

**Development of an Automatic Code Generator and
Implementation of Multireference Equation of Motion
Coupled-Cluster Theory in the ORCA Program Package**

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

The contents of chapter 5 of this thesis have been published in: L. M. J. Huntington and M. Nooijen, “Application of multireference equation of motion coupled-cluster theory to transition metal complexes and an orbital selection scheme for the efficient calculation of excitation energies”, *J. Chem. Phys.* **142**, 194111 (2015). Some of the single reference calculations in this chapter were performed by M. Nooijen. All other work contained in chapter 5 of this thesis, relating to this publication, is solely my own.

The contents of chapters 3 and 6 have been submitted for publication in: L. M. J. Huntington, O. Demel, and M. Nooijen, “Benchmark studies of variations of multireference equation of motion coupled-cluster theory”, *J. Chem. Theory Comput.*, submitted (2015). I acknowledge that O. Demel and M. Nooijen have written the code used to perform the calculations in the ACES II program package and that M. Nooijen has performed some of the calculations reported in chapter 6. My contributions to this work include performing the remaining calculations, data analysis and writing the manuscript.

I further acknowledge that I am the sole author of the remaining chapters of this thesis.

Abstract

Over the past 50 years, single-reference coupled-cluster theory has emerged as a cornerstone of quantum chemistry. While it is an accurate methodology for the calculation of the properties of the electronic states of many systems, there are still many strongly-correlated (multireference) systems which cannot be adequately treated with single-reference coupled-cluster theory. Hence, in the past four decades, there have been significant efforts to develop multireference generalizations of coupled-cluster theory to treat such systems. In this work, we review some of the major developments in single-reference and multireference molecular electronic structure theory. We discuss the details of the Multireference Equation of Motion (MR-EOM) coupled-cluster approach, developed in the Nooijen group, and introduce a new variant which makes use of a Hermitizing transformation. The MR-EOM methodology constitutes a transform and diagonalize approach to electronic structure theory, that is applicable to both ground and excited states. A major topic of this thesis concerns the development of an automatic code generation tool, that has been used to implement the MR-EOM approach in the ORCA quantum chemistry software package. The implementation in ORCA is employed for the characterization and calculation of the excitation energies of transition metal complexes. We also introduce an orbital selection scheme which can be used to extend the applicability of the MR-EOM approach to larger systems for the calculation of excitation spectra. A variety of MR-EOM approaches are then considered in benchmark applications to organic molecules and the various approximations, introduced in the ORCA implementation of MR-EOM, are studied for several transition metal complexes. Finally, we discuss how the implementation in ORCA might be improved in the future, in order to push applications to larger systems and larger active spaces.

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This thesis is dedicated to the life
and memory of my dear friend
Marc Méthé

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List of Abbreviations

AO	Atomic Orbital
BCH	Baker-Campbell-Hausdorff
BLAS	Basic Linear Algebra Subprograms
BW-MRCC	Brillouin-Wigner Multireference Coupled-Cluster theory
CASCI	Complete Active Space Configuration Interaction
CASPT2	Complete Active Space second-order Perturbation Theory
CASSCF	Complete Active Space Self-Consistent Field
CAS	Complete Active Space
CC	Coupled-Cluster
CC3	Coupled-Cluster model which includes single and double excitations and an approximate (iterative) treatment of triple excitations
CCSD	Coupled-Cluster theory with Single and Double excitations
CCSD(T)	Coupled-Cluster theory with Single and Double excitations and a non-iterative perturbative correction for Triple excitations
CCSDT	Coupled-Cluster theory with Single, Double and Triple excitations
CI	Configuration Interaction
CISD	Configuration Interaction with Single and Double excitations

CT	Canonical Transformation
CTSD	Canonical Transformation theory with Single and Double excitations
DLPNO	Domain based Local Pair Natural Orbitals
DMRG	Density Matrix Renormalization Group
EA	Electron Attachment
EE	Excitation Energy
EKT	Extended Koopman's Theorem
EOM-CC	Equation Of Motion Coupled-Cluster
EOM-CCSD	Equation of Motion Coupled-Cluster theory with Single and Double excitations
EOM-CCSD(T)	Equation of Motion Coupled-Cluster theory with Single and Double excitations and a non-iterative perturbative correction for Triple excitations
EOM-CCSDT-3	Equation of Motion Coupled-Cluster theory with Single and Double excitations and an approximate (iterative) scheme for Triple excitations
GWT	Generalized Wick's Theorem
ic-MRCI	Internally Contracted Multireference Configuration Interaction
ic-MRCC	Internally Contracted Multireference Coupled-Cluster
ic-MRCCSD	Internally Contracted Multireference Coupled-Cluster theory with Single and Double excitations
ic-MRCCSD(T)	Internally Contracted Multireference Coupled-Cluster theory with Single and Double excitations and a non-iterative perturbative correction for Triple excitations
IP	Ionization Potential
KM	Kutzelnigg-Mukherjee

MO	Molecular Orbital
MR-ACPF	Multireference Approximate Coupled-Pair Functional
MR-AQCC	Multireference Averaged Quadratic Coupled-Cluster
MR-CI	Multireference Configuration Interaction
MR-CIS	Multireference Configuration Interaction with Single excitations
MR-CISD	Multireference Configuration Interaction with Single and Double excitations
MRCI+Q	Multireference Configuration Interaction with Single and Double excitations and the Davidson Q correction
MR-EOM-CC	Multireference Equation Of Motion Coupled-Cluster
MRCC	Multireference Coupled-Cluster
Mk-MRCC	Mukherjee's Multireference Coupled-Cluster theory
NEVPT2	<i>n</i> -Electron Valence second-order Perturbation Theory
RDM	Reduced Density Matrix
SAC-CI	Symmetry Adapted Cluster Configuration Interaction
STEOM-CC	Similarity Transformed Equation Of Motion Coupled-Cluster

Example Code

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Chapter 1

Introduction

Modern quantum chemical methods have become powerful tools for the accurate prediction of properties relating to molecular structure and reactivity (*e.g.* geometries, potential energy surfaces, thermochemistry and kinetics, *etc.*) and for the simulation and/or interpretation of spectra, an essential tool for probing the fundamental properties of matter. With current computer technology and the availability of sophisticated software packages, quantum chemical methods are also routinely employed by non-specialists in academia and industry. Density Functional Theory (DFT) has emerged as the most popular methodology in the computational chemistry community, as a result of its favourable cost/accuracy ratio and wide range of applicability [1]. Even so, it is well known that DFT is not as robust and accurate as the more computationally demanding wavefunction based methods (see Ref. [1] and references therein).

In particular, single-reference Coupled-Cluster (CC) theory provides a systematically improvable hierarchy of methods, which rapidly converge toward the exact solution of the molecular electronic Schrödinger equation for ground states [2]. The CCSD(T) (Coupled-Cluster theory with Single and Double excitations with a non-iterative, perturbative correction for Triple excitations) approach [3] is widely hailed as the “gold-standard” of modern *ab-initio* quantum chemistry due to its overall accuracy and reliability in the treatment of a variety of systems [2, 4]. As a result, it is often used as a benchmark for more approximate methodologies. Furthermore, this approach can be combined with local correlation schemes, which take advantage of the short-range nature of dynamical correlation, in order to extend its applicability to much larger systems. Of particular note, is the recent domain-based local pair natural orbital (DLPNO) [5, 6, 7, 8] implementation of CCSD(T), reported in Ref. [9]. The DLPNO-CCSD(T) method achieves near linear scaling and its application to a small protein (crambin), consisting of 644 atoms, provides a testa-

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ment to the efficiency of this approach [9]. Moreover, single-reference methods for the calculation of excited electronic states are firmly established. These include Coupled-Cluster Linear Response Theory (CC-LRT) [10, 11, 12], Equation of Motion Coupled-Cluster (EOM-CC) [13, 14, 15] theory, Similarity Transformed Equation of Motion Coupled Cluster (STEOM-CC) [16, 17] theory and the Symmetry Adapted Cluster Configuration Interaction (SAC-CI) [18, 19] approach.

The methods described above are referred to as single-reference approaches, since they are all based on a single-determinantal zeroth order wavefunction, obtained from a mean-field (Hartree-Fock) calculation. The major assumption underlying these approaches is therefore, that the single-determinantal zeroth order (reference) wavefunction provides a qualitatively correct description of the system. This is true for many closed-shell molecules, near the equilibrium geometry. However, there are many systems where a linear combination of two or more dominant configurations is required to provide a correct qualitative zeroth order description of the wavefunction. This is the case when electronic states become degenerate or nearly (quasi-) degenerate. Some representative examples include transition states, excited states, open-shell systems (*e.g.* bi-radicals), stretched bonds, many transition metal complexes, *etc.* In principle, these systems can be treated with single-reference methods, as long as sufficiently high level excitations are included in the definition of the methodology. However, these calculations quickly become prohibitive, as the computational scaling increases drastically with increasing excitation rank. Thus, in order to achieve a quantitative description of these systems, a much more effective approach is to develop correlated methods which are based on a multi-configurational zeroth order wavefunction.

Such methods are aptly referred to as multireference correlation approaches. The development of multireference coupled-cluster methods is still a very active field of research (*e.g.* see Ref. [20] and references therein). This thesis will be concerned with further developments and the implementation of the Multireference Equation Of Motion Coupled-Cluster (MR-EOM-CC) approach [21, 22, 23] in the ORCA electronic structure program package [24]. In analogy with single-reference EOM-CC [13, 14, 15] and STEOM-CC [16, 17], this method can be characterized as a transform and diagonalize scheme that is applicable to ground and excited states. An MR-EOM calculation involves a single state-averaged CASSCF calculation, incorporating a small number of low-lying states and the solution of a single set of cluster amplitudes, which define the final similarity transformed Hamiltonian. This transformed Hamiltonian can then be diagonalized over a compact manifold of configurations to provide access to a large number of electronic states. Let us now provide a brief outline of the structure of the remainder of this thesis.

In chapter 2, we provide an overview of both single-reference and multireference correlation methods. The goal of this discussion is not to provide an exhaustive review of wavefunction based quantum chemistry, but rather to expose some of the theoretical aspects of the various formalisms. The main objective

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is to compare various multireference methodologies and highlight their salient features and the issues associated with their use. This then provides some perspective and motivation for the discussion of the MR-EOM approach. The theoretical foundations of MR-EOM are introduced in chapter 3. Several different variants are detailed, since we wish make a critical assessment of these variations in the benchmark applications which are described in chapter 6. These variants of MR-EOM are characterized by the following aspects: 1. the operators included in the sequence of similarity transformations of the molecular electronic Hamiltonian, 2. whether or not permutational symmetries (*i.e.* Hermitization, vertex-symmetry) are imposed on the final elements of the similarity transformed Hamiltonian, 3. the size of the manifold over which the similarity transformed Hamiltonian is diagonalized, 4. whether or not the two-body cumulant is included in the expressions defining the amplitudes and the elements of the transformed Hamiltonian. One reason to investigate a number of variations of MR-EOM, is to establish a suitable scheme that may be employed in routine calculations. Moreover, the study of different variants of the MR-EOM methodology provides further insight into the workings of the approach.

The implementation of MR-EOM in the ORCA package has been achieved using an automatic code generation system, written in the Python programming language [25], which is described in detail in chapter 4. The discussion begins with a brief description of the tensorial equations which can be treated by the code generator. An overview of the structure of the code is then presented and includes an outline of the data structures which are used for the internal representation of the tensorial equations, the information which needs to be extracted from the equations in order to generate code and the structure of the Mako templates [26] which are used to generate the final code. In order to achieve a considerably more efficient implementation, we describe how the code generator can make use of the BLAS (Basic Linear Algebra Subprograms) [27, 28, 29, 30, 31] wrappers defined within ORCA. The code generator has been interfaced with the equation generation module of the Automatic Program Generator (APG) [32] and has the ability to automatically implement the defining equations for a wide variety of methods in the ORCA program package.

Chapter 5 presents the first application of the multireference equation of motion coupled-cluster approach to the calculation and characterization of excitation energies of transition metal complexes. The calculated MR-EOM excitation energies are compared with experimental UV/Vis. band maxima, Brueckner STEOM and EOM-CCSD(T) calculations and results calculated with other methods from the literature. The agreement of the excitation energies with experiment is found to be reasonable and suitable rationalization is given for the discrepancies. An orbital selection scheme is also introduced, which can be employed to extend the applicability of the MR-EOMCC methodology to considerably larger systems.

In chapter 6, the variants of MR-EOM, which are defined in chapter 3, are benchmarked for the

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calculation of the excitation energies of a subset of the organic molecules from the test suite of Thiel and coworkers [33]. With the availability of reliable benchmark data for this test set it is possible to gauge the relative accuracy of several variants of MR-EOM. Furthermore, as discussed above, we investigate the effects of different transformation schemes, the imposition of permutational symmetries on the final elements of the transformed Hamiltonian, the size of the final diagonalization manifold and the exclusion of two-body cumulants from the defining equations. In a second set of applications, we employ the five transition metal complexes of chapter 5 to investigate the effects of the various approximations, inherent in the ORCA implementation of MR-EOM, on the calculation of the excitation energies of these systems. The goal is to determine whether or not these approximations have a large effect on the results. We also demonstrate that these systems prove to be particularly difficult for single-reference coupled-cluster methods.

There are several important improvements which can be made in the current implementation of MR-EOM in the ORCA program package. These are detailed in chapter 7 and include a discussion of factorization of the defining equations, parallelization of the code and the possible interface of MR-EOM with the Density Matrix Renormalization Group (DMRG) [34, 35, 36, 37, 38, 39, 40], to allow for the use of much larger active spaces. A major goal is to implement a DLPNO [5, 6, 7, 8, 9] based version of MR-EOM, as this would greatly extend its applicability to much larger systems.

Chapter 2

A Survey of Wavefunction Based Molecular Electronic Structure Methods

2.1 Introduction

In this chapter, we wish to give an overview of wavefunction based molecular electronic structure theory. This constitutes a vast subfield of chemical physics, spanning a wide range of topics and methodologies, and we will be selective in our discussion. We begin by discussing some basic elements of the theory, including the formalism of second quantization, which all of the correlated methods herein, are based upon. We then introduce the Hartree-Fock (mean-field) approximation for a single determinantal wavefunction and discuss the basic formulation of configuration interaction and single-reference coupled-cluster theory for ground and excited states. A primary goal of this chapter is to discuss the details of multireference correlation methods, which are based on a multi-configurational zeroth order wavefunction. We begin by contrasting the concepts of dynamic and static correlation and introduce the complete active space self-consistent field (CASSCF) approach for obtaining a multi-configurational zeroth order wavefunction. The multireference configuration interaction method is then introduced as a straightforward generalization of single-reference configuration interaction. We then provide an overview of the development of methods which make use of an exponential parametrization of the wavefunction. These include methods based on the Jeziorski-Monkhorst [41] ansatz, like Brillouin-Wigner [42, 43, 44, 45] and Mukherjee's [46, 47, 48] multireference coupled-cluster theory, as well as internally contracted multireference coupled-cluster ansätze. In the latter case, we provide an overview of the internally contracted multireference coupled-cluster

approach [49, 50, 51, 52], as well as canonical transformation theory [53, 54, 55, 56, 57, 58], which employs a unitary parametrization of the wavefunction.

2.2 Fundamental Concepts in Electronic Structure Theory

2.2.1 The Molecular Electronic Hamiltonian and Slater Determinants

The field of *ab-initio* molecular electronic structure theory is concerned with the determination of approximate solutions of the time-independent Schrödinger equation,

$$\hat{H} |\Psi\rangle = \left[\sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_{\alpha=1}^{\mathcal{N}} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} \right) + \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\beta>\alpha}^{\mathcal{N}} \frac{Z_{\alpha} Z_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} \right] |\Psi\rangle = E |\Psi\rangle, \quad (2.1)$$

at a fixed nuclear configuration (geometry) $\{\mathbf{R}_{\alpha}\}_{\alpha=1}^{\mathcal{N}}$. In Eq. (2.1), $\hat{H}$, $|\Psi\rangle$ and E are respectively, the molecular electronic Hamiltonian, wavefunction and energy [59]. The first term in the Hamiltonian of Eq. (2.1) is the kinetic energy operator for the system of N electrons. The second term represents the nuclear-electron attraction potential, in which Z_{α} is the charge on the α^{th} nucleus, $\mathbf{r}_i$ is the position vector for the i^{th} electron, $\mathbf{R}_{\alpha}$ is the position vector for the α^{th} nucleus and $r_{i\alpha} = |\mathbf{r}_i - \mathbf{R}_{\alpha}|$ is the Euclidean distance between electron i and nucleus α . The third term is the inter-electronic repulsion potential and the last term represents the inter-nuclear repulsion. The latter term is often excluded from the definition of the electronic Hamiltonian of Eq. (2.1), since it simply represents a constant shift of the electronic energy. It is important to note that Eq. (2.1) is only valid within the Born-Oppenheimer approximation [60], in which it is assumed that the motion of the nuclei and electrons is decoupled and can be treated as two separate problems. However, the electronic wavefunction and energy still have a parametric dependence on the fixed positions of the nuclei (clamped nuclei), owing to the presence of the electrostatic nuclear-electron attraction potential in Eq. (2.1) [59]. Hence, the energies obtained by solving Eq. (2.1), for a given electronic state, define a multidimensional (*i.e.* $3\mathcal{N}-6$ ($3\mathcal{N}-5$) for a non-linear (linear) molecule composed of $\mathcal{N}$ atoms) potential energy surface for that electronic state. For a particular state, this potential energy surface governs the motion of the nuclei (*i.e.* translation, vibration and rotation), since it represents the potential energy of the nuclei in the field generated by the electrons, within the Born-Oppenheimer approximation [59].

In order to simplify the task of (approximately) solving the molecular electronic Schrödinger equation of Eq. (2.1), it is convenient to expand the many electron wavefunction in a basis of one-electron functions.

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These functions have a dependence on both the position and spin of an electron and are obtained from a mean-field theory (*e.g.* Hartree-Fock), as will be discussed below. Let $\sigma_i(\omega)$ represent the spin of electron i , as a function of an undefined spin coordinate ω . This function can take on one of two forms, corresponding to spin up or spin down, that are represented by the orthonormal functions $\alpha(\omega)$ and $\beta(\omega)$, respectively. We collect the spatial and spin coordinates of a given electron i into a single set of coordinates as $\mathbf{x}_i = (\mathbf{r}_i, \omega_i)$. Given an orthonormal set $\{\phi_1(\mathbf{r}), \phi_2(\mathbf{r}), \dots, \phi_K(\mathbf{r})\}$ of K spatial one-electron functions or orbitals, one can form an orthonormal set $\{\varphi_1(\mathbf{x}), \varphi_2(\mathbf{x}), \dots, \varphi_{2K}(\mathbf{x})\}$ of $2K$ spin-orbitals via [59],

$$\begin{aligned}\varphi_{2p-1}(\mathbf{x}) &= \phi_p(\mathbf{r})\alpha(\omega), \\ \varphi_{2p}(\mathbf{x}) &= \phi_p(\mathbf{r})\beta(\omega).\end{aligned}\tag{2.2}$$

Since electrons are fermions, the electronic wavefunction must be antisymmetric under the interchange of the space-spin coordinates of any two electrons,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) = -\Psi(\mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_3, \dots, \mathbf{x}_N).\tag{2.3}$$

A Slater determinant,

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\varphi_{p_1} \varphi_{p_2} \dots \varphi_{p_N}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{p_1}(\mathbf{x}_1) & \varphi_{p_2}(\mathbf{x}_1) & \dots & \varphi_{p_N}(\mathbf{x}_1) \\ \varphi_{p_1}(\mathbf{x}_2) & \varphi_{p_2}(\mathbf{x}_2) & \dots & \varphi_{p_N}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{p_1}(\mathbf{x}_N) & \varphi_{p_2}(\mathbf{x}_N) & \dots & \varphi_{p_N}(\mathbf{x}_N) \end{vmatrix},\tag{2.4}$$

constructed by distributing N electrons in N spin-orbitals $\{\varphi_{p_1}, \varphi_{p_2}, \dots, \varphi_{p_N}\}$, is an elementary N -electron wavefunction which satisfies the antisymmetry property [4]. In principle, if we had a complete basis set of spin-orbitals, we could write the exact N -electron wavefunction as a linear combination of all possible Slater determinants, formed from this set of spin-orbitals (*i.e.* this set spans the complete N -electron Hilbert space). However, a finite basis set of one-electron functions is always employed in all practical applications.

2.2.2 Second Quantization

We will now discuss an alternative representation of many-electron wavefunctions and operators within the formalism of second quantization. For a given N -electron Slater determinant $|\varphi_{p_1} \varphi_{p_2} \dots \varphi_{p_N}\rangle$, constructed from an ordered set $\{\varphi_1(\mathbf{x}), \varphi_2(\mathbf{x}), \dots, \varphi_M(\mathbf{x})\}$ of M spin-orbitals, we associate an occu-

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pation number n_p with each spin-orbital φ_p from the set. The occupation number $n_p = 1$, if the Slater determinant contains the spin-orbital φ_p (*i.e.* φ_p is occupied by an electron) and $n_p = 0$ if it does not (*i.e.* φ_p is unoccupied). This Slater determinant can then be represented as an occupation number vector

$$|\mathbf{n}\rangle = |n_1, n_2, n_3, \dots, n_M\rangle. \quad (2.5)$$

The complete set of occupation number vectors span a 2^M dimensional orthonormal vector space, called Fock space $\mathcal{F}$, which is the direct sum of the p -electron (*i.e.* $p = 0, 1, \dots, M$) Hilbert spaces $\mathcal{H}_p$ [4],

$$\mathcal{F} = \bigoplus_{p=0}^M \mathcal{H}_p = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \dots \oplus \mathcal{H}_M. \quad (2.6)$$

The 0-electron occupation number vector $|0\rangle = |0_1, 0_2, 0_3, \dots, 0_M\rangle$, in which none of the spin-orbitals are occupied, is referred to as the physical vacuum state.

We introduce the elementary creation $\hat{a}_p^\dagger$ and annihilation $\hat{a}_p$ operators, which are defined by their action on the occupation number vectors. The creation operator $\hat{a}_p^\dagger$ creates an electron in spin-orbital φ_p if it is not already occupied and gives a result of zero if it is occupied, [61]

$$\hat{a}_p^\dagger |n_1, n_2, \dots, 0_p, \dots, n_M\rangle = (-1)^{\eta_p} |n_1, n_2, \dots, 1_p, \dots, n_M\rangle, \quad (2.7)$$

$$\hat{a}_p^\dagger |n_1, n_2, \dots, 1_p, \dots, n_M\rangle = 0, \quad (2.8)$$

Here, $\eta_p = \sum_{q=1}^{p-1} n_q$ is equal to the number of occupied spin-orbitals that appear before φ_p in the occupation number vector. The action of the annihilation operator $\hat{a}_p$ on an occupation number vector is [61]

$$\hat{a}_p |n_1, n_2, \dots, 1_p, \dots, n_M\rangle = (-1)^{\eta_p} |n_1, n_2, \dots, 0_p, \dots, n_M\rangle, \quad (2.9)$$

$$\hat{a}_p |n_1, n_2, \dots, 0_p, \dots, n_M\rangle = 0. \quad (2.10)$$

Thus, it deletes an electron from the spin-orbital φ_p if it is occupied and gives a result of 0 if it is not. We can represent an N -electron Slater determinant as a string of creation operators acting on the physical vacuum state,

$$|\Phi\rangle = \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \dots \hat{a}_{p_N}^\dagger |0\rangle. \quad (2.11)$$

Furthermore, an annihilation operator gives a result of 0 when acting on the vacuum state (*i.e.* this follows from Eq. (2.10)),

$$\hat{a}_p |0\rangle = 0 \quad \forall p, \quad (2.12)$$

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and by taking the adjoint of this expression, one can see that the creation operator obeys the relation,

$$\langle 0 | \hat{a}_p^\dagger = 0 \quad \forall p, \quad (2.13)$$

From the defining relations in Eqs. (2.7), (2.8), (2.9) and (2.10), it is a simple exercise to show that the anticommutation relations,

$$\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = \hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = 0, \quad (2.14)$$

$$\{\hat{a}_p, \hat{a}_q\} = \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0, \quad (2.15)$$

$$\{\hat{a}_p^\dagger, \hat{a}_q\} = \hat{a}_p^\dagger \hat{a}_q + \hat{a}_q \hat{a}_p^\dagger = \delta_{pq}, \quad (2.16)$$

are satisfied for any p and q (*e.g.* see Refs. [4, 61]), in which δ_{pq} is the Kronecker delta. These anticommutation relations ensure that determinants, resulting from the action of the creation and annihilation operators, will remain antisymmetric with respect to interchange of any two electrons.

The formalism of second-quantization also provides a convenient representation of operators such as the molecular electronic Hamiltonian of Eq. (2.1). If we define the one-electron integrals as

$$h_q^p = \langle p | \hat{h} | q \rangle = \int \varphi_p^*(\mathbf{x}) \left(-\frac{1}{2} \nabla^2 - \sum_{\alpha=1}^N \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} \right) \varphi_q(\mathbf{x}) d\mathbf{x}, \quad (2.17)$$

and the antisymmetrized two-electron integrals as

$$v_{rs}^{pq} = \langle pq || rs \rangle = \int \left[\varphi_p^*(\mathbf{x}_1) \varphi_q^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_r(\mathbf{x}_1) \varphi_s(\mathbf{x}_2) - \varphi_p^*(\mathbf{x}_1) \varphi_q^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_s(\mathbf{x}_1) \varphi_r(\mathbf{x}_2) \right] d\mathbf{x}_1 d\mathbf{x}_2, \quad (2.18)$$

and let

$$h_{\text{nuc.}} = \sum_{\beta > \alpha}^N \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}, \quad (2.19)$$

denote the internuclear repulsion term, then it can be demonstrated (*e.g.* see Refs. [4, 61]) that the molecular electronic Hamiltonian of Eq. (2.1) can be written, in second quantization, as

$$\hat{H} = \sum_{p,q} h_q^p \hat{e}_q^p + \frac{1}{4} \sum_{p,q,r,s} v_{rs}^{pq} \hat{e}_{rs}^{pq} + h_{\text{nuc.}}. \quad (2.20)$$

Here, we have introduced the notation

$$\hat{e}_q^p = \hat{a}_p^\dagger \hat{a}_q, \quad (2.21)$$

$$\hat{e}_{rs}^{pq} = \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r, \quad (2.22)$$

for the single and double substitution operators, respectively. The operator $\hat{e}_q^p$, is a single substitution operator, as it removes an electron from the spin-orbital φ_q and places it in the spin-orbital φ_p . Similarly, the operator $\hat{e}_{rs}^{pq}$, is a double substitution operator, since it simultaneously promotes an electron from φ_r to φ_p and another electron from φ_s to φ_q . In general, an n -tuple substitution operator may be written as

$$\hat{e}_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n} = \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \dots \hat{a}_{p_n}^\dagger \hat{a}_{q_n} \dots \hat{a}_{q_2} \hat{a}_{q_1}. \quad (2.23)$$

It is important to discuss the concepts of normal ordering and Wick's theorem as they are essential elements of the formalism of second quantization. A normal-ordered product of second quantized operators is a string of such operators, that has been manipulated so that the creation operators appear to the left of the annihilation operators. For example, $\{\hat{a}_p^\dagger \hat{a}_q\} = \hat{a}_p^\dagger \hat{a}_q$, $\{\hat{a}_q \hat{a}_p^\dagger\} = -\hat{a}_p^\dagger \hat{a}_q$ and $\{\hat{a}_p^\dagger \hat{a}_s \hat{a}_q^\dagger \hat{a}_r\} = -\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$ are normal ordered products, where the braces are used to indicate normal-ordering with respect to the vacuum state. A minus sign arises from each of the permutations of adjacent operators that is required to produce the final normal-ordered product. The expectation value of any normal-ordered product in the vacuum state is zero, which follows from Eq. (2.12). For any two elementary second-quantized operators $\hat{A}$ and $\hat{B}$, the difference [61],

$$\overline{\hat{A}\hat{B}} = \hat{A}\hat{B} - \{\hat{A}\hat{B}\}, \quad (2.24)$$

between the original product and the normal-ordered product is called a contraction $\overline{\hat{A}\hat{B}}$. There are four different cases to be considered,

$$\overline{\hat{a}_p^\dagger \hat{a}_q^\dagger} = \hat{a}_p^\dagger \hat{a}_q^\dagger - \{\hat{a}_p^\dagger \hat{a}_q^\dagger\} = \hat{a}_p^\dagger \hat{a}_q^\dagger - \hat{a}_p^\dagger \hat{a}_q^\dagger = 0, \quad (2.25)$$

$$\overline{\hat{a}_p^\dagger \hat{a}_q} = \hat{a}_p^\dagger \hat{a}_q - \{\hat{a}_p^\dagger \hat{a}_q\} = \hat{a}_p^\dagger \hat{a}_q - \hat{a}_p^\dagger \hat{a}_q = 0, \quad (2.26)$$

$$\overline{\hat{a}_p \hat{a}_q} = \hat{a}_p \hat{a}_q - \{\hat{a}_p \hat{a}_q\} = \hat{a}_p \hat{a}_q - \hat{a}_p \hat{a}_q = 0, \quad (2.27)$$

$$\overline{\hat{a}_q \hat{a}_p^\dagger} = \hat{a}_q \hat{a}_p^\dagger - \{\hat{a}_q \hat{a}_p^\dagger\} = \hat{a}_q \hat{a}_p^\dagger - (-\hat{a}_p^\dagger \hat{a}_q) = \{\hat{a}_p^\dagger, \hat{a}_q\} = \delta_{pq}, \quad (2.28)$$

where the anticommutation relation of Eq. (2.16) was used in Eq. (2.28). A normal ordered product with contractions can be written as

$$\{\overline{\hat{A}\hat{B}\hat{C}\hat{D}} \dots \overline{\hat{P}\hat{Q}\hat{R}\hat{S}} \dots\} = (-1)^n \overline{\hat{P}\hat{R}\hat{Q}\hat{S}} \dots \{\hat{A}\hat{B}\hat{C}\hat{D} \dots\}, \quad (2.29)$$

in which η denotes the number of interchanges that are required for the reordering. The time-independent Wick's theorem [62] states that any string of second quantized operators can be written as a sum of the normal ordered products and all of the possible partially and fully contracted normal products, that is

$$\begin{aligned}
 \hat{A}\hat{B}\hat{C}\hat{D}\dots &= \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \underbrace{\left[\{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \dots + \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \dots \right]}_{\text{all possible single contractions}} \\
 &+ \underbrace{\left[\{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \dots \right]}_{\text{all possible double contractions}} + \dots + \sum_{\text{fully contracted}} \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} \\
 &= \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\} + \sum_{\text{all possible contractions}} \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\}
 \end{aligned} \tag{2.30}$$

As a consequence of Wick's theorem, Eq. (2.12) and Eq. (2.16), the vacuum expectation value of a string of creation and annihilation operators is equal to the sum of the fully contracted normal products,

$$\langle 0 | \hat{A}\hat{B}\hat{C}\hat{D}\dots | 0 \rangle = \sum_{\text{fully contracted}} \{\hat{A}\hat{B}\hat{C}\hat{D}\dots\}. \tag{2.31}$$

A generalization of Wick's theorem, (GWT or Generalized Wick's Theorem) [62] provides a prescription for the evaluation of contractions between an arbitrary number of products of normal ordered products of creation and annihilation operators. Since contractions within a normal ordered product must vanish, the GWT yields

$$\begin{aligned}
 \{\hat{A}_1\hat{A}_2\dots\}\{\hat{B}_1\hat{B}_2\dots\}\{\hat{C}_1\hat{C}_2\dots\}\dots &= \{\hat{A}_1\hat{A}_2\dots\hat{B}_1\hat{B}_2\dots\hat{C}_1\hat{C}_2\dots\} \\
 &+ \sum' \{\hat{A}_1\hat{A}_2\dots\hat{B}_1\hat{B}_2\dots\hat{C}_1\hat{C}_2\dots\},
 \end{aligned} \tag{2.32}$$

in which the primed sum runs over all possible single contractions, double contractions, *etc.* with the exception that contractions must be formed from two different normal ordered products (*i.e.* the sum excludes internal contractions such as $\hat{A}_1\hat{A}_2$ or $\hat{C}_1\hat{C}_2$) [61]. The Wick's theorem and GWT are extremely useful for the derivation of working equations for a wide variety of methods in electronic structure theory (*e.g.* the Coupled-Cluster residual equations). A diagrammatic representation of second-quantized operators is also frequently employed as an alternative to the algebraic application of Wick's theorem and the

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GWT (*e.g.* see Refs. [61, 2] and references therein for a detailed discussion).

Since operators, such as the Hamiltonian of Eq. (2.20), act on a reference determinant $|\Phi_0\rangle$ (*i.e.* the Fermi vacuum state) rather than the true vacuum state, it is convenient to modify the definitions of the creation and annihilation operators and the concept of normal ordering accordingly before proceeding. Let i, j, k, l label occupied orbitals, a, b, c, d label unoccupied (virtual) orbitals and p, q, r, s label general orbitals (*i.e.* run over both hole and particle orbitals) in the reference state $|\Phi_0\rangle$. A result of zero is obtained when the creation ($\hat{a}_i^\dagger$) and annihilation ($\hat{a}_a$) operators are applied to the reference state $|\Phi_0\rangle$,

$$\hat{a}_i^\dagger |\Phi_0\rangle = 0, \quad (2.33)$$

$$\hat{a}_a |\Phi_0\rangle = 0, \quad (2.34)$$

since the orbital φ_i is occupied in the reference and φ_a is unoccupied. These operators are often called *quasi-annihilation* operators, since their action on the reference state is analogous to that of the original annihilation operators on the physical vacuum. The action of the creation ($\hat{a}_a^\dagger$) and annihilation ($\hat{a}_i$) operators on the determinant (*e.g.* $|\Phi_0\rangle = |\varphi_i\varphi_j\varphi_k\varphi_l\cdots\rangle$) is

$$\hat{a}_a^\dagger |\Phi_0\rangle = \hat{a}_a^\dagger |\varphi_i\varphi_j\varphi_k\varphi_l\cdots\rangle = |\varphi_a\varphi_i\varphi_j\varphi_k\varphi_l\cdots\rangle = |\Phi^a\rangle, \quad (2.35)$$

$$\hat{a}_i |\Phi_0\rangle = \hat{a}_i |\varphi_i\varphi_j\varphi_k\varphi_l\cdots\rangle = |\varphi_j\varphi_k\varphi_l\cdots\rangle = |\Phi_i\rangle. \quad (2.36)$$

Hence, the action of $\hat{a}_a^\dagger$ on the reference is analogous to that of the original creation operators on the physical vacuum, while $\hat{a}_i$ creates a vacancy in the orbital φ_i . As such, these operators are often referred to as *quasi-creation* operators. The definition of quasi-creation and quasi-annihilation operators, with respect to their action on the reference (Fermi vacuum) state $|\Phi_0\rangle$, forms the basis of the so-called hole-particle formalism [63]. Within this formalism, the occupied spin-orbitals in the reference state $|\Phi_0\rangle$, are referred to as “hole” orbitals (*i.e.* $\hat{a}_i$ creates a vacancy or hole in the occupied orbital φ_i) and the unoccupied spin-orbitals are “particle” orbitals (*i.e.* $\hat{a}_a^\dagger$ creates a particle (electron) in the unoccupied orbital φ_a). Note that we will often use the notation $|\Phi_{ijkl\cdots n}^{abcd\cdots g}\rangle = \hat{e}_{ijkl\cdots n}^{abcd\cdots g} |\Phi_0\rangle$ to denote (arbitrarily) excited determinants, constructed by deleting electrons from occupied orbitals and promoting them to unoccupied (virtual) orbitals (*e.g.* singly excited determinants: $|\Phi_i^a\rangle = \hat{e}_i^a |\Phi_0\rangle$, doubly excited determinants: $|\Phi_{ij}^{ab}\rangle = \hat{e}_{ij}^{ab} |\Phi_0\rangle$, *etc.*). Moreover, normal ordering, with respect to the reference state, is defined such that all of the *quasi-creation* operators lie to the left of the *quasi-annihilation* operators. According to Eqs. (2.25), (2.26), (2.27) and (2.28), the only non-vanishing contractions for these *quasi-creation* and *quasi-annihilation* operators

are

$$\hat{a}_a \hat{a}_b^\dagger = \delta_{ab}, \quad (2.37)$$

$$\hat{a}_i^\dagger \hat{a}_j = \delta_{ij}. \quad (2.38)$$

With this new definition of normal ordering and the expressions for the contractions in Eqs. (2.37) and (2.38), the Wick's theorem (Eq. (2.30)) and the GWT (Eq. (2.32)) can be applied to the hole-particle operators, with respect to the Fermi vacuum, in the same way as for the operators defined with respect to the physical vacuum. For example, application of Wick's theorem (in the hole-particle formalism) to the Hamiltonian of Eq. (2.20) yields

$$\begin{aligned} \hat{H} &= h_{\text{nuc.}} + \sum_{i,j} h_i^i + \frac{1}{2} \sum_{ij} v_{ij}^{ij} + \sum_{p,q} h_q^p \{ \hat{e}_q^p \} + \sum_{p,q,i} v_{qi}^{pi} \{ \hat{e}_q^p \} + \frac{1}{4} \sum_{p,q,r,s} v_{rs}^{pq} \{ \hat{e}_{rs}^{pq} \} \\ &= E_0 + \sum_{p,q} f_q^p \{ \hat{e}_q^p \} + \frac{1}{4} \sum_{p,q,r,s} v_{rs}^{pq} \{ \hat{e}_{rs}^{pq} \}, \end{aligned} \quad (2.39)$$

where in the last line, we have defined the Fock matrix and the reference energy (*e.g.* Hartree-Fock energy) respectively, as

$$f_q^p = h_q^p + \sum_i v_{qi}^{pi}, \quad (2.40)$$

$$E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = h_{\text{nuc.}} + \sum_{i,j} h_i^i + \frac{1}{2} \sum_{i,j} v_{ij}^{ij}. \quad (2.41)$$

Before leaving the discussion of second quantization, it is important to discuss the concept of spin-adaptation, since many of the expressions which appear in this thesis are written in a spin-adapted (spin-free) form. The term spin-adaptation signifies that the summation over the spin functions has been carried out explicitly, such that the resulting expressions are represented exclusively in terms of spatial orbitals. The implementation of the spin-adapted formulation of a given methodology is significantly more computationally efficient than one expressed in terms of spin-orbitals, since the orbital ranges are reduced by a factor of one half (*i.e.* K spatial orbitals v.s. $2K$ spin-orbitals). A fairly comprehensive discussion of the consideration of spin in second quantization can be found in chapter 2 of Ref. [4]. For reasons of brevity, we only discuss the form of the spin-adapted Hamiltonian, since it is most relevant in the current context. Let σ and τ label the spin functions, with the two possible values α and β and let p, q, r, s label general spatial orbitals. Then we can write the spin-free, single and double excitation operators $\hat{E}_q^p$ and

$\hat{E}_{rs}^{pq}$, respectively, as [4]

$$\hat{E}_q^p = \sum_{\sigma} \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} = \hat{a}_{p\alpha}^{\dagger} \hat{a}_{q\alpha} + \hat{a}_{p\beta}^{\dagger} \hat{a}_{q\beta}, \quad (2.42)$$

$$\hat{E}_{rs}^{pq} = \sum_{\sigma, \tau} \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\tau}^{\dagger} \hat{a}_{s\tau} \hat{a}_{r\sigma} = \hat{E}_r^p \hat{E}_s^q - \delta_r^q \hat{E}_s^p. \quad (2.43)$$

The spin-free form of the second-quantized Hamiltonian of Eq. (2.20) can then be written as [4]

$$\hat{H} = \sum_{p,q} h_q^p \hat{E}_q^p + \frac{1}{2} \sum_{p,q,r,s} V_{rs}^{pq} \hat{E}_{rs}^{pq} + h_{\text{nuc.}}, \quad (2.44)$$

in which the spin-free one- and two-electron integrals are respectively, given by

$$h_q^p = \langle p | \hat{h} | q \rangle = \int \phi_p^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 - \sum_{\alpha=1}^{\mathcal{N}} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \right) \phi_q(\mathbf{r}) d\mathbf{r}, \quad (2.45)$$

$$V_{rs}^{pq} = \langle pq | rs \rangle = \int \phi_p^*(\mathbf{r}_1) \phi_q^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (2.46)$$

Similarly, for closed-shell systems, the spin-free form of the Hamiltonian of Eq. (2.39) (*i.e.* written in normal-order with respect to the closed-shell reference state) can be expressed as

$$\hat{H} = E_0 + \sum_{p,q} F_q^p \{ \hat{E}_q^p \} + \frac{1}{2} \sum_{p,q,r,s} V_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \}, \quad (2.47)$$

in which the spin-free Fock matrix F_q^p and the spin-free expression for E_0 are given respectively, by (*i.e.* i and j label occupied spatial orbitals)

$$F_q^p = h_q^p + \sum_i \left(2V_{qi}^{pi} - V_{iq}^{pi} \right), \quad (2.48)$$

$$E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = h_{\text{nuc.}} + 2 \sum_i h_i^i + \sum_{i,j} \left(2V_{ij}^{ij} - V_{ji}^{ij} \right). \quad (2.49)$$

2.3 Single Reference Correlation Methods

2.3.1 The Hartree-Fock Method

The Hartree-Fock (HF) method plays a central role in electronic structure theory, since it provides a starting point for more rigorous *ab-initio* single-reference correlation methods. In the Hartree-

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Fock approximation, the N -electron wavefunction is represented as a single Slater determinant $|\Phi_0\rangle = |\varphi_1\varphi_2\varphi_3\cdots\varphi_N\rangle$, constructed by distributing N electrons over N spin-orbitals. Recall that the spin-orbitals, from which the Slater determinant is constructed, are referred to as occupied (hole) spin-orbitals and the remaining spin-orbitals (from the finite set) are referred to as unoccupied (virtual or particle) spin-orbitals. Furthermore, we recognize that Eq. (2.41) gives the functional dependence $E_{SD}(\{\varphi_i\})$ of the reference energy (*i.e.* SD = Slater determinant) in terms of the occupied spin-orbitals, namely,

$$E_{SD}(\{\phi_i\}) = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = h_{\text{nuc.}} + \sum_{i,j} h_i^i + \frac{1}{2} \sum_{i,j} v_{ij}^{ij} \quad (2.50)$$

We wish to find the set of N spin-orbitals $\{\varphi_1, \varphi_2, \varphi_3, \dots, \varphi_N\}$, which minimize the energy functional of Eq. (2.50), subject to the constraint that the orbitals remain orthonormal. We can therefore, use the method of Lagrange multipliers to incorporate this constraint into the optimization problem, via the Lagrange functional [4]

$$\mathcal{L}(\{\varphi_i\}) = E_{SD}(\{\varphi_i\}) - \sum_{i,j} \varepsilon_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}), \quad (2.51)$$

in which the ε_{ij} ($= \varepsilon_{ji}^*$) are the so-called undetermined Lagrange multipliers. For an infinitesimal variation of the occupied orbitals (*i.e.* $\varphi_i \rightarrow \varphi_i + \delta\varphi_i$), the first variation in $\mathcal{L}(\{\varphi_i\})$ (*i.e.* the functional derivative with respect to the occupied spatial orbitals) must vanish, that is

$$\left. \frac{\delta \mathcal{L}(\{\varphi_i\})}{\delta \varphi_k} \right|_{\varphi_i \neq \varphi_k} = 0, \quad (2.52)$$

After some rather tedious manipulations (*e.g.* see Ref. [59]), one finds that Eq. (2.52) is satisfied if

$$\hat{F} |\varphi_i\rangle = \hat{h} \varphi_i(\mathbf{x}_1) + \sum_k \left[\left(\int \varphi_k^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_k(\mathbf{x}_2) d\mathbf{x}_2 \right) \varphi_i(\mathbf{x}_1) - \left(\int \varphi_k^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_i(\mathbf{x}_2) d\mathbf{x}_2 \right) \varphi_k(\mathbf{x}_1) \right] = \varepsilon_i |\varphi_i\rangle, \quad (2.53)$$

in which ε_i is the energy of the occupied spin-orbital φ_i (*i.e.* the Lagrange multipliers satisfy the condition $\varepsilon_{ij} = \varepsilon_i \delta_{ij}$) and $\hat{F} = \hat{h} + \sum_k (\hat{J}_k - \hat{K}_k)$ is the Fock operator in which,

$$\hat{J}_k = \int \varphi_k^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_k(\mathbf{x}_2) d\mathbf{x}_2 \quad (2.54)$$

is the Coulomb operator and the exchange operator $\hat{K}_k$, can be defined by its action on the spin-orbital $\varphi_i(\mathbf{x}_1)$,

$$\hat{K}_k \varphi_i(\mathbf{x}_1) = \left(\int \varphi_k^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_i(\mathbf{x}_2) d\mathbf{x}_2 \right) \varphi_k(\mathbf{x}_1). \quad (2.55)$$

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The expression of Eq. (2.53) therefore, dictates that the occupied spin-orbitals are eigenfunctions of the Fock matrix with energy eigenvalues (orbital energies) of ε_i . In principle, the Fock matrix should admit an infinite number of eigenfunctions and corresponding eigenvalues. However, in practice, we always have a finite set of N_v virtual spin-orbitals $\{\varphi_{N+1}, \varphi_{N+2}, \dots, \varphi_{N_v}\}$, which are eigenfunctions of the Fock matrix, with corresponding eigenvalues of $\varepsilon_{N+1}, \varepsilon_{N+2}, \dots, \varepsilon_{N_v}$ (*i.e.* the virtual orbital energies). Thus, for a given finite set of spin-orbitals the Hartree-Fock equations, in the molecular spin-orbital basis, can be written as

$$\hat{F}|\varphi_p\rangle = \varepsilon_p |\varphi_p\rangle, \quad p = 1, 2, 3, \dots, N, N+1, N+2, \dots, N_v. \quad (2.56)$$

In order to solve the Hartree-Fock equations of Eq. (2.56), we introduce a basis $\{\chi_\mu\}$ of known atomic orbitals. Usually, these atomic orbitals are constructed from contracted spherical Gaussian functions (*e.g.* see Ref. [4] for a detailed discussion). Let $\mu, \nu, \kappa, \lambda$ label the N_{AO} atomic orbitals, then we can expand the molecular orbitals as a linear combination of atomic orbitals (LCAO),

$$\varphi_p(\mathbf{x}) = \sum_{\mu=1}^{N_{\text{AO}}} C_{\mu p} \chi_\mu(\mathbf{x}). \quad (2.57)$$

Substituting this expression into Eq. (2.56), left multiplying $\chi_\mu^*(\mathbf{x})$ and integrating yields

$$\sum_{\nu=1}^{N_{\text{AO}}} C_{\nu p} \int \chi_\mu^*(\mathbf{x}) \hat{F} \chi_\nu(\mathbf{x}) d\mathbf{x} = \varepsilon_p \sum_{\nu=1}^{N_{\text{AO}}} C_{\nu p} \int \chi_\mu^*(\mathbf{x}) \chi_\nu(\mathbf{x}) d\mathbf{x}. \quad (2.58)$$

If we then define the elements of the Fock matrix F_ν^μ and overlap matrix S_ν^μ , in the atomic orbital basis, as

$$F_\nu^\mu = \int \chi_\mu^*(\mathbf{x}) \hat{F} \chi_\nu(\mathbf{x}) d\mathbf{x}, \quad (2.59)$$

$$S_\nu^\mu = \int \chi_\mu^*(\mathbf{x}) \chi_\nu(\mathbf{x}) d\mathbf{x}, \quad (2.60)$$

the expression of Eq. (2.58) takes the form

$$\sum_{\nu} F_\nu^\mu C_{\nu p} = \sum_{\nu} S_\nu^\mu C_{\nu p} \varepsilon_p \Rightarrow \mathbf{FC} = \mathbf{SC}\varepsilon \quad (2.61)$$

which are the Hartree-Fock Roothaan equations [64]. These equations cannot simply be solved as a generalized eigenvalue problem, since the Fock operator itself, depends on the occupied spin-orbitals (*cf.* Eq. (2.53)). Therefore, the Hartree-Fock Roothaan equations must be solved using an iterative procedure,

often referred to as a "self-consistent field" (SCF) procedure. Let us briefly outline the details of this procedure. If we note that $h_\nu^\mu = \sum_{p,q} C_{\mu p} h_q^p C_{\nu q}^*$ and $v_{\nu i}^{\mu i} = \sum_{p,q} C_{\mu p} v_{q i}^{p i} C_{\nu q}^*$, then the elements of the Fock matrix of Eq. (2.40) (*i.e.* in the molecular spin-orbital (MO) basis) can be transformed to the atomic orbital (AO) basis as

$$\begin{aligned} F_\nu^\mu &= \sum_{p,q} C_{\mu p} F_q^p C_{\nu q}^* = h_\nu^\mu + \sum_{\kappa,\lambda} \sum_i C_{\lambda i} C_{\kappa i}^* v_{\nu\lambda}^{\mu\kappa} \\ &= h_\nu^\mu + \sum_{\kappa,\lambda} D_\lambda^\kappa v_{\nu\lambda}^{\mu\kappa}, \end{aligned} \quad (2.62)$$

in which we have defined the one-electron density matrix $D_\mu^\nu = \sum_i C_{\mu i} C_{\nu i}^* = (\mathbf{C}\mathbf{C}^\dagger)_{\mu\nu}$, in the atomic orbital basis. Similarly, the Hartree-Fock energy expression of Eq. (2.41) can be written in the atomic orbital basis as

$$E_0 = h_{\text{nuc.}} + \sum_{\mu,\nu} D_\nu^\mu h_\nu^\mu + \frac{1}{2} \sum_{\mu,\nu,\kappa,\lambda} D_\nu^\mu D_\lambda^\kappa v_{\nu\lambda}^{\mu\kappa} \quad (2.63)$$

For a given molecular geometry and an atomic orbital basis set, one can construct an initial guess (*e.g.* Hückel theory, superposition of atomic densities, *etc.*) for the coefficients $C_{\mu p}$. The self-consistent field iterations then proceed as follows [4]:

1. Form the density $D_\mu^\nu = \sum_i C_{\mu i} C_{\nu i}^*$ from the orbital coefficients $C_{\mu p}$.
2. Calculate the Fock matrix in the atomic orbital (AO) basis from Eq. (2.62). At this point, we can solve the generalized eigenvalue problem $\mathbf{F}^{\text{AO}}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon$ of Eq. (2.61), using the current AO Fock matrix $\mathbf{F}^{\text{AO}}$, to obtain the orbital energies ϵ_p and coefficients $C_{\mu p}$. The current value of the Hartree-Fock energy can also be obtained from Eq. (2.63) (as it is often printed in each iteration, in most electron structure program packages).
3. Transform the Fock matrix to the molecular orbital (MO) basis via $\mathbf{F}^{\text{MO}} = \mathbf{C}^\dagger \mathbf{F}^{\text{AO}} \mathbf{C}$.
4. Calculate the error vector $\mathbf{e}$, which depends on the occupied-virtual (*i.e.* f_a^i) block of the MO Fock matrix (*e.g.* see Ref. [4]).
5. If the norm of the error vector is below a given threshold $\mathcal{T}$ (*i.e.* $|\mathbf{e}| < \mathcal{T}$), such that we have reached a desired level of accuracy, we return from the iterations. Otherwise, we return to step 1 and use the current coefficients $C_{\mu p}$ (from step 2) to begin another iteration.

It is important to note that the procedure described above is a naive approach for solving the Hartree-Fock Roothaan equations and more sophisticated algorithms have been developed over the years, to speed up convergence (*e.g.* DIIS (Direct Inversion of the Iterative Subspace) [65, 66], QC-SCF (Quadratically Convergent SCF) [67], *etc.*) and to make calculations more efficient (*e.g.* integral direct SCF [68], density-based Hartree-Fock for large systems [69, 70, 71, 72, 73, 74], *etc.*). In any case, from the self-consistent Hartree-Fock solution, we acquire several quantities that are absolutely essential for all post Hartree-Fock *ab-initio* correlation methods. Namely, we obtain the optimized coefficients $C_{\mu p}$, for the LCAO expansion (Eq. (2.57)) of the self-consistent molecular orbitals in terms of atomic orbitals (*i.e.* allow transformations from the AO basis to MO basis and vice versa), the set of two electron integrals $v_{\kappa\lambda}^{\mu\nu}$ in the AO basis (*i.e.* can be transformed to the MO basis, using the coefficients $C_{\mu p}$), the Fock matrix in the MO basis, the orbital energies ε_p and the Hartree-Fock reference energy E_0 .

The Hartree-Fock approximation is intrinsically a mean-field theory (or independent particle approximation), as the Fock matrix, an effective one-particle operator, only includes the interaction of an electron with the average field of all the other electrons through the Coulomb and exchange operators. Even though it often yields more than 99% of the total electronic energy (*i.e.* as a variational upper bound to the exact energy), the Hartree-Fock approximation is insufficient to accurately model chemical phenomena and a more systematic treatment of the inter-electronic repulsion term in Eq. (2.1) is required. The probability distribution of the electrons in a molecule is "correlated" and methods which provide a more realistic treatment of the effects of the inter-electronic interaction are aptly referred to as electron correlation methods. It is possible to accurately model the effects of electron correlation by including excited configurations in the wavefunction, involving excitations out of the single determinantal Hartree-Fock configuration. The difference

$$E_C = E - E_0 \quad (2.64)$$

between the total energy E of a given single-reference correlated *ab-initio* method and the Hartree-Fock energy E_0 , is the correlation energy for the corresponding approach in a given basis set. In the remainder of section 2.3, we will briefly review the details of some single-reference correlation methods and discuss the advantages and disadvantages associated with each of these approaches.

2.3.2 Configuration Interaction

Conceptually, configuration interaction (CI) is the simplest approach for including excited configurations in the description of the molecular electronic wavefunction $|\Psi\rangle$. The full CI (FCI) wavefunction $|\Psi_{\text{FCI}}\rangle$, provides an exact representation of the N -electron wavefunction in a given (finite) basis of one-

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electron functions and is written as a linear combination of the reference determinant ($|\Phi_0\rangle$) and all possible non-redundant, singly ($|\Phi_i^a\rangle$), doubly ($|\Phi_{ij}^{ab}\rangle$), triply ($|\Phi_{ijk}^{abc}\rangle$), ..., N -tuply ($|\Phi_{ijkl\dots}^{abcd\dots}\rangle$) excited determinants,

$$\begin{aligned} |\Psi_{\text{FCI}}\rangle &= c_0 |\Phi_0\rangle + \sum_{i,a} c_i^a |\Phi_i^a\rangle + \sum_{\substack{j>i \\ b>a}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{\substack{k>j>i \\ c>b>a}} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots + \sum_{\substack{\dots>k>j>i \\ \dots>c>b>a}} c_{ijkl\dots}^{abcd\dots} |\Phi_{ijkl\dots}^{abcd\dots}\rangle \\ &= \sum_I c_I |\Phi_I\rangle. \end{aligned} \quad (2.65)$$

Here, the index I runs over the basis of N -electron Slater determinants, which constitute the wavefunction $|\Psi_{\text{FCI}}\rangle$. It is also common to work in intermediate normalization, such that $\langle\Phi_0|\Psi_{\text{FCI}}\rangle = 1$ and $c_0 = 1$. The number $N_{\text{det.}}$, of N -electron Slater determinants which can be formed from a basis of M spin-orbitals is

$$N_{\text{det.}} = \binom{M}{N} = \frac{M!}{N!(M-N)!}. \quad (2.66)$$

With the form of the wavefunction in Eq.(2.65), the molecular electronic Schrödinger equation (Eq. (2.1)) can be written as

$$\sum_J \hat{H} |\Phi_J\rangle c_J = E \sum_J |\Phi_J\rangle c_J, \quad (2.67)$$

and projection of this equation onto the possible configurations $|\Phi_I\rangle$, leads to a set of equations

$$\sum_J \langle\Phi_I|\hat{H}|\Phi_J\rangle c_J = E \sum_J \langle\Phi_I|\Phi_J\rangle c_J. \quad (2.68)$$

If we further assume that the various determinants have been constructed from a set of orthonormal spin-orbitals, then the determinants constitute an orthonormal set (*i.e.* $\langle\Phi_I|\Phi_J\rangle = \delta_{IJ}$). If we let $H_{IJ} = \langle\Phi_I|\hat{H}|\Phi_J\rangle$, Eq. (2.68) can be simplified as

$$\sum_J H_{IJ} c_J = E c_I \Rightarrow \mathbf{H}\mathbf{c} = E\mathbf{c}. \quad (2.69)$$

Let us examine the structure of the Hamiltonian matrix in some detail. Simple application of the GWT (Eq. (2.32)) or Slater's rules (*e.g.* see Ref. [59]) yields

$$\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = \langle\Phi_i^a|\hat{H}|\Phi_0\rangle = f_i^a = f_a^i, \quad (2.70)$$

where for a Hartree-Fock reference state ($f_i^a = f_a^i = 0$), we must have that

$$\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = \langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = 0. \quad (2.71)$$

This is the so-called Brillouin theorem [75, 76], which stipulates that the molecular electronic Hamiltonian cannot couple singly excited determinants $|\Phi_i^a\rangle$ with the Hartree-Fock reference determinant $|\Phi_0\rangle$. Furthermore, since the molecular electronic Hamiltonian is a two-body operator (*cf.* Eq. (2.39)), it can only couple determinants which differ by at most an excitation level (rank) of two, as dictated by the GWT of Eq. (2.32) or Slater's rules (*e.g.* $\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_i^a \rangle \neq 0$ and $\langle \Phi_{ijkl}^{abcd} | \hat{H} | \Phi_{ij}^{ab} \rangle \neq 0$, while $\langle \Phi_{ijkl}^{abcd} | \hat{H} | \Phi_i^a \rangle = 0$ and $\langle \Phi_{ijklm}^{abcde} | \hat{H} | \Phi_{ij}^{ab} \rangle = 0$). Let $|\mathcal{S}\rangle$, $|\mathcal{D}\rangle$, $|\mathcal{T}\rangle$ and $|\mathcal{Q}\rangle$ denote blocks of singly, doubly, triply and quadruply excited configurations, then the block structure of the Full CI Hamiltonian matrix in Eq. (2.69) can be written as

$$\mathbf{H} = \begin{bmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = E_0 & 0 & \langle \Phi_0 | \hat{H} | \mathcal{D} \rangle & 0 & 0 & \dots \\ 0 & \langle \mathcal{S} | \hat{H} | \mathcal{S} \rangle & \langle \mathcal{S} | \hat{H} | \mathcal{D} \rangle & \langle \mathcal{S} | \hat{H} | \mathcal{T} \rangle & 0 & \dots \\ \langle \mathcal{D} | \hat{H} | \Phi_0 \rangle & \langle \mathcal{D} | \hat{H} | \mathcal{S} \rangle & \langle \mathcal{D} | \hat{H} | \mathcal{D} \rangle & \langle \mathcal{D} | \hat{H} | \mathcal{T} \rangle & \langle \mathcal{D} | \hat{H} | \mathcal{Q} \rangle & \dots \\ 0 & \langle \mathcal{T} | \hat{H} | \mathcal{S} \rangle & \langle \mathcal{T} | \hat{H} | \mathcal{D} \rangle & \langle \mathcal{T} | \hat{H} | \mathcal{T} \rangle & \langle \mathcal{T} | \hat{H} | \mathcal{Q} \rangle & \dots \\ 0 & 0 & \langle \mathcal{Q} | \hat{H} | \mathcal{D} \rangle & \langle \mathcal{Q} | \hat{H} | \mathcal{T} \rangle & \langle \mathcal{Q} | \hat{H} | \mathcal{Q} \rangle & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}. \quad (2.72)$$

Iterative diagonalization (*e.g.* using the Davidson procedure [77]) of this Hamiltonian over all possible N -electron configurations, in the single particle space spanned by the K spin-orbitals, yields the CI coefficients (*i.e.* excitation amplitudes) in Eq. (2.65) and state energies of the given system. The variational principle ensures that the lowest energy eigenvalue corresponds to an upper bound to the true ground state energy, while the other eigenvalues are upper bounds to the excited state energies [59].

It is known that FCI gives the exact solution to the molecular electronic Schrödinger equation of Eq. (2.1) in a given basis set of one-electron functions and thus, provides a benchmark for testing approximate correlation methods. The disadvantage of FCI is that $N_{\text{det.}} = \binom{M}{N}$ (*i.e.* Eq. (2.66)) determinants must be included in the FCI wavefunction¹ of Eq. (2.65) and hence, it is extremely computationally demanding. For example, the efficient determinant based Full CI algorithm of Olsen and coworkers [78] has a computational cost which scales as $\mathcal{O}(N_{\text{det.}} N^2 (M - N/2)^2)$ for a closed-shell molecule. These high level calculations can only be performed on the smallest of systems, in relatively small basis sets and practical CI calculations usually involve a truncation of the Full CI wavefunction to a given excitation level.

¹The number of determinants can be reduced considerably if one imposes spin and symmetry restrictions (*i.e.* the coefficients (amplitudes) of configurations that do not have the same spin and/or spatial symmetry as the total wavefunction, for a

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Note that truncated CI methods still retain the following properties of the Full CI approach: 1. They are variational such that the energy eigenvalue for a given state is an upper bound to the exact energy for that state. 2. The wavefunction and energy are invariant under rotations of the orbitals in the occupied and virtual subspaces. 3. A CI wavefunction which includes up to n -fold excited determinants is exact for an n -electron system, in a given basis of one-electron functions (*e.g.* CISD (including singly and doubly and excited determinants) is exact for two-electron systems, CISDT (including singly, doubly and triply excited determinants) is exact for three-electron systems, *etc.*). Nevertheless, the major drawback of the use of truncated CI approaches is that they are not size-consistent or size-extensive [61, 2].

A given method is said to be size-consistent if the correlation energy is additively separable. Namely, size consistency requires that the correlation energy $E_C(AB)$ of a system AB , composed of two non-interacting subsystems A and B (*i.e.* at infinite separation) with respective energies of $E_C(A)$ and $E_C(B)$, be equal to the sum of the energies $E_C(AB) = E_C(A) + E_C(B)$, of the isolated subsystems [79, 80, 81]. In general, in order for a method to be size extensive, the correlation energy of a (periodic) system composed of n interacting subsystems A , must scale linearly with the size n of the system, in the thermodynamic limit ($n \rightarrow \infty$),

$$\lim_{n \rightarrow \infty} \frac{E_C(nA)}{n} \rightarrow C, \quad (2.73)$$

in which C is a constant that is greater than zero [80, 81, 82]. For example, even for a system of n non-interacting two-electron subsystems (*e.g.* H_2 or He), it can be shown that the CISD correlation energy is proportional to $\sqrt{n}$, such that the correlation energy per particle is zero in the thermodynamic limit (*i.e.* $\lim_{n \rightarrow \infty} \frac{E_C(nHe)}{n} \propto \lim_{n \rightarrow \infty} \frac{\sqrt{n}}{n} = 0$) [83]. The lack of size-extensivity in truncated CI approaches is a result of the fact that the so-called residual equations, which determine the coefficients in the wavefunction (*e.g.* the amplitudes c_i^a , c_{ij}^{ab} , *etc.* in a given truncation of Eq. (2.65)), contain the correlation energy [2]. For example, consider the CISD approach, with the wavefunction

$$|\Psi_{\text{CISD}}\rangle = |\Phi_0\rangle + \sum_{i,a} c_i^a |\Phi_i^a\rangle + \frac{1}{4} \sum_{i,j,a,b} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle = (1 + \hat{C}_1 + \hat{C}_2) |\Phi_0\rangle, \quad (2.74)$$

in which $\hat{C}_1 = \sum_{i,a} c_i^a \hat{e}_i^a$ and $\hat{C}_2 = \frac{1}{4} \sum_{i,j,a,b} c_{ij}^{ab} \hat{e}_{ij}^{ab}$, are respectively single and double excitation operators. If we let $\hat{H}_N = \hat{H} - E_0$, then the correlation energy for this model is given as $E_C = \langle \Phi_0 | \hat{H}_N (\hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle$ and iterative solution of the residual equations

$$R_i^a = \langle \Phi_i^a | \hat{H}_N (1 + \hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle - E_C c_i^a = 0, \quad (2.75)$$

given state, are rigourously zero)

$$R_{ij}^{ab} = \langle \Phi_{ij}^{ab} | \hat{H}_N (1 + \hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle - E_C c_{ij}^{ab} = 0, \quad (2.76)$$

determines the single (c_i^a) and double (c_{ij}^{ab}) excitation amplitudes and hence, the wavefunction and correlation energy [2, 6]. The contributions that contain the correlation energy in Eqs. (2.75) and (2.76) are said to be disconnected since the correlation energy itself is a fully contracted quantity (*i.e.* the sum of closed diagrams) and thus, is not contracted to the amplitudes in either equation [61]. In a perturbative expansion of the CISD correlation energy, these disconnected contributions lead to renormalization terms which scale as N^p with $p > 1$, thus resulting in a non size-extensive energy [2]. This will be true for any truncated CI expansion.

2.3.3 Single Reference Coupled-Cluster Theory for Ground States

Coupled Cluster (CC) theory was first introduced in the context of nuclear physics [84, 85]. Soon thereafter, Čížek developed the first working model which could be applied to the many-electron problem of quantum chemistry [86]. It has since become one of the most popular hierarchies of *ab-initio* methods in quantum chemistry and a recent review of CC theory for ground and excited states is given by Bartlett and Musiał [2]. In single reference CC theory, an exponential ansatz is employed to introduce excitations into the model wavefunction,

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle, \quad (2.77)$$

where the cluster operator $\hat{T}$ is the sum $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$ of single ($\hat{T}_1$), double ($\hat{T}_2$) and higher order excitations out of the reference (Hartree-Fock) determinant and an arbitrary N -fold excitation operator $\hat{T}_N$ can be written as [86]

$$\hat{T}_N = \left(\frac{1}{N!} \right)^2 \sum_{\substack{i,j,k,l,\dots \\ a,b,c,d,\dots}} t_{ijkl\dots}^{abcd\dots} \hat{c}_{ijkl\dots}^{abcd\dots}. \quad (2.78)$$

Inserting the exponential ansatz of Eq. (2.77) into the molecular electronic Schrödinger equation of Eq. (2.1), we obtain

$$\hat{H} e^{\hat{T}} |\Phi_0\rangle = E e^{\hat{T}} |\Phi_0\rangle. \quad (2.79)$$

Let $\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ denote the similarity transformed Hamiltonian, then multiplication of Eq. (2.79) by $e^{-\hat{T}}$ yields the similarity transformed Schrödinger equation as,

$$\hat{\bar{H}} |\Phi_0\rangle = e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle = E |\Phi_0\rangle. \quad (2.80)$$

Evidently, this equation admits that the reference (Hartree-Fock) determinant is an eigenfunction of the similarity transformed Hamiltonian $\widehat{\bar{H}}$, with an eigenvalue equal to the ground state (Coupled-Cluster) energy E . From the well-known Baker-Campbell-Hausdorff (BCH) expansion, the similarity transformed Hamiltonian in Eq. (2.80) can be written as a series of nested commutators,

$$\widehat{\bar{H}} = e^{-\widehat{T}} \widehat{H} e^{\widehat{T}} = \widehat{H} + [\widehat{H}, \widehat{T}] + \frac{1}{2} [[\widehat{H}, \widehat{T}], \widehat{T}] + \frac{1}{6} [[[\widehat{H}, \widehat{T}], \widehat{T}], \widehat{T}] + \frac{1}{24} [[[[\widehat{H}, \widehat{T}], \widehat{T}], \widehat{T}], \widehat{T}], \quad (2.81)$$

where the series terminates after the 4th-fold nested commutator, since $\widehat{H}$ is a two-body operator and can at most, be contracted to four $\widehat{T}$ operators (*cf.* the GWT of Eq. (2.32)). Furthermore, using the GWT, we can expand the similarity transformed Hamiltonian as

$$\widehat{\bar{H}} = \bar{h}_0 + \sum_{i,a} \bar{h}_q^p \{ \hat{e}_q^p \} + \frac{1}{4} \sum_{p,q,r,s} \bar{h}_{rs}^{pq} \{ \hat{e}_{rs}^{pq} \} + \frac{1}{36} \sum_{p,q,r,s,t,u} \bar{h}_{stu}^{pqr} \{ \hat{e}_{stu}^{pqr} \} + \dots, \quad (2.82)$$

in which the braces $\{ \}$ indicate normal ordering of the products of second-quantized operators with respect to the Hartree-Fock reference state. The various elements, $\bar{h}_0$, $\bar{h}_q^p$, $\bar{h}_{rs}^{pq}$, *etc.* of $\widehat{\bar{H}}$ can be expressed as a series of tensor contractions involving the elements of the bare Hamiltonian (*i.e.* the Fock matrix and two-electron integrals) and the amplitudes defining the cluster operator $\widehat{T}$.

An expression for the CC energy (*i.e.* for any truncation of the cluster operator $\widehat{T}$) is obtained by projecting Eq. (2.80) onto the reference determinant and using the BCH expansion and the GWT of Eq. (2.32),

$$E = \bar{h}_0 = \langle \Phi_0 | \widehat{\bar{H}} | \Phi_0 \rangle = E_0 + E_C = E_0 + \sum_{i,a} f_a^i t_i^a + \frac{1}{4} \sum_{i,j,a,b} v_{ab}^{ij} (2t_i^a t_j^b + t_{ij}^{ab}). \quad (2.83)$$

Projecting Eq. (2.80) onto the various excited determinants we obtain the residual equations

$$\begin{aligned} R_i^a &= \langle \Phi_i^a | \widehat{\bar{H}} | \Phi_0 \rangle = \bar{h}_i^a = 0, \\ R_{ij}^{ab} &= \langle \Phi_{ij}^{ab} | \widehat{\bar{H}} | \Phi_0 \rangle = \bar{h}_{ij}^{ab} = 0, \\ &\vdots \\ R_{ijkl\cdots}^{abcd\cdots} &= \langle \Phi_{ijkl\cdots}^{abcd\cdots} | \widehat{\bar{H}} | \Phi_0 \rangle = \bar{h}_{ijkl\cdots}^{abcd\cdots} = 0, \end{aligned} \quad (2.84)$$

which determine the cluster amplitudes $t_i^a, t_{ij}^{ab}, \dots, t_{ijkl\cdots}^{abcd\cdots}$. Even though the CC energy expression of Eq. (2.83) only depends on the single and double cluster amplitudes, these amplitudes are coupled to the higher rank excitation amplitudes via the residual equations of Eq. (2.84). In contrast with the CI residual

equations (*e.g.* the CISD equations of Eqs. (2.75) and (2.76)), the energy does not enter the residual equations of Eq. (2.84) and this is the key to the correct linear scaling of the energy, with system size, in CC theory [4]. Furthermore, the nested commutators in the BCH expansion of $\hat{H}$ in Eq. (2.81) imply that $\hat{H}$ and $\hat{T}$ always have spin-orbital indices in common (*i.e.* they are always contracted through at least one index) and hence, every contribution in the series is connected [2]. This implies that the exponential form of the wavefunction in Eq. (2.77) and the energy of Eq. (2.83) contain only connected contributions and hence, CC theory is size-extensive/consistent by construction [2]. This is true for any truncation of the cluster operator $\hat{T}$. Furthermore, CC is invariant to rotations of occupied/virtual orbitals, systematically improved by adding higher order excitations to the cluster operator $\hat{T}$ and when truncated to N -fold excitations, CC theory is exact for N -electron systems in a given spin-orbital basis.

The CCSD approach [87] (with single and double excitations) is defined by taking a cluster operator $\hat{T} = \hat{T}_1 + \hat{T}_2$, composed of single and double excitation operators (*i.e.* $|\Psi_{\text{CCSD}}\rangle = e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle$). The set of residual equations which determine the cluster amplitudes t_i^a and t_{ij}^{ab} are then given by

$$R_i^a = \bar{h}_i^a = \langle \Phi_i^a | e^{-\hat{T}_1 - \hat{T}_2} \hat{H} e^{\hat{T}_1 + \hat{T}_2} | \Phi_0 \rangle = \langle \Phi_i^a | \left(\hat{H} \left(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \frac{1}{6} \hat{T}_1^3 \right) \right)_C | \Phi_0 \rangle, \quad (2.85)$$

$$R_{ij}^{ab} = \bar{h}_{ij}^{ab} = \langle \Phi_{ij}^{ab} | e^{-\hat{T}_1 - \hat{T}_2} \hat{H} e^{\hat{T}_1 + \hat{T}_2} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \left(\hat{H} \left(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{6} \hat{T}_1^3 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{24} \hat{T}_1^4 \right) \right)_C | \Phi_0 \rangle, \quad (2.86)$$

in which the notation $()_C$ indicates that all contributions within the parentheses are connected [61]. Application of the GWT of Eq. (2.32) to the various contributions in Eqs. (2.85) and (2.86) then yields the working equations for the CCSD methodology. The asymptotic scaling of the cost of a CCSD calculation is dominated by the contribution $\frac{1}{2} \sum_{c,d} v_{cd}^{ab} (t_{ij}^{cd} + 2t_i^c t_j^d)$, to Eq. (2.86). In a spin-adapted implementation, the cost of a CCSD calculation therefore scales as $\mathcal{O}(n_o^2 n_v^4)$, where n_o is the number of occupied spatial orbitals and n_v is the number of virtual spatial orbitals. Note that this is the same asymptotic scaling as for the CISD method, since Eq. (2.76) contains the contribution $\frac{1}{2} \sum_{c,d} v_{cd}^{ab} c_{ij}^{cd}$. In general, the spin-adapted formulations of both CC and CI approaches, truncated to m -fold excitations, have an asymptotic scaling of $\mathcal{O}(n_o^m n_v^{m+2})$. The CCSD(T) approach [3], which includes a (non-iterative $\mathcal{O}(n_o^3 n_v^4)$ scaling) perturbative correction for triple excitations to the CCSD energy, is often called the “gold-standard” of modern *ab-initio* quantum chemistry, as it provides a good trade-off between computational cost and accuracy. However, it is known that it is insufficient to model (multireference) systems where the Hartree-Fock reference provides a poor first order description of the wavefunction (*i.e.* bond-breaking, bi-radicals, transition states, many transition metal complexes, *etc.*). These systems may be adequately described by including higher excitations in CC theory, beyond singles and doubles. However, these calculations quickly become

prohibitive since the computational cost scales as $\mathcal{O}(n_o^m n_v^{m+2})$, for a given excitation rank m . We will discuss alternative approaches to dealing with these systems in section 2.4.

Let us briefly describe the algorithm that is used for solving the CCSD equations, as it is particularly relevant to the discussion which follows in later chapters. The two-electron integrals in the atomic orbital (AO) basis, obtained from a converged Hartree-Fock calculation (*cf.* section 2.3.1), are transformed to the molecular orbital (MO) basis, using the coefficients $C_{p\mu}$ from the self-consistent field solution. Typically, one uses the first order approximation

$$t_{ij}^{ab(1)} = \frac{v_{ij}^{ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \quad (2.87)$$

as a guess to the doubles amplitudes, before entering the first CCSD iteration [61]. The Brillouin theorem (Eq. (2.71)) dictates that the first order singles amplitudes are zero (*i.e.* $t_i^{a(1)} = 0$). With this guess for the amplitudes, we then begin the CCSD residual equation iterations:

1. Calculate the residual equations of Eqs. (2.85) and (2.86), using the current values of the amplitudes $(t_i^a)_n$ and $(t_{ij}^{ab})_n$.
2. If the largest element of the current residuals R_i^a or R_{ij}^{ab} falls below a predetermined threshold $\mathcal{T}$, then terminate the iterations. Otherwise, calculate a new set of single and double amplitudes via

$$(t_i^a)_{n+1} = (t_i^a)_n + \frac{R_i^a}{\varepsilon_i - \varepsilon_a}, \quad (2.88)$$

$$(t_{ij}^{ab})_{n+1} = (t_{ij}^{ab})_n + \frac{R_{ij}^{ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \quad (2.89)$$

and return to step 1 to begin another iteration.

It is also important to note that in modern implementations of CC methods, the DIIS procedure of Pulay [65, 66] is almost always used to accelerate the convergence of these iterations.

2.3.4 Equation of Motion Coupled-Cluster Methods for Excited States

The Excitation-Energy Equation of Motion Coupled-Cluster (EE-EOM-CC) approach [13, 14, 15] is a generalization of the ground state Coupled-Cluster method to excited states. Over the years, other EOM-CC approaches have also been reported, for calculating ionization potentials (IP-EOM-CC) [88, 89] and electron affinities (EA-EOM-CC) [90, 91], in addition to further generalizations (*e.g.* EOM-CC for double

ionization potentials (DIP-EOM-CC) [92]). The EE-EOM-CC wavefunction $|\Psi_{\mathbf{m}}\rangle$, for a given excited state $\mathbf{m} = 1, 2, 3, \dots$ can be written as [61]

$$|\Psi_{\mathbf{m}}\rangle = \hat{R}^{[\mathbf{m}]} |\Psi_0\rangle = \hat{R}^{[\mathbf{m}]} e^{\hat{T}} |\Phi_0\rangle, \quad (2.90)$$

in which $|\Psi_0\rangle = e^{\hat{T}} |\Phi_0\rangle$ is the CC ansatz of Eq. (2.77), for the ground state wavefunction, and $\hat{R}^{[\mathbf{m}]}$ is a linear excitation operator for the $\mathbf{m}^{\text{th}}$ excited state,

$$\hat{R}^{[\mathbf{m}]} = r_0^{[\mathbf{m}]} + \sum_{i,a} r_i^{a[\mathbf{m}]} \hat{e}_i^a + \sum_{\substack{j < i \\ b < a}} r_{ij}^{ab[\mathbf{m}]} \hat{e}_{ij}^{ab} + \dots \quad (2.91)$$

The excitation amplitudes, which define the cluster operator $\hat{T}$, are taken from a ground state coupled-cluster calculation (*i.e.* $\hat{R}^{[0]} = 1$ for the ground state $\mathbf{m} = 0$) [61]. Substituting the EE-EOM-CC ansatz of Eq. (2.90) into the Schrödinger equation of Eq. (2.1), we obtain

$$\hat{H} \hat{R}^{[\mathbf{m}]} e^{\hat{T}} |\Phi_0\rangle = E_{\mathbf{m}} \hat{R}^{[\mathbf{m}]} e^{\hat{T}} |\Phi_0\rangle, \quad (2.92)$$

in which $E_{\mathbf{m}}$ is the energy of the $\mathbf{m}^{\text{th}}$ excited state. Also, since $\hat{R}^{[\mathbf{m}]}$ in Eq. (2.91) is an excitation operator, it commutes with the cluster operator $\hat{T}$ and hence, $e^{\hat{T}}$, such that Eq. (2.92) can be written as [61]

$$\hat{H} e^{\hat{T}} \hat{R}^{[\mathbf{m}]} |\Phi_0\rangle = E_{\mathbf{m}} e^{\hat{T}} \hat{R}^{[\mathbf{m}]} |\Phi_0\rangle. \quad (2.93)$$

Left multiplication of both sides of this equation by $e^{-\hat{T}}$ then yields,

$$\hat{\bar{H}} \hat{R}^{[\mathbf{m}]} |\Phi_0\rangle = E_{\mathbf{m}} \hat{R}^{[\mathbf{m}]} |\Phi_0\rangle, \quad (2.94)$$

where once again $\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$, is the similarity transformed Hamiltonian operator [61]. Furthermore, from Eq. (2.91) we have that

$$\hat{R}^{[\mathbf{m}]} |\Phi_0\rangle = \sum_I r_I^{[\mathbf{m}]} |\Phi_I\rangle, \quad (2.95)$$

in which the index I runs over the basis of N -electron Slater determinants (*cf.* Eq. (2.65)). Hence, Eq. (2.94) can be written as

$$\sum_I r_I^{[\mathbf{m}]} \hat{\bar{H}} |\Phi_I\rangle = E_{\mathbf{m}} \sum_I r_I^{[\mathbf{m}]} |\Phi_I\rangle, \quad (2.96)$$

in analogy with Eq. (2.67) in (Full-)CI. However, since the similarity transformed Hamiltonian $\widehat{\bar{H}} = e^{-\widehat{T}}\widehat{H}e^{\widehat{T}}$, is not Hermitian, it must also have a set of left hand eigenvectors $\langle\Phi_0|\widehat{L}^{[m]}$ such that

$$\langle\Phi_0|\widehat{L}^{[m]}\widehat{\bar{H}} = \langle\Phi_0|\widehat{L}^{[m]}E_m \Rightarrow \sum_I \langle\Phi_I|l_I^{[m]}\widehat{\bar{H}} = E_m \sum_I \langle\Phi_I|l_I^{[m]}, \quad (2.97)$$

in which $\widehat{L}^{[m]}$ is a de-excitation operator for the m^{th} state [61],

$$\widehat{L}^{[m]} = l_0^{[m]} + \sum_{i,a} l_a^{i[m]} \hat{e}_{ab}^{ij} + \sum_{\substack{j < i \\ b < a}} l_{ab}^{ij[m]} \hat{e}_{ab}^{ij} + \dots \quad (2.98)$$

Let us once again assume that the determinants are mutually orthonormal (*i.e.* $\langle\Phi_I|\Phi_J\rangle = \delta_{IJ}$) and let $\bar{H}_{IJ} = \langle\Phi_I|\widehat{\bar{H}}|\Phi_J\rangle$ denote the elements of the (non-symmetric, $\bar{H}_{IJ} \neq \bar{H}_{JI}$) similarity transformed Hamiltonian, in the basis of Slater determinants. Projection of Eq. (2.96) onto the possible determinants $|\Phi_I\rangle$, then gives the set of equations

$$\begin{aligned} \sum_J \langle\Phi_I|\widehat{\bar{H}}|\Phi_J\rangle r_J^{[m]} &= E_m \sum_J r_J^{[m]} \langle\Phi_I|\Phi_J\rangle \Rightarrow \sum_J \bar{H}_{IJ} r_J^{[m]} = E_m r_I^{[m]} \\ &\Rightarrow \bar{\mathbf{H}}\mathbf{r}^{[m]} = E_m \mathbf{r}^{[m]}, \end{aligned} \quad (2.99)$$

which is an eigenvalue problem yielding the expansion coefficients of the right-hand eigenvector, in the basis of Slater determinants, and the energy for the m^{th} excited state [4]. In an analogous fashion, we obtain the following eigenvalue problem by projecting Eq. (2.97) onto the possible determinants $|\Phi_I\rangle$,

$$\sum_J l_J^{[m]} \bar{H}_{JI} = E_m l_I^{[m]} \Rightarrow \mathbf{l}^{[m]} \bar{\mathbf{H}} = E_m \mathbf{l}^{[m]} \quad (2.100)$$

which determines the expansion coefficients of the left-hand eigenvector, in the basis of Slater determinants, and the energy for the m^{th} excited state [4]. If one is simply interested in the excited state energies, then it is only necessary to solve Eq. (2.99) for each excited state of interest, while the calculation of properties of excited states (*e.g.* transition moments, multipole moments, *etc.*) also requires the solution of Eq. (2.100) [61].

In order to illustrate the effectiveness of the EE-EOM-CC approach, let us consider the EE-EOM-CCSD method. One first solves the CCSD equations of Eqs. (2.85) and (2.86) (*i.e.* $\bar{h}_i^a = \bar{h}_{ij}^{ab} = 0$) for the t_i^a and t_{ij}^{ab} amplitudes, which determine the ground state CCSD energy $E_{\text{CCSD}} = \langle\Phi_0|\widehat{\bar{H}}|\Phi_0\rangle$ (from Eq. (2.83)). The block structure of the similarity transformed Hamiltonian matrix $\bar{\mathbf{H}}$ can then be

represented schematically as

$$\begin{array}{c|ccccc}
 \bar{\mathbf{H}} & |\Phi_0\rangle & |\mathcal{S}\rangle & |\mathcal{D}\rangle & |\mathcal{T}\rangle & |\mathcal{Q}\rangle \\
 \hline
 \langle\Phi_0| & E_{\text{CCSD}} & X & X & 0 & 0 \\
 \langle\mathcal{S}| & \bar{h}_i^a = 0 & X & X & X & 0 \\
 \langle\mathcal{D}| & \bar{h}_{ij}^{ab} = 0 & X & X & X & X \\
 \hline
 \langle\mathcal{T}| & \sim & \sim & X & X & X \\
 \langle\mathcal{Q}| & \sim & \sim & \sim & X & X
 \end{array} \tag{2.101}$$

in which an X is used to indicate a block containing many sizeable elements, 0 indicates a block of vanishing elements and $\sim$ is used to indicate a block containing many small elements. If one is interested in the accurate calculation of singly excited states (*i.e.* excited states dominated by singly excited configurations $|\Phi_i^a\rangle$), as is often the case, it is only necessary to diagonalize the similarity transformed Hamiltonian $\bar{\mathbf{H}}$, over the manifold of singly and doubly excited determinants (as indicated by the dashed line in Eq. (2.101)). This is due to the fact that many of the important elements of the $\langle\mathcal{T}|\hat{H}|\mathcal{S}\rangle$ block have been eliminated as a result of the satisfaction of the CCSD residual condition $\bar{h}_{ij}^{ab} = 0$ (*i.e.* the two-body excitation operators $\{\hat{e}_{ij}^{ab}\}$ no longer couple the determinants in this block) and many of the remaining elements that couple triply excited determinants to singly excited determinants are typically small [93]. In order to get reasonably accurate excitation energies (for singly excited states) from a CI calculation, one would have to diagonalize the bare Hamiltonian of Eq. (2.72) over the manifold of singly, doubly and triply excited determinants, since there are many sizeable elements in the $\langle\mathcal{T}|\hat{H}|\mathcal{S}\rangle$ block [93]. It is important to note that, for each excited state of interest, the latter CISDT diagonalization has a computational scaling of $\mathcal{O}(n_o^3 n_v^5)$, while the EE-EOM-CCSD calculation (for each state) scales as $\mathcal{O}(n_o^2 n_v^4)$.

One deficiency of the EE-EOM-CC methodology is that it is not size-extensive for charge-transfer (CT) excitations (*e.g.* see Refs. [80, 94]). This is a consequence of the disconnected diagrams which arise in the EE-EOM-CC wavefunction of Eq. (2.90) and excited state energy eigenvalues, upon truncation of the (CI-like) linear excitation operator of Eq. (2.91) [94]. Nevertheless, EE-EOM-CC is still widely employed for the calculation of excitation energies in molecular systems. Alternatively, the Similarity Transformed Equation of Motion CCSD approach (STEOM-CCSD) [16, 17] treats charge-transfer excitations in a rigorously size-extensive fashion [80]. It involves a sequence of two similarity transformations, the first of which is identical to that in EE-EOM-CCSD (*i.e.* $\hat{\bar{H}} = e^{-\hat{T}_1 - \hat{T}_2} \hat{H} e^{\hat{T}_1 + \hat{T}_2}$, with t_i^a and t_{ij}^{ab} amplitudes obtained from a converged CCSD calculation for the ground state). The second similarity transformation

defines a transformed Hamiltonian $\widehat{G}$ [16, 17],

$$\widehat{G} = \{e^{\widehat{S}}\}^{-1} \widehat{H} \{e^{\widehat{S}}\}, \quad (2.102)$$

where the operator $\widehat{S}$ is given by

$$\widehat{S} = \widehat{S}_- + \widehat{S}_+, \quad (2.103)$$

with

$$\widehat{S}_- = \sum_{i,m} s_{i'}^m \{\hat{e}_{i'}^m\} + \frac{1}{2} \sum_{i,j,a,m} s_{ij}^{am} \{\hat{e}_{ij}^{am}\}, \quad (2.104)$$

$$\widehat{S}_+ = \sum_{e,a} s_e^{a'} \{\hat{e}_e^{a'}\} + \frac{1}{2} \sum_{i,e,a,m} s_{ie}^{ab} \{\hat{e}_{ie}^{ab}\}. \quad (2.105)$$

Here, we use m to denote a set of “active” occupied orbitals chosen as a subset of the occupied orbitals and e to denote a set of “active” virtual orbitals chosen from the set of virtual orbitals. Furthermore, i' is used to label the “inactive” occupied orbitals and a' is used to label the “inactive” virtual orbitals. In analogy with Eq. (2.82), we can write the transformed Hamiltonian $\widehat{G}$ in normal-ordered, second quantized form as

$$\widehat{G} = g_0 + \sum_{i,a} g_q^p \{\hat{e}_q^p\} + \frac{1}{4} \sum_{p,q,r,s} g_{rs}^{pq} \{\hat{e}_{rs}^{pq}\} + \frac{1}{36} \sum_{p,q,r,s,t,u} g_{stu}^{pqr} \{\hat{e}_{stu}^{pqr}\} + \dots, \quad (2.106)$$

in which the elements g_0 , g_q^p , g_{rs}^{pq} , *etc.* are expressed in terms of a series of tensor contractions between the elements of $\widehat{H}$, in Eq. (2.82), and the s -amplitudes which define the operator $\widehat{S}$ in Eq. (2.103). It can be shown [95] that vanishing elements of the first similarity transformation are preserved in the second transformation of Eq. (2.102), namely,

$$g_0 = \bar{h}_0 = E_{\text{CCSD}}, \quad (2.107)$$

$$g_i^a = \bar{h}_i^a = 0, \quad (2.108)$$

$$g_{ij}^{ab} = \bar{h}_{ij}^{ab} = 0. \quad (2.109)$$

The $s_{i'}^m$ and s_{ij}^{am} amplitudes, which define the operator $\widehat{S}_-$ in Eq. (2.104), can be obtained by iteratively solving the coupled set of non-linear equations

$$g_{i'}^m = \langle \Phi_{i'} | \widehat{G} | \Phi_m \rangle = 0, \quad (2.110)$$

$$g_{ij}^{am} = \langle \Phi_{ij}^a | \widehat{G} | \Phi_m \rangle = 0. \quad (2.111)$$

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Similarly, the $s_e^{a'}$ and s_{ie}^{ab} amplitudes, defining the operator $\hat{S}_+$ in Eq. (2.105), can be determined as iterative solutions of the equations

$$g_e^{a'} = \langle \Phi^{a'} | \hat{G} | \Phi^e \rangle = 0, \quad (2.112)$$

$$g_{ie}^{ab} = \langle \Phi_i^{ab} | \hat{G} | \Phi^e \rangle = 0. \quad (2.113)$$

In Ref. [17], it is demonstrated that the amplitudes satisfying Eqs. (2.110) and (2.111), are obtained by solving the IP-EOM-CCSD equations for a number of principal ionization potentials and that the solution of the EA-EOM-CCSD equations, for a selection of principle electron affinities, yields the amplitudes which satisfy Eqs. (2.112) and (2.113). Since the inverse $\{e^{\hat{S}}\}^{-1}$ in Eq. (2.102) is not known, the explicit algebraic expressions for the required elements of $\hat{G}$ have been obtained from the expression

$$\hat{G} = \left(\hat{H} \{e^{\hat{S}}\} \right)_C - \left(\{e^{\hat{S}} - 1\} \hat{G} \right)_C, \quad (2.114)$$

by back-substitution and the application of diagrammatic techniques [17]. With these expressions in hand, one can then evaluate the elements of the matrix representation of $\hat{G}$ from the converged s -amplitudes. The block structure of the $\mathbf{G}$ matrix can then be represented as

$\mathbf{G}$	$ \Phi_0\rangle$	$ \mathcal{S}\rangle$	$ \mathcal{D}\rangle$	$ \mathcal{T}\rangle$	$ \mathcal{Q}\rangle$
$\langle \Phi_0 $	E_{CCSD}	X	X	0	0
$\langle \mathcal{S} $	$g_i^a = 0$	X	X	X	0
$\langle \mathcal{D} $	$g_{ij}^{ab} = 0$	$\sim$	X	X	X
$\langle \mathcal{T} $	$\sim$	$\sim$	$\sim$	X	X
$\langle \mathcal{Q} $	$\sim$	$\sim$	$\sim$	$\sim$	X

(2.115)

where once again, X is used to indicate a block containing many sizeable elements, 0 indicates a block of vanishing elements and $\sim$ is used to indicate a block containing many small elements. The elimination of the operators $\{\hat{e}_{ij}^{am}\}$ and $\{\hat{e}_{ie}^{ab}\}$, due to the satisfaction of the residual conditions of Eqs. (2.111) and (2.113), respectively, removes the most important contributions to the $\langle \mathcal{D} | \hat{G} | \mathcal{S} \rangle$ block (*i.e.* these operators are the primary contributors to the coupling between singles and doubles configurations in this block). Accurate excitation energies of singly excited states can then be obtained by diagonalizing this transformed Hamiltonian over the relatively small manifold of singly excited determinants [93, 16, 17], as shown by the dashed line in Eq. (2.115). Hence, in addition to providing a size-extensive description of charge-transfer excitations, the STEOM-CCSD approach is considerably less computationally demanding than EE-EOM-CCSD for the calculation of excitation energies.

2.4 Multireference Correlation Methods

2.4.1 The Distinction between Dynamic and Static Correlation

Let us reconsider the Full-CI wavefunction of Eq. (2.65), in section 2.3.2, and write it as

$$|\Psi\rangle = c_0 |\Phi_0\rangle + \sum_I c_I |\Phi_I\rangle. \quad (2.116)$$

For many closed-shell molecules, near the equilibrium geometry of the ground electronic state, the Hartree-Fock approximation provides a qualitatively correct description of the wavefunction [61]. When this is the case, the Hartree-Fock reference determinant $|\Phi_0\rangle$ is the dominant contribution to the FCI wavefunction of Eq. (2.116) (*i.e.* $|c_0|^2 \gg |c_I|^2 \quad \forall \quad I > 0$). The role of the numerous excited determinants, which enter Eq. (2.116) with small weights, is to include the effects of *dynamic correlation* in the description of the molecular electronic wavefunction. Dynamic correlation refers to the differential correlation beyond the mean-field approximation, which is due to electrostatic repulsion and is inherently a short-range correlation effect [61]. The word dynamic is used universally throughout the literature although nothing is moving in the theoretical description (*i.e.* time-independent quantum mechanics). As we have seen, all of the post Hartree-Fock correlation approaches, discussed in section 2.3, model the effects of dynamic correlation by including excited configurations in the wavefunction. Also, the fact that a single Slater determinant is taken as the zeroth order reference wavefunction explains why these approaches are aptly referred to as single-reference correlation methods.

In a wide variety of systems, such as biradicals, open-shell molecules, closed-shell molecules with stretched bonds, excited states, transition states, many transition metal complexes, *etc.*, there are two or more nearly degenerate configurations that make a large contribution to the wavefunction of Eq. (2.116). This signifies that the Hartree-Fock reference determinant no longer provides a qualitatively correct zeroth order description of the wavefunction for these systems. The term *static correlation* is used to describe the correlation effects which are included within the multi-determinantal expansion of the zeroth order wavefunction for these systems. Namely, static correlation describes the correlation effects resulting from near degeneracies and other deficiencies inherent in a single-determinantal zeroth order description of the wavefunction [61]. Static electron correlation is inherently a non-local correlation effect since it is often enhanced or even only present when electrons are separated by large distances (*e.g.* internuclear separations corresponding to a broken bond). This can be viewed as the entanglement of electrons in distant orbitals. As mentioned previously, static correlation effects can be treated with single-reference correlation methods that include sufficiently high rank excitation operators, however, the cost of calculations quickly

become prohibitive for all but the smallest of systems. Hence, one can see the need for multireference correlation methods, which treat static correlation by taking a multi-determinantal expansion for the zeroth order wavefunction and include dynamic correlation effects by considering excitations out of the multi-configurational reference space.

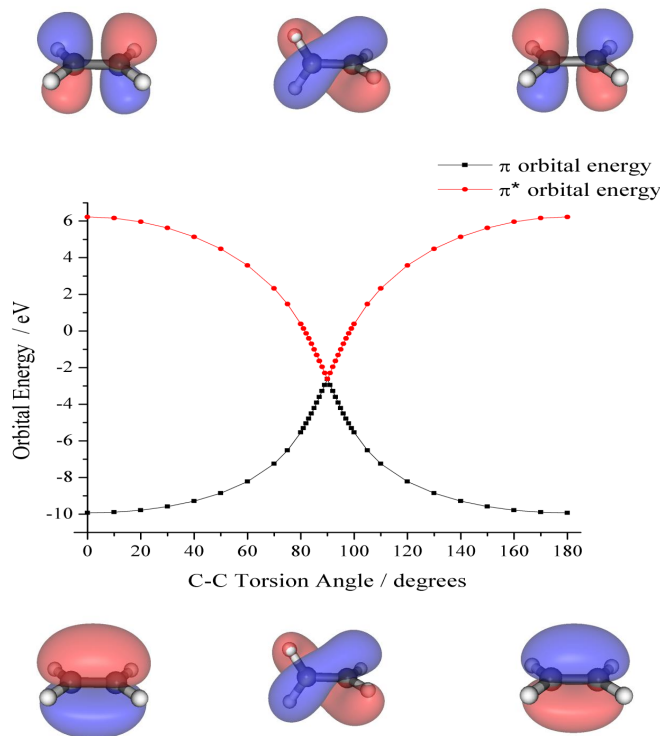


Figure 2.1: The CASSCF(2,2) orbital energies of the π (HOMO) and π^* (LUMO) orbitals as a function of the C-C torsion angle of ethylene, in a def2-TZVPP basis.

Let us discuss a simple example to illustrate the usefulness of multireference correlation methods. We will consider various methods for the calculation of the potential energy curve along the internal rotation (torsion) coordinate about the carbon-carbon double bond of the ethylene molecule, in a def2-TZVPP basis [96]. In Figure 2.1, we plot the CASSCF(2,2) (*i.e.* Complete Active Space Self-Consistent Field approach with two-electrons in two orbitals) orbital energies for the Highest Occupied (π) Molecular Orbital (HOMO) and the Lowest Unoccupied (π^*) Molecular Orbital (LUMO) as a function of the C-C torsion angle (*i.e.* the angle between the plane containing one CH_2 group and the plane containing the

second CH_2 group). The CASSCF(m_a, n_a) (m_a electrons distributed among n_a “active” orbitals) approach is a general procedure for obtaining a multi-configurational reference wavefunction and will be discussed in some detail in section 2.4.2. One important thing to note, at this point, is that the CASSCF(2,2) wavefunction is a linear combination of four Slater determinants, one which includes the doubly occupied π orbital, one which has a spin up electron in the π orbital and a spin down electron in the π^* orbital, another which has a spin down electron in the π orbital and a spin up electron in the π^* orbital and the last determinant consists of a doubly occupied π^* orbital. The CASSCF(2,2) reference wavefunction, however, is a mixture of these four configurations and thus, each of the two “active” molecular orbitals will have fractional occupation numbers. From the plot in Figure 2.1, it is observed that the energies of the π and π^* orbitals are separated by a large gap (~ 16 eV) at the equilibrium geometry, when the torsion angle is 0° . In contrast, as the torsion angle approaches 90° , the energy difference decreases abruptly until the two orbitals become degenerate at 90° . At this geometry, we find that the CASSCF(2,2) occupation numbers of both orbitals are exactly 1, indicating that ethylene behaves as a biradical. In the case of the RHF approach, which only considers a single determinant with a doubly occupied π HOMO, the difference in the orbital energies of the π and π^* orbitals is always large for all values of the C-C torsion angle.

In Figure 2.2, the molecular electronic energy is plotted as a function of the C-C torsion angle, for various methods in a def2-TZVPP basis. The unphysical (nearly linear) rise of the energy to a cusp, as the torsion angle approaches 90° in Figure 2.2 a), clearly demonstrates the failure of the single determinantal RHF approach in describing the potential energy surface in this region. The inclusion of dynamic correlation effects out of the RHF reference wavefunction lowers the energy considerably, as expected, but does little to remedy the situation, since the potential energy curves calculated with the single-reference CCSD and CCSD(T) approaches display the same unphysical rise to a cusp near a torsion angle of 90° , which can clearly be observed in Figure 2.2 b). In contrast, the CASSCF(2,2) potential energy curve is smooth over the entire range of the C-C torsion angles (*cf.* Figure 2.2 a)). This is not surprising, as the zeroth order CASSCF(2,2) wavefunction is able to correctly describe the degeneracy of the π and π^* orbitals when the torsion angle is 90° (*i.e.* Figure 2.1) and will thus, have the correct qualitative behaviour in the vicinity of this geometry. The potential energy curves, calculated with the MR-EOM (MultiReference Equation Of Motion) and MRCI+Q (MultiReference Configuration Interaction with single and double excitations and the Davidson Q correction [97, 98]) approaches, which include dynamic correlation effects on top of the CASSCF reference wavefunction, are also smooth over the entire range of torsion angles. The details of the MRCI approach will be briefly discussed in section 2.4.3, while the MR-EOM method will constitute one of the major topics of this thesis. In any case, the results of Figure 2.2 demonstrate the usefulness of multireference correlation methods in quantum chemistry. Namely, by using the CASSCF approach to treat static correlation effects, resulting in a qualitatively correct zeroth order wavefunction, multiref-

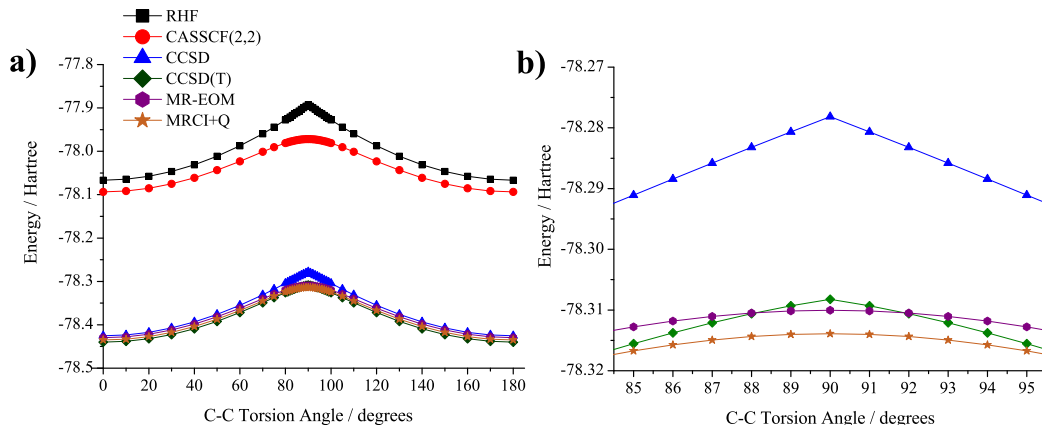


Figure 2.2: The molecular electronic energy, calculated with various methods, as a function of the C-C torsion angle for ethylene in a def2-TZVPP basis. The plot in a) shows the potential energy, for all the methods considered, over the full range of torsion angles and the in plot b) shows the behaviour of the single-reference (CCSD and CCSD(T)) and multireference (MR-EOM and MRCI+Q) correlation methods in the vicinity of the 90° torsion angle.

reference correlation methods can be employed to incorporate dynamic correlation effects by introducing excitations out of this multi-determinantal reference space. Moreover, these methods provide a much more cost effective alternative to the treatment of these systems than highly excited single-reference correlation methods.

2.4.2 CASSCF: Complete Active Space Self-Consistent Field

As we have already discussed in the previous section, the Complete Active Space Self-Consistent Field (CASSCF) approximation [99] defines a multi-determinantal wavefunction which allows for a proper treatment of static correlation effects in molecular systems [4]. In addition to a set of N_i doubly occupied inactive core spin-orbitals (i', j', k', l') and a set of N_v unoccupied virtual spin-orbitals (a, b, c, d), the CASSCF reference orbital space also contains a set of N_a active orbitals, labeled by w, x, y, z , which are partially occupied. The labels i, j, k, l now run over the full set of the $N_o = N_i + N_a$ occupied orbitals, which are either inactive or active. Here, we use M_a to denote the number of active electrons. The

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CASSCF(M_a, N_a) wavefunction for a given electronic state (of a given spin multiplicity) can be written as

$$|\Psi_0\rangle = \sum_{\alpha=1}^{N_{\text{Ref.}}} c_{\alpha} |\Phi_{\alpha}\rangle, \quad (2.117)$$

in which α runs over the set $\{|\Phi_{\alpha}\rangle\}$, of $N_{\text{Ref.}}$ reference determinants formed by distributing the M_a active electrons among the N_a active orbitals, in all possible ways [4, 99]. The CASSCF wavefunction is therefore, equivalent to a Full-CI wavefunction within the active orbital space. In analogy with Eq. (2.69), variational minimization of the energy with respect to the coefficients c_{α} (assuming orthonormality, $\langle\Psi_0|\Psi_0\rangle = \sum_{\alpha} |c_{\alpha}|^2 = 1$) leads to the following (CASCI) eigenvalue problem

$$\sum_{\beta} H_{\alpha\beta} c_{\beta} = E_{\text{CAS}} c_{\alpha} \Rightarrow \mathbf{H}\mathbf{c} = E_{\text{CAS}}\mathbf{c}, \quad (2.118)$$

for the CASSCF energy and coefficients of a particular electronic state. Furthermore, one can write the CASSCF energy, for a given state, as

$$E_{\text{CAS}} \equiv E_{\text{CAS}}(\{\phi_p\}, \mathbf{c}) = \langle\Psi_0|\hat{H}|\Psi_0\rangle = \sum_{\alpha,\beta} c_{\alpha}^* c_{\beta} H_{\alpha\beta}, \quad (2.119)$$

in which the energy is a functional of the orbitals (*i.e.* appearing in the elements $H_{\alpha\beta} = \langle\Phi_{\alpha}|\hat{H}|\Phi_{\beta}\rangle$ of the Hamiltonian) and the vector of coefficients $\mathbf{c}$, appearing in Eq. (2.117) and we have once again, used the orthonormality condition $\langle\Psi_0|\Psi_0\rangle = \sum_{\alpha} |c_{\alpha}|^2 = 1$.

Employing the second-quantized Hamiltonian of Eq. (2.20), the energy expression of Eq. (2.119) can be rewritten as

$$E_{\text{CAS}} = \sum_{p,q} h_q^p \langle\Psi_0|\hat{e}_q^p|\Psi_0\rangle + \frac{1}{2} \sum_{p,q,r,s} V_{rs}^{pq} \langle\Psi_0|\hat{e}_{rs}^{pq}|\Psi_0\rangle + h_{\text{nuc.}}, \quad (2.120)$$

where we define the one- and two-body reduced density matrices (RDMs), respectively, as [4]

$$\gamma_q^p = \langle\Psi_0|\hat{e}_q^p|\Psi_0\rangle = \sum_{\alpha,\beta} c_{\alpha}^* c_{\beta} \langle\Phi_{\alpha}|\hat{e}_q^p|\Phi_{\beta}\rangle, \quad (2.121)$$

$$\gamma_{rs}^{pq} = \langle\Psi_0|\hat{e}_{rs}^{pq}|\Psi_0\rangle = \sum_{\alpha,\beta} c_{\alpha}^* c_{\beta} \langle\Phi_{\alpha}|\hat{e}_{rs}^{pq}|\Phi_{\beta}\rangle. \quad (2.122)$$

If we assume that the orbitals are real, as will always be the case for any methods considered herein, then the one-body density matrix is symmetric,

$$\gamma_q^p = \gamma_p^q, \quad (2.123)$$

and the two-body density matrix admits the following permutational symmetries [4],

$$\gamma_{rs}^{pq} = \gamma_{qp}^{sr} \quad (2.124)$$

$$\gamma_{rs}^{pq} = \gamma_{sr}^{qp} = -\gamma_{rs}^{qp} = -\gamma_{sr}^{pq}. \quad (2.125)$$

Since the virtual orbitals are not occupied in the CASSCF wavefunction, the one- and two-electron RDMs vanish if at least one of the labels is a virtual orbital [100, 101]. Hence, the labels p, q, r, s in the above expressions for the RDMs are constrained to be either inactive core or active orbitals (*i.e.* they are occupied orbitals i, j, k, l). Also, the inactive-inactive block of the one-body density matrix is diagonal with elements

$$\gamma_{j'}^{i'} = \delta_{i'j'}, \quad (2.126)$$

and all of the elements of the inactive-active (active-inactive) block are rigourously zero [100],

$$\gamma_w^{i'} = \gamma_{i'}^w = 0. \quad (2.127)$$

Furthermore, it can be demonstrated that when one or more of the indices are inactive, the only non-vanishing elements of the two-body RDM are given by [101]

$$\gamma_{k'l'}^{i'j'} = \delta_{i'k'}\delta_{j'l'} - \delta_{i'l'}\delta_{j'k'}, \quad (2.128)$$

$$\gamma_{i'x}^{i'w} = \gamma_{xi'}^{wi'} = \gamma_x^w, \quad (2.129)$$

$$\gamma_{i'x}^{wi'} = \gamma_{wi'}^{i'x} = -\gamma_x^w. \quad (2.130)$$

The relations of Eqs. (2.126)-(2.130) allow any expression, containing the one- and/or two-body RDMs (*e.g.* the CASSCF energy of Eq. (2.120)), to be written in terms of the active part of the corresponding RDM(s) and hence, one only ever needs to calculate the active one- (γ_x^w) and two-body (γ_{yz}^{wx}) RDMs. Note that the eigenvalues n_w , of the one-body density matrix γ_x^w are the (fractional) occupation numbers of the active orbitals and the eigenvectors are the so-called natural orbitals [59, 4].

Let us expand the molecular orbitals in a basis of atomic orbitals,

$$\phi_p(\mathbf{x}) = \sum_{\mu=1}^{N_{\text{AO}}} C_{\mu p} \chi_{\mu}(\mathbf{x}), \quad (2.131)$$

as was done in the case of the Hartree-Fock approximation in section 2.3.1 (*cf.* Eq. (2.57)). The matrix of basis transformation coefficients $\mathbf{C}$, which variationally optimizes the CASSCF energy of Eq. (2.120), can

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be written as a unitary transformation $\mathbf{C} = \mathbf{C}_0 \mathbf{U}$ of the original matrix of orbital coefficients $\mathbf{C}_0$ [100]. The unitary transformation matrix $\mathbf{U}$ can be written as the exponential

$$\mathbf{U} = e^{\boldsymbol{\kappa}} = \mathbf{1} + \boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^2 + \dots, \quad (2.132)$$

of a matrix $\boldsymbol{\kappa}$ which is anti-Hermitian (*i.e.* $\boldsymbol{\kappa}^\dagger = -\boldsymbol{\kappa}$) [100]. Note that this unitary transformation of the orbital coefficients is completely equivalent to the following parametrization of the CASSCF wavefunction,

$$|\Psi'_0\rangle = e^{-\hat{\kappa}} |\Psi_0\rangle = e^{-\hat{\kappa}} \sum_{\alpha} c_{\alpha} |\Phi_{\alpha}\rangle \quad (2.133)$$

in which $|\Psi\rangle$ is the CASSCF wavefunction of Eq. (2.117) and $\hat{\kappa}$ is an anti-Hermitian single excitation operator of the form,

$$\hat{\kappa} = \sum_{p>q} \kappa_{pq} (\hat{e}_q^p - \hat{e}_p^q), \quad (2.134)$$

and κ_{pq} are the elements of the anti-Hermitian matrix $\boldsymbol{\kappa}$ [4]. It is known that variational minimization of the energy functional $E_{\text{CAS}} = \langle \Psi_0 | e^{\hat{\kappa}} \hat{H} e^{-\hat{\kappa}} | \Psi_0 \rangle$ with respect to the κ_{pq} leads to the following variational condition for the CASSCF orbital optimization (*e.g.* see Refs. [4, 99] and references therein),

$$\langle \Psi_0 | \hat{H} (\hat{e}_q^p - \hat{e}_p^q) | \Psi_0 \rangle = 0, \quad (2.135)$$

which is the so-called *generalized-Brillouin theorem* [102, 103].

The CASSCF approximation searches for the simultaneous solutions of Eqs. (2.118) and (2.135), yielding the optimum CASCI coefficients and molecular orbitals, respectively. Various computational approaches have been developed over the years to accomplish this task and a comprehensive discussion of these methods can be found in Refs. [4, 104]. With the current memory and disk space limitations of modern high-performance computers, CASSCF(M_a, N_a) calculations can be performed for wavefunctions (Eq. (2.117)) comprised of $N_{\text{Ref.}} \sim 10^8$ Slater determinants, which corresponds to $M_a \approx 16$ electrons distributed among $n_a = \frac{N_a}{2} \approx 16$ spatial orbitals. From a converged CASSCF calculation, we obtain various quantities which are required for the subsequent treatment of dynamic correlation effects. Namely, the CASSCF method yields the one- and two-body density matrices in the active space, the molecular orbital coefficients $C_{\mu p}$ (which allow transformations of quantities between the molecular and atomic orbital bases), the two-electron integrals in the atomic orbital basis (*i.e.* they can be transformed to the molecular

orbital basis using the coefficients $C_{\mu p}$), the CASSCF Fock matrix

$$f_q^p = h_q^p + \sum_{i'} v_{qi'}^{pi'} + \sum_{w,x} \gamma_x^w v_{qx}^{pw}, \quad (2.136)$$

in the molecular orbital basis and the corresponding orbital energies. The rest of this chapter will be devoted to a discussion of multireference correlation methods, which treat dynamic correlation effects through the inclusion of excitations out of the CASSCF wavefunction.

2.4.3 Multireference Configuration Interaction

The multireference configuration interaction (MRCI) approach [105, 106, 107] is a generalization of the single-reference configuration interaction method of section 2.3.2 for the incorporation of dynamic correlation effects on top of a multi-determinantal zeroth order wavefunction. In practice, one typically only includes up to single and double excitations in the MRCI wavefunction, which defines the so-called MR-CISD methodology. In particular, the MR-CISD approach considers all single and double excitations out of each of the $\alpha = 1, 2, \dots, N_{\text{Ref.}}$ reference determinants $|\Phi_\alpha\rangle$, appearing in the CASSCF wavefunction of Eq. (2.117). Since the MR-CISD formalism finds such common use in the literature, it is often abbreviated simply as MRCI, as it is understood that only single and double excitations are being considered. The MR-CISD wavefunction can be written as

$$|\Psi_{\text{MRCI}}\rangle = \sum_{\alpha} c_{\alpha} |\Phi_{\alpha}\rangle + \sum_{\alpha} \sum_{p,q} c_q^p(\alpha) \hat{e}_q^p |\Phi_{\alpha}\rangle + \frac{1}{4} \sum_{\alpha} \sum_{p,q,r,s} c_{rs}^{pq}(\alpha) \hat{e}_{rs}^{pq} |\Phi_{\alpha}\rangle, \quad (2.137)$$

in which the $c_q^p(\alpha)$ and $c_{rs}^{pq}(\alpha)$ are the coefficients associated with the excitation operators $\hat{e}_q^p$ and $\hat{e}_{rs}^{pq}$, respectively, acting on the reference determinant $|\Phi_{\alpha}\rangle$. The permissible excitation operators $\hat{e}_q^p$ and $\hat{e}_{rs}^{pq}$ appearing in Eq. (2.137) and the corresponding excitation classes are summarized in Table 2.1, where we use h to denote hole (*i.e.* doubly occupied inactive core) orbitals and p to denote particle (*i.e.* unoccupied or virtual) orbitals. These excitation operators are said to span the first-order interacting space, that is, the space that includes all configurations that contribute to the first-order correction to the wavefunction in perturbation theory [108]. Note that there are vanishing configurations (*e.g.* $\hat{e}_x^a |\Phi_{\alpha}\rangle = 0$ if φ_x is not occupied in $|\Phi_{\alpha}\rangle$) and redundant configurations which appear in the wavefunction of Eq. (2.137) [104]. The redundant configurations arise since an excitation in one reference determinant can generate the same configuration as an excitation in another reference determinant. The vanishing and redundant configurations must be eliminated from Eq. (2.137) before proceeding with the MRCI calculation [104].

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The wavefunction of Eq. (2.137), may be written in the familiar form (*cf.* Eqs. (2.69) and (2.117))

$$|\Psi_{\text{MRCI}}\rangle = \sum_I a_I |\Phi_I\rangle, \quad (2.138)$$

in which the label I runs over the reference determinants and all of the non-vanishing and unique singly and doubly excited determinants included in Eq. (2.137). The variational theorem then leads to the following eigenvalue problem for the coefficients a_I and the MRCI energy E_{MRCI} of a given state,

$$\sum_J H_{IJ} a_J = E_{\text{MRCI}} a_I \Rightarrow \mathbf{H}\mathbf{a} = E_{\text{MRCI}}\mathbf{a}. \quad (2.139)$$

It is important to note that the set of coefficients $\{a_I\}$, includes the reference coefficients c_α , in addition to the single ($c_q^p(\alpha)$) and double ($c_{rs}^{pq}(\alpha)$) excitation amplitudes associated with each of the reference determinants. Hence, the reference coefficients c_α are reoptimized (*i.e.* relaxed) in the presence of dynamic correlation effects.

Table 2.1: The allowed excitation operators and corresponding excitation classes which appear in the MR-CISD wavefunction of Eq. (2.137)

Excitation operator	Excitation class
$\hat{e}_{i'}^a$	1p1h
$\hat{e}_w^a$	1p
$\hat{e}_{i'}^w$	1h
$\hat{e}_{i'j'}^{ab}$	2p2h
$\hat{e}_{i'w}^{ab}$	2p1h
$\hat{e}_{i'x}^{wa}$	1p1h
$\hat{e}_{wx}^{ab}$	2p
$\hat{e}_{xy}^{wa}$	1p
$\hat{e}_{i'j'}^{wa}$	1p2h
$\hat{e}_{i'j'}^{wx}$	2h
$\hat{e}_{i'y}^{wx}$	1h
$\hat{e}_{yz}^{wx}$	

Since the MRCI wavefunction of Eq. (2.137) includes all possible single and double excitations out of each of the reference determinants, comprising the CASSCF reference wavefunction, the number of configurations in Eq. (2.137) grows very rapidly with the size of the reference space. This imposes severe limitations on the size of the CASSCF reference spaces which can be used in a subsequent MRCI treatment of dynamic correlation. Alternatively, one can employ a so-called *internally-contracted* ansatz for the MRCI (ic-MRCI) wavefunction $|\Psi_{\text{ic-MRCI}}\rangle$ [109, 110, 111], in which the allowed excitation operators (Table 2.1) act on the entire CASSCF reference wavefunction $|\Phi_0\rangle$ of Eq. (2.117),

$$\begin{aligned} |\Psi_{\text{ic-MRCI}}\rangle &= \tilde{c}_0 |\Phi_0\rangle + \sum_{p,q} \tilde{c}_q^p \hat{e}_q^p |\Phi_0\rangle + \frac{1}{4} \sum_{p,q,r,s} \tilde{c}_{rs}^{pq} \hat{e}_{rs}^{pq} |\Phi_0\rangle \\ &= \sum_{\alpha} \tilde{c}_0 c_{\alpha} |\Phi_{\alpha}\rangle + \sum_{\alpha} \sum_{p,q} c_{\alpha} \tilde{c}_q^p \hat{e}_q^p |\Phi_{\alpha}\rangle + \frac{1}{4} \sum_{\alpha} \sum_{p,q,r,s} c_{\alpha} \tilde{c}_{rs}^{pq} \hat{e}_{rs}^{pq} |\Phi_{\alpha}\rangle. \end{aligned} \quad (2.140)$$

The reference coefficients c_{α} , are constrained to their CASSCF values and therefore, one of the primary disadvantages of this ic-MRCI scheme is that it does not incorporate relaxation effects. Since there is a single set of single ($\tilde{c}_q^p$) and double ($\tilde{c}_{rs}^{pq}$) excitation amplitudes for the entire CASSCF reference wavefunction, the number of coefficients to optimize is commensurate with that in a single reference CISD wavefunction (*c.f.* Eq. (2.74)) [104]. Consequently, the ic-MRCI scheme is significantly less computationally demanding than the uncontracted MRCI approach and much larger CASSCF reference spaces can be considered in ic-MRCI calculations. It is important to note that the ic-MRCI approach is an approximation to uncontracted MRCI. This signifies that the ic-MRCI energy $E_{\text{ic-MRCI}}$, is a variational upper bound to the uncontracted MRCI energy E_{MRCI} , where the difference $\Delta E_{\text{contr.}} = E_{\text{ic-MRCI}} - E_{\text{MRCI}}$, is referred to as the contraction error [104]. Many of the implementations of ic-MRCC are only partially internally-contracted, because some of the excitations are still treated in an uncontracted fashion. For example, in the production level code of Werner and Knowles [112, 113, 114] and the more recent implementation of Shamasundar *et al.* [115], the singles excitations are left uncontracted and only selected double excitations are internally contracted. These partially contracted ic-MRCI approaches also allow for the relaxation of the reference coefficients during the ic-MRCI calculation [115].

The MRCI and ic-MRCI methods suffer from the same deficiency as single-reference CI, in that they are not size-consistent or size-extensive. However, over the years there has not yet been any consensus on a multireference CC ansatz that inherits all of the desirable properties of single-reference CC methods and therefore, MRCI and related methods are still widely applied to problems in computational chemistry [116]. One commonly used correction for the size-extensivity/consistency error is the multireference generalization

[98] of the Davidson Q correction [97] to the MRCI energy E_{MRCI} ,

$$\Delta E_{\text{Davidson}} = \left(1 - \sum_{\alpha=1}^{N_{\text{Ref.}}} c_{\alpha} \right) (E_{\text{MRCI}} - E_{\text{CAS}}) \quad (2.141)$$

in which the c_{α} are the reference coefficients and E_{CAS} is the CASSCF reference energy. This is an *a posteriori* correction to the MRCI energy which attempts to estimate the contribution of unlinked quadruples (*i.e.* $\frac{1}{2}\hat{T}_2^2$) to the energy. The resulting MRCI+Q and ic-MRCI+Q approaches have been applied to many interesting problems in the literature and the uncontracted MRCI+Q approach is often used as a benchmark for the calculation of potential energy surfaces (*e.g.* see Ref. [104] for an overview). Other *a posteriori* corrections to the MRCI energy also exist and the interested reader is referred to Ref. [104] for a detailed discussion. Alternatively, the MRCI (ic-MRCI) energy functional can be modified to estimate the effects of unlinked higher excitations to the energy in an *a priori* fashion (*i.e.* before optimization). These approaches can be viewed as multireference generalizations of the single-reference Coupled Electron Pair Approximations (CEPA) [117, 118, 119, 120, 121, 122] and are generally preferred over using *a posteriori* corrections, like the Davidson correction. Arguably, the most popular of these methods are the MR-ACPF (Averaged Coupled-Pair Functional) [123, 124] and MR-AQCC (Averaged Quadratic Coupled-Cluster) [125, 126] approaches [104]. Many of the interesting applications of MR-ACPF and MR-AQCC are reviewed in Ref. [104]. In the following section we briefly review the details of various multireference coupled-cluster schemes and discuss their advantages and disadvantages.

2.4.4 Multireference Coupled-Cluster Theory based on the Jeziorski-Monkhorst Ansatz

The Jeziorski-Monkhorst (JM) ansatz [41] provides a natural generalization of the single-reference coupled-cluster formalism of section 2.3.3 to the case of a multi-determinantal zeroth order wavefunction (*e.g.* CASSCF). The JM ansatz for the multireference Coupled-Cluster (MRCC) wavefunction of the m^{th} electronic state is given by

$$|\Psi_m\rangle = \hat{\Omega} |\Psi_0^m\rangle = \sum_{\alpha=1}^{N_{\text{Ref.}}} c_{\alpha}^m e^{\hat{T}_{\alpha}} |\Phi_{\alpha}\rangle, \quad (2.142)$$

in which

$$|\Psi_0^m\rangle = \sum_{\alpha=1}^{N_{\text{Ref.}}} c_{\alpha}^m |\Phi_{\alpha}\rangle, \quad (2.143)$$

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is the reference wavefunction for the m^{th} electronic state, $\hat{T}_\alpha$ is the cluster operator,

$$\hat{T}_\alpha = \hat{T}_1^\alpha + \hat{T}_2^\alpha + \dots = \sum_{i,a} t_i^a(\alpha) \hat{e}_i^a + \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab}(\alpha) \hat{e}_{ij}^{ab} + \dots, \quad (2.144)$$

for the α^{th} reference determinant and the wave operator $\hat{\Omega}$ is defined as

$$\hat{\Omega} = \sum_{\alpha=1}^{N_{\text{Ref.}}} e^{\hat{T}_\alpha} |\Phi_\alpha\rangle \langle \Phi_\alpha|. \quad (2.145)$$

Here, the labels $i, j, k, l, \dots$ run over the occupied orbitals in the reference determinant $|\Phi_\alpha\rangle$ and $a, b, c, d, \dots$ run over the virtual orbitals in said determinant. Moreover, the summations in Eq. (2.144) exclude any (internal) excitations that generate another determinant in the reference (model) space [61, 2, 41, 20]. For the sake of simplicity, we will assume that we are dealing with a complete model space obtained from a CASSCF calculation. Other model spaces are often employed due to the prohibitive computational costs associated with the use of a complete model space. We refer the interested reader to the recent review of Lyakh and coworkers [20] and references therein for more details on these alternative model spaces.

Let us define a projection operator $\hat{P}$, onto the reference space,

$$\hat{P} = \sum_{\alpha=1}^{N_{\text{Ref.}}} |\Phi_\alpha\rangle \langle \Phi_\alpha| = \sum_{\alpha=1}^{N_{\text{Ref.}}} \hat{P}_\alpha, \quad (2.146)$$

and a projection operator $\hat{Q}$, onto the orthogonal complimentary (external) space,

$$\hat{Q} = 1 - \hat{P} = \sum_{\mathcal{I}} |\Phi_{\mathcal{I}}\rangle \langle \Phi_{\mathcal{I}}|, \quad (2.147)$$

in which the index $\mathcal{I}$ runs over all of the determinants $|\Phi_i^a(\alpha)\rangle$, $|\Phi_{ij}^{ab}(\alpha)\rangle$, $|\Phi_{ijk}^{abc}(\alpha)\rangle$, *etc.* which are generated by excitations out of the $\alpha = 1, 2, \dots, N_{\text{Ref.}}$ reference determinants [61, 2, 41, 20]. It is typical to work in intermediate normalization,

$$\langle \Psi_0^m | \Psi_m \rangle = \langle \Psi_0^m | \hat{\Omega} | \Phi_0^m \rangle = 1, \quad (2.148)$$

such that [2, 41, 20]

$$\hat{P}\hat{\Omega} = \hat{P}. \quad (2.149)$$

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Furthermore, it can be shown that the wave-operator of Eq. (2.145) satisfies the following relations [41, 20],

$$\hat{\Omega}\hat{P} = \hat{\Omega}, \quad (2.150)$$

$$\hat{\Omega}^2 = \hat{\Omega}. \quad (2.151)$$

One can then define an effective Hamiltonian,

$$\hat{H}_{\text{eff.}} = \hat{P}\hat{H}\hat{\Omega}\hat{P}, \quad (2.152)$$

that satisfies the generalized Bloch equation [127, 128, 129, 130],

$$\hat{H}\hat{\Omega}\hat{P} = \hat{\Omega}\hat{H}_{\text{eff.}}\hat{P}, \quad (2.153)$$

and the following eigenvalue problem (*i.e.* Schrödinger equation for the effective Hamiltonian),

$$\hat{H}_{\text{eff.}} |\Psi_0^{\mathbf{m}}\rangle = E_{\mathbf{m}} |\Psi_0^{\mathbf{m}}\rangle \quad (2.154)$$

for the energy $E_{\mathbf{m}}$ of a given electronic state $\mathbf{m}$ (*i.e.* $\mathbf{m} \leq N_{\text{Ref.}}$), with wavefunction $|\Psi_{\mathbf{m}}\rangle = \hat{\Omega} |\Psi_0^{\mathbf{m}}\rangle$ [61, 2, 41, 20]. If we let $H_{\beta\alpha}^{\text{eff.}}$ denote the matrix elements of $\hat{H}_{\text{eff.}}$,

$$H_{\beta\alpha}^{\text{eff.}} \equiv \langle \Phi_{\beta} | \hat{H}_{\text{eff.}} | \Phi_{\alpha} \rangle = \langle \Phi_{\beta} | \hat{H} e^{\hat{T}_{\alpha}} | \Phi_{\alpha} \rangle, \quad (2.155)$$

substitute the definition of Eq. (2.143) for $|\Psi_0^{\mathbf{m}}\rangle$ in Eq. (2.154) and project the resulting equation onto a given reference determinant $|\Phi_{\beta}\rangle$, we obtain the following matrix eigenvalue problem,

$$\sum_{\alpha=1}^{N_{\text{Ref.}}} H_{\beta\alpha}^{\text{eff.}} c_{\alpha}^{\mathbf{m}} = E_{\mathbf{m}} c_{\beta}^{\mathbf{m}} \Rightarrow \mathbf{H}_{\text{eff.}} \mathbf{c}_{\mathbf{m}} = E_{\mathbf{m}} \mathbf{c}_{\mathbf{m}}, \quad (2.156)$$

for the vector $\mathbf{c}_{\mathbf{m}}$ of (relaxed) reference coefficients and energy $E_{\mathbf{m}}$ for each of the states $\mathbf{m} = 1, 2, \dots, N_{\text{Ref.}}$.

In the State-Universal MRCC (SU-MRCC) approach, initially proposed by Jeziorski and Monkhorst [41], the equations for the cluster amplitudes ($t_i^a(\alpha)$, $t_{ij}^{ab}(\alpha)$, *etc.*) are obtained directly from the Bloch equation of Eq. (2.153). Inserting the definition of Eq. (2.145), for the wave operator, into Eq. (2.153), we obtain,

$$\sum_{\beta=1}^{N_{\text{Ref.}}} \hat{H} e^{\hat{T}_{\beta}} \hat{P}_{\beta} = \sum_{\beta=1}^{N_{\text{Ref.}}} e^{\hat{T}_{\beta}} \hat{P}_{\beta} \hat{H}_{\text{eff.}} \hat{P}. \quad (2.157)$$

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Multiplying on the left by $e^{-\hat{T}_\alpha}$ and on the right by $\hat{P}_\alpha = |\Phi_\alpha\rangle\langle\Phi_\alpha|$ yields the expression,

$$e^{-\hat{T}_\alpha} \hat{H} e^{\hat{T}_\alpha} \hat{P}_\alpha = \sum_{\beta=1}^{N_{\text{Ref.}}} e^{-\hat{T}_\alpha} e^{\hat{T}_\beta} \hat{P}_\beta \hat{H}_{\text{eff.}} \hat{P}_\alpha, \quad (2.158)$$

and finally letting $\hat{H}_\alpha \equiv e^{-\hat{T}_\alpha} \hat{H} e^{\hat{T}_\alpha}$ and projecting on the right by the reference determinant $|\Phi_\alpha\rangle$ and on the left by a given excited determinant $|\Phi_{ij\dots}^{ab\dots}(\alpha)\rangle$, we obtain the residual equation,

$$\langle\Phi_{ij\dots}^{ab\dots}(\alpha)|\hat{H}_\alpha|\Phi_\alpha\rangle = \sum_{\beta=1}^{N_{\text{Ref.}}} \langle\Phi_{ij\dots}^{ab\dots}(\alpha)|e^{-\hat{T}_\alpha} e^{\hat{T}_\beta} |\Phi_\beta\rangle H_{\beta\alpha}^{\text{eff.}}, \quad (2.159)$$

which determines the amplitudes $t_{ij\dots}^{ab\dots}(\alpha)$ [61, 2, 41, 20].

Due to the presence of the so-called “coupling term” on the r.h.s. of Eq. (2.159), the amplitudes associated with the α^{th} reference determinant are dependent on the values of the excitation amplitudes corresponding to the other reference determinants (*i.e.* they are coupled). Hence, for each of the $\alpha = 1, 2, \dots, N_{\text{Ref.}}$ model functions, the corresponding amplitudes are iteratively solved from Eq. (2.159), using the current values of the amplitudes associated with all the other reference determinants on the r.h.s. and the procedure is continued until a self-consistent solution is reached [61]. The final amplitudes thus obtained are then employed to calculate the effective Hamiltonian, which is then diagonalized to determine the energies and reference coefficients for the $\mathbf{m} = 1, 2, \dots, N_{\text{Ref.}}$ electronic states (*i.e.* see Eq. (2.156)). The newly determined matrix elements of the effective Hamiltonian are then used to solve Eq. (2.159) for a new set of amplitudes and the entire two-step procedure is repeated until convergence is attained. It is important to note that the SU-MRCC approach must involve the simultaneous solution of the same number of electronic states as there are reference determinants in the reference wavefunction (*i.e.* $N_{\text{Ref.}}$ states) [41, 20]. Otherwise, the residual equation of Eq. (2.159) is underdetermined, as the number of amplitudes exceeds the number of equations. As explained in detail in Ref. [20], this is a result of the inherent redundancy of the JM ansatz of Eq. (2.142). For example, a given operator $\hat{T}_m^\alpha$ acting on the reference determinant $|\Phi_\alpha\rangle$ can generate the same excited configuration as another operator $\hat{T}_n^\beta$ acting on $|\Phi_\beta\rangle$.

The use of a CAS and intermediate normalization (Eq. (2.148)) ensure that the SU-MRCC approach is size-extensive [20]. However, it is well known that this approach suffers from the so-called intruder-state problem, especially when larger active spaces are employed. Intruder-states are electronic states belonging to the external space (*i.e.* dominant character from excited configurations) whose zeroth-order energy eigenvalues are nearly degenerate with those of states belonging to the (reference) model space

(see Refs. [131, 132, 133, 134, 135, 20] and references therein for a detailed discussion of the intruder-state problem). The intruder-state problem is a serious issue as it wreaks havoc on the convergence of the iterations of the SU-MRCC equations, producing severely divergent behaviour. In order to avoid the intruder-state problem, SU-MRCC approaches based on a general model space (GMS) can be employed. As the name suggests, the GMS is more general than a complete model space as it can be incomplete or complete depending on the system considered. With the use of any incomplete model space, special care is needed as internal excitations no longer rigourously vanish. This results in the presence of disconnected contributions in the SU-MRCC equations and thus, destroys the size-extensivity of the approach [61, 20]. One GMS based SU-MRCC methodology, developed by Mukherjee and coworkers [136, 137, 136] and Meissner and coworkers [138, 139], manages to preserve rigourous size-extensivity by disposing of the intermediate normalization condition. The more recent GMS based SU-MRCC method of Paldus and coworkers [140, 141, 142] takes a different approach in restoring approximate size-extensivity by introducing the so-called C-conditions (or connectivity conditions). However, as discussed by Nooijen *et al.* [80], there are still disconnected contributions which enter the equations, even after imposing the C-conditions. Hence, this approach is not rigourously size-extensive, but it is size-consistent [80] and core-extensive [20].

Alternatively, one can avoid the intruder state problem, inherent in the SU-MRCC method, by adopting a state-specific formalism of the MRCC approach, based on the JM ansatz of Eq. (2.142). Rather than treating all $\mathbf{m} = 1, 2, \dots, N_{\text{Ref.}}$ states in a single calculation, these state-specific methods only consider a single electronic state in a given calculation. As mentioned previously, if one does not consider the calculation of all of the $N_{\text{Ref.}}$ states simultaneously, the amplitude equations of Eq. (2.159) constitute an underdetermined system of equations, due to the redundancy of the JM ansatz. Hence, one must impose sufficiency conditions to eliminate the redundancies in the external space and obtain a well-defined system of amplitude equations, in which the number of equations is equal to the number of unknown amplitudes. There are various possibilities for the choice of sufficiency conditions (*i.e.* not unique) and different choices give rise to different state-selective MRCC methods such as the Brillouin-Wigner MRCC (BW-MRCC) method [42, 43, 44, 45] and Mukherjee's MRCC (Mk-MRCC) approach [46, 47, 48]. An alternative scheme is the MRexpT method of Hanrath [143, 144], which establishes additional constraints on the amplitudes, such that redundant excitations are removed from the JM ansatz and a proper residual equation can be defined, without resorting to the invocation of sufficiency conditions.

Let us briefly discuss the details of the BW-MRCC and Mk-MRCC methods and outline the advantages and disadvantages associated with each approach. Inserting the JM ansatz of Eq. (2.142) into the Schrödinger equation for a given electronic state $\mathbf{m}$,

$$\hat{H} |\Psi_{\mathbf{m}}\rangle = E_{\mathbf{m}} |\Psi_{\mathbf{m}}\rangle, \quad (2.160)$$

and rearranging, yields the expression,

$$\sum_{\alpha=1}^{N_{\text{Ref}}} \left(\hat{H} e^{\hat{T}_\alpha} |\Phi_\alpha\rangle c_\alpha^{\text{m}} - E_{\text{m}} e^{\hat{T}_\alpha} |\Phi_\alpha\rangle c_\alpha^{\text{m}} \right) = 0. \quad (2.161)$$

In order to derive the BW-MRCC residual equation for the excitation amplitudes $t_{ij\dots}^{ab\dots}(\alpha)$, we project on the left by the excited determinants $|\Phi_{ij\dots}^{ab\dots}(\alpha)\rangle$ to obtain,

$$\sum_{\alpha=1}^{N_{\text{Ref}}} \left(\langle \Phi_{ij\dots}^{ab\dots}(\alpha) | \hat{H} e^{\hat{T}_\alpha} |\Phi_\alpha\rangle c_\alpha^{\text{m}} - \langle \Phi_{ij\dots}^{ab\dots}(\alpha) | e^{\hat{T}_\alpha} |\Phi_\alpha\rangle E_{\text{m}} c_\alpha^{\text{m}} \right) = 0. \quad (2.162)$$

In analogy with Eq. (2.159), in the state-specific case, this constitutes an underdetermined system of equations for the amplitudes due to the redundancy of the JM ansatz. Hence, we note that a sufficient condition for the satisfaction of Eq. (2.162) is that the summand vanishes for each of the $\alpha = 1, 2, \dots, N_{\text{Ref}}$ reference determinants. Applying this sufficiency condition yields the BW-MRCC amplitude equations [42, 43, 44, 45],

$$\langle \Phi_{ij\dots}^{ab\dots}(\alpha) | \hat{H} e^{\hat{T}_\alpha} |\Phi_\alpha\rangle = E_{\text{m}} \langle \Phi_{ij\dots}^{ab\dots}(\alpha) | e^{\hat{T}_\alpha} |\Phi_\alpha\rangle \quad \forall \alpha, \quad (2.163)$$

for the amplitudes $t_{ij\dots}^{ab\dots}(\alpha)$.

One advantage of the BW-MRCC method is the relative simplicity of these amplitude equations, as they are formally quite similar to those which arise in single-reference CC theory. However, due to the presence of disconnected contributions on both sides of Eq. (2.163), the BW-MRCC method is not size-extensive and this constitutes a major drawback of this approach [61, 20]. Corrections for size-extensivity can be included in an *a-posteriori* fashion [145, 146] or during the iteration of the amplitude equations [147]. Even so, the fact that the BW-MRCC approach is not manifestly size-extensive makes it much less attractive than state-specific MRCC methods which are size-extensive (*e.g.* Mk-MRCC).

In order to derive the amplitude equations for the Mk-MRCC method, we start from Eq. (2.161) and introduce the resolution of the identity,

$$1 = e^{-\hat{T}_\alpha} e^{\hat{T}_\alpha} = e^{-\hat{T}_\alpha} (\hat{P} + \hat{Q}) e^{\hat{T}_\alpha}, \quad (2.164)$$

in the first term to obtain,

$$\sum_{\alpha,\beta} e^{\hat{T}_\alpha} |\Phi_\beta\rangle H_{\beta\alpha}^{\text{eff.}} c_\alpha^{\text{m}} + \sum_{\alpha} e^{\hat{T}_\alpha} \hat{Q} \hat{H}_\alpha |\Phi_\alpha\rangle c_\alpha^{\text{m}} - \sum_{\alpha} E_{\text{m}} e^{\hat{T}_\alpha} |\Phi_\alpha\rangle c_\alpha^{\text{m}} = 0, \quad (2.165)$$

where we have used the relation $H_{\beta\alpha}^{\text{eff.}} = \langle \Phi_\beta | \hat{H} e^{\hat{T}_\alpha} | \Phi_\alpha \rangle$ and the definition of $\hat{P}$ in Eq. (2.146). By interchanging the dummy summation labels α and β in the first term of Eq. (2.165), multiplying on the left by $e^{-\hat{T}_\alpha}$ and projecting onto the left by the excited determinants $|\Phi_{ij\cdots}^{ab\cdots}(\alpha)\rangle$, we can rewrite this equation as

$$\sum_{\alpha} \left[\sum_{\beta} \langle \Phi_{ij\cdots}^{ab\cdots}(\alpha) | e^{-\hat{T}_\alpha} e^{\hat{T}_\beta} | \Phi_\alpha \rangle H_{\alpha\beta}^{\text{eff.}} c_{\beta}^{\text{m}} + \langle \Phi_{ij\cdots}^{ab\cdots}(\alpha) | \hat{H}_\alpha | \Phi_\alpha \rangle c_{\alpha}^{\text{m}} \right] = 0. \quad (2.166)$$

Once again, in the state-specific case, this constitutes an underdetermined system of equations. The sufficiency condition, which leads to a well-defined set of amplitude equations, is to set the summand within brackets to zero for each value of α [46]. This then yields the following residual equations,

$$\sum_{\beta \neq \alpha} \langle \Phi_{ij\cdots}^{ab\cdots}(\alpha) | e^{-\hat{T}_\alpha} e^{\hat{T}_\beta} | \Phi_\alpha \rangle H_{\alpha\beta}^{\text{eff.}} c_{\beta}^{\text{m}} + \langle \Phi_{ij\cdots}^{ab\cdots}(\alpha) | \hat{H}_\alpha | \Phi_\alpha \rangle c_{\alpha}^{\text{m}} = 0 \quad \forall \alpha \quad (2.167)$$

for the amplitudes $t_{ij\cdots}^{ab\cdots}(\alpha)$.

These amplitude equations only contain connected terms and therefore, the Mk-MRCC approach is rigorously size-extensive [46, 47]. Another advantage of Mk-MRCC is that it can be implemented as a relatively straightforward modification of any available single-reference CC implementation. The fact that it is size-extensive and relatively easy to implement have certainly contributed to the fact that Mk-MRCC has become the preferred state-selective MRCC scheme, in recent years. A major drawback of Mk-MRCC and any other approach based on the JM ansatz, is that they are not orbital invariant. This signifies that results from these calculations can vary depending on the choice of orbitals and this is evidently an undesirable feature of these methods. Another deficiency of these approaches is that for every sector $|\Phi_\alpha\rangle$, of the model space, a different projection manifold ($\langle \Phi_{ijk\cdots}^{abc\cdots} |$) is employed. Only in the MRexpT approach of Hanrath [143, 144], is a common projection manifold used, such that

$$\langle \Phi_{\mathcal{I}} | (\hat{H} - E) | \Phi_0 \rangle = 0, \quad (2.168)$$

for all the functions $|\Phi_{\mathcal{I}}\rangle$, comprising the external space. Furthermore, for all the JM based MRCC methods, the computational cost scales factorially with the size of the active space, such that calculations become prohibitive for larger active spaces. This can be partially remedied by employing the so-called anonymous parentage approximation in which excitations operators which involve inactive excitations (*e.g.* $h \rightarrow p$, $2h \rightarrow 2p$, *etc.*) are treated in an internally-contracted fashion (*i.e.* makes use of an ansatz of the form $|\Psi_{\text{m}}\rangle = e^{\hat{T}} \sum_{\alpha=1}^{N_{\text{Ref.}}} c_{\alpha}^{\text{m}} e^{\hat{T}_{\alpha}} | \Phi_{\alpha} \rangle$ in which the single (internally contracted) $\hat{T}$ operator generates purely inactive excitations and the $\hat{T}_{\alpha}$ include all other excitations out of each reference determinant)

[148, 149, 150]. In the following section, we will describe approaches which do not invoke the JM ansatz for the wavefunction and treat the excitations in an internally-contracted fashion.

2.4.5 Internally-Contracted Multireference Coupled-Cluster Approaches

2.4.5.1 A Brief Overview of Kutzelnigg-Mukherjee Normal-Ordering

Since the methodologies discussed below (*i.e.* ic-MRCC [49, 50, 51] and canonical transformation (CT) theory [53, 54, 55, 56, 57, 58]) as well as MR-EOM [21, 22, 23], make use of the concept of Kutzelnigg-Mukherjee (KM) normal ordering [151, 152, 153], in one way or another, it is useful to give a brief introduction to the details underlying this concept. Mukherjee and Kutzelnigg [151, 152, 153] have described a generalization of normal ordering and Wick's theorem (see section 2.2.2) with respect to an arbitrary multi-configurational wavefunction $|\Phi_0\rangle$. In this generalized normal ordering formalism, the corresponding Wick's theorem gives rise to n -body contractions (*i.e.* involving n pairs of creation and annihilation operators for $n \geq 2$) and these n -body contractions evaluate to n -body cumulants of the reduced density matrices (RDMs). This is in contrast to the single-reference case of section 2.2.2, where only one-body contractions are permissible and evaluate to Kronecker deltas.

As usual, we let $\hat{e}_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n}$ denote a general product consisting of n creation operators $\hat{a}_{p_1}^\dagger, \hat{a}_{p_2}^\dagger, \dots, \hat{a}_{p_n}^\dagger$ and n annihilation operators $\hat{a}_{q_1}, \hat{a}_{q_2}, \dots, \hat{a}_{q_n}$, and we let $\tilde{e}_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n}$ denote the corresponding normal ordered product with respect to a multi-configurational reference wavefunction $|\Phi_0\rangle$. We define the reduced density matrices (RDMs) as

$$\gamma_{q_1}^{p_1} = \langle \Phi_0 | \hat{e}_{q_1}^{p_1} | \Phi_0 \rangle, \quad (2.169)$$

$$\gamma_{q_1 q_2}^{p_1 p_2} = \langle \Phi_0 | \hat{e}_{q_1 q_2}^{p_1 p_2} | \Phi_0 \rangle, \quad (2.170)$$

$$\vdots$$

$$\gamma_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n} = \langle \Phi_0 | \hat{e}_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n} | \Phi_0 \rangle. \quad (2.171)$$

and the corresponding cumulants (see Refs. [154, 155, 156, 157, 101, 158, 159, 160, 161, 162, 163, 164, 165, 166] and references therein) are obtained as,

$$\lambda_{q_1}^{p_1} = \gamma_{q_1}^{p_1}, \quad (2.172)$$

$$\lambda_{q_1 q_2}^{p_1 p_2} = \gamma_{q_1 q_2}^{p_1 p_2} - (\lambda_{q_1}^{p_1} \lambda_{q_2}^{p_2} - \lambda_{q_2}^{p_1} \lambda_{q_1}^{p_2}) = \gamma_{q_1 q_2}^{p_1 p_2} - \mathcal{A}(\lambda_{q_1}^{p_1} \lambda_{q_2}^{p_2}), \quad (2.173)$$

$$\lambda_{q_1 q_2 q_3}^{p_1 p_2 p_3} = \gamma_{q_1 q_2 q_3}^{p_1 p_2 p_3} - \mathcal{A}(\lambda_{q_1}^{p_1} \lambda_{q_2}^{p_2} \lambda_{q_3}^{p_3}) - \mathcal{A}(\lambda_{q_1}^{p_1} \lambda_{q_2 q_3}^{p_2 p_3}), \quad (2.174)$$

⋮

Here the operator $\mathcal{A}$ is the so-called antisymmetrizer, which can be formally defined for any quantity $X_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n}$, representing a single tensor or a product of tensors (*e.g.* $X_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n} = B_{q_1 q_2 \dots}^{p_1 p_2 \dots} C_{q_k \dots q_n}^{p_k \dots p_n}$), (*e.g.* see Ref. [32]),

$$\mathcal{A}X_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n} = \frac{1}{\mathcal{F}_{\text{sym.}}} \sum_{\substack{u_1 u_2 \dots u_n \in \text{permutations} \\ \text{of } p_1 p_2 \dots p_n}} \sum_{\substack{v_1 v_2 \dots v_n \in \text{permutations} \\ \text{of } q_1 q_2 \dots q_n}} (-1)^{\mathcal{P}} X_{v_1 v_2 \dots v_n}^{u_1 u_2 \dots u_n}, \quad (2.175)$$

in which the first sum runs over all possible permutations of the sequence $p_1 p_2 \dots p_n$ of the upper indices and the second sum runs over all possible permutations of the sequence $q_1 q_2 \dots q_n$ of the lower indices. In this expression, $X_{v_1 v_2 \dots v_n}^{u_1 u_2 \dots u_n} = \hat{P}_{p_1 p_2 \dots p_n}^{u_1 u_2 \dots u_n} \hat{P}_{q_1 q_2 \dots q_n}^{v_1 v_2 \dots v_n} X_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n}$, where $\hat{P}_{p_1 p_2 \dots p_n}^{u_1 u_2 \dots u_n}$ is a permutation operator which permutes the original sequence of upper labels $p_1 p_2 \dots p_n$ to the sequence $u_1 u_2 \dots u_n$ and $\hat{P}_{q_1 q_2 \dots q_n}^{v_1 v_2 \dots v_n}$ permutes the sequence of lower labels $q_1 q_2 \dots q_n$ to $v_1 v_2 \dots v_n$. The quantity $\mathcal{P}$ is the parity of the permutation and it is equal to the number of transpositions of indices in $X_{v_1 v_2 \dots v_n}^{u_1 u_2 \dots u_n}$, that are required to achieve the same upper-lower index pairing as in the original quantity $X_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n}$ (*i.e.* p_1 above q_1 , p_2 above q_2 and so on) [32]. Furthermore, we note that terms related by antisymmetry are redundant and that certain permutations in products of tensors of the same type generate duplicates (*e.g.* $\lambda_q^p \lambda_s^r = \lambda_s^r \lambda_q^p$). The factor $\mathcal{F}_{\text{sym.}}$ therefore, ensures that redundant contributions appear with a factor of unity in the final expression.

In analogy with Eq. (2.30), Wick's theorem allows us to write a string of elementary second quantized operators ($\hat{c}_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n} = \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \dots \hat{a}_{p_n}^\dagger \hat{a}_{q_n} \dots \hat{a}_{q_2} \hat{a}_{q_1}$) as the sum of the normal ordered product $\hat{c}_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n} = \{\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \dots \hat{a}_{p_n}^\dagger \hat{a}_{q_n} \dots \hat{a}_{q_2} \hat{a}_{q_1}\}$ and all possible normal ordered products with contractions. We also recall that there is no longer a restriction to binary (one-body) contractions, as n -body contractions are permitted and evaluate to n -body cumulants (for $n \geq 2$). Application of Wick's theorem to the string $\hat{c}_{q_1 q_2 \dots q_n}^{p_1 p_2 \dots p_n}$ then yields,

$$\begin{aligned} \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \dots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1} &= \{\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \dots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1}\} + \underbrace{\{\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \dots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1}\}}_{\text{all single one-body contractions}} + \dots \\ &+ \underbrace{\{\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \dots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1}\}}_{\text{all two-fold one-body contractions}} + \dots + \underbrace{\{\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \dots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1}\}}_{\text{all three-fold one-body contractions}} + \dots + \dots \\ &+ \underbrace{\{\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \dots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1}\}}_{\text{all single two-body contractions}} + \dots + \underbrace{\{\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \dots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1}\}}_{\text{all single two-body contractions and single one-body contractions}} + \dots + \dots \end{aligned}$$

$$+ \underbrace{\left\{ \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \cdots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1} \right\}}_{\text{all single three-body contractions}} + \dots + \dots, \quad (2.176)$$

or more compactly, we can write this as

$$\hat{e}_{q_1 q_2 \cdots q_n}^{p_1 p_2 \cdots p_n} = \tilde{e}_{q_1 q_2 \cdots q_n}^{p_1 p_2 \cdots p_n} + \sum_{\substack{\text{all possible contractions} \\ \text{(including 1-, 2-, \dots, n-body} \\ \text{contractions)}}} \left\{ \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \cdots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1} \right\}. \quad (2.177)$$

It is also important to note that the reference (vacuum) expectation value of any normal ordered operator vanishes,

$$\langle \Phi_0 | \tilde{e}_{q_1 q_2 \cdots q_n}^{p_1 p_2 \cdots p_n} | \Phi_0 \rangle = 0, \quad (2.178)$$

if the λ 's are taken as cumulants of the reduced density matrices, but that other choices are possible as suggested in Ref. [167]. The fact that Eq. (2.178) is satisfied also further implies that the vacuum expectation value of any string $\hat{e}_{q_1 q_2 \cdots q_n}^{p_1 p_2 \cdots p_n}$, of creation and annihilation operators, must be equal to the sum of the fully contracted normal ordered products (*cf.* Eq. (2.31)),

$$\langle \Phi_0 | \hat{e}_{q_1 q_2 \cdots q_n}^{p_1 p_2 \cdots p_n} | \Phi_0 \rangle = \sum_{\text{fully contracted}} \left\{ \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \cdots \hat{a}_{q_3} \hat{a}_{q_2} \hat{a}_{q_1} \right\} \quad (2.179)$$

Let us proceed to determine the contraction rules for the one- and two-body contractions. From Eq. (2.179), one can see that the contraction $\overline{\hat{a}_p^\dagger \hat{a}_q}$ is equal to the vacuum expectation value of $\hat{e}_q^p$, which is the definition of the one-body RDM in Eq. (2.169) or equivalently the one-body cumulant of Eq. (2.172), that is,

$$\overline{\hat{a}_p^\dagger \hat{a}_q} = \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q | \Phi_0 \rangle = \gamma_q^p = \lambda_q^p. \quad (2.180)$$

Similarly, with the use of the anticommutation relation of Eq. (2.16), we have that

$$\overline{\hat{a}_q \hat{a}_p^\dagger} = \langle \Phi_0 | \hat{a}_q \hat{a}_p^\dagger | \Phi_0 \rangle = \langle \Phi_0 | (\delta_q^p - \hat{a}_p^\dagger \hat{a}_q) | \Phi_0 \rangle = \delta_q^p - \gamma_q^p = \eta_q^p, \quad (2.181)$$

in which η_q^p is the so-called hole density. In order to derive an expression for the two-body contraction $\overline{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r}$, we take the vacuum expectation value of the operator string $\hat{e}_{r s}^{p q} = \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$ and apply Eq. (2.179) (*i.e.* retaining only the fully contracted terms) to obtain,

$$\langle \Phi_0 | \hat{e}_{r s}^{p q} | \Phi_0 \rangle = \left\{ \overline{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r} \right\} + \left\{ \overline{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r} \right\} + \left\{ \overline{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r} \right\} \quad (2.182)$$

$$= -\overbrace{\hat{a}_p^\dagger \hat{a}_s \hat{a}_q^\dagger \hat{a}_r} + \overbrace{\hat{a}_p^\dagger \hat{a}_r \hat{a}_q^\dagger \hat{a}_s} + \overbrace{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r} \quad (2.183)$$

$$= -\lambda_s^p \lambda_r^q + \lambda_r^p \lambda_s^p + \overbrace{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r}, \quad (2.184)$$

where in the last line, we employed the definition of the one-body contraction given in Eq. (2.180). Noting that the vacuum expectation value of $\hat{e}_{rs}^{pq}$ is the definition of the two-body RDM γ_{rs}^{pq} in Eq. (2.170) and solving for the two-body contraction, we obtain,

$$\overbrace{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r} = \gamma_{rs}^{pq} - \lambda_r^p \lambda_s^p + \lambda_s^p \lambda_r^q = \lambda_{rs}^{pq}, \quad (2.185)$$

where the final equality follows from the definition of the two-body cumulant in Eq. (2.173). In general, the n -body contractions, for $n \geq 2$, are equal to the corresponding elements of the n -body cumulant [153].

Some simple examples of the application of the Wick theorem of Eq. (2.177) are given by [167]

$$\tilde{e}_q^p = \hat{e}_q^p - \lambda_q^p, \quad (2.186)$$

$$\tilde{e}_{rs}^{pq} = \hat{e}_{rs}^{pq} - \mathcal{A}(\lambda_r^p \tilde{e}_s^q) - \mathcal{A}(\lambda_r^p \lambda_s^q) - \lambda_{rs}^{pq}, \quad (2.187)$$

$$\tilde{e}_{stu}^{pqr} = \hat{e}_{stu}^{pqr} - \mathcal{A}(\lambda_s^p \tilde{e}_{tu}^{qr}) - \mathcal{A}(\lambda_s^p \lambda_t^q \tilde{e}_u^r) - \mathcal{A}(\lambda_{st}^{pq} \tilde{e}_u^r) - \mathcal{A}(\lambda_s^p \lambda_t^q \lambda_u^r) - \mathcal{A}(\lambda_s^p \lambda_{tu}^{qr}) - \lambda_{stu}^{pqr}, \quad (2.188)$$

$\vdots$

A rigorous algebraic proof of the generalized Wick's theorem (GWT), within the framework of KM normal ordering, is provided in Ref. [167]. In analogy with the single-reference case (see Eq. (2.32)), this gives a prescription for evaluating the product of two (or more) normal ordered products of elementary second quantized operators. For example, for the simplest case of the product $\tilde{e}_r^p \tilde{e}_s^q$, simple application of the GWT yields the following expression [153, 167],

$$\tilde{e}_r^p \tilde{e}_s^q = \tilde{e}_{rs}^{pq} + \eta_r^q \tilde{e}_s^p - \lambda_s^p \tilde{e}_r^q - \lambda_s^p \eta_r^q + \lambda_{rs}^{pq}. \quad (2.189)$$

We refer the interested reader to Refs. [153, 167] for more information regarding the GWT in KM normal order theory.

2.4.5.2 ic-MRCC: Internally-Contracted Multireference Coupled-Cluster Theory

In recent years, there has been considerable interest in the development of internally-contracted multireference coupled-cluster methods. One particularly attractive scheme is the ic-MRCC theory developed by Evangelista and Gauss [49] and Hanauer and Köhn [50, 51, 52], which builds upon the early work

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of Banerjee and Simons [168, 169, 170, 171]. The ansatz for the ic-MRCC wavefunction takes the simple form,

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle = e^{\hat{T}} \sum_{\alpha=1}^{N_{\text{Ref.}}} c_{\alpha} |\Phi_{\alpha}\rangle, \quad (2.190)$$

in which a single cluster operator $\hat{T}$, is employed to generate excitations out of the entire reference manifold. This is analogous to the strategy employed in the ic-MRCI approach discussed in section 2.4.3. Here, we let $i, j, k, l, \dots$ run over the orbital subspace spanned by the union of the inactive core orbitals and the active orbitals, $a, b, c, d, \dots$ run over the union of the active and virtual orbital subspaces and let w, x, y, z denote active orbitals. Then the cluster operator in Eq. (2.190) can be written as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots = \sum_{i,a} t_i^a \hat{e}_i^a + \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab} \hat{e}_{ij}^{ab} + \dots, \quad (2.191)$$

in which purely internal excitations (*i.e.* those involving only active orbitals and which generate another model space determinant) are excluded. For future reference, it is useful to introduce the compound index ρ ($\rho \equiv \overset{ab\dots}{ij\dots}$) which runs from 1 (all single excitations) to $n_{\text{exc.}}$ (all $n_{\text{exc.}}$ -tuple excitations), where $n_{\text{exc.}}$ is the maximum excitation rank of the cluster operator (*e.g.* $n_{\text{exc.}} = 2$ for ic-MRCCSD (up to doubles excitations), $n_{\text{exc.}} = 3$ for ic-MRCCSDT (up to triples excitations), *etc.*) [49, 50, 51, 52]. Then we can write Eq. (2.191) in the compact form,

$$\hat{T} = \sum_{\rho=1}^{n_{\text{exc.}}} \hat{\tau}^{\rho} t_{\rho} = \hat{\tau} \mathbf{t}, \quad (2.192)$$

in which $\mathbf{t}$ is a column vector containing the amplitudes (*i.e.* $\mathbf{t} = (t_1, t_2, \dots, t_{n_{\text{exc.}}})^T$) and $\hat{\tau}$ is a row vector containing the corresponding excitation operators (*i.e.* $\hat{\tau} = (\hat{\tau}_1, \hat{\tau}_2, \dots, \hat{\tau}_{n_{\text{exc.}}})$).

One can proceed in a manner analogous with single-reference coupled-cluster theory (see section 2.3.3) in order to derive expressions for the energy and amplitude equations. Namely, substituting the ansatz of Eq. (2.190) into the Schrödinger equation and multiplying on the left by $e^{-\hat{T}}$, we obtain the similarity transformed Schrödinger equation (*cf.* Eq. (2.80) in the single-reference case) as

$$\hat{\bar{H}} |\Phi_0\rangle = e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle = E |\Phi_0\rangle. \quad (2.193)$$

Projection of this equation onto the reference wavefunction gives the following expression for the ic-MRCC energy,

$$E = \langle \Phi_0 | \hat{\bar{H}} | \Phi_0 \rangle, \quad (2.194)$$

while projection onto the excited manifold of functions of the form $|\rho\rangle = \hat{\tau}^\rho |\Phi_0\rangle$, yields the preliminary equations for the amplitudes,

$$R_\rho = \langle \rho | \hat{H} | \Phi_0 \rangle = 0 \quad (2.195)$$

which can be written in vectorized form as

$$\mathbf{R} = \langle \Phi_0 | \hat{\tau}^\dagger \hat{H} | \Phi_0 \rangle = \mathbf{0}. \quad (2.196)$$

The r.h.s. of this equation (*i.e.* $E \langle \Phi_0 | \hat{\tau}^\dagger | \Phi_0 \rangle$) only vanishes because internal excitations have been excluded from the cluster operator. We note that in the absence of this restriction, relaxation effects would automatically be incorporated into the reference wavefunction. However, the BCH expansion of Eq. (2.81) does not terminate if these excitations are incorporated into the ic-MRCC ansatz. Alternatively, relaxation effects can be included through the reoptimization of the reference coefficients c_α by simultaneously solving the CI-like expression,

$$\sum_\beta \langle \Phi_\alpha | \hat{H} | \Phi_\beta \rangle c_\beta = E c_\alpha, \quad (2.197)$$

during the course of the amplitude iterations [50, 51, 52].

It is important to note that there are redundant configurations which arise in the manifold of excited functions $\{\hat{\tau}^\rho |\Phi_0\rangle\}$, since a given configuration can be generated more than once by the action of the excitation operators on the individual reference determinants. This signifies that the amplitude equations of Eq. (2.196) constitute an overdetermined system of equations. There are several different ways in which the linear dependencies can be removed from the amplitude equations (*e.g.* see Refs. [49, 50, 51, 52]). However, there is only one such procedure that has been found to preserve the size-extensivity of the methodology [50, 51, 52]. The procedure makes use of the metric matrix,

$$\mathbf{S} = \langle \Phi_0 | \hat{\tau}^\dagger \hat{\tau} | \Phi_0 \rangle, \quad (2.198)$$

in which the operators $\hat{\tau}$ are expressed in Kutzelnigg-Mukherjee (KM) normal ordering [151, 152, 153], as described in the previous section. The metric matrix can then be diagonalized according to

$$\mathbf{s} = \mathbf{U}^\dagger \mathbf{S} \mathbf{U}, \quad (2.199)$$

and the eigenvalues which fall below a threshold η are discarded (*i.e.* singular value decomposition (SVD)).

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The remaining $n_{\text{ind.}}$ linearly independent components are employed to form a transformation matrix,

$$\mathbf{X} = \mathbf{U}\mathbf{s}_\eta, \quad (2.200)$$

in which $\mathbf{s}_\eta$ is a rectangular matrix of dimension $n_{\text{exc.}} \times n_{\text{ind.}}$. The transformation matrix satisfies the relation,

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}_\eta, \quad (2.201)$$

in which $\mathbf{1}_\eta$ is the $n_{\text{ind.}} \times n_{\text{ind.}}$ identity matrix. A linearly independent set of residual equations $\mathbf{R}'$ is then obtained by transforming the original set $\mathbf{R}$ in Eq. (2.196), according to

$$\mathbf{R}' = \mathbf{X}\mathbf{R}. \quad (2.202)$$

Another issue of the ic-MRCC approach involves the formal truncation of the BCH expansion,

$$\widehat{H} = e^{-\widehat{T}} \widehat{H} e^{\widehat{T}} = \widehat{H} + [\widehat{H}, \widehat{T}] + \frac{1}{2} [[\widehat{H}, \widehat{T}], \widehat{T}] + \frac{1}{6} [[[\widehat{H}, \widehat{T}], \widehat{T}], \widehat{T}] + \dots \quad (2.203)$$

resulting from the non-commutativity of the operators in $\widehat{T}$. In contrast with single-reference CC theory, the BCH expansion does not rigorously terminate after the fourth-fold commutator in the evaluation of the ic-MRCC amplitude equations. The maximum number $n_{\text{comm.}}$ of commutators appearing in the residual equations is related to the excitation rank $n_{\text{exc.}}$ [50, 52],

$$n_{\text{comm.}} = 4 + 2n_{\text{exc.}}. \quad (2.204)$$

Hence, the formulation of the ic-MRCCSD equations ($n_{\text{exc.}} = 2$) requires the evaluation of up to eight-fold commutators and involves terms which contain the eight-body reduced density matrix (RDM). Therefore the resulting equations are incredibly complex and their derivation and implementation necessitates the use of automatic expression and code generation software. In practical applications of ic-MRCCSD, the BCH expansion is truncated up to two-fold commutators [50, 52]. This leads to equations that are at most quadratic in the amplitudes and the highest rank density matrix appearing in the equations is the five-body RDM [50, 52]. As mentioned in Refs. [50, 52], when large active spaces are employed in the current ic-MRCC scheme, the formation of the higher order RDM's, the SVD procedure and the evaluation of terms which have a high polynomial scaling w.r.t. the number of active orbitals (*e.g.* $n_a^{10} n_v$ where n_a is the number of active orbitals and n_v is the number of virtual orbitals) can become computational bottlenecks of the procedure.

In initial applications [50, 52], the ic-MRCCSD approach was found to be highly accurate for the calculation of potential energy surfaces of small molecules. An implementation of the ic-MRCCSD(T) method has also recently been reported [172, 52], which includes perturbative triples excitations in a non-iterative fashion (*i.e.* the internally-contracted multireference analogue of single-reference CCSD(T)). This method is found to be highly accurate for the treatment of static and dynamic correlation effects in initial applications to various systems, with relatively small active spaces [172]. It is also observed that ic-MRCCSD(T) results are considerably less sensitive to the size of the active space than those obtained from ic-MRCCSD calculations [172, 173]. Explicitly correlated versions of ic-MRCCSD (ic-MRCCSD(F_{12}^*)) and ic-MRCCSD(T) (ic-MRCCSD(F_{12}^*)+(T)) have also been developed to significantly enhance the basis set convergence of these approaches [173]. Moreover, a linear-response theory for the ic-MRCC approach has recently been reported, which allows applications of this methodology to excited electronic states [174].

2.4.5.3 Canonical Transformation Theory

The work of Chan and coworkers on the canonical transformation (CT) theory [53, 54, 55, 56, 57, 58] constitutes another notable recent development in the area of internally-contracted multireference coupled-cluster theory. In CT theory, the internally-contracted ansatz for the wavefunction is given by

$$|\Phi\rangle = e^{\hat{A}} |\Phi_0\rangle, \quad (2.205)$$

in which $\hat{A}$ is an antisymmetric operator (*i.e.* $\hat{A}^\dagger = -\hat{A}$), that is the difference between an excitation ($\hat{T}$) and de-excitation operator ($\hat{T}^\dagger$),

$$\hat{A} = \hat{T} - \hat{T}^\dagger \quad (2.206)$$

As in the previous section, we let $i, j, k, l, \dots$ denote union of the inactive core orbitals and the active orbitals, $a, b, c, d, \dots$ denote the union of the active and virtual orbital subspaces and let w, x, y, z denote active orbitals. Then the excitation operator $\hat{T}$ has the same form as that used in ic-MRCC (Eq. (2.191)),

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots = \sum_{i,a} t_i^a \hat{e}_i^a + \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab} \hat{e}_{ij}^{ab} + \dots, \quad (2.207)$$

and the de-excitation operator is the Hermitian conjugate of the excitation operator,

$$\hat{T}^\dagger = \hat{T}_1^\dagger + \hat{T}_2^\dagger + \dots = \sum_{i,a} t_a^i \hat{e}_a^i + \frac{1}{4} \sum_{i,j,a,b} t_{ab}^{ij} \hat{e}_{ab}^{ij} + \dots \quad (2.208)$$

In analogy with ic-MRCC, the sums in Eqs. (2.207) and (2.208) are restricted such that they do not include purely internal excitations or de-excitations, respectively. Evidently, Eq. (2.205) constitutes a unitary transformation of the reference wavefunction, since the exponential of an anti-Hermitian operator is a unitary operator (*i.e.* $\hat{U}^\dagger \hat{U} = e^{\hat{A}^\dagger} e^{\hat{A}} = e^{-\hat{A}} e^{\hat{A}} = 1$). Inserting the ansatz of Eq. (2.205) into the Schrödinger equation and left multiplying by $e^{-\hat{A}}$ yields the so-called canonically (unitary) transformed Schrödinger equation as

$$\hat{\bar{H}}|\Phi_0\rangle = e^{-\hat{A}}\hat{H}e^{\hat{A}}|\Phi_0\rangle = E|\Phi_0\rangle. \quad (2.209)$$

In contrast with the similarity transformed Hamiltonian in Eq. (2.193), which is employed in ic-MRCC, the canonically (unitary) transformed Hamiltonian in Eq. (2.209) is Hermitian. The BCH expansion can be used to write the canonically transformed Hamiltonian as

$$\hat{\bar{H}} = e^{-\hat{A}}\hat{H}e^{\hat{A}} = \hat{H} + [\hat{H}, \hat{A}] + \frac{1}{2}[[\hat{H}, \hat{A}], \hat{A}] + \frac{1}{6}[[[\hat{H}, \hat{A}], \hat{A}], \hat{A}] + \dots, \quad (2.210)$$

where we note that the expansion does not terminate for an anti-Hermitian operator $\hat{A}$.

Let us restrict our discussion to the so-called Canonical Transformation method with Single and Double excitations (CTSD), which was first introduced in Ref. [53]. The operator $\hat{A}$ is then given by

$$\hat{A} = \sum_{i,a} A_i^a (\hat{e}_i^a - \hat{e}_a^i) + \sum_{i,j,a,b} A_{ij}^{ab} (\hat{e}_{ij}^{ab} - \hat{e}_{ab}^{ij}) \quad (2.211)$$

in which A_i^a and A_{ij}^{ab} are the amplitudes which are to be determined. An expression for the energy is obtained by projection of the canonically transformed Schrödinger equation of Eq. (2.209) onto the reference wavefunction,

$$E = \langle \Phi_0 | \hat{\bar{H}} | \Phi_0 \rangle. \quad (2.212)$$

The amplitudes A_i^a and A_{ij}^{ab} are respectively, determined by solving the residual equations [53, 54, 55, 56, 57, 58],

$$R_i^a = \langle \Phi_0 | [\hat{\bar{H}}, (\hat{e}_i^a - \hat{e}_a^i)] | \Phi_0 \rangle, \quad (2.213)$$

$$R_{ij}^{ab} = \langle \Phi_0 | [\hat{\bar{H}}, (\hat{e}_{ij}^{ab} - \hat{e}_{ab}^{ij})] | \Phi_0 \rangle, \quad (2.214)$$

which are of the same form as the generalized Brillouin conditions described in Ref. [103].

In CTSD, the BCH expansion of Eq. (2.210) is approximated by

$$\hat{\bar{H}} \approx \hat{H} + [\hat{H}, \hat{A}]_{1,2} + \frac{1}{2}[[\hat{H}, \hat{A}]_{1,2}, \hat{A}]_{1,2} + \dots, \quad (2.215)$$

in which the subscript 1, 2 on the commutators indicates that higher than two-body operators are approximated by operator decompositions which contains only one- and two-body operators. This same operator decomposition procedure is used in the evaluation of the commutators entering the residual equations of Eqs. (2.213) and (2.214), namely,

$$R_i^a = \langle \Phi_0 | [\hat{H}, (\hat{e}_i^a - \hat{e}_a^i)]_{1,2} | \Phi_0 \rangle, \quad (2.216)$$

$$R_{ij}^{ab} = \langle \Phi_0 | [\hat{H}, (\hat{e}_{ij}^{ab} - \hat{e}_{ab}^{ij})]_{1,2} | \Phi_0 \rangle. \quad (2.217)$$

Note that the approximation of Eq. (2.215) is used for the transformed Hamiltonian $\hat{\bar{H}}$, appearing in these equations. Current incarnations of the methodology include only the first commutator in Eq. (2.215) (*i.e.* the Linearized or LCTSD method [53, 54]) or both the first commutator and second nested commutator (*i.e.* the Quadratic or QCTSD approach [55]). Hence, contributions involving three body operators arise in LCTSD, while terms with three- and four-body operators occur in QCTSD. We also note that in QCTSD, the second nested commutator is treated more carefully by using one, rather than two, separate operator decomposition steps [55]. This is in contrast with the usual CT formalism, where the terms in the BCH expansion are evaluated recursively [58]. For example, let $\hat{\bar{H}}^{(n)}$ denote the n^{th} term appearing in the approximate BCH expansion of Eq. (2.215), then each term is evaluated recursively as,

$$\hat{\bar{H}}^{(n)} = [\hat{\bar{H}}^{(n-1)}, \hat{A}]_{1,2}, \quad (2.218)$$

where we note that $\hat{\bar{H}}^{(0)} = \hat{H}$.

In order to achieve the desired operator decomposition in the commutators, the Wick theorem, defined within the KM normal order formalism [151, 152, 153] of section 2.4.5.1, is employed to expand the three-body and four-body operators in terms of lower rank operators. The contributions containing higher than two-body operators are discarded. For example, as shown in Ref. [153], the three-body operator $\hat{e}_{stu}^{pqr}$ can be expanded as

$$\hat{e}_{stu}^{pqr} = \tilde{e}_{stu}^{pqr} + \mathcal{A}(\gamma_s^p \hat{e}_{tu}^{qr}) + \mathcal{A}(\gamma_{st}^{pq} \hat{e}_u^r) + \gamma_{stu}^{pqr}. \quad (2.219)$$

This expression follows from the cumulant based expansion of Eq. (2.188) and the relations between the RDMs and cumulants given in Eqs. (2.172), (2.173) and (2.174). The approximation,

$$\hat{e}_{stu}^{pqr} \approx \mathcal{A}(\gamma_s^p \hat{e}_{tu}^{qr}) + \mathcal{A}(\gamma_{st}^{pq} \hat{e}_u^r) + \gamma_{stu}^{pqr}, \quad (2.220)$$

which excludes the KM normal ordered three body-operator $\tilde{e}_{stu}^{pqr}$ (*i.e.* only includes one- and two-body

operators) is then employed in the evaluation of the various commutators. Furthermore, while the one- and two-body RDMs are obtained from the CASSCF calculation, the three- (and four-body) RDMs occurring in the CTSD methods, must be computed separately. In order to avoid the computational overhead associated with their calculation, the three- and four-body RDMs are expanded in terms of cumulants and the terms containing the three- and four-body cumulants, which arise in the resulting decompositions, are discarded. For example, the final approximation of the three-body operator (*i.e.* in terms of one- and two-body RDMs) is given by [55]

$$\hat{e}_{stu}^{pqr} \approx \mathcal{A}(\gamma_s^p \hat{e}_{tu}^{qr}) + \mathcal{A}(\gamma_{st}^{pq} \hat{e}_u^r) - 2\mathcal{A}(\gamma_s^p \gamma_t^q \hat{e}_u^r) - \mathcal{A}(\gamma_s^p \gamma_{tu}^{qr}) + 4\mathcal{A}(\gamma_s^p \gamma_t^q \gamma_u^r). \quad (2.221)$$

The CT theory is rigorously size-extensive and size-consistent and has a similar scaling of the computational cost as single-reference CCSD (*i.e.* $\mathcal{O}(N^6)$) [58]. Since CT theory makes use of an internally-contracted ansatz, there are linear dependencies which must be dealt with in solving the amplitude equations of Eqs. (2.216) and (2.217). One approach is to use a numerical truncation of the overlap matrix, however, this can cause problems with convergence, it is expensive for larger active spaces (*i.e.* scales as n_a^9 with the number n_a of active orbitals) and the arbitrary choice of the truncation threshold can have a significant effect the computed energies [57]. Furthermore, while the operator and cumulant decompositions preserve orbital invariance in the active space, the numerical truncations of the overlap matrix destroy this property [53]. We note that the use of strongly contracted excitation operators, first introduced within the context of NEVPT2 (n -electron valence second-order perturbation theory) [175, 176], has been suggested as an alternative approach to the overlap truncation [57]. The CT theory can also make use of the reference densities from a DMRG [34, 35, 36, 37, 38, 39, 40] calculation, which allows for the use of much larger active spaces than are possible in CASSCF [56]. We refer the interested reader to the review of Lyakh *et al.* [20] and references therein for more details on other internally-contracted MRCC approaches.

2.5 Concluding Remarks

In this chapter, we have provided a fairly extensive overview of both single-reference and multireference correlation methods. We reiterate that the former methodology is well established and the coupled-cluster approach, with its exponential parametrization of the wavefunction, has emerged as a cornerstone of *ab-initio* quantum chemistry for systems that are qualitatively well described by a single-determinantal zeroth-order wavefunction [2]. In contrast, for multireference systems, there is not yet a consensus on a preferred methodology, which possesses all of the desirable features of the single-reference coupled-cluster

formulation. While the MRCI and related MR-ACPF [123, 124] and MR-AQCC [125, 126] approaches are conceptually straightforward, these methods are not rigorously size-consistent or size-extensive. As a consequence, fairly large active spaces are required to obtain accurate results, especially in the case of MRCI. This can be an issue if these methods are based on a partially uncontracted formalism, since calculations quickly become prohibitively expensive as the size of the active space grows.

The success of single-reference coupled-cluster theory provides the impetus to explore the possibilities for a multireference generalization of the formalism. The most straightforward approaches are based on the Jeziorski-Monkhorst ansatz [41], and include methods such as BW-MRCC [42, 43, 44, 45] and Mk-MRCC [46, 47, 48]. However, these methods are mainly employed with limited active spaces as the cost of the calculations scale factorially with the size of the active space. In order to avoid the steep scaling of these approaches with the size of the active space, methods which make use of an internally contracted ansatz have been developed. The ic-MRCC approach [49, 50, 51, 52] has many excellent properties which make it a very promising methodology. Notably, the current formulation described in Refs. [50, 51, 52] is size-extensive and orbital invariant. The ic-MRCCSD(T) approach [172] is particularly auspicious as initial applications show that it is highly accurate and that results are fairly insensitive to the size of the active space. Even so, the equations defining the methodology are incredibly complex and require up to the five-body RDM, which becomes prohibitively expensive to compute for larger active spaces. The canonical transformation theory [53, 54, 55, 56, 57, 58] is less computationally demanding, but also has other problems associated with its formulation. The most important issue is with linear dependencies and the arbitrariness of the overlap truncation scheme used to deal with it. In the following chapter, we discuss the details of a novel internally-contracted multireference coupled-cluster method (*i.e.* the Multireference Equation of Motion Coupled-Cluster (MR-EOM-CC) approach), which constitutes one of the major topics of this thesis.

Chapter 3

MR-EOM-CC: Multireference Equation of Motion Coupled-Cluster Theory¹

In recent years, a major research effort of the Nooijen group has been focused on the development and implementation of a novel internally-contracted multireference coupled-cluster theory. This approach has been coined Multireference Equation of Motion Coupled-Cluster (MR-EOM-CC) theory [21, 22, 23], due to the use of a similar transform and diagonalize strategy as that employed in single-reference EOM-CC [13, 14, 15] and STEOM-CC [16, 17]. In general, the MR-EOM methodology involves a sequence of similarity transformations of the bare molecular electronic Hamiltonian. The ultimate goal of these many-body transformations is to effectively decouple the CAS configurations from important excited configurations (*e.g.* 2p2h, 2p1h, 1p1h, *etc.*) which comprise the first-order interacting subspace (*i.e.* the excitation classes of Table 2.1 that enter the MR-CISD wavefunction of Eq. (2.137)). Through the definition of suitable cluster operators, in each of the transformations, the majority of these excitations can be included in an internally-contracted fashion. Hence, the resulting final transformed Hamiltonian can be diagonalized over a small subspace of the original first-order interacting space.

The first step in any MR-EOM calculation involves the solution of the state-averaged CASSCF problem. From the CASSCF calculation, one obtains the total Fock matrix, the two-electron integrals and the one- and two-body Reduced Density Matrices (RDMs) in the active space, which are required for the subsequent MR-EOM treatment of dynamic correlation effects. If $|\Phi_{\mathbf{m}}\rangle$ is the wavefunction corresponding to the $\mathbf{m}^{\text{th}}$ electronic state included in the state-averaged CASSCF, with weight $w_{\mathbf{m}}$, the state-averaged

¹The contents of this chapter and chapter 6 have been submitted for publication in *J. Chem. Theory Comput.*

one-body RDM can be written as

$$\Gamma_x^w = \sum_{\mathbf{m}} w_{\mathbf{m}} \langle \Phi_{\mathbf{m}} | \hat{E}_x^w | \Phi_{\mathbf{m}} \rangle, \quad (3.1)$$

and the state-averaged two-body RDM is given by

$$\begin{aligned} \Gamma_{yz}^{wx} &= \sum_{\mathbf{m}} w_{\mathbf{m}} \langle \Phi_{\mathbf{m}} | \hat{E}_{yz}^{wx} | \Phi_{\mathbf{m}} \rangle \\ &= \sum_{\mathbf{m}} w_{\mathbf{m}} \langle \Phi_{\mathbf{m}} | \hat{E}_y^w \hat{E}_z^x - \delta_y^x \hat{E}_z^w | \Phi_{\mathbf{m}} \rangle. \end{aligned} \quad (3.2)$$

Here, the operators $\hat{E}_x^w$ and $\hat{E}_{yz}^{wx}$ are spin-free single and double excitation operators, respectively. The MR-EOM approach makes extensive use of the Kutzelnigg-Mukherjee (KM) concept of normal ordering [151, 152, 153] and as such, the defining equations contain one- and two-body cumulants [101] of the state-averaged RDMs, rather than the RDMs themselves. The one-body cumulant is equal to the one-body RDM,

$$\Lambda_x^w = \Gamma_x^w, \quad (3.3)$$

while the two-body cumulant is obtained as [101]

$$\Lambda_{yz}^{wx} = \Gamma_{yz}^{wx} - \Gamma_y^w \Gamma_z^x - \frac{1}{2} \Gamma_z^w \Gamma_y^x. \quad (3.4)$$

For the reasons discussed at length in Ref. [177], the MR-EOM equations contain the α, β component of the two-body spin-orbital cumulant [162, 163],

$$\lambda_{yz}^{wx} \equiv \lambda_{Y_{\alpha} Z_{\beta}}^{W_{\alpha} X_{\beta}} = \frac{1}{6} (2\Lambda_{yz}^{wx} - \Lambda_{zy}^{wx}), \quad (3.5)$$

rather than the spatial two-body cumulant of Eq. (3.4) itself.

As mentioned previously, the MR-EOM methodology can be characterized as a transform and diagonalize scheme for the approximate solution of the molecular electronic structure problem. One first applies a sequence of many-body similarity transformations to the molecular electronic Hamiltonian and the resulting transformed operator is diagonalized over a compact subspace of configurations (including the CAS configurations and other excited configurations) in order to calculate a desired number of excited states. The MR-EOM-T[SXD]U approach, which was introduced in Ref. [23] and benchmarked for transition metal atoms in Ref. [178], is an extension of the MR-EOM-T [21] and MR-EOM-T[S]U [22] methods. Here, the notation T[SXD]U is used to denote that a sequence of similarity transformations is

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being applied to the Hamiltonian, the first involving the $\hat{T}$ operator, the second involving the $\hat{S} + \hat{X} + \hat{D}$ operator and the final transformation based on the $\hat{U}$ operator. Let us proceed to examine the details of this sequence of many-body transformations. The indices i, j, k, l are used to label the occupied (inactive core or active) orbitals, i', j', k', l' label the inactive core orbitals, w, x, y, z label the active orbitals, a, b, c, d label the virtual orbitals and p, q, r, s correspond to general orbitals in the state-averaged CASSCF reference space. It is important to note that *these labels refer to spatial orbitals rather than spin-orbitals*. The first similarity transformation is defined by

$$\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}, \quad (3.6)$$

in which the cluster operator $\hat{T}$ takes the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a \hat{E}_i^a + \frac{1}{2} \sum_{i,j,a,b} t_{ij}^{ab} \hat{E}_{ij}^{ab}, \quad (3.7)$$

where t_i^a and t_{ij}^{ab} are respectively, the single and double excitation amplitudes, which are to be determined. Since i and j run over both inactive core and active orbitals, the $\hat{T}_1$ operator generates 1h1p and 1p excitations out of the state-averaged CAS, while the $\hat{T}_2$ operator induces 2h2p, 1h2p and 2p type excitations. Here, we use ‘h’ to refer to hole (inactive core) orbitals and ‘p’ to refer to particle (virtual orbitals) orbitals. The transformed Hamiltonian of Eq. (3.6) can be expanded in KM normal order as

$$\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}} = \bar{h}_0 + \sum_{p,q} \bar{h}_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} \bar{h}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots \quad (3.8)$$

The curly braces in $\{ \hat{E}_q^p \}$ and $\{ \hat{E}_{rs}^{pq} \}$ indicate that these operators are written in KM normal order and $\bar{h}_0$, $\bar{h}_q^p$ and $\bar{h}_{rs}^{pq}$ are the KM normal ordered, 0-, 1- and 2-body elements of the similarity transformed Hamiltonian, respectively. In order to determine the single and double excitation amplitudes, one must iteratively solve the following set of residual equations [21, 22, 23, 177],

$$R_i^a = \sum_m w_m \langle \Phi_m | \hat{E}_a^i \hat{\bar{H}} | \Phi_m \rangle = 0, \quad (3.9)$$

$$R_{ij}^{ab} = \bar{h}_{ij}^{ab} = 0. \quad (3.10)$$

It is also important to note that in Eqs. (3.8)-(3.10), we discard terms that contain more than two $\hat{T}$ -amplitudes.

As discussed in Refs. [21, 22, 177], a projected residual equation (Eq. (3.9)) is employed for the

singles amplitudes so that the Brillouin condition is satisfied at first order. This signifies that the first-order approximation for the singles amplitudes, obtained from Eq. (3.9), rigorously vanishes for all i and a . This would not be the case if the many-body equation $\bar{h}_i^a = 0$, would be used in place of the projected equation of Eq. (3.9) and therefore, the many-body singles equation does not constitute a proper residual condition [177]. While the projected singles equation does contain contributions from the 3-body cumulant, such terms are discarded in practice as they are expected to have a small effect on the resulting singles amplitudes. Evidently, the equation for the doubles amplitudes (Eq. (3.10)) is a many-body residual equation, obtained by equating the $\bar{h}_{ij}^{ab}$ elements of $\hat{\bar{H}}$ in Eq. (3.6) to zero, and its use provides several benefits over the use of a projected residual equation. For one, the many-body equations are considerably less complex than their projected counterparts and only contain 1- and 2-body cumulants, for the reasons outlined in detail in Ref. [177]. Also, the many-body equations are non-singular and thus, in principle, one does not have to discard any amplitudes in order to solve these equations. However, in practical applications, it is sometimes necessary to discard some of the $\hat{T}_2$ -amplitudes in order to overcome convergence difficulties. From experience, it is found that the amplitudes which lead to convergence issues are those of the form t_{wx}^{ab} , where the active pairs (w, x) correspond to small eigenvalues of the two-body RDM (*i.e.* the metric matrix). Hence, in these cases, we use the projection scheme described in Ref. [177] (Scheme I), with the 2-body RDM as the metric matrix, to discard the offending amplitudes (*i.e.* eigenvalues below 0.01) and replace them with suitable perturbative estimates [22].

The second transformation in the MR-EOM-T|SXD|U scheme is given by

$$\begin{aligned}\hat{\bar{F}} &= \left\{ e^{\hat{S} + \hat{X} + \hat{D}} \right\}^{-1} \hat{\bar{H}}_2 \left\{ e^{\hat{S} + \hat{X} + \hat{D}} \right\} \\ &= \bar{f}_0 + \sum_{p,q} \bar{f}_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} \bar{f}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots,\end{aligned}\tag{3.11}$$

in which $\hat{\bar{H}}_2$ is the similarity transformed Hamiltonian of Eq. (3.8), truncated to two-body operators. Since the operators in $\hat{S}$, $\hat{X}$ and $\hat{D}$ do not commute, the transformation of Eq. (3.11) is written in terms of KM normal-ordered exponentials, in which there are no contractions among these operators. In order to evaluate this type of similarity transformation, which involves the inverse of a normal-ordered exponential, the procedure outlined in Ref. [95] is employed (*i.e.* see also appendix A of Ref. [22]). Here, the various cluster operators are defined as

$$\hat{S} = \hat{S}_1 + \hat{S}_2 = \sum_{i,a} s_i^a \{ \hat{E}_i^a \} + \sum_{i',j',w,a} s_{i'j'}^{aw} \{ \hat{E}_{i'j'}^{aw} \},\tag{3.12}$$

$$\hat{X} = \hat{X}_2 = \sum_{i',w,x,a} x_{xi'}^{aw} \{ \hat{E}_{xi'}^{aw} \},\tag{3.13}$$

$$\hat{D} = \hat{D}_2 = \sum_{i',w,x,a} d_{i'x}^{aw} \{ \hat{E}_{i'x}^{aw} \}. \quad (3.14)$$

The $\hat{S}_1$ operator generates 1h1p and 1p type excitations out of the state-averaged CAS (just like $\hat{T}_1$ in the first transformation). The $\hat{S}_2$ operator induces 2h1p excitations out of the CAS, while the $\hat{X}$ operator generates 1h1p exchange type excitations and the $\hat{D}$ operator generates 1h1p direct type excitations that in addition, act in the active space. Hence, they represent semi-internal excitations in MRCI language [111, 112, 113]. The 1p excitation operators of the form $\{ \hat{E}_{xy}^{aw} \}$, are excluded from this transformation, since it is observed that some of the associated amplitudes are large for a small set of test cases, as already pointed out in Ref. [22]. In addition, the introduction of these operators gives rise to three-body operators in $\hat{F}$, which only have active labels. Since such operators are not treated in the final MRCI diagonalization, it is best to not generate them in the first place. In order to satisfy the Brillouin condition, the s_i^a amplitudes are determined from a projected residual equation of the form,

$$R_i^a = \sum_m w_m \langle \Phi_m | \hat{E}_a^i \hat{F} | \Phi_m \rangle = 0, \quad (3.15)$$

while the $s_{i'j'}^{aw}$, $x_{xi'}^{aw}$ and $d_{i'x}^{aw}$ amplitudes are, respectively, obtained as solutions of the following many-body residual equations

$$R_{i'j'}^{aw} = \bar{f}_{i'j'}^{aw} = 0, \quad (3.16)$$

$$R_{xi'}^{aw} = \bar{f}_{xi'}^{aw} = 0, \quad (3.17)$$

$$R_{i'x}^{aw} = \bar{f}_{i'x}^{aw} = 0. \quad (3.18)$$

Once again, we only retain terms that are at most quadratic in the various amplitudes, in Eqs. (3.11) and (3.15)-(3.18).

The third and final transformation of the MR-EOM-T|SXD|U approach can be written as

$$\hat{G} = e^{-\hat{U}} \hat{\bar{F}}_2 e^{\hat{U}} \quad (3.19)$$

$$= g_0 + \sum_{p,q} g_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} g_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots \quad (3.20)$$

where the subscript 2 in $\hat{\bar{F}}_2$ indicates that the transformed Hamiltonian $\hat{\bar{F}}$ of Eq. (3.11) has been truncated

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up to two-body operators. The cluster operator $\widehat{U}$, appearing in this transformation, is given by

$$\widehat{U} = \widehat{U}_2 = \frac{1}{2} \sum_{i',j',w,x} u_{i'j'}^{wx} \{\widehat{E}_{i'j'}^{wx}\}, \quad (3.21)$$

and this operator generates 2h type excitations out of the state-averaged CAS. The $u_{i'j'}^{wx}$ amplitudes are determined as iterative solutions of the many body residual equation,

$$R_{i'j'}^{wx} = g_{i'j'}^{wx} = 0. \quad (3.22)$$

The single excitations of the form $\{\widehat{E}_{i'}^w\}$ have not been included in this transformation, since the corresponding projected residual equation is difficult to converge and is rather computationally expensive to solve due to its complexity. Furthermore, the 1h excitations of the form $\{\widehat{E}_{yi'}^{wx}\}$ and $\{\widehat{E}_{i'y}^{wx}\}$ have been excluded from the transformation since the amplitudes associated with these excitations are typically large [22]. For this reason, the final diagonalization space in MR-EOM, will always include the 1h configurations and this is another reason not to be concerned with the incorporation of the excitations of the form $\{\widehat{E}_{i'}^w\}$ (*i.e.* $\widehat{U}_1$) in the transformation. As already mentioned in Ref. [22], there can also be issues in the solution of Eq. (3.22) and a suitable metric matrix, based on the two body RDM, is always used to project out the nearly singular $\widehat{U}$ -amplitudes, replacing them with suitable perturbative estimates.

In the MR-EOM-TSXD approach, the similarity transformation of the molecular electronic Hamiltonian $\widehat{H}$ is defined as

$$\widehat{G} = \{e^{\widehat{T}+\widehat{S}_2+\widehat{X}+\widehat{D}}\}^{-1} \widehat{H} \{e^{\widehat{T}+\widehat{S}_2+\widehat{X}+\widehat{D}}\} \quad (3.23)$$

$$= g_0 + \sum_{p,q} g_q^p \{\widehat{E}_q^p\} + \sum_{p,q,r,s} g_{rs}^{pq} \{\widehat{E}_{rs}^{pq}\} + \dots, \quad (3.24)$$

in which $\widehat{T} = \widehat{T}_1 + \widehat{T}_2$ is the cluster operator of Eq. (3.7) and $\widehat{S}_2$, $\widehat{X}$ and $\widehat{D}$ are respectively, the operators given in Eqs. (3.12), (3.13) and (3.14). Evidently, since the $\widehat{S}_1$ operator is equivalent to the $\widehat{T}_1$ operator, it is not included in this transformation. The following equations,

$$R_i^a = \sum_m w_m \langle \Phi_m | \widehat{E}_a^i \widehat{G} | \Phi_m \rangle = 0, \quad (3.25)$$

$$R_{ij}^{ab} = g_{ij}^{ab} = 0, \quad (3.26)$$

$$R_{i'j'}^{aw} = g_{i'j'}^{aw} = 0, \quad (3.27)$$

$$R_{xi'}^{aw} = g_{xi'}^{aw} = 0, \quad (3.28)$$

$$R_{i'x}^{aw} = g_{i'x}^{aw} = 0, \quad (3.29)$$

must then be solved simultaneously for the respective amplitudes, t_i^a , t_{ij}^{ab} , $s_{i'j'}^{aw}$, $s_{xi'}^{aw}$ and $s_{i'x}^{aw}$. These equations are considerably more complex than in the sequential MR-EOM-T|SXD case (*i.e.* Eqs. (3.9), (3.10), (3.16), (3.17), and (3.18)) and therefore, require more computational effort in their solution. However, from a theoretical standpoint, this non-sequential transformation is more adequate as the desired elements of the final transformed Hamiltonian will be rigourously zero. Since there has not yet been any comparison of the MR-EOM-T|SXD and MR-EOM-TSXD approaches, we will investigate the relative accuracy of these methods in the benchmark applications of chapter 6.

One of the issues associated with sequential transformations of the type used in the MR-EOM-T|SXD|U approach, is that subsequent transformations do not rigourously preserve the vanishing components in a previous transformation. For example, after the MR-EOM-T transformation of Eq. (3.8), the operator components $\{\hat{E}_{ij}^{ab}\}$ are eliminated by virtue of Eq. (3.10) (*i.e.* $\bar{h}_{ij}^{ab} = 0$). However, after the subsequent SXD transformation, the $\bar{f}_{ij}^{ab}$ elements of Eq. (3.11) are not zero (although they are typically quite small) and hence, the operator components $\{\hat{E}_{ij}^{ab}\}$ can still contribute in the final diagonalization step. Despite this fact, in a previous study [22], it was observed that the methods making use of a non-sequential $\hat{T}$ and $\hat{S}$ transformation (*i.e.* MR-EOM-TS and MR-EOM-TS|U) did not provide more accurate results, for the calculation of excitation energies of transition metal atoms and small organic molecules, than the methods employing sequential $\hat{T}$ and $\hat{S}$ transformations (*i.e.* MR-EOM-T|S and MR-EOM-T|S|U). In chapter 6, we will make a similar comparison between MR-EOM-T|SXD (*i.e.* sequential T|SXD transformation) and MR-EOM-TSXD (*i.e.* makes use of a single transformation which incorporates the $\hat{T}$, $\hat{S}_2$, $\hat{X}$ and, $\hat{D}$ operators). Also, as noted in Ref. [22], the $\hat{U}$ transformation (Eq. (3.20)) has no effect on vanishing elements from a previous transformation, given that these elements have at least a single virtual label. This is why this transformation is always performed sequentially.

In this thesis, we will also consider another sequence of transformations which constitutes the so-called MR-EOM-T|T[†]|SXD approach. This methodology has been implemented in the ORCA program package [24] and important details regarding the symmetrization and Hermitization of the elements of the final similarity transformed Hamiltonian, in this implementation, are discussed below. The MR-EOM-T|T[†]|SXD approach begins with the $\hat{T}$ transformation of Eq. (3.8), with $\hat{T}$ -amplitudes obtained as solutions of Eqs. (3.9) and (3.10). The second transformation, which is not included in the MR-EOM-T|SXD approach, takes the form

$$\hat{\mathcal{H}} = e^{\hat{T}^\dagger} \hat{H}_2 e^{-\hat{T}^\dagger}$$

$$= \tilde{h}_0 + \sum_{p,q} \tilde{h}_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} \tilde{h}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots, \quad (3.30)$$

in which $\hat{H}_2$ includes the 0-, 1- and 2-body elements of $\hat{H}$ in Eq. (3.8). The de-excitation operator $\hat{T}^\dagger$ is given by

$$\hat{T}^\dagger = \sum_{i,a} t_a^i \hat{E}_a^i + \frac{1}{2} \sum_{i,j,a,b} t_{ab}^{ij} \hat{E}_{ab}^{ij}, \quad (3.31)$$

and the de-excitation amplitudes are approximated by the excitation amplitudes,

$$t_a^i \approx t_i^a, \quad (3.32)$$

$$t_{ab}^{ij} \approx t_{ij}^{ab}. \quad (3.33)$$

The transformation of Eq. (3.30) is performed so that the resulting Hamiltonian $\hat{\mathcal{H}}$ is approximately Hermitian. In the ORCA [24] implementation of MR-EOM-T|T[†]|SXD, the elements of the final transformed Hamiltonian are symmetrized before the MRCI diagonalization step (*vide infra*) due to a current technical limitation of the MRCI module. Namely, this module assumes that the elements of the final transformed Hamiltonian have the same permutational symmetries as the bare two-electron integrals. We plan to modify the program to lift this restriction in the future. However, this will require considerable effort and is beyond the scope of the current study. It is therefore, advantageous to Hermitize the Hamiltonian in some approximate fashion so that the effects of the symmetrization can be mitigated.

While the remaining SXD transformation step proceeds in a similar way as that in the MR-EOM-T|SXD (or MR-EOM-T|SXD|U) approach, there is one important difference. Namely, the single excitation operator $\hat{S}_1$, is excluded from the transformation. The final SXD transformation is therefore given by

$$\begin{aligned} \hat{G} &= \{ e^{\hat{S}_2 + \hat{X} + \hat{D}} \}^{-1} \hat{\mathcal{H}}_2 \{ e^{\hat{S}_2 + \hat{X} + \hat{D}} \} \\ &= g_0 + \sum_{p,q} g_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} g_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots \end{aligned} \quad (3.34)$$

in which $\hat{\mathcal{H}}_2$ is the transformed Hamiltonian of Eq. (3.30), truncated to two-body operators, the operator $\hat{S}_2$ is given by

$$\hat{S}_2 = \sum_{i',j',w,a} s_{i'j'}^{aw} \{ \hat{E}_{i'j'}^{aw} \}, \quad (3.35)$$

and $\hat{X}$ and $\hat{D}$ are the operators of Eqs. (3.13) and (3.14), respectively. In analogy with Eqs. (3.16), (3.17) and (3.18), the respective $s_{i'j'}^{aw}$, $x_{xi'}^{aw}$ and $d_{i'x}^{aw}$ amplitudes are determined as solutions of the many-body

residual equations,

$$R_{i'j'}^{aw} = g_{i'j'}^{aw} = 0, \quad (3.36)$$

$$R_{xi'}^{aw} = g_{xi'}^{aw} = 0, \quad (3.37)$$

$$R_{i'x}^{aw} = g_{i'x}^{aw} = 0. \quad (3.38)$$

The decision to discard the $\hat{S}_1$ operator from this transformation was arrived at, based on the observation that the s_i^a amplitudes are typically quite small in many of the calculations that we have performed with the MR-EOM-T|SXD method. Hence, the effects of excluding the $\hat{S}_1$ operator from the SXD transformation are minimal. We also note that the $\hat{S}_1$ operator is basically a $\hat{T}_1$ operator, which has already been included in the previous transformation. Furthermore, by excluding the $\hat{S}_1$ operator from the transformation, we eliminate the additional computational cost that is associated with solving the rather complex projected residual equation for the s_i^a amplitudes. Furthermore, the expressions for the elements of $\hat{G}$ in Eq. (3.34) (including the many-body residual equations of Eqs. (3.36), (3.37) and (3.38)) are considerably less complex than those for the elements of $\hat{F}$ in Eq. (3.11) (including the many-body residual equations of Eqs. (3.16), (3.17) and (3.18)), since the terms containing the s_i^a amplitudes have been discarded from the elements of $\hat{G}$ in Eq. (3.34).

In the MR-EOM-T|T[†]|SXD approach, we also approximate the 3p1h elements of each of the transformed Hamiltonians to be equal to the bare two electron integrals,

$$\tilde{h}_{bc}^{ia} \approx \bar{h}_{bc}^{ia} \approx v_{bc}^{ia}. \quad (3.39)$$

where $v_{ia}^{bc} = v_{bc}^{ia}$ (*i.e.* $\tilde{h}_{ia}^{bc} \approx \bar{h}_{ia}^{bc} \approx v_{ia}^{bc} = v_{bc}^{ia}$). Note that the elements g_{bc}^{ia} and g_{ia}^{bc} , of the final similarity transformed Hamiltonian $\hat{G}$ in Eq. (3.34), are not required since they do not enter the final MRCI diagonalization. The only reason to calculate the 3p1h and 4p elements in a given transformation, is that they are required as input for the subsequent transformation. By adopting the approximation of Eq. (3.39), we never have to compute the numerous 3p1h or 4p elements of any of the similarity transformed Hamiltonians involved in the sequence of transformations (*i.e.* the 4p elements of a given Hamiltonian are required for the computation of the 3p1h elements of the Hamiltonian in the subsequent transformation). This provides a significant reduction of the computational time required in the calculation of the elements of the various transformed Hamiltonians and we avoid the $n_v^3 n_o$ and n_v^4 storage costs associated with writing the respective 3p1h and 4p elements to disk (*i.e.* n_o is the number of occupied orbitals and n_v is the number of virtual orbitals). Note that the $\tilde{h}_{ia}^{bc}$ and $\tilde{h}_{bc}^{ia}$ elements of $\hat{\mathcal{H}}$ in Eq. (3.30), only enter terms, in the many-body amplitude equations of the SXD transformation (*i.e.* Eqs. (3.36), (3.37) and (3.38)),

which are quadratic in the amplitudes. These terms tend to be small and we expect that there will only be small differences between the elements $\tilde{h}_{bc}^{ia}$ and $\bar{\tilde{h}}_{bc}^{ia}$. Hence, the approximation of Eq. (3.39) is robust. In chapter 6, we will further investigate the combined effects of this approximation and the exclusion of $\hat{S}_1$ from the SXD transformation on the calculation of excitation energies. Let us also note that we do not perform additional transformations to include the de-excitation operators $\hat{S}^\dagger$, $\hat{X}^\dagger$, $\hat{D}^\dagger$ and $\hat{U}^\dagger$. The reason for this is that the resulting expressions for the various transformed elements have a significant number of contributions containing the three-body cumulant, which we wish to avoid for technical reasons. Moreover, the inclusion of these operators would generate a significant number of 3-body elements of $\hat{G}$ in Eq. (3.34), which only have active labels and this is undesirable.

In addition to studying the effects of different many-body transformations on the calculation of excitation energies, it is also important to investigate the consequences of imposing various permutational symmetries on the elements of the final similarity transformed Hamiltonian $\hat{G}$ of Eq. (3.34), in the MR-EOM-T|T † |SXD approach. As mentioned above, the only elements of $\hat{G}$ which are not required in the final MRCI diagonalization step are the 4p (g_{cd}^{ab}) and 3p1h elements (g_{ic}^{ab} and g_{ab}^{ic}). For the remaining elements, we will consider two different types of permutational symmetries:

1. *Hermitization*:

$$\tilde{g}_q^p = \tilde{g}_p^q, \quad (3.40)$$

$$\tilde{g}_{rs}^{pq} = \tilde{g}_{pq}^{rs}, \quad (3.41)$$

2. *Vertex-symmetry*:

$$\tilde{g}_{rs}^{pq} = \tilde{g}_{ps}^{rq} = \tilde{g}_{rq}^{ps}. \quad (3.42)$$

Here we will use a tilde to distinguish the symmetrized elements from the original elements of $\hat{G}$.

The one-body elements g_j^i (hh block) and g_b^a (pp block) are respectively, Hermitized according to

$$\tilde{g}_j^i = \tilde{g}_i^j = \frac{1}{2}(g_j^i + g_i^j), \quad (3.43)$$

$$\tilde{g}_b^a = \tilde{g}_a^b = \frac{1}{2}(g_b^a + g_a^b). \quad (3.44)$$

Similarly, the two-body elements g_{kl}^{ij} (4h), g_{ba}^{ic} (2p2h exchange) and g_{jb}^{ia} (2p2h direct) are respectively, Hermitized as

$$\tilde{g}_{kl}^{ij} = \tilde{g}_{ij}^{kl} = \frac{1}{2}(g_{kl}^{ij} + g_{ij}^{kl}), \quad (3.45)$$

$$\tilde{g}_{bj}^{ia} = \tilde{g}_{ia}^{bj} = \frac{1}{2}(g_{bj}^{ia} + g_{ia}^{bj}), \quad (3.46)$$

$$\tilde{g}_{jb}^{ia} = \tilde{g}_{ia}^{jb} = \frac{1}{2}(g_{jb}^{ia} + g_{ia}^{jb}). \quad (3.47)$$

However, for the remaining elements, we proceed in a different manner. The satisfaction of Eq. (3.10) implies that $\bar{h}_{ij}^{ab} = 0$ and due to the second transformation of Eq. (3.30), we have that $\tilde{h}_{ab}^{ij} \approx 0$ and hence, we set the corresponding final elements of $\hat{G}$ to zero (*i.e.* $\tilde{g}_{ij}^{ab} = \tilde{g}_{ab}^{ij} = 0$). Also, due to the solution of Eq. (3.9), the final elements of the ph block g_i^a are small, while there are still many potentially sizeable elements in the hp block (g_a^i). The fact that the elements g_i^a are small, contributes to the effective decoupling of the CAS configurations from the 1h1p configurations in the final MRCI diagonalization. If we were to Hermitize these elements in the usual way, by averaging the small g_i^a elements with the considerably larger g_a^i elements (*i.e.* via $\frac{1}{2}(g_a^i + g_i^a)$), the resulting sizeable elements would lead to the destruction of this decoupling of the CAS configurations from the 1h1p configurations. Hence, to avoid this, we equate the g_a^i elements to the values of the g_i^a elements, that is,

$$\tilde{g}_a^i = \tilde{g}_i^a. \quad (3.48)$$

Moreover, the satisfaction of Eqs. (3.36), (3.37) and (3.38), respectively, implies that $g_{i'j'}^{aw} = 0$, $g_{xi'}^{aw} = 0$ and $g_{i'x}^{aw} = 0$, while the elements $g_{aw}^{i'j'}$, $g_{aw}^{xi'}$ and $g_{aw}^{i'x}$ are non-zero and likely large. The condition $g_{i'j'}^{aw} = 0$, leads to a decoupling of the CAS configurations from the 2h1p configurations in the final MRCI diagonalization, whereas the satisfaction of $g_{xi'}^{aw} = g_{i'x}^{aw} = 0$ contributes to the decoupling of the CAS configurations from the 1h1p configurations. In order to avoid disrupting this decoupling by mixing in the large $g_{aw}^{i'j'}$, $g_{aw}^{xi'}$ and $g_{aw}^{i'x}$ elements through the standard Hermitization procedure of the 3h1p elements (*i.e.* by averaging as $\frac{1}{2}(g_{ij}^{ak} + g_{ak}^{ij})$), we set $\tilde{g}_{ak}^{ij} = \tilde{g}_{ij}^{ak}$ or more explicitly,

$$\tilde{g}_{aw}^{i'j'} = \tilde{g}_{i'j'}^{aw} = 0, \quad (3.49)$$

$$\tilde{g}_{aw}^{xi'} = \tilde{g}_{xi'}^{aw} = 0, \quad (3.50)$$

$$\tilde{g}_{aw}^{i'x} = \tilde{g}_{i'x}^{aw} = 0, \quad (3.51)$$

$$\tilde{g}_{aw}^{xy} = \tilde{g}_{xy}^{aw}, \quad (3.52)$$

$$\tilde{g}_{ak'}^{ij} = \tilde{g}_{ij}^{ak'}. \quad (3.53)$$

Since the elements g_{xy}^{aw} and $g_{ij}^{ak'}$ do not vanish, the Hermitization of these elements according to Eqs. (3.52) and (3.53), respectively, is less justified and could be further investigated (*e.g.* one could compare Hermitization by averaging, as in Eqs. (3.45), (3.46), (3.47), with the current scheme adopted in Eqs. (3.52) and

(3.53)) . However, this has not been pursued in this work.

As mentioned above, in the implementation of the MR-EOM-T|T[†]|SXD method in the ORCA program package, the full (eightfold) permutational symmetries of the bare two-electron integrals are imposed on the final elements of the transformed Hamiltonian in Eq. (3.34). This signifies that in addition to Hermitization, we require that the final elements of the transformed Hamiltonian have vertex-symmetry (*i.e.* Eq. (3.42)). The vertex symmetrization proceeds as follows,

$$\tilde{g}_{rs}^{pq} = \frac{1}{4}(2g_{rs}^{pq} + g_{ps}^{rq} + g_{rq}^{ps}), \quad (3.54)$$

after the Hermitization of the elements has been imposed, according to the procedure outlined above. In this work, will study the effects of Hermitization and vertex-symmetrization on the calculation of excitation energies. More precisely, we will examine to what extent the calculated excitation energies (with no symmetrization) vary when the elements of the final transformed Hamiltonian are simply Hermitized and when they are both Hermitized and vertex-symmetrized.

The characteristics of the various MR-EOM schemes studied in chapter 6, appear in Table 3.1. The nomenclature used for each method, the various operators included in the similarity transformation(s) and the definition of the final MRCI diagonalization manifold are provided in Table 3.1. Furthermore, any additional characteristics which define a given method (*i.e.* exclusion of λ_2 terms or symmetrization of the final $\hat{G}$ elements) are also indicated in the table. Note that, as indicated in Table 3.1, we will also investigate the consequences of excluding the two-body cumulant from the defining equations, as well as the effects of employing different MRCI diagonalization manifolds. The purpose of investigating all of these variations is not to generate a plethora of methods. Rather we wish to gain an understanding of the role of these variations and arrive at a solid final methodology. We note that each of these approaches has been implemented in (a development version of) the ACES II [179] program package and that the working equations were derived and implemented with the use of the Automatic Program Generator (APG) [32]. Furthermore, the MR-EOM-T|T[†]|SXD-h-v approach of Table 3.1, has been implemented within the ORCA electronic structure package [24], using an automatic code generation system written in Python (*i.e.* described in detail in the following chapter) and equations derived with the use of the APG.

Table 3.1: The characteristics of the various MR-EOM schemes investigated in this thesis.

Method	Transformation(s) ^a	Diagonalization space	Additional characteristics
Bare H	none	CAS, 1h, 1p, 2h, 1h1p, 2h1p	
MR-EOM-T	$\hat{T}_1 + \hat{T}_2$	CAS, 1h, 1p, 2h, 1h1p, 2h1p	
MR-EOM-T S	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2$	CAS, 1h, 1p, 2h, 1h1p	
MR-EOM-T SXD	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T SXD-noG λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	- λ_2 terms excluded from all equations (except the projected singles equations)
MR-EOM-T SXD-no λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	- λ_2 terms excluded from the many-body amplitude equations
MR-EOM-T SXD-full	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h, 1h1p	
MR-EOM-TSXD	$\hat{T}_1 + \hat{T}_2 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T SXD U	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p	
MR-EOM-T SXD U-noG λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p	- λ_2 terms excluded from all equations (except the projected singles equations)
MR-EOM-T SXD U-no λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p	- λ_2 terms excluded from the many-body amplitude equations
MR-EOM-T SXD U-full	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p, 2h, 1h1p	
MR-EOM-T T [†] (S ₁ + S ₂)XD	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T T [†] (S ₁ + S ₂)XD-h	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	-Hermitization of $\hat{G}$ elements
MR-EOM-T T [†] SXD	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T T [†] SXD-h	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	-Hermitization of $\hat{G}$ elements
MR-EOM-T T [†] SXD-h-v	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	-Hermitization and vertex-symmetrization of $\hat{G}$ elements

^a As usual, we employ a vertical bar (|) to separate one transformation sequence from another.

Chapter 4

Automatic Code Generation in ORCA

4.1 Introduction

In general, the development of an efficient production-level implementation of a new method in electronic structure theory involves a sequence of three steps. In the first step, the algebraic equations, which define the approach, and consist of a series of tensor contractions, are derived either by employing diagrammatic techniques (*e.g.* see Ref. [61]) or through tedious manipulations of strings of second-quantized operators (*i.e.* normal ordering of the string of operators and application of the Generalized Wick's Theorem (GWT) [62]). In the second step, the equations must be reworked into an efficient format for the subsequent implementation. For example, the tensor multiplications are reordered so that the scaling of the computational cost is minimized and the equations are factorized, through the formation of reusable intermediate tensors, so as to reduce the pre-factor of the scaling. The algorithm by which the multiplication order is optimized, in a set of equations, is called strength reduction. In the final step, the resulting equations are translated into an efficient implementation, making use of the optimized BLAS (Basic Linear Algebra Subprograms) libraries [27, 28, 29, 30, 31] for matrix operations and ensuring that the ordering of loops and read/write statements minimizes cache misses (redundant I/O operations). There are also many other ways of optimizing the performance of the implemented code (*i.e.* loop transformations, parallelization, *etc.*). Due to the fact that these tasks are arduous and repetitive in nature, they are most certainly fallible and the process of tracking down errors in the resulting equations and code becomes extremely daunting and time-consuming. Furthermore, as the complexity of the method increases, each of these steps becomes progressively more laborious and hence, imposes severe limitations on the complexity of methods

that can be manually implemented.

Consequently, tools for the automation of these tasks have become essential for the development of new methodologies in electronic structure theory. The first application of automatic expression generation dates back to the early seventies, when Paldus and Wong [180, 181] developed a program for the generation of all distinct contributions (Feynman diagrams of the Hugenholtz type [182]) to n^{th} order Many-Body Perturbation Theory (MBPT- n). In the time since the publication of this pioneering work, there has been much progress in the development of software for the automation of expression derivation and manipulation and code generation in quantum chemistry. The SQSYM (Second Quantization SYmbol Manipulator) program of Janssen and Schaefer [183] is the earliest example of a fully functional automatic implementation system. In addition to being able to derive equations, through manipulation of second quantized operators, it was also capable of performing strength reduction and identifying reusable intermediates within a series of tensor contractions. The equations thus produced, could then be interpreted by a Fortran program called CORR [183]. The SQSYM and CORR programs were employed to derive and implement two different high-spin open-shell CCSD methods, which were studied in detail in Ref. [183]. The first incarnation of the Automatic Program Generator (APG), reported by Nooijen and Lotrich, was developed for the purpose of exploring novel open-shell and multireference coupled-cluster methodologies [184]. This software made extensive use of the GWT for expression generation, had strength reduction and rudimentary factorization capabilities and was interfaced to a set of optimized subroutines for computing binary contractions in the ACES II program package [179]. It was used to implement and evaluate an open-shell CCSD method for doublet states, involving two sequential similarity transformations of the Hamiltonian [184], a Brueckner based generalization of CCSD that mimics higher order correlation effects via inclusion of special two-body operators in the wavefunction [185], an extension of the Similarity-Transformed Equation of Motion (STEOM) coupled-cluster method (extended-STEOM) [186] and a state-selective multireference coupled-cluster approach [187]. One ingenious development is that of Kállay and Surján [188], in which the diagrams appearing in coupled-cluster theory are represented as a 13-fold string of integers and techniques from string-based configuration interaction theory are employed to evaluate contractions. The derivation of equations, strength reduction and factorization are all achieved using diagrammatic techniques. The algorithm is completely general, in that it can be applied to coupled-cluster theory truncated to any arbitrary excitation order [188]. The Tensor Contraction Engine (TCE), developed by Hirata [189] and others [190], is another example of an advanced implementation system. It makes use of the GWT for the derivation of equations and strength reduction and factorization are treated as a coupled optimization problem. Furthermore, much work has been dedicated to the optimization of the performance of the generated code in terms of memory-minimization, space-time tradeoffs and data partitioning (*cf.* Ref. [191] and references therein for more details). The TCE has been employed to implement fully parallelized

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programs for configuration-interaction, many-body perturbation theory and coupled-cluster methods for ground and excited states [191]. A comprehensive review of these and other developments is provided within Ref. [191].

Some more recent developments include the work of Hanrath and Engels-Putzka, in which a genetic algorithm is used to solve the coupled strength reduction and factorization problem [192]. The automatic implementation program of Datta and Gauss is capable of deriving spin-adapted coupled-cluster methods, using the contraction topology of equations derived from Wick’s theorem [193]. Namely, each contribution in the equations is represented as a non-antisymmetric (spin-free) Goldstone diagram [194], which affords certain simplifications for identifying identical terms and common intermediates in the factorization algorithm [193]. It was used to implement the Combinatorial Open-Shell Coupled-Cluster (COSCC) approach [195, 196] for doublets. Another recent development by Kong [32], which constitutes the second incarnation of the APG, is based on the GWT [62] and the Kutzelnigg-Mukherjee (KM) concept of normal ordering, with respect to a multi-configurational reference state [151, 152, 153]. It has been developed for the purposes of deriving working equations and generating code for novel multireference coupled-cluster theories in the ACES II program package [179]. The implementation module uses the same optimized subroutines as the APG of Nooijen and Lotrich [184]. The equation generation module currently performs strength reduction and ensures that the formation of three-body intermediate quantities (6th rank tensors) are avoided, but does not have any factorization capabilities at this time. The APG has been used for the implementation of a multireference State-Selective Equation of Motion Coupled-Cluster method (SS-EOM-CC) [197] and the Multireference Equation of Motion Coupled-Cluster (MR-EOM-CC) method [177, 21, 22, 23].

The code generator, described in this chapter, has been written for the express purpose of generating code in the ORCA electronic structure package [24]. It is written in the Python programming language [25] and has been interfaced with the equation generator in the APG [32]. However, with small modifications, equations can be read from any source and transferred into an internal storage format. It is assumed that the equations have been written in strength reduced format (see section 4.2.1 for a more detailed discussion). As mentioned previously, the equation generator within the APG ensures that the equations are written in this format. We currently do not perform any global factorization of the tensorial equations. Each term is calculated explicitly and there is no formation of reusable intermediate quantities. This would be a major source for improvement in the code, as it would significantly reduce the pre-factor associated with the computational scaling. The implementation of coupled-pair methods (*e.g.* CCSD) within ORCA [24], is based on the Self-Consistent Electron-Pairs (SCEP) formalism of Meyer [198] and coworkers [199]. In this formalism, two-body quantities (4-index tensors), with at least two occupied indices, are stored as

matrices for each pair of occupied orbitals (*vide infra*) [198, 199]. Otherwise, the quantities are still stored as matrices, but the pair list now includes one or two virtual orbital labels. In the generated ORCA code, we follow the same storage conventions as in the SCEP formalism, as will be discussed in detail in section 4.3. Let us proceed with a discussion of the tensorial equations that are processed by the code generator and the general structure of the generated code in ORCA, before exposing the details of the code generator itself.

4.2 Overview of the General Structure of the Equations and Generated Code

4.2.1 Structure of the Equations Defining MR-EOM

As an example of the tensor equations that can be treated by the code generator described herein, let us consider those that arise in the Multireference Equation of Motion Coupled-Cluster (MR-EOM-CC) theory [21, 22, 23, 177], discussed in the previous chapter. It is important to recall that the MR-EOM- $T|T^\dagger|$ SXD-h-v approach of Table 3.1 has been implemented in the ORCA program package [24], using the code generator described herein. We first solve the state-averaged CASSCF problem to obtain the zeroth order (mean-field) multi-determinantal wavefunction and energy. The optimized molecular orbitals from the CASSCF, can be partitioned into three types: inactive (doubly-occupied), active (partially occupied) and virtual (unoccupied). We will also use the term occupied to denote orbitals that are either inactive or active. Furthermore, we will often refer to the orbital types by their hole-particle character. Namely, in the language of second quantization, the occupied orbitals are often referred to as “hole” states and the virtual orbitals, as “particle” states. In Table 4.1, we have summarized the various types of *spatial* molecular orbitals, along with their hole-particle types and the indices that are used for their representation. In the following discussion, we will use i, j, k, l to denote occupied (inactive + active) orbitals, w, x, y, z to denote active orbitals, a, b, c, d to denote virtual orbitals and p, q, r, s to denote general orbitals.

From the state-averaged CASSCF calculation, we also obtain the one- and two-particle density matrices over the active space, Γ_x^w and Γ_{yz}^{wx} , respectively. The one-particle density matrix is already diagonal since we choose to work in the natural orbital basis and the diagonal elements are the occupation

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Table 4.1: The various types of spatial molecular orbitals, their hole-particle character and the labels that are used to represent them.

Molecular Orbital Type	Hole-Particle Type	Labels Used ¹
inactive	hole (h)	i, j, k, l or i_1, i_2, i_3, i_4
occupied (inactive + active)	hole (h)	i, j, k, l or i_1, i_2, i_3, i_4
active	hole (h) ²	w, x, y, z or m_1, m_2, m_3, m_4
virtual	particle (p)	a, b, c, d or a_1, a_2, a_3, a_4

¹ The labels i, j, k, l or i_1, i_2, i_3, i_4 are most often reserved for the general occupied orbitals, but might be used to describe inactive orbitals where it is explicitly specified (or in any discussion concerning single-reference CC equations, where there are no active labels).

² We will sometimes refer to an active labels as a hole (h) or define its type as ‘a’ (for active), to distinguish it from the inactive labels in the context of the code generator.

numbers of the corresponding active orbitals. Hence, we form an occupation number vector n_i , where,

$$n_i = \begin{cases} 2 & \text{if } i \in \text{inactive (i.e. doubly occupied)} \\ \Gamma_i^i & \text{if } i \in \text{active} \end{cases}. \quad (4.1)$$

From the occupation numbers and the two-particle density matrix, we form the spin-free cumulant,

$$\Lambda_{yz}^{wx} = 2 \Gamma_{yz}^{wx} - \delta_y^w \delta_z^x n_w n_x + \frac{1}{2} \delta_z^w \delta_y^x n_w n_x, \quad (4.2)$$

in the active space, in which δ_x^w is the Kronecker delta. The spin-orbital cumulant λ_{yz}^{wx} , which is used in the MR-EOM equations, can then be computed as,

$$\lambda_{yz}^{wx} = \frac{1}{3} \Lambda_{yz}^{wx} + \frac{1}{6} \Lambda_{zy}^{wx}. \quad (4.3)$$

From the CASSCF calculation, we also obtain the Fock matrix and two-electron integrals in the atomic orbital basis, as well as a set coefficients to transform between the atomic orbital and molecular orbital bases. Using these coefficients in a subsequent transformation step, we obtain the two-electron integrals in the molecular orbital basis,

$$V_{rs}^{pq} = \langle pq | rs \rangle = \int \phi_p^*(\mathbf{r}_1) \phi_q^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (4.4)$$

in which the ϕ_p are real spatial molecular orbitals and r_{12}^{-1} is the electrostatic repulsion operator which appears in the molecular electronic Hamiltonian. We also obtain the Fock matrix in the molecular orbital basis as,

$$F_q^p = h_q^p + \frac{1}{2} \sum_i n_i \left(2 V_{qi}^{pi} - V_{iq}^{pi} \right), \quad (4.5)$$

in which $h_q^p = \langle p | \hat{h} | q \rangle = \int \phi_p^*(\mathbf{r}_1) \hat{h} \phi_r(\mathbf{r}_1) d\mathbf{r}_1$ is a one electron integral. The one-electron operator $\hat{h}$ itself, is defined as,

$$\hat{h} = -\frac{1}{2} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}}, \quad (4.6)$$

in which ∇^2 is the Laplacian operator and the second term comprises the attraction potential felt by the electron, due to the nucleus α (*i.e.* Z_{α} is the electrostatic charge on nucleus α). We then have all of the quantities required for the subsequent MR-EOM calculation.

The examples that are considered in this chapter will be mainly concerned with the equations defining single-reference CCSD [87] (see section 2.3.3 for a detailed discussion of single-reference coupled-cluster theory) and the equations defining the first transformation in MR-EOM [21, 22, 23, 177]. In a similar fashion as CCSD, the first similarity transformation of the molecular electronic Hamiltonian in MR-EOM is defined as,

$$\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}, \quad (4.7)$$

in which the cluster operator $\hat{T}$ includes both single $\hat{T}_1$, and double excitations $\hat{T}_2$ out of the reference state,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a \hat{E}_i^a + \frac{1}{2} \sum_{i,j,a,b} t_{ij}^{ab} \hat{E}_{ij}^{ab}, \quad (4.8)$$

where once again, $\hat{E}_i^a = \hat{a}_{a\alpha}^\dagger \hat{a}_{i\alpha} + \hat{a}_{a\beta}^\dagger \hat{a}_{i\beta}$ and $\hat{E}_{ij}^{ab} = \hat{E}_i^a \hat{E}_j^b$ (*N.B.* $\hat{E}_{rs}^{pq} = \hat{E}_r^p \hat{E}_s^q - \delta_r^q \hat{E}_s^p$ for general orbitals p, q, r, s) are the spin-free excitation operators (see Eqs. (2.42) and (2.43) in section 2.2.2). We wish to solve for the single and double excitation amplitudes, t_i^a and t_{ij}^{ab} , respectively. In CCSD, this is achieved by projecting the similarity transformed Schrödinger equation onto the singly and doubly excited determinants, respectively. However, in MR-EOM the equations defining the amplitudes are different. Making use of the GWT [62], the similarity transformed Hamiltonian of Eq. (4.7) can be expanded as,

$$\hat{\bar{H}} = \bar{h}_0 + \sum_{p,q} \bar{h}_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} \bar{h}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots, \quad (4.9)$$

in which the curly braces $\{ \}$ indicate KM normal ordering of the second-quantized operators, with respect to the multi-configurational reference state (*i.e.* the CASSCF wavefunction). In single-reference CCSD,

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the projected residuals are equivalent to certain elements of the corresponding similarity transformed Hamiltonian, namely, $R_i^a = \langle \Phi_i^a | \widehat{H} | \Psi_0 \rangle = \bar{h}_i^a$ and $R_{ij}^{ab} = \langle \Phi_{ij}^{ab} | \widehat{H} | \Psi_0 \rangle = \bar{h}_{ij}^{ab}$. However, in MR-EOM the projected equations are only equivalent to the corresponding $\bar{h}$ elements when the occupied labels correspond to (doubly occupied) inactive core orbitals (*e.g.* the elements $\bar{h}_i^a$ and $\bar{h}_{i'j'}^{ab}$ are equivalent to the corresponding elements of the projected singles and doubles residual equations, respectively). In MR-EOM, the equation defining the singles amplitudes t_i^a , is taken to be the projected equation,

$$R_i^a = \sum_{\mathbf{m}} w_{\mathbf{m}} \langle \Psi_{\mathbf{m}} | \widehat{E}_a^i \widehat{H} | \Psi_{\mathbf{m}} \rangle = 0, \quad (4.10)$$

in which $|\Psi_{\mathbf{m}}\rangle$ is the $\mathbf{m}^{\text{th}}$ state appearing in the state-averaged CAS with a weight of $w_{\mathbf{m}}$. The equation defining the doubles amplitudes t_{ij}^{ab} is taken to be equal to the set of $\bar{h}_{ij}^{ab}$ elements,

$$R_{ij}^{ab} = \bar{h}_{ij}^{ab} = 0. \quad (4.11)$$

In order to expose the types of tensor contractions arising in these equations, we provide the full set of R_{ij}^{ab} equations defined by Eq. (4.11),

$$\begin{aligned} R_{ij}^{ab} = \bar{h}_{ij}^{ab} = & \left(1 + \widehat{P}_{ij}^{ab}\right) \left(\frac{1}{2} V_{ij}^{ab} + F_c^a t_{ji}^{bc} + V_{cj}^{ab} t_i^c + \frac{1}{2} V_{cd}^{ab} t_{ij}^{cd} + \frac{1}{2} V_{cd}^{ab} t_i^c t_j^d - V_{ij}^{ak} t_k^b - F_i^k t_{jk}^{ba} \right. \\ & - \frac{1}{2} V_{ij}^{kl} t_{kl}^{ab} - F_c^k t_{ji}^{bc} t_k^a - V_{cj}^{ak} t_i^c t_k^b - V_{ci}^{ka} t_j^c t_k^b - V_{cd}^{ak} t_{ij}^{cd} t_k^b - F_c^k t_i^c t_{jk}^{ba} - V_{cj}^{kl} t_i^c t_{kl}^{ab} \\ & - \frac{1}{2} V_{cd}^{kl} t_{ij}^{cd} t_{kl}^{ab} + \frac{1}{2} V_{ij}^{kl} t_k^a t_l^b - \frac{1}{2} V_{ci}^{ak} t_{jk}^{bc} n_k + V_{ci}^{ka} t_{jk}^{bc} n_k - \frac{1}{2} V_{cj}^{ak} t_{ki}^{bc} n_k - \frac{1}{2} V_{ci}^{ka} t_{kj}^{bc} n_k \\ & - \frac{1}{2} V_{cd}^{ak} t_k^c t_{ji}^{bd} n_k + V_{cd}^{ak} t_k^d t_{ji}^{bc} n_k + V_{cd}^{ak} t_i^c t_{jk}^{bd} n_k - \frac{1}{2} V_{cd}^{ak} t_i^d t_{jk}^{bc} n_k - \frac{1}{2} V_{cd}^{ak} t_i^c t_{kj}^{bd} n_k \\ & - \frac{1}{2} V_{cd}^{ak} t_j^d t_{ki}^{bc} n_k + \frac{1}{4} V_{cd}^{kl} t_{kl}^{ac} t_{ji}^{bd} n_k n_l - \frac{1}{2} V_{cd}^{kl} t_{lk}^{ac} t_{ji}^{bd} n_k n_l - \frac{1}{2} V_{cd}^{kl} t_{ki}^{ac} t_{jl}^{bd} n_k n_l \\ & + \frac{1}{2} V_{cd}^{kl} t_{ik}^{ac} t_{jl}^{bd} n_k n_l + \frac{1}{4} V_{cd}^{kl} t_{jl}^{bc} t_{ki}^{ad} n_k n_l - \frac{1}{4} V_{cd}^{kl} t_{il}^{ac} t_{jk}^{bd} n_k n_l + \frac{1}{8} V_{cd}^{kl} t_{ki}^{ac} t_{lj}^{bd} n_k n_l \\ & + \frac{1}{8} V_{cd}^{kl} t_{lj}^{ac} t_{ki}^{bd} n_k n_l + \frac{1}{2} V_{ij}^{kl} t_{lk}^{ba} n_l + \frac{1}{2} V_{ci}^{kl} t_{jl}^{bc} t_k^a n_l - V_{ci}^{kl} t_{jk}^{bc} t_l^a n_k + \frac{1}{2} V_{cj}^{kl} t_{li}^{bc} t_k^a n_l \\ & + \frac{1}{2} V_{ci}^{kl} t_{kj}^{bc} t_l^a n_k + \frac{1}{2} V_{cj}^{kl} t_i^c t_{lk}^{ba} n_l + \frac{1}{2} V_{cj}^{kl} t_i^c t_{kl}^{ab} n_k + \frac{1}{2} V_{ci}^{kl} t_l^c t_{jk}^{ba} n_l - V_{ci}^{kl} t_k^c t_{jl}^{ba} n_k \\ & + \frac{1}{2} V_{cd}^{kl} t_{ij}^{cd} t_{lk}^{ba} n_l + \frac{1}{2} V_{cd}^{kl} t_{li}^{cd} t_{jk}^{ba} n_l - V_{cd}^{kl} t_{il}^{cd} t_{jk}^{ba} n_l + V_{cd}^{wx} \lambda_{wx}^{yz} t_{yz}^{ac} t_{ji}^{bd} - 2 V_{cd}^{wx} \lambda_{wx}^{yz} t_{zy}^{ac} t_{ji}^{bd} \\ & - 2 V_{cd}^{wx} \lambda_{wx}^{yz} t_{yi}^{ac} t_{jz}^{bd} + V_{cd}^{wx} \lambda_{wx}^{yz} t_{jz}^{bc} t_{yi}^{ad} + 2 V_{cd}^{wx} \lambda_{wx}^{yz} t_{iy}^{ac} t_{jz}^{bd} - V_{cd}^{wx} \lambda_{wx}^{yz} t_{iz}^{ac} t_{jy}^{bd} \\ & \left. + \frac{1}{2} V_{cd}^{wx} \lambda_{wx}^{yz} t_{zi}^{ac} t_{yj}^{bd} + \frac{1}{2} V_{cd}^{wx} \lambda_{wx}^{yz} t_{zj}^{ac} t_{yi}^{bd} \right). \quad (4.12) \end{aligned}$$

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These equations were produced using the equation generation module of the Automatic Program Generator (APG) [32]. In Eq. (4.12), we make use of the Einstein summation convention, such that repeated indices in the equations are summed over without explicit inclusion of a summation operator. As one can see, these equations consist of a series of tensor contractions that are added to a target quantity, the residual R_{ij}^{ab} in this case. We will often refer to indices that are summed over as free (*i.e.* the indices k, l, c, d, w, x, y, z in Eq. (4.12)) and the indices that are not contracted and which appear on the target, as fixed indices (*i.e.* the indices i, j, a, b in Eq. (4.12)). It is important to note that, in the terms containing occupation numbers, an occupied label can appear more than twice. For example, in the term $V_{ci}^{ka} t_{jk}^{bc} n_k$, the label k is contracted in $V_{ci}^{ka} t_{jk}^{bc}$, but it also appears in the occupation number vector.

The operator $\hat{P}_{ij}^{ab}$, appearing in Eq. (4.12), is a permutation operator which swaps the fixed labels i and j and a and b , simultaneously. For example, consider the term $-V_{cj}^{ak} t_i^c t_k^b$, in Eq. (4.12), the action of this permutation operator on this term is,

$$\hat{P}_{ij}^{ab} (-V_{cj}^{ak} t_i^c t_k^b) = -V_{ci}^{bk} t_j^c t_k^a. \quad (4.13)$$

The permutation operator is present in Eq. (4.12) in order to preserve the inherent vertex symmetry of this residual equation and to ensure that the resulting doubles amplitudes, that satisfy the residual condition $R_{ij}^{ab} = 0$, also possess this vertex symmetry. The term vertex symmetry refers to the permutational symmetries $R_{ij}^{ab} = R_{ji}^{ba}$ and $t_{ij}^{ab} = t_{ji}^{ba}$ of the doubles residuals and amplitudes, respectively. In the generated code, the doubles residual equations $R_{ij}^{ab} = 0$, for the t_{ij}^{ab} amplitudes (*i.e.* either in CCSD [87] or MR-EOM [177, 21, 22, 23]), are vertex-symmetrized on a term by term basis, since we loop over the full ranges of i, j, a and b . For example, let X_{ij}^{ab} denote one of the contributions appearing in Eq. (4.12), then in a single loop over i, j, a and b , we would perform the vertex symmetrization as,

$$R_{ij}^{ab} \leftarrow (1 + \hat{P}_{ij}^{ab}) X_{ij}^{ab} = X_{ij}^{ab} + X_{ji}^{ab}. \quad (4.14)$$

Another approach that is often used, is to expand the symmetrized residual $R_{ij}^{ab} = (1 + \hat{P}_{ij}^{ab}) \tilde{R}_{ij}^{ab}$ explicitly, where $\tilde{R}_{ij}^{ab}$ includes all the contributions to the right of $(1 + \hat{P}_{ij}^{ab})$ in Eq. (4.12), and use the loop restriction $i \geq j$. In both cases, one only needs to store the final R_{ij}^{ab} residual and t_{ij}^{ab} amplitudes for $i \geq j$.

The two-body cumulants/density matrices and two-electron integrals possess vertex symmetry (*i.e.* $\lambda_{yz}^{wx} = \lambda_{zy}^{xw}$ and $V_{rs}^{pq} = \langle pq|rs \rangle = \langle qp|sr \rangle = V_{sr}^{qp}$). The Fock matrix and one-electron Hamiltonian are Hermitian and hence they are symmetric matrices, *i.e.* $h_q^p = h_p^q$ and $F_q^p = F_p^q$. The two-electron integrals are also Hermitian, such that,

$$V_{rs}^{pq} = \langle pq|rs \rangle = \langle rs|pq \rangle = V_{pq}^{rs}, \quad (4.15)$$

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and combining the Hermiticity with the vertex symmetry, we have that,

$$V_{rs}^{pq} = \langle pq|rs \rangle = \langle sr|qp \rangle = V_{qp}^{sr}, \quad (4.16)$$

For the case of real orbitals, the integral is unchanged if we permute p and r or q and s [200]. In combination with Eqs. (4.15) and (4.16), this leads to the following eightfold permutational symmetries for the two electron integrals [200],

$$\langle pq|rs \rangle = \langle qp|sr \rangle = \langle rs|pq \rangle = \langle sr|qp \rangle = \langle rq|ps \rangle = \langle sp|qr \rangle = \langle ps|rq \rangle = \langle qr|sp \rangle. \quad (4.17)$$

In the code generator, we will use a different notational convention for two-electron integrals than the Dirac notation used in Eqs. (4.15), (4.16) and (4.17). In this notation, referred to as Mulliken notation, two-electron integrals over spatial orbitals are written as,

$$V_{qs}^{pr} = \langle pq|rs \rangle = \int \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \frac{1}{r_{12}} \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (4.18)$$

whereas in Dirac notation, the same integrals are written as [59],

$$V_{qs}^{pr} = \langle pr|qs \rangle = \int \phi_p^*(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_q(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (4.19)$$

Hence, it is clear that the relationship between the two notational conventions is simply $\langle pq|rs \rangle = \langle pr|qs \rangle$. The latter relation also applies to “dressed” integrals or intermediates (*e.g.* the two-body elements of the similarity transformed Hamiltonian $\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$) if one wishes to convert between the two notational conventions. Our reasons for employing Mulliken notation are that it is ubiquitously used in ORCA [24] and it allows us to easily identify where symmetric data structures for storage should be employed (*i.e.* triangular storage). In Mulliken notation, the expression of Eq. (4.17) becomes,

$$\langle pq|rs \rangle = \langle qp|rs \rangle = \langle pq|sr \rangle = \langle qp|sr \rangle = \langle sr|pq \rangle = \langle rs|qp \rangle = \langle sr|qp \rangle = \langle rs|pq \rangle, \quad (4.20)$$

for general and real spatial orbitals p, q, r, s [200]. It is important to note that we only store the two-electron integrals $\langle ia|jb \rangle$, $\langle ij|ab \rangle$, $\langle ik|jl \rangle$ for $i \geq j$ and the integrals $\langle ac|bd \rangle$ for $a \geq b$, as a result of the symmetries inherent in Eq. (4.20). The symmetries of Eq. (4.20) are not present in the two-body elements of a similarity transformed Hamiltonian $\hat{\bar{H}}$, which only exhibit vertex symmetry, $\bar{h}_{rs}^{pq} = \bar{h}_{sr}^{qp}$.

One important point to discuss is how the non-linear terms, appearing in equations like Eq. (4.12), are treated in the code. As an example, let us consider the contribution $\frac{1}{2} V_{cd}^{kl} t_{lk}^{ac} t_{ji}^{bd} n_k n_l$ in Eq. (4.12). The

computational cost of computing this term in one loop construct would be $n_o^4 n_v^4$ where n_o is the number of occupied orbitals and n_v , the number of virtual orbitals. Another naive way of computing this contribution, would be to first form the three-body intermediate quantity $W_{cji}^{klb} = \sum_d V_{cd}^{kl} t_{ji}^{bd}$ with a computational cost of $n_o^4 n_v^3$ and a cost of $n_o^4 n_v^2$ for the storage of this three-body intermediate on disk. Then in a second loop construct, we would add the contribution $\frac{1}{2} \sum_{k,l,c} W_{cji}^{klb} t_{lk}^{ac} n_k n_l$ to the residual with a computational cost of $n_o^4 n_v^3$. The most cost effective way to proceed is to form the two-body intermediate $W_d^a = \sum_{k,l,c} V_{cd}^{kl} t_{lk}^{ac}$ with a computational cost of $n_o^2 n_v^3$ and a storage cost of n_v^2 . Then in another loop construct, we would add the contribution $\frac{1}{2} \sum_d W_d^a t_{ji}^{bd}$ to the residual at a computational cost of $n_o^2 n_v^3$. Hence, it is evident that the order with which the contractions are performed (*i.e.* the multiplication order) is extremely important in order to achieve an optimal scaling of the computational cost. As mentioned previously, this strength reduction has been implemented in the APG and the equations produced on output are written such that the ordering of the multiplications, in each non-linear term, optimizes the computational scaling of the cost for the given term [32]. Furthermore, the algorithm in the APG also avoids the formation of any three-body intermediates [32]. The strength reduction thus, guarantees that the generated code will have the same asymptotic scaling as a hand-coded implementation (*e.g.* CCSD (and MR-EOM) exhibits $\mathcal{O}(n_o^2 n_v^4)$ asymptotic scaling of the computational cost).

4.2.2 A Brief Description of the Data Structures in ORCA and the Generated Code

Before proceeding with a detailed description of the various aspects of the code generator, it will be useful to discuss some of the data structures defined within the ORCA program [24] and briefly outline the structure of the generated code. In ORCA, there is a special class to deal with matrices and operations on matrices. For matrices of real numbers, the **TRMatrix** class is used to represent matrices as linear arrays (vectorized) and for symmetric matrices, the **TRMatrixSym** class can be employed to store only the lower triangle of the matrix [24]. An analogous class, **TRVector**, also exists for vectors and there are many functions implemented to deal with matrix and vector manipulations and operations [24]. For two-body quantities, such as the two-electron integrals and $\hat{H}$ elements, are stored as instances of the **TMatrixContainer** class in ORCA. A matrix container is an array of matrices from which each of the matrices in the container can be accessed by providing a pair of addressing indices. Additionally, there is a special class, **TMDCIState**, that is used for the matrix containers of residuals and amplitudes, which keeps track of pairs of occupied indices and defines special data structures (*e.g.* member functions GetSingles, SetSingles and AddSingles) for reading and writing singles amplitudes from disk. Furthermore, in a **TMDCIState** container, the doubles residuals/amplitudes are only stored for $i \geq j$, since these quantities

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have vertex symmetry (*i.e.* $R_{ij}^{ab} = R_{ji}^{ba}$ and $t_{ij}^{ab} = t_{ji}^{ba}$). A complete list of the data structures that appear in the generated code is provided in Table 4.2. In the analysis of the timings, we also make use of a small built-in routine `GetTime()`, which extracts the current runtime of a calculation in seconds [24].

Table 4.2: The various ORCA data structures appearing in the generated code.

Class	Description	Attributes or Member Functions Used in the Code Generator
TRMatrix	class for real matrices	- <code>NewMat(r,c)</code>: Initialize a new TRMatrix instance with <code>r</code> rows and <code>c</code> columns. - <code>DelMat()</code>: Delete the TRMatrix instance.
TRMatrixSym	class for real symmetric matrices	- <code>NewMat(r,c)</code>: Initialize a new TRMatrixSym instance with <code>r</code> rows and <code>c</code> columns. - <code>DelMat()</code>: Delete the TRMatrixSym instance.
TRVector	class for real vectors	- <code>NewVec(N)</code>: Initialize a new TRVector instance with <code>N</code> elements. - <code>DelVec()</code>: Delete the TRVector instance.
DMDCIINP	contains data from the input file	- <code>GetMOSpaces()</code>: Get a pointer to the array of orbital index ranges. - <code>UpdateTime(index,tm)</code>: Update the element of the timing array, corresponding to <code>index</code>, with the time <code>tm</code>.
TOrcaInfo	general calculation information	- <code>BaseName</code>: Get the name of the input file, excluding the file extension.
TMatrixContainer	class for storage of two-body quantities as matrix containers	- <code>GetMatrix(p,q,M)</code>: Get the TRMatrix <code>M</code> from the container which corresponds to address labels <code>p</code> and <code>q</code>. - <code>SetMatrix(p,q,M)</code>: Set the TRMatrix <code>M</code> to the container for the address labels <code>p</code> and <code>q</code>. - <code>SetFileName(name)</code>: Set the matrix container file name to the string <code>name</code>. - <code>SetData(cut,type,comp,disk)</code>: Set the data storage options, where elements smaller than <code>cut</code> are not stored, <code>type</code> indicates the data type of the elements (<i>e.g.</i> <code>double</code>), <code>comp</code> is a flag to indicate whether or not the data is compressed and <code>disk</code> is a flag to indicate whether the matrix container should be stored on disk or in core memory. - <code>SetMaxDim(Np,Nq)</code>: Set the maximum dimensions of the container - <code>OpenFileRead()</code>: Open the matrix container file for reading. - <code>OpenFileWrite()</code>: Open the matrix container file for writing. - <code>CloseFileRead()</code>: Close the matrix container file for reading. - <code>CloseFileWrite()</code>: Close the matrix container file for writing. - <code>RemoveFiles()</code>: Delete the matrix container file.
TMDCIState	special class for the storage of amplitudes and residuals	- <code>GetSingles(M1)</code>: Get the singles amplitudes/residual TRMatrix <code>M1</code>. - <code>SetSingles(M1)</code>: Set the singles amplitudes/residual TRMatrix <code>M1</code>. - <code>GetT()</code>: Get a pointer to the TMatrixContainer for the doubles amplitudes/residual. - <code>GetInfo()</code>: Get a pointer to the DMDCIINP instance.
TMDCIContainer	class used for the organization of two-electron integral containers	- <code>GetIKJL()</code>, <code>GetIKJA()</code>, <code>GetIJAB()</code>, <code>GetIAJB()</code>, <code>GetIBAC()</code>: Get a pointer to the TMatrixContainer corresponding to the $(ik jl)$, $(ik ja)$, $(ij ab)$, $(ia jb)$ and $(ib ac)$ integrals, respectively.

In order to give a brief overview of the structure of the generated code, we refer the reader to

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appendix A.1, where we have produced some C++ code for several terms appearing in Eq. (4.12). Here, we use the notation i_1, i_2, i_3, i_4 for occupied orbitals and a_1, a_2, a_3, a_4 for virtual orbitals. We note that by default, 2p2h integrals, as well as all the amplitudes (*i.e.* $\hat{T}$ and $\hat{S}$) and corresponding residuals are kept in core memory, given that enough memory is available to accommodate these quantities in a given calculation. For each target quantity that we wish to compute, the code generator produces a function in C++, which is written to an output file with the extension .cpp. In this case, the target is the MR-EOM residual $R_{i_1 i_2}^{a_1 a_2}$ of Eq. (4.12) and the function is appropriately named `Calc_R2_example`. In lines 1-30 of Example Code A.1, several libraries are imported into the file and in lines 32-38, we declare the function `Calc_R2_example` and its input parameters. Namely, the parameters consist of the **TOrcaInfo** instance `DAT`, the **TMDCIState** instances `STATE` and `SIGMA` for the amplitudes and residuals, respectively, the **TMDCIContainer** instance `MOINTS` for the two-electron integrals, the two-particle cumulant `Lambda_so` as a 4-dimensional array of doubles, the occupation number vector `n` as a **TRVector** and the Fock Matrix `FT` as a **TRMatrixSym**. In line 44, we get a pointer to the **DMDCIINP** instance `INF` and in line 45, the array `MOSpaces` of orbital index ranges is extracted from `INF`. In lines 46-51, the various orbital index ranges are extracted from the `MOSpaces` array and the dimensions of the various orbital spaces are defined in lines 52-54. The pointers to the **TMatrixContainer** files for the $(ib|ac)$ and $(ia|jb)$ integrals, respectively, are obtained from `MOINTS` in lines 56 and 57. The various indices are declared in lines 58-61. We then declare various **TRMatrix** instances in lines 62-66 (see Table 4.3 for a description of these quantities). For the simple example that will be considered here, we will use `t2_i2i1` for the amplitudes $t_{i_2 i_1}^{a_2 a_3}$ obtained from the amplitude matrix container for a given i_1 and i_2 . In line 68, we obtain the pointer to the amplitude **TMatrixContainer** file from the **TMDCIState** instance `STATE` and in lines 70-71, the singles amplitudes are extracted from `STATE`. The **TRMatrix** for the residuals is declared in line 73 and a pointer to the residual **TMatrixContainer** file is extracted from the **TMDCIState** instance `SIGMA` in line 74. Finally, in lines 76-77, the amplitude file is opened for reading.

We will consider the generated code of Example Code A.2, in section A.1.2 of appendix A, for the calculation of the second term, $F_{a_3}^{a_1} t_{i_2 i_1}^{a_2 a_3}$, in Eq. (4.12). In lines 1-3, we simply print a comment indicating the contribution which is being computed. We extract the current runtime `tm` in line 5 and proceed to loop over the indices `i1` and `i2` in lines 7-11. The index offsets `i1_0` and `i2_0` are not needed in this particular term, but they are always computed by default for each loop for the time being. The **TRMatrix** `Rili2`, corresponding to the residual $R_{i_1 i_2}^{a_1 a_2}$, is then retrieved from the residual **TMatrixContainer** file for the given addressing labels `i1` and `i2`, in lines 13-17. Since the residual is only stored when values of the first addressing label are larger or equal to the second, is symmetrized on a term by term basis and the loops over run over the full ranges (*i.e.* no triangular loops), as discussed above, we always read the residual with the largest label as the first address index and the smallest as the second. This is achieved by making use of

the `imax` and `imin` functions defined within ORCA [24]. Namely, the function `imax(i,j)` returns `i` if `i > j` and returns `j` otherwise. Conversely, the function `imin(i,j)` returns `i` if `i < j` and returns `j` otherwise. In lines 19-20, we retrieve the current values of the $t_{i_2 i_1}^{a_2 a_3}$ amplitudes from the amplitude **TMatrixContainer** file, in a similar fashion, but transpose the matrix if `i1 > i2` (*i.e.* $t_{i_2 i_1}^{a_2 a_3} = t_{i_1 i_2}^{a_3 a_2}$) since the amplitudes from the last iteration are vertex-symmetric. We then loop over `a1`, `a2` and `a3`, forming the appropriate offsets, in lines 23-30 and calculate the contribution `FT(a3,a1)*t2_i2i1(a2_0,a3_0)` to the residual in lines 32-41. Notice the presence of the **if** statements that are employed to properly perform the symmetrization of the contribution to the residual. Specifically, when `i1 > i2` (lines 32-34), the contribution is added to the **TRMatrix** `Ri1i2`, when `i2 > i1` (lines 35-37), the contribution is added to the transpose of `Ri1i2` and if `i1` is equal to `i2`, the contribution is added to both `Ri1i2` and its transpose (*i.e.* since $R_{i_1 i_1}^{a_1 a_2} = R_{i_1 i_1}^{a_2 a_1}$ in this case). The loops over the virtual labels are then closed in lines 42-44 and the value of the **TRMatrix** `Ri1i2` is written to the residual matrix container file using the **SetMatrix** function in lines 46-49. The loops over the occupied labels are closed in lines 50 and 51 and the matrices contained within `Ri1i2` and `t2_i2i1` are deleted in lines 52 and 53, respectively. In line 54, the current runtime is retrieved using `GetTime()` and `tm` is subtracted from it to give a new value of `tm`, which represents the total wall clock time for the computation of this contribution. Then in line 56, the timing array element, corresponding to the total wall-clock time for the calculation of the Fock matrix terms in the residuals, is updated with the value of `tm`. The quantity `_MREOM_TM_SIGMA_FOCK` is simply an integer (defined externally) which is used to keep track of this element of the timing array. Now that we have given a brief overview of the output of the generated code, let us proceed to discuss the inner workings of the code generator in detail.

4.3 Data Structures and Processing of Equations

4.3.1 Data Structures for Equations

Equations produced by the APG [32] are read in by the code generator and are stored as a list of **Term** objects. These **Term** objects are somewhat similar to and inspired by those employed in the APG. For illustration purposes, let us consider the following contribution to the doubles residual equations $R_{ij}^{ab} = 0$ of Eq. (4.12), which define the t_{ij}^{ab} amplitudes in MR-EOM theory [177, 21, 22, 23],

$$R_{ij}^{ab} += \frac{1}{4} \sum_{k,l,c,d} V_{cd}^{kl} t_{kl}^{ac} t_{ij}^{bd} n_k n_l. \quad (4.21)$$

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The expression of Eq. (4.21) can be represented as an instance of the **Term** class which has the following four attributes:

- **factor** : A float corresponding to the constant numerical factor which multiplies a given term. For the expression of Eq. (4.21), **factor** = 0.25.
- **factor2**: This attribute is only used in the definition of **Intermediate** objects (*vide infra*) to represent the occupation number(s) having labels that are contracted in the formation of the given intermediate quantity. For example, in Eq. (4.21), we can form the one-body intermediate $W_d^a = \sum_{k,l,c} n_k n_l V_{cd}^{kl} t_{kl}^{ac}$, which consists of a binary contraction of two tensors, V_{cd}^{kl} and t_{kl}^{ac} . The right hand side of this expression can also be represented as a **Term** object, whose **factor2** attribute would be set to the string '**n(k)*n(l)**', so that it could be used directly as written in the generated code. For linear terms, we do not set this attribute, as the string corresponding to **factor2** can easily be extracted while looping through the list of term objects during the code generation process.
- **tensors**: A list of **Tensor** objects.
- **hp_type**: A string corresponding to the hole-particle type of the integral or intermediate entering the given term in Mulliken notation. Here, active labels are treated as hole labels and **hp_type** is an empty string if the term does not contain a two-body integral or intermediate. The two-electron integral appearing in the expression of Eq. (4.21) is V_{cd}^{kl} (*i.e.* $(kc|ld)$ in Mulliken notation) and hence, **hp_type** = '**hphp**'. Note that this attribute is needed since integrals are modified, at a later stage, for storage purposes and the hole-particle character of the original integrals are lost as a result (see further discussion on p. 90 at the beginning of section 4.3.2)

As discussed above, each **Term** object has a tensor attribute which contains a list of **Tensor** objects. The **Tensor** class has the following attributes:

- **name**: A string corresponding to the name of the tensor. For the expression in Eq. (4.21), the list **Term.tensors** would contain three **Tensor** objects, one with **Tensor.name** = '**v**', corresponding to the name of V_{cd}^{kl} and two others with **Tensor.name** = '**t2**', corresponding to the names of t_{kl}^{ac} and t_{ij}^{bd} , respectively (*i.e.* the 2 in t2 is to denote that these are double excitation amplitudes).
- **uppIndices**: A list of the upper indices of the tensor (**Index** objects).
- **lowIndices**: A list of the lower indices of the tensor (**Index** objects).

Note that for two-electron integrals (or the two-body elements of a similarity transformed Hamiltonian), such as V_{cd}^{kl} in Eq. (4.21), the **uppIndices** and **lowIndices** take on a different meaning. Since we wish to represent these integrals in Mulliken notation (*e.g.* $V_{cd}^{kl} = (kc|ld)$), we use the **uppIndices** to represent the **Index** objects corresponding to the first two indices (*i.e.* kc in V_{cd}^{kl}), in this notation, and **lowIndices** to represent those corresponding to the last two indices (*i.e.* ld in V_{cd}^{kl}). The **Index** objects which comprise the **uppIndices** and **lowIndices** attributes of the **Tensor** class have the following attributes:

- **ind_name**: A string corresponding to the name of the index. For example consider the tensor t_{kl}^{ac} in Eq. (4.21), the **ind_name** attribute of two **Index** objects in the **Tensor.uppIndices** list would be 'a' and 'c', respectively. The **ind_name** attribute of the two **Index** objects in the **Tensor.lowIndices** list would be 'k' and 'l', respectively.
- **ind_type**: A string corresponding to the type of index (*e.g.* 'p' for particle (virtual), 'h' for hole (inactive), 'a' for active). Again if we consider the tensor t_{kl}^{ac} in Eq. (4.21), the **ind_type** attribute of the **Index** objects in the **Tensor.uppIndices** list would both be 'p'. The **ind_type** attribute of the **Index** objects in the **Tensor.lowIndices** list would both be 'h'.
- **fix**: An integer which is equal to 1 if the index is fixed (*i.e.* if it is not summed over in the expression) or 0 if it is free (*i.e.* if it is summed over in the expression). For the tensor t_{kl}^{ac} in Eq. (4.21), the **fix** attribute of two **Index** objects in the **Tensor.uppIndices** list would have values of 1 and 0, respectively. The **fix** attribute of the two **Index** objects in the **Tensor.lowIndices** list would both have values of 0.

For non-linear terms, such as that in Eq. (4.21), we also collect the sequence of binary contractions in a **TermIntermediates** object. This is done on a term by term basis during the code generation phase. The **TermIntermediates** class has a single attribute, **intermediates**, a list of **Intermediate** objects which serve to represent a single binary contraction. As previously discussed, we can form the one-body intermediate,

$$W_d^a = \sum_{k,l,c} n_k n_l V_{cd}^{kl} t_{kl}^{ac} \quad (4.22)$$

from the first binary contraction in Eq. (4.21). Then, the contribution of Eq. (4.21) to the MR-EOM residual equation $R_{ij}^{ab} = 0$ would read,

$$R_{ij}^{ab} += \frac{1}{4} \sum_d W_d^a t_{ij}^{bd}. \quad (4.23)$$

We can then use the **TermIntermediates** class to represent these two binary contractions as a list of **Intermediate** objects.

For each intermediate, the external indices (*i.e.* those that are not summed over) are collected as **Index** objects in a list and sorted according to type. The active labels are placed first, then the occupied labels appear next and finally the virtual indices are put at the end of the list. This list is then used to define the upper and lower indices of the **Intermediate** objects. For one-body intermediates, the first element of this list is set to upper index and the lower index is set to the second element. In the case of two-body intermediates, which are 4th rank tensors, the first two elements of the list become the upper indices and the last two elements are set to the lower indices.

The main reason for the sorting step is to achieve an ideal representation for the storage of these intermediates in ORCA [24]. One-body intermediates are stored as matrices (**TRMatrix**) and the upper index of the **Intermediate** instance is used as the row index of the matrix, while the lower index serves as the column index. Since ORCA is written in C++ [201], a programming language in which arrays are stored in row-major order¹, it is advantageous to have the index with the smallest range as the row index and that with the largest range as the column index. This is especially true if we want to make efficient use of the BLAS [27, 28, 29, 30, 31] routines for matrix operations, as discussed in section 4.5. Two-body intermediates are stored as instances of the **TMatrixContainer** class in ORCA [24]. In Table 4.3, we have summarized the matrix representation of various tensor quantities in ORCA. We will often use the notation,

$$M[p, q](r, s), \quad (4.24)$$

to denote the elements of a matrix container M in which p and q are the addressing labels and r and s are the row and column indices, respectively, of the matrix obtained from the container for a given p and q . In the case of a two-body **Intermediate** instance, the upper indices are used as the addressing indices and the lower indices provide the set of matrix indices of a given matrix, retrieved from the container. Since we wish to minimize the number of times we access these quantities from disk, it is necessary to have the indices with the smallest ranges as the addressing labels of the matrix container. As mentioned previously, this storage convention for two-body quantities is the same as that used in the SCEP formalism [198, 199]. Furthermore, the sorting step also ensures that the range of the row label of a matrix, belonging to the container, is also smaller or equal to the range of its column label.

The **Intermediate** objects themselves, have the following attributes:

- **name**: A string which defines the name of the intermediate. Note that we use the string 'W' to denote the base name of intermediates of this type. For one-body intermediates, we concatenate this string

¹Row-major ordering refers to the linear storage (vectorization) of a two-dimensional array in such a way that successive rows of the array are placed one after another in memory [201].

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Table 4.3: Representation of various tensors in the generated code.

Quantity	Tensor Format ¹	Format in ORCA ²	Description ⁴
two-body spin-orbital cumulant	$\lambda_{m_3 m_4}^{m_1 m_2}$	Lambda_so[m1][m2][m3][m4]	four index array over active space
single excitation amplitude	$t_{i_1}^{a_1}$	t1(i1_0,a1_0)	TRMatrix obtained from a TMDCIState instance
double excitation amplitude	$t_{i_1 i_2}^{a_1 a_2}$	t2_ili2(a1_0,a2_0)	TRMatrix obtained from a TMDCIState container with elements $t2[i1, i2](a1, a2)$
single de-excitation amplitude	$t_{a_1}^{i_1}$	tt1(i1_0,a1_0)	TRMatrix obtained from a TMDCIState instance
double de-excitation amplitude	$t_{a_1 a_2}^{i_1 i_2}$	tt2_ili2(a1_0,a2_0)	TRMatrix obtained from a TMDCIState container with elements $tt2[i1, i2](a1, a2)$
doubles S-amplitude	$s_{i_1 i_2}^{a_1 m_1}$	s2_ili2(m1_1,a1_0)	TRMatrix obtained from a TMatrixContainer with elements $s2[i1, i2](m1, a1)$
one-electron quantities ³ (e.g. the Fock matrix)	$F_{q_2}^{q_1}$	FT(q1,q2)	TRMatrix or TRMatrixSym
two-electron quantities ³ , excluding 3p1h types and 2p2h direct types (e.g. two-electron integrals)	$V_{q_1 q_2}^{i_1 i_2} = (i_1 q_1 i_2 q_2)$	Vili2(q1_0,q2_0)	TRMatrix obtained from a TMatrixContainer with elements $V[i1, i2](q1, q2)$
two-electron quantities ³ of the 2p2h direct (Coulomb) type	$V_{i_2 a_2}^{i_1 a_1} = (i_1 i_2 a_1 a_2)$ or $V_{a_2 i_2}^{a_1 i_1} = (a_1 a_2 i_1 i_2)$	Vili2(a1_0,a2_0)	TRMatrix obtained from a TMatrixContainer with elements $V[i1, i2](a1, a2)$
two-electron quantities ³ of the 3p1h type (e.g. two-electron integrals)	$V_{a_2 a_3}^{i_1 a_1} = (i_1 a_2 a_1 a_3)$	Vila1[a1_0](a2_0,a3_0)	array of TRMatrix objects obtained from a TMatrixContainer with elements $V[i1, a1](a2, a3)$

¹ The m_n , a_n and q_n , for $n = 1, 2, \dots$, refer to active, virtual and general orbitals, respectively. The i_n can either be occupied (inactive + active) or active orbitals here.

² The $\_0$ refers to an offset, namely, it indicates that the index of the first orbital of the set is subtracted from the current index so that the indexing starts from 0. The only exception is for active orbitals, where $\_0$ refers to subtracting the index of the first occupied orbital (*i.e.* only matters when we have a frozen-core and the core-orbitals are not correlated) and $\_1$ refers to subtracting the index of the first active orbital.

³ For the elements of a similarity transformed Hamiltonian, f , v , FT and V would be replaced by a user defined string. In the case of intermediates of the **Intermediate** class, for binary contractions in non-linear terms, f , v , FT and V would be replaced by the appropriate string corresponding to the intermediate name (see section 4.3.1 for the naming conventions and note that $\_tmp$ is added to the name of two-body intermediates to distinguish the matrix name from the matrix container name). Furthermore, all row and column labels of the matrices would start from 0 (*i.e.* $\_1$ offset for active labels and $\_0$ offset for all other labels).

⁴ *N.B.* The amplitudes $t_{i_1 i_2}^{a_1 a_2}$, $t_{a_1 a_2}^{i_1 i_2}$, residuals $R_{i_1 i_2}^{a_1 a_2}$, as well as the two-electron integrals $(i_1 i_3 | i_2 i_4)$, $(i_1 i_3 | i_2 a_1)$, $(i_1 i_2 | a_1 a_2)$, $(i_1 a_1 | i_2 a_2)$, are only stored for $i_1 > i_2$.

with the index types of both indices, add a number corresponding to the type of intermediate (*i.e.* 1-body or 2-body) and indicate the order of the binary contraction (*i.e.* first contraction, second contraction, *etc.*). Hence, for the intermediate in Eq. (4.22), **Intermediate.name** = 'Wpp_1_1'. For two-body intermediates, the string is concatenated with two strings corresponding to the index types of the addressing labels (the upper indices) of the intermediate and a number corresponding to the order of the binary contraction. For example, for the term $-F_c^k t_{ji}^{bc} t_k^a$, appearing in the MR-EOM doubles residual of Eq. (4.12), we would first form the two-body intermediate $W_{ji}^{bk} = F_c^k t_{ji}^{bc}$ and then contract it with $-t_k^a$ to form the contribution to the residual, $R_{ij}^{ab} += -W_{ji}^{bk} t_k^a$. The address labels of this intermediate are $[i, j]$ such that **Intermediate.name** would be 'Whh_2_1'.

- **uppIndices**: a list of **Index** objects corresponding to the upper indices of the intermediate
- **lowIndices**: a list of **Index** objects corresponding to the lower indices of the intermediate
- **term**: A **Term** object corresponding to the binary contraction of two tensors which define the given intermediate. In the case of Eq. (4.22), this would correspond to the **Term** object representing the right-hand side of this equation (*i.e.* $\sum_{k,l,c} n_k n_l V_{cd}^{kl} t_{kl}^{ac}$).

4.3.2 Processing of Equations and Data Collection for Code Generation

Before proceeding with the code generation step, the equations first need to be modified appropriately and several items of data need to be extracted from them. In a given set of equations, if the terms contain two-electron integrals or elements of a two-body intermediate (*e.g.* the two-body elements of a similarity transformed Hamiltonian $\widehat{\widehat{H}}$), we modify these elements for the purposes of storing them as matrix containers. The following modifications are made:

- The 2p2h $((ph|hp), (hp|ph)$ and $(ph|ph))$ exchange elements are mapped to the form $(hp|hp)$.
- The 1p3h $((hh|ph), (hp|hh)$ and $(ph|hh))$ elements are mapped to the form $(hh|hp)$.
- The 3p1h $((pp|hp), (ph|pp)$ and $(pp|ph))$ elements are mapped to the form $(hp|pp)$.

Note that if we replace an occupied label (denoted by h) by an active label, the above mapping is still applied. Once this transformation has been effected, then the 2p2h elements have the form $(ia|jb)$ and the 1p3h elements have the form $(ik|ja)$ and in both cases we would take i and j (*i.e.* 1st and 3rd indices) to be the addressing labels of the matrix container corresponding to the integral or intermediate. In the case of the 2p2h elements, a and b would be the row and column labels, respectively, of a matrix obtained from the

container, while for the 1p3h elements, k would be the row label and a would be the column label (*i.e.* 2nd and 4th indices in both cases). Hence, according to the notation introduced in Eq. 4.24, we could write the matrix container elements, corresponding to the $(ia|jb)$ integrals, as $V[i,j](a,b)$ and those corresponding to the $(ik|ja)$ integrals as $V[i,j](k,a)$. Furthermore, following the mapping discussed above, the 3p1h elements would have the form $(ib|ac)$. We would also take the 1st and 3rd indices as the addressing labels (i and a) of the matrix container and the 2nd and 4th indices (b and c) to be the row and column indices of a matrix obtained from the container. In the notation of Eq. 4.24, we would write the elements of the container as $V[i,a](b,c)$. In summary, we see that the global modification of these quantities makes it easy to extract the addressing indices and matrix indices for these three types of integrals/intermediates, as the rules for extracting them from the **Term** objects are identical in each case.

The transformation discussed above is perfectly legitimate, in the physical sense, for two-electron integrals (*i.e.* the permutational symmetries of Eq. (4.20)), but is not, in the case of “dressed” integrals like the elements of $\widehat{H}$, which only exhibit the vertex symmetry, $\bar{h}_{rs}^{pq} = \bar{h}_{sr}^{qp}$. In the latter situation, the mapping is only useful to define a convenient storage format for these quantities, as matrix containers, in ORCA. This is also the reason for keeping track of the original hole-particle type of the integral through the **hp_type** attribute of the **Term** class, as discussed in section 4.4.1. In Table 4.4, we have listed the naming conventions used for two-electron integral and two-body intermediate types in the code generator. For the time being, the only differences lie in the 1p3h and 2p2h exchange types, as we currently treat the 3p1h types as bare two-electron integrals in the MR-EOM code. This approximation is used, since it has negligible effects on the calculated results and one avoids the expensive storage of these 3p1h intermediates. Terms containing integrals with four virtual labels, namely $(pp|pp)$ type two-body quantities, are removed from the list of terms since these contributions are treated with an optimized hand-coded procedure, which is described in Ref. [5] and makes use of ideas from Refs. [198, 199, 202]. In both the closed-shell (*i.e.* Restricted Hartree-Fock (RHF) reference) single-reference CCSD equations [87] and the MR-EOM equations [177, 21, 22, 23], this type of contribution appears only twice in the doubles residual equations defining the $\widehat{T}$ -amplitudes. The total contribution of the terms containing integrals with four virtual labels, in both cases, can be written as

$$R_{ij}^{ab} += \sum_{c,d} V_{cd}^{ab} (t_{ij}^{cd} + t_i^c t_j^d) = \sum_{c,d} V_{cd}^{ab} \tau_{ij}^{cd}, \quad (4.25)$$

in which i, j are doubly occupied orbitals in the closed-shell CCSD case and can be either doubly occupied (inactive) or active orbitals in the MR-EOM equations and $\tau_{ij}^{cd} = t_{ij}^{cd} + t_i^c t_j^d$ is a so-called tau intermediate defined in the ORCA program. Since the computational scaling (*i.e.* $n_o^2 n_v^4$, where n_o is the number of occupied orbitals and n_v , the number of virtual orbitals) of Eq. (4.25), represents the dominant scaling

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Table 4.4: Naming conventions used for various two-electron integral and two-body intermediate types in the generated code.

hp Types	Two-Electron Integral Types	Two-Body Intermediate Types
$(hh hh)$	IKJL	IKJL
$(pp pp)$	ACBD	ACBD
$(hh pp), (pp hh)$	IJAB	IJAB
$(ph hp), (hp ph)$	IAJB	IAJB
$(hp hp), (ph ph)$	IAJB	IAJB_2
$(hp pp), (ph pp),$ $(pp hp), (pp ph)$	IBAC	IBAC
$(hh hp), (hp hh)$	IKJA	IKJA
$(ph hh), (hh ph)$	IKJA	IKJA_2

contribution to both the closed-shell CCSD and MR-EOM equations, it is imperative that it is treated in the most efficient way possible.

For each target quantity that we wish to calculate (*i.e.* residual, block of a similarity transformed Hamiltonian, target intermediate, *etc.*), the code generator will produce a function in C++ to calculate this quantity. Hence, one needs to collect all the information required for the function declaration and the declaration of all variables, matrices and matrix containers defined within the function. Looping through the list of **Term** objects, we collect the data in Table 4.5 for this purpose. Specialized functions have been written to collect this data from the **Term** objects in the list of terms. All of the data collected gets neatly organized in the form of a dictionary in Python. A dictionary is an associative array which allows one to associate keys (strings, numbers or tuples) with values of any data type [203]. It is similar to a list, except that the index or key referencing a certain value can be a string, number or a tuple [203]. For example, say that we had a list `fixed_list`, of fixed indices and a list `free_list`, of free indices and we wanted the string 'fixed' to be associated with the fixed index list and the string 'free' to be associated with the free index list, we could create a dictionary `dict`,

```
dict = {'fixed':fixed_list, 'free':free_list}.
```

Then the command `dict['fixed']` would return the list `fixed_list` and `dict['free']` would return `free_list`. The reason for using a dictionary to associate these strings with lists, strings or other data types in the code generator, is that the dictionary can be passed to a template, which automatically recognizes the associations made in the dictionary. A detailed description of these templates will be given

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Table 4.5: The data collected from the list of **Term** objects, corresponding to a given target quantity, which is employed for the declaration of a function in C++ and the declaration of all the variables, matrices and matrix containers used in the calculation of the target.

Name	Description
free_indlist	list of all unique free indices
fixed_indlist	list of all unique fixed indices
fixed_indtype	list of the index types of the indices in fixed_indlist
inter_active_inds	list of all unique active indices appearing in binary contraction intermediates
amplist	list of all unique amplitude matrix names
integ_containers ¹	list of all unique integral matrix container names, excluding 3p1h types
integ_names ¹	list of all unique integral matrix names, excluding 3p1h types
IBAC_names ¹	list of all unique matrix names corresponding 3p1h integrals
intermediate_list	list of all unique matrix names corresponding to binary contraction intermediates
intermediate_list2	list of all unique matrix container names corresponding to two-body binary contraction intermediates
target_inter_name	this contains the name of the matrix corresponding to the target
target_inter_container	if the target is not a residual, this contains the name of the matrix container corresponding to the target, otherwise it is an empty string
target_types	if the target is not a residual, this contains a list of the target index types (<i>i.e.</i> 'h', 'p' and 'a') and is set using the first list element of the the target_indlists list described in Table 4.7 below
IBAC_inter_list	list of all unique 3p1h binary contraction intermediate matrix names
IBAC_inter_list2	list of all unique 3p1h binary contraction intermediate matrix container names

¹ These are also used if the integrals are “dressed” quantities, like the elements of a similarity transformed Hamiltonian $\hat{\bar{H}}$

in section 4.4. We only mention that once the data is passed to a template, it is rendered to a string which contains the function declaration and the declaration of all variables, matrices and matrix containers needed for the remainder of the code.

To generate code for each of the terms in the list of **Term** objects, we loop through the list and first determine whether the term is linear or non-linear. For non-linear terms, we form the **Term_Intermediates** object which contains each of the binary contractions involved as a list of **Intermediate** objects. For a **Term** object or **Intermediate.term** instance in **Term_Intermediates**, we collect the information tabulated in Table 4.6. For each linear term or binary contraction intermediate, this information gets collected in the form of a dictionary, which is then passed to a template. The template gets rendered into a string representing the C++ code used to calculate the particular contribution. After looping through all the terms, one last template is used to terminate the defined function and perform any required operations (clean up, symmetrization of certain targets) before leaving the function body. This template uses a subset of the information that is passed to the declaration template, which was employed for declaring the function and all variables, matrices and matrix containers, needed for the calculation of a given target, as

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Table 4.6: The data collected from a **Term** or **Intermediate.term** instance. This information is used to generate C++ code for the corresponding contribution to the target or binary contraction intermediate.

Name	Description
inter_name	the name of the matrix corresponding to the target or binary contraction intermediate to which a contribution is added
inter_def	the matrix corresponding to the target or binary contraction intermediate to which a contribution is added, written in the format of the third column of Table 4.3
inter_def2	the matrix corresponding to the target or binary contraction intermediate to which a contribution is added, written in the format of the third column of Table 4.3, with the row and column indices interchanged
inter_container	the name of the matrix container corresponding to the target or binary contraction intermediate to which a contribution is added
inter_name2	if a contribution contains a binary contraction intermediate, this contains the name of the matrix for one-body intermediates and the name of the matrix container for two-body intermediates (<i>i.e.</i> the corresponding matrix name is obtained by adding <code>_tmp</code> to the matrix container name)
inter_inds	if a contribution contains a binary contraction intermediate, this contains a list of its indices
inter_indtypes	if a contribution contains a binary contraction intermediate, this contains a list of its index types
integ_name	for a contribution containing an integral or $\bar{h}$ element, this contains the corresponding name of the matrix
integ_address_list	for a contribution containing an integral or $\bar{h}$ element, this contains the list of address labels of the corresponding matrix container
integ_address_type	for a contribution containing an integral or $\bar{h}$ element, this contains the list of address label types (<i>i.e.</i> 'h', 'p' or 'a') of the corresponding matrix container
integ_address_fix	for a contribution containing an integral or $\bar{h}$ element, this contains a list of integers indicating whether a given address label, of the corresponding matrix container, is fixed (1) or free (0)
integ_container	for a contribution containing an integral or $\bar{h}$ element, this contains the name of the corresponding matrix container
ind_list	list of all indices involved in the computation of the given target or binary contraction intermediate
ind_type	list of all the index types of the indices involved in the computation of the given target or binary contraction intermediate
fix_indlist	list of the fixed indices (<i>i.e.</i> those that are not summed over in the calculation of the target or binary contraction intermediate)
fix_indtype	list of the types of the fixed indices
fix_address_list	list of the addressing labels of a two-body target or binary contraction intermediate
fix_address_type	list of the types of the addressing labels of a two-body target or binary contraction intermediate
tensor_list	list of the matrix representation (<i>i.e.</i> in the format of the 3 rd column of Table 4.3) of the tensor(s) contributing to the target or binary contraction intermediate
factor	string representing the numerical factor multiplying the contribution
factor2	string representing the occupation number or product of occupation numbers entering a contribution
amp_inds	list of the indices of the amplitude entering a given contribution
amplitude	name of the matrix corresponding to the amplitude entering a contribution
amp_address_list	list of the addressing labels of the matrix container for a doubles amplitude entering the contribution
amp_address_type	list of the types of the addressing labels of a doubles amplitude entering the contribution
amp_address_fix	list of integers indicating whether a given addressing label of a doubles amplitude is fixed (1) or free (0)
last	an integer which is 0 if the contribution is added to a binary contraction intermediate and 1 if it is added to a target quantity

discussed above. The templates themselves will be discussed in detail in section 4.4.

4.4 A Template Based Approach to Code Generation

4.4.1 The Mako Template Engine in Python

In our code generator, we make use of templates to produce source code that can easily be integrated into the ORCA program package [24]. Templates are strings or text files which contain placeholders for value or expression substitution. The placeholders are replaced by values or data structures extracted from a model, in our case, the equations defining a target intermediate (*e.g.* residual, $\hat{H}$ elements, *etc.*). The placeholder can also contain any valid Python expression (*e.g.* list elements, math functions, *etc.*) as the contents of a placeholder are evaluated directly by Python [25]. A template engine is used to perform the substitution of data values or expressions from the model into the proper placeholders within the templates and thus, is responsible for producing the final source code. The Mako template engine [26] is a text-based template processor written in Python [25]. We have chosen to use Mako as the templating engine in our code generator, since the templating language is very similar to Python’s syntax. In addition to the placeholders, Mako templates can contain blocks of Python code, control flow statements (*e.g.* loops and conditional statements), functions (defined within the template or imported from a separate Python module), as well as many other features which are not used in our code generator.

In order to demonstrate how the Mako template engine works and to familiarize the reader with the syntax used in the templates, we will consider a simple example. Note that placeholders are denoted by the syntax `${}` and control structures begin with `%` and must end with `%end<name>` where `<name>` is the name of the control statement (*i.e.* **if**, **while**, **for**, *etc.*). In Example Code 4.1, we have a Mako template which can be used to add a linear contribution to a target quantity, assuming that we have looped over all relevant indices and retrieved the relevant matrices from disk. This template is actually a small snippet of code which is contained within one of the main templates in the code generator and is responsible for dealing with the addition of tensors and binary contractions to a target within loop constructs when BLAS usage is not activated or warranted for a particular contribution (see section 4.5). The only exception is for a doubles residual of the type $R_{i_1 i_2}^{a_1 a_2} = 0$, which defines a set of amplitudes $t_{i_1 i_2}^{a_1 a_2}$ (*e.g.* CCSD [87] and MR-EOM [177, 21, 22, 23]), since the explicit vertex-symmetrization is needed in each term.

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Example Code 4.1: A simple example of a mako template for adding a linear contribution to a target within a loop construct.

```

1 %if len(tensor_list) == 1:
2     ${target} += ${factor}*${tensor_list[0]};
3 %else:
4     ${target} += ${factor}*${tensor_list[0]}*${tensor_list[1]};
5 %endif

```

Let us assume that we have saved the template of Example Code 4.1 to a text file `mako_example.txt`. We can then write a small Python script in order to render the template of Example Code 4.1. This Python script appears in Example Code 4.2, in which we consider two different linear contributions to the closed-shell single-reference CCSD equations [87] $R_{i_1}^{a_1} = 0$, for the single excitation amplitudes $t_{i_1}^{a_1}$. The first contribution consists of the addition of the occupied-virtual block of the Fock matrix to the residual,

$$R_{i_1}^{a_1} += F_{i_1}^{a_1}, \quad (4.26)$$

while the second contribution involves the contraction of a 3h1p integral with a double excitation amplitude,

$$R_{i_1}^{a_1} += -2.0 \sum_{i_2, i_3, a_2} (i_1 i_2 | i_3 a_2) t_{i_2 i_3}^{a_1 a_2}. \quad (4.27)$$

Note that in Eqs. (4.26) and (4.27), i_1 , i_2 and i_3 refer to doubly occupied orbitals, while a_1 and a_2 refer to virtual orbitals. Here we use a notational convention for the indices that is consistent with that used in the interface between the equation generator of the APG [32] and the code generator described herein.

Example Code 4.2: A Python script used to render the template in Example Code 4.1 for two different contributions to the CCSD singles residual equations.

```

1 # import the Template class from the mako module
2 from mako.template import Template
3
4 # set the template to be the file mako_example.txt
5 mytemplate = Template(filename='mako_example.txt')
6
7 # define the target as the singles residual  $R_{i_1}^{a_1}$ 
8 target = 'R(i1_0,a1_0)'
9
10 #-----
11 # Example 1:  $R_{i_1}^{a_1} += F_{i_1}^{a_1}$ 
12 #-----
13
14 # define the factor
15 factor = '1.0'

```

```

16
17 # define the tensor_list
18 tensor_list = ['FT(i1,a1)']
19
20 # declare a dictionary to pass variables to the template
21 dic = {'target':target, 'factor':factor, 'tensor_list':tensor_list}
22
23 # render the template to a string and print it
24 print 'Example 1 output:'
25 print mytemplate.render(**dic)
26
27 # -----
28 # Example 2:  $R_{i_1}^{a_1} += -2.0 \sum_{i_2, i_3, a_2} (i_1 i_2 | i_3 a_2) t_{i_2 i_3}^{a_1 a_2}$ 
29 # -----
30
31 # define the factor
32 factor = '-2.0'
33
34 # define the tensor_list
35 tensor_list = ['Vili3(i2_0,a2_0)', 't2_i2i3(a1_0,a2_0)']
36
37 # declare a dictionary to pass variables to the template
38 dic = {'target':target, 'factor':factor, 'tensor_list':tensor_list}
39
40 # render the template to a string and print it
41 print 'Example 2 output:'
42 print mytemplate.render(**dic)

```

In the script of Example Code 4.2, we begin by importing the `Template` class of the `mako` module. The name of the text file `mako_example.txt`, which contains the template of Example Code 4.1, is then passed to `Template` in order to create an instance of the `Template` class, `mytemplate`, which corresponds to this template. We then define `target` which corresponds to the CCSD singles residual in both examples. For both of the examples, we declare the `factor`, `tensor_list` and a dictionary to associate the names contained within the placeholders in the template (*i.e.* strings `'target'`, `'factor'` and `'tensor_list'`) with the values defined in the Python script (*i.e.* the string in `target`, the string in `factor` and the list in `tensor_list`). Note that the code generator would automatically collect this information from the equations, as discussed in section 4.3.2. In both examples, the dictionary is passed to the member function `render` of the `Template` class (*i.e.* lines 25 and 42 of Example Code 4.2), which automatically compiles into a pure Python module [26]. As is discussed in the Mako documentation [26], there is a function `render_body()` in the module which is tasked with generating the output as a string. For more details, see the extensive documentation in Ref. [26]. Evidently, for the first example in Example Code 4.2, `len(tensor_list) == 1` will evaluate to `true` in the `if` statement of line 1 in Example Code 4.1 (*i.e.* simple

addition of a tensor to the target), while it will evaluate to **false** in the second example (*i.e.* addition of the result of a binary contraction to the target). Hence, following the execution of the Python script in Example Code 4.2, we obtain the following output:

Example Code 4.3: Output from the Python script of Example Code 4.2, using the Mako template of Example Code 4.1.

```

1 Example 1 output:
2 R(i1_0,a1_0) += 1.0*FT(i1,a1);
3 Example 2 output:
4 R(i1_0,a1_0) += -2.0*Vi1i3(i2_0,a2_0)*t2_i2i3(a1_0,a2_0);

```

4.4.2 Mako Templates in the Code Generator

As discussed in section 4.3.2, the code generator produces a C++ function for each target quantity that we wish to calculate. To this end, we use the following three Mako templates to generate the body of the function:

- **T1: definition_template.txt:** This template performs the declaration of the C++ function used to calculate a given target and declares all required variables, matrices and matrix containers.
- **T2: template_for_loops.txt:** For a linear **Term** object or an **Intermediate.term** instance consisting of a binary contraction, this template is responsible for generating the C++ code (*i.e.* for loops, disk read and write statements, matrix multiplication and deletion of memory after usage) required to compute the given contribution
- **T3: clean_up_template.txt:** This template closes any open matrix container files, deletes the matrix for the singles amplitudes, writes the final value of the one-body targets to disk, symmetrizes targets that have vertex symmetry (*e.g.* hhhh type “dressed” elements, $\bar{h}_{i_1 i_2}^{i_3 i_4} = \bar{h}_{i_1 i_2}^{i_3 i_4} + \bar{h}_{i_2 i_1}^{i_4 i_3}$) and produces the return statements and closing brace of the function.

In addition to the data of section 4.3.2, which is collected by the Python module of the code generator, the templates require several items of user-defined data. In Table 4.7, we list the various user-defined quantities and the templates in which they are used, using T1 to denote definition_template.txt, T2 to denote template_for_loops.txt and T3 to denote clean_up_template.txt. Let us examine the details of each template more closely to demonstrate how they work in the code generator.

Table 4.7: The user-defined data employed by the templates in the code generator.

Name	Templates	Description
sigma	T1, T2, T3	an integer which is 1 if the target is a residual and 0 otherwise
res_amp_storage	T1, T2, T3	an integer which is 1 if the residuals/amplitudes are to be stored as TMDCIState type containers and 0 if they are to be stored as TMatrixContainer objects
MR	T1, T2, T3	an integer which is 1 if the method is a multi-reference method and 0 otherwise
sym	T2	an integer which is 0 if a doubles residual is to be vertex-symmetrized and 1 otherwise
bare	T1, T2	an integer which is 1 if the integrals are just regular two-electron integrals and 0 if the integrals are “dressed” quantities, like $\hat{H}$ elements
permu_sym	T1, T2	an integer which is 1 if the “dressed” integrals, present in the contributions, have the full eight-fold symmetries ¹ of the bare two-electron integrals and 0 if they only have vertex-symmetry
filename	T1	a string corresponding to the C++ file name where the function, corresponding to a given target, is written to (<i>i.e.</i> has the extension .cpp)
basename ²	N/A	a string corresponding to the base name of the targets corresponding to intermediates (<i>e.g.</i> for the $\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ elements in MR-EOM, <code>basename = 'H.T_'</code>)
integ_basename ²	T2	a string corresponding to the base name of the $\hat{H}$ elements appearing in the contributions
target_indlists	T2, T3	if the target is not a residual, this contains a list of index lists for the indices appearing in a given target (<i>i.e.</i> typically the list of lists only contains one list, corresponding to the indices of a given target, however, in the case of the $\hat{G} = \{e^S\}^{-1} \hat{H} \{e^S\}$ elements in MR-EOM, this is a list of lists for some of the $\hat{G}$ elements, for example, the $\hat{G}(i_1 i_3 i_2 i_4)$, $\hat{G}(m_1 i_2 i_1 i_3)$ and $\hat{G}(m_1 i_1 m_2 i_2)$ contributions are all added to the same matrix container and thus, the list of lists contains the indices of the three types of contributions)
BLAS	T2	an integer which is 1 if one wishes to enable the BLAS [27, 28, 29, 30, 31] in the generated code and is 0 otherwise (see section 4.5 for the details of BLAS usage in the generated code)
timers	T2	an integer which is 1 if one wishes to use timers in the generated code and 0 otherwise

¹ The bare two-electron integrals have the eight-fold permutational symmetries of Eq. (4.20).

² For bare integrals, the names in Table 4.4 are used to designate the matrix containers for the $(hh|hh)$, $(hh|hp)$, $(hh|pp)$, $(hp|hp)$, $(hp|pp)$ integrals, respectively. In the case of “dressed” targets, `basename` is added to the string corresponding to the container name in Table 4.4 (*i.e.* in the Python script, `target_container` already contains this string before being passed to any template) and if a list of terms contains “dressed” integral contributions, `integ_basename` contains the base name string to be added to the integral container names. A concatenated string, consisting of the first character (*e.g.* H, G, *etc.*), is also used in the definition of matrix names corresponding to these quantities in the generated code (rather than the string ‘V’ used for bare integrals).

4.4.2.1 T1: definition_template.txt

As mentioned above, the template `definition_template.txt` is responsible for the declaration of the C++ function and all the variables, matrices and matrix containers required for the calculation of a given target quantity. The code in Example Code A.1 of section A.1.1 of appendix A shows the output of `definition_template.txt` (excluding the include statements) for the three contributions of Eqs. (A.1), (A.2) and (A.3) which contribute to the doubles residual equation of Eq. (4.12). A detailed description of this code snippet is provided in section 4.2.2. The part of the template `definition_template.txt`, which declares the C++ function for each target, is represented in Example Code 4.4. This code snippet makes

use of the quantities defined within Tables 4.5 and 4.7. The actual subsection of the template is more complex than what is shown therein, since it can account for multiple types of amplitudes (*e.g.* $\hat{T}$ - and $\hat{S}$ -amplitudes treated together, as well as singles $\hat{S}$ -amplitudes) in a single target and residuals defining single $\hat{S}$ -amplitudes. In order to simplify the discussion, we have not taken these special cases under consideration, as the current implementation of MR-EOM [177, 21, 22, 23] in ORCA [24], makes use of a sequential transformation in which $\hat{T}$ - and $\hat{S}$ -amplitudes are treated separately and singles $\hat{S}$ -amplitudes are discarded from the equations. In line 1 of Example Code 4.4, one can see that the C++ function is defined with an integer return value and contains the name in filename without the extension .cpp. The DAT object is passed into the function, since it contains some crucial information about the calculation that is being performed. In the 12 lines that follow, it is decided whether or not the amplitudes are passed in as a **TMDCIState** instance or a **TMatrixContainer** instance and if the target is a residual, the same decision is made regarding the residual storage format. The **DMDCIINP** instance is needed when the inputs are **TMatrixContainer** instances, since it contains the ranges of the orbital spaces. In contrast, the **DMDCIINP** object is contained within a **TMDCIState** instance and thus, can be retrieved from the latter data structure. Scalar target quantities are passed to the function as is evidenced by lines 14-16 of Example Code 4.4. In line 17, the **MOINTS TMDCIContainer** instance is passed to the function. This object can be used to retrieve pointers to all of the bare two-electron integral files by using the Getter member functions of the **TMDCIContainer** class (*e.g.* `GetIAJB()`, `GetIKJL()`, *etc.*). If the method we are considering is a multireference method, then lines 18-21 make sure that the two-particle cumulant (**Lambda_so**) and occupation numbers of the one-particle density matrix enter the function. Lines 22-30 ensure that the proper one-body operator is passed to the function. In the case of bare integrals, this signifies that the Fock matrix (FT) should be used. Furthermore, if we impose the eightfold symmetries of the two-electron integrals (*i.e.* `permu_sym = 1`) then the one-electron operator will be a symmetric matrix, by construction, otherwise it possesses no symmetry. The function declaration is then closed with a `)` and the body of the function begins with the brace `{`.

Example Code 4.4: A simplified representation of the part of definition_template.txt, responsible for the C++ function declaration corresponding to a given target.

```

1  int Calc_${filename[: -4]}(TOrcaInfo &DAT,
2  %if res_amp_storage:
3      TMDCIState &STATE,
4      %if sigma:
5          TMDCIState &SIGMA,
6      %endif
7  %else:
8      DMDCIINP &INF,
9      TMatrixContainer &S2,
```

```

10     %if sigma:
11         TMatrixContainer &R2,
12     %endif
13 %endif
14 %if not sigma and len(target_indlist) == 0:
15     double &${target_inter_name},
16 %endif
17 TMDCIContainer    &MOINTS,
18 %if MR:
19     double ****Lambda_so,
20     TRVector &n,
21 %endif
22 %if bare:
23     TRMatrixSym &FT
24 %else:
25     %if permu_sym:
26         TRMatrixSym &${integ_basename}_pq
27     %else:
28         TRMatrix &${integ_basename}_pq
29     %endif
30 %endif
31 )
32 {
33 ## the function body begins here

```

For reasons of brevity, we will simply discuss the details of the remaining body of `definition_template.txt`. We start by defining the orbital ranges and numbers of occupied and virtual orbitals, as well as the number of active orbitals in the case of a multireference method. The orbital ranges are retrieved by using the `GetMOSpaces()` member function of the `DMDCIINP` instance. In what follows, we refer to the various definitions listed in Table 4.5. By looping through `free_indlist` and `fixed_indlist`, we declare all of the indices that are used in the calculation of the target and all of the required index offsets. The matrices corresponding to the integrals, amplitudes and binary contraction intermediates are declared as **TRMatrix** instances by looping through the lists `integ_names`, `amplitudes` and `intermediate_list`, respectively. The 3p1h integrals in `IBAC_names` are declared as an array of **TRMatrix** instances. For the two-body binary contraction intermediates, the **TMatrixContainer** instances are also declared from the contents of `intermediate_list2`. Then the array of **TRMatrix** instances and the **TMatrixContainer** instances for the 3p1h binary contraction intermediates are declared by looping through `IBAC_inter_list` and `IBAC_inter_list2`, respectively.

In the next part of this template, the integral matrix containers are defined as **TMatrixContainer** instances by looping through `integ_containers`. If the integrals appearing in the target are bare two-electron integrals or $\hat{H}$ elements of the type `IAJB_2` or `IBAC` (see Table 4.4), then a pointer to the integral

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file is retrieved using the getter member functions of the **MOINTS TMDICContainer** instance. For example, for the **IKJL** elements, the syntax would be,

```
TMatrixContainer *IKJL = MOINTS.GetIKJL();
```

Note that the $\hat{H}$ elements of the type **IAJB_2** are in fact the bare two-electron 2p2h exchange integrals, while we approximate the 3p1h $\hat{H}$ elements by the bare two-electron integrals of the type **IBAC**, as discussed in section 4.3.2. For the remaining $\hat{H}$ elements appearing in a given target, the declaration of the **TMatrixContainer** instances are achieved by defining the filename in which they are stored, using the **SetFileName** member function of the **TMatrixContainer** class. For example, for the **IKJA** elements of $\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$, for which `integ_basename = H_T_`, the syntax is

```
TMatrixContainer H_T_IKJA;
sprintf(msg,"%s.h_t_ikja_tmp.tmp", DAT.BaseName);
H_T_IKJA.SetFileName(msg);
```

in which `H_T_IKJA` is the name of the matrix container, `DAT.BaseName` contains the basename of the calculation file (*e.g.* if the input file for a calculation was `mreom.inp`, then `DAT.BaseName` would be `mreom`), and `basename.h_t_ikja_tmp.tmp` is the file containing the `H_T_IKJA` elements. Note that the code generator always defines the file name using the lower case version of the integral container name concatenated with `_tmp.tmp`. If the amplitudes come from a **TMDICState** instance `STATE`, (`res_amp_storage = 1`), we retrieve the singles amplitudes using the **GetSingles** member function of the **TMDICState** class and declare a pointer to the doubles amplitude file using the **GetT()** member function of the **TMDICState** class. The syntax for retrieving the singles amplitudes is,

```
res = STATE.GetSingles(Tia);
```

in which `res` is an integer which is 0 if the retrieval is successful and another integer otherwise and `Tia` is the matrix name of the singles amplitudes. For the doubles amplitudes, we have,

```
TMatrixContainer *T = STATE.GetT();
```

in which `T` is a pointer to the amplitude file. If the target quantity is a residual, then the next step in the template is to declare the matrices and matrix containers for the residuals. Whether the residual comes from a **TMDICState** instance (`res_amp_storage = 1`) or a **TMatrixContainer** instance (`res_amp_storage = 0`), we declare the matrix name, corresponding to the amplitude, as a **TRMatrix**. In the former case, if the target consists of singles amplitudes, we get the amplitude matrix using the **GetSingles** function of the

TMDCIState class in the same way as for the amplitudes above. Similarly, if the target is a doubles residual and `res_amp_storage = 1`, we declare a pointer R to the residual file as a **TMatrixContainer** instance, employing the `GetT` member function of the **TMDCIState** class. If the target quantity is an intermediate, then the code snippet in Example Code 4.5 is employed.

Example Code 4.5: A subsection of `definition_template.txt` tasked with declaring target intermediate quantities.

```

1  <%
2  def find_dim(index):
3      if index == 'a':
4          dim = 'NActive'
5      elif index == 'h':
6          dim = 'NOccupied'
7      elif index == 'p':
8          dim = 'NVirtual'
9      return dim
10 %>
11 %if sigma == 0:
12     %if len(fixed_indlist) == 4:
13         TMatrixContainer ${target_inter_container};
14         sprintf(msg, "%s.${target_inter_container.lower()}_tmp.tmp", DAT.BaseName);
15         ${target_inter_container}.SetFileName(msg);
16         ${target_inter_container}.SetData(1e-15,_MC_DOUBLE,_MC_UNCOMPRESSED,
17             _MC_ONDISK);
18         ${target_inter_container}.SetMaxDim(DIM, DIM);
19         TRMatrix ${target_inter_name};
20         ${target_inter_name}.NewMat(${find_dim(target_types[2])}, ${find_dim(
21             target_types[3])});
22     %elif len(fixed_indlist) == 2:
23         TRMatrix ${target_inter_name};
24         ${target_inter_name}.NewMat(${find_dim(target_types[0])},${find_dim(
25             target_types[1])});
26     %elif len(fixed_indlist) == 0:
27         ${target_inter_name} = 0.0;
28     %endif
29 %endif

```

Lines 1-10 of Example Code 4.5 illustrate the use of a pure Python function within a template. This function simply converts the strings 'a', 'h' and 'p' into the strings **NActive**, **NOccupied** and **NVirtual**, which are the number of active, occupied and virtual orbitals, respectively. For two-body intermediates (`len(fixed_indlist)= 4`), we define the target matrix container as a **TMatrixContainer** and we set the file name of the container which contains the name of the target matrix container in lower case letters (*i.e.* through the use of the `lower()` function). In line 16, we use the `SetData` member function of the

TMatrixContainer class to set the precision, type, compression and storage of the container. In the next line, we set the maximum dimension of the addressing labels of the container, using the **SetMaxDim** function, in which **DIM** has been defined to contain the dimension of the entire orbital space. The name of the matrix, retrieved from the target container, is then declared and initialized using the dimensions of the row and column indices, which are determined by applying **find_dim** to the last two elements of **target_types**. If the target is a one-body intermediate (**len(fixed_indlist)= 2**), the corresponding matrix is declared and initialized employing the dimensions of the row and column indices, by applying **find_dim** to the two elements of **target_types**. Finally, if the target is a scalar (**len(fixed_indlist)= 0**), the corresponding double, which is passed into the function, is initialized to 0. The final action of **definition_template.txt** is to open the doubles amplitude file for reading via the **OpenFileRead** function of the corresponding matrix container class.

4.4.2.2 T2: template_for_loops.txt

The template **template_for_loops.txt** is responsible for the generation of the body of the generated C++ function, which comprises the code necessary to calculate a given target quantity. In section 4.2.2, we discussed the details of the output of this template for one of the contributions appearing in the MR-EOM residual of Eq. (4.12), which appears in Example Code A.2 in appendix A.1.2. Before proceeding with a discussion of the structure of this template, let us consider two more examples from appendix A.1. In Code Example A.3 of appendix A.1.3, the code output of **template_for_loops.txt** is provided for the calculation of the contribution,

$$R_{i_1 i_2}^{a_1 a_2} += \sum_{a_3} (i_2 a_2 | a_3 a_1) t_{i_1}^{a_3}, \quad (4.28)$$

to the MR-EOM doubles residual $R_{i_1 i_2}^{a_1 a_2}$ of Eq. (4.12). Note that this contribution contains a 3p1h integral and is a special case in **template_for_loops.txt**, as will be discussed below. In lines 1-3, we print out a comment indicating the contribution that is being calculated. Then we get the current wall-clock time as **tm**. The **IBAC** integral buffer is then opened for reading in lines 7 and 8 and **Vi2a1** is defined as an array of **TRMatrix** instances of length **NVirtual** (*i.e.* the number of virtual orbitals), in lines 10 and 11. We then loop over **i2** in line 13 and define the offset **i2_0**, in line 14. In line 16, we loop over **a1** and define the offset **a1_0** in line 17. For a given value of **i2**, we gather all of the **TRMatrix** instances for each value of **a1_0** into the array **Vi2a1**, using the **GetMatrix** function in line 19 and then close the loop over **a1**, in line 21. This is done to avoid the **NVirtual** redundant reads of any quantity that is read from disk below (*i.e.* which would occur if we kept the loop over **a1** open throughout the calculation of the contribution). In this case, we would have **NVirtual** redundant reads of the residual if we didn't choose to collect the

integrals into an array of **TRMatrix** instances. In line 23, we loop over **i1** and define the offset **i1_0** in line 24. In lines 26-30, we open the residual buffer for reading, get the value of the residual as the **TRMatrix** **Ri1i2**, for the given values of **i1** and **i2**, using the **GetMatrix** function and then close the residual buffer. We then loop over the virtual labels **a1**, **a2** and **a3** and define the corresponding offsets **a1_0**, **a2_0** and **a3_0** in lines 32-39. In lines 41-50, the contribution of Eq. (4.28) is then added to the residual, for the given values of **i1** and **i2**, taking care to properly symmetrize the residual, as described in section 4.2.2. We then close the loops over **a1**, **a2** and **a3**, in lines 51-53 and then reopen the residual buffer, set the new value of the residual (for the given values of **i1** and **i2**), using the **SetMatrix** function and close the residual buffer, in lines 55-58. The loops over **i1** and **i2** are then closed in lines 59 and 60. In lines 61-66, we close the integral buffer, delete the **TRMatrix** **Ri1i2** from memory and delete the array of **TRMatrix** instances **Vi2a1**. Finally, we update the appropriate element of the timing array, in lines 67 and 69.

Example Code A.4 of appendix A.1.4 provides an example of the output of `template_for_loops.txt` for a non-linear term. Namely, this code snippet performs the calculation of the contribution,

$$R_{i_1 i_2}^{a_1 a_2} += - \sum_{i_3, i_4, a_3, a_4} n_{i_4} (i_3 a_3 | i_4 a_4) t_{i_1 i_4}^{a_3 a_4} t_{i_2 i_3}^{a_2 a_1} \quad (4.29)$$

to the MR-EOM doubles residual $R_{i_1 i_2}^{a_1 a_2}$ equation of Eq. (4.12). The calculation of this contribution is achieved by first calculating the one-body binary contraction intermediate,

$$W_{i_1}^{i_3} = \sum_{i_4, a_3, a_4} n_{i_4} (i_3 a_3 | i_4 a_4) t_{i_1 i_4}^{a_3 a_4}, \quad (4.30)$$

and then the contribution to the residual is computed as,

$$R_{i_1 i_2}^{a_1 a_2} += \sum_{i_3} W_{i_1}^{i_3} t_{i_2 i_3}^{a_2 a_1}. \quad (4.31)$$

The output of `template_for_loops.txt` for the calculation of the intermediate of Eq. (4.30) is provided in lines 5-46 of Example Code A.4, while the output of this template for the calculation of Eq. (4.31) is given in lines 48-101. In lines 1-3, a comment is printed indicating the non-linear contribution that is being computed. In lines 5-7, another comment is printed to indicate the binary contraction intermediate that is being calculated. Once again, the current wall-clock time is retrieved as the value of **tm**, in line 9. In line 11, the **TRMatrix** instance **Whh_1_1**, corresponding to the one-body intermediate, is initialized with a row and column dimension of **NOccupied** (*i.e.* the number of occupied orbitals). Then in lines 12 and 13, the integral buffer **IAJB** is opened for reading. We then loop over **i3** and **i4** and define the corresponding

offsets `i3_0` and `i4_0` in lines 15-19. For the given values of `i3` and `i4`, the integral $(i_3 a_3 | i_4 a_4)$ is retrieved as the **TRMatrix** `Vi3i4` in lines 21-23. As mentioned in Table 4.3, the integral $(i_3 a_3 | i_4 a_4)$ is only stored for $i_3 \geq i_4$ since $(i_3 a_3 | i_4 a_4) = (i_4 a_4 | i_3 a_3)$ (cf. the symmetries of two-electron integrals in Eq. (4.20)). Hence, when $i_4 > i_3$, we retrieve the integral as `(*IAJB).GetMatrix(i4,i3,Vi3i4)` (i.e. recall the description of the `imax` and `imin` functions in section 4.2.2) and transpose the retrieved **TRMatrix** to get the proper integral (i.e. $V[i_3, i_4](a_3, a_4) = V[i_4, i_3](a_4, a_3)$). We then loop over `i1` and define `i1_0` in lines 25 and 26 and retrieve the amplitudes $t_{i_1 i_4}^{a_3 a_4}$ as the **TRMatrix** `t2_i1i4` in lines 28-30. In a similar fashion as for the integrals, the amplitudes are only stored for $i_1 \geq i_4$, since $t_{i_1 i_4}^{a_3 a_4} = t_{i_4 i_1}^{a_4 a_3}$. Hence, we follow a similar procedure as what was done for the integrals in the retrieval of the amplitudes. Also, note that the amplitudes are read from disk `NOccupied` times more than is needed, as there is a loop over `i3` open during their retrieval. These types of cache misses are unavoidable in the implementation and are even present in the optimized, hand-coded CCSD implementation in ORCA [24, 5]. In lines 32-36, we loop over the virtual labels `a3` and `a4` and define the offset `a4_0` and `a3_0`. In line 38, the contribution of Eq. (4.30) is added to the binary contraction intermediate `Whh_1_1`. In lines 39-43, the loops over `a4`, `a3`, `i1`, `i4` and `i3` are closed. Then in lines 44-46, the integral container buffer is closed and the **TRMatrix** instances `Vi3i4` and `t2_i1i4` are deleted.

We then proceed with the calculation of the contribution of Eq. (4.31) to the doubles residual $R_{i_1 i_2}^{a_1 a_2}$. Once again, a comment is printed, indicating the contribution that is being computed, in lines 48-50. We then loop over the occupied labels `i1` and `i2` and define the corresponding offsets, in lines 52-56. The current value of the residual, for given values of `i1` and `i2`, is retrieved as the **TRMatrix** `Ri1i2`. We then loop over `i3` and define `i3_0`, in lines 64 and 65 and retrieve the amplitudes $t_{i_2 i_3}^{a_2 a_1}$ from the amplitude buffer in lines 67-69. Then we loop over the virtual labels `a1` and `a2` and add the contribution of Eq. (4.31) to the residual, in lines 77-86, for the given values of `i1` and `i2`. Once again, we ensure the proper symmetrization of the residual, as discussed previously. Then we close the loops over `a2`, `a1` and `i3`, in lines 87-89. For the given values of `i1` and `i2`, the matrix `Ri1i2` is written to the residual buffer, in lines 90-93 and the loops over `i2` and `i1` are closed, in lines 94 and 95. The **TRMatrix** instances `Ri1i2`, `Whh_1_1` and `t2_i2i3` are then deleted, in lines 96-98. Finally, the proper element of the timings array is updated, in lines 100 and 101. Lines 103-107 constitute the output of the template `clean_up_template.txt`

There are several function definitions (Mako defs) within `template_for_loops.txt` which facilitate the generation of code. The function `loop_function`, which is employed for producing for loops and index offsets in a contribution, is given in Example Code 4.6.

Example Code 4.6: The function `loop_function`, which is responsible for the generation of for loops and index offsets in `template_for_loops.txt`.

```

1  <%def name = "loop_function(index,indtype,amp_inds,fixed_indlist,inter_inds2,MR)" >
2      %if indtype == 'h':
3          %if MR:
4              <% end = 'LastActive' %>
5              <% start = 'FirstInactive' %>
6          %else:
7              <% end = 'LastInactive' %>
8              <% start = 'FirstInactive' %>
9          %endif
10     %elif indtype == 'p':
11         <% end = 'LastVirtual' %>
12         <% start = 'FirstVirtual' %>
13     %elif indtype == 'a':
14         <% end = 'LastActive' %>
15         <% start = 'FirstActive' %>
16     %endif
17     for (${index} = ${start} ; ${index} <= ${end} ; ${index}++) {
18         %if indtype == 'h':
19             ${index}_0 = ${index} - FirstInactive;
20         %elif indtype == 'p':
21             ${index}_0 = ${index} - FirstVirtual;
22         %elif indtype == 'a':
23             ${index}_0 = ${index} - FirstInactive;
24             %if (index in inter_inds) or (index in inter_inds2) or (index in
                fixed_indlist) or (index in amp_inds):
25                 ${index}_1 = ${index} - FirstActive;
26             %endif
27         %endif
28     </%def>

```

Note that pure Python code is contained within the `<% %>` construct. We can see that the input parameters to the function are `index`, `indtype`, `amp_inds`, `fixed_indlist`, `inter_inds2` and `MR`. These are respectively, the string corresponding to the index that is being looped over, the string corresponding to the index type, the list of indices appearing in an amplitude present in the contribution, the list of indices appearing in the quantity that is being computed (residual or intermediate), the list of indices appearing in a binary contraction intermediate present in the contribution and the integer `MR` described in Table 4.7. In lines 2-15 of Code Example 4.6, the function first decides where the for loop starts and ends based on the type of index that is being looped over. It also ensures that the loops over occupied orbitals end at `LastActive` (last active index) in a multireference method, rather than `LastInactive` (last inactive index) as in a single reference theory. Line 17 then produces the proper for loop for the given input index in C++. Then lines 18-27 generate the definition of the index offset(s), which are employed in the various matrices

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defining a given contribution, since the row and column indices need to start at 0 (*cf.* Table 4.3). Note that for active labels, if the index appears in any one of `amp_inds`, `fixed_indlist` or `inter_inds2`, then a second index offset must be defined so that the indexing of certain matrices starts from 0 (*cf.* Table 4.3).

The second function appearing in `template_for_loops.txt` is tasked with the retrieval of bare/dressed integrals from matrix containers. The function `get_integrals` appears in Example Code 4.7.

Example Code 4.7: The function `get_integrals`, in `template_for_loops`, which is employed for the retrieval of bare/dressed integral matrices from a matrix container file.

```

1  <%def name = "get_integrals(address_labels,integ_name,integ_type,integ_basename)" >
2      %if integ_basename != '':
3          <% int_typ = integ_type.replace(integ_basename + '_', '') %>
4          %if int_typ == 'IAJB_2':
5              res = (*${integ_type}).GetMatrix(imax(${address_labels[0]}},${
6                  address_labels[1]}),imin(${address_labels[0]}},${address_labels[1]}),${
7                  integ_name});
8              if (res!=0) AbortMessage("Error, failed to get integrals ${integ_type} \
9                  n",res);
10             if ( ${address_labels[1]} > ${address_labels[0]} ) ${integ_name}.
11                 Transpose();
12         %elif int_typ == 'IBAC':
13             res = (*${integ_type}).GetMatrix(${address_labels[0]}},${
14                 address_labels[1]},${integ_name});
15             if (res!=0) AbortMessage("Error, failed to get integrals ${integ_type} \
16                 n",res);
17         %else:
18             res = ${integ_type}.GetMatrix(${address_labels[0]}},${address_labels[1]},$
19                 {integ_name});
20             if (res!=0) AbortMessage("Error, failed to get integrals ${integ_type} \
21                 n",res);
22         %endif
23     %else:
24         %if (integ_type in ['IAJB','IJAB','IKJL']):
25             res = (*${integ_type}).GetMatrix(imax(${address_labels[0]}},${
26                 address_labels[1]}),imin(${address_labels[0]}},${address_labels[1]}),${
27                 integ_name});
28             if (res!=0) AbortMessage("Error, failed to get integrals  ${integ_type}
29                 \n",res);
30         %else:
31             res = (*${integ_type}).GetMatrix(${address_labels[0]}},${address_labels
32                 [1]},${integ_name});
33             if (res!=0) AbortMessage("Error, failed to get integrals  ${integ_type}
34                 \n",res);
35         %endif
36         %if (integ_type in ['IAJB','IKJL']):
37             if ( ${address_labels[1]} > ${address_labels[0]} ) ${integ_name}.
38                 Transpose();

```

```

25         %endif
26     %endif
27 </%def>

```

The function `get_integrals` in Example Code 4.7 takes five parameters as input, `address_labels`, `integ_name`, `integ_type` and `integ_basename`. These are respectively, a list of the addressing labels of the integral matrix container, the name corresponding to the **TRMatrix** instance retrieved from the container, the integral container name and `integ_basename`, as described in Table 4.7. For dressed integrals, `integ_basename` is not an empty string and the integral type (`int_tpy`) is extracted from `integ_type`, using the `replace` function to replace `integ_basename` with an empty string in `integ_type`. In order to retrieve a matrix from a matrix container, the `GetMatrix` member function of the **TMatrixContainer** class is employed. This function takes the addressing labels as its first two arguments and the name of the matrix to be retrieved from the container as its third argument. The matrix is automatically initialized when `GetMatrix` is called. As discussed previously, the **IBAC** and **IAJB_2** $\hat{h}$ elements are set to regular two-electron integrals and as such, are retrieved from the bare integral matrix containers. To this end, lines 4-7 of Example Code 4.7 ensure that the **IAJB_2** type integrals are retrieved from the bare **IAJB** container and lines 8-10 guarantee that the dressed **IBAC** integrals are retrieved from the bare **IBAC** container. Lines 11-13 are then used to retrieve the remaining integral types from the dressed integral matrix containers. Note that we use a pointer to the bare integral matrix containers (*e.g.* denoted by the `*` in `(*${integ_type}).GetMatrix(${address_labels[0]},${address_labels[1]},${integ_name})`), for reasons discussed above, while the actual name of the matrix container is used for the dressed integrals. Lines 15-25 of Code Example 4.7 are then used for the retrieval of bare two-electron integrals. Recalling the eightfold symmetries of the bare two-electron integrals in Eq. (4.20), we must have,

$$(ik|jl) = (jl|ik), \quad (4.32)$$

$$(ij|ab) = (ji|ab), \quad (4.33)$$

$$(ia|jb) = (jb|ia). \quad (4.34)$$

Here, we once again let i, j, k, l label occupied orbitals and a, b label virtual orbitals. As a result of the symmetries inherent in Eqs. (4.32)-(4.34), the bare integral matrix containers **IKJL**, **IJAB** and **IAJB** contain only the integrals for $i \geq j$. In the notation of Eq. (4.24), the respective matrix container elements corresponding to Eqs. (4.32), (4.33) and (4.34), are thus, related as follows,

$$V[i, j](k, l) = V[j, i](l, k), \quad (4.35)$$

$$V[i, j](a, b) = V[j, i](a, b), \quad (4.36)$$

$$V[i, j](a, b) = V[j, i](b, a). \quad (4.37)$$

Hence, we make use of the functions `imax(i, j)` and `imin(i, j)`, defined in ORCA [24], within the `GetMatrix` calls (see section 4.2.2 for the description of these functions). Hence, the syntax ,

```
(*${integ_type}).GetMatrix(imax(${address_labels[0]}, ${address_labels[1]}), imin(${address_labels[0]}, ${address_labels[1]}), ${integ_name});
```

ensures that within the loops over `address_label[0]` and `address_label[1]`, when `address_label[1]` becomes larger than `address_label[0]`, `address_label[1]` becomes the first argument of the `GetMatrix` function and `address_label[0]`, its second argument. For example, in the case of the **IAJB** integrals with addressing labels, i and j , the syntax `(*IAJB).GetMatrix(imax(i, j), imin(i, j), Vij)` would reduce to `(*IAJB).GetMatrix(i, j, Vij)` for $i > j$ and would be `(*IAJB).GetMatrix(j, i, Vij)` otherwise. Furthermore, in the case of the **IKJL** and **IAJB** integrals, Eqs. (4.35) and (4.36) imply that we must also transpose the matrix retrieved from the container when $j > i$. This is achieved in lines 7 and lines 23-25 of Example Code 4.7, with the syntax,

```
if(${address_labels[1]} > ${address_labels[0]}) ${integ_name}.Transpose();
```

where the `Transpose` member function of the **TRMatrix** class transposes the matrix in place. For example, after the operation `Vij.Transpose()`, `Vij` contains the transpose of the original **TRMatrix** instance, `Vij`. It is also important to note that the doubles residuals/amplitudes coming from a **TMDCIState** instance are also retrieved in an analogous fashion to the **IAJB** and **IKJL** bare integrals, from their respective containers, since we have that $R_{ij}^{ab} = R_{ji}^{ba}$ and $t_{ij}^{ab} = t_{ji}^{ba}$, as discussed above.

The final function, that is used within `template_for_loops.txt`, is responsible for generating the code for adding a contribution to a target or binary contraction intermediate within a loop construct. The example in section 4.4.1, constituted a simplified version of what this function does. The function is more general in that it also performs the vertex symmetrization ($R_{ij}^{ab} = R_{ij}^{ab} + R_{ji}^{ba}$) of doubles residuals R_{ij}^{ab} , in each term, as discussed in section 4.2. The function `tensor_multiplication` is given in Example Code 4.8.

Example Code 4.8: The function `tensor_multiplication` which produces the code for adding a contribution to a target or binary contraction intermediate within a loop construct.

```

1  <%def name = "tensor_multiplication(inter_def, inter_def2, factor, factor2,
    tensor_list, fix_address_list, sym)" >
2      <% factor = str(factor) %>
3      %if factor2 != '':
4          <% factor += '*' + str(factor2) %>
5      %endif
6      %if sym:
7          %if len(tensor_list) == 1:
8              ${inter_def} += ${tensor_list[0]};
9          %else:
10             ${inter_def} += ${tensor_list[0]}*${tensor_list[1]};
11         %endif
12     %else:
13         %if len(tensor_list) == 1:
14             if(${fix_address_list[0]} > ${fix_address_list[1]}) {
15                 ${inter_def} += ${tensor_list[0]};
16             }
17             if(${fix_address_list[0]} < ${fix_address_list[1]}) {
18                 ${inter_def2} += ${tensor_list[0]};
19             }
20             if(${fix_address_list[0]} == ${fix_address_list[1]}) {
21                 ${inter_def} += ${tensor_list[0]};
22                 ${inter_def2} += ${tensor_list[0]};
23             }
24         %else:
25             if(${fix_address_list[0]} > ${fix_address_list[1]}) {
26                 ${inter_def} += ${tensor_list[0]}*${tensor_list[1]};
27             }
28             if(${fix_address_list[0]} < ${fix_address_list[1]}) {
29                 ${inter_def2} += ${tensor_list[0]}*${tensor_list[1]};
30             }
31             if(${fix_address_list[0]} == ${fix_address_list[1]}) {
32                 ${inter_def} += ${tensor_list[0]}*${tensor_list[1]};
33                 ${inter_def2} += ${tensor_list[0]}*${tensor_list[1]};
34             }
35         %endif
36     %endif
37 </%def>

```

The function in Example Code 4.8, takes `inter_def`, `inter_def2`, `factor`, `factor2`, `tensor_list`, `fix_address_list` and `sym` as input. The first six parameters are as described in Table 4.6 and `sym` is described in Table 4.7. In line 4, `factor2` is concatenated with `factor`, using a multiplication sign (*) to join the two strings. Lines 6-11 perform exactly the same function as the template of Example Code 4.1 above. The remaining part of the template, on the other hand, adds the contribution to the target, while

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simultaneously performing the symmetrization of the target (if `sym = 0`). For example, in the case of a contribution $-\sum_{i_3}(i_2i_3|i_1a_1)t_{i_3}^{a_2}$ to the residual $R_{i_1i_2}^{a_1a_2}$ (*i.e.* once again, using notation consistent with the interface between the APG and the code generator), the function `tensor_multiplication` would produce the output given in Example Code 4.9. Note the transposition of the matrix `Rili2` in lines 5 and 9.

Example Code 4.9: Example output of Example Code 4.8 demonstrating the symmetrization of a doubles residual (`sym = 0`).

```

1  if (i1 > i2) {
2      Rili2(a1_0,a2_0) += -1.0*Vi2i1(i3_0,a1_0)*t1(i3_0,a2_0);
3  }
4  if (i1 < i2) {
5      Rili2(a2_0,a1_0) += -1.0*Vi2i1(i3_0,a1_0)*t1(i3_0,a2_0);
6  }
7  if (i1 == i2) {
8      Rili2(a1_0,a2_0) += -1.0*Vi2i1(i3_0,a1_0)*t1(i3_0,a2_0);
9      Rili2(a2_0,a1_0) += -1.0*Vi2i1(i3_0,a1_0)*t1(i3_0,a2_0);
10 }
```

In the interest of concision, let us describe the algorithmic details of the template `template_for_loops.txt` in the form of pseudo-code in Example Code 4.10. In the code generator, there are significant features to deal with 3plh intermediates. However, in the current version of MR-EOM [177, 21, 22, 23] in ORCA, there are no 3plh intermediates that arise in the definition of the equations. Hence, these features are not used and therefore, will not be discussed in the pseudo-code below.

Example Code 4.10: Pseudo-code describing the algorithmic details of `template_for_loops.txt`.

```

1  -print a comment indicating the contribution which is being computed
2
3  if timers:
4      -get the current wall clock time tm (i.e. tm = GetTime()) if this
5      is a linear term or the first binary contraction
6
7  if not sigma and len(fix_address_list) == 2:
8      -for the first term, open the target container for writing
9
10 if not last:
11     -initialize the matrix corresponding to the binary contraction
12     intermediate and the corresponding matrix container if it is
13     a two-body intermediate
14
15 if 'p' in integ_address_type:
16     -initialize the 3plh integrals, appearing in a contribution, as
17     arrays (of TRMatrix instances) of dimension NVirtual
```

```

18
19 if integ_container != '':
20     -open the integral container file for reading
21
22 if 'p' in integ_address_type:
23     if the corresponding 'h' label appears in fix_address_list:
24         -call loop_function, looping first over the 'h' label, then
25         over the 'p' label
26         -call get_integrals with integ_address_list and
27         integ_address_types as the input parameters, address_labels
28         and address_types and close the loop over the 'p' label
29
30 elif len(fix_address_list) == 2
31     -loop over fix_address_list and call loop_function for each element
32     in the list
33
34 if last and len(fix_address_list) == 2:
35     if sigma:
36         -get the doubles residual from the proper container, using the
37         two indices in fix_address_list as the addressing labels
38     else:
39         -if this is the first term, initialize the matrix in
40         target_inter_name, otherwise get the current matrix
41         target_inter_name from target_inter_container
42
43 if not last and len(fix_address_list) == 2:
44     -initialize the matrix corresponding to the binary contraction
45     intermediate being computed
46
47 if the contribution contains a doubles amplitude with both addressing
48 labels appearing in fix_address_list:
49     -get the amplitude from its container, using the two indices in
50     fix_address_list as the addressing labels
51
52 if 'p' not in integ_address_type:
53     -loop over the members of integ_address_list and call loop_function
54     for each of the elements which do not already appear in
55     fix_address_list
56     -call get_integrals with integ_address_list and integ_address_types
57     as the input parameters
58
59 elif the corresponding 'h' label does not appear in fix_address_list:
60     -call loop_function, looping first over the 'h' label, then
61     over the 'p' label
62     -call get_integrals with integ_address_list and
63     integ_address_types as the input parameters, address_labels
64     and address_types and close the loop over the 'p' label
65
66 if len(inter_inds) == 4:
67     -loop over the addressing labels of the binary contraction

```

```

68     intermediate (using loop_function) and then retrieve the matrix
69     from its container using these addressing labels
70
71     for i in range(len(amp_address_list):
72         if amp_address_list[i] has not already been looped over:
73             -call loop_function for amp_address_list[i]
74
75     if len(amp_address_list) == 2:
76         -get the amplitude from its container, using the two indices in
77         amp_address_list as the addressing labels
78
79     for i in range(len(ind_list)):
80         if ind_list[i] has not already been looped over:
81             -call loop_function for ind_list[i]
82
83     if BLAS:
84         -see section 2.3
85     else:
86         -call tensor_multiplication
87
88     for i in range(len(ind_list)):
89         if ind_list not in fix_address_list:
90             }
91
92     if len(fix_address_list) == 2:
93         if last:
94             if sigma:
95                 -store the new residual matrix in the corresponding matrix
96                 container
97             else:
98                 -store the new target matrix in the corresponding matrix
99                 container
100         else:
101             -store the new binary contraction intermediate matrix in the
102             corresponding matrix container
103     I
104     for i in range(len(fix_address_list)):
105         }
106
107     if not sigma and len(fix_address_list) == 2:
108         -for the first term, close the target container for writing
109
110     if inter_name2 != '':
111         -close the matrix container (for reading) corresponding to
112         inter_name2 and delete it
113
114     if not last:
115         -close the matrix container (for writing) corresponding to
116         inter_name
117

```

```

118 if integ_container != '':
119     -close integ_container for reading
120
121 -delete all matrices used in the calculation of the contribution, with
122 the exception of singles amplitudes/residuals and one-body targets
123
124 if timers and last:
125     -get the current wall-clock time and subtract from it the value of
126     tm to give the new value of tm (i.e. the time required for the
127     calculation of the term)
128     -update the appropriate element of the timing array with tm (i.e.
129     using the UpdateTime member function of the DMDCIINP class)

```

Let us describe the contents of Example Code 4.10 in some detail. We first print a comment containing a string specifying the contribution that is being calculated. If the timers are requested, we then get the current wall-clock time as `tm` for a linear term or the first binary contraction formed for a non-linear term. For a contribution to any target quantity other than a residual, the matrix container file corresponding to the target is opened for the purposes of writing. This is achieved by using the `OpenFileWrite` member function of the `TMatrixContainer` class. Lines 9-12 pertain to the calculation of a binary contraction intermediate in a non-linear term (*i.e.* `last = 0`). In this case, we need to initialize the matrix corresponding to the binary contraction intermediate and the corresponding matrix container for a two-body intermediate. This is done in precisely the same way as for the target quantities in Example Code 4.5. If the given contribution contains a 3p1h integral, we initialize it as an array of `TMatrix` instances, with a dimension of `NVirtual`. For example, given that `definition_template.txt` has declared `Vilal` as an array of `TMatrix` objects, the syntax for the initialization would be `Vilal = new TMatrix[NVirtual]`. If the contribution contains an integral, we open the matrix container file for reading, using the `OpenFileRead` function of the matrix container class.

Following the initialization procedure described above, we enter the main algorithm responsible for the generation of the loops. First we check if the contribution contains a 3p1h integral by verifying that a particle label appears in the address index list of the integral. If it does, we then verify whether or not the hole label in the address index list also appears in `fix_address_list`, the list of addressing indices of the target or binary contraction intermediate that is being computed. Given that the contribution contains a 3p1h intermediate and that the corresponding hole label also appears in the addressing label list of the target, we first loop over the hole label. Looping over the particle label, we then collect all of the `TMatrix` instances, for the given hole label into the initialized array and then the loop over the particle index is closed. For any other two-body target, we loop over both indices in `fix_address_list`. We must always loop over the addressing labels in `fix_address_list` first, since we need to retrieve (or

initialize) the matrix from the container for a given pair of these addressing indices and then we also need to set the new value of the matrix for this pair after the contribution has been added to it. If `last = 1`, we retrieve the matrix, for the given pair of addressing indices, from the appropriate container by using the `GetMatrix` function. If the target is not a residual and this is the first term, we initialize the matrix for each pair of addressing indices before adding the contribution to it by employing the `Init` member function of the **TRMatrix** class. Similarly, if `last = 0`, we must initialize the matrix corresponding to the binary contraction intermediate for each pair of addressing labels. If both addressing labels appear in the addressing label list of a doubles amplitude, present in the contribution, we retrieve it from the appropriate matrix container. If the contribution contains a two-electron integral, we loop over any hole labels in `integ_address_list` which do not appear in `fix_address_list` and we get the integral from the corresponding container using the addressing labels in `integ_address_list`. The 3plh integrals are retrieved to as an array of **TRMatrix** instances in the same way as if the corresponding hole label appeared in the `fix_address_list`. If instead, the contribution contains a two-body, binary contraction intermediate, we loop over the addressing labels of the intermediate (which do not appear in `fix_address_list`) and retrieve the matrix from the corresponding container. If the contribution contains a doubles amplitude, we then loop over the members of `amp_address_list`, that have not yet been looped over, and retrieve the matrix for this pair of addressing labels from the appropriate container. Then we loop over the remaining indices in `ind_list` and call `tensor_multiplication` to calculate the contribution. We then close the loops over all indices not appearing in `fix_address_list`. For two-body targets, doubles residuals and two-body binary contraction intermediates, we store the new value of the calculated matrix in the corresponding container, using the `SetMatrix` member function of the matrix container class, employing the addressing labels in `fix_address_list`. We then close the loops over the labels in `fix_address_list`, close all of the opened matrix container files and delete any matrices that can be deleted. If the timers are used, we get the current wall-clock time and subtract `tm` from it to get the new value of `tm`. Then the appropriate element of the timing array is updated with `tm`.

4.4.2.3 T3: `clean_up_template.txt`

The template `clean_up_template.txt` is then rendered in order to complete the definition of the C++ function used to calculate a given target quantity. We will simply describe the tasks that it performs in its execution. If the target is a one-body quantity, we store the corresponding matrix to a file by employing the `StoreMatrix` function of the **TRMatrix** class and then delete the matrix from memory, using the `DelMat` function. For singles residuals, we store the corresponding matrix in the **TMDCIState** instance `SIGMA` by using the `SetSingles` function and then delete the matrix from memory. For 4h target intermediates, we

perform the vertex symmetrization the contribution (*i.e.* $\bar{h}_{i_3 i_4}^{i_1 i_2} = \bar{h}_{i_3 i_4}^{i_1 i_2} + \bar{h}_{i_4 i_3}^{i_2 i_1}$). We first define the final matrix container file, open it for writing and open the original 4h container for reading. Then we initialize the temporary matrices that are needed to hold $\bar{h}[i_1, i_2](i_3, i_4)$ and $\bar{h}[i_2, i_1](i_4, i_3)$, respectively, for a given pair of addressing labels i_1, i_2 . We then loop over i_1 and $i_2 \leq i_1$, and retrieve both $\bar{h}[i_1, i_2](i_3, i_4)$ and $\bar{h}[i_2, i_1](i_4, i_3)$ from the original container that was created in the body of the function. Looping over i_3 and i_4 , we then calculate the contribution $\bar{h}_{\text{final}}[i_1, i_2](i_3, i_4) = \bar{h}[i_1, i_2](i_3, i_4) + \bar{h}[i_2, i_1](i_4, i_3)$ and close the loops over i_3 and i_4 . Then we use the **AddMatrix** member function of the **TMatrixContainer** class to add $\bar{h}_{\text{final}}[i_1, i_2](i_3, i_4)$ and $\bar{h}_{\text{final}}[i_2, i_1](i_4, i_3)$ to the final matrix container. We then close the loops over i_1 and $i_2 \leq i_1$, close and delete the original matrix container for reading, close the new container for writing and delete all of the **TRMatrix** instances used. The template then verifies if any **TRMatrix** instances were used for singles amplitudes and makes sure that they are deleted from memory. The template then generates the **return 0** statement (*i.e.* the function returns an integer which is 0 if no errors occur during its execution) and the closing brace **}** for the function.

We finally add a string containing some necessary include statements to the string containing the code for the entire C++ function and then write the resulting string to a .cpp file whose name is contained within **filename** (*cf.* Table 4.6). We then call an external program (within the Python module) called Uncrustify [204], in order to "beautify" the resulting code. This program is freely available for download through the links given at the webpage of Ref. [204]. This program ensures that proper indentation and various styles are adhered to in the final code, so that it looks nice and readable. Hence, it is merely used for esthetic reasons, as the code produced without this post processing step is still completely functional. As discussed previously, in appendix A.1 we demonstrate what the final output looks like by generating some code for three terms which appear in the MR-EOM equations [177, 21, 22, 23] of Eq. (4.12).

4.5 BLAS Usage in the Generated Code

The BLAS (Basic Linear Algebra Subprograms) [27, 28, 29, 30, 31] library provides a set of optimized procedures for performing linear algebra operations on large arrays. In ORCA [24], there is a fairly extensive set of specialized functions (wrappers) that have been written as an interface to the C version of the BLAS library, for operations on objects like the **TRMatrix** instances that we have previously described. At this time, we make use of the following three wrappers in the code generator,

- **BLAS_Add_Mat_x_Vec(double *V2, double fac, TRMatrix &M, double *V1, bool transpose)**: The input parameters for this function are the arrays of doubles **V1** and **V2**, the

double `fac`, the **TRMatrix** `M` and the **bool** `transpose`. The function calls the `dgemv` function of the BLAS library [27, 28, 29, 30, 31] to perform a matrix vector operation. Namely, this function performs the matrix-vector multiplication (for all `i`) $V2_i += fac \sum_j M_{ij} V1_j$ if the boolean `transpose` is `false` and $V2_i += fac \sum_j M_{ji} V1_j$ if it is `true` (*i.e.* the matrix `M` is transposed before performing the matrix-vector multiplication). Notice that the result of the matrix-vector multiplication is always added to the vector `V2`.

- **BLAS_Add_Mat_x_Mat(TRMatrix &C, TRMatrix &A, TRMatrix &B, bool transposeA, bool transposeB, double fac)**: The input parameters for this function are the **TRMatrix** instances `A`, `B` and `C`, the booleans `transposeA` and `transposeB` and the **double** `factor`. The function calls the `dgemm` function of the BLAS library [27, 28, 29, 30, 31] to perform a matrix-matrix operation. Specifically, this function performs the matrix-matrix multiplication of `A` and `B` multiplied by the scalar `fac` and adds the result to the matrix `C` (*i.e.* $C_{ij} += fac \sum_k A_{ik} B_{kj}$ for all `i` and `j`). Note that before the matrix-matrix multiplication, the matrix `A` will be transposed if `transposeA` is `true` and `B` will be transposed if `transposeB` is `true`.
- **BLAS_Trace(TRMatrix &A, TRMatrix &B, bool transpose)**: The parameters entering this function are the **TRMatrix** instances `A` and `B` and the **bool** `transpose`. This function returns a **double** `c` which is defined by $c = \sum_{ij} A_{ij} B_{ji}$ if `transpose` is `false` and $c = \sum_{ij} A_{ij} B_{ij}$ if `transpose` is `true`. This function makes use of the `ddot` function of the BLAS library [27, 28, 29, 30, 31].

It is important to note that the use of **BLAS_Add_Mat_x_Vec** requires casting the columns of some **TRMatrix** instances into linear arrays of doubles. In ORCA [24], this is done inline while calling the function. For example, consider the contribution,

$$R_{i_1}^{a_1} += 2 \sum_{i_2, a_2} (i_1 a_1 | i_2 a_2) t_{i_2}^{a_2}, \quad (4.38)$$

to the singles residual equations $R_{i_1}^{a_1} = 0$ defining the single excitation amplitudes $t_{i_1}^{a_1}$ in single-reference CCSD [87]. The current value of the residual $R_{i_1}^{a_1}$ is contained within a **TRMatrix** instance `Ria`, while the singles amplitudes are contained within a **TRMatrix** instance `t1`. Let us assume that we have looped over both `i1` and `i2` and that we have retrieved the **TRMatrix** `Vili2` from the integral matrix container `IAJB`, for a given pair values of `i1` and `i2` within the loop. We would then call **BLAS_Add_Mat_x_Vec**, within the loop construct, as follows,

```
BLAS_Add_Mat_x_Vec(&(Ria(i1_0, 0)), 2.0, Vili2, &(t1(i2_0, 0)), false);
```

in order to perform the matrix-vector multiplication. By passing the residual to the function as `&(Ria(i1_0, 0))` and the amplitudes, as `&t1(i2_0, 0)`, we ensure that entire column of **Ria**, for the given row corresponding to `i1_0`, is cast into a linear array of doubles and that the entire column of **t1**, for the corresponding row label of `i2_0`, is cast into an array of doubles. In effect, the syntax `&Ria(i1_0, 0)` denotes a pointer to the first element of the column of **Ria**, for the corresponding row label of `i1_0`. Let $\mathbf{Ri1}_{a1}$ denote the $a1^{\text{th}}$ element of the residual array for a given `i1_0` and $\mathbf{ti2}_{a2}$, the $a2^{\text{th}}$ element of the amplitude array for a given `i2_0`. The function `BLAS_Add_Mat_x_Vec` performs the operation $\mathbf{Ri1}_{a1} += \sum_{a2} \mathbf{V}i1i2_{a1a2} \mathbf{ti2}_{a2}$ for all `a1` and replaces the corresponding column of the original **TRMatrix** **Ria** with the new value contained within the computed array **Ri1**. Note that the row index `i1` (`i2`) is not involved in the BLAS, while the column index `a1` (`a2`), with the larger range, is involved in the BLAS operation. Hence, we see that the way that we have chosen to store these matrices becomes important for the BLAS operation (*i.e.* row major ordering).

For each contribution, consisting of a binary contraction, we use a selection procedure to determine whether or not BLAS will be employed in its computation. We compute a measure of the computational scaling of the cost of the binary contraction as a tuple (O, V) where O is the number of occupied and/or active labels appearing in the contribution and V is the number of virtual labels. For example, in Eq. (4.38), we have $O = 2$ (2 occupied labels) and $V = 2$ (2 virtual labels) so the actual scaling of the cost for this contribution is $n_o^2 n_v^2$ where n_o is the number of occupied orbitals and n_v is the number of virtual orbitals. We do *not* perform the BLAS, for a given contribution,

- if $V = 0$,
- if $V = 1$,
- if $V = 2$ and $O = 0$ or 1.

The second criterion that is used for the BLAS selection is the contraction order for the virtual labels. This is simply the number of virtual labels that are summed over in a contribution. For the expression of Eq. (4.38), the virtual contraction order is 1, since only one virtual label is contracted in this contribution. Given that the cost criterion has been satisfied, we only perform the BLAS, if the virtual contraction order is greater or equal to 1. In the Python module of the code generator, the function that verifies whether or not both of these criteria are satisfied is called `Do_BLAS`. This function takes a **Term** instance, consisting of a binary contraction, as input (*i.e.* a linear **Term** instance or **Intermediate.term** instance) and returns an integer which is 1 if the criteria for BLAS usage have been met and is 0 otherwise.

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The various contributions, which satisfy the selection criteria for BLAS, are classified according to the type of BLAS operation that should be performed. In the Python module of the code generator, there is a function `find_BLAS_type`, which returns,

- `BLAS_type = 1` if the BLAS operation is `BLAS_Add_Mat_x_Vec`,
- `BLAS_type = 2` if the BLAS operation is `BLAS_Add_Mat_x_Mat`,
- `BLAS_type = 3` if the BLAS operation is `BLAS_Trace`.

The classification is based on the virtual contraction order and the indices of the two matrices/vectors involved in the BLAS. A function `BLAS_indices`, is responsible for extracting the indices of each of the two matrices/vectors involved in the BLAS operation. It returns a list of two lists, the first list, containing the label(s) of the first matrix/vector and the second, the label(s) of the second matrix/vector. If the virtual contraction order is 1 and one of the lists is of length 1, then `BLAS_type = 1`, if both lists are of length 2, then `BLAS_type = 2`. If the virtual contraction order is 2, then `BLAS_type = 3`.

The Python module also contains a function, `BLAS_format`, which is tasked with producing the information needed for calling the BLAS functions in the generated code. The output of the function is contained within a single list called `BLAS_list`. In the case where `BLAS_type = 1`, the list takes the form,

`BLAS_list = [v1,fact,mat,v2,transpose,targ_tr_flag]`

in which `v1` and `v2` are the strings corresponding to the two vectors, as they appear in the code, `fact` is a string corresponding to the factor multiplying the contribution, `mat` is a string corresponding to the matrix as it appears in the code, `transpose` is a string which is `'true'` if the matrix is to be transposed and `'false'` otherwise and `targ_tr_flag` is 1 if the **TRMatrix** corresponding to `v1` needs to be transposed before the BLAS operation. For example, in the case of Eq. (4.38), the elements of the `BLAS_list` would be `v1 = 'Ria(i1_0,0)'`, `fact='2.0'`, `mat = 'Vili2'`, `v2 = 't1(i2_0,0)'`, `transpose = 'false'` and `targ_tr_flag = 0`. As an example of a situation where `targ_tr_flag` is 1, consider the following contribution to $\bar{h}_{a_1}^{a_2}$ in MR-EOM [177, 21, 22, 23],

$$\bar{h}_{a_1}^{a_2} += -\frac{1}{2} \sum_{i_1, a_3} n_{i_1} (i_1 a_2 | a_1 a_3) t_{i_1}^{a_3}. \quad (4.39)$$

The **TRMatrix** corresponding to $\bar{h}_{a_1}^{a_2}$ has the form `hab(a2_0,a1_0)`, however the label `a1` is not involved in the BLAS since it is an addressing index of the 3p1h integral (*i.e.* it is the array label in the array of

TRMatrix instances `Vilal[a1_0](a2_0,a3_0)`). In this case the flag `targ_tr_flag` would be 1, indicating that we need to transpose the matrix `hab` so that `a1_0` appears as the row label of the matrix for the BLAS operation. Within the loop construct over the labels `i1` and `a1`, we would have,

```
hab.Transpose();
BLAS_Add_Mat_x_Vec(&(hab(a1_0, 0)), -0.5*n(i1), Vilal[a1_0],&(t1(i1_0, 0)), false);
hab.Transpose();
```

In the case where `BLAS_type = 2`, the `BLAS_list` would take the form,

```
BLAS_list = [C,fact,A,B,trA,trB]
```

in which `A`, `B` and `C` are strings corresponding to the **TRMatrix** instances of the three matrices involved in the `BLAS_Add_Mat_x_Mat` operation, `fact` is a string corresponding to the factor multiplying the contribution, `trA` is a string which is 'true' if `A` is to be transposed and 'false' otherwise and `trB` is a string which is 'true' if `B` is to be transposed and 'false' otherwise. In this case, the function also finds the correct order of multiplication of the two matrices involved in the contribution. As an example, let us consider the contribution,

$$R_{i_1 i_2}^{a_1 a_2} += 2 \sum_{i_3, a_3} (i_1 a_1 | i_3 a_3) t_{i_2 i_3}^{a_2 a_3}, \quad (4.40)$$

to the doubles residual equations $R_{i_1 i_2}^{a_1 a_2} = 0$, defining the doubles amplitudes $t_{i_1 i_2}^{a_1 a_2}$, in single-reference CCSD [87]. Let us assume that we have looped over i_1 and i_2 and retrieved the **TRMatrix** `Rili2` from the residual container, for the given values of i_1 and i_2 . Let us further assume that we have looped over i_3 and retrieved the **TRMatrix** `Vili3` from the **IAJB** integral matrix container and the **TRMatrix** `t2_i2i3` from the amplitude container. Recalling the symmetrization procedure that is used for doubles residuals (*cf.* the discussion pertaining to Example Code 4.8 and 4.9 in section 4.4.2), we would then have,

```
if (i1 > i2) {
    BLAS_Add_Mat_x_Mat(Rili2, Vili3, t2_i2i3, false, true, 2.0);
}
if (i1 < i2) {
    BLAS_Add_Mat_x_Mat(Rili2, t2_i2i3, Vili3, false, true, 2.0);
}
if (i1 == i2) {
    BLAS_Add_Mat_x_Mat(Rili2, Vili3, t2_i2i3, false, true, 2.0);
    BLAS_Add_Mat_x_Mat(Rili2, t2_i2i3, Vili3, false, true, 2.0);
}
```

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Notice the reversal of the ordering of the matrix multiplication when $i_1 < i_2$ (and $i_1 = i_2$). This is taken care of in the `BLAS_operation` function, defined within `template_for_loops.txt`, which is described in Example Code 4.11 below. Thus, `BLAS_format` produces a single `BLAS_list`, in which `C = 'Rili2'`, `A = 't2_i2i3'`, `B = 'Vili3'`, `trA = 'false'`, `trB = 'true'` and `fact = '2.0'`. For the purposes of comparison, the corresponding code for the same contribution without the usage of BLAS is (assuming that we have looped over i_1 , i_2 and i_3 and retrieved the relevant **TRMatrix** instances `Rili2`, `Vili3` and `t2_i2i3`, as described above),

```

for (a1 = FirstVirtual; a1 <= LastVirtual; a1++) {
    a1_0 = a1 - FirstVirtual;

    for (a2 = FirstVirtual; a2 <= LastVirtual; a2++) {
        a2_0 = a2 - FirstVirtual;

        for (a3 = FirstVirtual; a3 <= LastVirtual; a3++) {
            a3_0 = a3 - FirstVirtual;

            if (i1 > i2) {
                Rili2(a1_0, a2_0) += 2.0 * Vili3(a1_0, a3_0) * t2_i2i3(a2_0, a3_0);
            }
            if (i1 < i2) {
                Rili2(a2_0, a1_0) += 2.0 * Vili3(a1_0, a3_0) * t2_i2i3(a2_0, a3_0);
            }
            if (i1 == i2) {
                Rili2(a1_0, a2_0) += 2.0 * Vili3(a1_0, a3_0) * t2_i2i3(a2_0, a3_0);
                Rili2(a2_0, a1_0) += 2.0 * Vili3(a1_0, a3_0) * t2_i2i3(a2_0, a3_0);
            }
        }
    }
}

```

In the final case, in which the `BLAS_type = 3`, the `BLAS_list` takes the form,

`BLAS_list = [c,fact,A,B,transpose]`

in which `c` is the string corresponding to the target (or binary contraction) matrix as it appears in the code, `fact` is the string corresponding to the factor multiplying the contribution, `A` and `B` are strings corresponding to the two matrices involved in the binary contraction as they appear in the code and `transpose` is the string `'true'` if `A` is to be transposed and `'false'` otherwise. As an example of this type of contribution, let us consider,

$$R_{i_1}^{a_1} \leftarrow 2 \sum_{i_2, a_2, a_3} (i_2 a_2 | a_1 a_3) t_{i_1 i_2}^{a_3 a_2}, \quad (4.41)$$

which is another contribution to the singles residual equation $R_{i_1}^{a_1} = 0$, in CCSD [87]. In this case, we have a 3plh integral and as such, we would loop over i_2 and a_1 and collect all of the matrices in the container into an array `Vi2a1[a1_0]` of **TRMatrix** instances and close the loop over a_1 . We would then loop over i_1 and get the **TRMatrix** `t2_ili2` from the amplitude container, then we would loop over a_1 once again and compute the contribution as,

```
Ria(i1_0,a1_0) += 2.0*BLAS_Trace(Vi2a1[a1_0], t2_ili2, false);
```

In this case, the elements of the `BLAS_list` are `c = 'Ria(i1_0,a1_0)'`, `fact = '2.0'`, `A = 'Vi2a1[a1_0]'`, `B = 't2_ili2'` and `transpose = 'false'`.

It is important to note that since the one-electron quantities (*i.e.* the Fock matrix, one-body $\bar{h}$ elements) are always stored over the full range of the orbital space, the appropriate sub-blocks must be extracted before they are employed in a BLAS wrapper. We define several templates as strings within the Python module to effectively cut out the appropriate blocks of these one-body quantities. Note that we never need to extract the occupied-occupied block of these quantities because these contributions never satisfy the conditions for BLAS usage, as described above. Since the templates for cutting out the virtual-virtual, occupied-virtual and virtual-occupied blocks (*i.e.* the virtual-occupied block is only required in the case of non-symmetric one-body quantities) are all very similar we only provide an example for the template dealing with the virtual-virtual block below.

```
cut_virtual_part = '''
// -----
// Cut out the virtual part of the one-electron matrix
// -----
TRMatrix ${op_name}_vv;
${op_name}_vv.NewMat(NExternal,NExternal);
for (a1=0;a1<NExternal;a1++){
    for (a2=0;a2<NExternal;a2++){
        ${op_name}_vv(a1,a2)= ${orig_name}(FirstExternal+a1,FirstExternal+a2);
    };
};
...
'''
```

This template is rendered with two input strings, `op_name` and `orig_name`. The string `op_name` is simply `F` for a Fock matrix element and is set to `integ_basename` for all other one-body elements. Note that the `BLAS_format` function also ensures that `BLAS_list` contains the proper name of the **TRMatrix** corresponding to the given block of the one-body matrix (*e.g.* `F_vv` for the virtual-virtual block of the Fock matrix) contained within a given contribution. The string `orig_name` simply contains the original

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name of the **TRMatrix** corresponding to the one-body quantity. If BLAS usage is activated, we extract the contributions containing virtual-virtual, occupied-virtual and virtual-occupied (if `permu_sym = 0`) from the list of terms and in each case, the respective template is rendered before commencing the calculation of the contributions. The code is then generated for all of the contributions containing that block of the one-body element and the **TRMatrix** instance corresponding to the sub-block is deleted from memory.

In addition to the data discussed in Table 4.6, the dictionary that is passed to `template_for_loops.txt` contains the following data,

- **Do_BLAS**: the result of the function `Do_BLAS` on the given contribution (*i.e.* an integer which is 1 if the contribution satisfies the criteria for BLAS and 0 otherwise)
- **BLAS_type**: if `Do_BLAS = 1`, this contains the result of the function `find_BLAS_type` on the contribution (*i.e.* either 1, 2 or 3 as discussed above)
- **BLAS_list**: if `Do_BLAS = 1`, this contains the list returned by the function `BLAS_format` for the given contribution

Lines 79-80 of the pseudo-code in Example Code 4.10 can now be modified to read,

```

if BLAS:
    if Do_BLAS:
        -call BLAS_operation
    else:
        -call tensor_multiplication

```

in which the function `BLAS_operation` is described in detail in Example Code 4.11 below.

Example Code 4.11: The function `BLAS_operation` which produces the code for adding a contribution to a target or binary contraction by employing a BLAS wrapper

```

1  <%def name = "BLAS_operation(BLAS_type, BLAS_format, inter_def, inter_def2, factor2,
    sym, fix_address_list)" >
2  <% factor = str(BLAS_list[1]) %>
3  %if factor2 != '':
4  <% factor += '*' + str(factor2) %>
5  %endif
6  %if sym:
7  %if BLAS_type == 1:
8  %if BLAS_list[5] == 0:
9  BLAS_Add_Mat_x_Vec(&({BLAS_list[0]}), ${factor}, ${BLAS_list[2]}, &({
    BLAS_list[3]}), ${BLAS_list[4]});
10 %else:

```

```

11         ${BLAS_list[0]}.partition('')[0]}.Transpose();
12         BLAS_Add_Mat_x_Vec(&(${BLAS_list[0]}),${factor},${BLAS_list[2]},&(${
13             BLAS_list[3]}),${BLAS_list[4]});
14         ${BLAS_list[0]}.partition('')[0]}.Transpose();
15     %endif
16 %elif BLAS_type == 2:
17     BLAS_Add_Mat_x_Mat(${BLAS_list[0]},${BLAS_list[2]},${BLAS_list[3]},${
18         BLAS_list[4]},${BLAS_list[5]},${factor});
19 %elif BLAS_type == 3:
20     ${inter_def} += ${factor}*BLAS_Trace(${BLAS_list[2]},${BLAS_list[3]},${
21         BLAS_list[4]});
22 %endif
23 %else:
24 %if BLAS_type == 1:
25     if(${fix_address_list[0]} > ${fix_address_list[1]}) {
26     %if BLAS_list[5] == 0:
27         BLAS_Add_Mat_x_Vec(&(${BLAS_list[0]}),${factor},${BLAS_list[2]},&(${
28             BLAS_list[3]}),${BLAS_list[4]});
29     %else:
30         ${BLAS_list[0]}.partition('')[0]}.Transpose();
31         BLAS_Add_Mat_x_Vec(&(${BLAS_list[0]}),${factor},${BLAS_list[2]},&(${
32             BLAS_list[3]}),${BLAS_list[4]});
33         ${BLAS_list[0]}.partition('')[0]}.Transpose();
34     %endif
35     }
36     if(${fix_address_list[0]} < ${fix_address_list[1]}) {
37     %if BLAS_list[5] == 1:
38         BLAS_Add_Mat_x_Vec(&(${BLAS_list[0]}),${factor},${BLAS_list[2]},&(${
39             BLAS_list[3]}),${BLAS_list[4]});
40     %else:
41         ${BLAS_list[0]}.partition('')[0]}.Transpose();
42         BLAS_Add_Mat_x_Vec(&(${BLAS_list[0]}),${factor},${BLAS_list[2]},&(${
43             BLAS_list[3]}),${BLAS_list[4]});
44         ${BLAS_list[0]}.partition('')[0]}.Transpose();
45     %endif
46     }
47     if(${fix_address_list[0]} == ${fix_address_list[1]}) {
48     BLAS_Add_Mat_x_Vec(&(${BLAS_list[0]}),${factor},${BLAS_list[2]},&(${
49         BLAS_list[3]}),${BLAS_list[4]});
50     ${BLAS_list[0]}.partition('')[0]}.Transpose();
51     }
52 %elif int(BLAS_type) == 2:
53     <% r_tr1 = str(not str2bool(str(BLAS_list[5])))>.lower() %>
54     <% r_tr2 = str(not str2bool(str(BLAS_list[4])))>.lower() %>
55     if(${fix_address_list[0]} > ${fix_address_list[1]}) {
56     BLAS_Add_Mat_x_Mat(${BLAS_list[0]},${BLAS_list[2]},${BLAS_list[3]},${
57         BLAS_list[4]},${BLAS_list[5]},${factor});
58     }

```

```

51         if(${fix_address_list[0]} < ${fix_address_list[1]}) {
52             BLAS_Add_Mat_x_Mat(${BLAS_list[0]},${BLAS_list[3]},${BLAS_list[2]},${
               r_tr1},${r_tr2},${factor});
53         }
54         if(${fix_address_list[0]} == ${fix_address_list[1]}) {
55             BLAS_Add_Mat_x_Mat(${BLAS_list[0]},${BLAS_list[2]},${BLAS_list[3]},${
               BLAS_list[4]},${BLAS_list[5]},${factor});
56             BLAS_Add_Mat_x_Mat(${BLAS_list[0]},${BLAS_list[3]},${BLAS_list[2]},${
               r_tr1},${r_tr2},${factor});
57         }
58     %endif
59 %endif
60 </%def>

```

The function `BLAS_operation`, defined in Example Code 4.11, takes seven parameters as input, `BLAS_type`, `BLAS_list`, `inter_def`, `inter_def2`, `factor2`, `sym` and `fix_address_list`. The description of `BLAS_list` and `BLAS_type` can be found above, while the remaining input parameters of the function are described in Table 4.6. For each `BLAS_type` value, the second element of `BLAS_list` is always the factor which multiplies the contribution and hence, we set `factor` to be equal to the corresponding string. If `factor2` is not an empty string (*i.e.* the contribution contains an occupation number or product of occupation numbers), we concatenate `factor` with a multiplication sign (*) and `factor2`. Since the elements of `BLAS_list` are exactly as they appear in the code, we simply extract the elements as they are needed in the definition of the various BLAS wrappers in Example Code 4.11. As a result of the similarity of `BLAS_operation` to the function `tensor_multiplication` in Example Code 4.8 and the detailed discussion above, concerning the various BLAS wrappers, we only discuss some details of Example Code 4.11 herein. It is important to note that when `BLAS_type = 1` and `targ_tr_flag = 1` (*i.e.* `BLAS_list[5] = 1`), the **TRMatrix** corresponding to the target or binary contraction intermediate is transposed before and after the BLAS operation. The result of the Python function `partition('(')` is a list consisting of three elements, the substring appearing before the substring '(', the substring '(' itself and the substring appearing after it. This function is used to extract the matrix name by taking the zeroth element of the list. In the symmetrization procedure for the doubles residuals (*i.e.* `sym = 0`), there are several important features to note. When `BLAS_type = 1`, the transposition of the matrix in `inter_def` is performed explicitly. In the case where `BLAS_type = 2`, rather than transposing the matrix in `inter_def`, the order of the matrix multiplication is reversed to achieve the same result. The reversal of the transpositions is also achieved by exchanging the roles of `trA` and `trB` and negating their boolean values. This is achieved, in part, by using the Python function `str2bool`, which is defined in the template and simply returns a bool `True` if the string is 'true' and returns `False` otherwise. Once the strings have been converted to Python booleans, they are negated by using the `not` statement and cast to a string of lower case letters so that

they are compatible with the C++ definition of booleans (*i.e.* the `.lower()` function is used). For example, in line 46 of Example Code 4.11, in the definition of `r_tr1` (*i.e.* meant to signify the new value of `tr1`, corresponding to the reversal of `tr2`), is formed by negating the string corresponding to the C++ boolean contained within `tr2` (`BLAS_list[5]`).

4.6 Evaluation of Timings for CCSD and MR-EOM Calculations, with and without BLAS Usage

In this section we will compare the timings of the CCSD code, produced by the code generator, with the optimized hand-coded CCSD implementation in ORCA [5]. We will also evaluate the timings of the code with and without BLAS usage and compare the timings of the CCSD iterations with those for the $\hat{T}$ -amplitude iterations in MR-EOM. Also, we will evaluate the timings for each part of the MR-EOM calculations (*i.e.* the $\hat{T}$ -amplitude iterations, the calculation of the $\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ and $\hat{F} = e^{\hat{T}^\dagger} \hat{H} e^{-\hat{T}^\dagger}$ elements, the $\hat{S}$ -amplitude iterations and the calculation of the $\hat{G} = \{e^{\hat{S}}\}^{-1} \hat{F} \{e^{\hat{S}}\}$ elements) and investigate how compiler optimizations and BLAS usage affect the performance of the calculation of these quantities. Furthermore, we will examine how the timings are distributed amongst the different types of contributions in each case (*i.e.* terms containing the Fock matrix or one-particle elements of $\bar{h}$, terms containing $(ia|jb)$ integrals or $\bar{h}$ elements, *etc.*). To this end, we will consider the benzene (C_6H_6) molecule in a def2-TZVP basis [96]. In the case of the MR-EOM calculations, we employ a state-averaged CASSCF reference with 6 electrons in 5 orbitals and 6 triplet states are included in the state averaging. The CASSCF reference is the same as that used in Ref. [22], with the exception of the larger basis used herein, and the optimized geometry of benzene was obtained from Ref. [33].

Table 4.8: Number of iterations, total timings and average time per iteration (in seconds) for the ORCA implementation of CCSD, CCSD with and without BLAS usage and the MR-EOM-T amplitude iterations, with and without BLAS, for benzene in a def2-TZVP basis.

	ORCA implementation of CCSD	CCSD with BLAS	CCSD without BLAS	MR-EOM-T with BLAS	MR-EOM-T without BLAS
Number of Iterations	12	12	12	19	19
Total Time / sec.	1163	3950	20027	9784	53254
Average Time per Iteration / sec.	99	329	1669	514	2802

CHAPTER 4. AUTOMATIC CODE GENERATION IN ORCA

In Table 4.8, we have tabulated the total timings, average time per iteration, as well as the number of iterations required to reach convergence for the ORCA implementation of CCSD [24, 5], the generated code for CCSD, with and without BLAS usage and the generated code for MR-EOM [177, 21, 22, 23], with and without BLAS usage. It is clearly apparent that the MR-EOM equations require more iterations, to solve for the converged amplitudes, than in CCSD. This is true in general, from our limited experience with MR-EOM calculations. Furthermore, the average time per iteration for the MR-EOM $\hat{T}$ -amplitude iterations is only about a factor of 1.5 larger than that for the CCSD iterations. Also, it is observed that the BLAS has a significant effect on the reduction of the timings of the calculations. Namely, in both CCSD and MR-EOM, the average time per iteration is reduced by a factor of ~ 5 when the BLAS wrappers are employed in the code. Furthermore, if we compare the generated code for CCSD, with BLAS, with the hand-coded implementation in ORCA, we see that the factorization, in the latter code, reduces the average timing per iteration further by a factor of ~ 3 . This demonstrates that factorization is an important means by which to optimize the performance of the implementation of such electronic structure methods.

Table 4.9: Evaluation of the effect of BLAS and compiler optimizations on the timings (in seconds) of various branches of the MR-EOM calculation, for benzene in a def2-TZVP basis.

	MR-EOM with BLAS and optimization	MR-EOM with BLAS	MR-EOM with optimization	MR-EOM
$\hat{T}$ -amplitude iterations ¹	514	556	2802	4641
calculation of $\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ elements	249	245	656	1720
calculation of $\hat{F} = e^{\hat{T}^\dagger} \hat{H} e^{-\hat{T}^\dagger}$ elements	109	104	262	805
$\hat{S}$ -amplitude iterations ¹	313	493	627	1677
calculation of $\hat{G} = \{e^{\hat{S}}\}^{-1} \hat{F} \{e^{\hat{S}}\}$ elements	783	1047	1426	3206

¹ average time per iteration

In Table 4.9, we investigate the effect of BLAS and loop optimizations, performed at compile-time, on the timings of various branches of the MR-EOM calculation, for benzene in a def2-TZVP basis. If we focus first on the last two columns, where explicit loops are used throughout the code, we see that the compiler optimizations have a significant effect on the reduction of the timings of the various parts of the calculation. When BLAS usage is enabled in the generated code, the effect of compiler optimizations is clearly not as important. It should be noted however, that the compiler optimizations have been enabled in the BLAS wrapper modules, even though they are turned off in the module containing the subroutines

for the calculation of the various residuals and similarity transformed elements of the Hamiltonian. It is observed that, with the usage of BLAS, the compiler optimizations are more important in the $\hat{S}$ -amplitude iterations and especially, in the calculation of the $\hat{G} = \{e^{\hat{S}}\}^{-1} \hat{F} \{e^{\hat{S}}\}$. This can be rationalized as the latter two branches of the code contain only `Mat_x_Vec` type BLAS operations, there are many more terms than in the other three branches and hence, many more contributions have no BLAS wrappers (explicit loops) in their computation. Therefore, it is not surprising that the compiler optimizations help to reduce the timings in the case of these two branches of the code.

Table 4.10: Percentage of the time spent calculating various contributions, in each branch of the MR-EOM calculation, for the benzene molecule in a def2-TZVP basis. The total time in seconds appears in the first row and the number of terms, for each type of contribution, appears in parentheses.

contributions	$\hat{T}$ -amplitude iterations ¹	calculation of $\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ elements	calculation of $\hat{F} = e^{\hat{T}^\dagger} \hat{H} e^{-\hat{T}^\dagger}$ elements	$\hat{S}$ -amplitude iterations ¹	calculation of $\hat{G} = \{e^{\hat{S}}\}^{-1} \hat{F} \{e^{\hat{S}}\}$ elements
total	514 s (130)	249 s (106)	109 s (56)	313 s (486)	783 s (1097)
one-body elements	0.7 % (12)	0.1 % (13)	0.4 % (13)	0.4 % (20)	0.5 % (65)
4p (ACBD)	5.0 % (2)	0 % (0)	0 % (0)	0 % (0)	0 % (0)
3p1h (IBAC)	38.0 % (16)	64.8 % (10)	86.3 % (10)	41.8 % (16)	35.4 % (20)
2p2h exchange (IAJB)	33.9 % (55)	28.9 % (53)	0.4 % (3)	0.7 % (4)	0.8 % (13)
2p2h direct (IJAB)	3.1 % (6)	0.2 % (3)	0.5 % (3)	0.7 % (4)	0.8 % (13)
1p3h (IKJA)	13.2 % (34)	5.9 % (25)	12.2 % (25)	56.3 % (431)	62.2 % (950)
4h (IKJL)	6.1 % (5)	0.1 % (2)	0.1 % (2)	0.2 % (11)	0.3 % (36)

¹ average time per iteration

In Table 4.10, we examine how the timings, in each branch of the MR-EOM calculation (with BLAS and optimization) for benzene in a def2-TZVP basis, are distributed amongst the various types of contributions. In the first row, we have the average timing per iteration for the $\hat{T}$ - and $\hat{S}$ -amplitude iterations and the total timings for the calculation of $\hat{H}$, $\hat{F}$ and $\hat{G}$, as well as the total number of terms (in parentheses), in each case. The other rows of Table 4.10 contain the percentage of time that is spent calculating various types of contributions (*i.e.* terms containing one-particle elements, 4p elements, 3p1h elements, 2p1h exchange and direct elements, 1p3h elements and 4h elements) and the number of terms of each type, in parentheses. For the $\hat{T}$ -amplitude iterations, the majority of the time is spent in the calculation of the terms containing 3p1h (38 %) and 2p2h exchange (33.9 %) integrals. This is not surprising since the 3p1h terms are rather expensive to compute (*i.e.* computational scaling of $n_o^p n_v^3$, where $p = 1, 2, 3$) and the 2p2h exchange terms are numerous (55 out of 130 terms). The 1p3h terms

also have a relatively large contribution to the timings, also due to the number of these terms appearing in the equations. This indicates that factorization would be advantageous to reduce the prefactor of the computational scaling associated with the calculation of the non-linear terms. For the calculation of the $\widehat{H}$ elements, the situation is similar, however the 3p1h terms clearly dominate the timings. In the case of the $\widehat{F}$, the number of terms containing 2p2h exchange integrals is small and therefore, the terms with 3p1h integrals take up the majority of the computational time. In the case of the $\widehat{S}$ -amplitude iterations and the calculation of the $\widehat{G}$ elements, the terms containing 3p1h integrals also make a significant contribution to the timings, but the terms containing 1p3h integrals dominate due to the large number of these terms appearing in both cases (*i.e.* 431 of 486 in the $\widehat{S}$ -amplitude equations and 950 of 1097 in the $\widehat{G}$ elements). Once again, it is important to note that factorization would help to reduce the prefactor associated with the scaling of these terms and would thus, have a significant effect on the performance of the code.

4.7 Concluding Remarks

The code generator, described in this chapter, consists of a single pure Python [25] module and makes extensive use of Mako [26] templates to achieve the generation of C++ [201] code in the ORCA program package [24]. It has been interfaced with the equation generator of the APG in Ref. [32], but can be readily modified to parse equations from any equation derivation program. This code generator has been successfully employed to implement the MR-EOM-CC method [21, 22, 23] in ORCA and further allowed us to numerically confirm that the initial implementation in ACES [179] was correct. Moreover, the implementation in ORCA will be freely available to thousands of users in the computational chemistry community in a future release of the program.

The code generator has been written with the intention of implementing multireference coupled pair theories (*i.e.* up to double excitations in the defining wavefunction) in ORCA, using the available data structures implemented therein. The definition of higher order densities and cumulants, in the generated code, is also possible even though we have restricted the discussion to one- and two-body cumulants in this chapter. The implementation of higher order excitations would require some modifications in the code generator and would also necessitate the definition of efficient storage data structures for higher order tensors in ORCA. However, the inclusion of higher order excitations is not the most pressing issue that we wish to tackle in the near future. In chapter 7, we will discuss some of the future improvements that can be made in the code generator in order to improve the efficiency of the generated code.

Chapter 5

Characterization of the Spectra of Transition Metal Complexes and an Orbital Selection Scheme for MR-EOM¹

5.1 Introduction

The Multireference Equation Of Motion Coupled-Cluster (MR-EOM-CC) methodology [21, 22, 23] has recently been introduced as a transform and diagonalize approach to the molecular electronic structure problem. The closely related state-specific partially internally contracted or pIC-MRCC approach is detailed in Ref. [177]. Through a succession of similarity transformations of the molecular electronic Hamiltonian, the majority of the excitation classes which couple configurations in the Complete Active Space (CAS) to other configurations (*i.e.* 1h1p, 2h2p, 2h1p, etc.), are included through the definition of internally contracted excitation operators that enter the transformed Hamiltonian. The remaining 1h, 1p and 2h excitations can then be incorporated through an uncontracted diagonalization of the similarity transformed Hamiltonian. Herein, we use ‘h’ or hole to specify an inactive (doubly occupied) orbital and ‘p’ or particle to denote a virtual orbital in the reference space. As discussed in chapter 3, the MR-EOM-T|T[†]|SXD-h-v approach (*i.e.* see Table 3.1) has been implemented in the ORCA quantum chemistry package [24]. The working equations for the MR-EOM-CC methodology were derived using the Automatic

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Program Generator (APG), described in Refs. [32, 197]. The resulting equations were implemented in the ORCA program package [24], employing the Python-based code generation tool described in chapter 4.

The MR-EOM methodology exhibits several attractive properties in that it is invariant to orbital rotations in the inactive, active and virtual subspaces, it is spin and symmetry adapted and the final diagonalization space is particularly compact, as it only includes 1h, 1p and 2h excitations out of the CAS. The transformed Hamiltonian is connected and the extensivity errors in MR-EOM tend to be small, as they arise from the relatively small number of excitations out of the CAS in the final diagonalization step. Most importantly, from a single state-averaged CAS orbital optimization and after solving a single set of cluster amplitudes, one can obtain a large number of excited states (10's to 100's) from a compact diagonalization. The states obtained in the final diagonalization can have an arbitrary excitation rank with respect to the ground state. However, only states that are dominated by active space configurations can be expected to be described accurately. The latter is the primary limitation of the MR-EOM approach, in addition to the need to define an active space and a set of active space reference states with appropriate weights. In initial applications [22, 23, 178], it has been found that, in general, results are not very sensitive to the precise nature of the state-averaged CAS.

Several successful benchmark applications of the variants of MR-EOM have been reported in Refs. [21, 22, 23, 178], which include excitation energies for transition metal atoms [21, 22, 23, 178] and organic molecules [22] as well as the calculation of potential energy surfaces [21] for C_2 and O_2 . For example, in Ref. [178], hundreds of excitation energies for the neutral and +1 and +2 charged cations of Cr, Mn, Fe and Co are compared with J-averaged experimental data and it is found that the RMS error is usually well below 0.1 eV. An ACES II [179] implementation, which mimics the ORCA [24] implementation of MR-EOM, has also been employed to benchmark this methodology for the excitation energies of a large test set of organic molecules and the excitation energies of transition metal atoms in chapter 6. In this work, we will apply the ORCA implementation of MR-EOM-T|T[†]|SXD-h-v (*i.e.* which will be referred to as simply MR-EOM for the remainder of this chapter) to the calculation of excitation energies of transition metal complexes. We have chosen five complexes, $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, ferrocene and cyclopentadienyl nickel nitrosyl ($CpNiNO$), for which experimental UV/Vis. band maxima are available in the literature. These systems have also been studied with other computational methods and the excitation energies from these studies will be compared with the MR-EOM results reported in this work. Furthermore, we introduce a novel orbital selection procedure which allows one to discard orbitals from the inactive and virtual subspaces in the calculation of excitation spectra. We will use the full MR-EOM excitation energies, for these five transition metal complexes, as benchmark data in order to make a critical assessment of the efficacy of this orbital selection scheme.

In section 5.2, we describe the formal aspects of the orbital selection procedure. A discussion of the benchmark systems and computational details of the calculations, reported in this chapter, is provided in section 5.3. In section 5.4.1, the MR-EOM excitation energies for the five transition metal complexes are presented and compared with Brueckner orbital [205, 206, 207, 208] based STEOM [16, 209, 17] (*i.e.* STEOM-ORB [210]) and EOM-CCSD(T) [13, 14, 15, 211] calculations, as well as other computational approaches and experimental results from the literature. Furthermore, a characterization of the various excited states is provided in terms of the active space orbitals. In section 5.4.2, the full MR-EOM results, in the complete orbital space, are used to benchmark various truncations of the inactive and virtual spaces, obtained by applying the orbital selection procedure described in section 5.2. To conclude, we then present summarizing remarks in section 5.5.

5.2 Orbital Selection Scheme

In applications of MR-EOM to larger molecules, we anticipate that the chromophore might be localized to a small part of the molecule. If excitation energies are of interest, rather than total energies, it is likely that one can truncate the orbital space by keeping only the important orbitals which are localized in the vicinity of the chromophore. In MR-EOM, the excitations of interest are always associated with orbitals in a compact active space. This allows the design of a general scheme for orbital selection. We wish to select the inactive and virtual orbitals which play an important role in the various types of excitations out of the CAS. To this end, we can construct one-body density matrices in the inactive and virtual orbital subspaces, using first order approximations to the $\hat{T}$, $\hat{S}$ and $\hat{U}$ excitation amplitudes, that all have at least one active orbital index. Since all excitations are dominated by configurations in the CAS space, one can expect these type of amplitudes to be most important for excitation energies that are dominated by differential correlation effects in the ground and excited states. The orbital selection is then based on the natural orbitals of these density matrices. In particular, the magnitude of the natural occupation numbers of the density matrices serve as an indicator of the importance of the corresponding inactive or virtual orbitals in the description of the excitations. The actual orbitals are defined by a canonicalization of the Fock matrix, which has been projected onto the subspace of interest.

5.2.1 Perturbative Estimates of the Excitation Amplitudes and the Inactive and Virtual Orbital Selection Densities

We first perform a partial AO to MO integral transformation to obtain the two-electron integrals V_{ij}^{kl} , V_{ij}^{ka} and V_{ij}^{ab} . The Fock matrix F_q^p in the MO basis is retrieved from the CASSCF calculation and the orbital energies of the inactive (ε_i) and virtual orbitals (ε_a) are obtained by diagonalizing (canonicalizing) the inactive and virtual blocks of the Fock matrix, respectively. In ORCA [24], the active orbitals are defined to be natural orbitals of the one-particle RDM Γ_x^w (Eq. (3.1)), such that it is diagonal with diagonal elements corresponding to the occupation numbers $n_w = \Gamma_w^w$, of the orbitals.

However, the natural orbitals are not those used in defining the perturbative estimates of the $\hat{T}$ -amplitudes. We distinguish between annihilation and creation operators in the active space and use orbitals and energies that are respectively, eigenvectors and eigenvalues of the corresponding Extended Koopman's Theorem (EKT) [212, 213, 214] eigenproblem. If a particular active orbital w is associated with a hole annihilation operator $\hat{a}_w$ (*i.e.* an electron is deleted from the orbital), then the corresponding orbital coefficient vector $\mathbf{C}_w$ and energy ε_w are taken as the eigenpair $(\mathbf{C}_w^{\text{IP}}, \varepsilon_w^{\text{IP}})$ of $\tilde{\mathbf{K}}^{\text{IP}}$ (Eq. (5.3)), the transformed EKT-IP matrix in the active space. On the other hand, if the active orbital w is associated with a particle creation operator $\hat{a}_w^\dagger$ (*i.e.* an electron is promoted into the orbital), then the corresponding orbital coefficient vector $\mathbf{C}_w$ and energy ε_w are chosen as the eigenpair $(\mathbf{C}_w^{\text{EA}}, \varepsilon_w^{\text{EA}})$ of $\tilde{\mathbf{K}}^{\text{EA}}$ (Eq. (5.8)), the transformed EKT-EA matrix in the active space.

The elements of the EKT-IP matrix $\mathbf{K}^{\text{IP}}$ are given by

$$K_{wx}^{\text{IP}} = \sum_m w_m \langle \Phi_m | \hat{a}_w^\dagger [\hat{H}, \hat{a}_x] | \Phi_m \rangle, \quad (5.1)$$

and the EKT-IP orbitals $\mathbf{C}^{\text{IP}}$ and energies ε^{IP} are determined as solutions of the generalized eigenvalue problem

$$\mathbf{K}^{\text{IP}} \mathbf{C}^{\text{IP}} = \mathbf{\Gamma} \mathbf{C}^{\text{IP}} \varepsilon^{\text{IP}}. \quad (5.2)$$

We can then define the matrix

$$\begin{aligned} \tilde{K}_{wx}^{\text{IP}} &= \sum_{yz} (\mathbf{\Gamma}^{-\frac{1}{2}})_{wy} K_{yz}^{\text{IP}} (\mathbf{\Gamma}^{-\frac{1}{2}})_{zx} \\ &= \frac{K_{wx}^{\text{IP}}}{\sqrt{n_w n_x}}, \end{aligned} \quad (5.3)$$

where the last line follows from the fact that we are working in the natural orbital basis. Diagonalization of

the transformed matrix $\tilde{\mathbf{K}}^{\text{IP}}$ then yields the desired EKT-IP orbitals and orbital energies. The expression for the elements of the EKT-EA matrix $\mathbf{K}^{\text{EA}}$ is

$$K_{wx}^{\text{EA}} = \sum_m w_m \langle \Phi_m | \hat{a}_w [\hat{H}, \hat{a}_x^\dagger] | \Phi_m \rangle, \quad (5.4)$$

and the generalized eigenvalue problem which determines the EKT-EA orbitals $\mathbf{C}^{\text{EA}}$ and orbital energies ϵ^{EA} is given by

$$\mathbf{K}^{\text{EA}} \mathbf{C}^{\text{EA}} = \mathbf{S} \mathbf{C}^{\text{EA}} \epsilon^{\text{EA}}. \quad (5.5)$$

In this case, the elements of the metric matrix $\mathbf{S}$ are obtained as

$$S_x^w = \sum_m w_m \langle \Phi_m | \hat{a}_w \hat{a}_x^\dagger | \Phi_m \rangle = \delta_x^w - \Gamma_x^w, \quad (5.6)$$

from which it is obvious that $\mathbf{S}$ is diagonal in the natural orbital basis and can be represented by the vector σ , with elements

$$\sigma_w = 1 - n_w. \quad (5.7)$$

Hence, the EKT-EA orbitals and orbital energies are obtained by diagonalization of the matrix

$$\tilde{K}_{wx}^{\text{EA}} = \frac{K_{wx}^{\text{EA}}}{\sqrt{\sigma_w \sigma_x}}. \quad (5.8)$$

To estimate the importance of the 2p-1h and 2p excitations in the first order interacting space, we compute the first order $t_{ij}^{ab(1)}$ amplitudes as

$$t_{ij}^{ab(1)} = \frac{V_{ij}^{ab}}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (5.9)$$

in which it is understood that $\epsilon_i = \epsilon_i^{\text{IP}}$, if i is active and $\epsilon_j = \epsilon_j^{\text{IP}}$, if j is active. It should also be noted that the active orbitals, in the integral in Eq. (5.9), are transformed to the EKT-IP basis before dividing by the denominator and are transformed back to the original basis afterward (*i.e.* using the orbital coefficients in $\mathbf{C}^{\text{IP}}$). The importance of the 2h-1p excitations is estimated by computing the first order $s_{i'j'}^{aw(1)}$ amplitudes and the importance of the 1h-1p excitations is estimated by computing the first order $s_{xj'}^{aw(1)}$ and $s_{i'x}^{aw(1)}$ amplitudes. The first order perturbative estimates of these amplitudes are obtained as

$$s_{i'j'}^{aw(1)} = \frac{V_{i'j'}^{aw}}{\epsilon_{i'} + \epsilon_{j'} - \epsilon_a - \epsilon_w^{\text{EA}}}, \quad (5.10)$$

$$s_{xj'}^{aw(1)} = \frac{V_{xj'}^{aw}}{\varepsilon_x^{\text{IP}} + \varepsilon_{j'} - \varepsilon_a - \varepsilon_w^{\text{EA}}}, \quad (5.11)$$

$$s_{i'x}^{aw(1)} = \frac{V_{i'x}^{aw}}{\varepsilon_{i'} + \varepsilon_x^{\text{IP}} - \varepsilon_a - \varepsilon_w^{\text{EA}}}. \quad (5.12)$$

Once again, we note that we must transform active orbitals to the corresponding EKT basis before dividing by the denominator and transform back to the original basis to obtain the final amplitudes. In order to estimate the important 2h excitations, in the first order interacting space, we can define an excitation operator $\hat{U}$ as

$$\hat{U} = \frac{1}{2} \sum_{w,x,i',j'} u_{i'j'}^{wx} \hat{E}_{i'j'}^{wx}, \quad (5.13)$$

as was done in Ref. [23] and to first order, the $u_{i'j'}^{wx(1)}$ amplitudes can be computed using

$$u_{i'j'}^{wx(1)} = \frac{V_{i'j'}^{wx}}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_w^{\text{EA}} - \varepsilon_x^{\text{EA}}}. \quad (5.14)$$

In our orbital selection scheme, we have also tried to estimate the effects of the 1p excitations via the first order expression

$$t_w^{a(1)} = \frac{F_w^a}{\varepsilon_w^{\text{IP}} - \varepsilon_a}. \quad (5.15)$$

However, this expression is only valid if the projected residual equation (Eq. (3.9)) is replaced by the expression $R_i^a = \bar{h}_i^a = 0$. Namely, the Brillouin condition, which is satisfied by the projected residual equation (Eq. (3.9)), rigourously dictates that $t_i^{a(1)} = 0$. Nevertheless, in appendix B, we show that the contribution of these amplitudes on the orbital selection scheme, has a negligible effect on the final excitation energies. We also note that the default settings in ORCA now exclude this contribution from the orbital selection procedure, but it has been used in all the calculations reported in this work.

Let us now proceed with a discussion of the construction of the orbital selection density matrices. The elements of the inactive orbital selection density matrix

$$D_{i'j'} = D_{i'j'}^t + \alpha (D_{i'j'}^s + D_{i'j'}^u), \quad (5.16)$$

consist of a contribution

$$D_{i'j'}^t = \sum_{w,a,b} t_{i'w}^{ab(1)} (2t_{j'w}^{ab(1)} - t_{j'w}^{ba(1)}), \quad (5.17)$$

from the first order $\widehat{T}$ -amplitudes of Eq. (5.9), a contribution

$$D_{i'j'}^s = \sum_{k,w,a} \left[s_{i'k}^{aw(1)} \left(2s_{j'k}^{aw(1)} - s_{kj'}^{aw(1)} \right) + s_{ki'}^{aw(1)} \left(2s_{kj'}^{aw(1)} - s_{j'k}^{aw(1)} \right) \right], \quad (5.18)$$

from the first order $\widehat{S}$ -amplitudes in Eqs. (5.10)-(5.12) and a contribution

$$D_{i'j'}^u = \sum_{k',w,x} u_{i'k'}^{wx(1)} \left(2u_{j'k'}^{wx(1)} - u_{k'j'}^{wx(1)} \right), \quad (5.19)$$

from the first order $\widehat{U}$ -amplitudes in Eq. (5.14). The factor α in Eq. (5.16) is defined as the ratio

$$\alpha = \frac{\text{Tr}(D^t)}{\text{Tr}(D^s) + \text{Tr}(D^u)}. \quad (5.20)$$

The factor α is introduced to get an equal weighting from the correlation effects due to $\widehat{T}_2$ and due to $\widehat{S}_2$ and $\widehat{U}_2$, in the orbitals. In general there are many more $\widehat{T}$ -amplitudes (*i.e.* sum over 2 virtual labels), than there are $\widehat{S}$ - and $\widehat{U}$ -amplitudes. We aim to restore a kind of balance. The elements of the virtual orbital selection density matrix

$$\rho_{ab} = \rho_{ab}^t + \beta \rho_{ab}^s, \quad (5.21)$$

are constructed from a contribution

$$\begin{aligned} \rho_{ab}^t &= \sum_{k,w,c} t_{wk}^{ac(1)} \left(2t_{wk}^{bc(1)} - t_{wk}^{cb(1)} \right) \\ &+ \sum_{i',w,c} t_{i'w}^{ac(1)} \left(2t_{i'w}^{bc(1)} - t_{i'w}^{cb(1)} \right) \\ &+ \sum_w t_w^a t_w^b, \end{aligned} \quad (5.22)$$

from the first order $t_{ij}^{ab(1)}$ amplitudes of Eq. (5.9) and the first order $t_w^{a(1)}$ amplitudes of Eq. (5.15) and a contribution

$$\begin{aligned} \rho_{ab}^s &= \sum_{i',k,w} s_{i'k}^{aw(1)} \left(2s_{i'k}^{bw(1)} - s_{ki'}^{bw(1)} \right) \\ &+ \sum_{i',w,x} s_{xi'}^{aw(1)} \left(2s_{xi'}^{bw(1)} - s_{i'x}^{bw(1)} \right), \end{aligned} \quad (5.23)$$

from the first order $\hat{S}$ -amplitudes of Eqs. (5.10)-(5.12). The factor β in Eq. (5.23) is defined as the ratio

$$\beta = \frac{\text{Tr}(\rho^t)}{\text{Tr}(\rho^s)}. \quad (5.24)$$

It can be verified that the inactive orbital selection density matrix of Eq. (5.16) and the virtual orbital selection density matrix of Eq. (5.21) are symmetric and positive definite. It is important to note that all of the $\hat{T}$ - and $\hat{S}$ -amplitudes which contribute to the density matrices of Eqs. (5.16) and (5.21) have at least one active label. This constitutes the basic mechanism to carve out the subset of orbitals which are important in the description of differential correlation effects.

In the following section, we will demonstrate how the orbital selection density matrices are employed to truncate the inactive and virtual orbital spaces. We will also discuss the procedure for the recanonicalization of the Fock matrix in the truncated basis and the transformation of the molecular orbital coefficients to the new basis.

5.2.2 Orbital Selection Procedure

Since the orbital selection procedure is identical for both the inactive and virtual orbital spaces, we will discuss it in general for an orbital selection density matrix D_{mn} . Here, we let m and n denote either the inactive orbitals i' and j' or the virtual orbitals a and b . The first step is to diagonalize the matrix D_{mn} to obtain a set of eigenvalues λ_n and eigenvectors V_{mn} . Here, the n^{th} column of the matrix $\mathbf{V}$ is the eigenvector corresponding to the eigenvalue λ_n . Given a threshold value of λ_{thresh} (to be determined), we select the eigenvectors we wish to keep according to the criterion

$$\lambda_{\tilde{m}} > \lambda_{\text{thresh}}, \quad (5.25)$$

in which we let $\tilde{m}$ label the truncated set of orbitals. This gives us a truncated set of eigenvectors $V_{m\tilde{m}}$. We then transform the corresponding block (*i.e.* inactive or virtual) of the Fock matrix to the truncated orbital basis,

$$F_{\tilde{m}\tilde{n}} = \sum_{m,n} V_{\tilde{m}m} F_{mn} V_{n\tilde{n}}, \quad (5.26)$$

and diagonalize it to obtain the eigenvectors $C_{\tilde{m}\tilde{n}}$ and eigenvalues $\varepsilon_{\tilde{n}}$. The $\varepsilon_{\tilde{n}}$ are the new orbital energies in the truncated orbital basis and the final set of coefficients $\tilde{V}_{m\tilde{n}}$ is given as

$$\tilde{V}_{m\tilde{n}} = \sum_{\tilde{n}} V_{m\tilde{m}} C_{\tilde{m}\tilde{n}}. \quad (5.27)$$

We can then define the new set of molecular orbital coefficients $\text{MO}_{\mu\tilde{n}}$ in the truncated basis as

$$\text{MO}_{\mu\tilde{n}} = \sum_m \text{MO}_{\mu m} \tilde{V}_{m\tilde{n}}, \quad (5.28)$$

in which μ runs over the atomic orbital space. These coefficients are then used in the integral transformation from the atomic orbital basis to the molecular orbital basis. The resulting integrals, as well as the Fock matrix of Eq. (5.26), are employed for the proceeding MR-EOM-CC calculation in the truncated orbital basis. Let us emphasize that the orbital selection is used for both the $\hat{T}$ - and $\hat{S}$ -amplitudes and in the final diagonalization procedure. For this reason total energies cannot be expected to be accurate. It would be possible to include a second order correction for the total energy to account for the missing amplitudes, but this correction is not included at present.

In the present implementation of the orbital selection scheme, the truncated orbital subspaces are used in the solution of the cluster amplitudes and in the final MRCI diagonalization step. Since these steps are comparable in terms of computational time, it is advantageous to use the orbital selection procedure to reduce the cost of both. This is probably also the most balanced strategy. In future work on a domain based local pair natural orbital (DLPNO) implementation of MR-EOM (*i.e.* see Refs. [6, 5] for information and a historical perspective on the development of the LPNO methodology and Refs. [7, 9, 8, 215] for the subsequent development of the DLPNO approach), a similar orbital selection scheme can be employed to select the 1h and 1p excitations in the final diagonalization step and the transformed matrix elements of $\hat{G}$ that need to be calculated. In this work, the focus will be on testing the efficacy of the orbital selection scheme. The selection is deemed successful if excitation energies converge sufficiently rapidly with the size of the orbital space. The tests presented herein can be considered quite stringent, as the molecules are not that large. If the scheme works for the systems considered in the present study, this signifies that the scheme will also likely be applicable for large molecules with clearly localized chromophores.

5.3 Discussion of Computational Methods and Benchmark Systems

In this work, we have selected five transition metal complexes, $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, ferrocene and cyclopentadienyl nickel nitrosyl (CpNiNO), which have previously been studied with other computational methods [216, 217, 218, 219, 220] and for which experimental band maxima have been measured in the literature [221, 222, 223, 224, 225]. In principle, these molecules are accessible to single-reference methods (*e.g.* TD-DFT [226] (Time-Dependent Density Functional Theory), SAC-CI [18, 19] (Symmetry-

Adapted-Cluster Configuration Interaction), EOM-CC [13, 14, 15] (Equation of Motion Coupled-Cluster), STEOM-CC [16, 209, 17] (Similarity Transformed Equation of Motion Coupled-Cluster), *etc.*), however, the $\text{Ni}(\text{CO})_4$, ferrocene and CpNiNO complexes prove to be particularly difficult for single-reference approaches. In particular, one finds that the use of Brueckner orbitals has a significant effect on the resulting excitation energies in STEOM-ORB [210] and EOM-CCSD(T) [211] calculations.

It is also important to note that there can be considerable difficulties associated with the comparison of the computed vertical excitation energies with experimental band maxima. The experimental bands for all these systems are quite diffuse, which signifies that there can be considerable uncertainty in the positions of the band maxima. Also, in the calculation of vertical excitation energies, we ignore various effects that can alter the positions of the band maxima in the experimental spectrum significantly. In particular, these calculations neglect the effects of vibrations (*e.g.* vibronic coupling, Jahn-Teller distortions, *etc.*), spin-orbit coupling and the solvent, in cases where the spectra have been measured in solution or in a condensed medium. Hence, without including these additional effects in our calculations, there can be considerable discrepancies between the computed excitation energies and experimental band maxima, even with higher levels of theory and large basis sets. Given the difficulties associated with the comparisons with experiment, there are several other ways to gauge the accuracy of the MR-EOM approach for the excitation energies of these transition metal complexes. Namely, we can compare the MR-EOM results with EOM-CCSD(T), which is an accurate approach for the calculation of excitation energies in single-reference systems. We can also examine basis set convergence to determine if the extension of the basis set has a considerable effect on the computed excitation energies. Furthermore, in general, the computed vertical excitation energies should be larger than the experimental band maxima. While there are some MR-ACPF (Multireference Averaged Coupled-Pair Functional) results that are available [218] for the $\text{Fe}(\text{CO})_5$ complex, it would be desirable to compare the MR-EOM results with other multireference calculations (*e.g.* MR-ACPF, MR-AQCC (Multireference Averaged Quadratic Coupled-Cluster)) or even higher level single reference results (EOM-CCSDtq) for the other systems considered herein. A more satisfactory comparison could also be made with the experimental results if we were to include vibronic and spin-orbit effects (and environmental effects, where applicable), but this is beyond the scope of present study. At present, there are no obvious best benchmark results available for the systems under consideration. We will employ Brueckner EOM-CCSD(T) results as our presumably, most accurate reference data for singlet states, but note that even these high level calculations may face difficulties for certain states.

The MR-EOM calculations reported in this work have been performed with a development version of the ORCA quantum chemistry program [24]. In Table 5.1, we have provided the details concerning the state-averaged CASSCF calculations and the reference geometries for the five molecules, $\text{Ni}(\text{CO})_4$,

Table 5.1: Details regarding the state-averaged CASSCF reference and the reference geometries for each of the five molecules considered in this study.

Molecule	CAS(M, N)	Active Orbitals by Irrep. ^a		(N _{singlets} , N _{triplets}) ^b	Reference Geometry
		strongly occupied	strongly unoccupied		
Ni(CO) ₄	CAS(10e, 8o)	$e(d), t_2(d)$	$2t_2(L)$	(15, 15)	BP86/QZVP from Ref. [227]
Fe(CO) ₅	CAS(8e, 6o)	$e'(d), e''(d)$	$2e''(d+L)$	(5, 8)	BP86/QZVP from Ref. [227]
Cr(CO) ₆	CAS(6e, 7o)	$t_{2g}(d)$	$t_{1u}(L), a_{1g}(L)$	(7, 12)	BP86/def2-TZVP
ferrocene	CAS(6e, 5o)	$a'_1(d), e'_2(d)$	$e''_1(d)$	(5, 6)	BP86/QZVP from Ref. [227]
CpNiNO	CAS(10e, 7o)	$a_1(d), e_2(d), e_1(d+L)$	$2e_1(L)$	(5, 10)	BP86/def2-TZVP

^a Strongly occupied orbitals refer to orbitals with occupation numbers greater than 1 and strongly unoccupied orbitals refer to orbitals with occupation numbers less than 1. We have used L to indicate orbitals that are primarily of ligand character and d to denote orbitals that are primarily of metal d character.

^b The number of singlet and triplet states included in the state-averaged CAS.

Fe(CO)₅, Cr(CO)₆, ferrocene and cyclopentadienyl nickel nitrosyl (CpNiNO), considered in this work. The reference geometries were all obtained with the BP86 density functional [228, 229]. The geometries from Ref. [227], were optimized in a QZVP basis [230], while we have employed the def2-TZVP basis [96, 231] in our geometry optimizations. The BP86/def2-TZVP optimized geometries of Cr(CO)₆ and CpNiNO are provided in appendix B, while the geometries for the other molecules can be found in Ref. [227]. Note that due to convergence difficulties of the $\hat{T}$ -amplitude equations in ferrocene, the nearly-singular $\hat{T}_2$ -amplitudes have been projected out according to the procedure described in Ref. [177]. The threshold for discarding the eigenvalues of the metric matrix (two-body cumulant) has been chosen as 0.05 rather than the 0.01 default threshold utilized in Refs. [21, 22, 177].

In all of the MR-EOM calculations, relativistic effects have been included by employing the second-order Douglas-Kroll-Hess (DKH2) Hamiltonian [232, 233, 234, 235]. The scalar relativistically recontracted (SARC) [236] variants of the def2-TZVPP [96, 231] and def2-SVP [237, 231] basis sets have been employed in the MR-EOM calculations. Note that the frozen-core approximation has been used in all of our calculations. The default settings in ORCA are to freeze the 3s and 3p electrons on the first row transition metals. We will demonstrate (*vide infra*) that the inclusion of these orbitals has little effect on the calculated excitation energies for Ni(CO)₄ and the default frozen core settings will be used for the remainder of the MR-EOM calculations performed herein.

Let us note that we employ an (*a-posteriori*) criterion, the %active value, to gauge the reliability of the MR-EOM excitation energy for a given excited state. The %active is defined as the squared length of the active space component of a normalized eigenvector of the transformed Hamiltonian of Eq. (3.8) (*i.e.* the reference weight of a particular state), times 100 %. It is therefore, a measure of the magnitude of the active space component of the given state. In general, the %active should be larger than 90 % (preferably > 95 %) to obtain suitably accurate results. If the %active falls below 85 %, for a particular excited state,

the MR-EOM excitation energy cannot be trusted. Let us note that the %active criterion has only a minor basis set dependence, as only the 1p excitations in the final diagonalization depend on the size of the basis set. The rationalization for our choice of active space therefore, depends on the resulting %active values for the states of interest. The %active criterion and the selection of the active space can first be determined in a small basis set by performing the (generally fast) MRCI calculation (*i.e.* including only the 1h, 1p and 2h configurations), using the untransformed Hamiltonian. In general, we find that the %active values in the final, more expensive, full MR-EOM calculation are also satisfactory and do not vary much from the initial bare MRCI values.

For the purposes of comparison, we have performed STEOM-CC [16, 209, 17] (Similarity Transformed Equation of Motion Coupled-Cluster) calculations of the excitation energies for all of the singly excited states of each of the five molecules considered in this work. In particular, a development version of the ACES II program package [179] has been used to perform these calculations with the STEOM-ORB scheme [210] and Brueckner orbitals [205, 206, 207, 208]. Herein, we will use the notation STEOM(n_o, n_v) to denote a Brueckner STEOM-ORB calculation with n_o active occupied orbitals and n_v active virtual orbitals. We have also performed Brueckner EOM-CCSD(T) calculations on the singly excited singlet states. In all of the Brueckner STEOM-ORB and Brueckner EOM-CCSD(T) calculations, we have employed a Wachters+F basis set [238, 239, 240] for the transition metal atoms and a cc-pVDZ basis [241] on all other atoms. This basis set has been used in an extensive study of the Cr(CO)₆ complex in Ref [242] and was shown to yield satisfactory results therein. It will be demonstrated that in general, excitation energies converge rapidly with the size of the basis. In order to approximately include scalar relativistic effects in the STEOM and Brueckner EOM-CCSD(T) calculations, the kinetic energy operator,

$$T = \frac{p^2}{m + \sqrt{\frac{p^2}{c^2} + m^2}},$$

is employed with $m = 1$ and $c \approx 137$ in atomic units.

In the STEOM-ORB approach, one first performs a regular STEOM-CC calculation and the STEOM eigenvectors are used to construct one-particle density matrices in the occupied and virtual spaces. The natural orbitals of these density matrices, with occupation numbers larger than 0.05, are kept as active orbitals and the remaining active-occupied and virtual orbitals are obtained by diagonalization of the respective blocks of the Fock matrix [210]. The details of this procedure are outlined in Ref. [210], where it has been shown that the electronic states obtained with this approach usually have 99 % or greater %active character. This is also the case here. While the effect of this scheme was rather insignificant for the systems considered in Ref. [210], it is required to obtain states with reasonable %active character for

some of the molecules in this work (*i.e.* $\text{Fe}(\text{CO})_5$ and ferrocene).

5.4 Results

5.4.1 Characterization of Excitation Spectra from MR-EOM Calculations

Let us first employ the MR-EOM methodology to characterize the singlet and triplet excited states and compute the corresponding excitation energies for each of the molecules listed in Table 5.1. For the $\text{Ni}(\text{CO})_4$ molecule, the calculated MR-EOM/def2-SVP and MR-EOM/def2-TZVPP results appear in Table 5.2. The character of the various states, in terms of the orbitals in the active space (*cf.* Table 5.1), has been computed at the MR-EOM/def2-TZVPP level of theory and is provided in Table 5.2. We have also included the MR-EOM/def2-TZVPP results for which the $3s3p$ electrons on nickel are correlated. The CASPT2(v) results from Ref. [216], the calculated STEOM(16o,16v) and Brueckner EOM-CCSD(T) results, the SAC-CI results from Ref. [217] and the experimental gas phase band maximum from Ref. [221], for the first T_2 singlet state, also appear in Table 5.2. Note that all of the singlet and triplet excited states have predominant single excitation character. Also, the %active is greater than 90 % for all of the excited states and is 90.6 % for the ground state.

Table 5.2: Singlet and triplet excited states and excitation energies (eV) for $\text{Ni}(\text{CO})_4$.

State	Character	%active	MR-EOM/ def2-SVP	MR-EOM def2-TZVPP		CASPT2 ^b	STEOM (16o,16v)	EOM- CCSD(T) ^c	SAC-CI ^d	Expt. ^e
				A ^a	B ^a					
Singlets										
¹ T ₁	88%(t ₂ → 2t ₂)	91.5	4.83	4.82	4.83	4.46	4.59	4.73	4.53	4.6
¹ E	86%(t ₂ → 2t ₂)	90.5	4.90	4.90	4.91	4.14	4.61	4.70	4.52	
¹ T ₂	87%(t ₂ → 2t ₂)	91.5	5.09	5.08	5.09	4.76	4.92	5.01	4.79	
¹ T ₁	89%(e → 2t ₂)	93.9	5.59	5.64	5.71	5.33	5.36	5.30	5.25	
¹ T ₂	88%(e → 2t ₂)	93.7	6.00	6.03	6.05	5.78	5.68	5.77	5.76	
Triplets										
³ A ₁	90%(t ₂ → 2t ₂)	92.7	4.05	4.03	4.06		3.73			
³ T ₂	89%(t ₂ → 2t ₂)	92.3	4.49	4.46	4.48		4.20			
³ E	89%(t ₂ → 2t ₂)	91.9	4.58	4.57	4.59		4.32			
³ T ₁	88%(t ₂ → 2t ₂)	91.6	4.71	4.71	4.71		4.43			
³ T ₁	90%(e → 2t ₂)	94.3	5.51	5.55	5.59		5.28			
³ T ₂	89%(e → 2t ₂)	94.1	5.61	5.66	5.68		5.53			

^a A refers to an MR-EOM/def2-TZVPP calculation with frozen $3s3p$ electrons and B refers to an MR-EOM/def2-TZVPP calculation with correlated $3s3p$ electrons.

^b CASPT2(v) from Ref. [216]

^c Brueckner EOM-CCSD(T)

^d Ref. [217]

^e gas phase spectrum from Ref. [221]

Comparing the MR-EOM results in the def2-SVP basis to those in the larger def2-TZVPP basis, one observes that the excitation energies only differ by as much as 0.05 eV. This signifies that the use of the larger basis has little effect on the MR-EOM excitation energies. Interestingly, for the excitations emanating from the active orbital with t_2 symmetry, the def2-TZVPP excitation energies are smaller than the corresponding def2-SVP values, whereas the converse is true for the excitations emanating from the active orbital of e symmetry. Furthermore, the difference between the def2-TZVPP and corresponding def2-SVP excitation energies is relatively smaller for the excitations coming from the t_2 orbital than those which originate out of the e orbital.

Let us then compare the MR-EOM/def2-TZVPP excitation energies, using the default frozen core settings in ORCA (*i.e.* frozen $3s3p$ electrons on nickel), with those for which the $3s3p$ electrons on nickel are correlated. We observe that the excitation energies in the latter case are all larger than those for which the $3s3p$ electrons are frozen in the correlation treatment. Furthermore, for the majority of excitation energies, the difference is only as much as 0.04 eV. The only exception is for the second T_1 singlet state, where the difference is 0.066 eV. Hence, we see that the inclusion of the $3s3p$ orbitals on the nickel atom, in the correlation treatment, has little effect on the calculated MR-EOM excitation energies. This signifies that the default frozen-core settings in ORCA are well justified and will thus, be employed in the remainder of this work.

Upon comparing the MR-EOM/def2-TZVPP results with the CASPT2 [216], STEOM(16o,16v) and SAC-CI [217] results, it is observed that the MR-EOM excitation energies are always significantly larger than those calculated with these other approaches. For the singlet states of dominant $t_2 \rightarrow 2t_2$ character, the MR-EOM excitation energies agree quite well with the Brueckner EOM-CCSD(T) values, in particular, for the states of T_1 and T_2 symmetry. Furthermore, the MR-EOM excitation energy, for the first singlet state of T_2 symmetry is 0.48 eV greater than the experimental value obtained from the gas phase UV spectrum of Ref. [221]. The corresponding values calculated with the other methods agree more closely with experiment, especially in the case of CASPT2 and SAC-CI. However, as mentioned previously, the comparison of vertical excitation energies with experimental values can be misleading due to the exclusion of vibrational effects, spin-orbit coupling and environmental effects (*i.e.* when comparing with spectra obtained in solution or condensed phases). We will return to the issue of vibrational effects at the end of this section and in appendix B.

Let us now consider the other two metal carbonyl complexes, as the details are similar to those for the $\text{Ni}(\text{CO})_4$ molecule. The assignment of the singlet and triplet excited states and corresponding excitation energies appear in Table 5.3 for $\text{Fe}(\text{CO})_5$ and in Table 5.4 for $\text{Cr}(\text{CO})_6$. The characterization of the the excited states in terms of the orbitals comprising the active space (see Table 5.1), has been determined

at the MR-EOM/def2-TZVPP level of theory. It is observed that the excitations are predominantly of single excitation character. The %active is also greater than 90 % for all of the excited states and is larger than 95 % in most cases. Furthermore, the %active for the ground state of $\text{Fe}(\text{CO})_5$ is 95 % and is 93.8 % for the ground state of $\text{Cr}(\text{CO})_6$. In the case of $\text{Fe}(\text{CO})_5$ in Table 5.3, we have included the calculated STEOM(13o,21v) and Brueckner EOM-CCSD(T) excitation energies and the MR-ACPF results from Ref. [218], as well as experimental band maxima from Refs. [221] (gas phase) and [222] (solution). The CASPT2(v) results from Ref. [216] (*i.e.* with the active space D), the calculated STEOM(14o,23v) and Brueckner EOM-CCSD(T) results and the experimental band maximum for the singlet state of T_{1u} symmetry have been included in Table 5.4 for $\text{Cr}(\text{CO})_6$.

 Table 5.3: Singlet and triplet excited states and excitation energies (eV) for $\text{Fe}(\text{CO})_5$.

State	Character	%active	MR-EOM/ def2-SVP	MR-EOM/ def2-TZVPP	STEOM (13o,21v)	EOM- CCSD(T) ^a	MR-ACPF ^b	Expt.
<i>Singlets</i>								
$^1A_1''$	94%($e' \rightarrow 2e''$)	96.2	4.54	4.55	4.04	4.73	4.43	
$^1E''$	93%($e' \rightarrow 2e''$)	95.2	4.84	4.84	4.27	4.91	4.63	
$^1A_2''$	94%($e' \rightarrow 2e''$)	96.1	4.90	4.87	4.56	5.17	4.70	4.4 ^c
$^1A'$	94%($e'' \rightarrow 2e''$)	95.2	5.63	5.71	5.57			
$^1E'$	90%($e'' \rightarrow 2e''$)	92.1	5.72	5.82	5.74			5.0 ^d
<i>Triplets</i>								
$^3A''$	94%($e' \rightarrow 2e''$)	95.7	4.28	4.30	3.85			
$^3E''$	94%($e' \rightarrow 2e''$)	95.7	4.43	4.43	3.95			
$^3A''$	93%($e' \rightarrow 2e''$)	95.6	4.53	4.52	4.11			
$^3A'$	93%($e'' \rightarrow 2e''$)	94.2	4.56	4.67	4.67			
$^3E'$	94%($e'' \rightarrow 2e''$)	95.4	5.12	5.21	5.13			
$^3A'$	92%($e'' \rightarrow 2e''$)	95.0	5.47	5.56	5.57			

^a Brueckner EOM-CCSD(T)

^b Ref. [218]

^c solvent (isopentane/methylcyclohexane mixture) spectrum from Ref. [222]

^d gas phase spectrum from Ref. [221]

In Table 5.3, we observe that the difference between the MR-EOM results in the def2-SVP and def2-TZVPP bases is small for the singlet and triplet excitations with $e' \rightarrow 2e''$ character and that the difference becomes significantly larger for the excitations of $e'' \rightarrow 2e''$ character. Similarly, in the case of $\text{Cr}(\text{CO})_6$ in Table 5.4, the differences between the def2-SVP and def2-TZVPP results are all ≤ 0.06 eV for the excitations of $t_{2g} \rightarrow t_{1u}$ character and are significantly larger (> 0.1 eV) for the singlet and triplet excitations of $t_{2g} \rightarrow a_{1g}$ character.

If we compare the MR-EOM/def2-TZVPP results for $\text{Fe}(\text{CO})_5$ with the MR-ACPF results in Table 5.3, we observe that the MR-EOM excitation energies are all larger than those calculated with this method. However, the MR-EOM excitation energies are always within 0.21 eV of the MR-ACPF results. One also observes that the MR-EOM values are considerably larger than the STEOM(13o,21v) values for

Table 5.4: Singlet and triplet excited states and excitation energies (eV) for $\text{Cr}(\text{CO})_6$.

State	Character	%active	MR-EOM/ def2-SVP	MR-EOM/ def2-TZVPP	STEOM (14o,23v)	EOM- CCSD(T) ^a	CASPT2 ^b	Expt. ^c
<i>Singlets</i>								
$^1A_{2u}$	96%($t_{2g} \rightarrow t_{1u}$)	96.1	4.31	4.30	4.04		3.66	
^1E_u	95%($t_{2g} \rightarrow t_{1u}$)	95.6	4.32	4.30	4.06	4.36	3.67	
$^1T_{2u}$	95%($t_{2g} \rightarrow t_{1u}$)	95.9	4.37	4.34	4.07	4.39	3.64	
$^1T_{1u}$	94%($t_{2g} \rightarrow t_{1u}$)	94.5	4.97	4.91	4.54	4.95	4.19	4.4
$^1T_{2g}$	96%($t_{2g} \rightarrow a_{1g}$)	96.7	5.95	6.08	5.95			
<i>Triplets</i>								
$^3A_{2u}$	97%($t_{2g} \rightarrow t_{1u}$)	97.3	4.36	4.31	4.11			
^3E_u	97%($t_{2g} \rightarrow t_{1u}$)	96.8	4.38	4.35	4.15			
^3T_u	98%($t_{2g} \rightarrow t_{1u}$)	97.3	4.45	4.40	4.15		3.78	
^3T_u	96%($t_{2g} \rightarrow t_{1u}$)	96.7	4.45	4.41	4.19			
$^3T_{2g}$	96%($t_{2g} \rightarrow a_{1g}$)	96.7	5.93	6.06	5.93			

^a Bruckner EOM-CCSD(T)

^b CASPT2(v) from Ref. [216] with the active space D

^c gas phase spectrum from Ref. [221]

the excitations of $e' \rightarrow 2e''$ character, while the deviations between the STEOM(13o,21v) and MR-EOM excitation energies are substantially reduced for the excitations of $e'' \rightarrow 2e''$ character. For the singlet states of $e' \rightarrow 2e''$ character, the Brueckner EOM-CCSD(T) results agree more closely with the corresponding MR-EOM values (deviations ≤ 0.3 eV) .

In Table 5.4, one can see that the MR-EOM excitation energies for $\text{Cr}(\text{CO})_6$ are all substantially larger than the corresponding CASPT2 values. On the other hand, even though the deviations are still significant, the STEOM(14o,23v) excitation energies are considerably closer to the corresponding MR-EOM values. Also, the deviations between the STEOM(14o,23v) and MR-EOM results are much smaller for the singlet and triplet states of $t_{2g} \rightarrow a_{1g}$ character, in comparison with the states of $t_{2g} \rightarrow t_{1u}$ character. Furthermore, one observes that the available Brueckner EOM-CCSD(T) excitation energies for the singlet states are in excellent agreement with the corresponding MR-EOM results. It is interesting to note that in general, for the metal carbonyls considered in this work, one finds that the majority of the STEOM and MR-EOM relative excitation energies of the singlets and triplets (*i.e.* the spacing between consecutive singlet or triplet states) have significantly better agreement than the excitation energies themselves.

Comparing the MR-EOM/def2-TZVPP results for $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ with the corresponding experimental values in Tables 5.3 (*i.e.* the singlets of A'_2 and E' symmetry) and 5.4 (the singlet of T_{1u} symmetry), respectively, it is observed that the computed values are all significantly larger than the experimental band maxima. In contrast, the STEOM results agree quite well with the experimental band maxima for the singlet of A'_2 symmetry in $\text{Fe}(\text{CO})_5$ and the singlet of T_{1u} symmetry in $\text{Cr}(\text{CO})_6$, while there is a significant deviation between the STEOM(13o,21v) excitation energy and the band maximum

CHAPTER 5. SPECTRA OF TM COMPLEXES AND ORBITAL SELECTION IN MR-EOM

for the state of E' symmetry in $\text{Fe}(\text{CO})_5$.

Table 5.5: Singlet and Triplet excited states and excitation energies (eV) for ferrocene.

State	Character	%active	MR-EOM/ def2-SVP	MR-EOM/ def2-TZVPP	STEOM (17o,30v)	EOM- CCSD(T) ^a	SAC-CI ^b	Expt.
<i>Singlets</i>								
$^1E''$	$48\%(a'_1 \rightarrow e''_1) + 46\%(e'_2 \rightarrow e''_1)$	95.7	2.70	2.71	1.69	3.06	2.27	2.81^c (2.70) ^d
$^1E''_2$	$96\%(e'_2 \rightarrow e''_1)$	96.4	2.75	2.77	1.86	3.12	2.11	2.81^c (2.98) ^d
$^1E''_1$	$44\%(a'_1 \rightarrow e''_1) + 47\%(e'_2 \rightarrow e''_1)$	93.5	4.41	4.32	2.90	4.35	4.03	3.82^c
$^1E'$	$69\%((a'_1)(e'_2) \rightarrow (e''_1)^2) + 16\%((e'_2)^2 \rightarrow (e''_1)^2) + 11\%((a'_1)^2 \rightarrow (e''_1)^2)$	97.2	5.38	5.41				
$^1E'$	$74\%((a'_1)(e'_2) \rightarrow (e''_1)^2) + 23\%((e'_2)^2 \rightarrow (e''_1)^2)$	97.3	5.52	5.55				
$^1A'$	$74\%((a'_1)(e'_2) \rightarrow (e''_1)^2) + 17\%((a'_1)^2 \rightarrow (e''_1)^2)$	97.0	5.65	5.66				
$^1E'$	$50\%((a'_1)(e'_2) \rightarrow (e''_1)^2) + 40\%((e'_2)^2 \rightarrow (e''_1)^2)$	96.9	5.72	5.75				
$^1E'$	$97\%((e'_2)^2 \rightarrow (e''_1)^2)$	97.6	5.82	5.86				
$^1A'$	$92\%((e'_2)^2 \rightarrow (e''_1)^2)$	95.4	6.41	6.40				
$^1A'$	$21\%((a'_1)(e'_2) \rightarrow (e''_1)^2) + 43\%((e'_2)^2 \rightarrow (e''_1)^2) + 31\%((a'_1)^2 \rightarrow (e''_1)^2)$	97.0	6.39	6.41				
<i>Triplets</i>								
$^3E''_1$	$18\%(a'_1 \rightarrow e''_1) + 77\%(e'_2 \rightarrow e''_1)$	95.8	1.66	1.75	0.93		1.40	1.65^e (1.74) ^f
$^3E''_2$	$94\%(e'_2 \rightarrow e''_1)$	95.6	1.77	1.86	1.11		1.68	2.01^e (2.05) ^f
$^3E''_1$	$73\%(a'_1 \rightarrow e''_1) + 17\%(e'_2 \rightarrow e''_1)$	92.9	2.59	2.61	1.52		2.60	(2.29) ^f
$^3A'$	$70\%((a'_1)(e'_2) \rightarrow (e''_1)^2) + 17\%((e'_2)^2 \rightarrow (e''_1)^2) + 9\%((a'_1)^2 \rightarrow (e''_1)^2)$	96.8	4.33	4.44				
$^3A'$	$88\%((a'_1)(e'_2) \rightarrow (e''_1)^2) + 8\%((e'_2)^2 \rightarrow (e''_1)^2)$	96.5	4.35	4.45				
$^3E'$	$92\%((a'_1)(e'_2) \rightarrow (e''_1)^2)$	97.2	4.44	4.53				

^a Brueckner EOM-CCSD(T)

^b Ref. [219]

^c gas phase spectrum from Ref. [223] (N.B. identical values are measured from the solvent spectrum in Ref. [223] and the solvent spectrum in Ref. [224])

^d low-temperature (77 K) glass matrix (ethyl ether/isopentane/ethanol mixture) spectrum from Ref. [224]

^e gas phase photoacoustic spectrum from Ref. [243]

^f solvent (ethanol) spectrum from Ref. [223]

The excitation energies and characters of the various singlet and triplet states of ferrocene, in terms of the active space orbitals (Table 5.1), appear in Table 5.5. Once again, the characterization of these states has been made at the MR-EOM/def2-TZVPP level of theory. The %active for all of the excited states exceeds 90 % and is greater than 95 % for the vast majority of them. The SAC-CI excitation energies from Ref. [219] and calculated STEOM(17o,30v) and Brueckner EOM-CCSD(T) results also appear in Table 5.5, along with excitation energies extracted from the solvent and gas phase UV/Vis. spectra from Ref. [223] and the low temperature (77 K) glass matrix UV/Vis. spectrum from Ref. [224].

In Table 5.5, it is observed that the first three singlets and triplets are single excitations in the active space. It should also be noted that the d-d transitions, involving the three (lowest lying) singly excited singlet states, are dipole forbidden. The higher lying singlet and triplet states are all double excitations within the active space. The notation $(a'_1)(e'_2) \rightarrow (e''_1)^2$, for example, specifies a double excitation involving the promotion of an electron from the orbital of a'_1 symmetry to the orbital of e''_1 symmetry and the

simultaneous excitation of an electron from the e'_2 orbital to the e''_1 orbital. Similarly, the notation $(e'_2)^2 \rightarrow (e''_1)^2$ denotes the excitation of two electrons from the e'_2 orbital into the e''_1 orbital. We will also use a similar notation (*e.g.* $(a_1)(e_2)(e_1) \rightarrow (2e_1)^3$) to denote triple excitation character in the discussion of the results for CpNiNO below. It is interesting to note that many of the excitations in ferrocene involve significant mixing of two or more types of excitations, while the excitations in the metal carbonyls were always characterized by a large fraction of one type of single excitation in the active space.

Considering the differences between the MR-EOM/def2-SVP and def2-TZVPP excitation energies for the singlet states in Table 5.5, it is observed that, with the exception of the second state of E''_1 symmetry, all of the def2-TZVPP are slightly larger (*i.e.* within 0.05 eV) than the def2-SVP values. For the triplet states, the def2-TZVPP excitation energies are also larger than the def2-SVP values, however, the difference approaches 0.1 eV in almost all the cases (*i.e.* except for the second state of E''_1 symmetry). This observation seems to indicate that the extension of the basis set has a different effect on the energies of the singlet states (including the ground state reference energy) than it does for the triplet states. It can be anticipated that extension of the basis set is somewhat more important for the dynamic correlation in the singlet states than for the triplet states. Hence, one might expect that the excitation energies of the triplet states would increase with the size of the basis set (lowering the singlet ground state energy), while the singlet states are less affected.

In Table 5.5, we also observe that the MR-EOM/def2-TZVPP excitation energies are larger than the corresponding SAC-CI [219] values for the majority of the singly excited states. The only exception is for the second triplet of E''_1 symmetry, where the MR-EOM/def2-TZVPP and SAC-CI values are nearly identical. It is also observed that the SAC-CI calculation predicts that the lowest lying singlet state is that of E''_2 symmetry, whereas the MR-EOM calculation gives the first singlet of E''_1 symmetry as the lowest lying singlet state. The STEOM(17o,30v) results are much lower than any of the other calculated excitation energies which indicates that the STEOM(17o,30v) excitation energies are very poor for this particular system. Not surprisingly, the IP and EA states in the STEOM calculation have a large double excitation character, which indicates a breakdown in the methodology. It is further observed that the Brueckner EOM-CCSD(T) results for the two lowest lying singlet states are 0.35 eV larger than the corresponding MR-EOM results, while the agreement is very good for the second singlet state of E''_1 symmetry. In general, the Brueckner EOM-CCSD(T) excitation energies are larger than those computed with any of the other methods considered in Table 5.5.

From the gas phase UV/Vis. spectrum in Ref. [223] and the solvent UV/Vis. spectra in Refs. [223, 224], there are two observed bands at 2.81 eV and 3.82 eV which have been assigned as symmetry forbidden d-d transitions at the ground-state geometry. In the low temperature (77 K) glass matrix spectrum of

Ref. [224], the 2.81 eV absorption band is resolved into two bands (2.70 eV and 2.98 eV) as indicated in Table 5.5. The three transitions have been assigned to dipole forbidden d-d excitations involving the three lowest singlet states (of $^1E_1''$, $^1E_2''$ and $^1E_1''$ symmetry, respectively) at the MR-EOM level of theory. The MR-EOM/def2-TZVPP excitation energy for the lowest lying singlet excited state is nearly the same as the low temperature experimental value in the glass matrix. This is almost certainly coincidental as the spectrum has been measured in a condensed phase. In contrast, the MR-EOM/def2-TZVPP value for the singlet of E_2'' symmetry is somewhat smaller (0.21 eV) than the experimental value obtained in Ref. [224]. Since the excitation energies associated with these two low-lying singlet states are so close in the MR-EOM calculations, it is not surprising that they are observed as one absorption band in the room temperature gas phase spectrum. Also, it is apparent that the MR-EOM excitation energies agree quite well with the gas phase value for this band. For the second singlet of E_1'' symmetry, the corresponding MR-EOM/def2-TZVPP excitation energy is significantly larger than the gas-phase experimental value from Ref. [223], but it agrees very well with the Brueckner EOM-CCSD(T) value.

There are two very weak intensity absorption bands observed in the gas phase photoacoustic absorption spectrum of Ref. [243], which have been attributed to spin-forbidden singlet to triplet transitions therein. Furthermore, three weak intensity absorption bands have been observed in the solvent UV/Vis. spectrum of Ref. [223] and have also been assigned to spin-forbidden singlet to triplet transitions. These absorption bands have been assigned to d-d transitions to the lowest triplet states (of $^3E_1''$, $^3E_2''$ and $^3E_1''$ symmetry, respectively) calculated with MR-EOM in Table 5.5. The MR-EOM/def2-TZVPP excitation energy for the lowest lying triplet is 0.10 eV larger than the gas phase experimental value and is nearly identical with the band maximum from the solvent spectrum. For the triplet state with E_2'' symmetry, the MR-EOM/def2-TZVPP value is smaller than the gas phase value by 0.15 eV and for the second triplet state of E_1'' symmetry, the MR-EOM/def2-TZVPP value is significantly larger than the experimental value from the solvent spectrum.

The composition of the singlet and triplet excitations of cyclopentadienyl nickel nitrosyl (CpNiNO) in terms of the active space orbitals (*cf.* Table 5.1) and the corresponding excitation energies appear in Table 5.6. The characterization of the various excited states has been carried out at the MR-EOM/def2-TZVPP level of theory. It is observed that the %active for the majority of the excited states is larger than 90 % and falls just below the threshold for two of the excited states in Table 5.6. The %active for the ground state is found to have a value of 94 %. The STEOM(12o,21v) and Brueckner EOM-CCSD(T) results have been included in Table 5.6. The experimental band maxima from the low temperature (20 K) glass matrix UV/Vis. spectrum of Ref. [225] also appear in Table 5.6. It is observed that the first five singlets and six triplets are predominantly of single excitation character, while the higher lying states are

dominated by double and even, triple excitation character.

Table 5.6: Singlet and Triplet excited states and excitation energies (eV) for cyclopentadienyl nickel nitrosyl (CpNiNO).

State	Character	%active	MR-EOM/ def2-SVP	MR-EOM/ def2-TZVPP	STEOM (12o,21v)	EOM- CCSD(T) ^a	Expt. ^b
<i>Singlets</i>							
¹ E ₁	50%(a ₁ → 2e ₁) + 31%(e ₂ → 2e ₁)	94.7	2.71	2.81	2.95	2.93	2.68
¹ E ₂	81%(e ₂ → 2e ₁)	94.9	2.82	2.98	3.04	3.00	
¹ A ₂	88%(e ₁ → 2e ₁)	89.9	3.48	3.49	2.55	3.06	3.22
¹ E ₁	35%(a ₁ → 2e ₁) + 49%(e ₂ → 2e ₁)	93.1	3.65	3.69	3.47	3.17	
¹ E ₂	86%(e ₁ → 2e ₁)	88.6	3.73	3.74	2.79	3.63	
¹ A	80%((e ₂) ² → (2e ₁) ²)	91.5	5.64	5.77			
¹ E ₂	79%((a ₁)(e ₂) → (2e ₁) ²) + 25%((a ₁)(e ₂)(e ₁) → (2e ₁) ³)	96.9	5.86	6.07			
¹ E ₁	59%((a ₁)(e ₁) → (2e ₁) ²) + 15%((e ₂)(e ₁) → (2e ₁) ²) + 8%((a ₁)(e ₁) ² → (2e ₁) ³)	91.4	6.57	6.66			
¹ E ₂	74%((e ₂)(e ₁) → (2e ₁) ²) + 11%((e ₂)(e ₁) ² → (2e ₁) ³)	92.3	6.60	6.77			
¹ E ₂	86%((e ₁) ² → (2e ₁) ²)	90.3	7.04	7.11			
<i>Triples</i>							
³ A ₁	86%(e ₁ → 2e ₁)	93.6	1.99	2.08	1.45		
³ E ₁	46%(a ₁ → 2e ₁) + 38%(e ₂ → 2e ₁)	94.6	2.58	2.67	2.75		
³ E ₂	87%(e ₁ → 2e ₁)	91.8	2.77	2.82	2.07		
³ E ₂	84%(e ₂ → 2e ₁)	94.6	2.68	2.84	2.93		
³ E ₁	39%(a ₁ → 2e ₁) + 47%(e ₂ → 2e ₁)	93.6	3.01	3.08	3.02		
³ A ₂	85%(e ₁ → 2e ₁)	90.4	3.19	3.25	2.53		
³ E ₁	45%((a ₁)(e ₁) → (2e ₁) ²) + 35%((e ₂)(e ₁) → (2e ₁) ²)	94.0	5.43	5.60			
³ E ₂	65%((e ₂)(e ₁) → (2e ₁) ²) + 16%((a ₁)(e ₁) → (2e ₁) ²) + 9%((e ₂)(e ₁) ² → (2e ₁) ³)	94.2	5.53	5.74			
³ E ₂	87%((e ₁) ² → (2e ₁) ²)	91.9	5.67	5.79			
³ E ₂	71%((a ₁)(e ₂) → (2e ₁) ²) + 24%((a ₁)(e ₂)(e ₁) → (2e ₁) ³)	96.6	5.73	5.93			
³ E ₁	50%((e ₂)(e ₁) → (2e ₁) ²) + 31%((a ₁)(e ₁) → (2e ₁) ²)	93.1	6.07	6.22			
³ E ₂	81%((e ₂)(e ₁) → (2e ₁) ²) + 12%((e ₂)(e ₁) ² → (2e ₁) ³)	93.6	6.02	6.23			

^a Brueckner EOM-CCSD(T)

^b low temperature (20 K) glass matrix (3-methylpentane) spectrum from Ref. [225]

Comparing the MR-EOM/def2-TZVPP excitation energies with the corresponding MR-EOM/def2-SVP values in Table 5.6, it is observed that the def2-TZVPP values are all consistently larger than those in the def2-SVP basis. Furthermore, the differences can be as large as ~ 0.2 eV in some cases and are non-negligible for the majority of the calculated states. Hence, the majority of the excitation energies for the CpNiNO molecule appear to be quite sensitive to the quality of the basis set. Given this observation and the fact that the differences approach 0.1 eV in several of the excitation energies for other molecules considered in this work, we recommend that basis sets, of at least triple- ζ quality, be employed for the calculation of excitation energies.

From Table 5.6, it is apparent that the STEOM(12o,21v) excitation energies for the states of dominant $e_1 \rightarrow 2e_1$ character are erratic, as they are much smaller than the corresponding MR-EOM and Brueckner EOM-CCSD(T) values. While the agreement between the STEOM(12o,21v) MR-EOM/def2-TZVPP results is quite good for many of the singly excited states (*i.e.* those with $e_2 \rightarrow 2e_1$ character

and the others which are a mixture of $a_1 \rightarrow 2e_1$ and $e_2 \rightarrow 2e_1$ character), it is very poor for the states which have dominant $e_1 \rightarrow 2e_1$ character. Comparing the MR-EOM/def2-TZVPP excitation energies with the corresponding Brueckner EOM-CCSD(T) values, we find that the values agree reasonably well for the lowest two singlet states and the second singlet state of E_2 symmetry, while the deviations are significantly larger for the A_2 state and the second singlet of E_1 symmetry.

The agreement between MR-EOM/def2-TZVPP and experiment is substantially better (0.13 eV) for the lowest lying singlet of E_1 symmetry than for the higher lying A singlet (0.27 eV). This is possibly due to the fact that the %active is relatively smaller for the latter state when compared with the state of E_1 symmetry. It is important to mention that the UV/Vis. spectrum of Ref. [225] has been measured in a glass matrix at low temperature (20 K). This can have a significant effect on the measured positions of certain band maxima, as was observed for the lowest two singlet states of ferrocene in Table 5.5.

Let us summarize the findings of this section. In general, MR-EOM calculations employing relatively small active spaces yield fairly robust and accurate results. Often the comparison with Brueckner based EOM-CCSD(T) is satisfactory (*i.e.* within 0.2 eV), but occasionally, larger discrepancies are observed. Often the Brueckner EOM-CCSD(T) excitation energies are larger than the corresponding MR-EOM values, with the exception of all the singlet states in $\text{Ni}(\text{CO})_4$, as well as the singlet state of A_1 symmetry and the second (higher lying) singlet states of E_1 and E_2 symmetry in CpNiNO (*i.e.* Table 5.6). The Brueckner STEOM-ORB results are usually somewhat lower than the corresponding MR-EOM values. For the metal carbonyl complexes, the STEOM results look reasonable and the allowed transitions agree very well with the experimental band maxima, except in the case of the singlet of E' symmetry in $\text{Fe}(\text{CO})_5$, in Table 5.3. However, in Table 5.5, one observes that the STEOM results for ferrocene are too low by about 1 eV and that the results for CpNiNO , in Table 5.6, are erratic. This seems to indicate that the STEOM results are not very reliable at the singles and doubles level. It is believed that these results could be improved significantly if triples corrections were considered in the EOM-IP and possibly, the EOM-EA parts of the calculation.

The agreement between the spacing of the excitation energies in MR-EOM, Brueckner STEOM-ORB and Brueckner EOM-CCSD(T) is often better than for the excitation energies themselves, which signifies that the calculation of the ground state energy can be problematic. This is perhaps also indicated by the fact that we think the use of Brueckner orbitals is imperative in the single-reference calculations. In future work, we will present a more detailed comparison of MR-EOM with single-reference EOM-CCSD and STEOM results. It is also believed that the use of Brueckner orbitals might be important in MR-EOM calculations. We find discrepancies between the MR-EOM-T|SXD results obtained in ACES II [179] and the MR-EOM-T|T[†]|SXD results in ORCA [24]. The major difference is in the use of both the $\hat{T}$

(Eq. (3.8)) and $\hat{T}^\dagger$ (Eq. (3.30)) transformations in the ORCA implementation. In effect, it is believed that the inclusion of the $\hat{T}^\dagger$ transformation of Eq. (3.30) can mimic the Brueckner orbital rotation. This aspect will be investigated in future work.

In comparison with other calculations, we think that MR-EOM performs quite satisfactorily. Let us emphasize the cost-effectiveness of the calculations. Solving for the $\hat{T}$ - and $\hat{S}$ -amplitudes in MR-EOM is about four times as expensive as a single-reference CCSD calculation. The final diagonalization step typically constitutes $\sim 30\%$ of the total calculation time. One finds that a MR-EOM calculation (including first order spin-orbit effects) on the Co atom (in a def2-TZVPP basis), which yields over 100 electronic states, takes about 30 min. In contrast, calculating the same number of states in the Co atom, using the (uncontracted) MR-AQCC/def2-TZVPP approach (with spin-orbit effects), takes over a week! The accuracy of MR-EOM for atoms is well established. For example, the RMS error for first row transition metal atoms is typically below 0.1 eV [178]. The systems considered in the present work have been selected to be accessible by single-reference methodologies for ease of comparison. However, MR-EOM is a generally applicable multireference method, as illustrated by applications to atomic systems.

There is one remaining issue that needs to be addressed. The agreement of MR-EOM with experiment, for the metal carbonyl complexes, leaves something to be desired (*i.e.* deviations are on the order of ~ 0.5 eV). What can we say about the possible sources of error? We think that the observed discrepancies likely originate from vibrational shifts of the experimental band maxima, to values which are considerably lower than the vertical excitation energies. For all of the metal carbonyls, the metal-carbon separation in the lowest triplet state increases by about 0.1 Å (at the B3PW91/cc-pVDZ level of theory), when compared with the ground state value. For Ni(CO)₄, we performed a more detailed investigation, which appears in appendix B. In summary, the adiabatic excitation energies are estimated to be 0.24-0.70 eV smaller than the vertical excitation energies. However, in a 1-dimensional Franck-Condon calculation, the band maximum did not shift from the vertical excitation energy. It is important to note that we have not considered changes in energy upon lowering the symmetry of the molecule (*e.g.* Jahn-Teller distortions). Due to the high degeneracy of the electronic states, an accurate assessment of vibrational effects will require the construction of vibronic models. We hope to be able to perform such calculations (based on MR-EOM results) in the future. This will require a major effort and is far beyond the scope of this work. However, we would be surprised if the band maxima, in such a calculation, would be identical to the calculated vertical excitation energies. If the band maxima are shifted from the vertical excitation energies, it would be to lower energies, improving the agreement of the computed results with experiment. Of course, a shift of 0.5 eV is very large and perhaps too much to hope for.

5.4.2 Orbital Selection in the Inactive and Virtual Spaces

In order to evaluate the orbital selection scheme described in section 5.2, we will consider the excitation energies of the five transition metal complexes of section 5.4.1, in a def2-TZVPP basis. The

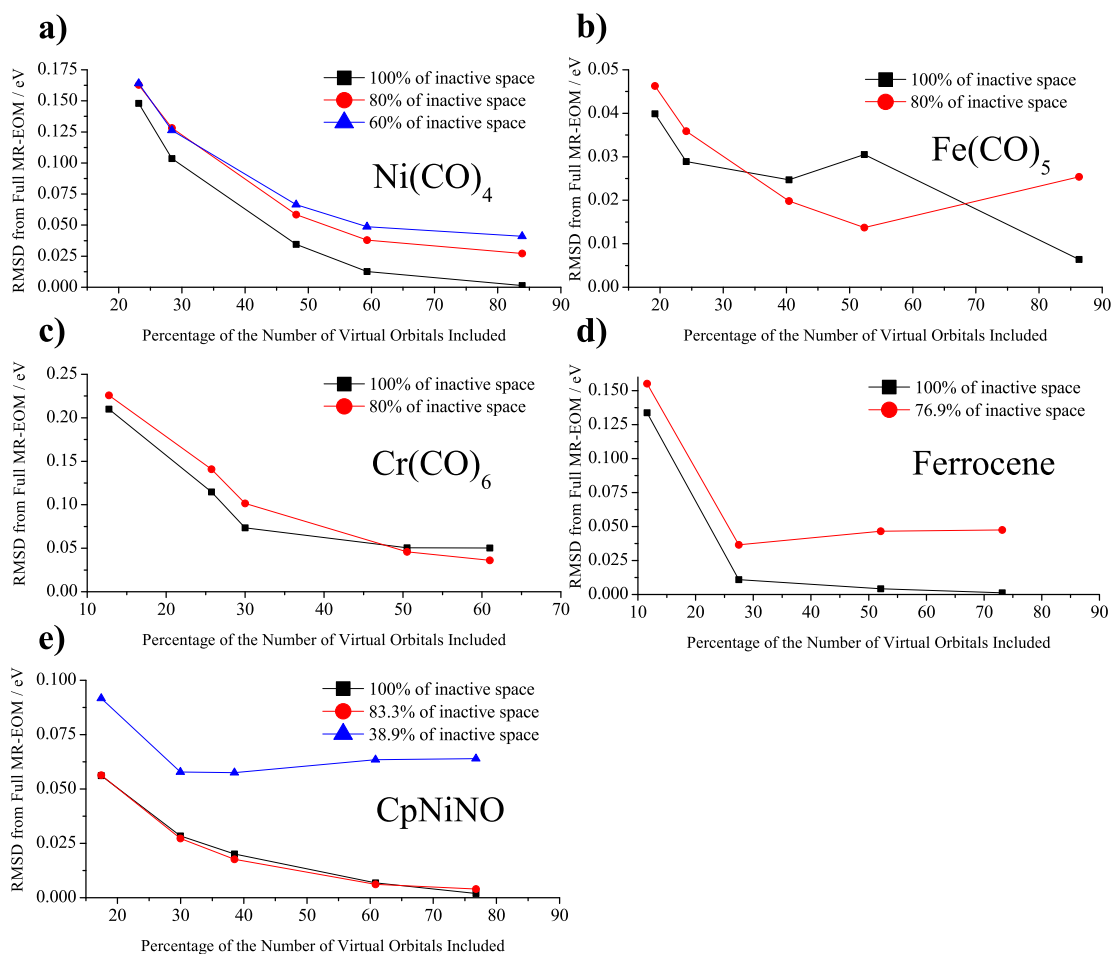


Figure 5.1: Variation in the Root Mean Squared Deviation (RMSD) in the calculated excitation energies, from full MR-EOM/def2-TZVPP, as a function of the percentage of the number of inactive and virtual orbitals included in the calculation for a) Ni(CO)₄, b) Fe(CO)₅, c) Cr(CO)₆, d) ferrocene and e) CpNiNO.

MR-EOM/def2-TZVPP excitation energies, reported in Tables 5.2 and 5.3-5.6, are employed as benchmark data to assess how various truncations of the inactive and virtual spaces affect the accuracy of the computed excitation energies. In Figure 5.1, the Root Mean Squared Deviation (RMSD), from the full MR-EOM excitation energies, is plotted as a function of the percentage of the inactive and virtual orbitals which have been included in a given calculation. Note that in the calculation of the RMSD, the excitation energies are weighted by the degeneracies of the corresponding excited states. The individual excitation energies (and statistics), for each molecule, are provided in appendix B. From the plots in Figure 5.1, one observes that the RMSD decreases monotonically as a function of the percentage of the virtual orbitals included, for the $\text{Ni}(\text{CO})_4$, $\text{Cr}(\text{CO})_6$, ferrocene and CpNiNO molecules, when 100 % of the inactive orbitals are included. For the most aggressive truncation of the inactive spaces in ferrocene and CpNiNO in Figure 5.1 d) and e), respectively, the RMSD decreases and then increases as the size of the virtual space is increased. The plots for $\text{Fe}(\text{CO})_5$ in Figure 5.1 b) are even less systematic and we will look more closely at the deviations in the individual excitation energies, from the full MR-EOM values, below. However, we note in this case that the RMSD is less than 0.05 eV for all of the truncations of the inactive and virtual spaces, even when the size of the virtual space falls below 20 %. Another case which deserves more careful scrutiny below, is that of the $\text{Cr}(\text{CO})_6$ molecule, for which the RMSD appears to converge considerably more slowly toward the full MR-EOM results with increasing size of the virtual space. Namely, when 100 % of the inactive space is included, the RMSD is still above 0.05 eV when the size of the virtual space is 61 % and for all other molecules, the RMSD falls below 0.05 eV at a significantly smaller value.

In Figure 5.2, the deviations in the computed excitation energies, from full MR-EOM/def2-TZVPP, for $\text{Fe}(\text{CO})_5$, are plotted as a function of the size of the virtual space for the case where there is no truncation of the inactive space (Figure 5.2 a)) and when 80 % of the inactive orbitals are included in the calculation (Figure 5.2 b)). We label the excited states from 1 to 11 in the same order as they appear in Table 5.3. In both Figures 5.2 a) and b), it becomes apparent that there are two groups of excited states for which the deviations in the excitation energies approach each other, as the number of virtual orbitals increases. This becomes especially evident in Figure 5.2 a), when the size of the virtual space is larger than 50 %. Upon closer inspection, we find that one group consists of states 1-3 and 6-8 while the other group is comprised of states 4, 5 and 9-11. In Table 5.3, we find that the states 1-3 correspond to singlets with $e' \rightarrow 2e''$ character and the states 6-8 are the triplets with $e' \rightarrow 2e''$ character. Furthermore, states 4 and 5 are singlets with $e'' \rightarrow 2e''$ character and the states 9-11 are triplets with $e'' \rightarrow 2e''$ character. This seems to indicate that states of different character are affected to a different extent by the orbital selection scheme.

The reasons for the relatively complicated behaviour of the RMSD in Figure 5.1 a) also become

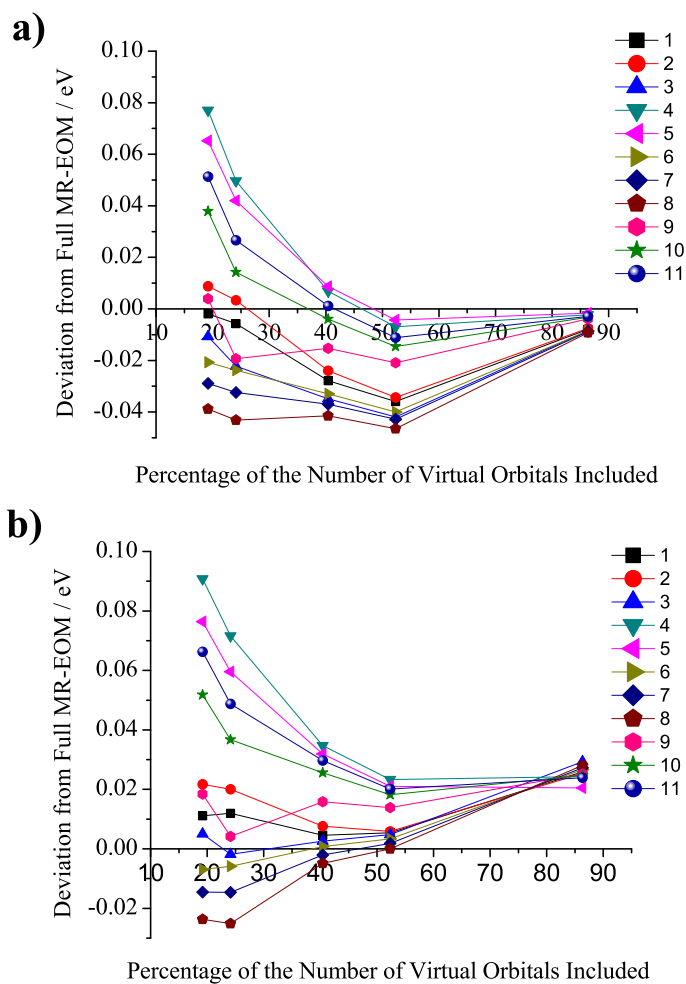


Figure 5.2: Deviations in the calculated excitation energies from full MR-EOM/def2-TZVPP as a function of the percentage of the number of virtual orbitals included in the calculation for $\text{Fe}(\text{CO})_5$ when a) 100 % of the inactive space is included and b) 80 % of the inactive space is included. The excited states are labelled from 1-11 in the order that they appear in Table 5.3.

clear when we observe the individual deviations in Figure 5.2. For example, in Figure 5.2 a), the majority of the deviations are decreasing in magnitude for the first three points in the plot, which explains the

decrease in the RMSD for these first three points. On going from 40.4 % to 52.3 %, all of the deviations move further downward and since the majority of the deviations move further away from 0 eV, this yields the subsequent rise in the RMSD as the size of the virtual space reaches 52.3 %. The individual deviations then become much smaller as the size of the virtual space approaches 90 %, explaining the subsequent decrease in the RMSD. Similar arguments can be applied to explain the behaviour of the RMSD plot when 80 % of the inactive space is included in the calculation.

Let us now consider the plots of the deviations in the excitation energies of $\text{Cr}(\text{CO})_6$, from full MR-EOM/def2-TZVPP, as a function of the size of the virtual space when there is no truncation of the inactive space (Figure 5.3 a)) and when 80 % of the inactive space is included (Figure 5.3 b)). We label the excited states from 1-10 as they appear in Table 5.4. From both plots, it is clear that the deviations for the singlet state 5 and the triplet state 10, behave very differently from those for the remaining states, as the size of the virtual space is increased. In fact, the deviations are nearly identical for both these states for all sizes of the virtual space in the plots of Figures 5.3 a) and b). The deviations for the remaining states, in both plots, also lie fairly closely together and show the same general trend in their behaviour. Not surprisingly, inspection of Table 5.4 reveals that the character of the states 5 and 10 ($t_{2g} \rightarrow a_{1g}$) is different from that of the rest of the excited states ($t_{2g} \rightarrow t_{1u}$). This gives further credence to the claim that states of different character can be affected differently by the orbital selection procedure.

The reasons for the relatively slow convergence of the RMSD plots for $\text{Cr}(\text{CO})_6$ (Figure 5.1 c)), with increasing size of the virtual space, become clear from the plots of the individual deviations (from MR-EOM/def2-TZVPP) in Figure 5.3. For example, let us focus on the plots in Figure 5.3 a). It is observed that the majority of the deviations in the excitation energies (*i.e.* corresponding to the excited states of $t_{2g} \rightarrow t_{1u}$ character) are within -0.02 and -0.035 eV, when 61 % of the virtual orbitals are included. In contrast, the two states of $t_{2g} \rightarrow a_{1g}$ character display significantly larger deviations of -0.089 eV, when 61 % of the virtual space is included in the calculation. Hence, the RMSD takes on an intermediate value of 0.05 eV, due to the presence of these two outliers. This seems to indicate that the RMSD might not always be the most reliable measure of the accuracy in this study. Namely, it is not representative of the true accuracy, since the majority of the absolute deviations fall below this value and the RMSD is overly sensitive to the presence of a few larger deviations.

When comparing Figure 5.2 a) with Figure 5.2 b) and Figure 5.3 a) with Figure 5.3 b), it becomes apparent that there can be large shifts in the values of the deviations as the size of the inactive space is reduced to 80 %. A similar observation can be made in the case of ferrocene (not shown), when the inactive space is reduced to 76.9 % (*i.e.* see the behaviour of the RMSD in Figure 5.1 d)). In the latter case, the spread in the deviations is also significantly increased on decreasing the size of the inactive space.

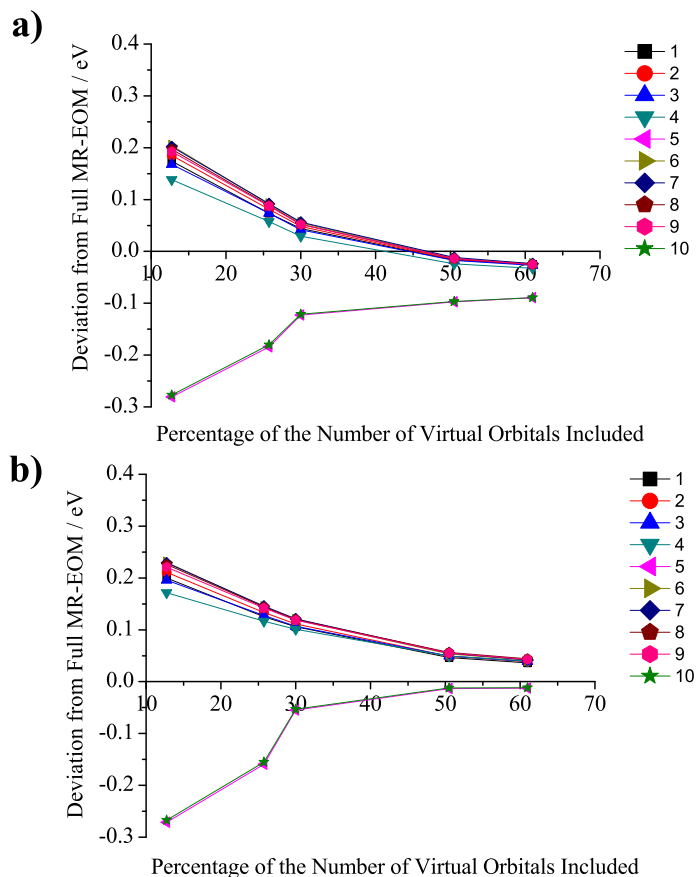


Figure 5.3: Deviations in the calculated excitation energies from full MR-EOM/def2-TZVPP as a function of the percentage of the number of virtual orbitals included in the calculation for $\text{Cr}(\text{CO})_6$ when a) 100 % of the inactive space is included and b) 80 % of the inactive space is included. The excited states are labelled from 1-10 in the order that they appear in Table 5.4.

It appears that since many inactive orbitals are already discarded in the frozen core approximation, the effect of discarding additional orbitals in the orbital selection scheme can be substantial. This behaviour is somewhat disconcerting and as a result, we suggest caution with the use of the inactive orbital selection scheme. We would anticipate, however, that the inactive orbital selection procedure would be applicable when the active space chromophore is localized within a sizeable molecule.

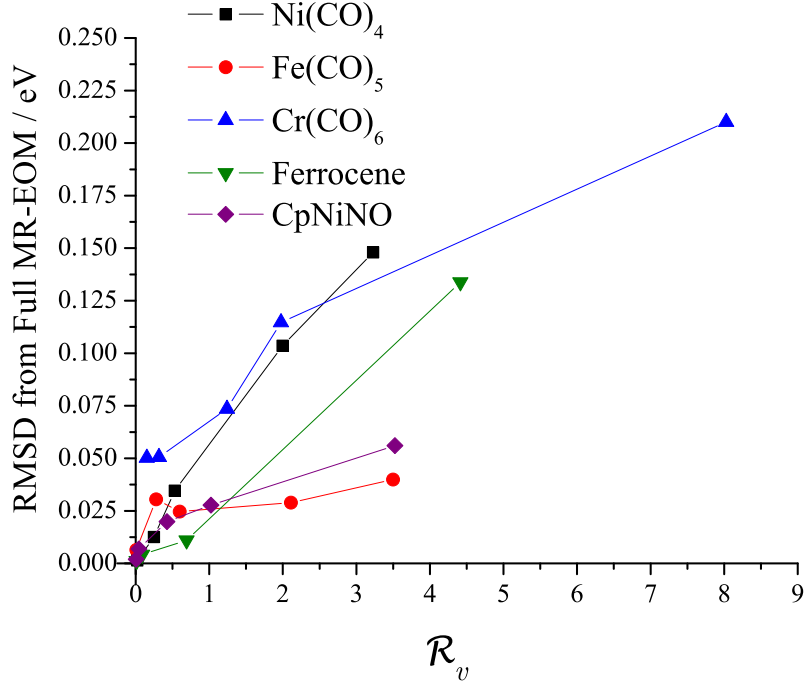


Figure 5.4: Root Mean Squared Deviation (RMSD) in the calculated excitation energies, from full MR-EOM/def2-TZVPP, as a function of the ratio $\mathcal{R}_v$ (in percent) defined in Eq. 5.29, for each of the five transition metal complexes considered in this work.

We wish to determine an alternative criterion for choosing the threshold for the eigenvalues of the orbital selection density matrix in the virtual space. To this end, we compute the ratio

$$\mathcal{R}_v = \frac{\sum_{a=1}^{n_v^{\text{excl.}}} \lambda_a}{\sum_{a=1}^{n_v} \lambda_a} \times 100 \%, \quad (5.29)$$

in which the λ_a are the eigenvalues of the virtual orbital selection density matrix ρ in Eq. (5.21), n_v is the total number of orbitals in the untruncated virtual space and $n_v^{\text{excl.}}$ is the number of virtual orbitals that have been discarded in the virtual orbital selection procedure. In order to obtain a reliable truncation of the virtual space, we would expect the ratio $\mathcal{R}_v$ to be small. More specifically, the sum of eigenvalues in the truncated space should only comprise a small percentage of the sum of all the eigenvalues. In Figure 5.4,

the RMSD (from full MR-EOM/def2-TZVPP) is plotted as a function of $\mathcal{R}_v$ for each of the five transition metal complexes considered in this study. It is observed that, with the exception of $\text{Cr}(\text{CO})_6$, the RMSD is well below 0.05 eV when $\mathcal{R}_v < 1$ %. Furthermore, in the case of $\text{Cr}(\text{CO})_6$, the RMSD approaches 0.05 eV when $\mathcal{R}_v < 1$ % (*i.e.* $\text{RMSD}(\mathcal{R}_v = 0.32 \%) = 0.0506$ eV and $\text{RMSD}(\mathcal{R}_v = 0.15 \%) = 0.0502$ eV). However, the majority of deviations are considerably less than 0.05 eV (*i.e.* for the $t_{2g} \rightarrow t_{1u}$ transitions) when $\mathcal{R}_v < 1$ % and there are only two outliers for which the deviations are significantly larger than 0.05 eV (*i.e.* for the $t_{2g} \rightarrow a_{1g}$ transitions). Furthermore, out of a total of 70 excitation energies, for the five transition metal complexes considered in this work, the latter two excitation energies are the only ones that deviate by more than 0.05 eV from the MR-EOM/def2-TZVPP values when $\mathcal{R}_v$ is less than 1 %. Hence, this seems to be a particularly useful and robust criterion to determine how many virtual orbitals can be discarded in the orbital selection scheme.

Table 5.7: The values of the ratio $\mathcal{R}_c$ corresponding to various truncations of the inactive space for each of the five transition metal complexes considered in this work, in a def2-TZVPP basis.

Molecule	% of inactive orbitals included	$\mathcal{R}_c$ (in %)
$\text{Ni}(\text{CO})_4$	80	2.79
	60	11.55
$\text{Fe}(\text{CO})_5$	80	2.10
$\text{Cr}(\text{CO})_6$	80	2.35
ferrocene	76.9	3.81
CpNiNO	83.3	1.20
	38.9	15.62

Similarly, we can define the ratio

$$\mathcal{R}_c = \frac{\sum_{i'=1}^{n_c^{\text{excl.}}} \lambda_{i'}}{\sum_{i'=1}^{n_c} \lambda_{i'}} \times 100 \%, \quad (5.30)$$

in which $\lambda_{i'}$ are the eigenvalues of the inactive orbital selection density D in Eq. (5.16), n_c is the total number of orbitals which constitute the untruncated inactive (core) space and $n_c^{\text{excl.}}$ is the number of inactive (core) orbitals that have been discarded in the inactive orbital selection procedure. In Table 5.7, we have tabulated the values of $\mathcal{R}_c$ for the different sizes of the inactive space considered in Figure 5.1, for each of the five transition metal complexes. We observe that in all cases, with the exception of CpNiNO , when 83.9% of the inactive space is kept, the $\mathcal{R}_c$ value is greater than 2%. In analogy with the virtual orbital selection procedure, we might postulate that a similar criterion of $\mathcal{R}_c < 1$ % would be required to

obtain consistently accurate results. Since the majority of the values of $\mathcal{R}_c$ in Table 5.7 are considerably larger than 1 %, this gives a possible rationalization for the unsatisfactory results achieved with the inactive orbital selection scheme (*e.g.* large shifts in the deviations in $\text{Fe}(\text{CO})_5$ (Figure 5.2), $\text{Cr}(\text{CO})_6$ (Figure 5.3) and ferrocene as the size of the inactive space is reduced). A more careful study would have to be carried out on larger systems (*i.e.* larger inactive spaces) to test the hypothesis that $\mathcal{R}_c < 1$ % is an appropriate criterion for the inactive orbital selection scheme.

Table 5.8: Comparison of timings for full MR-EOM with various truncations of the virtual space for the $\text{Ni}(\text{CO})_4$ molecule in a def2-TZVPP basis.

% of virtual orbitals included	$\mathcal{R}_v^a$ (in %)	total wall clock time (min.)	% of time for the calculation of amplitudes and many-body transformations	% of time for the MRCI diagonalization	average time / iteration for $\hat{T}$ -amplitudes ^b (sec.)	average time / iteration for $\hat{S}$ -amplitudes ^b (sec.)
100	0	12211	65.0	34.9	8260 (30)	9081 (22)
83.9	0.02	7917	67.2	32.6	5777 (27)	6828 (21)
59.3	0.25	3842	67.1	32.4	2250 (27)	3962 (21)
48.1	0.53	2675	63.3	36.1	1287 (27)	2835 (21)
28.4	2.00	1440	48.3	46.5	390 (27)	1306 (21)
23.2	3.23	865	36.6	60.6	173 (27)	566 (22)

^a $\mathcal{R}_v$ as defined in Eq. (5.29).

^b The number of iterations required to reach convergence is given in parentheses.

In Table 5.8, the timings for the full MR-EOM/def2-TZVPP calculation on $\text{Ni}(\text{CO})_4$ are compared with the timings for various truncations of the virtual space. The % of time spent in the calculation of the amplitudes and various elements of the similarity transformed Hamiltonians also appears in Table 5.8 and this also includes the time for the orbital selection procedure. However, the average time spent doing the orbital selection (4.89 min.) only represents a small fraction of the total time spent in this part of the calculation. Table 5.8 also includes the percentage of time spent in the MRCI diagonalization and the average time per iteration for the calculation of the $\hat{T}$ - and $\hat{S}$ -amplitudes.

If one includes 48.1 % of the virtual orbitals such that $\mathcal{R}_v$, defined in Eq. (5.29), is 0.53 %, the RMSD is 0.035 eV and all of the deviations in the excitation energies from full MR-EOM are less than 0.05 eV. In Table 5.8, one observes that the total wall clock time (2675 min.) for this particular truncation of the virtual space is reduced by a factor of 4.6 from the full MR-EOM/def2-TZVPP calculation (12211 min.). This represents a considerable reduction of the computation time without having a significant effect on the accuracy of the excitation energies. It might also be possible to discard a larger fraction of the virtual space (*i.e.* given that $\mathcal{R}_v$ would still be smaller than 1 %), in order to reduce the computation time even further. It is also interesting to note that the MRCI diagonalization step constitutes a significant

fraction of the total wall clock time in each case. It is also observed that the average time per iteration for the $\hat{S}$ -amplitudes is always larger than that for the $\hat{T}$ -amplitudes for this particular molecule, even though the number of $\hat{S}$ -amplitudes ($\sim n_c^3 n_v$) is far less than the number of $\hat{T}$ -amplitudes ($\sim n_c^2 n_v^2$). This is a result of the fact that there are many more terms in the residual equations defining the $\hat{S}$ -amplitudes. Future factorization of the equations is expected to have a large effect on the efficiency of the solution of the $\hat{S}$ -amplitude equations, in particular.

It should also be stressed that the $\hat{T}$ - and $\hat{S}$ -amplitude iterations, in canonical MR-EOM, are both of comparable cost to the $\hat{T}$ -amplitude iterations in single reference CCSD [87]. For example, if we use the APG [32] and our code generator to implement the unfactorized CCSD equations in ORCA [24], we find that the total time for a single point energy calculation for $\text{Ni}(\text{CO})_4$, in a def2-TZVPP basis, is 1495 min. and that the $\hat{T}$ -amplitude equations (98.7 % of the total time) are converged in 19 iterations with an average time per iteration of 4446 sec. From Table 5.8, it is observed that for the same system and basis set, the average time per iteration for the $\hat{T}$ -amplitudes (8260 sec.) and the $\hat{S}$ -amplitudes (9081 sec.) are both about a factor of 2 more expensive than for the single reference CCSD iterations. With the solution of two sets of equations and the subsequent MRCI step (34.9 % of the total time), it is not surprising that the MR-EOM calculation is about 10 times more expensive than the single reference CCSD calculation. The truncated MR-EOM calculation which includes 48.1 % of the virtual space, however, is only about a factor of 2 more expensive than the ground state CCSD calculation and we obtain 11 excitation energies that are accurate to within 0.05 eV from the full MR-EOM results. In order to obtain these 11 excitation energies in single reference EOM-CCSD [13, 14, 15], we would first solve the CCSD equations for the ground state amplitudes and energy. Then for each of the 11 excited states we would have to iteratively solve the so-called EOM-EE (EE = excitation energy) equations, which are of a similar expense as the CCSD equations. Thus, the EOM-CCSD calculation would likely be significantly more expensive than the corresponding MR-EOM calculation for this particular system. It should also be stressed that factorization (and other improvements, such as batching) can greatly reduce the timings for these calculations. For example, the timings for $\text{Ni}(\text{CO})_4$, with the production level CCSD code (*i.e.* see Ref. [5] and references therein) in ORCA (total time = 391.56 min., average time per iteration = 996.16 sec.), are much better than those for the unfactorized generated code. Thus, inclusion of a factorization scheme within the code generator is one of the more important efficiency-related issues that we wish to tackle in the near future. Let us summarize by noting that the cost of the solution of the $\hat{T}$ - and $\hat{S}$ -amplitudes does not depend on the size of the CAS configuration space, and this cost is comparable (within a factor of 2 perhaps) to single reference CCSD. The final diagonalization step does depend on the size of the CAS configuration space, and in the limit of a large CAS, this step will dominate the cost of the calculation. This latter step is not directly comparable to single reference EOM-CC. However, compared to internally contracted MRCI, the

cost of MR-EOM is dramatically smaller, as only 1h, 1p and 2h configurations out of the CAS need to be considered. Moreover, results are more nearly size-extensive, without the use of a Davidson correction.

5.5 Concluding Remarks

Let us first summarize the salient features of an MR-EOM calculation. In MR-EOM, the starting point is a state-averaged CASSCF calculation. In general, the size of the active space can be quite compact. The major requirement is that the excited states of interest are qualitatively well described by the CASCI calculation. This can be verified by a subsequent MRCI calculation including the CAS configurations and the 1h, 1p and 2h excitations out of the CAS, in a small basis. If the %active or weights in the reference space are large enough ($> 90\%$) for the electronic states of interest, the corresponding MR-EOM excitation energies will likely be reliable. Also, the choice of states to be included in the state-averaged CASSCF is not very critical. To a very large degree, the solution of the $\hat{T}$ and $\hat{S}$ equations only depends on the one-body density matrix in the state-averaged CAS [22]. This aspect is very important for the robustness of the MR-EOM results.

The subsequent solution of the $\hat{T}$ and $\hat{S}$ cluster amplitudes, takes about four times as long as a conventional single-reference CCSD calculation. However, in the current implementation, based on the unfactorized equations from the APG [32], it is about a factor of 10 more expensive. The amplitude iterations only need to be performed once and account for the 1p-1h, 2p-1h, 2h-1p and the 2p-2h excitations in a conventional MRCI calculation. This part of the calculation is fully size-extensive. The resulting transformed Hamiltonian, is a spin scalar and has the correct point-group symmetry. The subsequent final MRCI diagonalization is over a quite compact, first-order interacting space comprised of 1h, 1p and 2h excitations out of the CAS. This part of the calculation is not size-extensive and provides some reason for concern. One can also eliminate the 2h excitations by employing an additional similarity transformation (*i.e.* the $\hat{U}_2$ transformation described in Refs. [22, 23, 178]). In typical calculations, the final MRCI diagonalization step takes approximately 30 % of the total calculation time. On the other hand, the single solution of the $\hat{T}$ and $\hat{S}$ cluster amplitudes is typically twice as expensive as the MRCI diagonalization step, in which dozens of excited state energies might be calculated.

Let us note that the calculation of 15 converged roots, corresponding to singlet excited states for the $\text{Ni}(\text{CO})_4$ molecule, with the Brueckner EOM-CCSD(T) approach (in ACES II [179] using C_{2v} symmetry), took approximately 36000 seconds. The MR-EOM calculation (in ORCA [24] using C_1 symmetry), in the correspondingly small def2-SVP basis, takes approximately 80000 seconds and includes 28 converged roots;

14 corresponding to singlet states (including the ground state) and 14 corresponding to triplet states. The accuracy of the MR-EOM approach seems to be comparable to such EOM-CCSD(T) calculations.

In summary, we think MR-EOM can become a very versatile tool in quantum chemistry. The calculations are fairly user-friendly. Most critically, they require the selection of an active space and the states which are to be included in the state-averaging, but this only has to be done once in order to obtain the (potentially many) excited states of interest. The most significant limitation of the MR-EOM methodology seems to be that excited states have to be dominated by configurations in the active space. We are working to lift this constraint by employing further similarity transformations akin to those which are used in the single-reference STEOM approach [16, 209, 17].

In section 5.4, we already summarized the findings for the current selection of benchmark calculations. The results for the orbital selection scheme are also quite clear-cut. For most states, the orbital selection works quite well, although there can be states that are particularly sensitive to the selection procedure. The latter states, usually have a different character from the majority (*e.g.* see Figure 5.3 for $\text{Cr}(\text{CO})_6$) and this perhaps reflects a limitation of the state-averaged CAS used in MR-EOM calculations. Even so, the errors are manageable (below 0.1 eV). With the use of the virtual orbital selection scheme described in this chapter, a large portion of the virtual space can be discarded without having a significant effect on the computed excitation energies. This will be useful to push the applications of MR-EOM to more sizeable systems. The current implementation of MR-EOM in ORCA is therefore, applicable to a wide variety of interesting systems.

Chapter 6

Benchmark Applications of Variations of Multireference Equation of Motion Coupled-Cluster Theory¹

6.1 Introduction

In a series of recent publications [21, 22, 23, 178, 244, 245], variants of the Multireference Equation of Motion Coupled-Cluster (MR-EOM-CC) methodology have been introduced and benchmark applications to a variety of systems have been reported. In analogy with single-reference Equation of Motion Coupled-Cluster (EOM-CC) [13, 14, 15] and Similarity Transformed Equation of Motion Coupled-Cluster (STEOM-CC) approaches [16, 17], the MR-EOM methodology can be characterized as a “transform and diagonalize” scheme for the calculation of ground and excited electronic states of molecular systems. In contrast with the single-reference approaches, which are based on a single-determinantal reference wavefunction (*e.g.* Hartree-Fock), MR-EOM is based on a multi-configurational reference manifold of states, obtained from a state-averaged Complete Active Space Self-Consistent Field (CASSCF) [99] calculation. A necessary requirement for the viability of MR-EOM results, is that the configurations comprising the state-averaged CAS provide a qualitative description of the excitations of interest. In particular, the character of the desired excited states should be dominated by contributions from the active space configurations. The

¹The contents of this chapter and chapter 3 have been submitted for publication in *J. Chem. Theory Comput.*

primary strategy which has been adopted in MR-EOM, is to effectively eliminate the coupling between the CAS configurations and many of the excited configurations (*e.g.* 2h2p, 1h2p, 1h1p, *etc.*) by means of a sequence of similarity transformations of the molecular electronic Hamiltonian, with suitably defined excitation operators. For example, in the MR-EOM-T|SXD scheme introduced in Refs. [23, 178] and described in detail below, we perform two sequential transformations of the Hamiltonian. The first transformation incorporates a $\hat{T}$ operator, which includes 2h2p, 1h2p, 2p, 1h1p and 1p excitations out of the CAS, while the second transformation involves the operators $\hat{S}$, $\hat{X}$ and $\hat{D}$, which incorporate 2h1p and additional 1h1p and 1p excitations out of the CAS (*vide infra*). As a result, in the final MRCI diagonalization step of the similarity transformed Hamiltonian, one only needs to include the CAS and 1h, 1p and 2h configurations, which greatly reduces the size of the diagonalization space compared to that used in MR-CISD [23, 178]. Note that h (hole) denotes a doubly occupied core orbital while p (particle) refers to a virtual orbital.

One of the principal advantages of the MR-EOM methodology is the fact that many excited states can be obtained from the diagonalization of a similarity transformed Hamiltonian over a relatively small diagonalization manifold. For example, in the MR-EOM-T|SXD|U approach (*i.e.* MR-EOM-T|SXD with an additional transformation involving the $\hat{U}$ operator, which generates 2h excitations out of the CAS) reported in Refs. [23, 178] and considered herein, the minimal diagonalization space only consists of the CAS, 1h and 1p configurations. The use of a minimal diagonalization space holds several advantages. In particular, it greatly reduces the computational cost of a calculation, especially for larger active spaces. In addition, it lowers the size extensivity errors significantly, as demonstrated in Refs [23, 22]. The elements of the similarity transformed Hamiltonians and residual equations in MR-EOM are comprised of connected contributions. Therefore, the size-extensivity errors only arise from the final MRCI diagonalization step. By including more of the excitation classes through the definition of appropriate similarity transformations of the molecular electronic Hamiltonian, we can reduce the size of the final diagonalization manifold and thereby reduce the size-extensivity errors. It has also been shown that this reduction in size-extensivity errors is correlated to the increased accuracy of the calculated excitation energies for various atomic systems (*e.g.* see Refs. [23, 178]), as more operators are included in the transformation. Another virtue of the MR-EOM approach is that one only requires a single state-averaged CASSCF calculation and the solution of a single set of amplitudes to define the final similarity transformed Hamiltonian. From a somewhat limited set of calculations [21, 22, 23, 178, 244, 245], it has been found that the MR-EOM methods are relatively insensitive to the specific details concerning the choice of reference states to be included in the state-averaged CAS. In general, it is sufficient to incorporate only a small number of low-lying states in the state-averaging. Moreover, other desirable features of the MR-EOM methodology include the preservation of both spin and spatial (point-group) symmetry and orbital invariance in each of the (inactive, active and virtual) orbital subspaces.

In this work, we wish to investigate the effects of various modifications of the MR-EOM methodology on the calculation of excitation energies. Specifically, it is of interest to examine how the calculated excitation energies of molecular systems are affected by the various transformations in the sequence (*e.g.* the $\hat{T}$ transformation, the $\hat{S}$, $\hat{X}$, $\hat{D}$ transformation and the $\hat{U}$ transformation) and the size of the diagonalization manifold. A similar study of the MR-EOM-T, TS (non-sequential), T|S and T|S|U methods (*i.e.* not considering the $\hat{X}$ and $\hat{D}$ operators) has been reported in Ref. [22], for transition metal atoms and a subset of the organic molecule test suite of Thiel and coworkers [33]. In more recent work [178], the MR-EOM-T, T|SXD and T|SXD|U methods have been benchmarked using experimental data for transition metal atoms. In general, one finds that the additional operators (excepting the $\hat{U}$ operator) lead to a significant increase in the accuracy of the results, especially for the transition metal atoms. Also, the results obtained with MR-EOM methods, which employ a minimal diagonalization space, are comparable with those calculated using a larger manifold (*e.g.* including 1h1p configurations in T|SXD or including 1h1p and 2h configurations in T|SXD|U). Furthermore, it is important to note that the MR-EOM methodology has recently been implemented in the ORCA program package [24], as reported in Ref. [244]. The effects of spin-orbit coupling have also been investigated using this implementation, as reported in Ref. [245]. In the ORCA implementation, we have introduced an additional $\hat{T}^\dagger$ transformation, following the $\hat{T}$ transformation, in order to obtain a more approximately Hermitian final transformed Hamiltonian $\hat{G}$. In addition, we have introduced the following three approximations: 1. the permutational symmetries of the bare two-electron integrals are enforced on the elements of the final similarity transformed Hamiltonian, 2. the $\hat{S}_1$ operator is excluded from the SXD transformation, 3. the required 3p1h elements of each of the similarity transformed Hamiltonians are approximated by the bare 3p1h elements of the two-electron integrals. Hence, a prime focus of this study is to determine the extent of the effects of these approximations and the $\hat{T}^\dagger$ transformation on the calculated excitation energies, since these issues have not yet been investigated in detail.

In order to evaluate the various MR-EOM schemes for the calculation of excitation energies, we consider a subset of the organic molecules from the test set of Thiel and coworkers [33]. In addition, the five transition metal complexes (*i.e.* Ni(CO)₄, Fe(CO)₅, Cr(CO)₆, ferrocene and CpNiNO (cyclopentadienyl nickel nitrosyl)) from Ref. [244] are also used to further investigate the details of the $\hat{T}^\dagger$ transformation, as well as the two approximations adopted in the ORCA implementation of the MR-EOM approach. In the latter case, we also compare the results of various single-reference calculations to demonstrate the difficulties that such methods have with a reliable treatment of these systems. The organic molecule test suite is ideal for the purposes of benchmarking new methodologies for the calculation of transition energies, since there are reliable CC3 reference data [33] and EOM-CCSDT-3 reference data [22] available for these systems. In the case of the transition metal complexes, there are experimental UV/Vis. results

available for each of these systems. However, as discussed in detail in our previous work [244], there are clear difficulties associated with the comparison of calculated vertical excitation energies with experimental values. Namely, in our calculations, we have not included vibrational effects (*e.g.* vibronic coupling, Jahn-Teller distortions, *etc.*), spin-orbit coupling and environmental effects, where applicable (*i.e.* experimental spectra obtained in solution or condensed phases). These effects can be non-negligible and thus, can lead to considerable differences between the calculated and experimental excitation energies, even with large basis sets and high levels of theory. In contrast, in the recent study of transition metal atoms [178], where a large amount of gas-phase experimental data exists, the comparisons of calculated excitation spectra with experiment are unambiguous. The effects of spin-orbit coupling have also been investigated using the ORCA implementation of MR-EOM, as reported in Ref. [245]. For the transition metal complexes considered in the present study, we have performed higher level single-reference calculations (*i.e.* EOM-CCSD(T) and EOM-CCSDT-3). However, as will be discussed in detail below, these “benchmark” results are not as reliable as those for the organic molecule test set. Hence, the main focus of the investigation of transition metal complexes will be on the comparison of the differences between various MR-EOM methods, rather than the comparison with high-level single-reference data.

Let us briefly summarize the details of the remainder of this chapter. In chapter 3, we have already discussed the formal theoretical details of the MR-EOM approaches considered in this work. Hence, we only provide a brief review of these methods in section 6.2. A discussion of the benchmark applications of a multitude of MR-EOM approaches, for the calculation of transition energies of a subset of the organic molecules from the test suite of Thiel and coworkers [33], appears in section 6.3. Various calculations are presented for the five transition metal complexes in section 6.4. In particular, we compare the singlet excitation energies obtained from various single-reference approaches and compare the results of several MR-EOM calculations with Brueckner based EOM-CCSD(T) values. Furthermore, we examine the differences between the transition energies, for both singlet and triplet states, calculated with a selection of the MR-EOM approaches. This chapter is then concluded with summarizing statements in section 6.5.

6.2 Theory

Since the formal, theoretical aspects of the various MR-EOM approaches studied in this chapter have been discussed at length in chapter 3, we will only briefly review the details here. The MR-EOM approach makes use of a state-averaged CASSCF calculation, in which the one- and two-particle density matrices and hence, the CASSCF energy are obtained as a weighted average over a manifold of $\mathbf{m} = 1, 2, \dots, n_{\text{states}}$ electronic states. Let us assume that we have solved the state-averaged CASSCF problem, to obtain

the Fock matrix, two-electron integrals and the one- and two-body reduced density matrices, which are respectively given by

$$\Gamma_x^w = \sum_m w_m \langle \Phi_m | \hat{E}_x^w | \Phi_m \rangle, \quad (6.1)$$

$$\begin{aligned} \Gamma_{yz}^{wx} &= \sum_m w_m \langle \Phi_m | \hat{E}_{yz}^{wx} | \Phi_m \rangle \\ &= \sum_m w_m \langle \Phi_m | \hat{E}_y^w \hat{E}_z^x - \delta_y^x \hat{E}_z^w | \Phi_m \rangle. \end{aligned} \quad (6.2)$$

Here $|\Phi_m\rangle$ is the m^{th} state entering the state-averaged CASSCF calculation with weight w_m and $\hat{E}_x^w$ and $\hat{E}_{yz}^{wx}$ are spin-free single and double excitation operators, respectively. As we have already noted in chapter 3, the expressions defining the MR-EOM approaches contain the one- and two-body cumulants [101] of these density matrices, rather than the RDMs themselves. The one-body cumulant is equivalent to the one-body RDM,

$$\Lambda_x^w = \Gamma_x^w, \quad (6.3)$$

while the two-body cumulant is obtained in terms of the one- and two-body RDMs as [101]

$$\Lambda_{yz}^{wx} = \Gamma_{yz}^{wx} - \Gamma_y^w \Gamma_z^x - \frac{1}{2} \Gamma_z^w \Gamma_y^x. \quad (6.4)$$

As discussed in detail in Ref. [177], the α, β component of the two-body spin-orbital cumulant [162, 163],

$$\lambda_{yz}^{wx} \equiv \lambda_{Y_\alpha Z_\beta}^{W_\alpha X_\beta} = \frac{1}{6} (2\Lambda_{yz}^{wx} - \Lambda_{zy}^{wx}), \quad (6.5)$$

arises in the equations defining the MR-EOM methodology, rather than the spatial two-body cumulant of Eq. (6.4) itself.

The general spatial orbitals p, q, r, s , which comprise the molecular orbital basis, are partitioned into (doubly occupied) inactive core orbitals i', j', k', l' , occupied orbitals i, j, k, l (*i.e.* the union of the inactive core and active orbital subspaces), active orbitals w, x, y, z and virtual orbital a, b, c, d . The first transformation that is included in all sequential variants of the MR-EOM methodology [21, 22, 23], was first introduced in the context of the state-specific partially internally-contracted (pIC) MRCC approach [177] and takes the form,

$$\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$$

$$= \bar{h}_0 + \sum_{p,q} \bar{h}_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} \bar{h}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots \quad (6.6)$$

in which

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a \hat{E}_i^a + \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab} \hat{E}_{ij}^{ab}. \quad (6.7)$$

It is important to note that the braces in Eq. (6.6) denote Kutzelnigg-Mukherjee normal ordering [151, 152, 153] of the operators with respect to the CAS reference state. The equations determining the cluster amplitudes t_i^a and t_{ij}^{ab} are respectively, given by [177, 21, 22, 23]

$$R_i^a = \sum_{\mathbf{m}} w_{\mathbf{m}} \langle \Phi_{\mathbf{m}} | \hat{E}_i^a \hat{H} | \Phi_{\mathbf{m}} \rangle = 0, \quad (6.8)$$

$$R_{ij}^{ab} = \bar{h}_{ij}^{ab} = 0. \quad (6.9)$$

This equation is a projected residual equation in that it is obtained by projecting onto a manifold of singly excited functions, while Eq. (6.9) for the doubles amplitudes is a so-called “many-body residual equation”, since it is defined by equating the elements $\bar{h}_{ij}^{ab}$ of the similarity transformed Hamiltonian to zero. In single-reference coupled-cluster theory, the expressions for the projected residuals are equivalent to the corresponding elements of the similarity transformed Hamiltonian (*e.g.* $R_i^a = \langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = \bar{h}_i^a$, $R_{ij}^{ab} = \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle = \bar{h}_{ij}^{ab}$). However, this is no longer true in the case of MR-EOM, since it makes use of a multi-configurational reference manifold of states (*i.e.* the state-averaged CAS). We note that the many-body residual equations are formally much simpler than the corresponding projected residual equations and they are also non-singular (*i.e.* form a linearly independent system of equations). However, we must make use of a projected residual equation for the singles amplitudes in order to satisfy the generalized Brillouin condition of Eq. (2.135), as discussed in detail in Refs. [21, 22, 177].

In general, all of the similarity transformations can be written in the same general form,

$$\begin{aligned} \hat{G} &= \{ e^{\hat{Y}} \}^{-1} \hat{\mathcal{H}}_2 \{ e^{\hat{Y}} \} \\ &= g_0 + \sum_{p,q} g_q^p \{ \hat{E}_q^p \} + \sum_{p,q,r,s} g_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots, \end{aligned} \quad (6.10)$$

in which $\hat{Y}$ is a cluster operator and $\hat{\mathcal{H}}_2$ is a similarity transformed Hamiltonian truncated up to two-body operators. The KM normal-ordered exponential, indicated by braces, only needs to be used in cases where the various operators entering $\hat{Y}$ do not commute. The various transformations, considered in this work, are summarized in Table 6.1 along with the definitions of the corresponding operators and the residual

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equations which determine the cluster amplitudes. It is important to note that in all residual equations and the expressions for the various elements of the similarity transformed Hamiltonians, we only keep up to quadratic terms in the amplitudes. Hence, the evaluation of these expressions only requires the one- and two-body RDMs. This is in stark contrast to ic-MRCCSD theory [49, 50, 51, 52], which requires up to five-body RDMs in the definition of the residual equations, when truncated to terms which are up to quadratic in the amplitudes.

Table 6.1: The details of the various MR-EOM transformations that are studied in this chapter. The equations for the operator components and the residual equations which determine the corresponding amplitudes also appear in the Table. Note that we use the usual (Einstein) convention that repeated indices are summed over.

Name	Transformation	Operators	Operator Components	Residual Equation
T	$\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ $= \bar{h}_0 + \bar{h}_q^p \{ \hat{E}_q^p \} + \bar{h}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots$	$\hat{T} = \hat{T}_1 + \hat{T}_2$	$\hat{T}_1 = t_i^a \hat{E}_i^a$ $\hat{T}_2 = \frac{1}{2} t_{ij}^{ab} \hat{E}_{ij}^{ab}$	$R_i^a = \sum_{\mathbf{m}} \langle \Phi_{\mathbf{m}} \hat{E}_a^i \hat{H} \Phi_{\mathbf{m}} \rangle$ $R_{ij}^{ab} = \bar{h}_{ij}^{ab}$
T [†]	$\hat{\bar{H}} = e^{\hat{T}^\dagger} \hat{H} e^{-\hat{T}^\dagger}$ $= \bar{h}_0 + \bar{h}_q^p \{ \hat{E}_q^p \} + \bar{h}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots$	$\hat{T}^\dagger = \hat{T}_1^\dagger + \hat{T}_2^\dagger$	$\hat{T}_1^\dagger = t_a^i \hat{E}_a^i$ $\hat{T}_2^\dagger = \frac{1}{2} t_{ab}^{ij} \hat{E}_{ab}^{ij}$	None (<i>i.e.</i> set $t_a^i \approx t_i^a$) None (<i>i.e.</i> set $t_{ab}^{ij} \approx t_{ij}^{ab}$)
SXD ^a	$\hat{\bar{F}} = \{ e^{\hat{S} + \hat{X} + \hat{D}} \}^{-1} \hat{H}_2 \{ e^{\hat{S} + \hat{X} + \hat{D}} \}$ $= \bar{f}_0 + \bar{f}_q^p \{ \hat{E}_q^p \} + \bar{f}_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots$	$\hat{S} = \hat{S}_1 + \hat{S}_2$ $\hat{X} = \hat{X}_2$ $\hat{D} = \hat{D}_2$	$\hat{S}_1 = s_i^a \hat{E}_i^a$ $\hat{S}_2 = s_{i'j'}^{aw} \hat{E}_{i'j'}^{aw}$ $\hat{X}_2 = x_{i'x}^{aw} \hat{E}_{i'x}^{aw}$ $\hat{D}_2 = d_{xi'}^{aw} \hat{E}_{xi'}^{aw}$	$R_i^a = \sum_{\mathbf{m}} \langle \Phi_{\mathbf{m}} \hat{E}_a^i \hat{F} \Phi_{\mathbf{m}} \rangle$ $R_{i'j'}^{aw} = \bar{f}_{i'j'}^{aw}$ $R_{i'x}^{aw} = \bar{f}_{i'x}^{aw}$ $R_{xi'}^{aw} = \bar{f}_{xi'}^{aw}$
U	$\hat{G} = e^{-\hat{U}} \hat{F}_2 e^{\hat{U}}$ $= g_0 + g_q^p \{ \hat{E}_q^p \} + g_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots$	$\hat{U} = \hat{U}_2$	$\hat{U}_2 = u_{i'j'}^{wx} \hat{E}_{i'j'}^{wx}$	$R_{i'j'}^{wx} = g_{i'j'}^{wx}$
TSXD	$\hat{\bar{G}} = \{ e^{\hat{T} + \hat{S} + \hat{X} + \hat{D}} \}^{-1} \hat{H} \{ e^{\hat{T} + \hat{S} + \hat{X} + \hat{D}} \}$ $= g_0 + g_q^p \{ \hat{E}_q^p \} + g_{rs}^{pq} \{ \hat{E}_{rs}^{pq} \} + \dots$	$\hat{T} = \hat{T}_1 + \hat{T}_2$ $\hat{S} = \hat{S}_2$ $\hat{X} = \hat{X}_2$ $\hat{D} = \hat{D}_2$	$\hat{T}_1 = t_i^a \hat{E}_i^a$ $\hat{T}_2 = \frac{1}{2} t_{ij}^{ab} \hat{E}_{ij}^{ab}$ $\hat{S}_2 = s_{i'j'}^{aw} \hat{E}_{i'j'}^{aw}$ $\hat{X}_2 = x_{i'x}^{aw} \hat{E}_{i'x}^{aw}$ $\hat{D}_2 = d_{xi'}^{aw} \hat{E}_{xi'}^{aw}$	$R_i^a = \sum_{\mathbf{m}} \langle \Phi_{\mathbf{m}} \hat{E}_a^i \hat{G} \Phi_{\mathbf{m}} \rangle$ $R_{i'j'}^{aw} = g_{i'j'}^{aw}$ $R_{i'x}^{aw} = g_{i'x}^{aw}$ $R_{xi'}^{aw} = g_{xi'}^{aw}$

^a Note that if the T[†] transformation has been performed, then the SXD transformation becomes $\hat{\bar{F}} = \{ e^{\hat{S}_2 + \hat{X} + \hat{D}} \}^{-1} \hat{H}_2 \{ e^{\hat{S}_2 + \hat{X} + \hat{D}} \}$ (*i.e.* $\hat{S}_1$ is excluded from the transformation). The only exception is for the MR-EOM-T|T[†]|(S₁ + S₂)XD approach, which includes the $\hat{S}_1$ operator.

In order to indicate the sequence of transformations employed in a given MR-EOM method, we separate each transformation by a bar (|) in the name of the method. For example, the MR-EOM-T|SXD|U approach consists of a T transformation (*i.e.* involving the $\hat{T}$ operator), followed by an SXD

transformation (*i.e.* including the $\hat{T} + \hat{S} + \hat{D}$ operator), which is then proceeded by a final U transformation (*i.e.* incorporating the $\hat{U}$ operator). It is important to note that we make two important approximations in the definition of the MR-EOM-T|T † |SXD approach, which includes the $\hat{T}^\dagger$ transformation. Namely, we do not include the $\hat{S}_1$ operator in the SXD transformation and the 3p1h elements of the required similarity transformed Hamiltonians are approximated by the 3p1h elements of the bare two-electron integrals (*N.B.* this does not need to be done for the elements of the final transformed Hamiltonian $\hat{G}$, since they do not enter the MRCI diagonalization step and are thus, never calculated),

$$\tilde{h}_{bc}^{ia} \approx \bar{h}_{bc}^{ia} \approx v_{bc}^{ia}. \quad (6.11)$$

where $v_{ia}^{bc} = v_{bc}^{ia}$ (*i.e.* $\tilde{h}_{ia}^{bc} \approx \bar{h}_{ia}^{bc} \approx v_{ia}^{bc} = v_{bc}^{ia}$). Conversely, the MR-EOM-T|T † |(S $_1$ + S $_2$)XD approach does not employ either of these approximations, as it includes the $\hat{S}_1$ operator in the SXD transformation and no approximation is used for the 3p1h elements of each of the required similarity transformed Hamiltonians.

As discussed in chapter 3, the so-called MR-EOM-T|T † |SXD-h-v approach has been implemented in the ORCA program package [24]. Furthermore, we recall that this method was the subject of the benchmark applications to transition metal complexes in chapter 5, which also included an assessment of the efficacy of the orbital selection scheme described therein. Moreover, in chapter 3, we explained the details of the Hermitization and vertex symmetrization (*i.e.* indicated by the h and v in MR-EOM-T|T † |SXD-h-v) of the elements of the similarity transformed Hamiltonian. This symmetrization is currently required due to a technical limitation of the MRCI module in the ORCA program, where it is expected that these elements have the full symmetry of the bare two-electron integrals. Let us briefly review how one imposes these symmetries on the elements of the final similarity transformed Hamiltonian. For the one-body elements, the Hermitization (*i.e.* the permutational symmetry $g_q^p = g_p^q$) is achieved by employing the the following expressions,

$$g_j^i = g_i^j = \frac{1}{2}(g_j^i + g_i^j), \quad (6.12)$$

$$g_b^a = g_a^b = \frac{1}{2}(g_b^a + g_a^b) \quad (6.13)$$

$$g_i^a = g_a^i \quad (6.14)$$

For the two-body elements, the Hermitization (*i.e.* $g_{rs}^{pq} = g_{pq}^{rs}$) is imposed as follows,

$$g_{kl}^{ij} = g_{ij}^{kl} = \frac{1}{2}(g_{kl}^{ij} + g_{ij}^{kl}), \quad (6.15)$$

$$g_{bj}^{ia} = g_{ia}^{bj} = \frac{1}{2}(g_{bj}^{ia} + g_{ia}^{bj}), \quad (6.16)$$

$$g_{jb}^{ia} = g_{ia}^{jb} = \frac{1}{2}(g_{jb}^{ia} + g_{ia}^{jb}), \quad (6.17)$$

$$g_{ij}^{ak} = g_{ak}^{ij}. \quad (6.18)$$

The reason why the 1h1p and 3h1p elements are treated differently was explained in detail in chapter 3 and we refer the reader to the discussion contained therein. The vertex-symmetrization of the two-body elements (*i.e.* the permutational symmetries $g_{rs}^{pq} = g_{ps}^{rq} = g_{rq}^{ps}$) is always performed after the Hermitization and is achieved through the use of the expression,

$$g_{rs}^{pq} = \frac{1}{4}(2g_{rs}^{pq} + g_{ps}^{rq} + g_{rq}^{ps}). \quad (6.19)$$

In this chapter, we will investigate how the calculated excitation energies of various systems are affected by the imposition of Hermitian and vertex symmetries.

In the final uncontracted MRCI diagonalization step of an MR-EOM calculation, the ground and excited state energies are obtained by diagonalizing the final similarity transformed Hamiltonian over the CAS configurations and some of the excited configurations. The minimal diagonalization space must at least incorporate configurations that are generated by excitation operators that are not included in the cluster operator(s) which define the similarity transformed Hamiltonian(s) for a given MR-EOM approach. Hence, in addition to the CAS configurations, the minimal diagonalization space for the MR-EOM-T|SXD, MR-EOM-TSXD and MR-EOM-T|T[†]|SXD approaches includes all 1h, 1p and 2h configurations, while that for the MR-EOM-T|SXD|U only includes the 1h and 1p configurations. As stated previously, the virtue of a minimal diagonalization space is that it reduces the computational cost of the calculation and reduces the size-extensivity errors. In section 6.3, we will further examine how the size of the final diagonalization manifold affects the excitation energies for a benchmark test set of organic molecules. Namely, we will compare the MR-EOM-T|SXD-full (including 1p1h configurations in the final diagonalization) excitation energies with those from MR-EOM-T|SXD calculations (excluding 1p1h configurations) and compare MR-EOM-T|SXD|U-full (including 2h and 1p1h in the final diagonalization) excitation energies with MR-EOM-T|SXD|U results (excluding 2h and 1p1h configurations). We will also examine the effects of excluding terms containing the two-body cumulant from the various residual equations and elements of the various similarity transformed Hamiltonians. The features of the MR-EOM variants, considered in this work, appear in Table 6.2.

Table 6.2: The characteristics of the various MR-EOM schemes investigated in this work.

Method	Transformation(s) ^a	Diagonalization space	Additional characteristics
Bare H	none	CAS, 1h, 1p, 2h, 1h1p, 2h1p	
MR-EOM-T	$\hat{T}_1 + \hat{T}_2$	CAS, 1h, 1p, 2h, 1h1p, 2h1p	
MR-EOM-T S	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2$	CAS, 1h, 1p, 2h, 1h1p	
MR-EOM-T SXD	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T SXD-noG λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	$-\lambda_2$ terms excluded from all equations (except the projected singles equations)
MR-EOM-T SXD-no λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	$-\lambda_2$ terms excluded from the many-body amplitude equations
MR-EOM-T SXD-full	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h, 1h1p	
MR-EOM-TSXD	$\hat{T}_1 + \hat{T}_2 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T SXD U	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p	
MR-EOM-T SXD U-noG λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p	$-\lambda_2$ terms excluded from all equations (except the projected singles equations)
MR-EOM-T SXD U-no λ_2	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p	$-\lambda_2$ terms excluded from the many-body amplitude equations
MR-EOM-T SXD U-full	$\hat{T}_1 + \hat{T}_2 \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D} \hat{U}$	CAS, 1h, 1p, 2h, 1h1p	
MR-EOM-T T [†] (S ₁ + S ₂)XD	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T T [†] (S ₁ + S ₂)XD-h	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_1 + \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	-Hermitization of $\hat{G}$ elements
MR-EOM-T T [†] SXD	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	
MR-EOM-T T [†] SXD-h	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	-Hermitization of $\hat{G}$ elements
MR-EOM-T T [†] SXD-h-v	$\hat{T}_1 + \hat{T}_2 \hat{T}_1^\dagger + \hat{T}_2^\dagger \hat{S}_2 + \hat{X} + \hat{D}$	CAS, 1h, 1p, 2h	-Hermitization and vertex-symmetrization of $\hat{G}$ elements

^a As usual, we employ a vertical bar (|) to separate one transformation sequence from another.

6.3 Excitation Energies for Organic Molecules

As a first benchmark application for the various MR-EOM approaches of Table 6.2, we will consider the calculation of excitation energies of the low-lying valence transitions (*i.e.* $\sigma \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) of a subset of the organic molecules from the test suite of Thiel and coworkers [33]. The MR-EOM calculations were performed in a development version of the ACES II program package [179]. The reference MP2/6-31G* ground state geometries for these molecules were taken from Ref. [33] and the TZVP basis of Ahlrichs and coworkers [246] is used in all of the calculations.

For each of the molecules considered, detailed information regarding the choice of active space and the state-averaged CAS, are provided in Table 6.3. Note that the active spaces include all of the pertinent orbitals involved in the electronic transitions of interest (*i.e.* the relevant σ , n (lone-pair), π and π^*

CHAPTER 6. BENCHMARK APPLICATIONS OF VARIATIONS OF MR-EOM

Table 6.3: The choice of active space and states included in the state-averaged CAS for each molecule comprising the organic molecule benchmark test set. For each molecule, we also indicate whether or not the projection scheme is employed for discarding the nearly singular $\hat{T}_2$ -amplitudes (*i.e.* project $\hat{T}_2$)

Molecule	Active orbitals by irrep.	$(n_e, n_o)^a$	Reference states by irrep.	Project $\hat{T}_2$
acetamide	$2 \times a'$, $4 \times a''$	(10, 6)	$1 \times {}^3A''$	no
benzene	$2 \times b_{1u}$, $1 \times b_{2g}$, $1 \times b_{3g}$, $1 \times a_u$	(6, 5)	$1 \times {}^3A_g$, $1 \times {}^3B_{1g}$, $2 \times {}^3B_{2u}$, $2 \times {}^3B_{3u}$	no
cyclopentadiene	$2 \times a_2$, $2 \times b_2$	(4, 4)	$2 \times {}^3A_1$, $1 \times {}^3B_1$	yes
cyclopropene	$1 \times a_1$, $1 \times a_2$, $1 \times b_1$, $1 \times b_2$	(6, 4)	$1 \times {}^3B_1$, $1 \times {}^3B_2$	no
E-butadiene	$2 \times a_u$, $2 \times b_g$	(4, 4)	$1 \times {}^3A_g$, $1 \times {}^3B_u$	yes
E-hexatriene	$3 \times a_u$, $2 \times b_g$	(6, 5)	$1 \times {}^3A_g$, $1 \times {}^3B_u$	yes
ethene	$1 \times b_{1u}$, $1 \times b_{2g}$	(2, 2)	$1 \times {}^3B_{1u}$	no
formaldehyde	$1 \times a_1$, $1 \times b_1$, $2 \times b_2$	(6, 4)	$1 \times {}^3A_1$, $1 \times {}^3A_2$, $1 \times {}^3B_2$	no
formamide	$2 \times a'$, $3 \times a''$	(6, 5)	$2 \times {}^3A'$, $2 \times {}^3A''$	yes
furan	$2 \times a_2$, $2 \times b_2$	(4, 4)	$1 \times {}^3A_1$, $1 \times {}^3B_1$	yes
imidazole	$1 \times a'$, $4 \times a''$	(6, 5)	$4 \times {}^3A'$, $2 \times {}^3A''$	yes
norbornadiene ^{S^b}	$1 \times a_1$, $1 \times a_2$, $1 \times b_1$, $1 \times b_2$	(4, 4)	$1 \times {}^1A_1$, $2 \times {}^1A_2$, $2 \times {}^1B_2$	yes
norbornadiene ^{T^c}	$1 \times a_1$, $1 \times a_2$, $1 \times b_1$, $1 \times b_2$	(4, 4)	$1 \times {}^3A_2$, $1 \times {}^3B_2$	yes
propanamide	$4 \times a'$, $3 \times a''$	(12, 7)	$2 \times {}^3A'$, $2 \times {}^3A''$	no
pyridazine	$1 \times a_1$, $2 \times a_2$, $1 \times b_1$, $2 \times b_2$	(8, 6)	$3 \times {}^1A_1$, $2 \times {}^1A_2$, $2 \times {}^1B_1$, $2 \times {}^1B_2$	no
pyridine	$1 \times a_1$, $2 \times a_2$, $3 \times b_2$	(8, 6)	$3 \times {}^3A_1$, $1 \times {}^3A_2$, $3 \times {}^3B_1$, $1 \times {}^3B_2$	no
pyrimidine	$2 \times a_1$, $2 \times b_1$, $1 \times b_2$	(6, 5)	$3 \times {}^1A_1$, $1 \times {}^1A_2$, $1 \times {}^1B_1$, $2 \times {}^1B_2$	no
pyrrole	$2 \times a_2$, $2 \times b_2$	(4, 4)	$1 \times {}^3A_1$, $1 \times {}^3B_1$	yes
triazine	$1 \times a_1$, $2 \times a_2$, $2 \times b_1$, $1 \times b_2$	(8, 6)	$2 \times {}^1A_1$, $2 \times {}^1A_2$, $2 \times {}^1B_1$, $1 \times {}^1B_2$	no

^a The CAS(n_e, n_o) active space consisting of n_e electrons distributed among n_o orbitals.

^b Used for the calculation of singlet states in norbornadiene.

^c Used for the calculation of triplet states in norbornadiene.

orbitals) and the Abelian symmetries of these orbitals are listed in Table 6.3. Also, for each molecule, the number of active electrons appears in the table, along with the Abelian symmetries of the various states included in the state-averaged CAS. Furthermore, in the last column of Table 6.3, we indicate whether or not the projection scheme of Ref. [177] is used to discard the nearly singular $\hat{T}_2$ -amplitudes (*i.e.* project $\hat{T}_2$), replacing them with suitable perturbative estimates.

For the majority of the systems, we employ a state-averaged CAS constructed from a manifold of triplet states. The only exceptions are for the pyridazine, pyrimidine and triazine molecules, as well as the state-averaged CAS used for the MR-EOM calculations of singlet states in norbornadiene, where a manifold of singlet states is employed to construct the CAS. One particularly powerful aspect of the MR-EOM methodology is that from a single state-averaged CASSCF calculation, one can access a large number of excited states by solving for a single set of cluster amplitudes and diagonalizing a many-body Hamiltonian over a compact first-order interacting space. It is important to note that the selection of

states to be included in the state-averaged CASSCF is not crucial and we have simply decided to employ a manifold of triplet states for the majority of the systems in Table 6.3. It is not a necessity, as long as the character of the final states of interest are dominated by CAS configurations.

The %active is an important (*a-posteriori*) criterion to determine whether or not a given electronic state is reliably described in a given MR-EOM calculation. The %active is a measure of the active space character of a particular state, since it is simply the square of the norm of the active space component of a normalized eigenvector of the final similarity transformed Hamiltonian (*i.e.* the reference weight), times 100%. Typically, if the %active value is larger than 90% for a given electronic state, this means that the MR-EOM energy can be trusted for that state. Generally, if the %active falls below 85%, the MR-EOM results for that particular state should be viewed as suspect. Note that the active spaces and states included in the state-averaging, for each of the molecules considered (see Table 6.3), were chosen such that the majority of states of interest have a corresponding %active value which is greater than 85%.

6.3.1 Evaluation of the Effects of Many-Body Transformations and the Size of the Diagonalization Manifold on the Calculated Excitation Energies

In order to assess the relative accuracy of the MR-EOM methods, the CC3 [247, 248, 249] excitation energies from Ref. [33] are used as benchmark data. In addition, the calculated excitation energies for the singlet states are compared with benchmark EOM-CCSDT-3 [250] results from Ref. [22]. Note that both the CC3 and EOM-CCSDT-3 methods include approximate triples corrections in an iterative fashion. However, EOM-CCSDT-3 is more complete from a theoretical standpoint, as it includes more of the contributions that are present in the EOM-CCSDT equations. The differences between the CC3 and EOM-CCSDT-3 results, for the singlet excited states comprising the full test set of Thiel and coworkers [33], has recently been investigated in Ref. [210]. It was observed that the deviations can be as large as 0.1 eV and that there are many which are greater than 0.05 eV. This is somewhat disconcerting, since these results serve as benchmark data in the present study and it is not known which of these two methods is more accurate relative to Full-CI. Nonetheless, since we currently do not have access to more reliable data (*e.g.* EOM-CCSDT calculations), we will compare the calculated excitation energies with the available CC3 and EOM-CCSDT-3 results. One important criterion for determining the reliability of the CC3 (or EOM-CCSDT-3) energy for a particular state is the %T1. This is a measure of the single excitation character of a given state and in general, if it is larger than 85%, the results are suitably accurate. As the %T1 decreases below this threshold, the double excitation character of a state becomes significant and this leads to considerable errors in the calculated excitation energies (*i.e.* methods such as CC3 and EOM-CCSDT-3 are designed for the explicit treatment of states dominated by single excitations). Note

that in the calculation of the statistics reported below, we have excluded states for which %T1 < 85% (*i.e.* we employ the CC3 values) and %active < 90%. For the interested reader, the individual excitation energies, from which the various statistics below are calculated, can be found in appendix C.

Table 6.4: Statistics for the deviations in the calculated excitation energies from CC3 and EOM-CCSDT-3 benchmark values (in eV) for the test set of organic molecules.

	Deviations from CC3					
	Bare H	T	T S	T SXD	TSXD	T SXD U
<i>Singlets</i>						
Average	0.141	0.125	0.082	-0.017	0.032	-0.005
MAD	0.207	0.130	0.091	0.062	0.070	0.061
RMSD	0.254	0.155	0.114	0.080	0.086	0.077
Standard deviation	0.214	0.094	0.080	0.079	0.080	0.078
MAX	0.536	0.319	0.266	0.181	0.218	0.152
<i>Triplets</i>						
Average	0.100	0.052	0.038	-0.036	-0.011	-0.043
MAD	0.162	0.058	0.048	0.067	0.056	0.065
RMSD	0.192	0.076	0.065	0.077	0.064	0.076
Standard deviation	0.166	0.056	0.053	0.069	0.064	0.064
MAX	0.428	0.220	0.179	0.159	0.115	0.135
	Deviations from EOM-CCSDT-3					
	Bare H	T	T S	T SXD	TSXD	T SXD U
<i>Singlets</i>						
Average	0.090	0.073	0.031	-0.068	-0.019	-0.056
MAD	0.182	0.087	0.065	0.087	0.061	0.077
RMSD	0.227	0.108	0.079	0.102	0.077	0.093
Standard deviation	0.211	0.080	0.073	0.077	0.075	0.075
MAX	0.506	0.249	0.196	0.241	0.199	0.200

The statistics for the deviations in the Bare H, MR-EOM-T, T|S, T|SXD, TSXD and T|SXD|U excitation energies from the CC3 benchmark results, for the singlet and triplet states of the organic molecules of Table 6.3, are provided in Table 6.4. For each of these methods, the statistics for the deviations from EOM-CCSDT-3 benchmark results, for the singlet states, also appear in Table 6.4. The reported statistics consist of the average deviation, the mean absolute deviation (MAD), the root mean square of the deviations (RMSD), the standard deviation and the maximum absolute deviation (MAX).

Let us consider the RMSD values in Table 6.4 in more detail. For each of the methods considered in Table 6.4, we also plot the RMSD from CC3 for the singlet and triplet states and the RMSD from EOM-

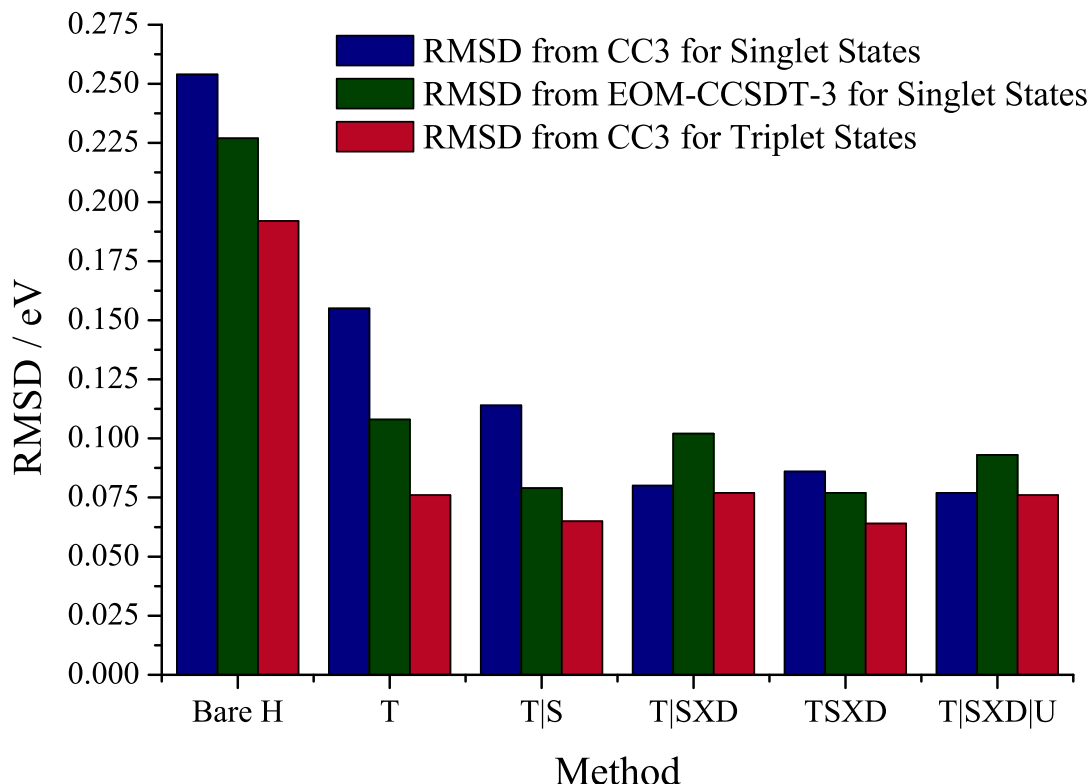


Figure 6.1: Bar plots of the RMSD from CC3 (in eV) for the singlet and triplet states and the RMSD from EOM-CCSDT-3 (in eV) for the singlets states for the organic molecule test set.

CCSDT-3 for the singlet states in the form of bar graphs in Figure 6.1. As expected, the RMSD for all of the MR-EOM approaches is significantly smaller than for the Bare H method. The standard deviation is also greatly reduced and is quite similar for all of the MR-EOM methods. One also observes that the RMSD from CC3, for the singlet states, decreases as additional operators are included in the similarity transformation(s), although the $\hat{U}$ transformation has very little effect on the results. In contrast, in the case of the triplet states, there is not much difference between the RMSD values for all of the MR-EOM approaches. Similar behavior is also observed for the RMSD from EOM-CCSDT-3 for the singlet states, however, the variation in the RMSD is larger. It is important to note that the diagonalization manifold is significantly more compact in the MR-EOM-T|SXD, TSXD (*i.e.* 1h, 1p and 2h) and T|SXD|U (*i.e.* 1h

and 1p) approaches and therefore, these methods are considerably less computationally demanding than the MR-EOM-T and T|S methods. Hence, while there is no clear indication that the accuracy of the excitation energies, for this test set of organic molecules, increases upon performing additional similarity transformations of the Hamiltonian, the large gains in computational efficiency are evident. The results of Table 6.4 also indicate that there is no significant difference between the MR-EOM-T|SXD (sequential) and TSXD (non-sequential) methods. Since the equations defining the T|SXD method are markedly less complex than the expressions which constitute the TSXD approach, the former methodology is more attractive from a computational efficiency perspective. As mentioned in Ref. [22], the EOM-CCSDT-3 excitation energies are always larger than the corresponding CC3 values and this provides an explanation for why the behaviour in the RMSD from CC3 is different from that of the RMSD from EOM-CCSDT-3. First, we note that the average deviations from CC3 for the Bare H approach and MR-EOM-T, T|S, TSXD are positive, while those for T|SXD and T|SXD|U approach are negative. Since the average deviation of the EOM-CCSDT-3 excitation energies from the CC3 results is 0.051 eV, it can be verified that the average deviations from EOM-CCSDT-3, for each of the methods in Table 6.4, are 0.051 eV smaller than those for CC3. Correspondingly, the RMSD in the Bare H and MR-EOM-T, T|S and TSXD approaches decreases (*i.e.* on average, the deviations are closer to 0 eV) upon going from CC3 to EOM-CCSDT-3, while the RMSD for MR-EOM-T|SXD and T|SXD|U methods increases (*i.e.* on average, the deviations become more negative).

Table 6.5: Statistics for the deviations in the MR-EOM-T|SXD, T|SXD|U and T|SXD|U-full excitation energies from the T|SXD-full results (in eV) for the test set of organic molecules.

	T SXD	T SXD U	T SXD U-full
<i>Singlets</i>			
Average	-0.013	-0.001	-0.002
MAD	0.036	0.033	0.004
RMSD	0.042	0.042	0.007
Standard deviation	0.041	0.043	0.006
MAX	0.105	0.089	0.025
<i>Triplets</i>			
Average	0.012	0.005	0.001
MAD	0.019	0.017	0.002
RMSD	0.031	0.025	0.002
Standard deviation	0.029	0.025	0.002
MAX	0.109	0.075	0.015

In Table 6.5, we report statistics for the deviations of the MR-EOM-T|SXD, T|SXD|U and T|SXD|U-

full excitation energies from the T|SXD-full values for the singlet and triplet states of the organic molecules. The results indicate that the differences between the T|SXD|U-full and T|SXD-full results are very small, which suggests that the $\hat{U}$ transformation has little effect on the calculated excitation energies. When the minimal diagonalization spaces are used in each case, one finds that the differences between T|SXD and T|SXD|U (not shown in Table 6.5) are larger (*e.g.* RMSD of 0.035 eV for singlet states and 0.018 eV for triplets) but still quite small. Furthermore, from the results of Table 6.5, it is evident that the deviations of the T|SXD and T|SXD|U methods from T|SXD-full are very similar and fairly small. This seems to indicate that the minimal diagonalization spaces employed are well justified, as they tend to only have a marginal effect on the excitation energies. This is further confirmed for the T|SXD|U method by comparing with the T|SXD|U-full results (not shown), where the RMSD is found to be 0.040 eV for the singlets and 0.026 eV for the triplets. Evidently, the use of smaller diagonalization manifolds is advantageous because they greatly reduce the computational cost of the calculations. Moreover, the reduction of the size of the final diagonalization space leads to a decrease of the size-extensivity errors (*e.g.* see Refs. [22, 23]). Hence, the size-extensivity errors in the T|SXD|U approach are expected to be smaller than those in the T|SXD approach, since it also includes 2h configurations in the final diagonalization manifold in addition to the CAS, 1h and 1p configurations which constitute the minimal diagonalization space of MR-EOM-T|SXD|U.

In practice, the final MRCI diagonalization for the most compact subspaces takes minor computational time for the molecules considered. Solving for the cluster amplitudes is the dominant step in the calculations and is about 3-5 times as expensive as a single-reference CCSD calculation. Hence, MR-EOM calculations are comparable in efficiency to EOM-CCSD, or even STEOM-CCSD calculations.

In a recent study [210], the STEOM methodology was benchmarked against CC3 and EOM-CCSDT-3 results for the calculation of the transition energies of the entire test set of organic molecules of Thiel and coworkers [33]. The accuracy of the MR-EOM-T|SXD and T|SXD|U approaches (see Table 6.4), for the truncated test set, is comparable to that of STEOM for the singlet states and these MR-EOM methods are markedly more accurate for the triplet states. Also, the MR-EOM-T|SXD and T|SXD|U calculations provide a significant improvement over the EOM-CCSD and CASPT2 (Complete Active Space Second-Order Perturbation Theory) results of Ref. [33] and the NEVPT2 (*n*-Electron Valence Second-Order Perturbation Theory) results from Ref. [251], especially in the case of the singlet states. The MR-EOM results for the triplet states tend to be slightly more accurate than for the singlet states. With the exception of the STEOM calculations, the same trend is observed in the EOM-CCSD, CASPT2 and NEVPT2 results, where excitation energies for the triplet states are considerably more accurate than for the singlet states.

6.3.2 Evaluation of the Effect of Discarding Terms Containing the Two-Body Cumulant from the Defining Equations on the Calculated Excitation Energies

Table 6.6: Statistics for the deviations in the MR-EOM-T|SXD-no λ_2 and T|SXD-noG λ_2 excitation energies from the T|SXD values (in eV) and for the deviations in the MR-EOM-T|SXD|U-no λ_2 and T|SXD|U-noG λ_2 excitation energies from the T|SXD|U results (in eV).

	Deviations from T SXD		Deviations from T SXD U	
	T SXD-no λ_2	T SXD-noG λ_2	T SXD U-no λ_2	T SXD U-noG λ_2
<i>Singlets</i>				
Average	0.003	0.001	0.002	0.000
MAD	0.003	0.005	0.002	0.004
RMSD	0.009	0.011	0.003	0.005
Standard deviation	0.008	0.011	0.001	0.005
MAX	0.056	0.063	0.005	0.014
<i>Triplets</i>				
Average	0.003	0.000	0.001	-0.002
MAD	0.004	0.006	0.001	0.004
RMSD	0.011	0.013	0.002	0.006
Standard deviation	0.010	0.013	0.001	0.005
MAX	0.059	0.064	0.005	0.016

It is interesting to explore to what extent the excitation energies are affected by discarding terms containing the two-body cumulant of Eq. (3.5), in the defining equations of the MR-EOM-T|SXD and T|SXD|U approaches. In particular, we investigate the effects of eliminating two-body cumulants from the many-body amplitude equations (*i.e.* the so-called no λ_2 methods), as well as the consequences of removing the cumulant terms from both the many-body residual equations and the elements of the similarity transformed Hamiltonians (*i.e.* the so-called noG λ_2 methods). Note that the two-body cumulants are not excluded from the projected residual equations (*i.e.* Eqs. (3.9) and (3.15)), since these terms are necessary to satisfy the Brillouin condition. Since the λ_2 contributions to the many-body residual equations are always quadratic in the amplitudes and involve small integrals/transformed Hamiltonian elements, we expect that the effects of these terms will be small. However, in the case of the elements of the similarity transformed Hamiltonians, there are λ_2 contributions which are linear in the amplitudes, which could have a more significant effect on the calculated excitation energies.

In Table 6.6, we have collected the statistics for the deviations in the MR-EOM-T|SXD-noG λ_2 and

T|SXD-no λ_2 excitation energies from the T|SXD results, as well as the statistics for the deviations in the MR-EOM-T|SXD|U-no $G\lambda_2$ and T|SXD|U-no λ_2 excitation energies from the T|SXD|U values. Evidently, the results of Table 6.6 demonstrate that the two-body cumulants have very little effect on the vast majority of the computed excitation energies in each case. The RMSD for the T|SXD-no $G\lambda_2$ and T|SXD-no λ_2 excitation energies from the T|SXD values are ~ 0.01 eV (for the singlets and triplets) and in both cases, there are only four absolute deviations which are larger than 0.02 eV (*i.e.* two of the singlet and two of the triplet excitation energies). Furthermore, the RMSD values for the T|SXD|U-no $G\lambda_2$ and T|SXD|U-no λ_2 excitation energies from the T|SXD|U results are even slightly smaller and the maximum absolute deviations are all below 0.02 eV. It is interesting to note that, while the deviations are very small in all the cases considered, the results of Table 6.6 seem to indicate that the effects of the two-body cumulant are even less important in the T|SXD|U calculations. The results of Table 6.6 are quite non-intuitive and provide a rationale for the fact that in MR-EOM, a single set of amplitudes can be used to describe a large number of excited states. While the one-particle density matrices for these states might be similar, the two-body cumulants are always different. This insensitivity of the amplitudes to the two-body cumulant is crucially dependent on the use of many-body residual equations and KM normal ordering. Terms in the amplitude equations that contain the two-body cumulant are quadratic in the amplitudes and hence, of lesser importance. The situation in MR-EOM is in clear contrast to experience in ic-MRCC, where up to five-body density matrices are included and results are sensitive to the five-body density [50, 52].

6.3.3 Evaluation of the Effects of the $\hat{T}^\dagger$ Transformation, the Approximations Inherent in the ORCA Implementation of MR-EOM and the Symmetrization of the Final Elements of the Similarity Transformed Hamiltonian on the Calculated Excitation Energies

In Table 6.7, we compare the MR-EOM-T|SXD and T| $T^\dagger|(S_1+S_2)$ XD approaches for the calculation of the excitation energies of the organic molecules. From Table 6.2, one can see that the only difference between these two methodologies is the additional $\hat{T}^\dagger$ transformation of Eq. (3.30), in MR-EOM-T| $T^\dagger|(S_1+S_2)$ XD. Hence, the results of Table 6.7 serve to illustrate the effects of this transformation on the calculation of the transition energies. Let us first focus on the statistics for the differences between the T| $T^\dagger|(S_1+S_2)$ XD and T|SXD excitation energies in the second column of Table 6.7. It is observed that the average of the deviations for the singlet excitations is positive, sizable and is nearly equal to the MAD, indicating that many of the MR-EOM-T| $T^\dagger|(S_1+S_2)$ XD excitation energies are considerably larger than the T|SXD values (*i.e.* in fact, one finds that there is only one deviation that is negative). Correspondingly, the

Table 6.7: Statistics for the deviations of the MR-EOM-T|SXD and T|T[†]|(S₁ + S₂)XD excitation energies from the benchmark CC3 and EOM-CCSDT-3 values (in eV) for the test set of organic molecules. The statistics for the differences between the MR-EOM-T|T[†]|(S₁ + S₂)XD and T|SXD excitation energies are also reported (in eV).

Difference between		Deviations from CC3		Deviations from EOM-CCSDT-3	
T T [†] (S ₁ + S ₂)XD and T SXD		T SXD	T T [†] (S ₁ + S ₂)XD	T SXD	T T [†] (S ₁ + S ₂)XD
<i>Singlets</i>					
Average	0.120	−0.017	0.103	−0.068	0.052
MAD	0.125	0.062	0.109	0.087	0.072
RMSD	0.137	0.080	0.132	0.102	0.092
Standard deviation	0.066	0.079	0.084	0.077	0.077
MAX	0.255	0.181	0.288	0.241	0.218
<i>Triplets</i>					
Average	0.049	−0.036	0.013	N/A	N/A
MAD	0.063	0.067	0.037	N/A	N/A
RMSD	0.074	0.077	0.052	N/A	N/A
Standard deviation	0.057	0.069	0.051	N/A	N/A
MAX	0.148	0.159	0.160	N/A	N/A

RMSD value is also large for the singlet excitations. The agreement between the T|T[†]|(S₁ + S₂)XD and T|SXD transition energies is significantly better for the triplet states, as the RMSD is about half the value calculated for the singlet states. Also, in the case of the triplets, the majority of the T|T[†]|(S₁ + S₂)XD excitation energies are larger than the T|SXD values (*i.e.* only 5 deviations which are negative out of 36). These results illustrate that the effect of the $\hat{T}^\dagger$ transformation, on the calculated excitation energies of the organic molecules, is substantial, especially for the singlet transitions. Comparing the MR-EOM-T|SXD and T|T[†]|(S₁ + S₂)XD excitation energies to the CC3 benchmark values for the singlet transitions, one observes that the agreement is much better for the T|SXD method. Conversely, in the case of the triplet states, the MAD and RMSD are somewhat smaller for the T|T[†]|(S₁ + S₂)XD approach. The same is true also, in the comparison of the deviations in the T|SXD and T|T[†]|(S₁ + S₂)XD transition energies for the singlets from the EOM-CCSDT-3 values. The latter observation can be rationalized since, as discussed above, the EOM-CCSDT-3 results are always larger than the CC3 results. Hence, as the MR-EOM-T|T[†]|(S₁ + S₂)XD are appreciably larger than the T|SXD results, it is not surprising that the MAD and RMSD for T|SXD and MR-EOM-T|T[†]|(S₁ + S₂)XD, respectively, increase and decrease upon changing the benchmark values from CC3 to EOM-CCSDT-3.

As discussed in section 6.2, the MR-EOM-T|T[†]|SXD-h-v approach has been implemented in the ORCA program package [24]. We reiterate that in addition to the $\hat{T}^\dagger$ transformation of Eq. (3.30), there are

Table 6.8: Statistics for the deviations of the MR-EOM- $T|T^\dagger|(S_1 + S_2)XD$ -h, $T|T^\dagger|SXD$, $T|T^\dagger|SXD$ -h and $T|T^\dagger|SXD$ -h-v excitation energies from the $T|T^\dagger|(S_1 + S_2)XD$ values (in eV) for the organic molecule test set.

	$T T^\dagger (S_1 + S_2)XD$ -h	$T T^\dagger SXD$	$T T^\dagger SXD$ -h	$T T^\dagger SXD$ -h-v
<i>Singlets</i>				
Average	-0.003	0.000	0.032	0.011
MAD	0.004	0.008	0.049	0.038
RMSD	0.005	0.011	0.060	0.051
Standard deviation	0.004	0.011	0.051	0.050
MAX	0.012	0.036	0.146	0.162
<i>Triplets</i>				
Average	0.001	-0.006	-0.006	-0.005
MAD	0.002	0.007	0.025	0.032
RMSD	0.002	0.010	0.035	0.046
Standard deviation	0.002	0.007	0.035	0.047
MAX	0.005	0.036	0.130	0.166

several characteristics which distinguish this approach from the $T|SXD$ method. Namely, the $\hat{S}_1$ operator is excluded from the final SXD transformation of Eq. (3.34), the 3p1h elements in each transformation are approximated by the bare two-electron integrals (see Eq. (6.11)) and the full permutational symmetries of the bare two electron integrals (*i.e.* Hermitization and vertex symmetry) are applied to the elements of the final similarity transformed Hamiltonian. In Table 6.8, we have compiled statistics for the deviations in the MR-EOM- $T|T^\dagger|(S_1 + S_2)XD$ -h, $T|T^\dagger|SXD$, $T|T^\dagger|SXD$ -h and $T|T^\dagger|SXD$ -h-v transition energies from MR-EOM- $T|T^\dagger|(S_1 + S_2)XD$ for the organic molecule test set. We note that there is no approximation for the 3p1h elements of the various similarity transformed Hamiltonians in the MR-EOM- $T|T^\dagger|(S_1 + S_2)XD$ method and the $\hat{S}_1$ operator is included in the final transformation. The very small magnitude of the various statistics for the deviations in the $T|T^\dagger|(S_1 + S_2)XD$ -h excitation energies from the $T|T^\dagger|(S_1 + S_2)XD$ values indicate that the Hermitization has little effect on the final results. Similarly, the statistics for the $T|T^\dagger|SXD$ deviations are also fairly insignificant, which implies that the approximation of Eq. (6.11) for the 3p1h elements and the neglect of the $\hat{S}_1$ operator in the final transformation, are well justified. It is interesting to note that the Hermitization has somewhat of a larger effect on the excitation energies in the $T|T^\dagger|SXD$ method, as evidenced by the values of the statistics for the $T|T^\dagger|SXD$ -h method in Table 6.8. Furthermore, with the inclusion of vertex symmetrization, the statistics for $T|T^\dagger|SXD$ -h-v are comparable to those for the $T|T^\dagger|SXD$ -h method.

6.4 Excitation Energies for Transition Metal Complexes

In a second set of applications, we will investigate the excitation spectra of five transition metal complexes, $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, ferrocene and cyclopentadienyl nickel nitrosyl (CpNiNO), using single reference methods and a selection of MR-EOM approaches. These systems were studied in our recent work [244], which involved the characterization of the excitation energies of these systems at the MR-EOM- $\text{T}|\text{T}^\dagger|\text{SXD-h-v}/\text{def2-TZVPP}$ level of theory (see Refs. [96, 231] for the details of the def2-TZVPP basis). Furthermore, this study involved the comparison of these calculations with other theoretical methods and available experimental UV/Vis. band maxima, as well as the assessment of an orbital selection scheme for reducing the computational cost of the MR-EOM- $\text{T}|\text{T}^\dagger|\text{SXD-h-v}$ excitation energy calculations. The contents of this study can be found in chapter 5 of this thesis.

In all of the current single-reference and MR-EOM calculations, we employ a cc-pVDZ basis [241] for the main-group atoms (*i.e.* hydrogen, carbon, oxygen, nitrogen) and a Wachters+F basis [238, 239, 240] for the transition metal atoms. This particular basis set was used for all of the single-reference Brueckner orbital [205, 206, 207, 208] based STEOM-ORB [16, 17, 210] and EOM-CCSD(T) [13, 14, 15, 211] calculations performed in Ref. [244] (see chapter 5) and in an extensive study of the $\text{Cr}(\text{CO})_6$ complex in Ref. [242]. For the $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ and ferrocene complexes, the ground state reference geometries, obtained from BP86 [228, 229] density functional theory calculations in a QZVP basis [230], are taken from Ref. [227]. In the case of $\text{Cr}(\text{CO})_6$ and CpNiNO , the ground state reference geometries are obtained from BP86 calculations in a def2-TZVP [96, 231] basis, which we have reported in Ref. [244]. Unless otherwise specified, relativistic effects are included in the calculations by employing the kinetic energy operator,

$$T = \frac{p^2}{m + \sqrt{\frac{p^2}{c^2} + m^2}}, \quad (6.20)$$

in the bare molecular electronic Hamiltonian, in which $m = 1$ and $c \approx 137$ in atomic units.

For the MR-EOM calculations, the details regarding the choice of active space and the states included in the state-averaged CAS are provided in Table 6.9. In each case, the state-averaged CAS has been chosen such that the excited states of interest are qualitatively well described by the CAS. Namely, with the use of the state-averaged CASSCF calculations described in Table 6.9, the majority of the calculated states in the final MR-EOM calculation have %active values of 90 % or greater. The active spaces are small compared with those which have been used in other multireference calculations on these systems (*e.g.* see Refs. [216, 218, 252]). One particular advantage of the MR-EOM approach, is that a small CAS can be employed. If the %active is large enough for a given electronic state ($> 90\%$), it is expected that it will be

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Table 6.9: The choice of active space and states included in the state-averaged CAS for each of the transition metal complexes.

Molecule	$(n_e, n_o)^a$	Active orbitals by irrep. ^b	Reference singlet states by irrep. ^c	Reference triplet states by irrep. ^b
Ni(CO) ₄	(10, 8)	e (d), t_2 (d), t_2 (L)	$1 \times {}^1A_1$ (${}^1A_1$), $2 \times {}^1T_1$ (${}^1A_1, {}^1B_1, {}^1B_2$), $2 \times {}^1T_2$ (${}^1A_2, {}^1B_1, {}^1B_2$), $1 \times {}^1E$ (${}^1A_1, {}^1A_2$)	$1 \times {}^3A_1$ (${}^3A_1$), $2 \times {}^3T_1$ (${}^3A_1, {}^3B_1, {}^3B_2$), $2 \times {}^3T_2$ (${}^3A_2, {}^3B_1, {}^3B_2$), $1 \times {}^3E$ (${}^3A_1, {}^3A_2$)
Fe(CO) ₅	(8, 6)	e' (d), e'' (d), e'' ($d + L$)	$1 \times {}^1A'_1$ (${}^1A_1$), $1 \times {}^1A'_2$ (${}^1B_1$), $1 \times {}^1A'_1$ (${}^1A_2$), $1 \times {}^1A'_2$ (${}^1B_2$), $1 \times {}^1E'$ (${}^1A_1, {}^1B_2$), $1 \times {}^1E''$ (${}^1A_2, {}^1B_1$)	$1 \times {}^3A'_1$ (${}^3A_1$), $1 \times {}^3A'_2$ (${}^3B_1$), $1 \times {}^3A'_1$ (${}^3A_2$), $1 \times {}^3A'_2$ (${}^3B_2$), $1 \times {}^3E'$ (${}^3A_1, {}^3B_2$), $1 \times {}^3E''$ (${}^3A_2, {}^3B_1$)
Cr(CO) ₆	(6, 7)	t_{2g} (d), t_{1u} (L), a_{1g} (L)	$1 \times {}^1A_{1g}$ (${}^1A_1$), $1 \times {}^1A_{2u}$ (${}^1A_2$), $1 \times {}^1E_u$ (${}^1A_1, {}^1A_2$), $2 \times {}^1T_{(1/2)u}$ (${}^1A_1, {}^1B_1, {}^1B_2$)	$1 \times {}^3A_{2u}$ (${}^3A_2$), $1 \times {}^3E_u$ (${}^3A_1, {}^3A_2$), $2 \times {}^3T_{(1/2)u}$ (${}^3A_1, {}^3B_1, {}^3B_2$)
ferrocene	(6, 5)	a'_1 (d), e'_2 (d), e'_1 (d)	$1 \times {}^1A'_1$ (${}^1A_1$), $3 \times {}^1E'_{(1/2)}$ (${}^1A_2, {}^1B_1$)	$3 \times {}^3E'_{(1/2)}$ (${}^3A_2, {}^3B_1$)
CpNiNO	(10, 7)	a_1 (d), e_2 (d), e_1 ($d + L$), e_1 (L)	$3 \times {}^1A_1$ (${}^1A'$), $2 \times {}^1A_2$ (${}^1A''$), $4 \times {}^1E_{(1/2)}$ (${}^1A', {}^1A''$)	$2 \times {}^3A_1$ (${}^3A'$), $3 \times {}^3A_2$ (${}^3A''$), $4 \times {}^3E_{(1/2)}$ (${}^3A', {}^3A''$)

^a The CAS(n_e, n_o) active space consisting of n_e electrons distributed among n_o orbitals.

^b Note that L is used to denote orbitals that are primarily of ligand character and d is used to denote orbitals that are primarily of metal d character.

^c The corresponding characters of the states in the Abelian subgroup representation appear in parentheses.

accurately described in the MR-EOM calculation. However, it is important to note that only states which are dominated by CAS configurations are accurately described in an MR-EOM calculation and this is one of the main drawbacks of the approach. Furthermore, the criteria that are currently used for the selection of active spaces in MR-EOM are based on anecdotal evidence from our somewhat limited experience with these calculations. A more stringent study will be required to determine whether or not the %active value provides a sufficient criterion for the selection of active spaces, in general.

Before proceeding with an evaluation of a selection of MR-EOM methods for the calculation of the excitation energies of the transition metal complexes, we will first investigate several single-reference approaches to expose some of the issues that can arise in the treatment of these systems. In Table 6.10, we have compiled a variety of computed excitation energies for the singlet states (dominated by single excitation character) of the five transition metal complexes. In particular, Table 6.10 contains STEOM-ORB [16, 17, 210], EOM-CCSD [13, 14, 15] and EOM-CCSD(T) [211] excitation energies, in addition to the results calculated with the Brueckner orbital [205, 206, 207, 208] based variants of these approaches. We have also included EOM-CCSD calculations that do not make use of the relativistic correction of Eq. (6.20) for the purposes of comparison. Furthermore, the CFOUR electronic structure package [253] was employed to calculate the excitation energies at the EOM-CCSDT-3 [250] level of theory, without inclusion of relativistic effects.

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Table 6.10: Comparison of various single-reference methods for the calculation of singlet state excitation energies (in eV) for the transition metal complexes.

State	STEOM-ORB	Brueckner STEOM-ORB	EOM-CCSD (no rel.) ^a	EOM-CCSD	Brueckner EOM-CCSD	EOM-CCSD(T)	Brueckner EOM-CCSD(T)	EOM-CCSDT-3 ^{a,b}
Ni(CO) ₄								
¹ T ₁	4.42	4.59	4.82	4.82	4.90	4.99	4.73	5.32 (76.3)
¹ E	4.45	4.61	4.85	4.85	4.93	4.97	4.70	5.30 (75.6)
¹ T ₂	4.74	4.92	5.16	5.16	5.26	5.27	5.01	5.59 (73.7)
¹ T ₁	5.16	5.36	5.53	5.51	5.62	5.58	5.30	5.92 (70.4)
¹ T ₂	5.49	5.68	N/A	N/A	6.17	N/A	5.77	N/A
Fe(CO) ₅								
¹ A'' ₁	3.99	4.04	4.60	4.63	4.66	4.75	4.73	4.37 (88.0)
¹ E''	4.20	4.27	4.78	4.79	4.84	4.91	4.91	4.59 (87.1)
¹ A'' ₂	4.53	4.56	5.18	5.21	5.21	5.21	5.17	4.69 (85.1)
¹ A'	5.49	5.57	6.03	N/A	6.08	N/A	N/A	N/A
¹ E'	5.64	5.74	6.43	6.45	6.52	6.42	6.47	N/A
Cr(CO) ₆								
¹ A _{2u}	3.98	4.04	4.52	N/A	N/A	N/A	N/A	4.35 (84.1)
¹ E _u	4.00	4.06	4.50	4.48	4.49	4.32	4.36	4.32 (84.6)
¹ T _{2u}	4.01	4.07	4.55	4.53	4.54	4.35	4.39	4.36 (84.2)
¹ T _{1u}	4.47	4.54	5.11	5.10	5.13	4.89	4.95	4.87 (83.0)
¹ T _{2g}	5.90	5.95	N/A	N/A	N/A	N/A	N/A	N/A
ferrocene								
¹ E'' ₁	0.93	1.69	2.88	2.90	2.92	3.13	3.06	2.82 (94.7)
¹ E'' ₂	1.08	1.86	2.90	2.91	2.98	N/A	3.12	2.80 (95.3)
¹ E'' ₁	2.22	2.90	4.37	4.38	4.28	4.46	4.36	4.03 (93.1)
CpNiNO								
¹ E ₁	2.79	2.95	3.17	3.20	3.18	3.13	2.93	3.23 (78.8)
¹ E ₂	2.85	3.04	3.35	3.37	3.34	3.31	3.00	3.40 (76.4)
¹ A ₂	2.53	2.55	3.09	3.14	3.04	3.18	3.06	2.90 (89.2)
¹ E ₁	3.33	3.47	3.31	3.33	3.26	3.23	3.17	3.06 (87.8)
¹ E ₂	2.77	2.79	4.03	4.05	4.02	3.89	3.63	3.94 (75.2)

^a Relativistic effects are not included in these calculations.

^b The %AEL (Approximate Excitation Level) value is given in parentheses.

Comparing the EOM-CCSD transition energies with the EOM-CCSD (no rel.) results (*i.e.* not accounting for relativistic effects), it is observed that all of the values agree to within 0.03 eV, with the exception of the ¹A₂ state in CpNiNO, where the difference is 0.05 eV. This evidently indicates that the inclusion of scalar relativistic effects has a relatively minor effect on the computed excitation energies. For many of the states in Table 6.10, the Brueckner STEOM-ORB and especially, the STEOM-ORB results are smaller in magnitude than those computed with the other methods. Also, as mentioned in Ref. [244], the STEOM approaches break down for the ferrocene molecule, yielding excitation energies that are far too small. Furthermore, the STEOM-ORB excitation energies are erratic for the CpNiNO molecule, in particular for the ¹A₂ state and the second state of ¹E₂ symmetry. While there is not much difference between the EOM-CCSD and Brueckner EOM-CCSD results ($\lesssim 0.1$ eV), the differences

between the STEOM and EOM-CCSD(T) excitation energies from the corresponding values obtained with the Brueckner based methods can be quite large in some cases. With the exception of ferrocene, where the differences are very large, there are somewhat larger differences between the STEOM-ORB and Brueckner STEOM-ORB results for $\text{Ni}(\text{CO})_4$ and CpNiNO . Furthermore, the differences between EOM-CCSD(T) and Brueckner EOM-CCSD(T) approach 0.3 eV for all the states in $\text{Ni}(\text{CO})_4$ and are sizeable for many of the states in CpNiNO . This seems to indicate that these systems are particularly difficult to treat at the single-reference level and that the reference orbitals and ground state, single excitation amplitudes have a non-negligible effect on the resulting excitation energies.

From the data in Table 6.10, one further observes large differences between the (Brueckner) EOM-CCSD(T) transition energies and the corresponding EOM-CCSDT-3 results. We have also included the %AEL (Approximate Excitation Level) values for the EOM-CCSDT-3 calculations in parentheses. Like the %T1 criterion, the %AEL is a measure of the single excitation character of a given state. If it is sufficiently large (preferably $> 90\%$), the states are of dominant single excitation character and the results are likely reliable. However, it is observed that for many of the states in Table 6.10, the %AEL values are smaller than 85 %, indicating that the calculated excitation energies are questionable. For this reason, we believe that the Brueckner EOM-CCSD(T) calculations probably provide better estimates of the excitation energies for these states, excepting the case of ferrocene molecule. For ferrocene, the %AEL values are all greater than 90% and hence, the EOM-CCSDT-3 results are likely the best available estimates of the excitation energies for this molecule

Let us now compare the excitation energies obtained from various MR-EOM calculations with the Brueckner EOM-CCSD(T) results. The MR-EOM- $\text{T}|\text{SXD}$, $\text{T}|\text{T}^\dagger|(S_1 + S_2)\text{XD}$, $\text{T}|\text{T}^\dagger|\text{SXD}$, $\text{T}|\text{T}^\dagger|\text{SXD-h}$, $\text{T}|\text{T}^\dagger|\text{SXD-h-v}$ and Brueckner EOM-CCSD(T) excitation energies, for the singlet states of dominant single excitation character, appear in Table 6.11. The EOM-CCSDT-3 results for ferrocene are also given in parentheses. For $\text{Ni}(\text{CO})_4$, there seems to be little difference between the $\text{T}|\text{SXD}$, $\text{T}|\text{T}^\dagger|(S_1 + S_2)\text{XD}$ and $\text{T}|\text{T}^\dagger|\text{SXD}$ excitation energies, while the Hermitization lowers the excitation energies slightly (*i.e.* $\text{T}|\text{T}^\dagger|\text{SXD-h}$) and the additional vertex symmetrization has only a small effect. The Brueckner EOM-CCSD(T) transition energies are all lower than those calculated with the MR-EOM approaches and the MR-EOM- $\text{T}|\text{T}^\dagger|\text{SXD-h-v}$ results have the best overall agreement with the Brueckner EOM-CCSD(T) values for $\text{Ni}(\text{CO})_4$. In the case of $\text{Fe}(\text{CO})_5$, the $\text{T}|\text{SXD}$ and $\text{T}|\text{T}^\dagger|\text{SXD}$ excitation energies are similar, while the $\text{T}|\text{T}^\dagger|(S_1 + S_2)\text{XD}$ are somewhat larger. Once again, the Hermitization lowers the transition energies in the $\text{T}|\text{T}^\dagger|\text{XD-h}$ approach and the vertex symmetrization (*i.e.* $\text{T}|\text{T}^\dagger|\text{XD-h-v}$) further reduces the values significantly (~ 0.1 eV). In this case, the $\text{T}|\text{SXD}$ transition energies show the best overall agreement with the Brueckner EOM-CCSD(T) values. For the $\text{Cr}(\text{CO})_6$ complex, one observes much

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Table 6.11: Comparison of the MR-EOM-T|SXD, $T|T^\dagger|(S_1 + S_2)XD$, $T|T^\dagger|SXD$, $T|T^\dagger|SXD-h$, $T|T^\dagger|SXD-h-v$ and the Brueckner EOM-CCSD(T) excitation energies (in eV) for the singlet states of the transition metal complexes, which are dominated by single excitation character.

State	Brueckner EOM-CCSD(T)	T SXD	$T T^\dagger (S_1 + S_2)XD$	$T T^\dagger SXD$	$T T^\dagger SXD-h$	$T T^\dagger SXD-h-v$
<i>Ni(CO)₄</i>						
¹ T ₁	4.73	4.97	5.00	4.99	4.88	4.88
¹ E	4.70	5.05	5.08	5.07	4.97	4.95
¹ T ₁	5.30	5.71	5.77	5.74	5.72	5.73
¹ T ₂	5.77	6.15	6.21	6.19	6.15	6.09
<i>Fe(CO)₅</i>						
¹ A ₁ ^{''}	4.73	4.74	4.86	4.75	4.68	4.61
¹ E ^{''}	4.91	5.04	5.19	5.08	5.00	4.90
¹ A ₂ ^{''}	5.17	5.14	5.25	5.11	5.09	4.96
¹ E'	6.47	6.12	6.23	6.18	6.01	5.88
<i>Cr(CO)₆</i>						
¹ E _u	4.36	5.22	4.98	4.60	4.29	4.33
¹ T _{2u}	4.39	5.27	5.01	4.66	4.35	4.37
¹ T _{1u}	4.95	5.94	5.68	5.32	5.06	4.96
<i>ferrocene</i>						
¹ E ₁ ^{''}	3.06 (2.82) ^a	2.49	2.82	2.79	2.96	2.91
¹ E ₂ ^{''}	3.12 (2.80) ^a	2.52	2.85	2.83	2.96	2.99
¹ E ₁ ^{''}	4.36 (4.03) ^a	3.95	4.23	4.22	4.33	4.31
<i>CpNiNO</i>						
¹ E ₁	2.93	2.79	2.90	2.90	2.94	2.94
¹ E ₂	3.00	2.87	2.98	2.98	3.03	3.04
¹ A ₂	3.06	3.28	3.36	3.39	3.36	3.39
¹ E ₁	3.17	3.48	3.58	3.62	3.59	3.60
¹ E ₂	3.63	3.49	3.63	3.65	3.69	3.70

^a The EOM-CCSDT-3 results for ferrocene are provided in parentheses.

larger variations in the values of MR-EOM excitation energies. The addition of the $\hat{T}^\dagger$ transformation lowers the excitation energies by approximately 0.25 eV (*i.e.* compare T|SXD with $T|T^\dagger|(S_1 + S_2)XD$), while the differences between T|SXD and $T|T^\dagger|SXD$ are even more extreme. The Hermitization also significantly reduces the excitation energies and the additional vertex symmetrization only has a relatively minor effect by comparison. The large variations that are observed in the MR-EOM excitation energies of Cr(CO)₆ can be attributed to disproportionate changes in the ground state energy, relative to those of the excited states, as will be discussed below. In this case, the MR-EOM-T|T[†]|SXD-h-v excitation energies agree remarkably well with the Brueckner EOM-CCSD(T) values. For the ferrocene molecule, we also

observe larger variations between the MR-EOM excitation energies. Also, all the methods which include the $\hat{T}^\dagger$ transformation give larger excitation energies than the T|SXD method. In contrast with the metal carbonyls, the Hermitization increases the excitation energies for ferrocene, while the vertex symmetrization seems to have only a small effect on the results. Overall, the MR-EOM-T| $T^\dagger$ |SXD-h excitation energies display the best agreement with the Brueckner EOM-CCSD(T) results. In contrast, the EOM-CCSDT-3 results are all lower in energy than those obtained from the Brueckner EOM-CCSD(T) calculations. For the two lowest energy excited states, the agreement between the T| $T^\dagger$ |(S₁ + S₂)XD, T| $T^\dagger$ |SXD and EOM-CCSDT-3 results is very good, while for the higher lying E_1'' state, the T|SXD excitation energy agrees more closely with the EOM-CCSDT-3 value. In the case of CpNiNO, one observes relatively small differences between the MR-EOM excitation energies. The $\hat{T}^\dagger$ transformation produces an increase in the excitation energies and there is little difference between the T| $T^\dagger$ |(S₁ + S₂)XD and T| $T^\dagger$ |SXD values. Furthermore, the Hermitization and vertex symmetrization result in very slight changes in the excitation energies. Each of the MR-EOM approaches provide excitation energies which show similar overall agreement with the Brueckner EOM-CCSD(T) results, but the MR-EOM-T| $T^\dagger$ |(S₁ + S₂)XD results are marginally better in this case. The statistics for the deviations in the MR-EOM excitation energies from Brueckner EOM-CCSD(T), for the singlet states of all five molecules, appear in Table 6.12. The RMSD and MAD are smallest for the MR-EOM-T| $T^\dagger$ |SXD-h approach and the T| $T^\dagger$ |SXD-h-v values are only slightly larger. The RMSD for the T| $T^\dagger$ |SXD method is also comparable with that of T| $T^\dagger$ |SXD-h and all these methods seem to provide significantly better excitation energies (compared to Brueckner EOM-CCSD(T)) than T| $T^\dagger$ |(S₁ + S₂)XD and especially, T|SXD.

Table 6.12: Statistics for the deviations in the MR-EOM-T|SXD, T| $T^\dagger$ |(S₁ + S₂)XD, T| $T^\dagger$ |SXD, T| $T^\dagger$ |SXD-h and T| $T^\dagger$ |SXD-h-v excitation energies from the Brueckner EOM-CCSD(T) values (in eV) for the singlet states of the transition metal complexes, which are dominated by single excitation character.

	T SXD	T $T^\dagger$ (S ₁ + S ₂)XD	T $T^\dagger$ SXD	T $T^\dagger$ SXD-h	T $T^\dagger$ SXD-h-v
Average	0.127	0.202	0.120	0.067	0.039
MAD	0.377	0.299	0.235	0.170	0.176
RMSD	0.469	0.364	0.276	0.226	0.243
Standard deviation	0.463	0.311	0.256	0.222	0.246
MAX	0.988	0.735	0.451	0.456	0.586

In Table 6.13, we have compiled the statistics for the deviations in the MR-EOM-T|SXD, T| $T^\dagger$ |SXD, T| $T^\dagger$ |SXD-h and T| $T^\dagger$ |SXD-h-v excitation energies from the T| $T^\dagger$ |(S₁ + S₂)XD values for all of the calculated excited states (*i.e.* singlet and triplet states of single excitation character and, in the case of ferrocene

and CpNiNO, some states of higher excitation character), for each of the transition metal complexes. As mentioned above, the differences in the ground state energies (*i.e.* when comparing two different MR-EOM calculations) can be disproportionately large compared to the differences in the excited state energies. In order to illustrate this fact, we have calculated the so-called shifted RMSD. We take the lowest singlet excitation energy as a reference and subtract it from the values of the higher lying singlets and the triplets. The shifted RMSD, for each of the MR-EOM approaches, is computed for the deviations in these “shifted” excitation energies from the $T|T^\dagger|(S_1 + S_2)$ XD values. In Table 6.13, we have also included the deviations in the lowest singlet excitation energies from the $T|T^\dagger|(S_1 + S_2)$ XD value (*i.e.* deviation in E_1), for the purposes of comparison.

If we first focus on the T|SXD results, we see that the statistics are fairly small for $\text{Ni}(\text{CO})_4$ and are relatively larger for the $\text{Fe}(\text{CO})_5$ and CpNiNO complexes. This indicates that the $\hat{T}^\dagger$ transformation has a non-negligible effect on the computed excitation energies in the latter two cases. Also, the statistical errors are much larger in the case of ferrocene and $\text{Cr}(\text{CO})_6$. The small value of the shifted RMSD in the case of $\text{Cr}(\text{CO})_6$, seems to indicate that the ground state energy is affected to much greater extent, by the $\hat{T}^\dagger$ transformation, than the excited states. The shifted RMSD is still large in the case of ferrocene and this signifies that this transformation has an important effect on the excited states, as well. In general, one observes that the electronic energy of the ground and excited states are increased by the $\hat{T}^\dagger$ transformation (*i.e.* the $T|T^\dagger|(S_1 + S_2)$ XD energies are larger than the T|SXD energies). The RMSD for the deviations in the $T|T^\dagger|$ SXD excitation energies from $T|T^\dagger|(S_1 + S_2)$ XD are quite small for $\text{Ni}(\text{CO})_4$, ferrocene and CpNiNO. This demonstrates that discarding the $\hat{S}_1$ operator from the SXD transformation and employing the approximation of Eq. (6.11) for the 3p1h elements of the similarity transformed Hamiltonians, doesn’t have a large effect on the computed excitation energies for these systems. The RMSD value is larger (0.114 eV) in the case of $\text{Fe}(\text{CO})_5$ and is much greater (0.351 eV) for the $\text{Cr}(\text{CO})_6$ complex. In contrast, the shifted RMSD is small for both of these systems, indicating that the effects of these approximations are much more important for the ground state. The RMSD can also increase quite significantly as the elements of the final similarity transformed Hamiltonian are Hermitized (*i.e.* MR-EOM- $T|T^\dagger|$ SXD-h). However, with the exception of CpNiNO, the ground state seems to be affected to a greater extent as suggested by the relatively small values of the shifted RMSD in each case. The vertex symmetrization appears to have a greater effect in $\text{Fe}(\text{CO})_5$ and ferrocene, as significant shifts are observed in the RMSD, but it has very little effect on the excitation energies of the other three molecules.

Let us briefly review the most important details of the current study of various MR-EOM approaches for the calculation of the excitation energies of the transition metal complexes. We note that it is particularly difficult to obtain good reference data for these systems. In a recent study [244] (see chapter

CHAPTER 6. BENCHMARK APPLICATIONS OF VARIATIONS OF MR-EOM

Table 6.13: Statistics for the deviations in the MR-EOM-T|SXD, T|T[†]|SXD, T|T[†]|SXD-h and T|T[†]|SXD-h-v excitation energies from the T|T[†]|(S₁ + S₂)XD values for the singlet and triplet states of each of the transition metal complexes.

	T SXD	T T [†] SXD	T T [†] SXD-h	T T [†] SXD-h-v
<i>Ni(CO)₄</i>				
Average	−0.039	−0.022	−0.085	−0.093
MAD	0.039	0.022	0.085	0.093
RMSD	0.045	0.023	0.090	0.099
Standard deviation	0.022	0.008	0.030	0.036
MAX	0.069	0.033	0.115	0.133
Shifted RMSD ^a	0.027	0.013	0.041	0.042
Deviation ^b for <i>E</i> ₁	0.025	0.012	0.112	0.114
<i>Fe(CO)₅</i>				
Average	−0.087	−0.110	−0.200	−0.295
MAD	0.087	0.110	0.200	0.295
RMSD	0.095	0.114	0.204	0.299
Standard deviation	0.042	0.034	0.040	0.054
MAX	0.151	0.149	0.265	0.363
Shifted RMSD ^a	0.056	0.034	0.044	0.070
Deviation ^b for <i>E</i> ₁	0.122	0.114	0.182	0.253
<i>Cr(CO)₆</i>				
Average	0.263	−0.351	−0.658	−0.653
MAD	0.263	0.351	0.658	0.653
RMSD	0.263	0.351	0.658	0.654
Standard deviation	0.014	0.014	0.020	0.027
MAX	0.292	0.376	0.689	0.720
Shifted RMSD ^a	0.035	0.031	0.032	0.032
Deviation ^b for <i>E</i> ₁	−0.292	0.326	0.635	0.639
<i>ferrocene</i>				
Average	−0.491	−0.039	0.200	0.130
MAD	0.491	0.039	0.200	0.130
RMSD	0.507	0.041	0.207	0.142
Standard deviation	0.133	0.013	0.053	0.059
MAX	0.606	0.059	0.263	0.227
Shifted RMSD ^a	0.215	0.014	0.081	0.071
Deviation ^b for <i>E</i> ₁	0.327	0.034	−0.140	−0.092
<i>CpNiNO</i>				
Average	−0.077	−0.006	−0.017	−0.005
MAD	0.080	0.016	0.044	0.040
RMSD	0.089	0.021	0.056	0.048
Standard deviation	0.044	0.020	0.054	0.049
MAX	0.147	0.040	0.140	0.102
Shifted RMSD ^a	0.058	0.021	0.078	0.065
Deviation ^b for <i>E</i> ₁	0.115	0.003	−0.037	−0.034

^a We take the difference between the various excitation energies and the excitation energy corresponding to the 1st excited state. The shifted RMSD is computed for the deviations in these “shifted” excitation energies from the T|T[†]|(S₁ + S₂)XD values.

^b The deviations in the 1st excited state energies (*E*₁) from the T|T[†]|(S₁ + S₂)XD value.

5), we compared the results of MR-EOM-T|T[†]|SXD-h-v with available band maxima from experimental UV/Vis. spectra. We reiterate that there are several difficulties associated with the comparison of calcu-

lated vertical excitation energies with experimental band maxima. In particular, the calculations do not take into account important vibrational effects (*e.g.* vibronic coupling, Jahn-Teller distortions), spin-orbit coupling effects and environmental effects, when comparing with experimental data obtained in solution or condensed phases. Also, the basis sets employed in this work are large enough for comparing the vertical excitation energies obtained from various calculations, but are probably somewhat small for comparisons with experiment. Furthermore, we have seen that single-reference calculations can be particularly difficult for some of these systems (*i.e.* rather small %AEL values for the EOM-CCSDT-3 calculations and large differences between Brueckner EOM-CCSD(T) and EOM-CCSD(T)). Due to the unsatisfactory %AEL values for many of the states calculated with EOM-CCSDT-3, we have chosen to compare the MR-EOM excitation energies with the Brueckner EOM-CCSD(T) values, even though we cannot be fully confident that they are always reliable.

In our investigation of the transition metal complexes, we have focussed on comparing the fine details of a small subset of the MR-EOM schemes from Table 6.2. In particular, we compare the MR-EOM-T|SXD, T|T[†]|(S₁+S₂)XD, T|T[†]|SXD, T|T[†]|SXD-h and T|T[†]|SXD-h-v approaches for the calculation of the excitation spectra of these systems. It is observed that the $\hat{T}^\dagger$ transformation can have a significant effect on the excitation energies, especially in the case of Cr(CO)₆ and ferrocene. For these particular molecules, the shifted RMSD is also significantly smaller than the RMSD, indicating that the effects of the $\hat{T}^\dagger$ transformation are more important for the ground state. It is important to note that the shifted RMSD for ferrocene is also much larger than that for any other molecule, which seems to indicate that, at least some of the excited states are also more sensitive to the additional transformation. For the other three molecules, the shifted RMSD is also somewhat smaller than the RMSD. Hence, the results of Table 6.13 indicate that the ground state energy is affected to a greater extent by the $\hat{T}^\dagger$ transformation.

In the comparison of the T|T[†]|SXD approach (*i.e.* discard $\hat{S}_1$ and approximate the 3p1h elements of the similarity transformed Hamiltonians by the bare two-electron integrals (Eq. (6.11))) with T|T[†]|(S₁ + S₂)XD, we can draw similar conclusions. Namely, the additional approximations in the T|T[†]|SXD approach have a larger effect on some molecules (*i.e.* Fe(CO)₅ and especially, Cr(CO)₆) than others. In the cases where the RMSD is large, the shifted RMSD is much smaller which implies once again, that the effects are greater for the ground state. For CpNiNO, the RMSD and shifted RMSD are the same, while the shifted RMSD is only slightly smaller than the RMSD for ferrocene and Ni(CO)₄. Therefore, for all molecules except CpNiNO, the ground state is more susceptible to the effects of the additional approximations applied in the T|T[†]|SXD calculations. The Hermitization of the elements of the final similarity transformed Hamiltonian (T|T[†]|SXD-h), is also observed to have a greater consequences for certain systems (*i.e.* Cr(CO)₆ and ferrocene), if one compares the difference in the RMSD between

$T|T^\dagger|SXD$ and $T|T^\dagger|SXD-h$. However, for these and the other molecules, the corresponding change in the shifted RMSD is small in each case. Thus, the ground state is more sensitive to the Hermitization for all molecules, other than $CpNiNO$. The additional vertex symmetrization has a relatively small effect in each case and the largest change in the RMSD between $T|T^\dagger|SXD-h$ and $T|T^\dagger|SXD-h-v$ (0.095 eV) is observed for $Fe(CO)_5$. This is in contrast to the recent results reported for transition metal atoms in Ref. [245], where the vertex-symmetrization was found to have a significantly larger effect on the computed excitation energies.

Let us attempt to rationalize why, in most cases, the ground state is more sensitive to the differences in the various MR-EOM methods considered in this section. Evidently, the state-averaging in the CASSCF calculation favours the excited states and therefore, there might be an imbalance in the description of the ground and excited states. In particular, it is conceivable that the excited states could have more metal to ligand charge-transfer (MLCT) character or that many of the excited states have a greater multireference character than the ground state. In either case, it is not clear if the situation can be easily remedied. One possibility is to perform a separate MR-EOM calculation for the ground and excited states, using a different CAS in each calculation. However, this strategy has already been attempted in a recent MR-EOM study of transition metal atoms [178], where it was discovered that it is not at all easy to achieve a balance between the different MR-EOM calculations.

6.5 Concluding Remarks

This chapter provides a detailed investigation of a wide variety of MR-EOM approaches for the calculation of the excitation energies of organic molecules and transition metal complexes. Let us briefly summarize some of the main conclusions that can be drawn from the study of the organic molecules. The incorporation of additional similarity transformations, following the $\hat{T}$ transformation, allows for a significant reduction in the size of the final diagonalization space and hence, leads to large gains in computational efficiency. The use of minimal diagonalization spaces in MR-EOM- $T|SXD$ and MR-EOM- $T|SXD|U$ is well justified and only has a relatively small effect on the resulting excitation energies. Therefore, the MR-EOM- $T|SXD|U$ approach, with a minimal diagonalization space consisting of the CAS, 1h and 1p configurations, is currently the most efficient variant of the MR-EOM methodology. We have found that the removal of the terms containing the two-body cumulant, from the many-body residual equations and the expressions for the elements of the various similarity transformed Hamiltonians, has a negligible effect on the calculated excitation energies. As discussed previously, this also provides a rationalization for the transferability of the various excitation amplitudes for different electronic states. The inclusion of the $\hat{T}^\dagger$ transformation,

after the $\hat{T}$ transformation, tends to increase the values of the excitation energies considerably. However, in comparisons with the available CC3 and EOM-CCSDT-3 benchmark data, there is insufficient evidence to indicate that the MR-EOM-T|SXD approach is more accurate than MR-EOM-T| $T^\dagger$ |($S_1 + S_2$)XD, in general. In addition, if we Hermitize the elements of the final similarity transformed Hamiltonian in the MR-EOM-T| $T^\dagger$ |($S_1 + S_2$)XD approach, the effects on the computed excitation energies are minimal. The additional approximations involved in the MR-EOM-T| $T^\dagger$ |SXD approach (*i.e.* no $\hat{S}_1$ in the SXD transformation and the approximation of Eq. (6.11) for the 3p1h elements of the various similarity transformed Hamiltonians) also have a fairly small effect on the computed excitation energies. Interestingly, it appears that Hermitization has a considerably greater effect on the excitation energies calculated with the MR-EOM-T| $T^\dagger$ |SXD method compared with those calculated with the MR-EOM-T| $T^\dagger$ |($S_1 + S_2$)XD approach. Furthermore, the variation in the excitation energies with the additional vertex symmetrization is relatively small.

There are also several important conclusions which can be drawn from the study of the transition metal complexes. The large differences in the excitation energies of the singly excited singlet states, calculated with a variety of single-reference methods, seems to indicate difficulties in the treatment of these systems with such approaches. This is further evidenced by the fact that many of the states calculated with the high-level EOM-CCSDT-3 method have %AEL values below 85%. In comparisons of various MR-EOM approaches with Brueckner based EOM-CCSD(T), it is observed that the MR-EOM-T| $T^\dagger$ |SXD, T| $T^\dagger$ |SXD-h and T| $T^\dagger$ |SXD-h-v approaches all perform similarly well and show considerably better agreement than the T| $T^\dagger$ |($S_1 + S_2$)XD and T|SXD methods. It is also important to mention that it is difficult to assess the reliability of the Brueckner EOM-CCSD(T) results for these transition metal complexes and hence, one should not put too much emphasis on the results of this comparison. From the comparisons of the MR-EOM-T|SXD, T| $T^\dagger$ |SXD, T| $T^\dagger$ |SXD-h and T| $T^\dagger$ |SXD-h-v excitation energies with the T| $T^\dagger$ |($S_1 + S_2$)XD, for each of the five molecules, one can see that there are large changes in the RMSD in certain cases, while the shifted RMSD is much more reasonably behaved. As mentioned above, this seems to indicate that the ground state energy is affected to a much greater extent by the differences between the various MR-EOM approaches than the excited states. The relative excitation energies (*i.e.* differences between a given excitation energy and that of the 1st excited singlet state) seem to be particularly robust as evidenced by the shifted RMSD values. As indicated previously, the increased sensitivity of the ground state to differences in the MR-EOM approaches might be due to an imbalance in the description of the ground and excited states resulting from the definition of the state-averaged CAS, which tends to favour the excited states. In future work, it might be interesting to investigate if a better balance might be achieved for the various states by employing suitable weights in the state-averaged CASSCF calculation. We also note that in CASPT2 studies of transition metal compounds, a second set of d-orbitals is often included in the

active space (*e.g.* see Refs. [216] (excitation energies of $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$), [254] (excitation energies of $\text{Fe}(\text{CO})_5$) and [252] (structure of ferrocene)). This second d shell is needed to describe the so-called double-shell effect (*i.e.* radial correlation effects in the 3d shell) and is essential for obtaining a balanced description of ground and excited states in CASPT2 and MRCI calculations [255, 256]. Hence, it would also be interesting to investigate if including a second d shell in the CAS would lead to an improved balance between ground and excited states in the MR-EOM calculations.

Let us emphasize the salient features of the MR-EOM methodology. An MR-EOM calculation involves a single state-averaged CASSCF calculation, including a small number of low-lying states and the solution of a single set of amplitudes (*i.e.* with the same scaling as single-reference CCSD) to define the similarity transformed Hamiltonians. Then from a compact diagonalization of the final similarity transformed Hamiltonian, one obtains a desired number of (potentially many) excited states. The approach is invariant to rotations of the orbitals in the inactive, active and virtual subspaces and is spin and spatial symmetry adapted. In contrast with Difference Dedicated Configuration Interaction (DDCI) [257], which yields fairly accurate excitation energies, the MR-EOM approach also provides accurate total energies for each state. Even though there is an additional cost associated with the calculation of the amplitudes, the final diagonalization manifold is particularly compact such that the MR-EOM approach is significantly cheaper than DDCI. One major limitation of the MR-EOM method is that only states that are dominated by CAS configurations can be expected to be described accurately.

Chapter 7

Summary and Future Research Directions

In this thesis, we report further developments of the MR-EOM methodology [21, 22, 23], the implementation of this approach in the ORCA program package [24] and benchmark applications of several variants of MR-EOM to organic molecules and transition metal complexes. The MR-EOM methodology employs a convenient transform and diagonalize strategy in order to provide access to a large number of electronic states. In particular, one first solves the state-averaged CASSCF problem, incorporating a small number of low-lying states and solves for a single set of cluster amplitudes to define a similarity transformed Hamiltonian, which is then diagonalized over a compact manifold of configurations. This approach is orbital invariant and rigourously spin- and spatially-adapted. Some of the main drawbacks of this methodology is that it is not rigourously size-extensive (but it is core-extensive) and the states of interest must be dominated by configurations from the CASSCF reference space.

Let us provide a brief outline of the original contributions presented in this work. A new variant of MR-EOM has been reported, which includes a Hermitizing $\hat{T}^\dagger$ transformation. A Python [25] based automatic code generation system has been developed for the implementation of the defining equations of general coupled-pair theories within the ORCA electronic structure package [24]. The automatic code generator has been successfully employed to implement the MR-EOM-T| $T^\dagger$ |SXD-h-v approach in ORCA. We have also developed an orbital selection procedure, which allows one to discard core and virtual orbitals in the calculation of excitation energies. This scheme can be used to extend the applicability of MR-EOM to considerably larger systems. We also present the first benchmark applications of the MR-EOM

implementation in ORCA to the characterization and calculation of excitation energies of transition metal complexes. Furthermore, we have benchmarked a wide variety of MR-EOM approaches for the calculation of excitation energies of a subset of the organic molecules from the Thiel test set [33] and further performed an assessment of the effects of the $\hat{T}^\dagger$ transformation and various approximations adopted in the MR-EOM- $T|T^\dagger|SXD$ -h-v approach for some transition metal complexes.

In general, we have found that the MR-EOM- $T|SXD$, $T|SXD|U$ and $T|T^\dagger|SXD$ -h-v approaches are accurate for the calculation of the excitation energies of the organic molecules and that the $T|T^\dagger|SXD$ -h-v method is a robust method for the calculation of the relative excitation energies of the transition metal complexes. As mentioned above, an orbital selection scheme has also been implemented within the ORCA implementation of MR-EOM- $T|T^\dagger|SXD$ -h-v, which allows one to discard inactive and virtual orbitals which are not important for the description of the excited states of interest. This orbital selection scheme was described in our previous paper [244] and was tested for the transition metal complexes which are also considered in this work. We reiterate that this scheme can be used to extend the applicability of the MR-EOM approach, for the calculation of excitation energies, to fairly sizeable systems and is expected to be more effective for larger systems, where the chromophore might be localized to a small part of the molecule. Another virtue of the implementation in ORCA, is that spin-orbit coupling effects can be included in the calculation of excitation spectra. This is made possible using the current implementation (see Refs. [258, 259]) in the ORCA MRCI module, in which spin-orbit coupling effects are included by means of Quasi-Degenerate Perturbation Theory (QDPT) with a Spin-Orbit Mean-Field (SOMF) Hamiltonian [260, 261]. It is important to note that the SOMF Hamiltonian has not been similarity transformed, so this constitutes a first order approximation within the framework of MR-EOM. Even so, in a recent investigation [245], we have shown that this approach works quite well for calculating the spin-orbit splitting in the excitation energies of transition metal atoms.

7.1 Future Research

In future work, we wish to make several improvements to the current implementation of MR-EOM in the ORCA program package. Firstly, it is desirable to include the $\hat{U}$ transformation in the sequence of similarity transformations, so that the final diagonalization space only consists of only the CAS, 1h and 1p configurations. This is currently the most cost-effective way to proceed within the MR-EOM formalism. Another relatively straightforward, but tedious task is to modify the MRCI module in ORCA so that it may accommodate integrals (*i.e.* the elements of a similarity transformed Hamiltonian) that are not Hermitian and vertex-symmetric. While the effects of this symmetrization are rather unimportant in the case of the

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organic molecules (*i.e.* even though the accuracy of the excitation energies slightly decreases), we have seen that it can have a greater effect on the excitation energies of the transition metal complexes and as shown in Ref. [245], it can lead to a significant decrease in accuracy of the excitation energies of transition metal atoms, in comparisons with J-averaged experimental data. Hence, it would be advantageous to lift this symmetry restriction in order to avoid the potential negative effects that might be associated with this approximation.

At the level of the code generator, there are a number of improvements that can be implemented. We have started work on the implementation of a scheme for term by term loop fusion. As the name suggests, loop fusion involves finding common loops that can be consolidated in a sequence of binary contractions, which define a given contribution to a target quantity (*e.g.* residual, elements of a transformed Hamiltonian). The main advantage of the scheme that we have considered is that, we can avoid the storage of some types of two-body intermediates on disk. Let us examine a simple example to illustrate how this procedure would work in practice. Consider the contribution,

$$R_{ij}^{ab} += \frac{1}{2} \sum_{k,c} v_{cd}^{kl} t_{ij}^{cd} t_{kl}^{ab}, \quad (7.1)$$

to the doubles residual equation of CCSD [87]. In the current implementation, we would first compute the intermediate,

$$W_{ij}^{kl} = \sum_{c,d} v_{cd}^{kl} t_{ij}^{cd}, \quad (7.2)$$

and store it in a matrix container `Whh_2_1[i,j](k,l)`, for each pair of addressing indices (i,j) . Then the final contribution to the residual would be evaluated, in a separate loop construct, by retrieving the intermediate matrix from the container for each pair (i,j) and computing the contribution to the target for each pair as

$$R_{ij}^{ab} += \frac{1}{2} \sum_{k,l} W_{ij}^{kl} t_{kl}^{ab}. \quad (7.3)$$

In contrast, in the loop fused code, we would only loop over i, j, k and l once to evaluate Eqs. (7.2) and (7.3). In particular, in the loop over i, j, k and l , we would compute the value of the intermediate of Eq. (7.2) (by summing over c and d) as a double precision variable `Whh_2_1` and evaluate the contribution to the residual as in Eq. (7.2) (by looping over a and b). Hence, we avoid having to store the intermediate of Eq. (7.2) on disk, the associated I/O operations involved and the redundancy associated with looping over i, j, k and l twice.

It is also highly desirable to be able to generate code that is parallelized, in order to increase the

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range of applicability of the implemented methods. We will follow a similar procedure as that adopted in Ref. [262], for the parallelization of the single reference Local Pair Natural Orbital or LPNO-CCSD equations in ORCA [24], using MPI (Message Passing Interface) [263]. In this implementation, parallelization is achieved by distributing loops over pairs of occupied indices over a set of processors [262]. Hence, we might envision that, when coupled with the loop fusion scheme described above, this could provide an extremely efficient scheme for parallelization in the generated code, since we would be able to avoid some rather expensive read/write operations. We would also like to be able to perform a batchwise evaluation of the most expensive contributions, containing 3p1h integrals/transformed Hamiltonian elements, as this would also lead to important efficiency gains. Namely, instead of having all matrices in memory, for all of the 3 virtual labels at one time, we would read batches of these matrices into an array, depending on the memory constraints provided on input. At the moment, these contributions severely limit the applicability of the methodology, since the memory required for these contributions increases dramatically with system size and the number of these terms is quite large. Nevertheless, the way that we have currently dealt with the implementation of these terms avoids extremely expensive cache misses (*i.e.* redundant I/O operations), by not having open loops over integral addressing labels consisting of virtual orbitals throughout the rest of the loop construct (*e.g.* we are not reading a set of amplitudes, with occupied addressing labels, from disk n_v times more than we should be).

Factorization of the equations would also provide a significant reduction of the computational cost of the implemented methodologies (*e.g.* MR-EOM), by reducing the prefactor associated with the scaling of the cost. This would be most important for the more expensive contributions containing 3p1h and 2p2h integrals or intermediates. It would also be important for lower order scaling contributions that have a large prefactor. A robust factorization algorithm would achieve a linearization of the equations, by identifying common factors appearing in the expression and by defining a set of reusable intermediates, which are then used to calculate the final linearized equations. This is what is done in the most efficient hand-coded implementations of methodologies such as CCSD (*e.g.* see Refs. [202, 264, 265] for efficient factorizations, which are still used in modern implementations of CCSD). A brute-force approach would consist of an exhaustive search algorithm which considers all possible orderings of multiplications in non-linear terms, as well as all possible permutations of the indices in the tensors in order to find a global minimum in the computational cost. However, it is well known that this exhaustive search algorithm is not feasible, as it scales exponentially with the number of terms (*i.e.* the optimization is NP-hard) [266]. More feasible solutions to the factorization problem have recently been reported in the literature. As mentioned in chapter 4, Hanrath and Engels-Putzka have developed a genetic algorithm to tackle the optimization problem and have demonstrated that the timings of their generated code are competitive with hand-coded implementations of CISD and CCSD [192]. Thus, given the recent success of this scheme,

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we might consider the factorization of expressions, using a similar genetic optimization algorithm.

A primary goal is to incorporate the Domain based Local Pair Natural Orbital (DLPNO) scheme within the MR-EOM implementation, since this would allow for applications of this methodology to much larger systems (*i.e.* see Refs. [6, 5] for the development of the LPNO based methods and a historical perspective, Refs. [7, 9, 215] for the more recent development and extensions of the DLPNO based approaches and Ref. [8] for a recent review of these methods). For example, this approach has been extremely successful within the framework of single-reference coupled-cluster theory, as highlighted by the application [9] of DLPNO-CCSD(T) to a small protein (Crambin) comprised of 644 atoms and its recent application in describing the asymmetric hydrogenation of olefins, promoted by phosphino-oxazoline iridium complexes, as described in Ref. [267]. In brief, the approach makes use of the ideas of Projected Atomic Orbitals (PAOs) and correlation domains [268, 269, 270, 271] and LPNOs, expanded in a basis of PAOs, in order to achieve near linear scaling for the CCSD [7] and CCSD(T) [9] methods. The residual equations, defining the amplitudes for a given approach, must be transformed to the LPNO basis. Hence, the equations of MR-EOM would need to be modified in order to accommodate this LPNO transformation. This would have to be done in an automated fashion, due to the inherent complexity of the expressions that define this methodology. The implementation should be relatively straightforward, given the current infrastructure within ORCA and can easily be combined with the orbital selection scheme of chapter 5, to provide a highly efficient scheme for the calculation of excitation energies. In summary, the incorporation of the DLPNO scheme within the MR-EOM equations would allow for unprecedented applications to large, highly correlated transition metal complexes.

It is also of interest to extend the current MR-EOM formalism so that excitations, that do not have dominant active space character, can be treated accurately. This will require the use of a larger first order interacting space than that underlying the MR-EOM approach described in this work. Hence, one possibility is to introduce additional similarity transformations, in the spirit of STEOM, in order to minimize the size of the final diagonalization manifold (*i.e.* MR-STEOM-CC). We also envision combining MR-EOM with DMRG [34, 35, 36, 37, 38, 39, 40], so that much larger active spaces can be employed in practical applications. In particular, it would be relatively easy to employ a DMRG wavefunction as the reference function, given that the DMRG methodology is already available in ORCA. We would simply need to take the Fock matrix, integrals and density matrices from a DMRG calculation, rather than from a CASSCF calculation. However, while an internally contracted DMRG-MRCI implementation has recently been reported [272], the implementation of DMRG-MRCI has not yet been implemented in the ORCA program package. Alternatively, the remaining single excitations that are treated within the uncontracted MRCI module (*i.e.* the 1h, 1p and 2h excitations) could be treated perturbatively at

CHAPTER 7. SUMMARY AND FUTURE RESEARCH DIRECTIONS

the NEVPT2 [175, 176] (or other multireference perturbative) level of theory. This might also greatly extend the applicability of the current MR-EOM methodology, without compromising the accuracy of the approach, especially when coupled with the DLPNO scheme and a DMRG reference wavefunction.

APPENDICES

Appendix A

Some Examples of Generated Code

A.1 Generation of Code for a Small Subset of the Contributions to the MR-EOM Equations for the $\hat{T}_2$ amplitudes, without BLAS Usage

Consider the expression,

$$R_{i_1 i_2}^{a_1 a_2} += \sum_{a_3} F_{a_3}^{a_1} t_{i_2 i_1}^{a_2 a_3} \quad (\text{A.1})$$

$$+ \sum_{a_3} (i_2 a_2 | a_3 a_1) t_{i_1}^{a_3} \quad (\text{A.2})$$

$$- \sum_{i_3, i_4, a_3, a_4} n_{i_4} (i_3 a_3 | i_4 a_4) t_{i_1 i_4}^{a_3 a_4} t_{i_2 i_3}^{a_2 a_1} \quad (\text{A.3})$$

which constitutes 3 of the 54 contributions to the doubles residual equations $R_{i_1 i_2}^{a_1 a_2} = 0$, in Eq. (4.12), that define the $t_{i_1 i_2}^{a_1 a_2}$ amplitudes in MR-EOM [177, 21, 22, 23]. The C++ function produced by the code-generator for the input expressions in Eqs. (A.1)-(A.3), without any BLAS usage in the code, is broken up into several code snippets below.

A.1.1 Include Statements and Declaration of the C++ Function and Data Structures

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

Example Code A.1: Include statements and the declaration of the C++ function and data structures for the calculation of the contributions of Eqs. (A.1)-(A.3) to the doubles residual equations in MR-EOM.

```

1  #include <stdlib.h>
2  #include <stdio.h>
3  #include <math.h>
4
5  #include "qcinpdat.h"
6  #include "qcinfo.h"
7  #include "qcmsg.h"
8  #include "qcmath.h"
9  #include "qcmat1.h"
10 #include "qcmat2.h"
11 #include "qcrdiag2.h"
12 #include "qcutil.h"
13 #include "qcmem.h"
14 #include "qctime.h"
15 #include "qcclineq.h"
16 #include "qcutil.h"
17 #include "readln.h"
18
19 #include "gtopac.h"
20 #include "qcmatstore.h"
21 #include "qccompress.h"
22 #include "qcciutil.h"
23 #include "qccitrafo2.h"
24 #include "qcilist.h"
25
26 #include "mdci_def.h"
27 #include "mdci_fock.h"
28 #include "mdci_util.h"
29 #include "mdci_rhf_util.h"
30 #include "mdci_mreom.h"
31
32 int Calc_R2_example(TorcaInfo&    DAT,
33                    TMDCIState&    STATE,
34                    TMDCIState&    SIGMA,
35                    TMDCIContainer& MOINTS,
36                    double          ****Lambda_so,
37                    TRVector&       n,
38                    TRMatrixSym&    FT
39                    )
40 {
41     char    msg[512];
42     int     res;
43     double  tm          = 0.0;
44     DMDCIINP *INF      = STATE.GetInfo();
45     int      *MOSpaces  = INF->GetMOSpaces();
46     int      FirstInactive = MOSpaces[0];
47     int      LastInactive  = MOSpaces[1];

```

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

```

48  int      FirstActive   = MOSpaces[2];
49  int      LastActive    = MOSpaces[3];
50  int      FirstVirtual  = MOSpaces[4];
51  int      LastVirtual   = MOSpaces[5];
52  int      NOccupied     = LastActive - FirstInactive + 1;
53  int      NActive       = LastActive - FirstActive + 1;
54  int      NVirtual      = LastVirtual - FirstVirtual + 1;
55
56  TMatrixContainer *IBAC = MOINTS.GetIBAC();
57  TMatrixContainer *IAJB = MOINTS.GetIAJB();
58  int      i1, i2, a1, a2;
59  int      i1_0, i2_0, a1_0, a2_0;
60  int      a3, i3, i4, a4;
61  int      a3_0, i3_0, i4_0, a4_0;
62  TRMatrix  Vi3i4;
63
64  TRMatrix t2_i2i1, t1, t2_i1i4, t2_i2i3;
65  TRMatrix Whh_1_1;
66  TRMatrix *Vi2a1 = 0;
67
68  TMatrixContainer *T = STATE.GetT();
69
70  res = STATE.GetSingles(t1);
71  if (res != 0) { AbortMessage("Error, failed to get t1 amplitudes \n", res); }
72
73  TRMatrix  R1i12;
74  TMatrixContainer *R = SIGMA.GetT();
75
76  res = (*T).OpenFileRead();
77  if (res != 0) { return(res); }

```

A.1.2 Generated Code for the Calculation of Eq. (A.1)

Example Code A.2: Generated code for the calculation of the contribution of Eq. (A.1) to the doubles residual in MR-EOM .

```

1  //////////////////////////////////////
2  //  R1i12(a1_0,a2_0) = 1.0*kmf(a3,a1)t2(i2i1,a2a3)  //
3  //////////////////////////////////////
4
5  tm = GetTime();
6
7  for (i1 = FirstInactive; i1 <= LastActive; i1++) {
8      i1_0 = i1 - FirstInactive;
9
10     for (i2 = FirstInactive; i2 <= LastActive; i2++) {
11         i2_0 = i2 - FirstInactive;

```

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

```

12
13     res = (*R).OpenFileRead();
14     if (res != 0) { AbortMessage("Error, failed to open residual buffer \n", res);
15         }
16     res = (*R).GetMatrix(imax(i2, i1), imin(i2, i1), Rili2);
17     (*R).CloseFileRead();
18     if (res != 0) { AbortMessage("Error, failed to get residual vector\n", res); }
19
20     res = (*T).GetMatrix(imax(i2, i1), imin(i2, i1), t2_i2i1);
21     if (res != 0) { AbortMessage("Error, failed to get amplitude t2_i2i1 in term 1
22         \n", res); }
23     if (i1 > i2) { t2_i2i1.Transpose(); }
24
25     for (a1 = FirstVirtual; a1 <= LastVirtual; a1++) {
26         a1_0 = a1 - FirstVirtual;
27
28         for (a2 = FirstVirtual; a2 <= LastVirtual; a2++) {
29             a2_0 = a2 - FirstVirtual;
30
31             for (a3 = FirstVirtual; a3 <= LastVirtual; a3++) {
32                 a3_0 = a3 - FirstVirtual;
33
34                 if (i1 > i2) {
35                     Rili2(a1_0, a2_0) += FT(a3, a1) * t2_i2i1(a2_0, a3_0);
36                 }
37                 if (i1 < i2) {
38                     Rili2(a2_0, a1_0) += FT(a3, a1) * t2_i2i1(a2_0, a3_0);
39                 }
40                 if (i1 == i2) {
41                     Rili2(a1_0, a2_0) += FT(a3, a1) * t2_i2i1(a2_0, a3_0);
42                     Rili2(a2_0, a1_0) += FT(a3, a1) * t2_i2i1(a2_0, a3_0);
43                 }
44             }
45         }
46     }
47
48     (*R).ReOpen();
49     res = (*R).SetMatrix(imax(i2, i1), imin(i2, i1), Rili2);
50     if (res != 0) { AbortMessage("Error, failed to set residual vector \n", res); }
51     (*R).CloseFileWrite();
52 }
53 Rili2.DelMat();
54 t2_i2i1.DelMat();
55 tm = GetTime() - tm;
56 INF->UpdateTime(_MREOM_TM_SIGMA_FOCK, tm);

```

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

A.1.3 Generated Code for the Calculation of Eq. (A.2)

Example Code A.3: Generated code for the calculation of the contribution of Eq. (A.2) to the doubles residual in MR-EOM.

```
1  ////////////////////////////////////////////
2  //  Rili2(a1_0,a2_0) = 1.0*kmv(i2a2,a1a3)t1(i1,a3)  //
3  ////////////////////////////////////////////
4
5  tm = GetTime();
6
7  res = (*IBAC).OpenFileRead();
8  if (res != 0) { AbortMessage("Error, failed to open integral container IBAC \n",
9    res); }
10
11  Vi2a1 = new TRMatrix[NVirtual];
12  if (!Vi2a1) { ABORT_MEMORY; }
13
14  for (i2 = FirstInactive; i2 <= LastActive; i2++) {
15    i2_0 = i2 - FirstInactive;
16
17    for (a1 = FirstVirtual; a1 <= LastVirtual; a1++) {
18      a1_0 = a1 - FirstVirtual;
19
20      res = (*IBAC).GetMatrix(i2, a1, Vi2a1[a1_0]);
21      if (res != 0) { AbortMessage("Error, failed to get integral container IBAC \n",
22        res); }
23    }
24
25    for (i1 = FirstInactive; i1 <= LastActive; i1++) {
26      i1_0 = i1 - FirstInactive;
27
28      res = (*R).OpenFileRead();
29      if (res != 0) { AbortMessage("Error, failed to open residual buffer \n", res);
30        }
31      res = (*R).GetMatrix(imax(i2, i1), imin(i2, i1), Rili2);
32      (*R).CloseFileRead();
33      if (res != 0) { AbortMessage("Error, failed to get residual vector\n", res); }
34
35      for (a1 = FirstVirtual; a1 <= LastVirtual; a1++) {
36        a1_0 = a1 - FirstVirtual;
37
38        for (a2 = FirstVirtual; a2 <= LastVirtual; a2++) {
39          a2_0 = a2 - FirstVirtual;
40
41          for (a3 = FirstVirtual; a3 <= LastVirtual; a3++) {
42            a3_0 = a3 - FirstVirtual;
43
44            if (i1 > i2) {
45              Rili2(a1_0, a2_0) += Vi2a1[a1_0](a2_0, a3_0) * t1(i1_0, a3_0);
46            }
47          }
48        }
49      }
50    }
51  }
```

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

```

43         }
44         if (i1 < i2) {
45             Rili2(a2_0, a1_0) += Vi2a1[a1_0](a2_0, a3_0) * t1(i1_0, a3_0);
46         }
47         if (i1 == i2) {
48             Rili2(a1_0, a2_0) += Vi2a1[a1_0](a2_0, a3_0) * t1(i1_0, a3_0);
49             Rili2(a2_0, a1_0) += Vi2a1[a1_0](a2_0, a3_0) * t1(i1_0, a3_0);
50         }
51     }
52 }
53 }
54
55 (*R).ReOpen();
56 res = (*R).SetMatrix(imax(i2, i1), imin(i2, i1), Rili2);
57 if (res != 0) { AbortMessage("Error, failed to set residual vector \n", res); }
58 (*R).CloseFileWrite();
59 }
60 }
61 (*IBAC).CloseFileRead();
62 Rili2.DelMat();
63 if (Vi2a1 != 0) {
64     delete[] Vi2a1;
65     Vi2a1 = 0;
66 }
67 tm = GetTime() - tm;
68
69 INF->UpdateTime(_MREOM_TM_SIGMA_IBAC, tm);

```

A.1.4 Generated Code for the Calculation of Eq. (A.3)

Example Code A.4: Generated code for the calculation of the contribution of Eq. (A.3) to the doubles residual in MR-EOM and termination of the C++ function declaration.

```

1  ///////////////////////////////////////////////////////////////////
2  // Rili2(a1_0, a2_0) = -kmv(i3a3, i4a4) t2(i1i4, a3a4) t2(i2i3, a2a1) n(i4) //
3  ///////////////////////////////////////////////////////////////////
4
5  //-----
6  // Whh_1_1(i1_0, i3_0) = 1.0*n(i4)*kmv(i3a3, i4a4) t2(i1i4, a3a4)
7  //-----
8
9     tm = GetTime();
10
11     Whh_1_1.NewMat(NOccupied, NOccupied);
12     res = (*IAJB).OpenFileRead();
13     if (res != 0) { AbortMessage("Error, failed to open integral container IAJB \n",
        res); }

```

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

```

14
15  for (i3 = FirstInactive; i3 <= LastActive; i3++) {
16      i3_0 = i3 - FirstInactive;
17
18      for (i4 = FirstInactive; i4 <= LastActive; i4++) {
19          i4_0 = i4 - FirstInactive;
20
21          res = (*IAJB).GetMatrix(imax(i3, i4), imin(i3, i4), Vi3i4);
22          if (res != 0) { AbortMessage("Error, failed to get integral container IAJB \n",
23                                     res); }
24          if (i4 > i3) { Vi3i4.Transpose(); }
25
26          for (i1 = FirstInactive; i1 <= LastActive; i1++) {
27              i1_0 = i1 - FirstInactive;
28
29              res = (*T).GetMatrix(imax(i1, i4), imin(i1, i4), t2_ili4);
30              if (res != 0) { AbortMessage("Error, failed to get amplitude t2_ili4 in term
31                                     3 \n", res); }
32              if (i4 > i1) { t2_ili4.Transpose(); }
33
34              for (a3 = FirstVirtual; a3 <= LastVirtual; a3++) {
35                  a3_0 = a3 - FirstVirtual;
36
37                  for (a4 = FirstVirtual; a4 <= LastVirtual; a4++) {
38                      a4_0 = a4 - FirstVirtual;
39
40                      Whh_1_1(i1_0, i3_0) += 1.0 * n(i4) * Vi3i4(a3_0, a4_0) * t2_ili4(a3_0,
41                                     a4_0);
42                  }
43              }
44          }
45      }
46      (*IAJB).CloseFileRead();
47      Vi3i4.DelMat();
48      t2_ili4.DelMat();
49
50      //-----
51      // Rili2(a1_0,a2_0) = -1.0*Whh_1_1(i1,i3)t2(i2i3,a2a1)
52      //-----
53
54      for (i1 = FirstInactive; i1 <= LastActive; i1++) {
55          i1_0 = i1 - FirstInactive;
56
57          for (i2 = FirstInactive; i2 <= LastActive; i2++) {
58              i2_0 = i2 - FirstInactive;
59
60              res = (*R).OpenFileRead();
61              if (res != 0) { AbortMessage("Error, failed to open residual buffer \n", res);
62                                     }

```

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

```

60     res = (*R).GetMatrix(imax(i2, i1), imin(i2, i1), Rili2);
61     (*R).CloseFileRead();
62     if (res != 0) { AbortMessage("Error, failed to get residual vector\n", res); }
63
64     for (i3 = FirstInactive; i3 <= LastActive; i3++) {
65         i3_0 = i3 - FirstInactive;
66
67         res = (*T).GetMatrix(imax(i2, i3), imin(i2, i3), t2_i2i3);
68         if (res != 0) { AbortMessage("Error, failed to get amplitude t2_i2i3 in term
69             3 \n", res); }
70         if (i3 > i2) { t2_i2i3.Transpose(); }
71
72         for (a1 = FirstVirtual; a1 <= LastVirtual; a1++) {
73             a1_0 = a1 - FirstVirtual;
74
75             for (a2 = FirstVirtual; a2 <= LastVirtual; a2++) {
76                 a2_0 = a2 - FirstVirtual;
77
78                 if (i1 > i2) {
79                     Rili2(a1_0, a2_0) += -1.0 * Whh_1_1(i1_0, i3_0) * t2_i2i3(a2_0, a1_0);
80                 }
81                 if (i1 < i2) {
82                     Rili2(a2_0, a1_0) += -1.0 * Whh_1_1(i1_0, i3_0) * t2_i2i3(a2_0, a1_0);
83                 }
84                 if (i1 == i2) {
85                     Rili2(a1_0, a2_0) += -1.0 * Whh_1_1(i1_0, i3_0) * t2_i2i3(a2_0, a1_0);
86                     Rili2(a2_0, a1_0) += -1.0 * Whh_1_1(i1_0, i3_0) * t2_i2i3(a2_0, a1_0);
87                 }
88             }
89         }
90         (*R).ReOpen();
91         res = (*R).SetMatrix(imax(i2, i1), imin(i2, i1), Rili2);
92         if (res != 0) { AbortMessage("Error, failed to set residual vector \n", res); }
93         (*R).CloseFileWrite();
94     }
95 }
96 Rili2.DelMat();
97 Whh_1_1.DelMat();
98 t2_i2i3.DelMat();
99
100 tm = GetTime() - tm;
101 INF->UpdateTime(_MREOM_TM_SIGMA_IAJB, tm);
102
103 (*T).CloseFileRead();
104
105 t1.DelMat();
106 return(0);
107 }

```

A.2 Differences in the Generated Code with and without BLAS Usage

In this section we will simply highlight the differences between the generated code with BLAS usage and that of section A.1, which does not include any BLAS operations. First of all, we would need to cut out the virtual-virtual block of the Fock matrix in order to use a BLAS wrapper to calculate the contribution of Eq. (A.1). This would appear directly before the computation of the term in Example Code A.2 as,

```
// -----
// Cut out the virtual part of the one-electron matrix
// -----
TRMatrix F_vv;
F_vv.NewMat(NVirtual, NVirtual);
for (a1 = 0; a1 < NVirtual; a1++) {
    for (a2 = 0; a2 < NVirtual; a2++) {
        F_vv(a1, a2) = FT(FirstVirtual + a1, FirstVirtual + a2);
    }
}
```

Then following line 56 in Example Code A.2, we would add a line containing `F_vv.DelMat();` in order to delete the virtual-virtual block of the Fock matrix from memory. In Example Code A.2, lines 23-44 would be replaced by the following code (*i.e.* the loops over `a1`, `a2` and `a3` are removed),

```
if (i1 > i2) {
    BLAS_Add_Mat_x_Mat(R1i12, F_vv, t2_i2i1, true, true, 1.0);
}
if (i1 < i2) {
    BLAS_Add_Mat_x_Mat(R1i12, t2_i2i1, F_vv, false, false, 1.0);
}
if (i1 == i2) {
    BLAS_Add_Mat_x_Mat(R1i12, F_vv, t2_i2i1, true, true, 1.0);
    BLAS_Add_Mat_x_Mat(R1i12, t2_i2i1, F_vv, false, false, 1.0);
}
```

Similarly in the calculation of Eq. (A.2), lines 35-52 of Code Example A.3 would be replaced with (*i.e.* the loops over `a2` and `a3` are removed),

```
if (i1 > i2) {
    BLAS_Add_Mat_x_Vec(&(R1i12(a1_0, 0)), 1.0, Vi2a1[a1_0], &(t1(i1_0, 0)), false);
}
```

APPENDIX A. SOME EXAMPLES OF GENERATED CODE

```

if (i1 < i2) {
    Rili2.Transpose();
    BLAS_Add_Mat_x_Vec(&(Rili2(a1_0, 0)), 1.0, Vi2a1[a1_0], &(t1(i1_0, 0)), false);
    Rili2.Transpose();
}
if (i1 == i2) {
    BLAS_Add_Mat_x_Vec(&(Rili2(a1_0, 0)), 1.0, Vi2a1[a1_0], &(t1(i1_0, 0)), false);
    Rili2.Transpose();
    BLAS_Add_Mat_x_Vec(&(Rili2(a1_0, 0)), 1.0, Vi2a1[a1_0], &(t1(i1_0, 0)), false);
    Rili2.Transpose();
}

```

In the calculation of the final contribution of Eq. (A.3), BLAS is only used in the calculation of the intermediate and not in adding the final contribution to the residual (*i.e.* it does not satisfy the criteria for BLAS usage discussed in section 4.6). In this case, lines 32-40 of Example Code A.4 would be replaced with (*i.e.* the loops over **a3** and **a4** are removed),

```

Whh_1_1(i1_0, i3_0) += 1.0 * n(i4) * BLAS_Trace(Vi3i4, t2_ili4, true);

```

Appendix B

Supporting Information for Chapter 5: Characterization of the Spectra of Transition Metal Complexes and an Orbital Selection Scheme for MR-EOM

B.1 BP86/def2-TZVP Optimized Cartesian Coordinates (Å)

1. $\text{Cr}(\text{CO})_6$

Cr	0.000000	0.000000	0.000000
C	0.000000	-1.907111	0.000000
C	0.000000	0.000000	1.907111
C	0.000000	1.907111	0.000000
C	0.000000	0.000000	-1.907111
C	1.907111	0.000000	0.000000
C	-1.907111	0.000000	0.000000
O	3.059590	0.000000	0.000000
O	0.000000	3.059590	0.000000
O	3.059590	0.000000	0.000000
O	0.000000	0.000000	3.059590
O	0.000000	-3.059590	0.000000
O	0.000000	0.000000	-3.059590

2. CpNiNO

N	-0.000000	-1.843444	0.000000
O	0.000000	-3.063930	0.000000
Ni	-0.000000	-0.248084	0.000000
C	0.998676	1.367063	0.725581
C	0.998676	1.367063	-0.725581
C	-0.381460	1.367063	1.174014
C	-1.234432	1.367063	0.000000
C	-0.381460	1.367063	-1.174014
H	1.873539	1.449309	1.361206
H	1.873539	1.449309	-1.361206
H	-0.715628	1.449309	2.202477
H	-2.315822	1.449309	0.000000
H	-0.715628	1.449309	-2.202477

B.2 Excitation Energies For various truncations of the inactive and virtual orbital spaces and statistics for the deviations from full Mr-EOM Results

The Mean Absolute Deviation (MAD), Root Mean Squared Deviation (RMSD) and Standard Deviation (SD), reported in this section, are defined as follows

$$\begin{aligned}
 \text{MAD} &= \frac{1}{\sum_i g_i} \sum_i g_i |\Delta E_{\text{Calc},i} - \Delta E_{\text{MR-EOM},i}|, \\
 \text{RMSD} &= \sqrt{\frac{1}{\sum_i g_i} \sum_i g_i (\Delta E_{\text{Calc},i} - \Delta E_{\text{MR-EOM},i})^2}, \\
 \text{SD} &= \sqrt{\frac{\sum_i g_i \left(\Delta E_{\text{Calc},i} - \Delta E_{\text{MR-EOM},i} - \left(\frac{1}{\sum_j g_j} \sum_j g_j (\Delta E_{\text{Calc},j} - \Delta E_{\text{MR-EOM},j}) \right) \right)^2}{\sum_i g_i - 1}},
 \end{aligned}$$

in which g_i , $\Delta E_{\text{Calc},i}$ and $\Delta E_{\text{MR-EOM},i}$ are respectively, the degeneracy, the calculated excitation energy (*i.e.* using a given truncation of the inactive and/or virtual spaces) and the full (complete orbital space) MR-EOM excitation energy of the i^{th} excited state. We also report the maximum absolute deviation (MAX) in each case.

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Table B.1: Singlet and triplet excitation energies (in eV) for Ni(CO)₄, calculated with full (complete orbital space) MR-EOM and various truncations of the inactive and virtual spaces, in a def2-TZVPP basis.

State	(n_c, n_v) values ^a							
	(20, 285) ^b	(20, 239)	(20, 169)	(20, 137)	(20, 81)	(20, 66)	(16, 239)	(16, 169)
<i>Singlets</i>								
¹ T ₁	4.82	4.82	4.83	4.85	4.93	4.97	4.84	4.85
¹ E	4.90	4.90	4.91	4.93	5.00	5.04	4.92	4.93
¹ T ₂	5.08	5.08	5.09	5.12	5.19	5.24	5.10	5.11
¹ T ₁	5.64	5.64	5.65	5.67	5.74	5.79	5.67	5.68
¹ T ₂	6.03	6.03	6.04	6.07	6.14	6.20	6.06	6.07
<i>Triplets</i>								
³ A ₁	4.03	4.03	4.04	4.05	4.10	4.13	4.06	4.07
³ T	4.46	4.46	4.47	4.49	4.56	4.59	4.49	4.50
³ E	4.57	4.57	4.59	4.61	4.68	4.71	4.60	4.61
³ T	4.71	4.71	4.72	4.74	4.82	4.85	4.73	4.74
³ T	5.55	5.55	5.56	5.58	5.65	5.70	5.59	5.59
³ T	5.66	5.66	5.67	5.69	5.76	5.81	5.69	5.70
State	(n_c, n_v) values ^a							
	(16, 137)	(16, 81)	(16, 66)	(12, 239)	(12, 169)	(12, 137)	(12, 81)	(12, 66)
<i>Singlets</i>								
¹ T ₁	4.87	4.95	4.98	4.85	4.86	4.88	4.94	4.98
¹ E	4.95	5.02	5.05	4.93	4.94	4.95	5.01	5.05
¹ T ₂	5.14	5.21	5.25	5.12	5.12	5.14	5.21	5.25
¹ T ₁	5.70	5.77	5.81	5.69	5.69	5.71	5.77	5.81
¹ T ₂	6.10	6.17	6.22	6.07	6.08	6.11	6.17	6.22
<i>Triplets</i>								
³ A ₁	4.07	4.13	4.14	4.08	4.08	4.09	4.13	4.15
³ T	4.51	4.58	4.60	4.50	4.51	4.52	4.58	4.61
³ E	4.63	4.70	4.73	4.61	4.62	4.63	4.70	4.73
³ T	4.76	4.84	4.87	4.74	4.75	4.77	4.83	4.86
³ T	5.61	5.68	5.72	5.60	5.61	5.62	5.68	5.72
³ T	5.72	5.79	5.83	5.70	5.71	5.73	5.79	5.83

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

^b The full MR-EOM $((n_c, n_v) = (20, 285))$ excitation energies.

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Table B.2: Statistics (in eV) for the deviations in the excitation energies obtained with various truncations of the inactive and virtual spaces from full (complete orbital basis) MR-EOM results, for $\text{Ni}(\text{CO})_4$, in a def2-TZVPP basis.

	(n_c, n_v) values ^a							
	(20, 239)	(20, 169)	(20, 137)	(20, 81)	(20, 66)	(16, 239)	(16, 169)	(16, 137)
MAD	0.001	0.012	0.034	0.103	0.147	0.027	0.038	0.058
RMSD	0.001	0.013	0.035	0.104	0.148	0.027	0.038	0.058
SD	0.001	0.003	0.005	0.010	0.015	0.004	0.003	0.006
MAX	0.002	0.016	0.042	0.115	0.168	0.032	0.042	0.070
	(n_c, n_v) values ^a							
	(16, 81)	(16, 66)	(12, 239)	(12, 169)	(12, 137)	(12, 81)	(12, 66)	
MAD	0.128	0.162	0.041	0.049	0.066	0.126	0.164	
RMSD	0.128	0.163	0.041	0.049	0.067	0.126	0.164	
SD	0.008	0.015	0.004	0.004	0.006	0.007	0.015	
MAX	0.140	0.185	0.047	0.055	0.077	0.137	0.186	

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

Table B.3: Singlet and triplet excitation energies (in eV) for $\text{Fe}(\text{CO})_5$, calculated with full (complete orbital space) MR-EOM and various truncations of the inactive and virtual spaces, in a def2-TZVPP basis.

State	(n_c, n_v) values ^a										
	(25, 344) ^b	(25, 297)	(25, 180)	(25, 139)	(25, 83)	(25, 66)	(20, 297)	(20, 180)	(20, 139)	(20, 83)	(20, 66)
<i>Singlets</i>											
$^1A''_1$	4.55	4.55	4.52	4.53	4.55	4.55	4.58	4.56	4.56	4.57	4.57
$^1E''$	4.84	4.83	4.81	4.82	4.84	4.85	4.87	4.85	4.85	4.86	4.86
$^1A''_2$	4.87	4.87	4.83	4.84	4.85	4.86	4.90	4.88	4.88	4.87	4.88
$^1A'$	5.71	5.70	5.70	5.71	5.76	5.78	5.73	5.73	5.74	5.78	5.80
$^1E'$	5.82	5.82	5.82	5.83	5.86	5.89	5.84	5.84	5.85	5.88	5.90
<i>Triplets</i>											
$^3A''$	4.30	4.29	4.26	4.27	4.28	4.28	4.33	4.30	4.30	4.30	4.29
$^3E''$	4.43	4.42	4.39	4.39	4.40	4.40	4.46	4.43	4.43	4.42	4.42
$^3A''$	4.52	4.51	4.47	4.48	4.48	4.48	4.55	4.52	4.52	4.49	4.50
$^3A'$	4.67	4.67	4.65	4.66	4.65	4.67	4.70	4.68	4.69	4.67	4.69
$^3E'$	5.21	5.21	5.20	5.21	5.23	5.25	5.24	5.23	5.24	5.25	5.27
$^3A'$	5.56	5.56	5.55	5.57	5.59	5.62	5.59	5.58	5.59	5.61	5.63

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

^b The full MR-EOM ($(n_c, n_v) = (25, 344)$) excitation energies.

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Table B.4: Statistics (in eV) for the deviations in the excitation energies obtained with various truncations of the inactive and virtual spaces from full (complete orbital basis) MR-EOM results, for $\text{Fe}(\text{CO})_5$, in a def2-TZVPP basis.

	(n_c, n_v) values ^a									
	(25, 297)	(25, 180)	(25, 139)	(25, 83)	(25, 66)	(20, 297)	(20, 180)	(20, 139)	(20, 83)	(20, 66)
MAD	0.006	0.026	0.021	0.025	0.032	0.025	0.011	0.015	0.029	0.037
RMSD	0.006	0.031	0.025	0.029	0.040	0.025	0.014	0.020	0.036	0.046
SD	0.003	0.016	0.018	0.030	0.038	0.002	0.009	0.015	0.031	0.038
MAX	0.009	0.047	0.042	0.050	0.077	0.029	0.023	0.035	0.072	0.091

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

Table B.5: Singlet and triplet excitation energies (in eV) for $\text{Cr}(\text{CO})_6$, calculated with full (complete orbital space) MR-EOM and various truncations of the inactive and virtual spaces, in a def2-TZVPP basis.

State	(n_c, n_v) values ^a										
	(30, 400)	(30, 244)	(30, 202)	(30, 120)	(30, 103)	(30, 51)	(24, 244)	(24, 202)	(24, 120)	(24, 103)	(24, 51)
<i>Singlets</i>											
¹ A_{2u}	4.30	4.27	4.28	4.34	4.37	4.47	4.33	4.34	4.40	4.42	4.50
¹ E_u	4.30	4.28	4.28	4.35	4.38	4.49	4.34	4.35	4.41	4.43	4.51
¹ T_{2u}	4.34	4.31	4.32	4.38	4.41	4.51	4.38	4.39	4.45	4.47	4.54
¹ T_{1u}	4.91	4.88	4.89	4.94	4.97	5.05	4.95	4.96	5.01	5.03	5.08
¹ T_{2g}	6.08	5.99	5.99	5.96	5.90	5.80	6.07	6.07	6.03	5.92	5.81
<i>Triples</i>											
³ A_{2u}	4.31	4.29	4.30	4.37	4.40	4.51	4.35	4.36	4.43	4.46	4.54
³ E_u	4.35	4.32	4.34	4.40	4.44	4.55	4.39	4.40	4.47	4.49	4.58
³ T_u	4.40	4.37	4.38	4.45	4.48	4.59	4.44	4.45	4.52	4.54	4.62
³ T_u	4.41	4.38	4.40	4.46	4.50	4.60	4.45	4.46	4.53	4.55	4.63
³ T_{2g}	6.06	5.97	5.97	5.94	5.88	5.79	6.05	6.05	6.01	5.91	5.80

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

^b The full MR-EOM ($(n_c, n_v) = (30, 400)$) excitation energies.

Table B.6: Statistics (in eV) for the deviations in the excitation energies obtained with various truncations of the inactive and virtual spaces from full (complete orbital basis) MR-EOM results, for $\text{Cr}(\text{CO})_6$, in a def2-TZVPP basis.

	(n_c, n_v) values ^a									
	(30, 244)	(30, 202)	(30, 120)	(30, 103)	(30, 51)	(24, 244)	(24, 202)	(24, 120)	(24, 103)	(24, 51)
MAD	0.042	0.037	0.065	0.105	0.205	0.034	0.042	0.098	0.140	0.224
RMSD	0.050	0.051	0.074	0.115	0.210	0.036	0.046	0.102	0.141	0.226
SD	0.028	0.036	0.075	0.116	0.204	0.024	0.029	0.074	0.129	0.212
MAX	0.089	0.097	0.123	0.184	0.281	0.044	0.056	0.121	0.160	0.271

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

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Table B.7: Singlet and triplet excitation energies (in eV) for Ferrocene, calculated with full (complete orbital space) MR-EOM and various truncations of the inactive and virtual spaces, in a def2-TZVPP basis.

State	(n_c, n_v) values ^a								
	(26, 484) ^b	(26, 354)	(26, 252)	(26, 133)	(26, 56)	(20, 354)	(20, 252)	(20, 133)	(20, 56)
<i>Singlets</i>									
$^1E''_1$	2.71	2.71	2.71	2.71	2.80	2.74	2.74	2.73	2.81
$^1E''_2$	2.77	2.77	2.77	2.76	2.84	2.81	2.81	2.79	2.86
$^1E''_1$	4.32	4.32	4.32	4.32	4.47	4.35	4.35	4.34	4.48
$^1E'$	5.41	5.41	5.40	5.40	5.58	5.46	5.46	5.45	5.60
$^1E'$	5.55	5.55	5.54	5.54	5.72	5.61	5.60	5.60	5.75
$^1A'$	5.66	5.66	5.66	5.66	5.84	5.71	5.71	5.71	5.86
$^1E'$	5.75	5.75	5.75	5.75	5.92	5.81	5.81	5.80	5.95
$^1E'$	5.86	5.86	5.86	5.85	6.04	5.93	5.93	5.92	6.08
$^1A'$	6.40	6.40	6.40	6.40	6.61	6.45	6.45	6.45	6.63
$^1A'$	6.41	6.41	6.41	6.40	6.60	6.48	6.48	6.47	6.63
<i>Triples</i>									
$^3E''_1$	1.75	1.75	1.75	1.74	1.77	1.79	1.79	1.77	1.79
$^3E''_2$	1.86	1.86	1.86	1.84	1.88	1.90	1.90	1.88	1.90
$^3E''_1$	2.61	2.61	2.61	2.61	2.68	2.63	2.63	2.63	2.69
$^3A'$	4.44	4.43	4.43	4.42	4.54	4.49	4.49	4.47	4.57
$^3A'$	4.45	4.45	4.44	4.43	4.56	4.50	4.50	4.49	4.59
$^3E'$	4.53	4.53	4.52	4.51	4.65	4.58	4.58	4.57	4.68

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

^b The full MR-EOM $((n_c, n_v) = (26, 484))$ excitation energies.

Table B.8: Statistics (in eV) for the deviations in the excitation energies obtained with various truncations of the inactive and virtual spaces from full (complete orbital basis) MR-EOM results, for Ferrocene, in a def2-TZVPP basis.

	(n_c, n_v) values ^a							
	(26, 354)	(26, 252)	(26, 133)	(26, 56)	(20, 354)	(20, 252)	(20, 133)	(20, 56)
MAD	0.001	0.004	0.010	0.120	0.045	0.044	0.034	0.142
RMSD	0.001	0.004	0.011	0.134	0.048	0.047	0.037	0.155
SD	0.001	0.002	0.006	0.060	0.016	0.016	0.014	0.065
MAX	0.002	0.007	0.018	0.201	0.072	0.073	0.056	0.223

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

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Table B.9: Singlet and triplet excitation energies (in eV) for Cyclopentadienyl Nickel Nitrosyl (CpNiNO), calculated with full (complete orbital space) MR-EOM and various truncations of the inactive and virtual spaces, in a def2-TZVPP basis.

State	(n_c, n_v) values ^a							
	(18, 327) ^b	(18, 251)	(18, 199)	(18, 126)	(18, 98)	(18, 57)	(15, 251)	(15, 199)
Singlets								
¹ E ₁	2.81	2.81	2.81	2.80	2.81	2.85	2.81	2.81
¹ E ₂	2.98	2.98	2.98	2.97	2.97	3.01	2.99	2.99
¹ A	3.49	3.49	3.49	3.51	3.54	3.58	3.49	3.50
¹ E ₁	3.69	3.69	3.69	3.70	3.73	3.79	3.70	3.70
¹ E ₂	3.74	3.74	3.75	3.78	3.80	3.84	3.75	3.75
¹ A	5.77	5.77	5.76	5.76	5.76	5.80	5.76	5.76
¹ E ₂	6.07	6.07	6.06	6.04	6.04	6.11	6.07	6.06
¹ E ₁	6.66	6.65	6.65	6.64	6.67	6.75	6.65	6.65
¹ E ₂	6.77	6.77	6.77	6.76	6.76	6.83	6.77	6.77
¹ E ₂	7.11	7.10	7.10	7.08	7.11	7.17	7.10	7.09
Triplets								
³ A	2.08	2.08	2.08	2.09	2.08	2.09	2.09	2.09
³ E ₁	2.67	2.67	2.67	2.67	2.67	2.71	2.68	2.68
³ E ₂	2.82	2.82	2.82	2.83	2.84	2.87	2.82	2.83
³ E ₂	2.84	2.84	2.84	2.83	2.82	2.87	2.84	2.84
³ E ₁	3.08	3.08	3.07	3.07	3.09	3.14	3.08	3.08
³ A	3.25	3.25	3.25	3.27	3.28	3.31	3.25	3.26
³ E ₁	5.60	5.60	5.59	5.58	5.57	5.63	5.60	5.60
³ E ₂	5.74	5.74	5.73	5.71	5.70	5.76	5.74	5.74
³ E ₂	5.79	5.79	5.79	5.77	5.77	5.82	5.79	5.78
³ E ₂	5.93	5.93	5.92	5.90	5.90	5.97	5.93	5.93
³ E ₁	6.22	6.22	6.22	6.20	6.20	6.28	6.22	6.22
³ E ₂	6.23	6.23	6.22	6.20	6.19	6.27	6.23	6.22
State	(n_c, n_v) values ^a							
	(15, 126)	(15, 98)	(15, 57)	(7, 251)	(7, 199)	(7, 126)	(7, 98)	(7, 57)
Singlets								
¹ E ₁	2.81	2.81	2.85	2.88	2.88	2.88	2.87	2.90
¹ E ₂	2.98	2.97	3.02	3.04	3.04	3.04	3.03	3.06
¹ A	3.51	3.54	3.58	3.49	3.49	3.51	3.53	3.56
¹ E ₁	3.70	3.73	3.79	3.76	3.76	3.76	3.79	3.84
¹ E ₂	3.77	3.80	3.84	3.75	3.76	3.77	3.79	3.83
¹ A	5.76	5.76	5.80	5.75	5.76	5.75	5.75	5.80
¹ E ₂	6.04	6.04	6.11	6.21	6.21	6.19	6.18	6.23
¹ E ₁	6.64	6.67	6.74	6.71	6.71	6.70	6.72	6.78
¹ E ₂	6.76	6.76	6.84	6.81	6.81	6.80	6.80	6.87
¹ E ₂	7.08	7.10	7.17	7.04	7.04	7.03	7.05	7.12
Triplets								
³ A	2.09	2.08	2.09	2.11	2.11	2.11	2.10	2.10
³ E ₁	2.67	2.67	2.71	2.74	2.74	2.73	2.73	2.76
³ E ₂	2.83	2.84	2.87	2.83	2.83	2.84	2.84	2.87
³ E ₂	2.83	2.83	2.87	2.89	2.89	2.88	2.87	2.91
³ E ₁	3.08	3.09	3.14	3.14	3.14	3.13	3.15	3.18
³ A	3.27	3.28	3.31	3.26	3.26	3.27	3.28	3.31
³ E ₁	5.58	5.57	5.63	5.66	5.66	5.64	5.63	5.68
³ E ₂	5.72	5.70	5.77	5.79	5.79	5.77	5.76	5.80
³ E ₂	5.77	5.77	5.82	5.77	5.76	5.76	5.75	5.80
³ E ₂	5.91	5.90	5.97	6.07	6.07	6.06	6.04	6.09
³ E ₁	6.20	6.20	6.28	6.26	6.26	6.25	6.24	6.31
³ E ₂	6.21	6.19	6.27	6.25	6.25	6.24	6.22	6.29

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

^b The full MR-EOM $((n_c, n_v) = (18, 327))$ excitation energies.

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Table B.10: Statistics (in eV) for the deviations in the excitation energies obtained with various truncations of the inactive and virtual spaces from full (complete orbital basis) MR-EOM results, for Cyclopentadienyl Nickel Nitrosyl (CpNiNO), in a def2-TZVPP basis.

	(n_c, n_v) values ^a							
	(18, 251)	(18, 199)	(18, 126)	(18, 98)	(18, 57)	(15, 251)	(15, 199)	(15, 126)
MAD	0.002	0.006	0.018	0.024	0.050	0.003	0.005	0.015
RMSD	0.002	0.007	0.020	0.028	0.056	0.004	0.006	0.018
SD	0.002	0.005	0.017	0.028	0.026	0.004	0.006	0.016
MAX	0.004	0.013	0.033	0.059	0.101	0.009	0.012	0.032

	(n_c, n_v) values ^a						
	(15, 98)	(15, 57)	(7, 251)	(7, 199)	(7, 126)	(7, 98)	(7, 57)
MAD	0.023	0.051	0.053	0.053	0.049	0.049	0.082
RMSD	0.027	0.056	0.064	0.063	0.058	0.058	0.092
SD	0.027	0.025	0.048	0.048	0.045	0.044	0.042
MAX	0.058	0.100	0.141	0.139	0.122	0.112	0.156

^a n_c and n_v are respectively, the number of inactive (core) and virtual orbitals included in the calculation.

B.2.1 Approximate Analysis of Vibrational Effects in Ni(CO)₄

Let us attempt to approximately determine the effects of vibrations on the excitation energy of the first singlet of T_2 symmetry in Table B.1. Since we do not currently have an implementation of analytic gradients for MR-EOM, we simply calculate one-dimensional potential energy surfaces for the ground and excited states along the symmetric Ni-C stretching coordinate. In particular, keeping the C-O bond distance fixed, we compute the ground and excited state energies as a function of the Ni-C bond distance $R(\text{Ni-C})$, at the MR-EOM/def2-SVP level of theory. The distance $R(\text{Ni-C})$, is varied in increments of 0.05Å and the ground and excited state energies are calculated at ten different points. For each of the potential energy curves, we use a least squares procedure to fit the energies to a quartic function

$$E(R) = a_4 R^4 + a_3 R^3 + a_2 R^2 + a_1 R + a_0,$$

of the Ni-C bond distance, which has been abbreviated as R . The MR-EOM/def2-SVP potential energy curves for the ground and excited states appear in Figure B.1, along with the quartic fits to the data. Note that the minimum of the quartic function, corresponding to the ground state, has been taken as the zero of the energy scale and all other values are given in eV relative to this value of the energy.

From Figure B.1, it is observed that the minimum in all of the excited state potential energy curves occurs at a significantly larger Ni-C bond distance than for the ground state (*i.e.* the minimum energy

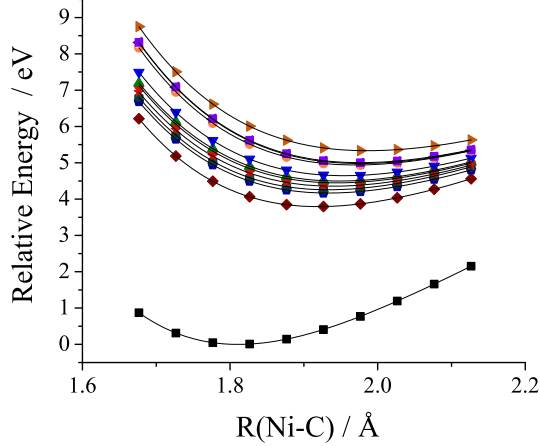


Figure B.1: MR-EOM/def2-SVP energies for $\text{Ni}(\text{CO})_4$ as a function of the Ni-C separation. The energy scale in eV is relative to the minimum of the quartic fit to the ground state potential energy curve. The quartic function fits to the data are also shown as solid lines.

Ni-C separation for the excited states, estimated from the quartic fits, are 0.109 Å to 0.166 Å larger than that of the ground state). In Table B.11, we also provide adiabatic excitation energies $\Delta E_{\text{ad.}}$, for each of the excited states, which are estimated by taking the difference between the minimum of the quartic function for the corresponding excited state and that of the ground state. Evidently, the estimated adiabatic excitation energies differ considerably from the vertical excitation energies (*i.e.* the vertical excitation energies are 0.26-0.66 eV larger than the adiabatic excitation energies) and specifically, for the first excited singlet state of T_2 symmetry (dipole allowed), the vertical excitation energy is 0.45 eV larger than the adiabatic value of 4.64 eV. Is it possible that there will also be a significant shift in the band maximum, corresponding to the first excited state of T_2 symmetry, such that it lies somewhere in between the vertical and adiabatic excitation energies?

In order to investigate whether or not there is a considerable shift in the band maximum, we have used the LEVEL 8.0 program [273] to compute the one-dimensional Franck-Condon spectrum corresponding to excitations from the $v = 0$ vibrational level of the ground state to various vibrational levels in the first excited T_2 singlet state. It is important to note that this calculation is very approximate since we are using the one-dimensional potential energy surfaces of Figure B.1, along the symmetric Ni-C stretching coordinate, and an estimated reduced mass of $\mu \approx 153.1 \text{ u}$ has been employed. This reduced mass is calculated from $\mu = k/4\pi^2 c^2 \omega^2$, in which the force constant $k = 1217 \text{ N}\cdot\text{m}^{-1}$, is estimated as the second

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Table B.11: Comparison of the estimated adiabatic ($\Delta E_{\text{ad.}}$) and calculated MR-EOM/def2-SVP, vertical ($\Delta E_{\text{vert.}}$) excitation energies of $\text{Ni}(\text{CO})_4$. The experimental excitation energy for the first singlet of T_2 symmetry is also provided.

State	$\Delta E_{\text{ad.}}$ (eV)	$\Delta E_{\text{vert.}}^{\text{a}}$ (eV)	$\Delta E_{\text{vert.}}(R_{\text{min}})^{\text{b}}$ (eV)	Expt. ^c
<i>Singlets</i>				
$^1T_1$	4.45	4.83	4.96	
^1E	4.50	4.90	5.03	
$^1T_2$	4.65	5.09	5.23	4.6
$^1T_1$	4.98	5.59	5.76	
$^1T_2$	5.33	6.00	6.17	
<i>Triplets</i>				
$^3A_1$	3.79	4.05	4.17	
^3T	4.17	4.49	4.61	
^3E	4.26	4.58	4.71	
^3T	4.36	4.71	4.84	
^3T	4.94	5.51	5.67	
^3T	5.00	5.61	5.78	

^a vertical excitation energies obtained from the MR-EOM/def2-SVP calculation at the BP86/QZVP geometry of Ref. [227]

^b vertical excitation energies obtained by using the estimated energies from the quartic fits, evaluated at the minimum Ni-C bond distance R_{min} (*i.e.* the minimum of the quartic fit to the ground state)

^c gas phase spectrum from Ref. [221]

derivative of the quartic fit to the ground state potential evaluated at the minimum and the vibrational frequency of the symmetric Ni-C stretching mode is taken as the experimental value of $\omega = 367.5 \text{ cm}^{-1}$, reported in Ref. [274]. The resulting one-dimensional Franck-Condon spectrum appears in Figure B.2. The band maximum in this spectrum occurs at an energy of 5.22 eV, which is nearly identical to the vertical excitation energy (*i.e.* evaluated at the minimum of the quartic fit to the ground state) of 5.23 eV in Table B.11. Hence, the spectrum of Figure B.2 provides no evidence that vibrational effects, due to the Ni-C symmetric stretching mode, lead to a shift of the band maximum away from the vertical excitation energy. Of course there are other effects, in particular, vibronic effects involving the non-symmetric normal modes, which for the $\text{Ni}(\text{CO})_4$ molecule, would lead to Jahn-Teller distortions. However, we have no information on this at present.

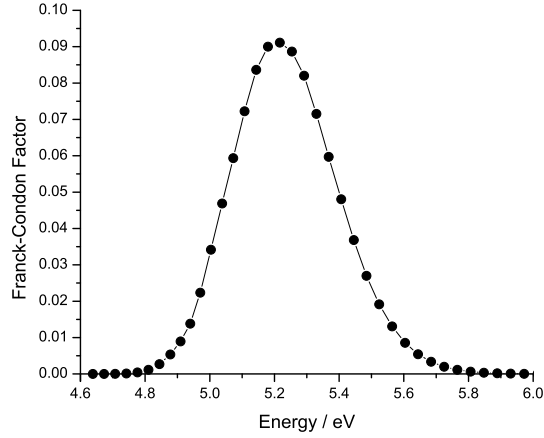


Figure B.2: One-dimensional Franck-Condon spectrum for $\text{Ni}(\text{CO})_4$, calculated using the MR-EOM/def2-SVP potential energy surfaces for the ground state and the first singlet excited state of T_2 symmetry.

B.3 Effect of the First order Perturbative Singles on the orbital selection scheme

Let us investigate the effects of excluding the first order singles amplitudes, in the virtual orbital selection density (*i.e.* the third term of ρ_{ab}^t in Eq. (5.22)), on the calculated excitation energies of $\text{Ni}(\text{CO})_4$ in a def2-TZVPP basis. As discussed in section 5.2.1, the first order singles amplitudes are rigorously zero due to the Brillouin condition, satisfied by the projected residual equation in Eq. (3.9). However, in all the calculations with a truncated virtual space reported in chapter 5, we have used the non-zero first order amplitudes defined by Eq. (5.15). For a particular truncation of the virtual space and a given excited state i , let ε_i denote the corresponding excitation energy calculated by including the first order singles in the density of Eq. (5.21) and ϵ_i denote the excitation energy which excludes the first order singles. We then define $\Delta\mathcal{E}_i$ as the difference

$$\Delta\mathcal{E}_i = \varepsilon_i - \epsilon_i, \quad (\text{B.1})$$

and plot the difference $\Delta\mathcal{E}_i$ for each of the considered states of $\text{Ni}(\text{CO})_4$ (*i.e.* the states $i = 1, 2 \dots 11$, numbered according to the order that they appear in Table B.1) in Figure B.3, for various truncations of the virtual space. As expected, the deviations typically increase as the size of the virtual space decreases.

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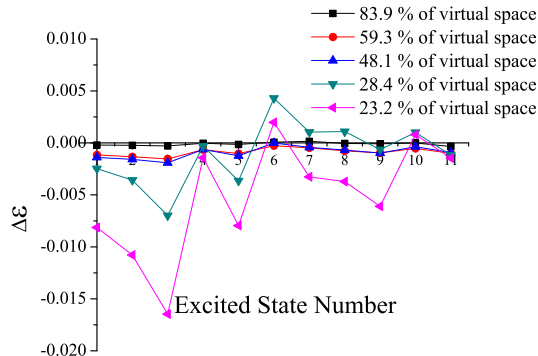


Figure B.3: Plot of the differences $\Delta\mathcal{E}$, between the excitation energies of $\text{Ni}(\text{CO})_4$, calculated using the virtual orbital selection density of Eq. (5.21) with and without the first order singles amplitudes (*cf.* Eq. (5.15)), for various sizes of the virtual space in a def2-TZVPP basis. The excited states are labelled from 1-11 in the order that they appear in Table B.1.

Even so, there are only two absolute deviations which are greater than 0.01 eV and they occur for the most aggressive truncation of the virtual space (*i.e.* 23.2 % of the virtual space included). This clearly demonstrates that the first order singles have only a small effect on the computed excitation energies, for reasonable truncations of the virtual space and that the results included in chapter 5 will not be significantly affected by their inclusion in the virtual orbital selection density of Eq. (5.21). However, we reiterate that the default in ORCA [24] is now to exclude the first order singles from the virtual orbital selection density.

Appendix C

Supporting Information for Chapter 6: Benchmark Applications of Variations of Multireference Equation of Motion Coupled-Cluster Theory

In the following tables, we provide the calculated excitation energies for each of the organic molecules considered in section 6.3. These excitation energies were used to calculate the various statistics reported therein. It is important to recall that the statistics have been computed by considering only the excitation energies which simultaneously satisfy the criteria $\%T1(CC3) \geq 85\%$ and $\%active \geq 90\%$. The relevant $\%T1(CC3)$ and $\%active$ (*i.e.* obtained from the MR-EOM-T|SXD-full calculation) values are provided in Tables C.1 (singlets) and C.4 (triplets), along with the benchmark CC3 and EOM-CCSDT-3 (*i.e.* for singlet states) reference data and the results obtained with several different MR-EOM approaches (*i.e.* MR-EOM-T, T|S, T|SXD, TSXD and T|SXD|U). The excitation energies calculated with the remaining MR-EOM approaches of Table 6.2 appear in Tables C.2 and C.3 for the singlet states and Tables C.5 and C.6 for the triplet states. Furthermore, the excitation energies for the five transition metals, considered in section 6.4 appear in Tables C.7 and C.8 for the singlet and triplet states, respectively.

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Table C.1: The reference CC3 and EOM-CCSDT-3 excitation energies for the singlet states of the organic molecule test set of chapter 6 and the corresponding MR-EOM-T, T|S, T|SXD, TSXD and T|SXD|U excitation energies, calculated in a TZVP basis set. The %T1(CC3) and %active (*i.e.* at the MR-EOM-T|SXD-full level) values are also included in the table.

Molecule	State	%active	%T1(CC3)	Method							
				CC3	EOM-CCSDT-3	Bare H	T	T S	T SXD	TSXD	T SXD U
ethene	$^1B_{1u}$	94.5	96.9	8.37	8.40	8.38	8.30	8.30	8.23	8.29	8.30
E-butadiene	^1A_g	98.4	72.8	6.77	6.89	6.72	6.61	6.60	6.43	6.48	6.44
	^1B_u	96.0	93.7	6.58	6.61	6.45	6.68	6.66	6.48	6.54	6.54
E-hexatriene	^1A_g	92.1	65.8	5.72	5.88	5.57	5.64	5.61	5.45	5.50	5.45
	^1B_u	94.6	92.6	5.58	5.61	5.43	5.76	5.75	5.69	5.75	5.73
cyclopropene	$^1B_1$	97.0	93.0	6.90	6.92	6.51	6.94	6.92	6.80	6.83	6.82
	$^1B_2$	85.7	95.5	7.10	7.14	6.90	7.08	7.14	7.15	7.20	7.17
cyclopentadiene	$^1B_2$	95.5	94.3	5.73	5.75	5.76	5.79	5.79	5.67	5.72	5.71
	$^1A_1$	98.3	79.3	6.61	6.71	6.56	6.56	6.54	6.38	6.42	6.39
norbornadiene	$^1A_1$	91.7	93.1	8.69	8.76	9.00	8.89	8.96	8.72	8.81	8.78
	$^1A_2$	96.7	93.4	5.64	5.68	5.57	5.69	5.69	5.62	5.66	5.63
	$^1B_2$	94.5	91.9	6.49	6.55	6.37	6.66	6.64	6.53	6.60	6.54
	$^1B_2$	94.2	93.8	7.64	7.68	7.64	7.78	7.74	7.61	7.67	7.61
benzene	$^1A_2$	95.0	93.0	7.71	7.74	7.58	7.87	7.83	7.72	7.78	7.73
	$^1B_{2u}$	94.1	85.8	5.07	5.10	5.39	5.15	5.12	4.99	5.00	5.00
	$^1B_{1u}$	97.4	93.6	6.68	6.69	7.08	6.65	6.66	6.52	6.56	6.53
	$^1E_{2g}$	94.6	92.2	7.45	7.52	7.82	7.62	7.60	7.42	7.48	7.42
furan	^1A_g	88.8	65.6	8.43	8.60	8.89	8.52	8.48	8.25	8.28	8.26
	$^1A_1$	97.9	84.9	6.62	6.69	6.67	6.63	6.55	6.41	6.45	6.44
	$^1B_2$	92.3	92.6	6.60	6.64	6.75	6.69	6.73	6.63	6.68	6.67
pyrrole	$^1A_1$	92.3	90.7	8.53	8.61	8.70	8.78	8.71	8.53	8.62	8.65
	$^1A_1$	97.3	86.0	6.40	6.46	6.53	6.38	6.36	6.22	6.26	6.26
	$^1B_2$	91.2	91.6	6.71	6.75	6.89	6.83	6.84	6.69	6.73	6.73
pyridine	$^1A_1$	91.7	90.2	8.17	8.24	8.36	8.40	8.34	8.13	8.22	8.24
	$^1B_1$	94.0	88.1	5.05	5.12	5.21	5.19	5.11	5.04	5.09	5.04
	$^1B_2$	92.9	85.9	5.15	5.18	5.59	5.30	5.28	5.12	5.14	5.12
	$^1A_2$	93.0	87.7	5.50	5.59	5.53	5.64	5.57	5.48	5.54	5.48
	$^1A_1$	96.1	92.8	6.85	6.87	7.25	6.84	6.85	6.70	6.74	6.71
	$^1B_2$	93.7	89.7	7.59	7.66	7.97	7.76	7.74	7.53	7.59	7.53
pyrimidine	$^1A_1$	92.8	91.5	7.70	7.78	8.16	7.96	7.93	7.69	7.76	7.69
	$^1A_1$	86.2	74.1	8.68	8.86	9.25	8.87	8.83	8.52	8.57	8.53
	$^1B_2$	87.1	65.2	8.77	8.97	9.41	9.07	9.03	8.78	8.82	8.79
	$^1B_1$	94.6	88.4	4.50	4.57	4.59	4.69	4.50	4.50	4.58	4.49
	$^1A_2$	92.7	88.2	4.93	5.00	5.05	5.25	5.03	4.98	5.05	5.01
	$^1B_2$	86.9	85.7	5.36	5.39	5.78	5.53	5.51	5.50	5.51	5.51
pyridazine	$^1A_1$	93.1	92.2	7.06	7.09	7.55	7.15	7.15	7.08	7.11	7.06
	$^1A_1$	91.5	89.7	7.74	7.81	8.23	8.01	7.92	7.87	7.93	7.85
	$^1B_2$	92.0	90.7	8.01	8.08	8.45	8.30	8.20	8.17	8.23	8.14
	$^1B_1$	93.6	89.0	3.92	4.00	4.14	4.15	4.09	4.02	4.05	4.02
	$^1A_2$	94.5	86.6	4.49	4.59	4.48	4.60	4.53	4.49	4.52	4.49
	$^1A_1$	85.3	85.2	5.22	5.25	5.80	5.49	5.52	5.49	5.50	5.48

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imidazole	$^1A_2$	91.3	86.6	5.74	5.82	6.00	5.94	5.94	5.87	5.91	5.87
	$^1B_1$	89.3	86.6	6.41	6.51	6.50	6.58	6.61	6.55	6.59	6.55
	$^1B_2$	81.1	90.7	6.93	6.96	7.41	7.09	7.20	7.11	7.15	7.08
	$^1B_2$	74.7	90.2	7.55	7.61	8.06	7.90	8.07	7.98	8.03	7.95
	$^1A_1$	90.3	90.5	7.82	7.91	8.38	8.22	8.31	8.38	8.44	8.39
	$^1A'$	94.7	87.2	6.58	6.64	6.80	6.64	6.60	6.47	6.51	6.47
	$^1A''$	96.4	87.6	6.82	6.89	6.70	6.85	6.80	6.71	6.76	6.71
	$^1A'$	91.2	89.8	7.10	7.14	7.31	7.17	7.18	7.05	7.10	7.07
triazine	$^1A''$	94.8	89.4	7.93	8.01	7.78	8.00	7.93	7.83	7.89	7.83
	$^1A'$	86.1	88.6	8.45	8.51	8.68	8.65	8.62	8.43	8.50	8.45
	$^1A''$	95.3	88.0	4.76	4.85	4.88	4.92	4.78	4.70	4.78	4.70
	$^1A''_2$	91.7	88.0	4.78	4.84	4.99	5.03	4.87	4.77	4.83	4.78
	$^1E''$	92.9	88.1	4.81	4.89	5.00	5.04	4.89	4.82	4.89	4.81
formaldehyde	$^1A'_2$	87.4	85.1	5.71	5.74	6.16	5.86	5.80	5.71	5.72	5.75
	$^1A'_1$	94.3	90.8	7.41	7.44	7.95	7.44	7.40	7.33	7.39	7.32
	$^1E'$	88.8	88.8	8.04	8.13	8.61	8.35	8.25	8.16	8.22	8.13
	$^1A_2$	96.8	91.2	3.95	3.96	3.85	3.99	3.96	3.96	4.00	3.92
	$^1B_1$	96.8	90.9	9.18	9.20	9.09	9.26	9.23	9.21	9.24	9.17
formamide	$^1A''$	97.7	90.7	5.65	5.66	5.69	5.69	5.66	5.65	5.67	5.65
	$^1A'$	92.1	87.9	8.27	8.35	8.46	8.46	8.42	8.30	8.32	8.31
acetamide	$^1A'$	84.6	86.6	10.93	11.09	10.88	10.88	10.84	10.67	10.74	13.26
	$^1A''$	98.3	90.6	5.69	5.71	5.76	5.70	5.66	5.82	5.77	5.78
	$^1A'$	82.8	89.1	7.67	7.76	7.72	7.84	7.94	8.78	8.76	7.48
propanamide	$^1A'$	42.7	88.7	10.50	10.60	10.53	10.45	10.57	11.62	11.63	10.18
	$^1A''$	97.3	90.6	5.72	5.73	5.67	5.74	5.71	5.67	5.69	5.64
	$^1A'$	86.8	89.2	7.62	7.74	7.66	7.73	7.73	7.55	7.62	7.54
	$^1A'$	84.8	89.0	10.06	10.15	10.28	10.23	10.20	10.14	10.21	10.14

Table C.2: The MR-EOM-T|SXD-full, T|SXD|U-full, T|SXD-no λ_2 , T|SXD-noG λ_2 , T|SXD|U-no λ_2 and T|SXD|U-noG λ_2 excitation energies for the singlet states of the organic molecule test set, calculated in a TZVP basis set.

Molecule	State	Method					
		T SXD-full	T SXD U-full	T SXD-no λ_2	T SXD-noG λ_2	T SXD U-no λ_2	T SXD U-noG λ_2
ethene	$^1B_{1u}$	8.27	8.27	8.22	8.22	8.29	8.29
E-butadiene	^1A_g	6.44	6.44	6.43	6.43	6.44	6.44
	^1B_u	6.53	6.53	6.48	6.48	6.54	6.54
E-hexatriene	^1A_g	5.41	5.41	5.45	5.45	5.45	5.45
	^1B_u	5.64	5.64	5.69	5.69	5.73	5.73
cyclopropene	$^1B_1$	6.79	6.79	6.85	6.86	6.83	6.83
	$^1B_2$	7.03	7.03	7.14	7.14	7.17	7.18
cyclopentadiene	$^1B_2$	5.71	5.71	5.67	5.67	5.71	5.71
	$^1A_1$	6.39	6.39	6.38	6.38	6.39	6.39
	$^1A_1$	8.77	8.77	8.73	8.72	8.79	8.78
norbornadiene	$^1A_2$	5.66	5.66	5.62	5.62	5.63	5.63

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benzene	$^1B_2$	6.59	6.59	6.53	6.53	6.54	6.54
	$^1B_2$	7.65	7.66	7.61	7.61	7.61	7.61
	$^1A_2$	7.75	7.76	7.72	7.72	7.73	7.73
	$^1B_{2u}$	4.97	4.98	4.99	4.99	5.00	5.00
	$^1B_{1u}$	6.53	6.54	6.52	6.52	6.53	6.53
	$^1E_{2g}$	7.45	7.45	7.42	7.42	7.42	7.42
furan	^1A_g	8.19	8.19	8.26	8.26	8.26	8.26
	$^1A_1$	6.42	6.42	6.41	6.41	6.45	6.44
	$^1B_2$	6.66	6.66	6.64	6.64	6.68	6.68
pyrrole	$^1A_1$	8.57	8.57	8.54	8.54	8.66	8.66
	$^1A_1$	6.23	6.23	6.22	6.22	6.26	6.26
	$^1B_2$	6.72	6.72	6.69	6.69	6.73	6.73
pyridine	$^1A_1$	8.18	8.19	8.14	8.14	8.24	8.24
	$^1B_1$	5.01	5.02	5.05	5.04	5.05	5.04
	$^1B_2$	5.12	5.13	5.12	5.12	5.12	5.13
pyrimidine	$^1A_2$	5.50	5.50	5.49	5.47	5.49	5.48
	$^1A_1$	6.72	6.73	6.70	6.70	6.71	6.71
	$^1B_2$	7.59	7.59	7.54	7.54	7.54	7.54
	$^1A_1$	7.75	7.75	7.69	7.70	7.69	7.70
	$^1A_1$	8.54	8.54	8.52	8.53	8.53	8.53
	$^1B_2$	8.77	8.77	8.78	8.79	8.79	8.79
	$^1B_1$	4.53	4.53	4.50	4.51	4.49	4.49
	$^1A_2$	5.02	5.00	4.99	4.98	5.01	5.01
	$^1B_2$	5.46	5.45	5.50	5.50	5.51	5.51
	$^1A_1$	7.12	7.12	7.08	7.08	7.06	7.06
pyridazine	$^1A_1$	7.93	7.91	7.88	7.88	7.86	7.86
	$^1B_2$	8.20	8.17	8.17	8.17	8.14	8.14
	$^1B_1$	4.01	4.01	4.02	4.01	4.02	4.02
	$^1A_2$	4.52	4.52	4.49	4.48	4.49	4.48
	$^1A_1$	5.36	5.34	5.49	5.49	5.48	5.48
	$^1A_2$	5.80	5.80	5.87	5.87	5.88	5.87
imidazole	$^1B_1$	6.51	6.50	6.55	6.55	6.56	6.55
	$^1B_2$	7.09	7.05	7.12	7.11	7.08	7.08
	$^1B_2$	7.81	7.79	7.98	7.98	7.96	7.96
	$^1A_1$	8.29	8.28	8.39	8.38	8.39	8.38
	$^1A'$	6.47	6.47	6.47	6.47	6.48	6.48
	$^1A''$	6.71	6.71	6.72	6.71	6.71	6.70
	$^1A'$	7.03	7.03	7.05	7.05	7.07	7.07
	$^1A''$	7.83	7.82	7.83	7.83	7.83	7.82
triazine	$^1A'$	8.39	8.39	8.43	8.43	8.46	8.46
	$^1A_1''$	4.72	4.73	4.71	4.71	4.70	4.70
	$^1A_2''$	4.82	4.80	4.77	4.77	4.79	4.79
	$^1E''$	4.86	4.85	4.82	4.82	4.82	4.82
	$^1A_2'$	5.78	5.77	5.71	5.71	5.75	5.75
	$^1A_1'$	7.40	7.39	7.33	7.33	7.32	7.32
formaldehyde	$^1E'$	8.19	8.16	8.16	8.17	8.13	8.13
	$^1A_2$	3.88	3.88	3.97	3.95	3.93	3.91
	$^1B_1$	9.17	9.17	9.22	9.20	9.18	9.16
formamide	$^1A''$	5.57	5.57	5.65	5.63	5.65	5.64
	$^1A'$	8.32	8.32	8.31	8.30	8.31	8.30

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acetamide	$^1A'$	10.68	10.69	13.25	13.22	13.26	13.23
	$^1A''$	5.71	5.71	5.82	5.81	5.78	5.77
	$^1A'$	7.85	7.85	7.48	7.49	7.48	7.49
propanamide	$^1A'$	10.55	10.55	10.18	10.18	10.18	10.19
	$^1A''$	5.64	5.64	5.68	5.67	5.64	5.64
	$^1A'$	7.52	7.52	7.54	7.55	7.54	7.55
	$^1A'$	10.04	10.04	10.14	10.14	10.14	10.14

Table C.3: The MR-EOM- $T|T^\dagger|(S_1+S_2)$ XD, $T|T^\dagger|(S_1+S_2)$ XD-h, $T|T^\dagger|$ SXD, $T|T^\dagger|$ SXD-h and $T|T^\dagger|$ SXD-h-v excitation energies for the singlet states of the organic molecule test set, calculated in a TZVP basis set

Molecule	State	Method				
		$T T^\dagger (S_1+S_2)$ XD	$T T^\dagger (S_1+S_2)$ XD-h	$T T^\dagger $ SXD	$T T^\dagger $ SXD-h	$T T^\dagger $ SXD-h-v
ethene	$^1B_{1u}$	8.42	8.42	8.42	8.51	8.49
E-butadiene	^1A_g	6.56	6.56	6.56	6.57	6.58
	^1B_u	6.67	6.66	6.67	6.77	6.76
E-hexatriene	^1A_g	5.52	5.52	5.51	5.54	5.55
	^1B_u	5.82	5.82	5.82	5.88	5.86
cyclopropene	$^1B_1$	6.88	6.88	6.87	6.87	6.88
	$^1B_2$	7.32	7.31	7.33	7.42	7.35
cyclopentadiene	$^1B_2$	5.84	5.83	5.85	5.94	5.93
	$^1A_1$	6.51	6.51	6.51	6.52	6.54
	$^1A_1$	8.98	8.97	8.99	9.06	9.04
norbornadiene	$^1A_2$	5.77	5.77	5.79	5.81	5.78
	$^1B_2$	6.69	6.69	6.69	6.72	6.69
	$^1B_2$	7.79	7.79	7.81	7.85	7.82
	$^1A_2$	7.88	7.87	7.88	7.90	7.87
benzene	$^1B_{2u}$	5.05	5.05	5.05	5.11	5.06
	$^1B_{1u}$	6.71	6.71	6.73	6.72	6.68
	$^1E_{2g}$	7.59	7.58	7.60	7.66	7.60
	^1A_g	8.39	8.39	8.39	8.47	8.36
furan	$^1A_1$	6.52	6.52	6.52	6.52	6.53
	$^1B_2$	6.77	6.78	6.79	6.87	6.87
	$^1A_1$	8.77	8.76	8.79	8.84	8.83
pyrrole	$^1A_1$	6.34	6.33	6.33	6.33	6.34
	$^1B_2$	6.83	6.84	6.84	6.90	6.90
	$^1A_1$	8.36	8.35	8.37	8.42	8.42
pyridine	$^1B_1$	5.14	5.14	5.13	5.12	5.13
	$^1B_2$	5.18	5.18	5.17	5.23	5.18
	$^1A_2$	5.61	5.60	5.60	5.65	5.63
	$^1A_1$	6.88	6.88	6.89	6.90	6.85
	$^1B_2$	7.70	7.69	7.70	7.78	7.70
	$^1A_1$	7.86	7.86	7.87	7.95	7.88

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pyrimidine	$^1A_1$	8.67	8.67	8.66	8.78	8.66
	$^1B_2$	8.91	8.91	8.90	9.00	8.88
	$^1B_1$	4.63	4.63	4.62	4.64	4.62
	$^1A_2$	5.11	5.10	5.09	5.12	5.12
	$^1B_2$	5.49	5.48	5.49	5.54	5.52
pyridazine	$^1A_1$	7.17	7.17	7.18	7.20	7.20
	$^1A_1$	7.96	7.95	7.97	8.04	8.01
	$^1B_2$	8.29	8.28	8.29	8.37	8.34
	$^1B_1$	4.06	4.06	4.06	4.07	4.05
	$^1A_2$	4.57	4.56	4.57	4.61	4.55
	$^1A_1$	5.49	5.49	5.49	5.51	5.49
	$^1A_2$	5.91	5.91	5.91	5.91	5.88
	$^1B_1$	6.63	6.63	6.64	6.67	6.62
	$^1B_2$	7.23	7.22	7.23	7.29	7.28
	$^1B_2$	8.10	8.09	8.10	8.22	8.16
imidazole	$^1A_1$	8.50	8.49	8.51	8.34	8.28
	$^1A'$	6.58	6.57	6.58	6.59	6.57
	$^1A''$	6.81	6.81	6.80	6.80	6.78
	$^1A'$	7.17	7.17	7.18	7.21	7.20
	$^1A''$	7.97	7.96	7.96	7.97	7.94
triazine	$^1A'$	8.59	8.58	8.59	8.66	8.64
	$^1A_1''$	4.84	4.84	4.83	4.83	4.85
	$^1A_2''$	4.89	4.89	4.89	4.98	4.97
	$^1E''$	4.94	4.93	4.93	4.99	4.90
	$^1A_2'$	5.70	5.69	5.70	5.80	5.71
formaldehyde	$^1A_1'$	7.44	7.44	7.45	7.48	7.52
	$^1E'$	8.29	8.28	8.30	8.43	8.35
	$^1A_2$	3.99	3.98	3.98	3.93	3.96
	$^1B_1$	9.24	9.23	9.23	9.19	9.18
formamide	$^1A''$	5.68	5.69	5.67	5.60	5.61
	$^1A'$	8.37	8.37	8.36	8.45	8.39
acetamide	$^1A'$	13.24	13.24	13.19	13.15	13.14
	$^1A''$	5.70	5.70	5.66	5.55	5.54
	$^1A'$	7.61	7.60	8.08	8.19	8.10
propanamide	$^1A'$	10.32	10.32	11.40	11.42	11.39
	$^1A''$	5.70	5.70	5.69	5.69	5.68
	$^1A'$	7.69	7.69	7.68	7.73	7.73
	$^1A'$	10.28	10.27	10.27	10.36	10.31

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Table C.4: The reference CC3 excitation energies for the triplet states of the organic molecule test set of chapter 6 and the corresponding MR-EOM-T, T|S, T|SXD, TSXD and T|SXD|U excitation energies, calculated in a TZVP basis set. The %T1(CC3) and %active (*i.e.* at the MR-EOM-T|SXD-full level) values are also included in the table.

Molecule	State	%active	%T1(CC3)	Method						
				CC3	Bare H	T	T S	T SXD	TSXD	T SXD U
ethene	$^3B_{1u}$	100.0	99.3	4.48	4.62	4.55	4.55	4.52	4.52	4.49
E-butadiene	^3B_u	99.3	98.5	3.32	3.41	3.35	3.35	3.28	3.30	3.27
	^3A_g	99.1	98.9	5.17	5.39	5.20	5.19	5.05	5.09	5.05
E-hexatriene	^3B_u	92.1	98.0	2.69	2.76	2.91	2.87	2.74	2.78	2.74
	^3A_g	96.9	98.4	4.32	4.50	4.34	4.33	4.23	4.25	4.23
cyclopropene	$^3B_2$	98.7	99.1	4.34	4.32	4.41	4.41	4.38	4.40	4.37
	$^3B_1$	97.8	98.1	6.62	6.19	6.66	6.64	6.56	6.59	6.59
cyclopentadiene	$^3B_2$	99.3	98.5	3.25	3.34	3.32	3.30	3.23	3.24	3.22
	$^3A_1$	99.1	98.7	5.09	5.27	5.18	5.17	5.03	5.07	5.03
norbornadiene	$^3A_2$	98.4	98.7	3.72	3.83	3.76	3.75	3.63	3.66	3.64
	$^3B_2$	98.0	99.0	4.16	4.28	4.22	4.24	4.08	4.12	4.08
benzene	$^3B_{1u}$	94.4	98.7	4.12	4.37	4.26	4.23	4.11	4.11	4.12
	$^3E_{1u}$	95.5	97.0	4.90	5.14	4.94	4.92	4.82	4.83	4.82
	$^3B_{2u}$	97.9	98.2	6.04	6.29	6.00	6.00	5.90	5.93	5.91
	$^3E_{2g}$	82.4	94.9	7.49	8.04	7.87	7.82	7.55	7.56	7.55
furan	$^3B_2$	99.1	98.5	4.17	4.39	4.19	4.16	4.08	4.09	4.06
	$^3A_1$	98.4	98.2	5.48	5.61	5.49	5.49	5.36	5.40	5.35
pyrrole	$^3B_2$	99.0	98.4	4.48	4.68	4.49	4.46	4.39	4.40	4.36
	$^3A_1$	97.3	97.8	5.51	5.62	5.48	5.52	5.40	5.44	5.38
pyridine	$^3A_1$	93.7	98.6	4.25	4.57	4.42	4.40	4.29	4.29	4.29
	$^3B_1$	94.8	97.1	4.50	4.53	4.60	4.51	4.46	4.51	4.46
	$^3B_2$	93.7	97.2	4.86	5.22	4.97	4.95	4.79	4.82	4.79
	$^3A_1$	94.0	97.0	5.05	5.37	5.15	5.13	5.02	5.03	5.02
	$^3A_2$	92.6	95.8	5.46	5.46	5.59	5.54	5.46	5.52	5.46
	$^3B_2$	96.6	97.8	6.40	6.62	6.38	6.37	6.28	6.31	6.29
	$^3A_1$	85.5	95.3	7.66	8.32	8.09	8.04	7.76	7.78	7.76
	$^3B_2$	83.2	94.4	7.83	8.54	8.36	8.31	8.05	8.06	8.04
imidazole	$^3A'$	97.6	98.4	4.69	4.89	4.70	4.68	4.61	4.63	4.61
	$^3A'$	96.6	97.9	5.79	5.98	5.82	5.80	5.69	5.72	5.70
	$^3A''$	96.7	97.4	6.37	6.23	6.39	6.33	6.27	6.31	6.26
	$^3A'$	87.9	97.9	6.55	6.63	6.63	6.77	6.65	6.70	6.65
	$^3A'$	90.1	97.1	7.42	7.47	7.46	7.55	7.48	7.52	7.49
	$^3A''$	94.5	96.0	7.51	7.26	7.57	7.52	7.43	7.49	7.42
formaldehyde	$^3A_2$	96.1	98.1	3.55	3.37	3.58	3.56	3.58	3.63	3.54
	$^3A_1$	99.4	99.2	5.83	6.07	5.93	5.92	5.92	5.95	5.88
formamide	$^3A''$	97.4	97.8	5.36	5.40	5.40	5.38	5.39	5.41	5.40
	$^3A'$	97.1	98.4	5.74	5.80	5.80	5.78	5.71	5.74	5.72
acetamide	$^3A''$	98.0	98.3	5.42	5.43	5.42	5.39	5.58	5.53	5.53
	$^3A'$	93.0	98.3	5.88	5.99	5.96	6.06	6.81	6.81	5.80
propanamide	$^3A''$	97.3	97.7	5.45	5.35	5.47	5.44	5.43	5.45	5.40
	$^3A'$	95.7	98.3	5.90	5.96	5.89	5.93	5.92	5.96	5.88

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Table C.5: The MR-EOM-T|SXD-full, T|SXD|U-full, T|SXD-no λ_2 ,T|SXD-noG λ_2 , T|SXD|U-no λ_2 and T|SXD|U-noG λ_2 excitation energies for the triplet states of the organic molecule test set, calculated in a TZVP basis set.

Molecule	State	Method					
		T SXD-full	T SXD U-full	T SXD-no λ_2	T SXD-noG λ_2	T SXD U-no λ_2	T SXD U-noG λ_2
ethene	$^3B_{1u}$	4.51	4.51	4.52	4.52	4.49	4.48
E-butadiene	^3B_u	3.28	3.28	3.28	3.28	3.28	3.27
	^3A_g	5.05	5.05	5.05	5.05	5.05	5.05
E-hexatriene	^3B_u	2.69	2.69	2.74	2.74	2.74	2.74
	^3A_g	4.23	4.23	4.23	4.23	4.23	4.23
cyclopropene	$^3B_2$	4.34	4.34	4.40	4.40	4.37	4.37
	$^3B_1$	6.57	6.57	6.62	6.63	6.59	6.59
cyclopentadiene	$^3B_2$	3.23	3.23	3.23	3.23	3.23	3.22
	$^3A_1$	5.03	5.03	5.03	5.03	5.03	5.03
norbornadiene	$^3A_2$	3.64	3.64	3.64	3.63	3.64	3.63
	$^3B_2$	4.07	4.07	4.08	4.08	4.08	4.08
benzene	$^3B_{1u}$	4.11	4.11	4.11	4.12	4.12	4.12
	$^3E_{1u}$	4.82	4.83	4.82	4.82	4.83	4.83
	$^3B_{2u}$	5.93	5.93	5.90	5.90	5.91	5.90
	$^3E_{2g}$	7.45	7.45	7.55	7.55	7.55	7.55
furan	$^3B_2$	4.08	4.08	4.08	4.08	4.06	4.06
	$^3A_1$	5.36	5.37	5.37	5.36	5.35	5.35
pyrrole	$^3B_2$	4.39	4.39	4.39	4.39	4.37	4.36
	$^3A_1$	5.40	5.40	5.40	5.40	5.38	5.38
pyridine	$^3A_1$	4.29	4.29	4.29	4.29	4.29	4.29
	$^3B_1$	4.46	4.46	4.46	4.45	4.47	4.46
	$^3B_2$	4.82	4.82	4.79	4.80	4.79	4.80
	$^3A_1$	5.02	5.03	5.02	5.02	5.02	5.03
	$^3A_2$	5.47	5.47	5.47	5.45	5.47	5.46
	$^3B_2$	6.30	6.31	6.28	6.28	6.29	6.29
	$^3A_1$	7.75	7.75	7.76	7.77	7.76	7.77
	$^3B_2$	8.02	8.01	8.05	8.05	8.04	8.05
imidazole	$^3A'$	4.61	4.62	4.61	4.61	4.61	4.61
	$^3A'$	5.69	5.69	5.69	5.69	5.70	5.70
	$^3A''$	6.26	6.26	6.27	6.26	6.27	6.26
	$^3A'$	6.57	6.56	6.65	6.65	6.65	6.65
	$^3A'$	7.41	7.40	7.48	7.47	7.49	7.48
	$^3A''$	7.43	7.43	7.43	7.42	7.43	7.42
formaldehyde	$^3A_2$	3.52	3.52	3.59	3.57	3.55	3.53
	$^3A_1$	5.90	5.90	5.92	5.91	5.88	5.87
formamide	$^3A''$	5.33	5.33	5.39	5.38	5.40	5.38
	$^3A'$	5.70	5.70	5.72	5.71	5.72	5.71
acetamide	$^3A''$	5.47	5.47	5.57	5.56	5.54	5.52
	$^3A'$	6.03	6.03	5.83	5.83	5.80	5.80
propanamide	$^3A''$	5.41	5.41	5.44	5.43	5.40	5.40
	$^3A'$	5.86	5.86	5.92	5.92	5.89	5.88

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Table C.6: The MR-EOM- $T|T^\dagger|(S_1+S_2)$ XD, $T|T^\dagger|(S_1+S_2)$ XD-h, $T|T^\dagger|$ SXD, $T|T^\dagger|$ SXD-h and $T|T^\dagger|$ SXD-h-v excitation energies for the triplet states of the organic molecule test set, calculated in a TZVP basis set

Molecule	State	Method				
		$T T^\dagger (S_1+S_2)$ XD	$T T^\dagger (S_1+S_2)$ XD-h	$T T^\dagger $ SXD	$T T^\dagger $ SXD-h	$T T^\dagger $ SXD-h-v
ethene	$^3B_{1u}$	4.48	4.48	4.47	4.45	4.46
E-butadiene	^3B_u	3.32	3.32	3.32	3.32	3.33
	^3A_g	5.14	5.14	5.14	5.13	5.14
E-hexatriene	^3B_u	2.79	2.80	2.79	2.82	2.82
	^3A_g	4.31	4.31	4.31	4.31	4.32
cyclopropene	$^3B_2$	4.38	4.38	4.37	4.33	4.34
	$^3B_1$	6.63	6.63	6.62	6.62	6.63
cyclopentadiene	$^3B_2$	3.26	3.26	3.26	3.26	3.27
	$^3A_1$	5.11	5.11	5.11	5.10	5.12
norbornadiene	$^3A_2$	3.72	3.72	3.71	3.72	3.73
	$^3B_2$	4.18	4.18	4.18	4.17	4.19
benzene	$^3B_{1u}$	4.12	4.12	4.11	4.17	4.21
	$^3E_{1u}$	4.88	4.88	4.88	4.92	4.94
	$^3B_{2u}$	6.05	6.05	6.06	6.06	6.07
	$^3E_{2g}$	7.65	7.65	7.65	7.76	7.74
furan	$^3B_2$	4.07	4.08	4.08	4.07	4.07
	$^3A_1$	5.43	5.43	5.43	5.42	5.42
pyrrole	$^3B_2$	4.40	4.40	4.40	4.38	4.38
	$^3A_1$	5.48	5.48	5.48	5.47	5.47
pyridine	$^3A_1$	4.30	4.30	4.29	4.33	4.36
	$^3B_1$	4.55	4.54	4.54	4.56	4.56
	$^3B_2$	4.87	4.87	4.87	4.92	4.94
	$^3A_1$	5.08	5.08	5.07	5.10	5.12
	$^3A_2$	5.58	5.58	5.58	5.62	5.60
	$^3B_2$	6.41	6.41	6.41	6.43	6.43
	$^3A_1$	7.86	7.86	7.86	7.95	7.92
	$^3B_2$	8.15	8.15	8.15	8.24	8.20
imidazole	$^3A'$	4.64	4.64	4.64	4.62	4.60
	$^3A'$	5.76	5.76	5.76	5.75	5.73
	$^3A''$	6.34	6.35	6.34	6.34	6.33
	$^3A'$	6.76	6.76	6.76	6.78	6.76
	$^3A'$	7.58	7.58	7.57	7.56	7.54
	$^3A''$	7.54	7.54	7.54	7.56	7.54
formaldehyde	$^3A_2$	3.61	3.60	3.60	3.58	3.56
	$^3A_1$	5.86	5.86	5.84	5.79	5.80
formamide	$^3A''$	5.41	5.42	5.40	5.35	5.32
	$^3A'$	5.74	5.74	5.72	5.71	5.70
acetamide	$^3A''$	5.44	5.45	5.40	5.31	5.27
	$^3A'$	5.88	5.88	6.08	6.00	5.97
propanamide	$^3A''$	5.45	5.45	5.45	5.46	5.44
	$^3A'$	5.95	5.95	5.93	5.93	5.93

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Table C.7: The MR-EOM-T|SXD, T|T[†]|(S₁ + S₂)XD, T|T[†]|SXD, T|T[†]|SXD-h and T|T[†]|SXD-h-v excitation energies for the singlet states of the five transition metal complexes considered in chapter 6

State	T SXD	T T [†] (S ₁ + S ₂)XD	T T [†] SXD	T T [†] SXD-h	T T [†] SXD-h-v
<i>Ni(CO)₄</i>					
¹ T ₁	4.97	5.00	4.99	4.88	4.88
¹ E	5.05	5.08	5.07	4.97	4.95
¹ T ₁	5.71	5.77	5.74	5.72	5.73
¹ T ₁	6.15	6.21	6.19	6.15	6.09
<i>Fe(CO)₅</i>					
¹ A'' ₁	4.74	4.86	4.75	4.68	4.61
¹ E''	5.04	5.19	5.08	5.00	4.90
¹ A'' ₂	5.14	5.25	5.11	5.09	4.96
¹ A'	6.04	6.12	6.05	5.89	5.79
¹ E'	6.12	6.23	6.18	6.01	5.88
<i>Cr(CO)₆</i>					
¹ A _{2u}	5.25	4.95	4.63	4.32	4.32
¹ E _u	5.22	4.98	4.60	4.29	4.33
¹ T _{2u}	5.27	5.01	4.66	4.35	4.37
¹ T _{1u}	5.94	5.68	5.32	5.06	4.96
<i>ferrocene</i>					
¹ E'' ₁	2.49	2.82	2.79	2.96	2.91
¹ E'' ₂	2.52	2.85	2.83	2.96	2.99
¹ E'' ₁	3.95	4.23	4.22	4.33	4.31
¹ E'	4.99	5.59	5.55	5.82	5.82
¹ A'	5.12	5.69	5.66	5.92	5.85
¹ E'	5.11	5.70	5.65	5.93	5.88
¹ E'	5.21	5.79	5.75	6.02	5.95
¹ E'	5.52	6.11	6.07	6.35	6.34
¹ A'	5.70	6.26	6.21	6.49	6.37
¹ E'	5.69	6.26	6.22	6.47	6.40
¹ A'	6.03	6.58	6.54	6.78	6.70
<i>CpNiNO</i>					
¹ E ₁	2.79	2.90	2.90	2.94	2.94
¹ E ₂	2.87	2.98	2.98	3.03	3.04
¹ A ₂	3.28	3.36	3.39	3.36	3.39
¹ E ₁	3.48	3.58	3.62	3.59	3.60
¹ E ₂	3.49	3.63	3.65	3.69	3.70
¹ A	5.78	5.80	5.80	5.72	5.74
¹ E ₂	6.28	6.39	6.35	6.38	6.37
¹ E ₁	6.63	6.74	6.73	6.69	6.72
¹ E ₂	6.65	6.75	6.74	6.72	6.74
¹ E ₂	7.21	7.18	7.17	7.04	7.08

APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER 6

Table C.8: The MR-EOM-T|SXD, T|T[†]|(S₁ + S₂)XD, T|T[†]|SXD, T|T[†]|SXD-h and T|T[†]|SXD-h-v excitation energies for the triplet states of the five transition metal complexes considered in chapter 6

State	T SXD	T T [†] (S ₁ + S ₂)XD	T T [†] SXD	T T [†] SXD-h	T T [†] SXD-h-v
<i>Ni(CO)₄</i>					
³ A ₁	4.15	4.17	4.15	4.07	4.06
³ T ₂	4.60	4.62	4.61	4.52	4.51
³ E	4.72	4.74	4.72	4.63	4.63
³ T ₁	4.85	4.87	4.86	4.76	4.76
³ T ₁	5.59	5.65	5.62	5.60	5.61
³ T ₂	5.69	5.75	5.72	5.70	5.71
<i>Fe(CO)₅</i>					
³ A''	4.51	4.60	4.46	4.43	4.37
³ E	4.61	4.71	4.56	4.55	4.48
³ A''	4.71	4.81	4.66	4.66	4.59
³ A'	5.11	5.12	4.99	4.85	4.76
³ E'	5.61	5.65	5.55	5.40	5.30
³ A'	5.91	5.96	5.88	5.72	5.62
<i>Cr(CO)₆</i>					
³ A _{2u}	5.26	4.99	4.64	4.33	4.35
³ E _u	5.29	5.02	4.67	4.36	4.38
³ T _u	5.34	5.08	4.73	4.42	4.43
³ T _u	5.35	5.09	4.74	4.42	4.44
<i>ferrocene</i>					
³ E'' ₁	1.42	1.73	1.70	1.89	1.76
³ E'' ₂	1.58	1.91	1.88	2.08	1.99
³ E'' ₁	2.32	2.59	2.57	2.71	2.61
³ A'	3.87	4.46	4.41	4.72	4.60
³ E'	3.96	4.55	4.50	4.81	4.74
³ E'	4.02	4.62	4.57	4.87	4.78
³ A'	4.23	4.81	4.75	5.05	4.90
<i>CpNiNO</i>					
³ A ₁	2.11	2.12	2.12	2.10	2.11
³ E ₁	2.59	2.70	2.70	2.75	2.75
³ E ₂	2.72	2.80	2.81	2.78	2.80
³ E ₂	2.76	2.84	2.83	2.89	2.90
³ E ₁	2.95	3.08	3.08	3.12	3.13
³ A ₂	3.12	3.18	3.20	3.17	3.17
³ E ₂	5.73	5.80	5.77	5.75	5.74
³ E ₂	5.84	5.86	5.85	5.75	5.78
³ E	5.88	5.90	5.87	5.86	5.87
³ E	6.12	6.23	6.19	6.23	6.23
³ E	6.34	6.40	6.37	6.34	6.35
³ E	6.37	6.43	6.40	6.37	6.38

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