of the MMCC(2,3)/PT calculations with the CR-EOMCCSD(T) results reported in Ref. 22. Let us recall that the CR-EOMCCSD(T) method is a “black-box” variant of the MMCC(2,3) approximation, in which we do not have to select active orbitals to determine the triples corrections to CCSD/EOMCCSD energies derived from the general MMCC formalism.

We begin our discussion with the vertical excitation energies at the equilibrium geometry. In this case, the doubly excited nature of the first-excited $^1\Sigma^+$ ($2\ ^1\Sigma^+$) state and the lowest-energy $^1\Delta$ ($1\ ^1\Delta$) state, and the partially biexcited character of the second $^1\Pi$ ($2\ ^1\Pi$) state (cf. Refs. 111, 124–127, 269) cause significant problems for the EOMCCSD approach. The errors in the EOMCCSD excitation energies for these three states, relative to the corresponding full CI values, are 0.560, 0.924, and 0.327 eV, respectively. The conventional linear response CC approach to triple excitations via the CC3 method of Jørgensen and co-workers^{10,121–123} reduces these large errors to 0.219–0.318 eV,¹²² which is a significant improvement, but if we want to obtain errors which are much than 0.1 eV with the standard EOMCC methodology, we must use the full EOMCCSDT approach (or its active-space EOMCCSDt variant^{125,24}).

The full EOMCCSDT approach reduces the relatively large unsigned errors in the EOMCCSD results for the $2\ ^1\Sigma^+$, $1\ ^1\Delta$, and $2\ ^1\Pi$ states to 0.074, 0.040, and 0.060 eV, respectively.

As shown in Table 7, the CR-EOMCCSD(T), MMCC(2,3)/CI, and MMCC(2,3)/PT methods, which represent three different flavors of the MMCC(2,3) theory and which are all much less expensive than the iterative CC3 and EOMCCSDT approaches, are capable of providing the results of near-EOMCCSDT quality. Indeed, the errors in the vertical excitation energies calculated at $R_{\text{C-H}} = R_e$ for the $2\ ^1\Sigma^+$, $1\ ^1\Delta$, and $2\ ^1\Pi$ states of CH^+ , which have significant double excitation components, obtained with the noniterative CR-EOMCCSD(T), MMCC(2,3)/CI, MMCC(2,3)/PT approximations, are 0.084–0.117 eV for the $2\ ^1\Sigma^+$ state, 0.027–0.090 eV for the $1\ ^1\Delta$ state, and 0.105–0.176 eV for the $2\ ^1\Pi$ state. This should be compared to the 0.560, 0.924, and 0.327 eV errors, respectively, in the EOM-CCSD results and the 0.230, 0.318, and 0.219 eV errors, respectively, obtained with the CC3 method. For the remaining two states shown in Table 7 (the third $^1\Sigma^+$ state and the lowest-energy $^1\Pi$ state), which at $R_{\text{C-H}} = R_e$ are dominated by single excitations,^{111,124–127,269} the errors in the CR-EOMCCSD(T), MMCC(2,3)/CI, and MMCC(2,3)/PT results are 0.000–0.051 eV and 0.007–0.015 eV, respectively. In this case, the CR-EOMCCSD(T), MMCC(2,3)/CI, and MMCC(2,3)/PT methods provide the results of the CC3 or near-EOMCCSDT quality. The standard EOMCC methods, including the basic EOMCCSD approximation, have no troubles with describing excited states dominated by one-electron transitions, but it is encouraging to observe that even in this case all three MMCC(2,3) methods, includ-

ing the MMCC(2,3)/PT approximation developed in this work, improve the EOM-CCSD results. The MMCC(2,4)/PT approach provides small improvements in the MMCC(2,3)/PT results for the $2^1\Sigma^+$ and 1Δ states, while keeping the high accuracy of the MMCC(2,3)/PT calculations for the remaining states.

The very good performance of the MMCC(2,3)/PT and other MMCC(2,3) methods is not limited to vertical excitation energies at the equilibrium geometry. As shown in Table 7, the CR-EOMCCSD(T), MMCC(2,3)/CI, and MMCC(2,3)/PT approaches are capable of providing a highly accurate description of excited-state potentials of CH^+ at larger values of $R_{\text{C-H}}$, where all excited states listed in Table 7 gain a considerable multi-reference character^{124–127}. The very large (even ~ 1 eV) errors in the EOMCCSD results for the excited-state potential energy curves of CH^+ , relative to the corresponding full CI potentials, are reduced in the CR-EOMCCSD(T), MMCC(2,3)/CI, and MMCC(2,3)/PT calculations to 0.1 eV or less. Indeed, the errors in the EOMCCSD excitation energies, relative to full CI, for the two lowest excited states of the $1\Sigma^+$ symmetry, the two lowest 1Π states, and the lowest 1Δ state are 0.668, 0.124, 0.109, 0.564, and 1.114, respectively, at $R_{\text{C-H}} = 1.5R_e$, and 0.299, 0.532, 0.234, 0.467, and 1.178 eV, respectively, at $R_{\text{C-H}} = 2R_e$. The MMCC(2,3)/PT method proposed in this work reduces these large unsigned errors to 0.102, 0.053, 0.083, 0.022, and 0.085 eV, respectively, at $R_{\text{C-H}} = 1.5R_e$, and 0.079, 0.021, 0.133, 0.123, and 0.005 eV, respectively, at $R_{\text{C-H}} = 2R_e$. As in the $R_{\text{C-H}} = R_e$ case, the only standard EOMCC approach that can provide the results of similar quality is the very expensive full EOMCCSDT method (cf. Table 7). The MMCC(2,4)/PT approach provides further improvements in a few cases or does not change the already very

good MMCC(2,3)/PT energies.

The results in Table 7 show that all three MMCC(2,3) approximations, including CR-EOMCCSD(T), MMCC(2,3)/CI, and MMCC(2,3)/PT, provide similar improvements in the EOMCCSD energies. The improvements are particularly substantial for excited states dominated by doubles and for excited-state potentials at stretched internuclear geometries, where all excited states of CH^+ gain a significant multi-reference character. It is interesting to learn that the basic and relatively simple MMCC(2,3) approximation is capable of providing considerable improvements in the EOMCCSD results, independent of the form of the wavefunction $|\Psi_\mu\rangle$ used in the MMCC(2,3) correction formula. The CR-EOMCCSD(T) approach uses the perturbative, EOMCCSDT-like, wavefunctions $|\Psi_\mu\rangle$, the MMCC(2,3)/CI method uses the MRCI-like wave functions $|\Psi_\mu\rangle$, and the MMCC(2,3)/PT scheme proposed in this work uses the MRMBPT-like wavefunctions $|\Psi_\mu\rangle$ defined by Eqs. (86) or (87), and yet the resulting MMCC(2,3) excitation energies for CH^+ are very similar. This demonstrates the robustness of the MMCC formalism, which is capable of improving the results of conventional CC and EOMCC calculations independent of the specific form of $|\Psi_\mu\rangle$ used to calculate the energy corrections $\delta_\mu^{(A)}$ or $\delta_\mu^{(\text{CCSD})}$. From the point of view of this work, it is important that we can considerably improve the CCSD and EOMCCSD results using low-order MRMBPT-like wavefunctions $|\Psi_\mu\rangle$ defined by Eq. (86). As explained earlier, the MMCC(2,3)/PT is much less expensive than the MMCC(2,3)/CI approach, since we do not have to solve iterative MRCI-like equations to obtain the wavefunctions $|\Psi_\mu\rangle$ that enter the MMCC(2,3)/PT energy expression. Also, if the active space is small, the MMCC(2,3)/PT method is less expensive than

the CR-EOMCCSD(T) approach, since the summation over $i < j < k, a < b < c$ in Eq. (93) includes only the selected types of triple excitations relative to $|\Phi\rangle$ that are included in the MRMBPT wavefunctions $|\bar{\Psi}_\mu^{(\text{MRMBPT})}\rangle$, Eqs. (86) or (87). Finally, it is worth noticing that there is no apparent need to reoptimize orbitals to obtain an accurate description of excited states of CH^+ in the MMCC(2,3)/PT calculations (the ordinary RHF orbitals seem to suffice), although it would be interesting to examine the role of orbital optimization in MRMBPT calculations that precede the MMCC(2,3)/PT calculations. The MMCC(2,4)/PT method improves the description of the CH^+ system somewhat, but not to a degree that would favor this approach over the less expensive MMCC(2,3)/PT approximation.

6 Summary, Concluding Remarks, and Future Perspectives

In this dissertation, a new electronic structure theory, termed MMCC/PT, which combines the CC/EOMCC method with low-order multi-reference perturbation theory, has been developed. The MMCC/PT approaches have been formulated using diagrammatic methods. The MMCC(2,3)/PT and MMCC(2,4)/PT methods have been efficiently implemented using the idea of diagram factorization. The performance of the basic MMCC/PT approximations has been illustrated by the results of test calculations for the bond breaking in HF, F₂, and H₂O, and the excited states of CH⁺. The test calculations show that the MMCC(2,3)/PT and MMCC(2,4)/PT approaches provide a good description of bond breaking and excited states dominated by doubles, eliminating the failures of the conventional CC/EOMCC methods at larger internuclear distances and for excited states dominated by two-electron transitions without invoking expensive steps of high-order CC/EOMCC methods.

Clearly, several issues need further study. The role of different choices of active orbitals should be examined. The majority of multi-reference calculations are performed with the orbitals optimized at the CASSCF level. In this work, we have only used the ground-state RHF orbitals. It would be also interesting to examine different types of the MRMBPT wavefunctions that enter the MMCC/PT corrections. In this work, we have tested a simplified MRMBPT-like scheme based on the partitioning of the Hamiltonian into the model-space (P -space) and Q -space components (the latter component originates from single and double excitations from a multi-dimensional

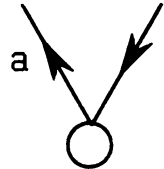
model space). The majority of contemporary MRMBPT calculations are performed with schemes, such as CASPT2, MC-QDPT, or MRMP2, mentioned in the Introduction. Several other low-order MRMBPT have been proposed in literature as discussed in the Chapter 1. It would be useful to test how the conclusions of this work depend on the particular form of the MRMBPT theory used to provide wavefunctions $|\Psi_\mu\rangle$ for MMCC calculations.

Appendices

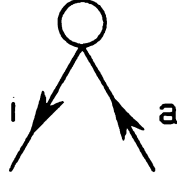
Appendix A. An Introduction to the Diagrammatic Methods of Many-Body Theory

To introduce the diagrammatic methods of many-body theory, we begin our considerations with selecting a Fermi vacuum state $|\Phi\rangle$, which is a single-determinantal state that is typically chosen to provide a reasonable approximation to the ground electronic state of a given many-fermion system of interest. The Fermi vacuum state (reference state) is diagrammatically represented by an empty space. All other Slater determinants are represented with *oriented lines*, pointing either *upward* for *particle states* (spin-orbitals unoccupied in the reference $|\Phi\rangle$) or *downward* for *hole states* (spin-orbitals occupied in the reference $|\Phi\rangle$), with labels associated with the corresponding spin-orbitals excitations relative to $|\Phi\rangle$, and outgoing or incoming into a simple vertex.

We represent the second-quantized operators entering a given operator product with basic diagrams. In the design of these diagrams, we use vertices with *incoming lines* representing *annihilation operators* and *outgoing lines* representing the *creation operators*. Each basic *vertex* contains information about matrix elements in a spin-orbital basis defining the operator. For instance, the Slater determinants $|\Phi_i^a\rangle = [a^a a_i]|0\rangle$ are represented by



and $\langle\Phi_i^a| = \langle 0|(a^a a_i)^\dagger = \langle 0|a^i a_a$ are represented by



We assign different vertices to represent different operators. Since the one-body operator brings a pair of creation and annihilation operators, its diagrammatic representation contains only two oriented lines. Likewise, the diagram representing the two-body operator, which brings two pairs of creation and annihilation operators, contains four oriented lines, and so on and so forth.

There are several diagrammatic representations; the most popular are the Hugenholtz and the Goldstone representations. The Hugenholtz representation employs the antisymmetrized matrix elements in the second-quantized definitions of operators (e.g., $v_{pq}^{rs} = \langle pq|v|rs\rangle - \langle pq|v|sr\rangle$ for the two-body operator V_N) while the Goldstone representation is based on the second-quantized form of operators that uses non-symmetric matrix elements (e.g. $\langle pq|v|rs\rangle$ in the case of V_N). In our analysis, we use the Hugenholtz representation, since this approach produces fewer distinct resulting diagrams than the Goldstone representation. The Goldstone representation is useful in developing spin-adapted formalisms for spin-free Hamiltonians.

The basic diagrams (in the Hugenholtz representation) for the one- and two-body parts of the electronic Hamiltonian in the normal-ordered form, F_N and V_N ,

$$F_N = \sum_{p,q} f_p^q N[a^p a_q] \equiv f_p^q N[a^p a_q] \quad (119)$$

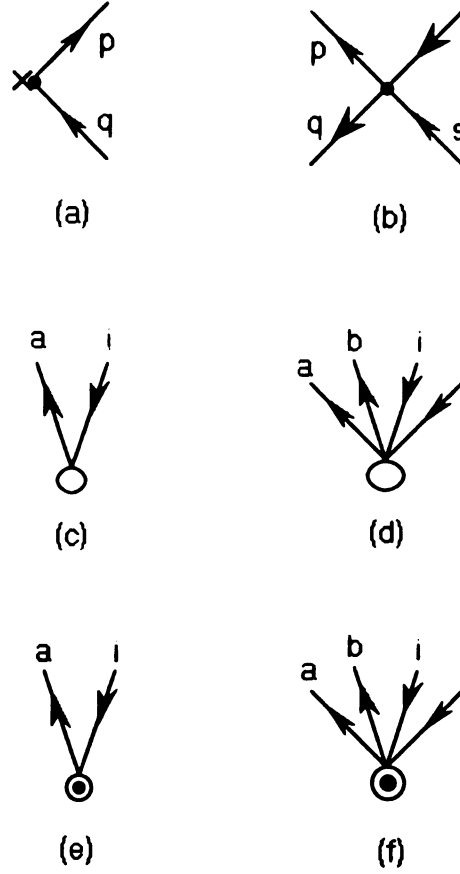


Figure 15: Hugenholtz representation of (a) F_N ; (b) V_N ; (c) T_1 ; (d) T_2 ; (e) $R_{\mu,1}$; and (f) $R_{\mu,2}$.

and

$$V_N = \frac{1}{4} \sum_{p,q,r,s} v_{pq}^{rs} N[a^p a^q a_s a_r] \equiv \frac{1}{4} v_{pq}^{rs} N[a^p a^q a_s a_r], \quad (120)$$

respectively, and the cluster and excitation operators T_1 , T_2 , $R_{\mu,1}$, and $R_{\mu,2}$ are shown in Figure 15.

The spin-orbitals that are attached to the oriented lines are referred to as *free* if they represent summation indices and as *fixed* otherwise. As shown in Figure 15, the cluster operators and the linear excitation operators have the same diagrammatic form, the only difference is with their corresponding vertices. In particular, T_1 and

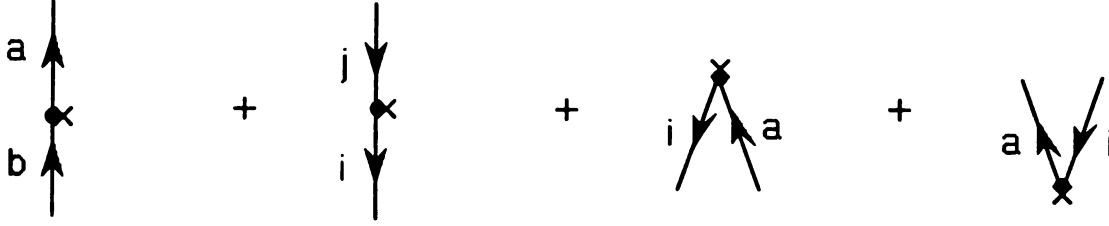


Figure 16: Hugenholtz representation of F_N .

T_2 use unfilled oval vertices, while $R_{\mu,1}$ and $R_{\mu,2}$ use circled dots. A diagram stripped of the free labels is called a *skeleton* or, better, the oriented skeleton. The oriented skeleton determines the weight of the diagram (a combinatorial coefficient that enters the algebraic expression). The spin-orbital indices p, q, r, s can either be occupied or unoccupied in the Fermi vacuum. According to standard convention, the indices $i, j, \dots$ label occupied spin-orbitals, while $a, b, \dots$ refer to unoccupied spin-orbitals in the Fermi vacuum $|\Phi\rangle$. For example, the one-body component of the Hamiltonian H_N can be expressed as

$$F_N = \sum_{a,b} f_a^b N[a^a a_b] + \sum_{i,j} f_i^j N[a^i a_j] + \sum_{i,a} f_i^a N[a^i a_a] + \sum_{i,a} f_a^i N[a^a a_i]. \quad (121)$$

The corresponding diagrams are shown in Figure 16. The two-body component of H_N , V_N , can be partitioned in a similar way, as shown in Figure 17.

After assigning skeletons (or diagrams) to the basic operators, the diagrammatic calculation proceeds as follows:

1. Represent the operators by appropriate skeletons following the vertical time axis (as described in Section 4.3), that is, placing the operators from the bottom to

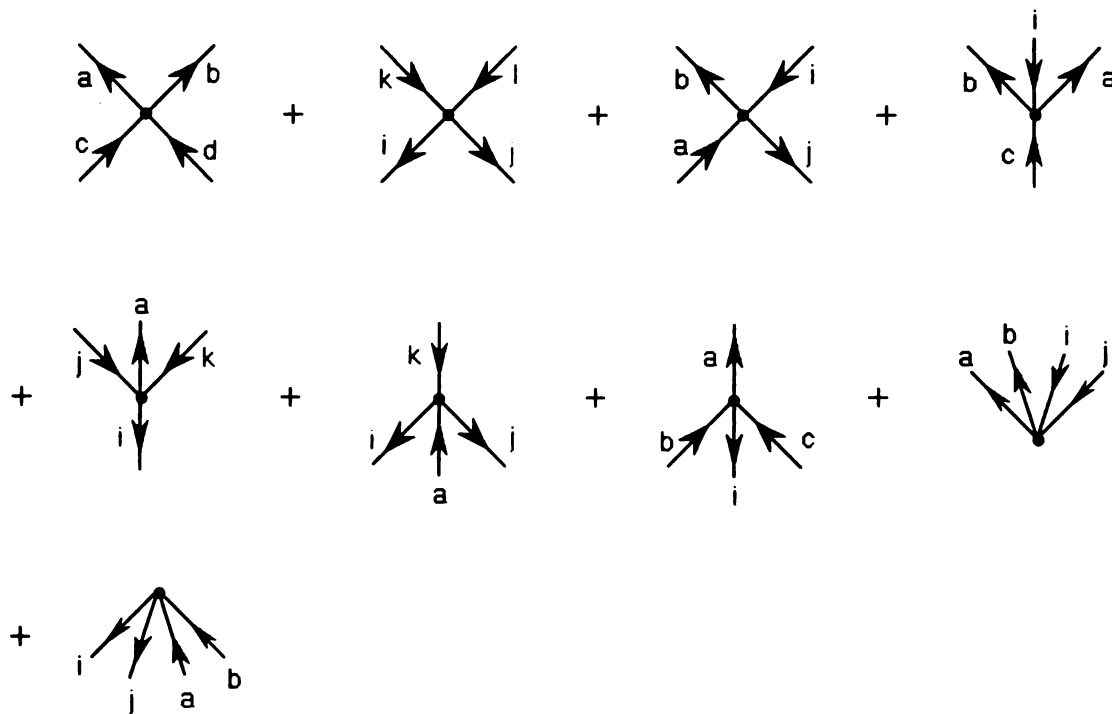
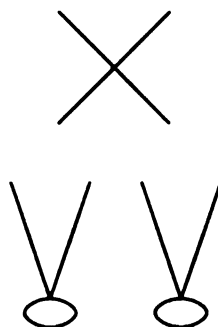


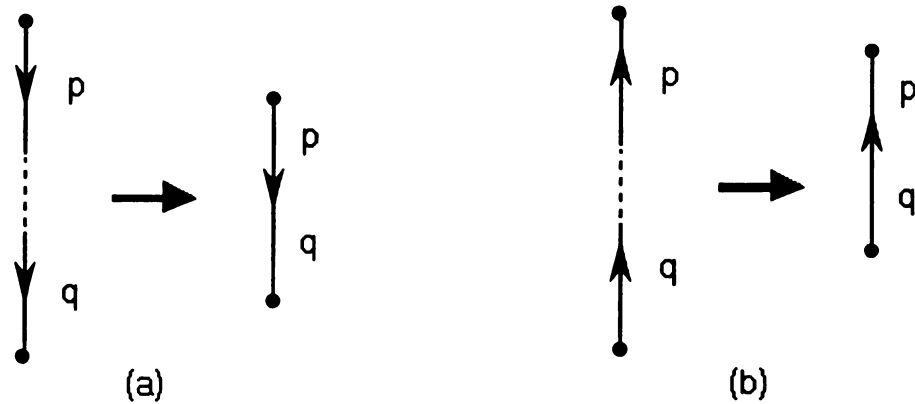
Figure 17: Hugenholtz representation of V_N .

the top corresponding to the left to right order of the operators, when they act on the functions (vectors) in the Fock space. For instance, the operator $\frac{1}{2}(V_N T_1^2)$ is represented as



2. Form all permissible resulting skeletons by connecting the lines in all possible ways. Then, form all nonequivalent resulting diagrams, in which the oriented

lines are labeled with their corresponding spin-orbital indices, representing only the nonvanishing contraction schemes that result when the Wick's theorem is applied, that is,



where (a) $\overline{a^p a_q} = \delta_{pq} H(q)$ and (b) $\overline{a_p a^q} = \delta_{pq} [1 - H(q)]$.

The $H(q)$ step function is equal to 1 for q being a hole and 0 for q representing a particle and δ_{pq} is the usual Kronecker delta.

3. Lastly, assign the algebraic expressions to all nonequivalent permissible resulting diagrams. The final expression for the operator product of interest is a sum of the algebraic expressions corresponding to all nonequivalent resulting diagrams allowed by a given many-body formalism. In general, the corresponding algebraic expression of a given diagram is a product of (a) the weight factor, (b) the sign factor, (c) the scalar factor, and (for example, in the wavefunction expressions) (d) the operator part, accompanied by a summation over all relevant hole and particle indices, if such summations exist in the operators. For the

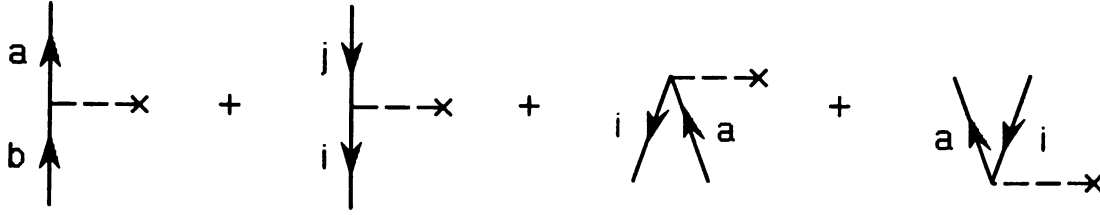


Figure 18: Bradow representation of F_N .

connected Hugenholtz diagrams, the weight factor is specified by $(\frac{1}{2})^m$ where m is the number of pairs of “equivalent” lines. A pair of equivalent lines is defined as being two lines originating at the same vertex and ending at another, but same vertex, and going in the same direction. We must remember that the identically oriented lines carrying fixed (i.e. not summed) spin-orbital indices can never be regarded as equivalent lines. The scalar factor is a product of matrix elements associated with the individual vertices entering the resulting diagram. The operator part (if it appears in the expression) is a product of the creation and annihilation operators associated with the uncontracted external lines.

The drawback of the Hugenholtz representation is that Hugenholtz diagrams do not specify the overall sign of the contribution of the diagram. This is due to the fact that the basic Hugenholtz diagrams, such as V_N or T_2 , use antisymmetrized matrix elements v_{pq}^{rs} , t_{ab}^{ij} , etc. In order to determine the sign, it is necessary to draw one Goldstone representative, called the Bradow diagram, for each Hugenholtz diagram. This can be done by “expanding” the Hugenholtz vertices. In other words, we replace all basic Hugenholtz vertices by Bradow vertices (the Bradow representations of

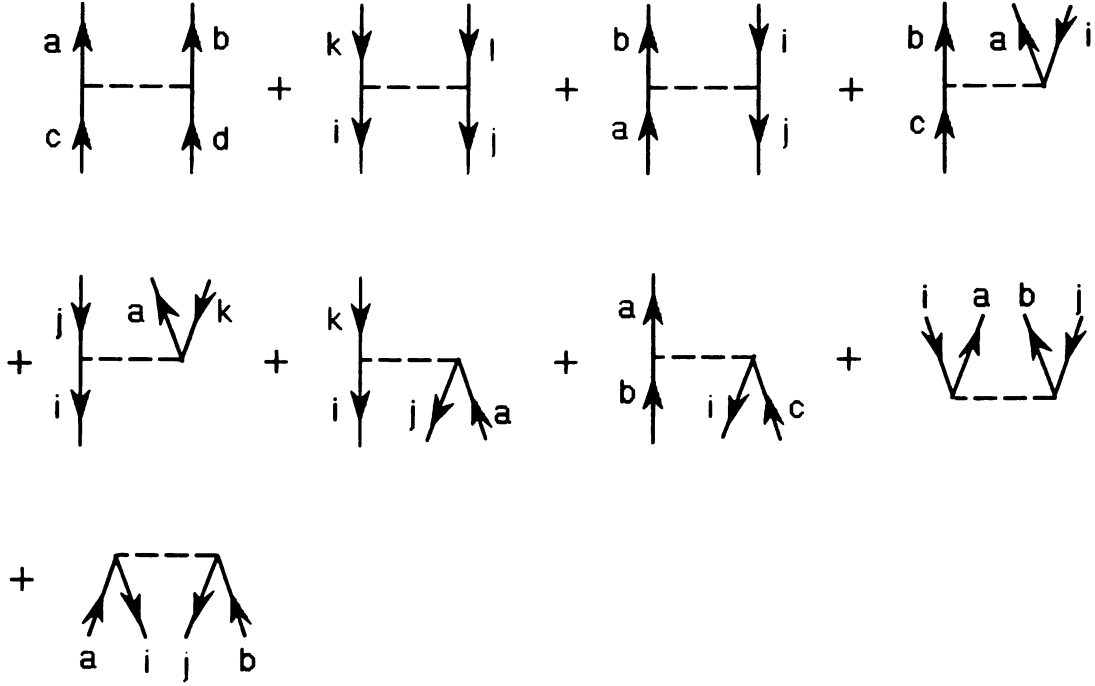


Figure 19: Brandow representation of V_N .

F_N and V_N are shown in Figures 18 and 19), while keeping the directions of the lines and the connectivity intact. Usually more than one possibility exists, since one can usually draw several Goldstone diagrams for each Hugenholtz diagram, but this is not a problem here: we choose any Goldstone representative of a given Hugenholtz diagram as a Brandow diagram. The final results do not depend on the choice. Once the Brandow diagram is drawn, we determine the sign factor for it by counting the number of loops (l) and the number of internal hole lines (h) and by using the sign formula $(-1)^{l+h}$.

Appendix B. The Structure of the Similarity-transformed Hamiltonian of the CCSD Theory

The $\bar{H} = e^{-T} H e^T$ operator is a quantity of interest for several reasons. Due to the Campbell-Hausdorff-Baker formula, $\bar{H}$ can be expanded in terms of commutators only, which is equivalent to its expansion in terms of the connected diagrams, as in Eqs. (9) and (12). This means that $\bar{H}$ is represented by a finite set of diagrams. The other reason $\bar{H}$ is worth considering is the fact that it is a quantity that occurs in various computational schemes based upon the CC wavefunction ansatz.

In order to construct the $\bar{H}^{(\text{CCSD})}$ diagrams, we follow the diagrammatic rules discussed in Appendix A. Thus, we contract the Hamiltonian in the normal ordered form, H_N , with a number of $T^{(\text{CCSD})}$ operators appearing in the $e^{T^{(\text{CCSD})}}$ expansion. Since Hamiltonians used in chemistry contain at most two-body interactions, H_N can be contracted with at most four cluster operators to produce connected diagrams of $\bar{H}_N^{(\text{CCSD})}$.

The one- and two-body components of the $\bar{H}^{(\text{CCSD})}$ have similar diagrammatic forms as the one- and two-body component of the Hamiltonian, H_N , the difference is only with the interaction line, the former uses the wavy interaction line, while the latter uses the dashed lines, as in Figures 18 and 19.

To illustrate how we use the diagrammatic methods in deriving the explicit algebraic expressions for $\bar{H}^{(\text{CCSD})}$,

$$\bar{H}^{(\text{CCSD})} = (H_N e^{T_1 + T_2})_C = \bar{h}_p^q a^p a_q + \frac{1}{4} \bar{h}_{pq}^{rs} a^p a^q a_s a_r + \dots, \quad (122)$$

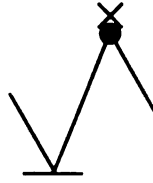
we show an example on how we obtain the contributing diagrams to $\bar{h}_a^b$,



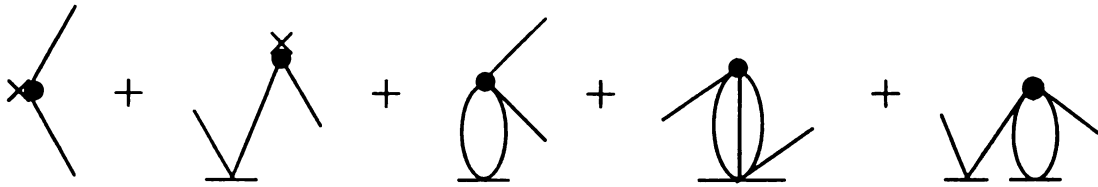
which is one of the one-body components of $\bar{H}^{(\text{CCSD})}$. In this case, our goal is to generate diagrams of this form from the connected product of H_N and $e^{T^{(\text{CCSD})}}$. The resulting diagrams must contain an oriented line above and below the vertex; both lines should be directed upward as particle lines a and b . We can expand the $\bar{H}^{(\text{CCSD})}$ operator in the following manner:

$$\begin{aligned}
 \bar{H}^{(\text{CCSD})} &= (H_N e^{T^{(\text{CCSD})}})_C \\
 &= [(F_N(1 + T_1 + T_2 + \tfrac{1}{2}T_1^2 + \dots) + \\
 &\quad V_N(1 + T_1 + T_2 + \tfrac{1}{2}T_1^2 + \dots))]_C.
 \end{aligned} \tag{123}$$

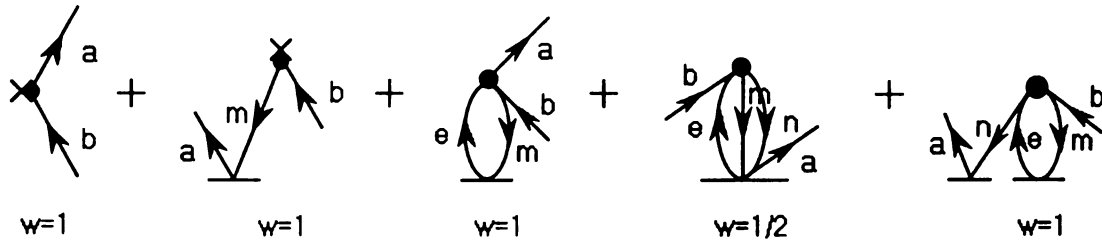
Let us identify which terms in Eq. (123) contributes to $\bar{h}_a^b$ by forming first the nonoriented Hugenholtz skeletons. We begin with the first term, F_N , which is represented diagrammatically in Figure 16. As shown in Figure 16, the leftmost diagram in that figure satisfies the above criteria and hence contributes to $\bar{h}_a^b$. Next, we consider the $(F_N T_1)_C$ terms, which produces one resulting nonoriented Hugenholtz skeleton that contains one line above the vertex as well as one line below the vertex as shown below:



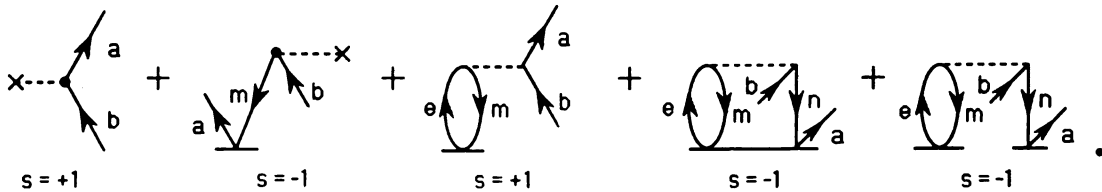
When we analyze other terms in Eq. (123) in the same fashion, we obtain all of the resulting nonoriented Hugenholtz skeletons of $\bar{h}_a^b$, which are



The corresponding oriented Hugenholtz diagrams for $\bar{h}_a^b$ with their respective weights are as follows:



The corresponding Brandow diagrams for $\bar{h}_a^b$ with their corresponding sign factors are shown below



These diagrams yield the following algebraic expression for $\bar{h}_a^b$:

$$\bar{h}_a^b = f_a^b - f_m^b t_a^m + v_{ma}^{eb} t_e^m - \frac{1}{2} v_{mn}^{eb} t_{ea}^{mn} - v_{mn}^{eb} t_e^m t_a^n. \quad (124)$$

All of the resulting diagrams for one-, two-, three-, and four-body components of $\bar{H}^{(\text{CCSD})}$ are obtained in a similar way. They are shown in Figures 20-23. Figures 24 and 25 show all of the resulting diagrams corresponding to ground-state triply and quadruply excited moments of the CCSD equations, $\mathfrak{M}_{0,abc}^{ijk}(2)$ and $\mathfrak{M}_{0,abcd}^{ijkl}(2)$, respectively, which can also be regarded as three- and four-body components of $\bar{H}^{(\text{CCSD})}$. Tables 8-11 summarize all the algebraic expressions of the one-, two-, three-, and four-body components of $\bar{H}^{(\text{CCSD})}$, including $\mathfrak{M}_{0,abc}^{ijk}(2)$ and $\mathfrak{M}_{0,abcd}^{ijkl}(2)$, which are obtained by reading the diagrams shown in Figures 20-25.

(a) $\bar{h}_i^a$

(b) $\bar{h}_a^b$

(c) $\bar{h}_i^j$

Figure 20: One-body components of $\bar{H}^{(\text{CCSD})}$.

(a) $\bar{h}_{ai}^{bc}$

(b) $\bar{h}_{ij}^{ka}$

(c) $\bar{h}_{ab}^{cd}$

(d) $\bar{h}_{ij}^{kl}$

Figure 21: Two-body components of $\bar{H}^{(\text{CCSD})}$.

Diagram (e) shows the decomposition of a wavy line between two vertical fermion lines. The left side is a wavy line connecting two vertical lines with external labels b, a on the left and i, j on the right. The right side is a sum of seven diagrams: a dashed line, a dashed line with a fermion loop, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, and a dashed line with a fermion loop and an external fermion line.

(e) $\bar{h}_{jb}^{ia}$

Diagram (f) shows the decomposition of a wavy line between two vertical fermion lines. The left side is a wavy line connecting two vertical lines with external labels b, c on the left and i, a on the right. The right side is a sum of twelve diagrams: a dashed line with a fermion loop, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, a dashed line with a fermion loop and an external fermion line, and a dashed line with a fermion loop and an external fermion line.

(f) $\bar{h}_{ab}^{ic}$

Figure 21: continued.

(a) $\tilde{h}_{abc}^{tjd}$

Figure 22: Three-body components of $\bar{H}^{(\text{CCSD})}$.

The diagram shows the decomposition of a four-point interaction (represented by a wavy line) into a sum of tree-level diagrams. The external lines are labeled with momenta k, l, i, j and indices a, b . The internal lines are labeled with momenta f, m, e, k, b, j, i, a and indices e, m, k, b, j, i, a . The diagrams are arranged in four rows, separated by plus signs, and the entire sum is preceded by an equals sign.

(b) $\bar{h}_{lba}^{kji}$

Figure 22: continued.

(c) $\bar{h}_{cba}^{dei}$

(d) $\bar{h}_{mla}^{kji}$

(e) $\bar{h}_{bka}^{cji}$

Figure 22: continued.

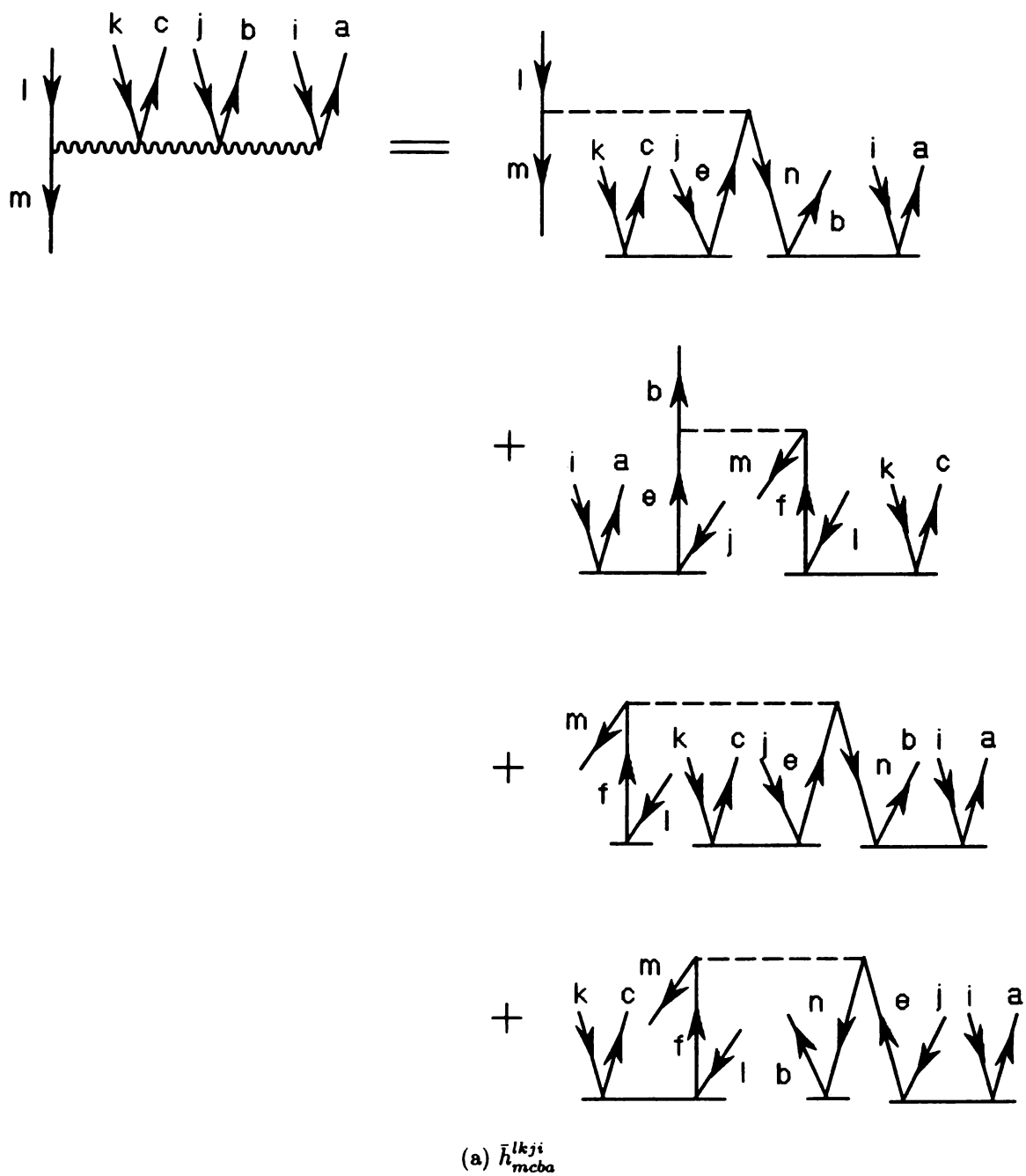
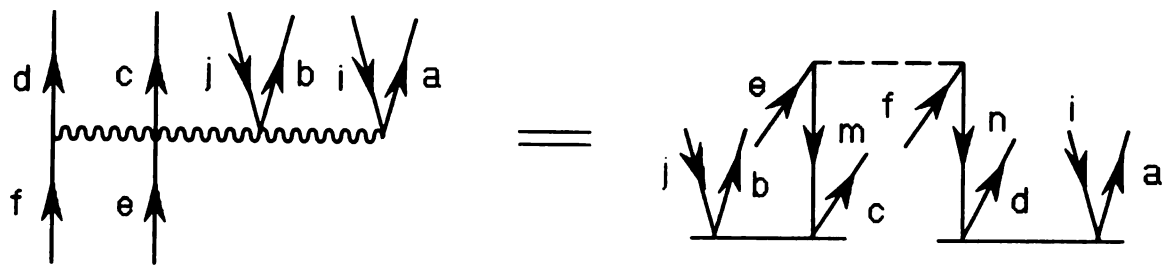


Figure 23: Four-body components of $\bar{H}^{(\text{CCSD})}$.

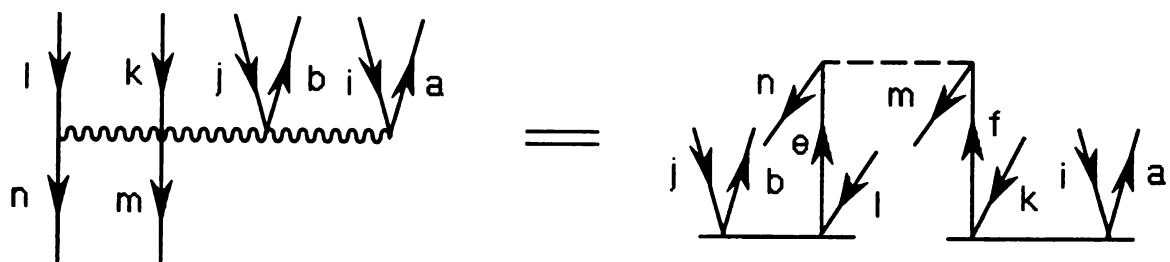
The diagram shows the decomposition of a four-point function into a sum of tree-level diagrams. The left side shows a four-point function with external lines labeled d (up), e (up), k (down), c (down), j (down), b (down), i (down), and a (down). The internal lines are a wavy line and a dashed line. The right side shows the sum of four tree-level diagrams, each with a different internal structure, connected by plus signs. The diagrams are labeled with various internal lines and vertices, including $k, c, j, b, i, a, d, e, m, n, f$.

(b) $\bar{h}_{dcba}^{ekji}$

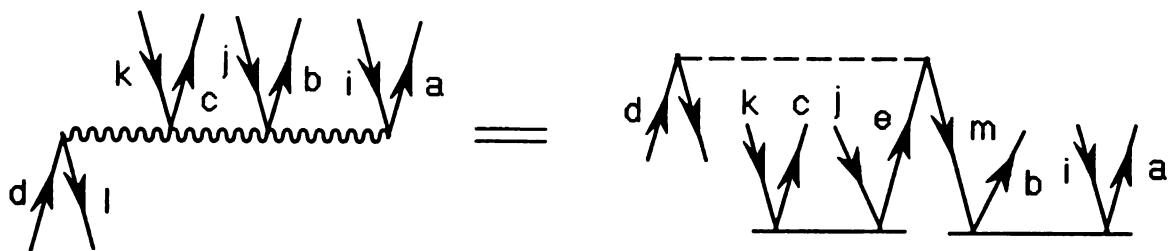
Figure 23: continued.



(c) $\bar{h}_{dcba}^{feji}$



(d) $\bar{h}_{nmba}^{lkji}$



(e) $\bar{h}_{lcba}^{dkji}$

Figure 23: continued.

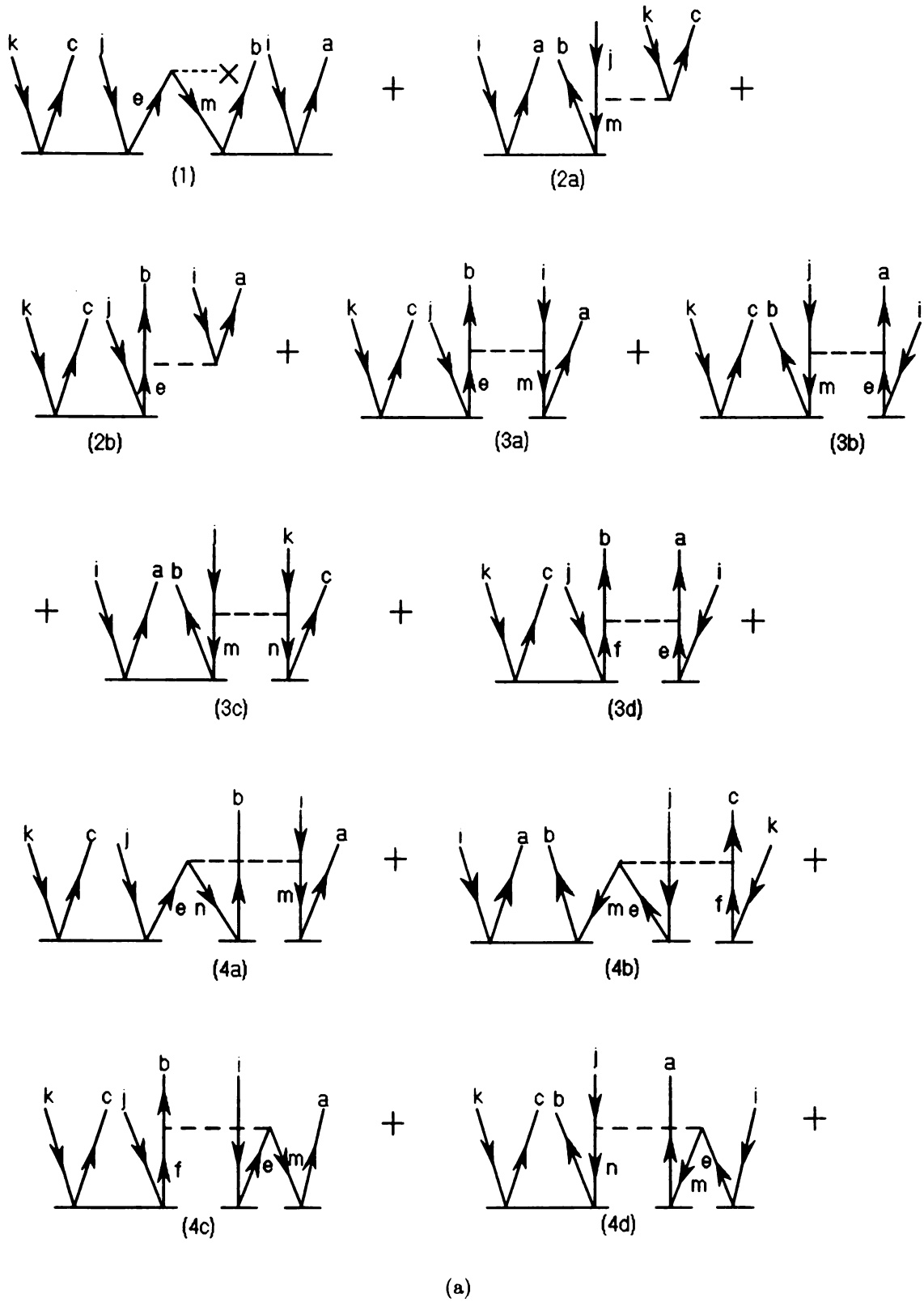
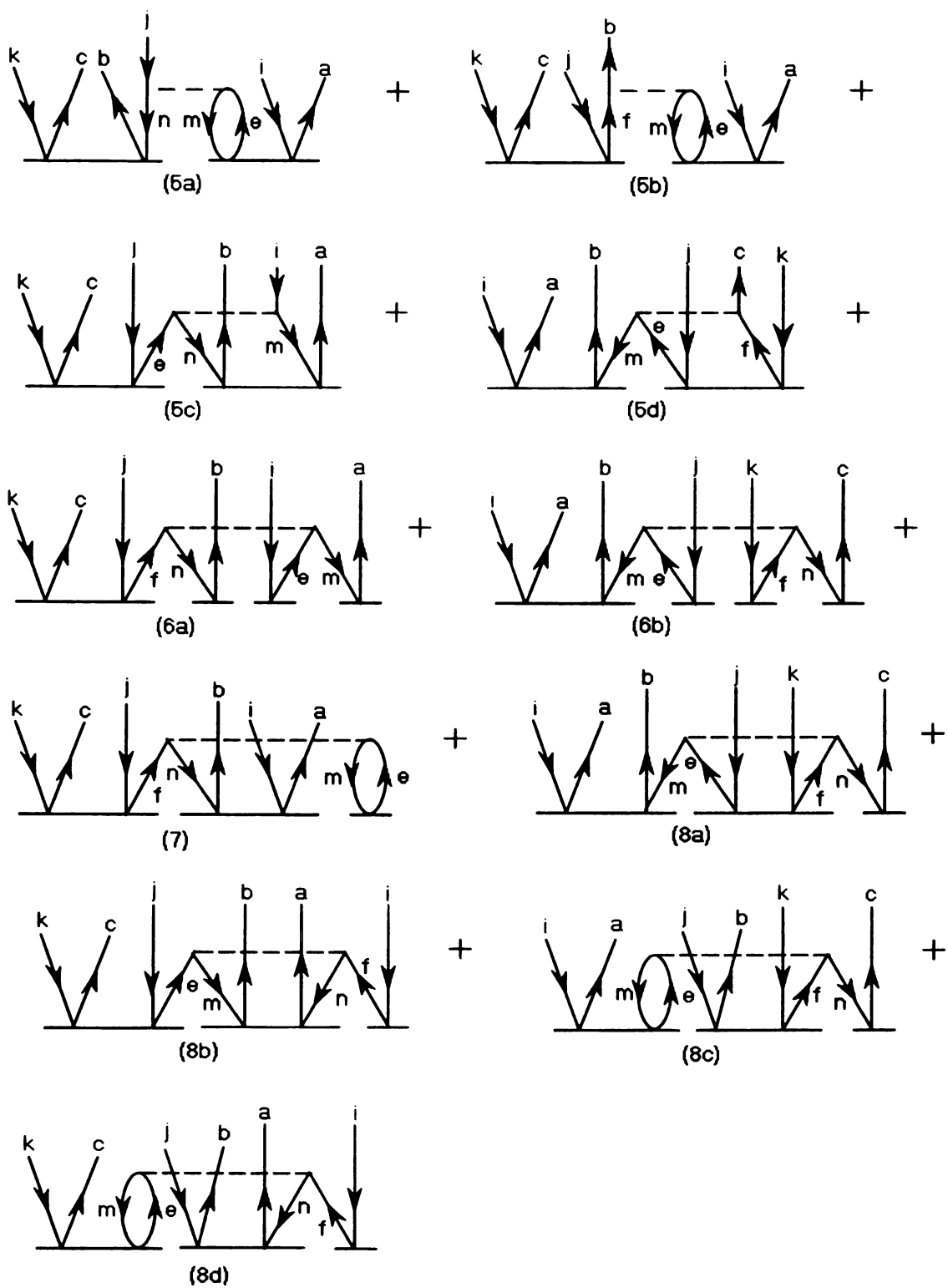


Figure 24: Diagrammatic representation of $\mathfrak{M}_{0,abc}^{ijk}(2)$.



(b)

Figure 24: continued.

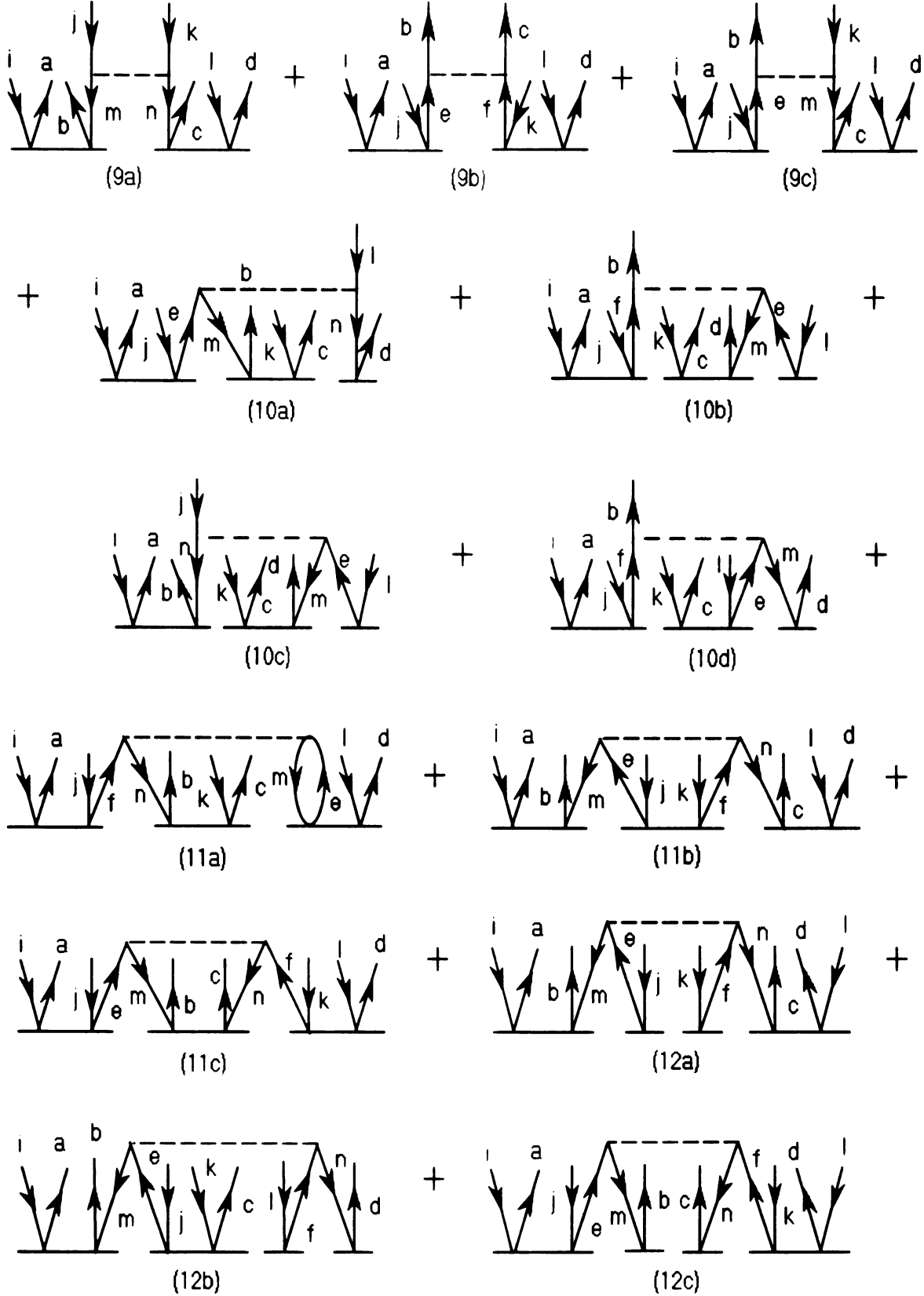


Figure 25: Diagrammatic representation of $\mathfrak{M}_{0,abcd}^{ijkl}(2)$.

Table 8: Explicit algebraic expressions for the one- and two-body matrix elements elements of $\bar{H}^{(\text{CCSD})}$ (designated by $\bar{h}$) shown in Figures 20-21.

Expression ^a		Figure
$\bar{h}_i^a$	$f_i^a + v_{im}^{ae} t_e^m$	20 (a)
$\bar{h}_a^b$	$f_a^b + v_{am}^{be} t_e^m - \frac{1}{2} v_{mn}^{eb} t_{ea}^{mn} - v_{mn}^{eb} t_e^m t_a^n - f_m^b t_a^m$	20 (b)
$\bar{h}_i^j$	$f_i^j + v_{im}^{je} t_e^m + \frac{1}{2} v_{mi}^{ef} t_{ef}^{mj} + v_{mi}^{ef} t_e^m t_f^j + f_i^e t_e^j$	20 (c)
$\bar{h}_{ai}^{bc}$	$v_{ai}^{bc} - v_{mi}^{bc} t_a^m$	21 (a)
$\bar{h}_{ij}^{ka}$	$v_{ij}^{ka} + v_{ij}^{ea} t_e^k$	21 (b)
$\bar{h}_{ab}^{cd}$	$v_{ab}^{cd} + \frac{1}{2} v_{mn}^{cd} t_{ab}^{mn} - \mathcal{A}_{ab} v_{am}^{cd} t_b^m + v_{mn}^{cd} t_a^m t_b^n$	21 (c)
$\bar{h}_{ij}^{kl}$	$v_{ij}^{kl} + \frac{1}{2} v_{ij}^{ef} t_{ef}^{kl} + \mathcal{A}^{kl} v_{ij}^{ke} t_e^l + v_{ij}^{ef} t_e^k t_f^l$	21 (d)
$\bar{h}_{jb}^{ia}$	$v_{jb}^{ia} + v_{bj}^{ea} t_e^i - v_{mj}^{ia} t_b^m + v_{mj}^{ea} t_{be}^{im} - v_{jm}^{ae} t_e^i t_b^m$	21 (e)
$\bar{h}_{ab}^{ic}$	$-f_m^c t_{ab}^{im} + v_{ab}^{ic} + v_{ab}^{ec} t_e^i - \mathcal{A}_{ab} v_{am}^{ic} t_b^m + \mathcal{A}_{ab} v_{mb}^{ec} t_{ae}^{im}$ $+ \frac{1}{2} v_{mn}^{ic} t_{ab}^{mn} + v_{mn}^{ic} t_a^m t_b^n - \mathcal{A}_{ab} v_{am}^{ec} t_e^i t_b^m + v_{mn}^{ec} t_a^m t_e^i t_b^n$ $- v_{mn}^{ec} t_e^m t_{ab}^{in} - \mathcal{A}_{ab} v_{mn}^{ec} t_{ae}^{im} t_b^n - \frac{1}{2} v_{mn}^{ec} t_{ab}^{mn} t_e^i$	21 (f)
$\bar{h}_{ia}^{jk}$	$f_i^e t_{ea}^{jk} + v_{ia}^{jk} - v_{im}^{jk} t_a^m + \mathcal{A}^{jk} v_{ia}^{ek} t_e^j + \mathcal{A}^{jk} v_{im}^{je} t_{ea}^{mk}$ $+ \frac{1}{2} v_{ia}^{fe} t_{fe}^{jk} - \mathcal{A}^{jk} v_{im}^{ek} t_a^m t_e^j + v_{ia}^{fe} t_f^j t_e^k - v_{im}^{fe} t_a^m t_e^k t_f^j$ $+ v_{im}^{fe} t_e^m t_{fa}^{jk} + \mathcal{A}^{jk} v_{im}^{fe} t_{ea}^{mk} t_f^j - \frac{1}{2} v_{im}^{fe} t_{fe}^{jk} t_a^m$	21 (g)

^a Summation over repeated upper and lower indices is assumed; $f_p^q = \langle p|f|q \rangle$ and $v_{pq}^{rs} = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$ are the one- and two-electron integrals in a molecular spin-orbital basis $\{p\}$ corresponding to the Fock operator (f) and the two-body part of the Hamiltonian (v).

Table 9: Explicit algebraic expressions for the three- and four-body matrix elements elements of $\bar{H}^{(\text{CCSD})}$ (designated by $\bar{h}$) shown in Figures 22-23.

	Expression ^a	Figure
$\bar{h}_{abc}^{ijd}$	$\mathcal{A}_{a/bc} v_{nm}^{de} t_c^{n_i} t_b^{m_j} t_{ea}^{j_i} + \mathcal{A}_{ab/c} \mathcal{A}^{ij} v_{nm}^{de} t_c^{n_i} t_e^{j_i} t_{ba}^{m_i}$ $- \mathcal{A}_{a/bc} \mathcal{A}^{ij} v_{nm}^{de} t_{bc}^{j_n} t_{ea}^{m_i} + \frac{1}{2} \mathcal{A}_{a/bc} v_{nm}^{de} t_{nm}^{j_n} t_{cb}^{m_i} t_{ea}^{j_i}$ $+ \mathcal{A}_{ab/c} \mathcal{A}^{ij} v_{nm}^{dj} t_c^{n_i} t_{ba}^{m_i} - \mathcal{A}_{abc} v_{mb}^{de} t_c^{m_i} t_{ea}^{j_i} - \mathcal{A}_{ac/b} \mathcal{A}^{ij} v_{bm}^{ed} t_e^{j_i} t_{ca}^{m_i}$ $+ \mathcal{A}_{a/bc} v_{cb}^{de} v_{ea}^{j_i} - \mathcal{A}_{ab/c} \mathcal{A}^{ij} v_{cm}^{dj} t_{ba}^{m_i}$	22 (a)
$\bar{h}_{lba}^{kji}$	$-\mathcal{A}_{ab} \mathcal{A}^{ij/k} v_{lm}^{fe} t_f^{k_i} t_b^{m_j} t_{ea}^{j_i} - \mathcal{A}^{i/jk} v_{lm}^{fe} t_f^{k_i} t_e^{j_i} t_{ba}^{m_i}$ $+ \mathcal{A}_{ab} \mathcal{A}^{i/jk} v_{lm}^{fe} t_{bf}^{j_k} t_{ea}^{m_i} - \frac{1}{2} \mathcal{A}^{i/jk} v_{lm}^{fe} t_{fe}^{k_j} t_{ba}^{m_i}$ $-\mathcal{A}^{ijk} v_{lm}^{ej} t_e^{k_i} t_{ba}^{m_i} + \mathcal{A}_{ab} \mathcal{A}^{ij/k} v_{bl}^{ef} t_e^{j_i} t_{fa}^{m_i}$ $-\mathcal{A}_{ab} \mathcal{A}^{ik/j} v_{ml}^{je} t_b^{m_i} t_{ea}^{k_i} + \mathcal{A}_{ab} \mathcal{A}^{ij/k} v_{lb}^{ke} t_{ea}^{j_i} - \mathcal{A}^{i/jk} v_{lm}^{kj} t_{ba}^{m_i}$	22 (b)
$\bar{h}_{cba}^{dei}$	$-\mathcal{A}_{ab/c} v_{cm}^{ed} t_{ba}^{m_i} + \mathcal{A}_{ab/c} v_{nm}^{ed} t_c^{n_i} t_{ba}^{m_i}$	22 (c)
$\bar{h}_{mla}^{kji}$	$\mathcal{A}^{ij/k} v_{ml}^{ke} t_{ea}^{j_i} + \mathcal{A}^{ij/k} v_{ml}^{fe} t_f^{k_i} t_{ea}^{j_i}$	22 (d)
$\bar{h}_{bka}^{cji}$	$\mathcal{A}_{ab} v_{bk}^{ce} t_{ea}^{j_i} - \mathcal{A}_{ab} v_{mk}^{ce} t_b^{m_i} t_{ea}^{j_i}$ $-\mathcal{A}^{ij} v_{km}^{jc} t_{ba}^{m_i} - \mathcal{A}^{ij} v_{km}^{ec} t_e^{j_i} t_{ba}^{m_i}$	22 (e)
$\bar{h}_{mcba}^{lkji}$	$-\mathcal{A}_{ab/c} \mathcal{A}^{i/jk/l} v_{mn}^{le} t_{ce}^{k_j} t_{ba}^{n_i} + \mathcal{A}_{ac/b} \mathcal{A}^{ij/kl} v_{mb}^{fe} t_{ae}^{j_i} t_{fc}^{k_i}$ $-\mathcal{A}_{ab/c} \mathcal{A}^{i/jk/l} v_{mn}^{fe} t_f^{l_i} t_{ce}^{k_j} t_{ba}^{n_i} - \mathcal{A}_{ac/b} \mathcal{A}^{ij/kl} v_{mn}^{fe} t_{cf}^{kl} t_b^{n_i} t_{ea}^{j_i}$	23 (a)
$\bar{h}_{dcba}^{ekji}$	$-\mathcal{A}_{ab/c/d} \mathcal{A}^{i/jk} v_{dm}^{ef} t_{cf}^{k_j} t_{ba}^{m_i} + \mathcal{A}_{ab/cd} \mathcal{A}^{ik/j} v_{mn}^{je} t_{ab}^{m_i} t_{dc}^{nk}$ $+ \mathcal{A}_{ab/c/d} \mathcal{A}^{i/jk} v_{nm}^{ef} t_d^{n_i} t_{cf}^{k_j} t_{ba}^{m_i} + \mathcal{A}_{ab/cd} \mathcal{A}^{ik/j} v_{nm}^{ef} t_{cd}^{kn} t_f^{j_i} t_{ba}^{m_i}$	23 (b)
$\bar{h}_{dcba}^{feji}$	$\mathcal{A}_{ad/bc} v_{mn}^{ef} t_{bc}^{j_m} t_{da}^{n_i}$	23 (c)
$\bar{h}_{nmba}^{lkji}$	$\mathcal{A}^{ik/jl} v_{nm}^{ef} t_{be}^{j_l} t_{fa}^{k_i}$	23 (d)
$\bar{h}_{lcba}^{dkji}$	$-\mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{lm}^{de} t_{ce}^{k_j} t_{ba}^{m_i}$	23 (e)

^a Summation over repeated upper and lower indices is assumed; $f_p^q = \langle p|f|q \rangle$ and $v_{pq}^{rs} = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$ are the one- and two-electron integrals in a molecular spin-orbital basis $\{p\}$ corresponding to the Fock operator (f) and the two-body part of the Hamiltonian (v).

Table 10: Explicit algebraic expressions for $\mathfrak{M}_{0,abc}^{ijk}(2)$ obtained by reading the diagrams shown in Figure 24.

Term	Expression ^a
1	$- \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} f_m^e t_{ab}^{im} t_{ec}^{jk}$
2a	$- \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mc}^{jk} t_{ab}^{im}$
2b	$\mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{ab}^{ie} t_{ec}^{jk}$
3a	$- \mathcal{A}_{abc} \mathcal{A}^{i/jk} v_{mb}^{ie} t_a^m t_{ec}^{jk}$
3b	$- \mathcal{A}_{a/bc} \mathcal{A}^{ijk} v_{am}^{ej} t_e^i t_{bc}^{mk}$
3c	$\mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mn}^{jk} t_{ab}^{im} t_c^{jn}$
3d	$\mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{ab}^{ef} t_e^i t_{fc}^{jk}$
4a	$\mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mn}^{ie} t_a^m t_b^n t_{ec}^{jk}$
4b	$- \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mc}^{ef} t_{ab}^{im} t_e^j t_f^{jk}$
4c	$- \mathcal{A}_{abc} \mathcal{A}^{i/jk} v_{bm}^{fe} t_{fc}^{jk} t_e^i t_a^m$
4d	$\mathcal{A}_{a/bc} \mathcal{A}^{ijk} v_{nm}^{je} t_e^i t_a^m t_{bc}^{nk}$
5a	$- \mathcal{A}_{a/bc} \mathcal{A}^{ijk} v_{mn}^{ej} t_{ae}^{im} t_{bc}^{nk}$
5b	$\mathcal{A}_{abc} \mathcal{A}^{i/jk} v_{mb}^{ef} t_{ae}^{im} t_{fc}^{jk}$
5c	$\frac{1}{2} \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mn}^{ie} t_{ab}^{mn} t_{ec}^{jk}$
5d	$-\frac{1}{2} \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mc}^{ef} t_{ab}^{im} t_{ef}^{jk}$
6a	$\mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mn}^{ef} t_a^m t_e^i t_b^n t_{fc}^{jk}$
6b	$\mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mn}^{ef} t_{ab}^{im} t_e^j t_f^{jk} t_c^{in}$
7	$- \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{ef}^{mn} t_{nc}^{jk} t_{ab}^{in} t_e^m$
8a	$\frac{1}{2} \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mn}^{ef} t_{ab}^{im} t_{ef}^{jk} t_c^{in}$
8b	$\frac{1}{2} \mathcal{A}_{ab/c} \mathcal{A}^{i/jk} v_{mn}^{ef} t_{ec}^{jk} t_{ba}^{mn} t_f^i$
8c	$- \mathcal{A}_{abc} \mathcal{A}^{i/jk} v_{mn}^{ef} t_{ae}^{im} t_{bf}^{jk} t_c^{in}$
8d	$- \mathcal{A}_{ab/c} \mathcal{A}^{ijk} v_{mn}^{ef} t_f^i t_{ab}^{nj} t_{ec}^{mk}$

^a Summation over repeated upper and lower indices is assumed; $f_p^q = \langle p|f|q \rangle$ and $v_{pq}^{rs} = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$ are the one- and two-electron integrals in a molecular spin-orbital basis $\{p\}$ corresponding to the Fock operator (f) and the two-body part of the Hamiltonian (v).

Table 11: Explicit algebraic expressions for $\mathfrak{M}_{0,abcd}^{ijkl}(2)$ obtained by reading the diagrams shown in Figure 25.

Term	Expression ^a
9a	$\mathcal{A}_{ab/cd} \mathcal{A}^{jk/il} v_{mn}^{jk} t_{ab}^{im} t_{cd}^{nl}$
9b	$\mathcal{A}_{bc/ad} \mathcal{A}^{ij/kl} v_{bc}^{ef} t_{ae}^{ij} t_{fd}^{kl}$
9c	$-\mathcal{A}_{a/b/cd} \mathcal{A}^{ij/k/l} v_{bm}^{ek} t_{ae}^{ij} t_{cd}^{ml}$
10a	$\mathcal{A}_{a/bc/d} \mathcal{A}^{ij/k/l} v_{mn}^{el} t_{ae}^{ij} t_{bc}^{mk} t_d^n$
10b	$-\mathcal{A}_{a/b/cd} \mathcal{A}^{ij/k/l} v_{mb}^{ef} t_{af}^{ij} t_{cd}^{km} t_e^l$
10c	$\mathcal{A}_{ab/cd} \mathcal{A}^{ik/j/l} v_{mn}^{ej} t_{ab}^{in} t_{cd}^{km} t_e^l$
10d	$-\mathcal{A}_{ac/b/d} \mathcal{A}^{ij/kl} v_{mb}^{ef} t_{af}^{ij} t_{ce}^{kl} t_d^m$
11a	$-\mathcal{A}_{a/bc/d} \mathcal{A}^{ij/k/l} v_{mn}^{ef} t_{af}^{ij} t_{bc}^{nk} t_{ed}^{ml}$
11b	$\frac{1}{2} \mathcal{A}_{ab/cd} \mathcal{A}^{il/jk} v_{mn}^{ef} t_{ab}^{im} t_{ef}^{jk} t_{cd}^{nl}$
11c	$\frac{1}{2} \mathcal{A}_{ad/bc} \mathcal{A}^{ij/kl} v_{mn}^{ef} t_{ae}^{ij} t_{bc}^{mn} t_{fd}^{kl}$
12a	$\mathcal{A}_{ab/cd} \mathcal{A}^{il/jk} v_{mn}^{ef} t_{ab}^{im} t_e^j t_f^k t_{cd}^{nl}$
12b	$\mathcal{A}_{ab/c/d} \mathcal{A}^{i/jk/l} v_{mn}^{ef} t_{ab}^{im} t_{ec}^{jk} t_f^l t_d^n$
12c	$\mathcal{A}_{ad/bc} \mathcal{A}^{ij/kl} v_{mn}^{ef} t_{am}^{ij} t_b^m t_c^n t_{fd}^{kl}$

^a Summation over repeated upper and lower indices is assumed; $f_p^q = \langle p|f|q \rangle$ and $v_{pq}^{rs} = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$ are the one- and two-electron integrals in a molecular spin-orbital basis $\{p\}$ corresponding to the Fock operator (f) and the two-body part of the Hamiltonian (v).

Appendix C. Factorization of Coupled-Cluster Diagrams

The diagrammatic technique is a very powerful tool, however, if we program the diagrams one by one, this will give an inefficient and hence impractical computer code, even in a situation where each of the diagrams is computed at a modest cost. The purpose of this section is to reformulate the one- and two-body components of $\bar{H}^{(\text{CCSD})}$ in such a way that all the common pieces could be factored out, computed only once, and then substituted in different places. This procedure is possible due to the fact that coupled-cluster diagrams are, in fact “denominator-less”, which means that the MBPT denominators are implicitly included in the cluster operator vertices, which avoids assigning the denominators to each diagram that are normally considered in MBPT diagrams. This enables us to sum over all internal lines belonging to one T vertex independent of the other T vertex, which helps the factorization.

In this section, we rederive the expressions for the one- and two-body components of $\bar{H}^{(\text{CCSD})}$, $\bar{H}_1^{(\text{CCSD})}$ and $\bar{H}_2^{(\text{CCSD})}$, respectively, in such a way that only linear terms with redefined vertices are retained in each equation. Thus, in each nonlinear term, we retain one t amplitude, usually (but not always) corresponding to the highest level of excitation, while the remaining amplitudes are absorbed to an effective vertex. Ultimately, the factorized forms of $\bar{H}_1^{(\text{CCSD})}$ and $\bar{H}_2^{(\text{CCSD})}$ are used to define the higher-rank components of $\bar{H}^{(\text{CCSD})}$, such as the three- and four-body components $\bar{H}_3^{(\text{CCSD})}$ and $\bar{H}_4^{(\text{CCSD})}$, as well as other intermediates entering the CC expressions of interest, such as $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ and $\mathfrak{M}_{\mu,abcd}^{ijkl}(2)$, which are naturally expressed via $\bar{H}_3^{(\text{CCSD})}$ and $\bar{H}_4^{(\text{CCSD})}$.

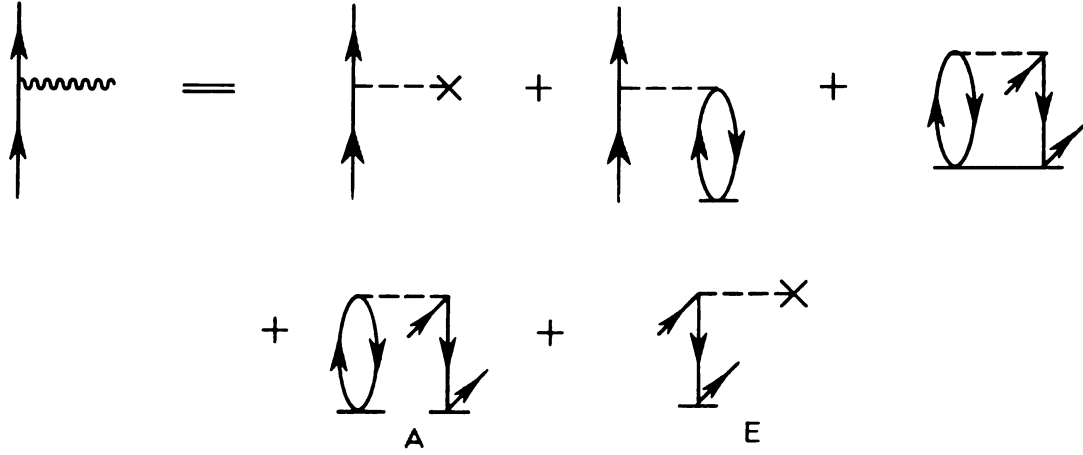


Figure 26: Diagrammatic representation of $\bar{h}_a^b$.

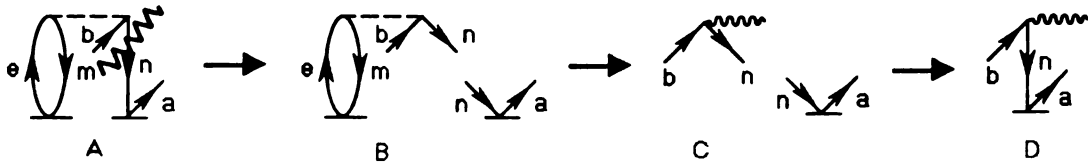


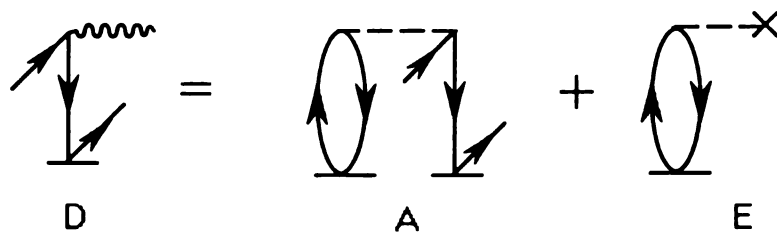
Figure 27: Example of diagram factorization.

To illustrate the diagrammatic factorization technique and computational benefits that it offers, we analyze an example of $\bar{h}_a^b$, which is expressed in a diagrammatic form in Figure 26.

Clearly, diagram A in Figure 26 is a nonlinear contribution. Hence, diagram A is a good candidate for demonstrating the idea and benefits of factorization. The cost of evaluating this diagram scales as $\mathcal{N}^5$ with the system size $\mathcal{N}$ or $n_o^2 n_u^3$.

Figure 27 presents the factorization of diagram A and its decomposition, for computational efficiency, into independently calculated parts. After factorization, the original computational cost associated with diagram A, $n_o^2 n_u^3$, is reduced to $n_o n_u^2$ (the

cost associated with diagram D) plus $n_o^2 n_u^2$ (the cost associated with the intermediate C which is defined as diagram B). Furthermore, if we realize that the intermediate C actually takes one of the forms of $\bar{H}_1^{(\text{CCSD})}$, which may have been calculated already, we can take advantage of this fact by extending the definition of the above intermediate C as one of the one-body components of $\bar{H}_1^{(\text{CCSD})}$, in this case the $\bar{h}_n^b$, which is defined in part (a) of Figure 20. As a result, diagram D, which has initially represented a single diagram A in Figure 27, becomes now equivalent to



corresponding to diagrams A and E in the original, not factorized, diagrammatic formulation of $\bar{h}_a^b$, as shown in Figure 26. Thus, the fully factorized version of $\bar{h}_a^b$, as shown in Figure 28, uses four diagrams, which are considerably cheaper to calculate than the original five diagrams shown in Figure 26.

The same factorization and cost reduction procedure can be applied to other components of $\bar{H}^{(\text{CCSD})}$. The computational savings offered by the factorization procedure in the case of the two-body and other many-body components of $\bar{H}^{(\text{CCSD})}$ are even more substantial than in the above example. Figures 29-30 shows the factorized diagrams of the one- and two-body components of $\bar{H}^{(\text{CCSD})}$, which can be generated in a recursive, fully vectorized (linearized) manner.

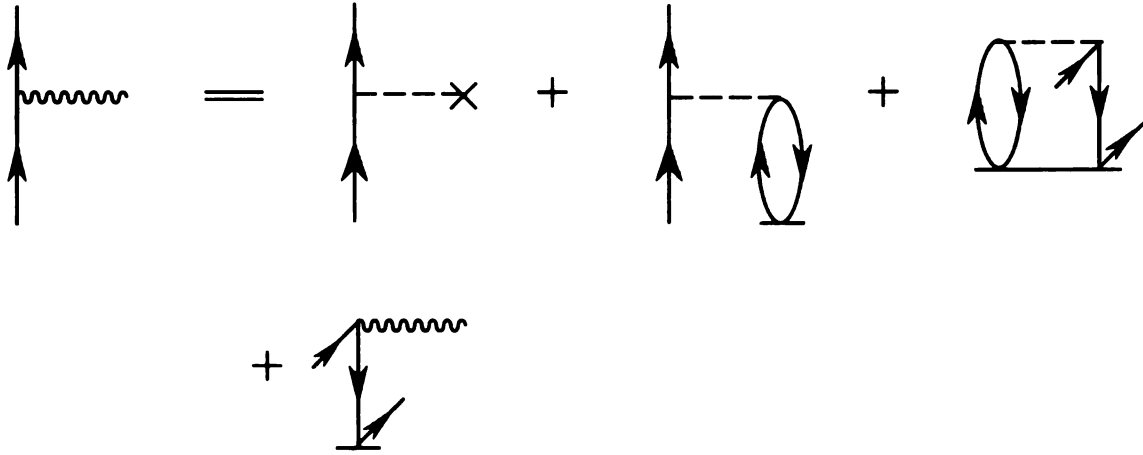
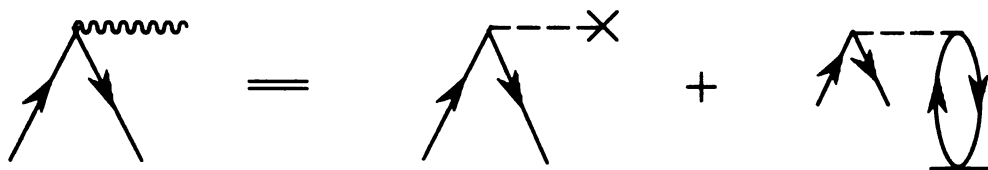
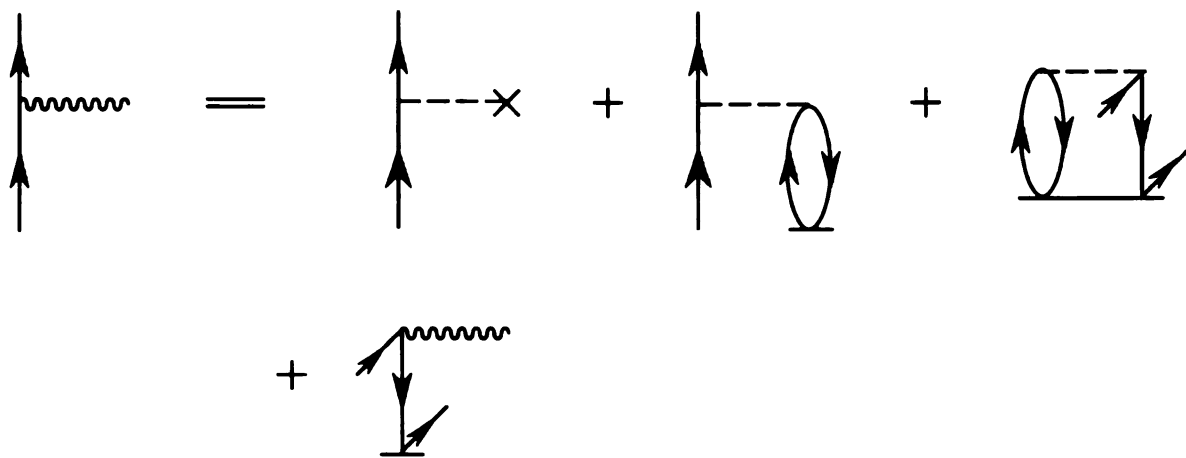


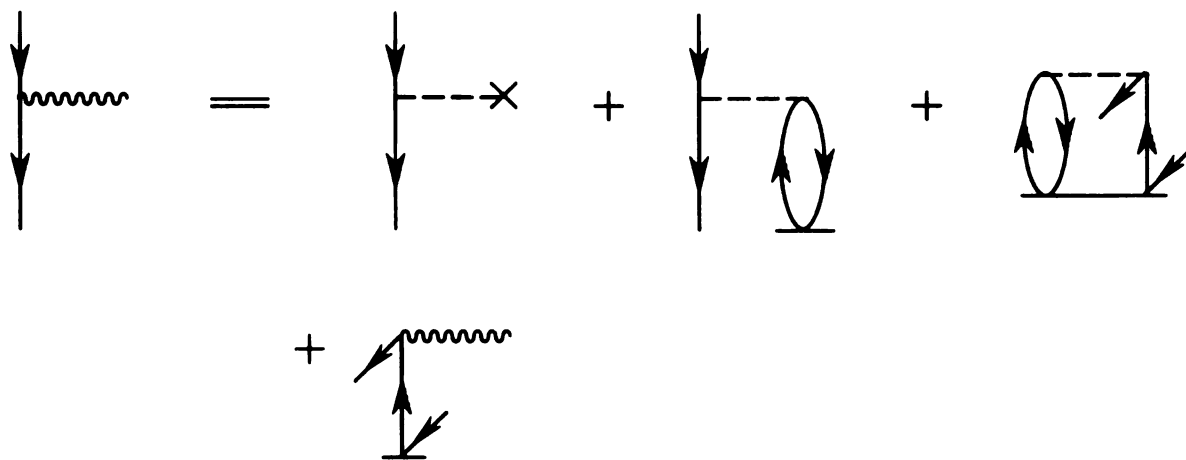
Figure 28: Fully Factorized Diagrammatic Formulation of $\bar{h}_a^b$



(a) $\bar{h}_i^a$

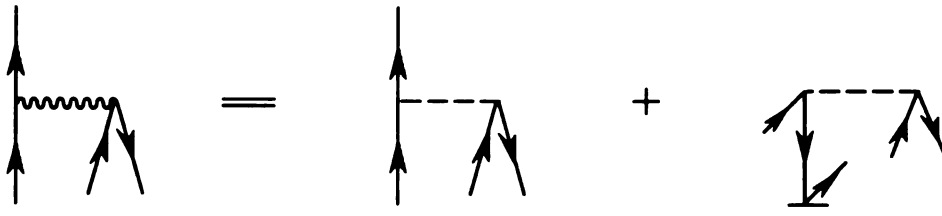


(b) $\bar{h}_a^b$

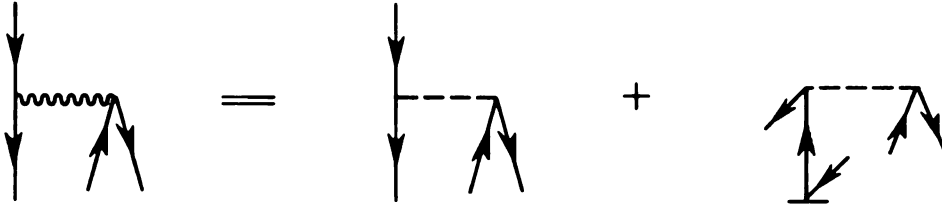


(c) $\bar{h}_i^j$

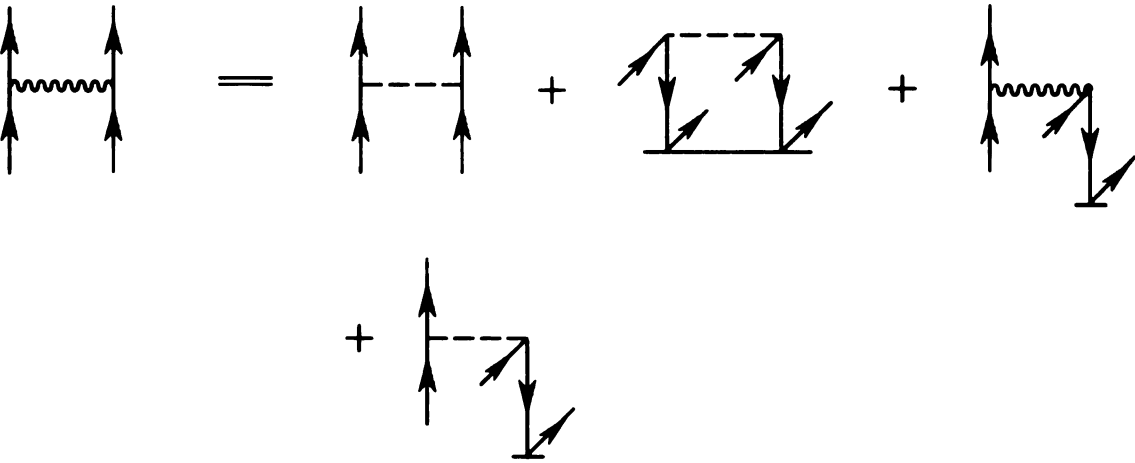
Figure 29: Factorized one-body components of $\bar{H}^{(\text{CCSD})}$.



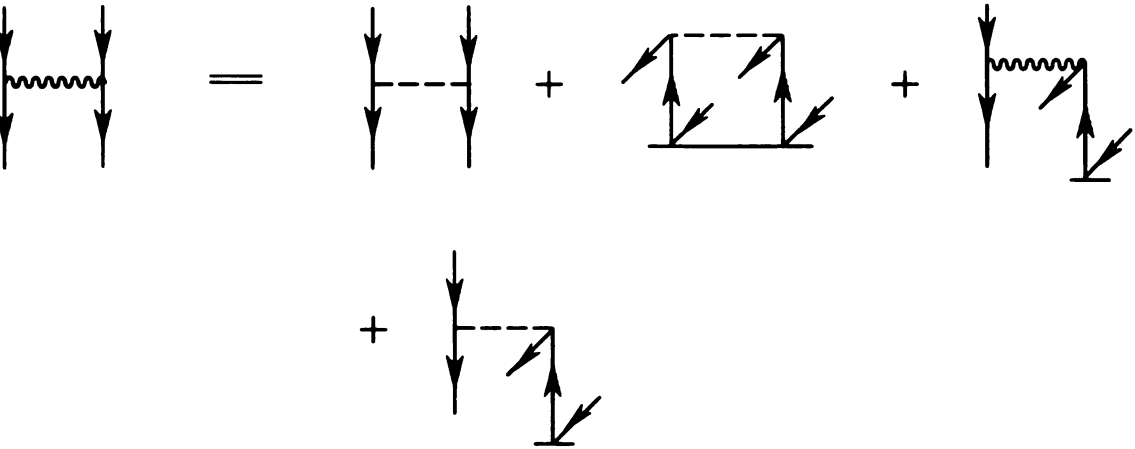
(a) $\bar{h}_{ai}^{bc}$



(b) $\bar{h}_{ij}^{ka}$



(c) $\bar{h}_{ab}^{cd}$



(d) $\bar{h}_{ij}^{kl}$

Figure 30: Factorized two-body components of $\bar{H}_1^{(\text{CCSD})}$.

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