Higher-Order Molecular Properties and Excitation Energies in Single-Reference and Multireference Coupled-Cluster Theory

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1. Introduction

Modern quantum chemistry is capable of quantitatively reproducing and predicting the outcome of chemical experiments [1]. It has gained a key role in chemical research as an indispensable tool not only for the interpretation of experimental results, but also for the design of new experiments. In some cases, quantum-chemical studies can even replace traditional approaches of chemistry. The range of application of quantum chemistry is still growing thanks to new methodological developments and increasing computational power.

Quantum chemistry relies on the application of quantum mechanics to the description of atoms and molecules. From a quantum-mechanical perspective, the chemistry of a system is largely driven by its electronic structure. The latter is determined by the electronic Schrödinger equation,¹ a multidimensional differential equation, whose solution yields the electronic energy and wave function of the system under consideration [1,2]. In a theoretical sense, this information on the quantum-mechanical state is sufficient for a unique characterization of the system, yet both the total energy and the wave function are inaccessible through experiment. Hence, the determination of further quantities is essential as soon as results from quantumchemical calculations are to be related to experimental findings [3,4]. Quantities of interest include, for example,

- energy differences that provide information on thermochemical parameters such as heats of formation,
- structural parameters (e.g., equilibrium bond lengths and angles), whose availability is crucial for a variety of applications such as rotational spectroscopy,
- vibrational frequencies and the corresponding intensities, which are experimentally accessible through infrared spectroscopy,
- electric properties such as the dipole moment, the polarizability tensor, etc., which govern the interaction of a molecule with an external electric field,
- magnetic properties such as nuclear magnetic shielding tensors, which govern the interaction of a molecule with an external magnetic field,
- electronic excitation energies and the corresponding transition moments, which can be measured using ultraviolet-visible spectroscopy and which are of great interest when photophysical or photochemical processes are under investigation.

The calculation of energy differences involves nothing but recomputing the energy for different systems. However, the determination of all further quantities in the list requires to go beyond the solution of the electronic Schrödinger equation. Two approaches have been used most often: analytic-derivative theory [5–10] and response theory [11–16]. Both rely on the idea that many molecular properties can be recast as the reaction of a system to an external perturbation. For the determination of so-called static properties, analytic-derivative theory can be applied. In this context, the system is studied in the presence of a time-independent perturbation such as, for example, a static electric field or a displacement of the nuclei. The

¹This holds if the motion of the atomic nuclei is not considered and if relativistic effects are neglected.

molecular properties then appear as derivatives of the energy with respect to the perturbation and can thus be calculated via differentiation. Conceptually simplest is to differentiate the energy numerically, but analytic-derivative theory is superior in several respects, for example, in terms of efficiency. According to how many differentiation steps have to be carried out, molecular properties can be classified as first-order properties, second-order properties, etc.

Response theory, in contrast, deals with the time evolution of an electronic state and hence is suited for the treatment of dynamic properties. In response theory, the system is studied under the influence of a time-dependent perturbation such as, for example, an oscillating electric field. Again, an expansion in orders of perturbation is carried out with the dynamic properties appearing as expansion coefficients. In addition, response theory provides access to electronic excitation energies and the corresponding transition moments. These quantities differ from the remaining ones in the introductory list in the regard that they involve information on more than one electronic state. Furthermore, excitation energies represent a property inherent to a system's electronic structure. As a consequence, their calculation does not require to consider any perturbation.

The electronic Schrödinger equation can be solved exactly only for a few model systems. Numerous methods have been developed for the approximate solution of this equation [1, 2]. This ranges from semi-empirical approaches, which aim at a qualitative description, to wavefunction based *ab initio* methods, which provide a more systematic approach and, in principle, the possibility of a solution of arbitrary accuracy. Among the methods that fall into the latter category, coupled-cluster (CC) theory [17–20] stands out due to its high accuracy and reliability. CC theory comprises a hierarchy of methods, which systematically converges to the exact solution of the electronic Schrödinger equation. Moreover, energies computed with CC methods show the correct scaling with respect to system size, a property referred to as size-extensivity. CC theory relies on the assumption that a single Slater determinant, i.e., an antisymmetrized product of one-electron wave functions, is a valid approximation to the many-electron wave function. If this is the case, the commonly used low-order truncated CC schemes such as CC with singles and doubles excitations (CCSD) [21] and especially CCSD augmented by a perturbative treatment of triples excitations (CCSD(T)) [22] provide excellent results. Energies computed with extrapolated CC schemes [23,24] are in many cases correct up to ≈ 1 kcal/mol, which sometimes surpasses the accuracy of the corresponding experimental values [24]. The advantages of CC theory come at the price of rather high computational cost and vet, CCSD(T) calculations for systems with up to 90 atoms have been carried out using special techniques [25].

Both analytic-derivative theory and response theory have been combined with the CC methodology [3,9,10,14,16]. The resulting schemes have been applied with great success to a variety of chemical problems. Especially noteworthy are cases (see, for example, Refs. 26 or 27), where exotic species have been under consideration such as they occur in atmospheric chemistry or astrochemistry. The experimental characterization of these species is often difficult or yields ambiguous results so that a complementary treatment by means of quantum chemistry is desirable. The availability of analytic CC energy gradients [8,9] has enabled the routine determination of molecular equilibrium structures [28] and numerous further first-order properties [3,4] with high accuracy. Analytic second derivatives of the CC energy [10] allow for the efficient evaluation of second-order properties such as the harmonic force constants, from which information on vibrational energy levels can be obtained. Applications of CC response theory include the calculation of vertical excitation spectra, the determination of excitedstate properties as well as the characterization of conical intersections [20]. These studies are of particular importance as the experimental characterization of electronically excited states is often more difficult than that of the respective ground state. However, there is a variety of molecular properties, which correspond to third or even higher derivatives of the energy [3,4]. In addition, it is sometimes necessary to consider higher-order corrections in order to meet the accuracy of contemporary spectroscopic approaches. This applies for example to vibrational frequencies, which can be determined within $\approx 1 \text{ cm}^{-1}$ using state-of-the-art experimental techniques. Such an accuracy cannot be achieved computationally regardless of the quantum-chemical method used if the vibrational frequencies are computed from the harmonic force constants [1]. As a consequence, anharmonic corrections [29] need to be taken into account, which again entails the need to evaluate higher than second derivatives. Such quantities have been calculated most often via numerical differentiation of analytic second derivatives even though a fully analytic evaluation is superior in terms of accuracy and computational cost [10]. In the context of CC theory, only selected third-order properties have been calculated analytically so far. Most noteworthy are implementations of hyperpolarizabilities [30–32] and polarizability gradients [33], where the latter property is of importance for the intensity of bands seen in Raman spectroscopy.

In this framework, the present thesis makes its first contribution: A generic expression for the third derivative of the CC energy has been derived and used for the fully analytic calculation of the dipole Hessian matrix. This third-order quantity plays a crucial role in the determination of infrared intensities when taking account of anharmonic effects. The further achievements of the present work, however, lie in the field of multireference CC (MRCC) theory, where first-order and second-order properties have been targeted.

The necessity of MRCC theory arises from the fact that CC theory in its single-reference formulation is subject to the aforementioned important constraint: Low-order truncated CC schemes require that the many-electron wave function is well represented by a single Slater determinant. Hence, methods such as CCSD or CCSD(T) fail for so-called multireference cases, where a linear combination of several Slater determinants needs to be employed [20,34, 35]. Multireference cases occur abundantly in chemistry. Typical examples include systems at non-equilibrium, e.g., the breaking of chemical bonds, but there are also molecules that possess a pronounced multireference character at their equilibrium structure. This is, for example, the case for most organic biradicals and a variety of transition-metal compounds. In addition, there are numerous molecules, where only the ground electronic state is accurately described by a single Slater determinant, while the excited states require a multireference treatment. Since CC theory has been first applied to chemistry more than 40 years ago, its generalization to the multireference case has been one of the most intriguing open problems in quantum chemistry and until today, a convincing solution has not been presented yet [20, 34, 35].

There are numerous pragmatic multireference approaches, which circumvent the theoretical difficulties that arise when formulating the CC ansatz in a multireference fashion. Such methods have been formulated, for example, within the multireference coupled-pair functional framework [36,37]. Moreover, extensions of the single-reference CC [38–43] and the equation-of-motion (EOM) CC methodology [44,45] have been suggested. Often, these methods yield results that are in very good agreement with experimental values, but there are also cases, where they fail completely [34,35]. Furthermore, they can rarely be used in a black-box manner, but rather require detailed knowledge on the electronic structure of the system of interest. Also, all these multireference methods suffer from a number of formal deficiencies, some of them, for example, lack size-extensivity. Hence, their reliability and applicability is not comparable to that of CC theory for single-reference cases.

A variety of genuine MRCC methods, which rely on the use of a multireference zeroth-order wave function as starting point, have been proposed [34,35,46–65]. They can be classified according to whether they target several or just one electronic state within one calculation. The

former class of methods, which comprises valence-universal (VU) [47–49] and state-universal (SU) [50–53] MRCC ansätze, suffers from a severe drawback, the so-called intruder-state problem, which leads to ill-conditioned working equations [20, 34]. Hence, the latter class, commonly referred to as state-specific (SS) MRCC ansätze [54–65], is generally considered more promising. Among the multitude of SS-MRCC approaches, the method suggested by Mukherjee and coworkers (Mk-MRCC) [55, 56, 59] has been studied extensively as it combines rigorous size-extensivity with conceptual simplicity. Following several encouraging pilot applications [66–72], Mk-MRCC has been implemented into production-level codes within the singles and doubles approximation (Mk-MRCCSDD) [69, 73, 74] and within the singles, doubles, and triples approximation (Mk-MRCCSDT) [73, 75]. An implementation for use with arbitrary excitation levels and reference spaces has been reported as well [76]. However, it should be mentioned that Mk-MRCC is subject to a number of theoretical problems such as an unfavorable scaling with respect to the size of the reference space [69], convergence problems in the case of larger reference spaces [76, 77], and the lack of invariance of the energy with respect to rotations among active orbitals [69, 78, 79].

The calculation of molecular properties and excitation energies within MRCC theory has been considered several times. Analytic first-order properties, in particular gradients for the determination of molecular equilibrium structures, have been implemented for several MRCC approaches [73,74,80–82]. Electronic excitation energies have been studied within the context of VU-MRCC and SU-MRCC [83–87], but such applications suffer from the drawbacks of VU-MRCC and SU-MRCC discussed above. In the context of Mk-MRCC, analytic gradients have been implemented within the Mk-MRCCSD and Mk-MRCCSDT approximations for closed-shell systems [73, 74]. In addition, various static electric properties [88] have been studied in pilot applications by means of numerical differentiation. Furthermore, excitation energies have been targeted in an EOM-CC fashion starting from a Mk-MRCCSD wave function [89]. Most recently, spin-orbit splittings calculated within Mk-MRCC theory have been reported [90]. However, neither static nor dynamic second-order properties have yet been calculated analytically for any MRCC approach.

As indicated, this thesis extends CC theory's range of application in two ways. First, it makes a contribution to the analytic evaluation of third-order properties within single-reference CC theory. And second, it deals with the determination of first-order and second-order properties as well as excitation energies within Mk-MRCC theory. The thesis is structured as follows. In Chapter 2, the theoretical background relevant to the determination of molecular properties and excitation energies in single-reference and multireference CC theory is reviewed. This comprises two aspects, i.e., the discussion of the quantum-chemical methods and that of the corresponding analytic-derivative and response-theory techniques. In Chapter 3, the Mk-MRCCSD approach is applied to the determination of molecular equilibrium structures and adiabatic excitation energies of various small and medium-sized molecules. The performance of Mk-MRCCSD is examined by means of comparison to other multireference and single-reference CC methods. Chapter 4 deals with the application of response theory to the Mk-MRCC wave function. The Mk-MRCC linear-response function is derived and subsequently used to determine the static and dynamic polarizability tensors of several molecules with strong multireference character within the Mk-MRCCSD approximation. Moreover, the response formalism is employed to study vertical excitation spectra within the Mk-MRCC framework. In Chapter 5, the third derivative of the single-reference CC energy is derived and used for the fully analytic calculation of the dipole Hessian matrix. Furthermore, analytical and numerical differentiation schemes are compared with respect to their accuracy in some pilot applications. Chapter 6 finally summarizes the results obtained in this work and presents an outlook regarding future developments.

2. Theoretical Foundations

2.1. The Electronic Schrödinger Equation

Non-relativistic quantum chemistry is governed by the Schrödinger equation

$$\hat{\mathcal{H}} |\psi\rangle = \mathcal{E} |\psi\rangle$$
 . (2.1)

This is a partial differential eigenvalue equation for the Hamiltonian $\hat{\mathcal{H}}$ defined in the space spanned by the spatial coordinates of all electrons and nuclei, which yields the wave function $|\psi\rangle$ as eigenvector and the total energy \mathcal{E} as eigenvalue. The Hamiltonian for a chemical molecule can be expressed as

$$\hat{\mathcal{H}} = \underbrace{-\sum_{A} \left(\frac{1}{2M_{A}} \nabla_{A}^{2}\right)}_{\hat{T}_{n}} - \underbrace{\sum_{\alpha} \left(\frac{1}{2} \nabla_{\alpha}^{2}\right)}_{\hat{T}_{e}} + \underbrace{\sum_{A < B} \frac{Z_{A} Z_{B}}{|R_{A} - R_{B}|}}_{\hat{V}_{nn}} - \underbrace{\sum_{A \alpha} \frac{Z_{A}}{|R_{A} - r_{\alpha}|}}_{\hat{V}_{ne}} + \underbrace{\sum_{\alpha < \beta} \frac{1}{|r_{\alpha} - r_{\beta}|}}_{\hat{V}_{ee}}$$
(2.2)

using atomic units. In Eq. (2.2), the first two terms \hat{T}_n and \hat{T}_e represent the kinetic energy of the nuclei and the electrons, respectively, while the remaining three terms describe the Coulomb interaction of all particles, namely the nucleus-nucleus repulsion \hat{V}_{nn} , the nucleuselectron attraction \hat{V}_{ne} , and the electron-electron repulsion \hat{V}_{ee} . Z_A and Z_B denote the charges of nuclei A and B and M_A is the mass of nucleus A.

As already hydrogen, the lightest nucleus, is about 2000 times heavier than an electron, the Born-Oppenheimer approximation [91], consisting in the separation of $|\psi\rangle$ into a nuclear and an electronic component according to

$$|\psi(\{r\},\{R\})\rangle = |\Psi(\{r\},\{R\})\rangle \cdot |\Psi_n(\{R\})\rangle , \qquad (2.3)$$

can be applied to Eq. (2.1), which greatly reduces its dimensionality. In Eq. (2.3), the nuclear wave function $|\Psi_n\rangle$ only depends on the position of the nuclei, whereas the electronic wave function $|\Psi\rangle$ depends on the position of the electrons and on that of the nuclei, but on the latter only in a parametric fashion. The electronic wave function is determined through the electronic Schrödinger equation

$$\hat{H} |\Psi\rangle = \left(\hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}\right) |\Psi\rangle = \left[\sum_{\alpha} \underbrace{\left(-\frac{1}{2}\nabla_{\alpha}^2 - \sum_{A} \frac{Z_A}{R_{A\alpha}}\right)}_{\hat{h}(\alpha)} + \sum_{\alpha < \beta} \frac{1}{r_{\alpha\beta}}\right] |\Psi\rangle = E |\Psi\rangle \quad (2.4)$$

with $h(\alpha)$ as the one-electron Hamiltonian for electron α , E as the electronic energy, and $R_{A\alpha}$ and $r_{\alpha\beta}$ defined as $R_{A\alpha} = |R_A - r_{\alpha}|$ and $r_{\alpha\beta} = |r_{\alpha} - r_{\beta}|$, respectively. Eq. (2.4) forms the basis of electronic-structure theory. However, it can be solved exactly only for one-electron systems. Hence, the study of chemical molecules requires schemes for the approximate solution of Eq. (2.4). The following section introduces all methods relevant to the present work.

2.2. Quantum-Chemical Methods

2.2.1. Hartree-Fock Theory

From fundamental considerations [2] one can deduce that the wave function of a manyelectron system must change its sign upon interchanging two arbitrary electrons. This fact motivates Hartree-Fock (HF) theory, where $|\Psi\rangle$ is approximated by a Slater determinant, i.e., an antisymmetrized product of spin orbitals $\{\varphi_i\}$, which represent a subset of an infinite set of orthonormal spin orbitals $\{\varphi_p\}$. $\{\varphi_i\}$ is commonly referred to as the set of occupied spin orbitals, whereas the complement $\{\varphi_a\} = \{\varphi_p\} \setminus \{\varphi_i\}$ constitutes the set of virtual spin orbitals. In the following, the letters i, j, k, \ldots are used to label occupied orbitals, while a, b, c, \ldots and p, q, r, \ldots refer to virtual and generic orbitals, respectively.

The HF wave function for a system comprising N electrons reads

$$|\Psi_{\rm HF}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix} , \qquad (2.5)$$

where $\varphi_i(\alpha)$ stands for the *i*-th spin orbital depending on the spatial coordinates r_{α} and spin coordinates σ_{α} of electron α according to

$$\varphi_i(\alpha) = |i\rangle = \phi_i(r_\alpha) \cdot s_i(\sigma_\alpha) \tag{2.6}$$

with ϕ_i and s_i denoting spatial orbital and spin function, respectively. If the same spatial orbitals are chosen for α - and β -spin orbitals, one speaks of restricted HF (RHF) and otherwise of unrestricted HF (UHF). The energy is obtained as

$$E_{\rm HF} = \langle \Psi_{\rm HF} | \hat{H} | \Psi_{\rm HF} \rangle = \sum_{i}^{N} h_{ii} + \frac{1}{2} \sum_{ij}^{N} \langle ij | | ij \rangle \quad .$$
 (2.7)

In this equation, the one-electron integrals h_{ii} are given as $h_{ii} = \langle i | \hat{h} | i \rangle$ with \hat{h} as the oneelectron Hamiltonian defined in Eq. (2.4), while the antisymmetrized two-electron integrals $\langle ij||ij \rangle$ are given as $\langle ij||ij \rangle = \langle ij|ij \rangle - \langle ij|ji \rangle$ and a generic two-electron integral $\langle pq|rs \rangle$ can be calculated from

$$\langle pq|rs\rangle = \int dr_1 \int d\sigma_1 \int dr_2 \int d\sigma_2 \,\varphi_p^*(1) \,\varphi_q^*(2) \,\frac{1}{r_{12}} \,\varphi_r(1) \,\varphi_s(2) \,. \tag{2.8}$$

To determine the molecular orbitals $\{\varphi_p\}$, the variational principle is used. Hence, a Lagrangian L is constructed by augmenting the energy with a constraint taking account of the orthonormality condition. This yields

$$L = E - \sum_{ij} f_{ij} \left(\langle i|j \rangle - \delta_{ij} \right) = \sum_{i} h_{ii} + \frac{1}{2} \sum_{ij} \langle ij||ij \rangle - \sum_{ij} f_{ij} \left(\langle i|j \rangle - \delta_{ij} \right)$$
(2.9)

with f_{ij} as Lagrange multiplier. As $\{\varphi_p\}$ constitutes a complete orthonormal basis, a new set of spin orbitals can be generated via

$$\varphi'_p = \sum_q U_{qp} \,\varphi_q \,\,. \tag{2.10}$$

Using this parametrization, the variational conditions can be obtained by invoking stationarity of the energy with respect to the orbital-rotation parameters U_{qp} , i.e.,

$$\left(\frac{\partial E}{\partial U_{qp}}\right)_{\mathbf{U}=\mathbf{1}} = 0 \ \forall \ p, q \ . \tag{2.11}$$

The conditions $(\partial E/\partial U_{ai})_{\mathbf{U}=\mathbf{1}} = 0$ and $(\partial E/\partial U_{ia})_{\mathbf{U}=\mathbf{1}} = 0$ give rise to

$$f_{ai} = h_{ai} + \sum_{k} \langle ak | |ik\rangle = 0 . \qquad (2.12)$$

This equation for the virtual-occupied block of the Fock matrix \mathbf{f} is known as the Brillouin theorem and forms the starting point for the determination of the orbitals $\{\varphi_p\}$. In contrast, the occupied-occupied and the virtual-virtual block of the Fock matrix¹ are defined as

$$f_{ij} = h_{ij} + \sum_{k} \langle ik || jk \rangle \quad , \tag{2.13}$$

$$f_{ab} = h_{ab} + \sum_{k} \langle ak || bk \rangle \quad . \tag{2.14}$$

 f_{ij} and f_{ab} are often chosen diagonal as $f_{pq} = \delta_{pq} f_p$ can be interpreted as the energy of the orbital φ_p in this case. The resulting orbitals are called canonical HF orbitals. In actual calculations, the conditions for the Fock matrix are converted into a pseudo-eigenvalue equation, which is then solved using self-consistent field (SCF) techniques [92,93]. For this purpose, the orbitals are expanded in a basis of atomic orbitals (AOs) { χ_{μ} } according to

$$\varphi_p = \sum_{\mu} C_{\mu p} \,\chi_\mu \tag{2.15}$$

with the molecular orbital (MO) coefficients $C_{\mu p}$ as expansion coefficients. Further simplifications to all equations presented in this section are possible when carrying out spin integration [2]. However, for the sake of consistency, the spin-orbital formalism is kept throughout the present work.

2.2.2. Electron Correlation

HF theory is a theory of independent particles, i.e., the Coulomb interaction between the electrons is described only in a mean-field manner and $|\Psi_{\rm HF}\rangle$ does not depend on the interelectronic distances $r_{\alpha\beta}$. In reality, however, the motion of the electrons is correlated and $|\Psi\rangle$ depends on $r_{\alpha\beta}$. The resulting difference between the HF energy and the exact non-relativistic energy from Eq. (2.4) defines the correlation energy $E_{\rm corr}$ as

$$E_{\rm corr} = E - E_{\rm HF} \ . \tag{2.16}$$

Although E_{corr} usually is a small number not exceeding a few per mille of the total energy for typical chemical systems, the impact of electron correlation on chemistry is substantial and HF theory often leads to qualitatively wrong results [2,20]. A straightforward way to improve upon HF theory consists in using a linear combination of Slater determinants as ansatz for the wave function $|\Psi\rangle$. This is formally justified by the fact that the set of all Slater determinants

¹The stationarity with respect to U_{ij} yields $f_{ij} - f_{ji} = 0$, which does not suffice to determine the corresponding Fock-matrix elements. The stationarity with respect to U_{ab} yields a trivial result as $E_{\rm HF}$ does not depend on the virtual spin orbitals.

 $\{\Phi_q\}$, which can be constructed from the orbitals $\{\varphi_p\}$, forms a complete many-particle basis. Hence, the full configuration-interaction (FCI) wave function

$$|\Psi_{\rm FCI}\rangle = \sum_{q} c_q |\Phi_q\rangle \quad , \tag{2.17}$$

where the coefficients c_q are determined using the variational principle, represents the exact solution to the electronic Schrödinger equation (Eq. (2.4)). Yet, the routine use of $|\Psi_{\text{FCI}}\rangle$ is beyond the reach of state-of-the-art computational facilities. As a consequence, truncations must be applied to Eq. (2.17) in order to include only determinants with a non-negligible weight c_q .

For the further discussion, it is advantageous to partition the correlation energy into a dynamic and a non-dynamic contribution. In many cases, one determinant $|\Phi_0\rangle$ delivers by far the most important contribution to $|\Psi_{\text{FCI}}\rangle$, i.e., $c_0 \gg c_q \forall q \neq 0$. All further determinants thus represent only small corrections to $|\Phi_0\rangle$ capturing dynamic electron correlation, i.e., effects resulting from the instantaneous repulsion of two electrons. HF theory represents a valid starting point for such cases and perturbative arguments can be applied to identify determinants to be included in the wave function. Methods to treat dynamic electron correlation include configuration-interaction (CI) approaches [94,95], Møller-Plesset (MP) perturbation theory [96], and coupled-cluster (CC) theory [17, 18], the latter two of which are introduced in Sections 2.2.4 and 2.2.5, respectively.

Non-dynamic electron correlation is present whenever more than one determinant delivers a considerable contribution to $|\Psi_{\rm FCI}\rangle$. This can occur due to spin or spatial symmetry, in which case certain coefficients c_q become equal up to a sign, but also in an arbitrary manner triggered just by the electronic structure of the system.² In particular, many systems of chemical interest like organic biradicals or transition-metal compounds possess an electronic structure where a number of determinants are quasidegenerate. For such multireference cases, the use of $|\Psi_{\rm HF}\rangle$ as zeroth-order approximation is not recommendable. Instead, a linear combination of several determinants should be employed.

2.2.3. Multiconfigurational Self-Consistent Field Theories

The multiconfigurational self-consistent field (MCSCF) wave function reads

$$|\Psi_{\rm MCSCF}\rangle = \sum_{\mu} c_{\mu} |\Phi_{\mu}\rangle \tag{2.18}$$

with the CI coefficients c_{μ} and the orbitals in $|\Phi_{\mu}\rangle$ as parameters to be determined [97,98]. The sum over μ comprises just the most important determinants. A common way to specify these "important" determinants relies on the idea of an active space constructed by distributing active electrons in a set of active orbitals. The latter comprises all orbitals that can be either occupied or virtual for different determinants $|\Phi_{\mu}\rangle$. If the active space comprises all determinants that arise from distributing m active electrons among n active orbitals, it is called a complete active space CAS(m, n).

The selection of active orbitals and active electrons is not straightforward, but requires a detailed analysis of the system under consideration. However, a multitude of multireference cases can already be correctly approximated by a MCSCF wave function based on a CAS(2,2). Such cases arise for example when stretching a single bond or in biradical systems, whose electronic structure is governed by a pair of energetically close frontier orbitals. In general, a

 $^{^{2}}$ A further distinction between non-dynamic and static correlation has sometimes been made [34]. However, these terms are used interchangeably in the present work.



Figure 2.1.: Determinants in a CAS(2,2) with active orbitals s and t.

CAS(2,2) includes the four determinants displayed in Figure 2.1, from which four electronic states can be constructed, namely one triplet state, one open-shell singlet state and two closed-shell states. If the active orbitals s and t transform under different irreducible representations, open-shell and closed-shell states are decoupled.

Hence, a suitable ansatz for the closed-shell states is the two-configurational SCF (TCSCF) wave function [99], which is given as

$$|\Psi_{\text{TCSCF}}\rangle = c_t |\Phi_1^{\text{cs}}\rangle + c_s |\Phi_2^{\text{cs}}\rangle = c_t |(\text{core})^2 \phi_t \overline{\phi}_t\rangle + c_s |(\text{core})^2 \phi_s \overline{\phi}_s\rangle$$
(2.19)

with ϕ_t and $\overline{\phi}_t$ referring to α and β spin orbitals. In analogy to Eq. (2.7), the energy is determined as

$$E_{\text{TCSCF}} = \langle \Psi_{\text{TCSCF}} | \hat{H} | \Psi_{\text{TCSCF}} \rangle$$

$$= c_t^2 \left[\sum_i^t h_{ii} + \frac{1}{2} \sum_{ij}^t \langle ij | | ij \rangle \right] + c_s^2 \left[\sum_i^s h_{ii} + \frac{1}{2} \sum_{ij}^s \langle ij | | ij \rangle \right] + c_t c_s \langle tt | ss \rangle ,$$

$$(2.20)$$

where the labels t and s adjacent to the summation symbol indicate that the sum includes the respective active orbital. The TCSCF orbitals and the CI coefficients c_t and c_s are obtained from the stationarity conditions for a suitable Lagrangian. As in HF theory, this includes as constraint the orthonormality of the orbitals, but in addition to that also the normalization of the CI vector. Explicit expressions for the TCSCF variational conditions have been presented, for example, in Ref. 100.

The open-shell states can be described with a special flavor of restricted open-shell HF (ROHF) theory [101] using the ansatz

$$|\Psi_{\rm ROHF}\rangle = c_t |\Phi_1^{\rm os}\rangle + c_s |\Phi_2^{\rm os}\rangle = \frac{1}{\sqrt{2}} \Big(|(\rm core)^2 \phi_t \overline{\phi}_s\rangle \pm |(\rm core)^2 \overline{\phi}_t \phi_s\rangle \Big) , \qquad (2.21)$$

where the coefficients c_t and c_s assume for symmetry reasons fixed values of $c_t = 1/\sqrt{2}$ and $c_s = \pm 1/\sqrt{2}$ and the plus and the minus sign refer to the $M_s = 0$ component of the triplet state and the singlet state, respectively. The energy is obtained as

$$E_{\rm ROHF} = \langle \Psi_{\rm ROHF} | \hat{H} | \Psi_{\rm ROHF} \rangle = \sum_{i}^{t,s} h_{ii} + \frac{1}{2} \sum_{ij}^{t,s} \langle ij | |ij\rangle \mp \langle tt | ss \rangle$$
(2.22)

with the label t,s indicating that the summation includes the two singly occupied orbitals tand s. Augmenting this expression with the orthonormality constraint for the orbitals leads to the ROHF Lagrangian, from which the ROHF variational conditions can be determined through stationarity conditions for orbital rotations. This gives rise to

$$f_{ai} = 0$$
 (virtual-occupied block), (2.23)

$$f_{at} - \frac{1}{2} \langle at|tt \rangle + \frac{1}{2} \langle as|st \rangle \mp \langle as|st \rangle \equiv 0 \quad \text{(virtual-active block)} , \qquad (2.24)$$

$$f_{ti} + \frac{1}{2} \langle tt|ti \rangle - \frac{1}{2} \langle ts|si \rangle \pm \langle ts|si \rangle = 0 \quad \text{(active-occupied block)}, \qquad (2.25)$$

 $\langle tt|ts \rangle - \langle ts|ss \rangle = 0$ (active-active block), (2.26)

where the Fock-matrix elements f_{ai} , f_{at} , and f_{ti} are defined in analogy to Section 2.2.1 and f_{as} as well as f_{si} can be constructed by replacing t by s. All remaining blocks of **f** can be chosen arbitrarily.³

If the active orbitals s and t in a CAS(2,2) transform under the same irreducible representation, all four determinants from Figure 2.1 are coupled. It is still possible to decouple the triplet state from the singlets, yet the distinction between open-shell and closed-shell singlet states becomes meaningless. However, Eqs. (2.19) and (2.21) both represent a valid ansatz in this case as the energy is invariant with respect to rotations among the active orbitals.

2.2.4. Møller-Plesset Perturbation Theory

A conceptually simple approach for the treatment of dynamical electron correlation is Møller-Plesset (MP) perturbation theory [2,96]. In the MP framework, the electronic Hamiltonian from Eq. (2.4) is partitioned as

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \tag{2.27}$$

with λ as the perturbation parameter. \hat{H}_0 is a mean-field operator chosen as

$$\hat{H}_0 = \sum_{\alpha} \hat{f}(\alpha) , \qquad (2.28)$$

where $\hat{f}(\alpha)$ is the Fock operator for electron α , which is defined through its elements in Eqs. (2.12), (2.13), and (2.14). Electron correlation is introduced via \hat{H}' , which is given as

$$\hat{H}' = \hat{H} - \hat{H}_0 . (2.29)$$

In MP perturbation theory, Eq. (2.27) is plugged into the Schrödinger equation, while the eigenstates and eigenvalues of \hat{H} are expanded into a power series in terms of λ . The resulting equation needs to be satisfied in each order of perturbation separately and can hence be split up. In first order of λ , the expression for the HF energy is recovered, whereas the second-order energy expression becomes

$$E^{(2)} = \sum_{n \neq 0} \frac{|\langle \Psi_n^{(0)} | \hat{H}' | \Psi_0^{(0)} \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$
(2.30)

with $|\Psi_n^{(0)}\rangle$ and $E_n^{(0)}$ denoting the *n*-th eigenstate and eigenvalue of \hat{H}_0 . Evaluation of Eq. (2.30) yields for canonical HF orbitals

$$E_{\rm MP2} = \frac{1}{4} \sum_{ijab} \frac{|\langle ij||ab\rangle|^2}{f_{ii} + f_{jj} - f_{aa} - f_{bb}} .$$
(2.31)

2.2.5. Coupled-Cluster Theory

Coupled-cluster (CC) theory [17–20] represents today's method of choice for the treatment of dynamical electron correlation. The CC ansatz for the wave function is

$$|\Psi_{\rm CC}\rangle = e^T |\Psi_0\rangle \quad , \tag{2.32}$$

³The variational condition for the active-active block is of importance for the singlet state only, for the triplet state this element of \mathbf{f} is also arbitrary.

where $|\Psi_0\rangle$ denotes the reference wave function, a single Slater determinant, which is usually chosen as the HF wave function. The cluster operator \hat{T} is given as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_n = \sum_q \hat{\tau}_q t_q .$$
 (2.33)

It consists of single (\hat{T}_1) , double (\hat{T}_2) , up to *n*-tuple (\hat{T}_n) excitations with the individual excitation operators $\hat{\tau}_q$ being defined via

$$\hat{\tau}_q = \dots \hat{a}_b^\dagger \hat{a}_j \hat{a}_a^\dagger \hat{a}_i , \qquad (2.34)$$

where \hat{a}^{\dagger} and \hat{a} denote creation and annihilation operators, respectively. The energy is obtained by projecting the Schrödinger equation on the reference state, which yields

$$E_{\rm CC} = \langle \Psi_0 | \hat{H} e^{\hat{T}} | \Psi_0 \rangle = \langle \Psi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle \quad .$$
 (2.35)

The amplitudes t_q are determined through projection of the Schrödinger equation onto the set of excited determinants $\langle \Phi_q | = \langle \Psi_0 | \hat{\tau}_q^{\dagger}$. This gives rise to the CC equations

$$0 = \langle \Phi_q | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle \quad . \tag{2.36}$$

Computationally tractable expressions are obtained from this set of non-linear equations by applying the Baker-Campbell-Hausdorff formula [1] to the similarity-transformed Hamiltonian $\overline{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$ followed by the use of Wick's theorem [19] or diagrammatic techniques [20]. If the complete set $\{\Phi_q\}$ of excited determinants is considered, $|\Psi_{CC}\rangle$ represents an alternative parametrization of the FCI wave function from Eq. (2.17). However, the success of CC theory results from the appealing features of truncated schemes like CC singles and doubles (CCSD) [21] or CC singles, doubles, and triples (CCSDT) [102], which represent a clear hierarchy of methods. The exponential ansatz ensures rigorous size-extensivity of the energy regardless of the truncation applied to \hat{T} [20]. In contrast, the analogous hierarchy of truncated CI methods, which employs a linear parametrization, does not yield size-extensive energies, i.e., the correlation energy does not scale properly with the size of the system [20].

Since \hat{H} contains pair interactions at most, only \hat{T}_2 contributes to the wave function at first order of perturbation theory, whereas at second order \hat{T}_1 and \hat{T}_3 appear. Hence, a wave function correct to second order requires taking account of \hat{T}_3 . As the full CCSDT method is computationally demanding, a number of approximate schemes have been developed, which seek to capture the effect of \hat{T}_3 in a perturbative manner. Among these, the CCSD(T) method [22] is used most often and has been termed the "gold standard of quantum chemistry" [34] for its high accuracy.

2.2.6. Multireference Coupled-Cluster Theory

A multitude of methods for the treatment of quasidegenerate systems with chemical accuracy has been proposed, but a truly convincing method, warranting a balanced description of dynamic and non-dynamic electron correlation, has not been presented yet. Most methods rely on the MCSCF wave function (Eq. (2.18)) as starting point and aim at adding dynamic electron correlation on top of it. Since the generalization of the CI approach to the multireference case is straightforward [103], several methods have been formulated within this context, which typically seek to correct the size-extensivity error of the parent multireference cI (MRCI) ansatz in an approximate manner. This includes a posteriori corrections to

the MRCI wave function [104, 105], but also the multireference averaged coupled-pair functional (MR-ACPF) method [36] and the multireference averaged quadratic coupled-cluster (MR-AQCC) method [37].

However, genuine multireference CC (MRCC) methods have also been developed [34,35,46–55,57,58,60,61,65], yet the generalization of CC theory to the multireference case is not obvious. Jeziorski and Monkhorst [50] devised the ansatz

$$|\Psi_{\rm JM}\rangle = \sum_{\mu=1}^{d} e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu}$$
(2.37)

with c_{μ} as weighting coefficients and the reference determinants $|\Phi_{\mu}\rangle$ forming a model space of dimension *d*. If the model space is a CAS, it is also called a complete model space (CMS). The cluster operators are defined as

$$\hat{T}_{\mu} = \sum_{q \in Q(\mu)} t_{q}^{\mu} \hat{\tau}_{q}^{\mu} , \qquad (2.38)$$

where $Q(\mu)$ denotes a reference-specific excitation manifold. Since \hat{T}_{μ} is a pure excitation operator, the methodology from single-reference CC theory can be used to evaluate all expressions that arise from applying \hat{H} to Eq. (2.37). Internal excitations, which create one reference determinant from another, are excluded from \hat{T}_{μ} to avoid redundancy in the wave function and to ensure intermediate normalization, i.e., $\langle \Psi_0 | \Psi \rangle = 1.^4$ The energy can then be obtained by inserting Eq. (2.37) into the Schrödinger equation followed by projection onto the model space. This yields the eigenvalue equation

$$\sum_{\nu} H^{\text{eff}}_{\mu\nu} c_{\nu} = E c_{\mu} , \qquad (2.39)$$

where the effective Hamiltonian is defined as

$$H_{\mu\nu}^{\text{eff}} = \langle \Phi_{\mu} | \hat{H} e^{\hat{T}_{\nu}} | \Phi_{\nu} \rangle \stackrel{\text{CMS}}{=} \langle \Phi_{\mu} | e^{-\hat{T}_{\nu}} \hat{H} e^{\hat{T}_{\nu}} | \Phi_{\nu} \rangle = \langle \Phi_{\mu} | \overline{H}_{\nu} | \Phi_{\nu} \rangle .$$
(2.40)

In Eq. (2.40), the second equality holds for a complete model space only. To obtain the cluster amplitudes, one cannot proceed in analogy to single-reference CC theory (cf. Eq. (2.36)) as the cluster amplitudes are underdetermined by the set of equations

$$\sum_{\mu} \left\langle \Phi_q \right| \left(\hat{H} - E \right) e^{\hat{T}_{\mu}} \left| \Phi_{\mu} \right\rangle c_{\mu} = 0 , \qquad (2.41)$$

which results from straightforward projection on the excited determinants. This problem arises from a redundancy intrinsic to the Jeziorski-Monkhorst ansatz: A generic excited determinant $|\Phi_q\rangle$ can be reached starting from different reference determinants according to $\hat{\tau}_p^{\mu} |\Phi_{\mu}\rangle = \hat{\tau}_q^{\nu} |\Phi_{\nu}\rangle$ as pictured in Figure 2.2. Hence, both the amplitude associated with $\hat{\tau}_p^{\mu}$ and the amplitude associated with $\hat{\tau}_q^{\nu}$ would need to be determined from the projection on $\langle \Phi_q |$, which is impossible.

Several ideas have been suggested to resolve this problem. In the original state-universal (SU) formulation of MRCC theory by Jeziorski and Monkhorst [50], no redundancy is encountered since the Schrödinger equation is solved for d states at the same time. The solution of Eq. (2.39) then yields energies for d electronic states. However, the applicability of SU-MRCC theory is limited by the intruder-state problem [20]: The SU-MRCC amplitude equations are

⁴This only holds for a complete model space, which is assumed here and in the following.



Figure 2.2.: Redundancy in the Jeziorski-Monkhorst ansatz: The excitations $\hat{\tau}_i^a(1)$ and $\hat{\tau}_{ij}^{ab}(2)$ give rise to the same excited determinant.

ill-defined whenever the energy difference between a reference determinant and an excited determinant becomes small. Actual calculations thus suffer from convergence problems. To avoid intruder states in the context of SU-MRCC theory, the use of incomplete model spaces has been advocated [53,83,106,107]. Yet, in addition to the intruder-state problem, the need to solve for d states at a time is another drawback of SU-MRCC theory.

If Eq. (2.37) is employed in a state-specific (SS) variant of MRCC theory [35], intruder states are avoided straight from the beginning as the Schrödinger equation is solved for only one electronic state. Hence, just one eigenvalue of the effective Hamiltonian is physically meaningful. To counteract the redundancy in Eq. (2.37), sufficiency conditions need to be introduced to allow for the unique determination of the cluster amplitudes [108]. One option consists in assigning the same value to amplitudes that are associated with excitations that give rise to the same excited determinant. This strategy is, for example, followed in MRexpT theory [57], yet the resulting scheme is not fully size-extensive.

A rigorously size-extensive theory (Mk-MRCC) is obtained when using the sufficiency conditions suggested by Mukherjee and coworkers [55, 56, 59]. In Mk-MRCC theory, the resolution of the identity in the form

$$1 = e^{\hat{T}_{\mu}} \left(\hat{P} + \hat{Q} \right) e^{-\hat{T}_{\mu}} = e^{\hat{T}_{\mu}} \left[\sum_{\nu} \left| \Phi_{\nu} \right\rangle \left\langle \Phi_{\nu} \right| + \sum_{q} \left| \Phi_{q} \right\rangle \left\langle \Phi_{q} \right| \right] e^{-\hat{T}_{\mu}}$$
(2.42)

is inserted into the Schrödinger equation

$$\sum_{\mu} \left[\hat{H} e^{\hat{T}_{\mu}} \left| \Phi_{\mu} \right\rangle c_{\mu} - E e^{\hat{T}_{\mu}} \left| \Phi_{\mu} \right\rangle c_{\mu} \right] = 0$$
(2.43)

in front of the Hamiltonian. This yields

$$\sum_{\mu} \left[e^{\hat{T}_{\mu}} \hat{Q} e^{-\hat{T}_{\mu}} \hat{H} e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu} + \sum_{\nu} e^{\hat{T}_{\mu}} |\Phi_{\nu}\rangle H_{\nu\mu}^{\text{eff}} c_{\mu} - E e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu} \right] = 0 .$$
 (2.44)

Interchanging the summation indices μ and ν in the second term leads to

$$\sum_{\mu} \left[e^{\hat{T}_{\mu}} \hat{Q} e^{-\hat{T}_{\mu}} \hat{H} e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu} + \sum_{\nu} e^{\hat{T}_{\nu}} |\Phi_{\mu}\rangle H^{\text{eff}}_{\mu\nu} c_{\nu} - E e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu} \right] = 0 .$$
 (2.45)

The Mk-MRCC sufficiency conditions consist in setting individual terms in the summation over μ in Eq. (2.45) equal to zero, which gives rise to

$$e^{\hat{T}_{\mu}}\hat{Q}e^{-\hat{T}_{\mu}}\hat{H}e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu} + \sum_{\nu} e^{\hat{T}_{\nu}} |\Phi_{\mu}\rangle H^{\text{eff}}_{\mu\nu}c_{\nu} - Ee^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu} = 0 .$$
(2.46)

Multiplication of this equation from the left by $e^{-\hat{T}_{\mu}}$ and subsequent projection onto excited determinants leads to the Mk-MRCC amplitude equations, which read

$$\langle \Phi^{\mu}_{q} | e^{-\hat{T}_{\mu}} \hat{H} e^{\hat{T}_{\mu}} | \Phi_{\mu} \rangle c_{\mu} + \sum_{\nu \neq \mu} \langle \Phi^{\mu}_{q} | e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} | \Phi_{\mu} \rangle H^{\text{eff}}_{\mu\nu} c_{\nu} = 0 . \qquad (2.47)$$

In this equation, $|\Phi_q^{\mu}\rangle$ is used instead of $|\Phi_q\rangle$ to emphasize that the excitation manifold explicitly depends on the reference determinant. As indicated above, Mukherjee and coworkers have given a proof that Eq. (2.47) is size-extensive regardless of the truncation applied to \hat{T}_{μ} [56]. Furthermore, it has been demonstrated that the solution of Eq. (2.47) yields the FCI wave function when the cluster operators are left untruncated. However, the Mk-MRCC method suffers from two formal deficiencies. First, the Mk-MRCC wave function does not fulfill the projected Schrödinger equation (Eq. (2.41)) as soon as the excitation manifolds spanned by different cluster operators do not completely overlap [34, 57, 108], i.e.,

$$\sum_{\mu} \langle \Phi_q | \left(\hat{H} - E \right) e^{\hat{T}_{\mu}} | \Phi_{\mu} \rangle c_{\mu} \neq 0 \quad \forall q \in Q \backslash \cap_{\mu} Q_{\mu} .$$
(2.48)

This is the case when truncating \hat{T}_{μ} according to standard schemes like Mk-MRCCSD or Mk-MRCCSDT. A straightforward solution to this problem is to explicitly choose the excitation manifolds in such a way that a complete overlap is ensured [79]. However, this comes at the price of increased computational cost. As a second drawback, the Mk-MRCC energy and hence all molecular properties computed with Mk-MRCC are not invariant with respect to rotations among the active orbitals [78,79]. While it has been demonstrated that the use of localized orbitals in general leads to superior results [109], there currently exists no MRCC scheme, which employs the Jeziorski-Monkhorst ansatz and is orbital invariant at the same time. From the perspective of implementation, a particular advantage of Eq. (2.47) is that it consists of a single-reference CC term and an additional coupling term. The first term in Eq. (2.47) equals Eq. (2.36) and is thus available from a single-reference CC code. The second term couples references $|\Phi_{\mu}\rangle$ and $|\Phi_{\nu}\rangle$, but has been shown to be easily evaluable. Explicit expressions for the coupling terms are available from the literature for Mk-MRCCSD [69] and Mk-MRCCSDT [70]. An implementation for use with arbitrary excitation levels has been achieved by means of string-based techniques [76].

2.3. Treatment of Molecular Properties and Excitation Energies

2.3.1. Molecular Properties as Energy Derivatives

Many molecular properties can be calculated as derivatives of the energy with respect to appropriate perturbation parameters χ_1, χ_2, \ldots [3,4]. This relies on the idea that the dependence of the energy on $\{\chi\}$ can be expressed through a Taylor expansion

$$E\left(\{\chi\}\right) = E(0) + \sum_{i} \chi_{i} \left(\frac{dE}{d\chi_{i}}\right)_{\chi_{i}=0} + \frac{1}{2} \sum_{ij} \chi_{i}\chi_{j} \left(\frac{d^{2}E}{d\chi_{i}d\chi_{j}}\right)_{\chi_{i}=0,\chi_{j}=0} + \dots$$
(2.49)

if the perturbations are sufficiently small. In the present work, two types of perturbations are of importance, namely electric fields and nuclear displacements.

Static electrical properties [4, 110] can be determined starting from the Hamiltonian in the presence of an electric field, which reads

$$\hat{H} = \hat{H}_0 - \sum_i \varepsilon_i \cdot \hat{\mu}_i \tag{2.50}$$

with \hat{H}_0 as the unperturbed Hamiltonian defined in Eq. (2.4) and $\hat{\mu}_i$ and ε_i denoting the components of the dipole operator and an external electric field, respectively. Taking the first derivative of the energy with respect to ε_i yields the corresponding component of the dipole moment μ_i . The elements of the static polarizability tensor $\boldsymbol{\alpha}$, which is studied in Chapter 4 based on the Mk-MRCC wave function, can be obtained as second derivatives of the energy, i.e.,

$$\alpha_{ij} = -\left(\frac{d^2 E}{d\varepsilon_i d\varepsilon_j}\right)_{\varepsilon_i, \varepsilon_j = 0} \,. \tag{2.51}$$

To determine equilibrium structures (cf. Chapter 3), minima on the potential hypersurface need to be located [28]. For this purpose, the first derivatives of the energy with respect to nuclear displacements $\{x\}$ are evaluated, which yields the forces acting on the nuclei. At a stationary point, this energy gradient vanishes. It should be noted that the Hamiltonian from Eq. (2.4) is a suitable starting point when studying geometrical properties such as equilibrium structures since the nuclear displacements $\{x\}$ do not represent external perturbations, rather the Hamiltonian intrinsically depends on them.

Energy derivatives can be calculated using either analytical or numerical differentiation schemes. Numerical differentiation is conceptually simpler as it only requires the computation of the energy in the presence of perturbations of different strength. For a generic first derivative, this yields

$$\left(\frac{dE}{d\chi}\right)_{\chi=0} = \frac{E(\Delta\chi) - E(-\Delta\chi)}{2\Delta\chi} \ . \tag{2.52}$$

Corresponding expressions for higher derivatives are available from the literature [111], but are also presented in Section 5.3. Such formulas can be easily implemented, yet the resulting schemes suffer from two drawbacks. First, their accuracy is limited, which is problematic especially if more than one differentiation step is carried out numerically, and second, the computational cost is higher than that of the corresponding analytical schemes. For example, the evaluation of the gradient according to Eq. (2.52) requires to compute the energy and the wave function 6N times with N as the number of nuclei. In contrast, the analytic approach involves only one calculation of the energy and the wave function. Hence, analyticderivative techniques [8–10] are in general superior to numerical differentiation even though their theoretical formulation and implementation is more demanding. In the context of the present work, numerical differentiation plays an important role as it has been used for the verification of all newly implemented analytic-derivative schemes.

2.3.2. Analytic Derivatives for Self-Consistent Field Wave Functions

If the energy is determined using the variational principle as done in HF and MCSCF theory, the respective Lagrangian (Eq. (2.9) for HF theory) can be used as starting point for the calculation of derivatives of the energy as no further constraints need to be taken into account. For the wave-function parameters, i.e., the coefficients $C_{\mu p}$, the (2n + 1) rule of derivative theory holds, which means that the *n*-th derivative of the wave function is sufficient for the calculation of the (2n + 1)-th derivative of the energy [112]. For the Lagrange multipliers, a (2n + 2) rule holds, which is defined in a similar manner [112]. As a consequence, the first derivative of the HF energy can be obtained from Eq. (2.9) by the replacements $h_{pq} \rightarrow h_{pq}^{\chi}$, $\langle pq|rs \rangle \rightarrow \langle pq|rs \rangle^{\chi}$, and $\langle p|q \rangle \rightarrow \langle p|q \rangle^{\chi} \equiv S_{pq}^{\chi}$, where quantities with the superscript χ represent derivatives of the AO integrals rotated into the MO basis [7]. Similar formulas are obtained for MCSCF wave functions and have been discussed in detail in the literature [113]. However, the second derivative of the SCF energy as well as all higher derivatives require the first derivative of the SCF wave function. Likewise, these contributions are needed in CC derivative theory as the CC energy is not variational with respect to the SCF wavefunction parameters. Taking the derivative of a generic orbital φ_p with respect to an arbitrary perturbation χ yields

$$\frac{d\varphi_p(\chi)}{d\chi} = \sum_{\mu} \left[C_{\mu p} \, \frac{d\chi_{\mu}}{d\chi} + \frac{dC_{\mu p}}{d\chi} \, \chi_{\mu} \right] \,, \tag{2.53}$$

where the first term delivers a contribution to the integral derivatives and the second term represents the dependence of the MO coefficients on the perturbation, which is unknown at first. To determine the latter contribution, it is reparametrized following Ref. 7 as

$$\frac{dC_{\mu p}(\chi)}{d\chi} = \frac{d}{d\chi} \left[\sum_{q} U_{qp} C_{\mu q}(\chi = 0) \right] = \sum_{q} \frac{dU_{qp}(\chi)}{d\chi} C_{\mu q} = \sum_{q} U_{qp}^{\chi} C_{\mu q}$$
(2.54)

with U_{qp}^{χ} as the so-called coupled-perturbed HF (CPHF) coefficients. This allows to rewrite the derivative of φ_p as

$$\frac{d\varphi_p}{d\chi} = \varphi_p^{\chi} + \sum_q U_{qp}^{\chi} \varphi_q \ . \tag{2.55}$$

For the perturbations considered in this work, i.e., electric-field components and nuclear displacements, all CPHF coefficients U_{pq}^{χ} with pq referring to a redundant orbital rotation can be obtained by differentiating the orthonormality constraint, which leads to

$$U_{pq}^{\chi} + U_{qp}^{\chi} + S_{pq}^{\chi} = 0 . (2.56)$$

For redundant orbital rotations, U_{pq}^{χ} can be chosen as

$$U_{pq}^{\chi} = U_{qp}^{\chi} = -\frac{1}{2}S_{pq}^{\chi} .$$
 (2.57)

Yet, for the determination of those CPHF coefficients where pq refers to a non-redundant orbital rotation, a system of linear equations needs to be solved. These CPHF equations [5,7] are obtained by differentiating the SCF variational conditions with respect to χ . In the case of HF theory, they read

$$\sum_{bj} A_{aibj} U^{\chi}_{bj} = B^{\chi}_{ai} \tag{2.58}$$

with the matrix **A** and the vector \mathbf{B}^{χ} defined as

$$A_{aibj} = \delta_{ij} f_{ab} - \delta_{ab} f_{ij} + \langle ab || ij \rangle + \langle aj || ib \rangle , \qquad (2.59)$$

$$B_{ai}^{\chi} = -f_{ai}^{(\chi)} + \sum_{j} S_{aj}^{\chi} f_{ij} + \sum_{jk} S_{jk}^{\chi} \langle aj || ik \rangle \quad , \tag{2.60}$$

and the partial derivative of the Fock matrix $f_{pq}^{(\chi)}$ given by

$$f_{pq}^{(\chi)} = h_{pq}^{\chi} + \sum_{j} \langle pj || qj \rangle^{\chi} \quad .$$

$$(2.61)$$

For a TCSCF wave function, a two-componential equation needs to be solved [114], from which the non-redundant coupled-perturbed TCSCF coefficients U_{pq}^{χ} and the derivatives of the CI coefficients are obtained simultaneously. Explicit expressions can be found, for example, in Ref. 100. For the ROHF wave function from Eq. (2.21), the resulting system of linear equations [115] can be schematically written as

$$\sum_{rs} A_{pqrs} U_{rs}^{\chi} = B_{pq}^{\chi}$$
(2.62)

with all index combinations pq and rs referring to non-redundant orbital rotations as defined in Eqs. (2.23) to (2.26). Detailed expressions for A_{pqrs} and B_{pq}^{χ} in the context of ROHF theory are presented in Section 3.1.

2.3.3. Analytic Gradients in Mk-MRCC Theory

As the Mk-MRCC wave function is determined in a non-variational manner, an appropriate Lagrangian [80, 112, 116] must be set up as the first step for the derivation of an expression for the first derivative of the Mk-MRCC energy. This Lagrangian is then made stationary with respect to all parameters involved. Following Ref. 74, the Mk-MRCC Lagrangian is given by

$$L = E + \sum_{\mu} \bar{c}_{\mu} \Big[\sum_{\nu} H_{\mu\nu}^{\text{eff}} c_{\nu} - E c_{\mu} \Big]$$

$$+ \sum_{\mu} \sum_{q \in Q(\mu)} \bar{c}_{\mu} \lambda_{q}^{\mu} \Big[\langle \Phi_{q}^{\mu} | \overline{H}_{\mu} | \Phi_{\mu} \rangle c_{\mu} + \sum_{\nu \neq \mu} \langle \Phi_{q}^{\mu} | e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} | \Phi_{\mu} \rangle H_{\mu\nu}^{\text{eff}} c_{\nu} \Big] ,$$

$$(2.63)$$

where \bar{c}_{μ} and λ_q^{μ} represent Lagrange multipliers corresponding to the constraints arising from Eqs. (2.39) and (2.47). Using the deexcitation operator $\hat{\Lambda}_{\mu}$ defined via

$$\hat{\Lambda}_{\mu} = \hat{\Lambda}_{\mu}^{\text{ext}} + \hat{\Lambda}_{\mu}^{\text{int}} , \qquad (2.64)$$

$$\hat{\Lambda}^{\text{ext}}_{\mu} = \sum_{q \in Q(\mu)} \hat{\tau}^{\mu\dagger}_q \lambda^{\mu}_q , \qquad (2.65)$$

$$\hat{\Lambda}^{\text{int}}_{\mu} = \sum_{\nu \neq \mu} \frac{\bar{c}_{\nu}}{\bar{c}_{\mu}} \left[1 + \sum_{q \in Q(\nu)} \lambda^{\nu}_{q} \langle \Phi^{\nu}_{q} | e^{-\hat{T}_{\nu}} e^{\hat{T}_{\mu}} | \Phi_{\nu} \rangle \right] | \Phi_{\mu} \rangle \langle \Phi_{\nu} | , \qquad (2.66)$$

the Lagrangian can be rewritten in a more compact form as

$$L = \sum_{\mu} \bar{c}_{\mu} c_{\mu} \langle \Phi_{\mu} | \left(1 + \hat{\Lambda}_{\mu} \right) \overline{H}_{\mu} | \Phi_{\mu} \rangle - \epsilon \left[\sum_{\mu} \bar{c}_{\mu} c_{\mu} - 1 \right], \qquad (2.67)$$

where the biorthonormality condition

$$\sum_{\mu} \bar{c}_{\mu} c_{\mu} = 1 \tag{2.68}$$

has been imposed as an additional constraint with corresponding Lagrange multiplier ϵ . While it is easy to identify the latter parameter as the energy, the Lagrange multipliers \bar{c}_{μ} and λ_{q}^{μ} need to be determined through additional sets of equations, which are obtained from the stationary conditions of L with respect to the CI coefficients c_{μ} and the amplitudes t_{q}^{μ} , respectively [74]. Once the Lagrange multipliers are determined, the first derivative of the Mk-MRCC energy can be calculated as

$$\frac{dE}{dx} = \frac{\partial L}{\partial x} = \sum_{\mu} \bar{c}_{\mu} c_{\mu} \langle \Phi_{\mu} | \left(1 + \hat{\Lambda}_{\mu} \right) e^{-\hat{T}_{\mu}} \frac{\partial H}{\partial x} e^{\hat{T}_{\mu}} | \Phi_{\mu} \rangle \quad , \tag{2.69}$$

where the (2n + 1) and (2n + 2) rules of derivative theory [112] have been exploited. Using a density-matrix based formalism [117], this expression is rewritten as

$$\frac{dE}{dx} = \sum_{\mu} \bar{c}_{\mu} c_{\mu} \left[\sum_{pq} D^{\mu}_{pq} \frac{df^{\mu}_{pq}}{dx} + \sum_{pqrs} \Gamma^{\mu}_{pqrs} \frac{d\langle pq | |rs \rangle}{dx} \right]$$
(2.70)

with f_{pq}^{μ} as elements of the Fock matrix defined with respect to $|\Phi_{\mu}\rangle$ as Fermi vacuum. D_{pq}^{μ} and Γ_{pqrs}^{μ} denote reference-specific one- and two-particle density matrices given as

$$D_{pq}^{\mu} = D_{pq}^{\text{SCF}}(\mu) + \langle \Phi_{\mu} | \left(1 + \hat{\Lambda}_{\mu} \right) e^{-\hat{T}_{\mu}} \{ \hat{a}_{p}^{\dagger} \hat{a}_{q} \}_{\mu} e^{\hat{T}_{\mu}} | \Phi_{\mu} \rangle \quad , \tag{2.71}$$

$$\Gamma^{\mu}_{pqrs} = \Gamma^{\rm SCF}_{pqrs}(\mu) + \frac{1}{4} \langle \Phi_{\mu} | \left(1 + \hat{\Lambda}_{\mu} \right) e^{-\hat{T}_{\mu}} \{ \hat{a}^{\dagger}_{p} \hat{a}^{\dagger}_{q} \hat{a}_{s} \hat{a}_{r} \}_{\mu} e^{\hat{T}_{\mu}} | \Phi_{\mu} \rangle \quad .$$
 (2.72)

In this equation, $D_{pq}^{\text{SCF}}(\mu)$ and $\Gamma_{pqrs}^{\text{SCF}}(\mu)$ represent the one- and two-particle density matrix for a single Slater determinant $|\Phi_{\mu}\rangle$. Further simplification is achieved by splitting the derivatives of f_{pq}^{μ} and $\langle pq || rs \rangle$ into an integral-derivative and an orbital-relaxation contribution. This yields

$$\frac{dE}{dx} = \sum_{\mu} \bar{c}_{\mu} c_{\mu} \left[D^{\mu}_{pq} f^{\mu(x)}_{pq} + \sum_{pqrs} \Gamma^{\mu}_{pqrs} \langle pq | | rs \rangle^{x} - 2 \sum_{pq} I^{\mu}_{pq} U^{x}_{pq} \right], \qquad (2.73)$$

where the last term comprises all CPHF contributions and I_{pq}^{μ} denotes a reference-specific one-particle intermediate [74].

2.3.4. Orbital Relaxation

The expression for the first derivative of the Mk-MRCC energy presented in Eq. (2.73) holds regardless of the underlying reference wave function. However, the coefficients U_{pq}^{χ} needed to evaluate the last term of this equation explicitly depend on the reference wave function as their determination requires the solution of the CPHF or coupled-perturbed MCSCF equations. To minimize the computational effort, the orbital-relaxation term in Eq. (2.73) is usually reformulated as

$$-2\sum_{pq}I_{pq}U_{pq}^{\chi} = -2\sum_{pq}^{\text{n.r.}}X_{pq}U_{pq}^{\chi} + \sum_{pq}^{\text{red.}}I_{pq}S_{pq}^{\chi} , \qquad (2.74)$$

where Eq. (2.57) has been exploited and $X_{pq} = I_{pq} - I_{qp}$ [118]. The labels "n.r." and "red." refer to non-redundant and redundant orbital rotations, respectively. The exact summation range depends on the SCF wave function used (cf. Sections 2.2.1 and 2.2.3). For a HF reference wave function, the first sum on the right-hand side of Eq. (2.74) includes only those elements, where p refers to a virtual orbital and q to an occupied one (cf. Section 2.3.2). However, special care is necessary if HF orbitals are employed in Mk-MRCC calculations as in this case the definition of occupied and virtual orbitals differs between the Mk-MRCC wave function and the HF reference.

For a HF or ROHF reference wave function, Eqs. (2.58) or (2.62) are used to recast the first term in Eq. (2.74) as

$$-2\sum_{pq}^{\text{n.r.}} X_{pq} U_{pq}^{\chi} = -2\sum_{pq}^{\text{n.r.}} Z_{pq} B_{pq}^{\chi}$$
(2.75)

with the elements of the Z-vector \mathbf{Z} defined through

$$\sum_{pq}^{\text{n.r.}} Z_{pq} A_{pqrs} = X_{rs} .$$
 (2.76)

A two-componential Z-vector equation is obtained for a TCSCF reference wave function as the calculation of U_{pq}^{χ} requires in this case to solve for the first derivative of the CI coefficients at the same time. Explicit expressions for these Z-vector equations are available from Ref. 82. Since **Z** does not depend on the perturbation χ , only Eq. (2.76) needs to be solved instead of N equations with N as the number of perturbations.

2.3.5. Response Theory

Response theory [11–16] is a formalism for the calculation of frequency-dependent properties and excitation energies. For this purpose, the time evolution of a stationary state is studied in the presence of a time-dependent Fourier-decomposable perturbation

$$\hat{V}(t) = \sum_{X} \varepsilon_X \hat{X} e^{-i\omega_X t}$$
(2.77)

with \hat{X} as a time-independent perturbation operator and ε_X and ω_X as the corresponding strength parameter and frequency, respectively. The Hamiltonian is partitioned as

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$
 (2.78)

with \hat{H}_0 denoting the time-independent Hamiltonian of the unperturbed system defined in Eq. (2.4). In principle, the time evolution of the system is governed by the time-dependent Schrödinger equation

$$\hat{H}(t) |\Psi(t)\rangle = i \frac{\partial}{\partial t} |\Psi(t)\rangle \quad . \tag{2.79}$$

However, the explicit determination of $|\Psi(t)\rangle$ can be avoided for small perturbations ε_X . In this case, an expansion in orders of perturbation can be applied instead.

Within the formalism of response theory [15, 16], frequency-dependent properties can be rewritten as response functions $\langle \langle X; Y, Z, \ldots \rangle \rangle_{\omega_Y, \omega_Z, \ldots}$, which appear as expansion coefficients in the expression for the time evolution of the expectation value $\langle X \rangle(t)$

$$\langle X \rangle(t) = \langle X \rangle(0) + \sum_{Y} \varepsilon_{Y} \langle \langle X; Y \rangle \rangle_{\omega_{Y}} e^{-i\omega_{Y}t} + \frac{1}{2} \sum_{Y,Z} \varepsilon_{Y} \varepsilon_{Z} \langle \langle X; Y, Z \rangle \rangle_{\omega_{Y},\omega_{Z}} e^{-i(\omega_{Y}+\omega_{Z})t} + \dots$$
 (2.80)

under the influence of the perturbations Y, Z, \ldots with frequencies $\omega_Y, \omega_Z, \ldots$. In particular, the dynamic polarizability, which is of importance for this work, can be obtained as the linear-response function

$$\alpha_{XY}(\omega_X, \omega_Y) = -\langle \langle \mu_X; \mu_Y \rangle \rangle_{\omega_Y}, \quad \omega_X = -\omega_Y , \qquad (2.81)$$

where μ_X and μ_Y represent components of the dipole operator.

Following the quasienergy formalism by Christiansen, Jørgensen, and Hättig [16], the linearresponse function may be calculated as

$$\langle\langle X; Y \rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm \omega} \frac{d^2 \{\dot{F}\}_T}{d\varepsilon_X d\varepsilon_Y} \Big|_{\varepsilon_X = \varepsilon_Y = 0} , \qquad (2.82)$$



Figure 2.3.: Interpretation of poles in the linear-response function. $\langle \langle X; Y \rangle \rangle_{\omega_Y}$ diverges if ω_Y approaches a frequency ω_i that corresponds to an excitation energy $E_i - E_0$.

where $C^{\pm\omega}$ symmetrizes a function with respect to a sign change of the frequencies. This expression should be seen in analogy to Eq. (2.51) for static second-order properties with the energy replaced by the time-averaged quasienergy $\{\dot{F}\}_T$. Time-averaging is defined via

$$\{\dot{F}\}_T = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0 + T} \dot{F}(t) dt ,$$
 (2.83)

while the time-dependent quasienergy $\dot{F}(t)$ is given as

$$\dot{F}(t) = \left\langle \Psi \right| \left(\hat{H}_0 - i \frac{\partial}{\partial t} \right) \left| \Psi \right\rangle \,. \tag{2.84}$$

As the time average of a periodic function is zero, the frequencies in Eqs. (2.80) and (2.81) are subject to the constraint $\sum_{I} \omega_{I} = 0$.

Similar to the time-independent case, it is advantageous to use an appropriate Lagrangian L(t) instead of the quasienergy in order to exploit the (2n+1) and (2n+2) rules of derivative theory [16,112]. This yields the following working equation for the linear-response function

$$\langle\langle X; Y \rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm \omega} \frac{\partial^2 \{L\}_T}{\partial \varepsilon_X \partial \varepsilon_Y} \Big|_{\varepsilon_X = \varepsilon_Y = 0} .$$
(2.85)

The expression for a static second derivative (cf. Eq. (2.51)) can be recovered from this equation by setting $\omega_Y = 0$.

Excitation energies can be extracted from the linear-response function by transferring Eq. (2.82) to a sum-over-state representation [14,16,119]. If $\langle \langle X; Y \rangle \rangle_{\omega_Y}$ is calculated starting from the exact wave function, this reads

$$\langle\langle X; Y \rangle\rangle_{\omega_Y} = \sum_{i \neq 0} \left[\frac{\langle \Psi_0 | \hat{X} | \Psi_i \rangle \langle \Psi_i | \hat{Y} | \Psi_0 \rangle}{\omega_Y - \omega_i} - \frac{\langle \Psi_0 | \hat{Y} | \Psi_i \rangle \langle \Psi_i | \hat{X} | \Psi_0 \rangle}{\omega_Y + \omega_i} \right]$$
(2.86)

with $|\Psi_i\rangle$ denoting the excited states and $|\Psi_0\rangle$ the ground electronic state, while ω_i is the energy difference between $|\Psi_i\rangle$ and $|\Psi_0\rangle$. From Eq. (2.86), it is clear that $\langle\langle X; Y \rangle\rangle_{\omega_Y}$ has

poles, i.e., diverges to infinity when ω_Y equals an excitation energy ω_i as shown in Figure 2.3. For CC response theory, Eq. (2.86) does not hold due to the non-linear parametrization of the wave function. However, it is still possible to identify excitation energies as poles of the CC linear-response function since the additional terms entering Eq. (2.86) do not give rise to further poles [16].

2.3.6. Anharmonic Effects in Quantum Chemistry

Infrared (IR) spectroscopy [29] is the experimental method of choice to study vibrational energy levels of molecules. IR spectra are characterized by two sets of parameters: The frequencies ν_i of the vibrational transitions, which reveal the energy differences between vibrational levels, and the associated intensities I_i , which are governed by the transition dipole moment $|\langle \Psi_i | \hat{\mu} | \Psi_f \rangle|^2$ with $|\Psi_i\rangle$ and $|\Psi_f\rangle$ denoting the wave functions for the vibrational states involved in the transition.

The quantum-chemical determination of these quantities can be carried out in zeroth order within the double harmonic approximation. This means that the potential V for the motion of the nuclei is approximated as harmonic and the electronic dipole moment μ^e is assumed to depend only linearly on the coordinates of the nuclei:

$$V(\{q_i\}) = V_0 + \frac{1}{2} \sum_i \omega_i q_i^2 , \qquad (2.87)$$

$$\mu^{e}(\{q_{i}\}) = \mu^{e}(\{q_{i}^{0}\}) + \sum_{i} \frac{d\mu^{e}}{dq_{i}} q_{i} .$$
(2.88)

In these equations, $\{q_i\}$ denotes the dimensionless normal coordinates of the molecule and ω_i the harmonic vibrational frequencies. Using the potential from Eq. (2.87), the motion of the nuclei is described by harmonic oscillators with no interaction between the vibrational modes. The resulting Schrödinger equation can be solved analytically, which yields equidistant energy levels as displayed in Figure 2.4. Furthermore, only transitions between adjacent energy levels are assigned a non-vanishing intensity. To determine the harmonic frequencies ω_i in a quantum-chemical calculation, the Hessian matrix, i.e., the matrix of second derivatives of the energy with respect to nuclear displacements $d^2E/dx_i dx_j$ needs to be evaluated. The frequencies and normal coordinates are then obtained as eigenvalues and eigenvectors of this matrix after introducing mass-weighted coordinates. Likewise, $d\mu_j^e/dq_i$ is also calculated as a second derivative of the energy, namely as $d^2E/dx_i d\varepsilon_j$.

However, the comparison to experiment shows the need to go beyond the double harmonic approximation when aiming at the accurate theoretical description of IR spectra [29, 120– 122]. In particular, overtone bands, where a transition takes place between non-adjacent energy levels, or combination bands, where two modes are excited simultaneously, cannot be described within the double harmonic approximation. Moreover, the theoretical treatment of enhanced IR-spectroscopical techniques like two-dimensional IR spectroscopy [123], where the interaction of vibrational modes is probed, requires to take account of anharmonicity. Two effects need to be distinguished: Mechanical and electrical anharmonicity. The former effect refers to the fact that the potential V possesses a more involved dependence on the nuclear coordinates than assumed in Eq. (2.87), i.e.,

$$V(\{q_i\}) = V_0 + \frac{1}{2} \sum_i \omega_i \, q_i^2 + \sum_{ijk} \phi_{ijk} \, q_i \, q_j \, q_k + \sum_{ijkl} \phi_{ijkl} \, q_i \, q_j \, q_k \, q_l + \dots \,, \tag{2.89}$$

where ϕ_{ijk} and ϕ_{ijkl} stand for cubic and quartic force constants. The latter effect relates to the dependence of the electronic dipole moment on the nuclear coordinates, which can be



Figure 2.4.: Vibrational transitions in the double harmonic approximation (left) and taking account of anharmonic effects (right).

generically expressed as

$$\mu^{e}(\{q_{i}\}) = \mu^{e}(\{q_{i}^{0}\}) + \sum_{i} \frac{d\mu^{e}}{dq_{i}} q_{i} + \frac{1}{2} \sum_{ij} \frac{d^{2}\mu^{e}}{dq_{i}dq_{j}} q_{i} q_{j} + \frac{1}{6} \sum_{ijk} \frac{d^{3}\mu^{e}}{dq_{i}dq_{j}dq_{k}} q_{i} q_{j} q_{k} + \dots \quad (2.90)$$

The Schrödinger equation for the motion of the nuclei resulting from the potential in Eq. (2.89) is usually solved using perturbative techniques such as, for example, second-order vibrational perturbation theory (VPT2) [29]. As shown in Figure 2.4, this yields energy levels that are no longer equidistant. Also, transitions between non-adjacent energy levels become possible and the intensities of transitions between different energy levels are in general no longer identical. The cubic and quartic force constants ϕ_{ijk} and ϕ_{ijkl} as well as the second and third derivatives of the dipole moment $d^2\mu^e/dq_i dq_j$ and $d^3\mu^e/dq_i dq_j dq_k$ are required as input for VPT2 calculations. Hence, this involves the evaluation of third derivatives of the energy, namely $d^{3}E/dx_{i}dx_{j}dx_{k}$ for cubic force constants and $d^{3}E/dx_{i}dx_{j}d\varepsilon_{k}$ for the elements of the dipole Hessian matrix $d^2 \mu_k^e / dq_i dq_j$. Numerical studies have shown that electron correlation has a significant impact on anharmonic effects. Accordingly, the cubic force constants and the dipole Hessian matrix ought to be evaluated using correlated methods. So far, this has been done only through numerical differentiation of analytic second derivatives [10]. However, a fully analytic evaluation of third derivatives is superior in terms of accuracy and computational cost as discussed in Section 2.3.1. All expressions required hereto are derived in Chapter 5.1.2 of this work at the MP2 and the CC level of theory.

3. Structure Optimizations Using Mk-MRCC Calculations

This chapter features molecular equilibrium structures as well as adiabatic excitation energies for the ground and low-lying excited states of the thirteen molecules *s*-tetrazine, naphthalene, cyclopentadiene, pyrrole, furan, thiophene, acetylene, vinylidene, *o*-benzyne, *m*-benzyne, *p*benzyne, 2,6-pyridyne, and 2,6-pyridynium. The principal method used for this investigation is the Mk-MRCCSD approach with corresponding analytic-derivative techniques as implemented in the quantum-chemical program package CFOUR [124]. In order to assess the performance of Mk-MRCCSD, the results are compared to those obtained using other multireference and single-reference CC methods.

3.1. Implementation of Analytic Mk-MRCC Gradients for Use with ROHF Orbitals

Using the expressions presented in Sections 2.3.3 and 2.3.4, analytic Mk-MRCCSD gradients for use with ROHF orbitals have been implemented into the quantum-chemical program package CFOUR [124]. The present implementation represents an extension of that described in Refs. 73, 74, 82, which is based on HF or TCSCF orbitals. The general course of calculation is outlined in Figure 3.1. As CFOUR was originally designed for single-reference CC theory, special techniques are required for the treatment of the active space in Mk-MRCCSD calculations. In order to keep the distinction between occupied and virtual orbitals, which is inherent to CFOUR, all active orbitals are duplicated and appended once to the space of occupied orbitals and once to the space of virtual orbitals before the Mk-MRCCSD calculation is carried out. Further details are available from Ref. 73. The use of different orbitals and reference wave functions, i.e., $|\Psi_{\text{ROHF}}\rangle$ (Eq. (2.21)) instead of $|\Psi_{\text{TCSCF}}\rangle$ (Eq. (2.19)) does not entail any changes to the Mk-MRCCSD amplitude or Λ equations. Likewise, the expressions for the density matrices D_{pq}^{μ} and Γ_{pqrs}^{μ} as well as the intermediates I_{pq}^{μ} are not affected. It is only necessary to employ a different set of CPHF coefficients U_{pq}^x in Eq. (2.73). The computational cost of a Mk-MRCCSD gradient calculation scales like $d \cdot n_o^2 \cdot n_v^4$, where d is the number of reference determinants and n_o and n_v stand for the number of occupied and virtual orbitals, respectively. Hence, the cost equals d times that of a single-reference CCSD gradient calculation. However, for an ROHF-based calculation of open-shell states within a CAS(2,2), the cost does not exceed that of a single-reference calculation since, due to spin symmetry, only one determinant needs to be considered when solving the amplitude or Λ equations. Moreover, c_{μ} and \bar{c}_{μ} are fixed by symmetry so that the corresponding equations can be skipped as well. Verification of the implementation has been achieved by means of numerical differentiation of the energy.

In the actual implementation, the last term in Eq. (2.73) is recast as discussed in Section 2.3.4. To evaluate this term, the integral derivatives $f_{\mu\nu}^{(x)}$, $\langle\mu\sigma|\nu\rho\rangle^x$, and $S_{\mu\nu}^x$ are computed by module vdint after the Mk-MRCCSD amplitude and Λ equations have been solved. Next, module cptcscf_incore is invoked for the solution of the ROHF Z-vector equations and the subsequent calculation of the orbital-relaxation contribution to the gradient. As this is



Figure 3.1.: Flowchart for the calculation of energy gradients at the Mk-MRCCSD level of theory using ROHF or TCSCF reference wave functions.

done in the MO basis, the first task of cptcscf_incore consists in constructing the integral derivatives $f_{pq}^{(x)}$, S_{pq}^x , $K_{pq}^{t(x)}$, and $K_{pq}^{s(x)}$, where the exchange-matrix derivatives $K_{pq}^{t(x)}$ and $K_{pq}^{s(x)}$ have been introduced as $K_{pq}^{t(x)} = (rt|t_{p})^{x} \quad \text{and} \quad K_{pq}^{s(x)} = (rt|t_{p})^{x} \quad \text{and} \quad K_{pq}^{s(x)} = (rt|t_{p})^{x}$

$$K_{pq}^{t(x)} = \langle pt|tq \rangle^x$$
 and $K_{pq}^{s(x)} = \langle ps|sq \rangle^x$. (3.1)

The calculation then proceeds with the solution of the ROHF Z-vector equations, the general form of which has been given in Eq. (2.76). The matrix **A** is set up in cptcscf_incore/amatrohf.f, its elements read

$$A_{aibj} = 4 \langle ab|ij \rangle - \langle ab|ji \rangle - \langle aj|bi \rangle + \delta_{ij} f_{ab} - \delta_{ab} f_{ij} , \qquad (3.2)$$

$$A_{aibt} = 2 \langle ab|it \rangle - \frac{1}{2} \langle ab|ti \rangle - \frac{1}{2} \langle at|bi \rangle - \delta_{ab} f_{ti} , \qquad (3.3)$$

$$A_{aitj} = 2 \langle at|ij \rangle - \frac{1}{2} \langle at|ji \rangle - \frac{1}{2} \langle aj|ti \rangle + \delta_{ij} f_{at} , \qquad (3.4)$$

$$A_{atbt} = \frac{1}{2} \langle ab|tt \rangle - \frac{1}{2} \langle at|bt \rangle + \frac{1}{2} f_{ab} - \frac{1}{4} K^t_{ab} + \frac{1}{4} K^s_{ab} \pm \frac{1}{2} K^s_{ab} - \delta_{ab} \Big(\frac{1}{2} f_{tt} - \frac{1}{4} K^t_{tt} + \frac{1}{4} K^s_{tt} \pm \frac{1}{2} K^s_{tt} \Big) , \qquad (3.5)$$

$$A_{titj} = \frac{1}{2} \langle tt|ij \rangle - \frac{1}{2} \langle ti|tj \rangle - \frac{1}{2} f_{ij} - \frac{1}{4} K^t_{ij} + \frac{1}{4} K^s_{ij} \pm \frac{1}{2} K^s_{ij}$$

$$+ S \left(\frac{1}{2} t_{ij} + \frac{1}{2} K^t_{ij} + \frac{1}{2} K^s_{ij} + \frac{1}{2} K^s_{i$$

$$+ \delta_{ij} \left(\frac{1}{2} f_{tt} + \frac{1}{4} K_{tt}^{t} - \frac{1}{4} K_{tt}^{s} \mp \frac{1}{2} K_{tt}^{s} \right) , \qquad (3.6)$$

$$A_{atbs} = \langle ab|ts \rangle \pm \frac{1}{2} \langle ab|st \rangle \pm \frac{1}{2} \langle as|bt \rangle , \qquad (3.7)$$

$$A_{tisj} = \langle ts|ij \rangle \pm \frac{1}{2} \langle ts|ji \rangle \pm \frac{1}{2} \langle tj|si \rangle , \qquad (3.8)$$

$$A_{attj} = \langle at|tj \rangle + \frac{1}{4}K^{t}_{aj} - \frac{1}{4}K^{s}_{aj} \mp \frac{1}{2}K^{s}_{aj} , \qquad (3.9)$$

$$A_{atsj} = \langle as|tj\rangle - \frac{1}{2} \langle as|jt\rangle - \frac{1}{2} \langle aj|st\rangle \mp \frac{1}{2} \langle as|jt\rangle \mp \frac{1}{2} \langle aj|st\rangle , \qquad (3.10)$$

where spin integration has been performed and the upper and the lower sign refer to the singlet and the triplet state, respectively. The exchange matrices K_{pq}^t and K_{pq}^s are defined in analogy to Eq. (3.1). Expressions for the remaining elements of **A** can be obtained by interchanging t and s. The actual algorithm for solving Eq. (2.76) relies on Pople's method [7] to solve the CPHF equations and has been adapted to the ROHF Z-vector equations. Spatial symmetry is exploited to lower the computational cost, but the current implementation requires the singly occupied orbitals t and s to transform under different irreducible representations. This limitation is due to the implementation of the ROHF-SCF equations in CFOUR and entails that **A** does not contain any matrix elements referring to the orbital rotations st or ts. Expressions for these additional elements in **A** can be deduced via differentiation of the corresponding variational condition, i.e., Eq. (2.26). However, if t and s transform under the same irreducible representation, additional terms will also appear in Eqs. (3.2) to (3.10). After the Z-vector has been obtained, it is contracted in routine cptcscf_incore/ bgeorohf.f with the vector \mathbf{B}^x , expressions for which are also obtained via differentiation of the variational conditions Eqs. (2.23) to (2.26). This yields

$$\begin{split} B_{ai}^{x} &= -f_{ai}^{(x)} + \sum_{j} S_{aj}^{x} f_{ij} + S_{at}^{x} f_{ti} + S_{as}^{x} f_{si} \\ &+ \sum_{jk} S_{jk}^{x} \left(2 \langle a j | ik \rangle - \langle a j | ki \rangle \right) + \sum_{j} S_{ij}^{x} \left(2 \langle a t | ij \rangle - \langle a t | ji \rangle \right) + \sum_{j} S_{sj}^{x} \left(2 \langle a s | ij \rangle - \langle a s | ji \rangle \right) \\ &+ \frac{1}{2} S_{tt}^{x} \left(2 \langle a t | it \rangle - \langle a t | ti \rangle \right) + \frac{1}{2} S_{ss}^{x} \left(2 \langle a s | is \rangle - \langle a s | si \rangle \right) , \qquad (3.11) \\ B_{at}^{x} &= -\frac{1}{2} f_{at}^{(x)} + \frac{1}{4} K_{at}^{t(x)} - \frac{1}{4} K_{at}^{s(x)} \mp \frac{1}{2} K_{at}^{s(x)} + \sum_{j} S_{aj}^{x} f_{tj} + S_{at}^{x} \left(\frac{1}{2} f_{tt} - \frac{1}{4} K_{tt}^{t} + \frac{1}{4} K_{st}^{s} \pm \frac{1}{2} K_{st}^{s} \right) \\ &+ \sum_{j} S_{tj}^{x} \left(-\frac{1}{4} K_{at}^{t} + \frac{1}{4} K_{aj}^{s} \pm \frac{1}{2} K_{aj}^{s} \right) + \frac{1}{2} \sum_{jk} S_{jk}^{x} \left(2 \langle a j | tk \rangle - \langle a j | kt \rangle \right) \\ &+ \frac{1}{2} \sum_{j} S_{tj}^{x} \left(\langle a t | tj \rangle - \langle a t | jt \rangle \right) + \sum_{j} S_{sj}^{x} \left(\langle a s | tj \rangle \pm \frac{1}{2} \langle a s | jt \rangle \pm \frac{1}{2} \langle a j | st \rangle \right) \\ &+ \frac{1}{2} S_{ss}^{x} \left(\langle a s | ts \rangle \pm \langle a s | st \rangle \right) , \qquad (3.12) \\ B_{ti}^{x} &= -\frac{1}{2} f_{ti}^{(x)} - \frac{1}{4} K_{ti}^{t(x)} + \frac{1}{4} K_{si}^{s(x)} \pm \frac{1}{2} K_{si}^{s(x)} + \sum_{j} S_{tj}^{x} \left(\frac{1}{2} f_{ij} + \frac{1}{4} K_{ij}^{s} \pm \frac{1}{2} K_{ij}^{s} \right) \\ &+ \frac{1}{2} \sum_{jk} S_{jk}^{x} \left(2 \langle tj | ik \rangle - \langle tj | ki \rangle \right) + \sum_{j} S_{tj}^{x} \langle tt | ij \rangle + \frac{1}{2} S_{tt}^{x} \langle tt | ti \rangle \\ &+ \sum_{j} S_{sj}^{x} \left(\langle ts | ij \rangle - \frac{1}{2} \langle ts | ji \rangle - \frac{1}{2} \langle tj | si \rangle \mp \frac{1}{2} \langle ts | ji \rangle \mp \frac{1}{2} \langle ts | si \rangle \right) , \qquad (3.13) \end{aligned}$$

where again spin integration has been carried out and the remaining elements are obtained by interchanging t and s. As discussed for the matrix **A**, an additional element B_{st}^x is, in principle, contained in **B**^x, but does not need to be considered here if t and s are of different spatial symmetry since the calculation of the gradient only requires totally symmetric elements of **B**^x. After the orbital-relaxation contribution has been evaluated, the calculation proceeds by transforming D_{pq}^{μ} and Γ_{pqrs}^{μ} to the AO basis. Thereafter, the integral derivatives $f_{\mu\nu}^{(x)}$ and $\langle \mu \sigma | \nu \rho \rangle^x$ are evaluated by module vdint and contracted on the fly with the corresponding density matrices.

3.2. Excited States of Arene Compounds

This section centers on equilibrium structures of the ground states and some low-lying excited states of s-tetrazine and naphthalene as well as the five-membered rings cyclopentadiene,

furan, thiophene, and pyrrole. Adiabatic excitation energies for all excited states of interest are reported as well. The molecular structure of the compounds under consideration is depicted in Figure 3.2. A common feature they share is that their electronic ground state is accurately described by single-reference CC theory, while their low-lying excited states are more challenging to treat. However, the present investigation is limited to states, whose wave function is dominated by one open-shell configuration, i.e., two determinants. In this case, the ROHF wave function (Eq. (2.21)) is a valid reference wave function for Mk-MRCCSD calculations. All states of interest are also targeted at the equation-of-motion (EOM) CCSD level of theory [125,126] for comparison purposes. Furthermore, all triplet states are examined in their $M_s = \pm 1$ component using the CCSD [127, 128] and the CCSD(T) [129] method in conjunction with ROHF molecular orbitals. The correlation-consistent core-valence polarized basis sets cc-pCVXZ (X=D,T) [130] are used and all electrons are included in the correlation treatment.



(a) Structure for the ground state of *s*tetrazine as computed at the CCSD level of theory using the cc-pCVTZ basis set.



(b) Structure for the ground state of naphthalene as computed at the CCSD level of theory using the ccpCVTZ basis set.



(c) Structures for the lowest excited singlet states of cyclopentadiene, furan, thiophene, and pyrrole (from left to right) as computed at the Mk-MRCCSD level of theory using the cc-pCVTZ basis set.

Figure 3.2.: Structures for some ground and low-lying excited states of arene compounds.

Adiabatic excitation energies for the lowest-lying excited singlet and triplet states of B_{3u} and A_u symmetry of *s*-tetrazine are presented in Table 3.1. The electronic ground state of this molecule is accurately described by single-reference CC theory using the configuration $|\Phi\rangle = |(\operatorname{core})^2 (3b_{3g})^2\rangle$ as reference [131]. The excited states of interest qualitatively arise from lifting an electron from the $3b_{3g}$ orbital to the lowest unoccupied orbitals of a_u and b_{3u} symmetry [131–134]. All computations are performed imposing D_{2h} symmetry as a constraint. Table 3.1 shows that Mk-MRCCSD consistently predicts smaller excitation energies than EOM-CCSD, but the discrepancy never exceeds 0.2 eV. For the triplet states, CCSD and Mk-MRCCSD agree within 0.03 eV, while CCSD(T) matches EOM-CCSD more closely with a maximum deviation of 0.09 eV. The best match with experimental values (2.248 eV for the ¹B_{3u} state [135] and 1.687 eV for the ³B_{3u} state [136]) is obtained at the CCSD(T) level of theory. However, a rigorous comparison to experiment is difficult as the results in Table 3.1 do not include zero-point vibrational energy (ZPVE) corrections.

Table 3.1.: Adiabatic excitation energies in eV for several low-lying excited states of *s*-tetrazine, naphthalene, cyclopentadiene, pyrrole, furan, and thiophene as computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory using the cc-pCVDZ and cc-pCVTZ basis sets.

State	Mk-MR-	EOM-	CCSD	CCSD(T)	Mk-MR-	EOM-	CCSD	CCSD(T)	
	CCSD	CCSD			CCSD	CCSD			
		cc-p	CVDZ			cc-p	CVTZ		
				s-Tet	razine				
$T_1({}^{3}B_{3u})$	2.043	1.842	2.017	1.827	2.038	1.832	2.011	1.799	
$T_2(^3A_u)$	2.836	2.670	2.839	2.621	2.854	2.705	2.858	2.614	
$\mathrm{S}_1(^1\mathrm{B}_{3u})$	2.693	2.564	—		2.642	2.515			
$S_2(^1A_u)$	3.020	2.916	—		3.020	2.931			
				Napht	halene				
$T_1(^{3}B_{2u})$	2.926	2.667	2.815	2.788	2.973	2.726	2.854	2.834	
$\mathrm{S}_1(^1\mathrm{B}_{2u})$	5.000	4.955	—		4.903	4.861			
				Cyclope	ntadiene				
$\mathrm{T}_{1}(^{3}\mathrm{B}_{2})^{a}$	2.610	2.524	2.486	2.571	2.679	2.601	2.549	2.648	
$\mathrm{S}_1(^1\mathrm{B}_2)^a$	5.266	5.426	—		5.167	5.322			
$S_1(^1A")^b$	5.040	5.190	—		4.919	5.065			
				Pyr	role				
$\mathrm{T}_{1}(^{3}\mathrm{B}_{2})^{a}$	3.990	3.974	3.890	3.991	4.005	3.982	3.893	4.008	
$T_1(^3A"$ -cis $)^b$	3.623	3.649	3.532	3.623	3.697	3.725	3.599	3.708	
$T_1(^3A"$ -trans) ^b	3.638	3.628	3.534	3.629	3.710	3.703	3.598	3.713	
$\mathrm{S}_1(^1\mathrm{B}_2)^a$	6.568	6.686	—		6.438	6.538	_		
$S_1(^1A"-cis)^b$	6.047	6.243	—		5.972	6.149	_		
				Fu	ıran				
$\mathrm{T}_{1}(^{3}\mathrm{B}_{2})^{a}$	3.608	3.611	3.512	3.608	3.633	3.628	3.524	3.637	
$T_1({}^{3}A")^b$	3.477	3.514	3.387	3.486	3.520	3.555	3.421	3.539	
$\mathrm{S}_1(^1\mathrm{B}_2)^a$	6.398	6.572	—		6.270	6.423	—		
$S_1(^1A")^b$	6.165	6.377	—		6.050	6.242	_		
				Thio	phene				
$\mathrm{T}_{1}(^{3}\mathrm{B}_{2})^{a}$	3.329	3.264	3.191	3.302	3.391	3.335	3.249	3.378	
$T_1({}^{3}A")^b$	3.267	3.234	3.141	3.250	3.331	3.312	3.206	3.331	
$\mathrm{S}_1(^1\mathrm{B}_2)^a$	5.900	6.013	—		5.734	5.847	—		
$S_1(^1A")^b$	5.502	5.704			5.371	5.559	—		

^{*a*}Imposing C_{2v} symmetry as constraint.

^bWithin C_s symmetry.

Optimized CN and NN bond distances corresponding to the excitation energies from Table 3.1 can be found in Table 3.2, while complete optimized structures have been published in Ref. 137. The results show that there is no generic order of the methods for the bond distances except for the fact that CCSD(T) always yields bonds elongated by ≈ 0.01 Å compared to CCSD. Mk-MRCCSD and CCSD nearly coincide for all states considered, while EOM-CCSD results deviate by at most 0.004 Å. For the states of B_{3u} symmetry, all methods predict a slight contraction of the CN and NN bond with respect to the ground state, whereas a longer CN bond and a distinctly shorter NN bond are forecast for the states of A_u symmetry. Equilibrium structures for the ground state and the excited states of B_{3u} symmetry have also been determined experimentally. For the ground state, CN bond lengths of 1.3405 Å [138] and 1.338 Å [139] as well as NN bond lengths of 1.3256 Å and 1.334 Å have been reported. The corresponding values for the ¹ B_{3u} state from the same studies are 1.324 Å and 1.358 Å for the CN bond as well as 1.349 Å and 1.280 Å for the NN bond. Concerning the ³ B_{3u} state, another experimental study [136] found shrinkages of 0.01 Å and 0.06 Å in CN and NN bond

Table 3.2.: CN and NN bond distances in angstrom for the ground and excited states of *s*-tetrazine as computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory using the cc-pCVTZ basis set.

State	CCSD	$\operatorname{CCSD}(T)$	Mk-MR-	EOM-	CCSD	CCSD(T)	Mk-MR-	EOM-	
			CCSD	CCSD			CCSD	CCSD	
		R(C	CN)		R(NN)				
$S_0(^1A_g)$	1.33026	1.33770			1.31269	1.32465			
$T_1(^3B_{3u})$	1.32382	1.33195	1.32368	1.32443	1.30901	1.31891	1.30850	1.30827	
$T_2(^3A_u)$	1.37855	1.38486	1.37871	1.37508	1.22092	1.23295	1.22099	1.22559	
$S_1(^1B_{3u})$			1.32470	1.32460	_		1.30938	1.30926	
$S_2(^1A_u)$			1.37946	1.37546			1.21994	1.22363	

Table 3.3.: C_1C_2 , C_2C_3 , C_1C_9 , and C_9C_{10} bond distances in angstrom for the ground and excited states of naphthalene as computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory using the cc-pCVTZ basis set.

-								
State	CCSD	CCSD(T)	Mk-MR-	EOM-	CCSD	$\operatorname{CCSD}(T)$	Mk-MR-	EOM-
			CCSD	CCSD			CCSD	CCSD
		$R(C_1$	(C_2)			$R(C_2$	$_{2}C_{3})$	
$S_0(^1A_g)$	1.36586	1.37358			1.41466	1.41670		
$T_1({}^{3}B_{2u})$	1.44092	1.43995	1.43875	1.43204	1.35228	1.36286	1.35353	1.36207
$\mathrm{S}_1(^1\mathrm{B}_{2u})$			1.42698	1.42089	_		1.36485	1.36992
		$R(C_1$	(C_9)			$R(C_9)$	$C_{10})$	
$S_0(^1A_g)$	1.41787	1.42011			1.41300	1.42160		_
$T_1({}^{3}B_{2u})$	1.39856	1.40697	1.39900	1.40505	1.44726	1.44366	1.44333	1.43638
$\mathrm{S}_1(^1\mathrm{B}_{2u})$			1.40010	1.40218			1.43512	1.43720

length, respectively, compared to the ground state. While the experimental findings for the ${}^{3}B_{3u}$ state are roughly in line with the results presented in Table 3.2, a qualitative mismatch is obtained for the ${}^{1}B_{3u}$ state. However, this latter discrepancy between theory and experiment has been addressed in detail in Ref. 133 and the revised structures agree with the values presented in this work.

Naphthalene in its closed-shell ground state is well described by the configuration $|\Phi\rangle = |(\operatorname{core})^2 (2b_{1u})^2 (1a_u)^2 \rangle$. The focus of this work is on the lowest singlet and triplet state of B_{2u} symmetry, which can be qualitatively described by promoting an electron from the $1a_u$ orbital to the $2b_{2g}$ lowest unoccupied orbital [140, 141]. Vertical excitation energies for these states have been calculated several times [140–143], while the corresponding adiabatic quantities and structural changes are less well explored [144]. It should be added that there are two low-lying states of B_{3u} symmetry, which have also been targeted several times. Yet, they require a reference space of four determinants in Mk-MRCCSD calculations and are thus excluded from the present investigation.

Adiabatic excitation energies for the ${}^{1}B_{2u}$ and the ${}^{3}B_{2u}$ state of naphthalene are available from Table 3.1. It is seen that Mk-MRCCSD and EOM-CCSD excitation energies almost coincide for the singlet state, while they differ by ≈ 0.25 eV for the triplet state with CCSD and CCSD(T) results falling in between. The experimentally determined excitation energy for the ${}^{3}B_{2u}$ state (2.60 eV) [145] agrees best with the EOM-CCSD value, but a quantitative comparison would require the inclusion of ZPVE corrections. Optimized CC bond distances for both states of interest are presented in Table 3.3. The remaining structural parameters have been published in Ref. 137. The largest difference in bond length between the methods is less than 0.01 Å for both states.

Table 3.4.: C_2C_3 and C_3C_4 distances in angstrom as well as dihedral angles δ^a in degrees for cyclopentadiene, pyrrole, furan, and thiophene as computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory using the cc-pCVTZ basis set.

State Method		$R(C_2C_3)$	$R(C_3C_4)$	δ	$R(C_2C_3)$	$R(C_3C_4)$	δ	
		Cyc	lopentadien	е	Pyrrole			
$S_0(^1A_1)$	CCSD	1.34112	1.47055	0.00	1.36926	1.42300	0.00	
	$\operatorname{CCSD}(T)$	1.34905	1.47026	0.00	1.37625	1.42505	0.00	
$T_1(^3B_2)^b$	Mk-MRCCSD	1.45368	1.35348	0.00	1.46946	1.34962	0.00	
	EOM-CCSD	1.45034	1.36024	0.00	1.46432	1.34135	0.00	
	CCSD	1.45795	1.35061	0.00	1.47122	1.34101	0.00	
	CCSD(T)	1.45816	1.36078	0.00	1.47235	1.35002	0.00	
$T_1(cis-^3A")^c$	Mk-MRCCSD				1.46847	1.34156	11.11	
	EOM-CCSD				1.46206	1.34799	9.86	
	CCSD				1.47030	1.34089	10.54	
	CCSD(T)			_	1.47074	1.34990	11.00	
$T_1(trans-^3A")^c$	Mk-MRCCSD				1.46693	1.34114	3.93	
	EOM-CCSD				1.46032	1.34921	3.97	
	CCSD				1.46980	1.34047	4.44	
	CCSD(T)				1.46945	1.34958	4.36	
$S_1(^1B_2)^b$	Mk-MRCCSD	1.42856	1.37585	0.00	1.45872	1.35185	0.00	
	EOM-CCSD	1.41967	1.38481	0.00	1.45132	1.36090	0.00	
$S_1(^1A")^c$	Mk-MRCCSD	1.41956	1.38887	22.13	1.44165	1.36761	21.40	
	EOM-CCSD	1.41125	1.39667	22.00	1.43517	1.37157	20.52	
			Furan		Г	Thiophene		
$S_0(^1A_1)$	CCSD	1.35066	1.43559	0.00	1.36031	1.42592	0.00	
	CCSD(T)	1.35795	1.43650	0.00	1.36858	1.42610	0.00	
$T_1({}^{3}B_2)^b$	Mk-MRCCSD	1.45965	1.34093	0.00	1.46290	1.34041	0.00	
	EOM-CCSD	1.45378	1.35000	0.00	1.45766	1.34841	0.00	
	CCSD	1.46178	1.34025	0.00	1.46552	1.33947	0.00	
	CCSD(T)	1.46231	1.34962	0.00	1.46627	1.34850	0.00	
$T_1(^{3}A")^c$	Mk-MRCCSD	1.46455	1.33905	3.80	1.46358	1.34203	10.11	
	EOM-CCSD	1.45837	1.34661	2.97	1.45802	1.34857	8.46	
	CCSD	1.46674	1.33839	3.14	1.46619	1.34066	8.92	
	CCSD(T)	1.46700	1.34747	3.56	1.46682	1.34969	9.37	
$S_1(^1B_2)^b$	Mk-MRCCSD	1.43791	1.35996	0.00	1.45628	1.34601	0.00	
· · ·	EOM-CCSD	1.43100	1.36609	0.00	1.44153	1.35785	0.00	
$S_1(^1A")^c$	Mk-MRCCSD	1.43288	1.37162	21.71	1.45083	1.35767	18.56	
	EOM-CCSD	1.42453	1.37688	20.03	1.43804	1.36641	18.49	

 ${}^{a}\delta$ is the dihedral angle defined by C₁, C₂, C₃, and C₄.

^bImposing C_{2v} symmetry as constraint.

^cWithin C_s symmetry.

The ring compounds cyclopentadiene, pyrrole, furan, and thiophene share a similar electronic structure and are thus discussed together in this section. The dominant configuration in the ground-state wave function is $|\Phi\rangle = |(\operatorname{core})^2(1a_2)^2\rangle$. Adiabatic excitation energies for the lowest non-totally symmetric singlet and triplet states are summarized in Table 3.1. These states arise from lifting an electron from the $1a_2$ orbital to the $4b_2$ (thiophene) or the $3b_2$ orbital (all other molecules). A noteworthy feature of some of these states is their non-planarity, which has been studied previously [146–153], albeit most investigations focused on vertical excitation energies [142, 143, 154–161]. Regarding furan, an in-plane distortion has also been proposed [162, 163], but this possibility is excluded from the present study. Table 3.1 shows that EOM-CCSD and Mk-MRCCSD yield consistent excitation energies for

Table 3.1 shows that EOM-CCSD and Mk-MRCCSD yield consistent excitation energies for all states of interest. The energetic differences between C_{2v} and C_s minima are in qualitative agreement as well. Yet, it is also seen that Mk-MRCCSD leads for all singlet states to values smaller by 0.1–0.2 eV, while a better match is found for the triplet states. For the latter, Mk-MRCCSD, EOM-CCSD, and CCSD(T) agree within 0.03 eV for all molecules with a single larger deviation of 0.08 eV occurring for cyclopentadiene, whereas CCSD delivers significantly smaller values.

 C_2C_3 and C_3C_4 distances as well as dihedral angles δ for the optimized structures of all states considered here are presented in Table 3.4. The remaining structural parameters are available from Ref. 137. Non-planar equilibrium structures are obtained for all excited states except for the triplet state of cyclopentaliene [146]. The optimized structures for the excited singlet states of all four molecules are also shown in Figure 3.2c. EOM-CCSD and Mk-MRCCSD agree within 0.01 Å for all bond lengths with a larger deviation of 0.015 Å occurring only for the singlet state of thisphene. Concerning the dihedral angle δ , the differences between all four methods do not exceed 1.5° . For the triplet state of pyrrole, all methods predict two minimum structures, which differ by the orientation of the NH bond with respect to the ring distortion and which are therefore labeled *cis* and *trans*. The energy gap between these structures is calculated to be less than 0.03 eV, but Mk-MRCCSD and CCSD(T) favor the *cis*-structure, while EOM-CCSD predicts a lower energy for the *trans*-structure and CCSD a negligible energy difference. It should be added that a corresponding pair of equilibrium structures has been reported for the singlet state of pyrrole based on CASPT2 calculations [151]. However, with all methods used in the present work, only the *cis*-structure is obtained as a minimum for the singlet state.

3.3. Excited States of Acetylene and Vinylidene

Much effort has been spent on the accurate description of the ground and excited states of acetylene [164–175]. Its closed-shell electronic ground state has $D_{\infty h}$ symmetry and is well represented by the configuration $|\Phi\rangle = |(\operatorname{core})^2(1\pi_u)^4\rangle$. Single-reference CC theory is the method of choice to target it [176], while a variety of methods has been applied to the low-lying excited valence states, which are more challenging to describe than the ground state. However, several extensive studies at the MRCI [166,167,175], CASPT2 [173], MR-AQCC [175], EOM-CCSD [170–172], and CCSD(T) [169,174] levels of theory have led to a good understanding of the local minima on the lower potential-energy surfaces. The focus in this work is to test the accuracy of the Mk-MRCCSD method for the four lowest excited singlet and triplet states. They all arise from the configuration $|\Phi\rangle = |(\operatorname{core})^2(1\pi_u)^3(1\pi_g)^1\rangle$, which yields the states ${}^{1,3}\Sigma_u^+$, ${}^{1,3}\Sigma_u^-$, and ${}^{1,3}\Delta_u$. As all these states are unstable with respect to a symmetry-lowering distortion along the CCH bending angle, cisoid and transoid equilibrium structures exist [177] as displayed in Figure 3.3. C_{2v} symmetry is imposed for all cisoid structures and C_{2h} symmetry for all transoid structures even though preceding studies [172, 175] indicate that higher-lying excited states may be subject to a further symmetry lowering. For all Mk-



Figure 3.3.: Structures for the ${}^{1}A_{2}$ state (left) and the ${}^{1}A_{u}$ state (center) of acetylene as well as the ${}^{1}A_{2}$ state of vinylidene (right) as computed at the Mk-MRCCSD level of theory using the cc-pCVTZ basis set.

7.070

1.947

2.527

2.796

4.011

Vinylidene

a

6.983

7.079

1.999

2.713

3.128

4.031

1.940

2.510

1.973

2.623

cc-l	pCVDZ a	nd cc-p(OVTZ b	asis sets.	u wik-witu		evels of	theory using	
State	Mk-MR	EOM-	CCSD	CCSD(T)	Mk-MR-	EOM-	CCSD	CCSD(T)	
	CCSD	CCSD			CCSD	CCSD			
	cc-pCVDZ cc-pCVTZ								
				Acet	ylene				
$T_1(^{3}B_2)$	3.785	3.652	3.553	3.618	4.001	3.893	3.771	3.859	
$T_1(^3B_u)$	4.171	3.915	3.915	3.968	4.386	4.156	4.127	4.210	
$T_2(^3A_u)$	4.226	4.533	4.238	4.296	4.424	4.720	4.437	4.509	
$T_2(^{3}A_2)$	4.574	4.872	4.580	4.643	4.737	5.028	4.745	4.821	
$S_1(^1A_u)$	5.089	5.471			5.204	5.575			
$S_1(^1A_2)$	5.511	5.884			5.580	5.944			

1.852

2.507

Table 3.5.: Adiabatic excitation energies in eV for acetylene and vinylidene as computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory using the cc-pCVDZ and cc-pCVTZ basis sets.

^{*a*}Mk-MRCCSD calculations for the S_2 (¹ B_u) state did not converge.

6.970

7.137

1.897

2.605

3.026

4.043

1.823

2.412

 $S_2(^1B_2)$

 $S_2(^{1}B_u)$

 $T_1(^{3}B_2)$

 $T_2(^{3}A_2)$

 $S_1(^1A_2)$

 $S_2(^1B_2)$

6.941

a

1.838

2.433

2.704

4.029

MRCCSD calculations, a reference of the form of Eq. (2.21) is used. For comparison purposes, calculations at the EOM-CCSD, CCSD, and CCSD(T) levels of theory are performed as discussed in Section 3.2. The cc-pCVXZ (X=D,T) basis sets [130] are employed in all calculations.

Adiabatic excitation energies for all states of interest computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory are summarized in Table 3.5. In accordance with previous investigations [165, 167, 173], the energetic order of the lowest excited states is found to be ${}^{1}A_{u} < {}^{1}A_{2} < {}^{1}B_{2} < {}^{1}B_{u}$ for singlet states and ${}^{3}B_{2} < {}^{3}B_{u} < {}^{3}A_{u} < {}^{3}A_{2}$ for triplet states. This holds for all methods used with the only exception being that Mk-MRCCSD calculations for the ${}^{1}B_{u}$ state did not converge. Table 3.5 shows that Mk-MRCCSD delivers smaller excitation energies than EOM-CCSD for all states of A_{μ} and A_{2} symmetry, while the reverse order is found for the states of B_u and B_2 symmetry. CCSD and Mk-MRCCSD agree within 0.02 eV for the ${}^{3}A_{u}$ state and the ${}^{3}A_{2}$ state, but differ by about 0.25 eV for the ${}^{3}B_{u}$ state and the ${}^{3}B_{2}$ state. CCSD(T) yields excitation energies, which are consistently about 0.08 eV higher than those at the CCSD level of theory. The maximum deviation between all methods is less than 0.10 eV for the ¹B₂ state and equals roughly 0.30 eV for all remaining states. A possible reason for the convergence problems of the Mk-MRCCSD equations encountered for the ${}^{1}B_{u}$ state is revealed by the analysis of the EOM-CCSD wave functions. These are dominated by one configuration for all states considered here except for the ${}^{1}B_{2}$ state and the ${}^{1}B_{u}$ state, where two configurations contribute roughly equally. Hence, Mk-MRCCSD calculations based on a CAS(2,2) are actually not suited to target the latter states. From this perspective, it is rather striking that EOM-CCSD and Mk-MRCCSD excitation energies agree within less than 0.10 eV for the ${}^{1}B_{2}$ state.

Structural parameters for the ground state and the low-lying excited states of acetylene are shown in Table 3.6. Qualitative agreement between EOM-CCSD and Mk-MRCCSD is obviously achieved for all states except for the ¹B₂ state, where the CCH bond angle is 15–17° smaller at the Mk-MRCCSD level of theory. This fact should be related to the different shape of the wave functions discussed above. The Mk-MRCCSD wave function is confined to one

State	Method	R(CC)	R(CH)	∡(CCH)	R(CC)	R(CH)	∡(CCH)
			cc-pCVDZ			cc-pCVTZ	
				Acet	ylene		
$S_0 (^1\Sigma_q^+)$	CCSD	1.21973	1.07589	180.00	1.20020	1.06157	180.00
	$\operatorname{CCSD}(T)$	1.22575	1.07731	180.00	1.20672	1.06331	180.00
$T_1 (^{3}B_2)$	Mk-MRCCSD	1.34186	1.10488	127.90	1.32341	1.08836	127.99
	EOM-CCSD	1.34854	1.10244	128.97	1.32870	1.08577	129.25
	CCSD	1.34814	1.10400	127.98	1.32941	1.08742	128.21
	$\operatorname{CCSD}(T)$	1.35459	1.10592	127.90	1.33619	1.08977	128.05
$T_1 (^3B_u)$	Mk-MRCCSD	1.34707	1.09602	131.12	1.32678	1.07989	131.68
	EOM-CCSD	1.36059	1.09428	132.21	1.33871	1.07797	132.75
	CCSD	1.35278	1.09629	130.94	1.33266	1.07989	131.56
	$\operatorname{CCSD}(T)$	1.36128	1.09747	131.03	1.34097	1.08151	131.59
$T_2 (^3A_u)$	Mk-MRCCSD	1.39661	1.10834	119.82	1.37510	1.09048	121.06
	EOM-CCSD	1.38606	1.10742	121.05	1.36528	1.08927	122.43
	CCSD	1.39573	1.10833	119.94	1.37417	1.09046	121.19
	$\operatorname{CCSD}(T)$	1.40324	1.11057	119.48	1.38228	1.09300	120.69
$T_2 (^{3}A_2)$	Mk-MRCCSD	1.36792	1.10798	130.17	1.34940	1.09096	130.66
	EOM-CCSD	1.35353	1.10802	132.51	1.33678	1.09030	133.00
	CCSD	1.36703	1.10820	130.36	1.34859	1.09115	130.85
	$\operatorname{CCSD}(T)$	1.37384	1.11041	129.96	1.35610	1.09366	130.41
$S_1 (^1A_u)$	Mk-MRCCSD	1.38858	1.11116	120.88	1.36791	1.09270	122.33
	EOM-CCSD	1.37505	1.11067	122.18	1.35564	1.09176	123.75
$S_1 (^1A_2)$	Mk-MRCCSD	1.35379	1.11347	131.90	1.33676	1.09487	132.50
	EOM-CCSD	1.33741	1.11348	134.41	1.32261	1.09407	134.97
$S_2 (^{1}B_2)$	Mk-MRCCSD	1.35278	1.13079	129.72	1.33250	1.11108	130.67
	EOM-CCSD	1.33018	1.11385	144.41	1.31387	1.08932	147.56
$S_2 (^1B_u)$	Mk-MRCCSD	a		—	a		—
	EOM-CCSD	1.34321	1.09129	146.60	1.32178	1.07263	150.46
				Viny	lidene		
S_0 (¹ A ₁)	CCSD	1.31969	1.09740	120.08	1.29881	1.08291	120.02
	$\operatorname{CCSD}(\mathrm{T})$	1.32377	1.09947	120.17	1.30318	1.08531	120.10
$T_1 ({}^{3}B_2)$	Mk-MRCCSD	1.33424	1.10118	121.01	1.31450	1.08629	121.04
	EOM-CCSD	1.33473	1.10005	120.87	1.31526	1.08519	120.93
	CCSD	1.33597	1.10075	120.94	1.31599	1.08590	121.01
	$\operatorname{CCSD}(\mathrm{T})$	1.34183	1.10247	120.85	1.32224	1.08795	120.90
$T_2 ({}^{3}A_2)$	Mk-MRCCSD	1.44787	1.10484	122.51	1.42760	1.08914	122.31
	EOM-CCSD	1.43745	1.10531	122.67	1.41729	1.08976	122.47
	CCSD	1.44888	1.10489	122.49	1.42855	1.08916	122.29
	CCSD(T)	1.45159	1.10690	122.58	1.43171	1.09150	122.36
$S_1 ({}^{_1}A_2)$	Mk-MRCCSD	1.46925	1.10583	122.33	1.44148	1.08985	122.14
	EOM-CCSD	1.44354	1.10677	122.57	1.42255	1.09101	122.38
$S_2 ({}^{_1}B_2)$	Mk-MRCCSD	1.34612	1.10519	119.90	1.32393	1.09048	120.11
	EOM-CCSD	1.34603	1.10509	119.90	1.32425	1.09014	120.04

Table 3.6.: CC and CH bond distances in angstrom and CCH bond angles in degrees for acetylene and vinylidene as computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory using the cc-pCVDZ and cc-pCVTZ basis sets.

 $^a\mathrm{Mk-MRCCSD}$ calculations for the S2 $(^1\mathrm{B}_u)$ state of acetylene did not converge.
configuration (i.e., two determinants), while two configurations are of importance in the EOM-CCSD picture for this state. It should be added that a deviation in bond angle of about 10° between different CASSCF calculations for the ¹B₂ state has been reported in the literature [173]. Regarding all other states, Mk-MRCCSD and EOM-CCSD deviate by less than 0.02 Å and 0.005 Å for the CC and the CH bond length, respectively, while the CCH bond angle differs by at most 2.5°. Furthermore, Table 3.6 reveals that the CC bond is longer at the Mk-MRCCSD level than at the EOM-CCSD level for all states of A_u and A_2 symmetry, whereas the opposite is true for the triplet states of B_u and B_2 symmetry. This pattern should be related to the order of Mk-MRCCSD and EOM-CCSD excitation energies discussed before. In contrast, the CCH angle is computed to be always smaller at the Mk-MRCCSD level of theory. CCSD and Mk-MRCCSD agree within 0.006 Å and 0.2° for all states, while the impact of the perturbative triples corrections is not uniform.

Vinylidene is an isomer of acetylene and can therefore be discussed in conjunction with the latter. Its ground state has been discussed most often with a special focus on the isomerization barrier with respect to acetylene [178–181], whereas comparatively little is known about the excited states of vinylidene. Calculations at the CCSD and EOM-CCSD levels of theory have established that the molecule possesses an ${}^{1}A_{1}$ ground state within C_{2v} symmetry and two low-lying excited singlet and triplet states of B_2 and A_2 symmetry [168, 172, 174, 182]. The ground state is well described by the configuration $|\Phi\rangle = |(\operatorname{core})^2 (5a_1)^2 (1b_1)^2\rangle$, while the two lowest excited states arise by excitation of a single electron from either the $5a_1$ or the $1b_1$ orbital to the $2b_2$ orbital. Adiabatic excitation energies for these four states are displayed in Table 3.5. All methods agree on the energetic order ${}^{3}B_{2} < {}^{3}A_{2} < {}^{1}A_{2} < {}^{1}B_{2}$. The fact that the lowest triplet state corresponds to the excitation of an electron out of the second highest occupied orbital has previously been discussed in detail [183]. From the values in Table 3.5 it is seen that EOM-CCSD leads to higher excitation energies than Mk-MRCCSD for all states considered. The maximum deviation in excitation energy is less than 0.06 eV for the states of B_2 symmetry, but equals roughly 0.20 eV and 0.33 eV for the ${}^{3}A_2$ and the $^{1}A_{2}$ state, respectively.

CC and CH bond distances as well as CCH bond angles computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory are summarized in Table 3.6. It can be seen that all methods predict a slight elongation of the CC bond for the states of B_2 symmetry and a strong elongation for the states of A_2 symmetry, both compared to the ground state. For the ${}^{1}B_{2}$ and the ${}^{3}B_{2}$ state, EOM-CCSD and Mk-MRCCSD agree within 0.002 Å on all bond lengths, whereas the CC bond is predicted to be 0.01 Å and 0.02 Å shorter for the ${}^{3}A_{2}$ and the ${}^{1}A_{2}$ state, respectively, when computed with Mk-MRCCSD. CCSD bond lengths are in good accordance with Mk-MRCCSD results and CCSD(T) calculations lead to elongations of about 0.003 Å to 0.006 Å for both bonds.

While there is no doubt that ground-state acetylene represents the global minimum on the S_0 potential hypersurface, the situation is not that obvious for the higher-lying potential hypersurfaces. In an earlier study [170] at the EOM-CCSD and MR-AQCC levels of theory, the vinylidene structure was found to be the global minimum on the S_1 surface. Regarding the T_1 hypersurface, another study [168] at the CCSD and CCSD(T) levels of theory reported energy differences of less than 0.1 eV between the vinylidene and the *cis*-acetylene structure. In the following, the question of the global minimum for the S_1 , S_2 , T_1 , and T_2 potential hypersurfaces is reexamined. Table 3.7 contains relative energies for the *cis*- and *trans*-acetylene structures with respect to the vinylidene structure. For the S_1 surface, both Mk-MRCCSD and EOM-CCSD predict that the 1A_2 state of vinylidene is lower in energy by 0.5-0.6 eV than the 1A_u state of *trans*-acetylene. For the S_2 surface, an even larger value of about 1.1 eV is obtained for the energy gap between *cis*-acetylene and vinylidene. Concerning

Table 3.7.: Energies in eV for the *cis*-acetylene and *trans*-acetylene structures relative to the vinylidene structure on the S₁, S₂, T₁, and T₂ potential hypersurfaces as computed at the CCSD, CCSD(T), EOM-CCSD, and Mk-MRCCSD levels of theory using the cc-pCVDZ and cc-pCVTZ basis sets.

Electronic	Mk-MR-	EOM-	CCSD	$\operatorname{CCSD}(T)$	Mk-MR-	EOM-	CCSD	$\operatorname{CCSD}(T)$		
State	CCSD	CCSD			CCSD	CCSD				
		cc-p6	CVDZ			cc-p6	CVTZ			
		cis-Acetylene								
$S_1(^1A_2)$	1.053	1.104		_	0.900	0.932		_		
$S_2(^{1}B_2)$	1.158	1.173	_		1.176	1.069	_	—		
$T_1(^{3}B_2)$	0.193	0.001	-0.030	-0.039	0.170	0.011	-0.053	-0.058		
$\mathrm{T}_{2}(^{3}\mathrm{A}_{2})$	0.387	0.513	0.414	0.330	0.326	0.431	0.351	0.255		
				trans-A	cetylene					
$S_1(^1A_u)$	0.632	0.691			0.525	0.562				
$S_2(^1B_u)$	a	1.340	_		a	1.164	_			
$T_1(^{3}B_u)$	0.580	0.265	0.333	0.311	0.555	0.274	0.303	0.293		
$T_2(^3A_u)$	0.039	0.175	0.072	-0.017	0.013	0.124	0.043	-0.058		

^{*a*}Mk-MRCCSD calculations for the S_2 (¹ B_u) state did not converge.

the triplet states, the energetic order of the structures is less clear. Mk-MRCCSD calculations claim that the vinylidene structure is the global minimum on the T₁ hypersurface with the *cis*acetylene structure lying 0.2 eV higher in energy. In contrast, EOM-CCSD yields a negligible energy difference, while CCSD and CCSD(T) favor the *cis*-acetylene structure by 0.05 eV. On the T₂ hypersurface, the vinylidene structure is found to be the global minimum by CCSD, EOM-CCSD, and Mk-MRCCSD although the calculated energy gaps vary considerably. The *trans*-acetylene structure is computed to be the global minimum only when using CCSD(T). Finally, Table 3.7 shows that all energy differences significantly depend on the basis set used, which makes a rigorous judgment of the results difficult.

3.4. Ground and Excited States of Aryne Compounds

Aryne compounds have served as a testing ground for numerous multireference methods as their biradical character requires a balanced description of static and dynamic electron correlation if accurate energies and structures are to be computed [184–186]. Optimized structures for the lowest singlet state of o-benzyne, m-benzyne, p-benzyne, 2,6-pyridyne, and the 2,6-pyridynium cation are shown in Figure 3.4. Most previous studies have focused on the three isomers of benzyne [61, 69, 71, 77, 187–199], but 2,6-pyridyne and the 2,6-pyridynium cation [74, 82, 200–204] share a similar electronic structure governed by the pair of frontier orbitals depicted in Figure 3.5, which can be qualitatively understood as bonding and antibonding combination of the orbitals accommodating the radical electrons [186]. Filling the frontier orbitals with two electrons results in two closed-shell and two open-shell configurations, which dominate the low-lying electronic states of the five molecules considered here. Since the energy difference between the frontier orbitals decreases from o-benzyne to p-benzyne, the multireference character increases in the same direction [69, 188, 189].

In the present investigation, all Mk-MRCCSD calculations for closed-shell states rely on a TCSCF wave function (Eq. (2.19)) as reference and those for open-shell states on a ROHF wave function (Eq. (2.21)). All states are also targeted at the MR-AQCC level of theory



(a) Structures for the ground states of *o*-, *m*-, and *p*-benzyne as computed at the Mk-MRCCSD level of theory using the cc-pCVTZ basis set.



(b) Structures for the lowest-lying singlet states of 2,6-pyridyne and the 2,6-pyridynium cation as computed at the Mk-MRCCSD level of theory using the cc-pCVTZ basis set.

Figure 3.4.: Structures for aryne compounds.

using the same reference wave functions.¹ In addition, the triplet states are studied in their $M_s = \pm 1$ component using CCSD and CCSD(T), while EOM-CCSD calculations [125, 126] are performed for the open-shell singlet states starting from CCSD wave functions. However, results from the latter calculations should be interpreted with caution as their reliability decreases with growing multireference character of the closed-shell ground state. Calculations on *p*-benzyne are carried out in D_{2h} symmetry with active orbitals of a_g and b_{3u} symmetry while calculations for the remaining molecules are performed imposing C_{2v} symmetry and using active orbitals of a_1 and b_2 symmetry.



Figure 3.5.: Active orbitals of *o*-benzyne, *m*-benzyne, and *p*-benzyne from TCSCF calculations for the S_0 ground state, structure optimized at the Mk-MRCCSD/cc-pCVTZ level of theory. The active orbitals of 2,6-pyridyne and the 2,6-pyridynium cation are of similar shape as those of *m*-benzyne.

Adiabatic excitation energies for the lowest pair of open-shell states of o-, m-, and p-benzyne are comprised in Table 3.8. It is seen at a glance that excitation energies computed with

¹These calculations have been carried out with the COLUMBUS program package [205].

Table 3.8.: Adiabatic excitation energies in eV for o-, m-, p-benzyne, 2,6-pyridyne, and the 2,6-pyridynium cation as computed at the CCSD, CCSD(T), EOM-CCSD, MR-AQCC, and Mk-MRCCSD levels of theory using the cc-pCVDZ and cc-pCVTZ basis sets.

State	Mk-MR-	MR-	EOM-	CCSD	CCSD(T)	Mk-MR-	EOM-	CCSD	CCSD(T)
	CCSD	$AQCC^a$	CCSD			CCSD	CCSD		
		С	c-pCVD2	Z			cc-p	CVTZ	
					o-Be	nzyne			
$T_1(^3B_2)$	1.545	1.403	1.349	1.237	1.463	1.675	1.496	1.364	1.608
$S_1(^1B_2)$	4.802	b	4.922			4.851	4.912		
					m-Be	enzyne			
$T_1(^3B_2)$	0.839	0.683	0.650	0.439	0.769	0.913	0.808	0.594	0.850
$S_1(^1B_2)$	4.794	b	4.632	_		4.718	4.622	_	
		<i>p</i> -Benzyne							
$\mathrm{T}_{1}(^{3}\mathrm{B}_{3u})$	0.216	0.125	-0.537	-0.706	0.192	0.211	-0.548	-0.752	0.152
$\mathrm{S}_1(^1\mathrm{B}_{3u})$	4.358	b	4.180			4.211	3.935		
					2,6-Py	vridyne			
$T_1(^3B_2)$	-0.040	-0.124	-0.328	-0.498	-0.036	-0.043	-0.323	-0.505	-0.041
$S_1(^1A_1)$	0.109	0.187		-0.018	0.123	0.034		-0.085	0.040
$S_2(^1B_2)$	2.013	2.092	2.686	—		2.040	2.724		
					2,6-Pyr	idynium			
$T_1(^3B_2)$	0.465	0.363	0.000	-0.187	0.444	0.495	0.006	-0.191	0.466
$S_1(^1B_2)$	4.880	b	4.076			c	4.040		

^aFor technical reasons, MR-AQCC calculations were limited to the cc-pCVDZ basis set.

^bNo minimum on the S_1 potential hypersurface could be determined at the MR-AQCC level of theory using a CAS(2,2).

 c No minimum on the S₁ potential hypersurface could be determined at the Mk-MRCCSD/cc-pCVTZ level of theory.

different methods deviate significantly from each other for all three benzynes. All methods predict the energy difference between the T_1 state and the ground state to shrink when going from o-benzyne to p-benzyne with Mk-MRCCSD consistently yielding the largest excitation energies, followed by CCSD(T), MR-AQCC, EOM-CCSD, and CCSD results. Concerning *p*-benzyne, CCSD and EOM-CCSD even predict a triplet ground state, which is not in line with previous theoretical and experimental studies [206]. The maximum deviation between the methods amounts to 0.31 eV for o-benzyne, 0.40 eV for m-benzyne, and 0.92 eV for pbenzyne. This decreasing agreement may be related to the multireference character of the S_0 ground state, which increases in the same direction. It should be interpreted as an indication that the CCSD method fails to correctly describe the ground state. Regarding the open-shell singlet state (S_1) , Mk-MRCCSD and EOM-CCSD both deliver excitation energies that decrease when going from o- to p-benzyne. Similar to the T_1 state, the deviation between the two methods increases in the same direction, but does not exceed 0.28 eV for p-benzyne. Furthermore, it is noteworthy that the minimum on the S_1 potential hypersurface is not found at the MR-AQCC level of theory when using a CAS(2,2). A potential reason may consist in a certain inadequacy of the orbitals used as indicated by large singles amplitudes in the corresponding Mk-MRCCSD calculations. While single excitations in CC theory efficiently account for orbital-relaxation effects, MR-AQCC calculations are more sensitive to the underlying orbitals due to the linear parametrization. The use of a larger reference space may potentially allow for a better description of the S_1 state at the MR-AQCC level of theory. Finally, it should be mentioned that experimental values [206] for the singlet-triplet splitting of the benzynes $((1.628 \pm 0.013) \text{ eV}$ for o-benzyne, $(0.911 \pm 0.014) \text{ eV}$ for m-benzyne, and

Table 3.9.: Distances between the radical centers (C_1C_2 distance for *o*-benzyne, C_2C_6 distance for *m*-benzyne, and C_1C_4 distance for *p*-benzyne) as computed at the CCSD, CCSD(T), EOM-CCSD, MR-AQCC, and Mk-MRCCSD levels of theory using the cc-pCVDZ and cc-pCVTZ basis sets. All values in angstrom.

State	Method	cc-pCVDZ	cc- $pCVTZ$	cc-pCVDZ	cc- $pCVTZ$	cc-pCVDZ	cc-pCVTZ	
		o-Benzyne		m-Be	nzyne	p-Benzyne		
S_0	Mk-MRCCSD	1.27067	1.25048	2.09361	2.01407	2.71936	2.68646	
	MR-AQCC	1.27438	a	2.13747	a	2.72374	a	
	CCSD	1.26369	1.24358	b	b	2.74064	2.70705	
	$\operatorname{CCSD}(T)$	1.27674	1.25671	2.12237	2.04318	2.74437	2.71830	
S_1	Mk-MRCCSD	1.43829	1.41868	2.31650	2.28116	2.54500	2.49918	
	EOM-CCSD	1.38360	1.36623	2.27741	2.23482	2.61234	2.56251	
T_1	Mk-MRCCSD	1.40664	1.39032	2.34960	2.31960	2.66015	2.62599	
	MR-AQCC	1.41248	a	2.35957	a	2.67332	a	
	EOM-CCSD	1.40726	1.38978	2.35297	2.32178	2.65994	2.62776	
	CCSD	1.41027	1.39362	2.35522	2.32492	2.66997	2.63528	
	$\operatorname{CCSD}(T)$	1.41500	1.39865	2.36471	2.33485	2.67874	2.64404	

^aFor technical reasons, MR-AQCC calculations were limited to the cc-pCVDZ basis set.

 b CCSD calculations for the S₀ state of *m*-benzyne favor a bicyclic structure without multireference character.

 (0.165 ± 0.016) eV for *p*-benzyne) agree within 0.05 eV with the Mk-MRCCSD/cc-pCVTZ results presented in Table 3.8.

As a consequence of the active orbitals' shape (cf. Figure 3.5), the structural differences between the examined states can be well understood by looking at the distances between the two radical centers. Values computed for these parameters are summarized in Table 3.9, while complete optimized structures are available from Ref. 137. All methods predict comparable structural changes upon excitation. For o-benzyne, the C_1C_2 distance is computed to be about 0.15 Å longer for the S_1 and the T_1 state compared to the ground state, while for pbenzyne, the C_1C_4 distance decreases by about 0.07 Å and 0.15 Å for the T_1 and the S_1 state, respectively. Concerning *m*-benzyne, all methods agree that the C_2C_6 distance is roughly 0.05 Å longer for the T₁ state than for the S₁ state. Yet, qualitatively different equilibrium structures are obtained for the ground state. CCSD calculations favor a bicyclic form with a very short C_2C_6 distance, which has no multireference character and is thus excluded from the present study. In contrast, Mk-MRCCSD, MR-AQCC, and CCSD(T) calculations lead to a monocyclic structure as depicted in Figure 3.4, whose C_2C_6 distance is approximately 0.2 Å shorter than that of the T_1 and the S_1 state. It is also noteworthy that better agreement of the methods is observed for the triplet states than for the singlet states. For the former, the maximum discrepancy does not exceed 0.02 Å, whereas it amounts to 0.045 Å for the ground states and 0.063 Å for the open-shell singlet states. A potential explanation regarding the latter states can be deduced from the EOM-CCSD wave functions. They show that the open-shell singlet states are not as clearly dominated by one configuration as the triplet states are. Mk-MRCCSD calculations would thus require the use of a larger reference space than a CAS(2,2) as discussed above for MR-AQCC.

Adiabatic excitation energies for 2,6-pyridyne and the 2,6-pyridynium cation can be found in Table 3.8. Both molecules are formally obtained from *m*-benzyne by replacing the C_1 carbon atom by either a nitrogen atom or a NH group. While the electronic structure of the 2,6-pyridynium cation is comparable to that of the parent benzyne, an intriguing difference occurs for 2,6-pyridyne as two near-degenerate closed-shell singlet states are found. Both of these states possess a distinct multireference character and are mainly composed of the

Table 3.10.: Distances between the radical centers (C_2C_6 distances) for 2,6-pyridyne and the 2,6-pyridynium cation as computed at the CCSD, CCSD(T), EOM-CCSD, MR-AQCC, and Mk-MRCCSD levels of theory using the cc-pCVDZ and cc-pCVTZ basis sets. All values in angstrom.

State	Method	cc-pCVDZ	cc- $pCVTZ$	cc-pCVDZ	cc-pCVTZ
		2,6-Py	ridyne	2,6-Pyri	idynium
$S_0 (^1A_1)$	Mk-MRCCSD	2.05856	2.02971	2.21826	2.18658
	MR-AQCC	2.08297	a	2.23427	a
	CCSD	1.91393	1.81834	2.16314	2.12139
	CCSD(T)	2.05441	2.01443	2.24016	2.20358
$S_1 (^1A_1)^b$	Mk-MRCCSD	2.39874	2.36782		
	MR-AQCC	2.40681	a		
	CCSD	2.42109	2.38829		
	CCSD(T)	2.42741	2.39543		
$S_2 (^1B_2)$	Mk-MRCCSD	2.37173	2.33860	2.29560	c
	MR-AQCC	2.39965	a		a
	EOM-CCSD	2.39959	2.34842	2.15853	2.13721
$T_1 (^{3}B_2)$	Mk-MRCCSD	2.24617	2.22395	2.32155	2.29662
	MR-AQCC	2.25976	a	2.33080	a
	EOM-CCSD	2.24355	2.21968	2.32511	2.29907
	CCSD	2.24195	2.21967	2.32540	2.30012
	CCSD(T)	2.25588	2.23507	2.33673	2.31229

^aFor technical reasons, MR-AQCC calculations were limited to the cc-pCVDZ basis set.

^bAll calculations indicate that such a state does not exist for the 2,6-pyridynium cation.

^cNo minimum on the S₁ potential hypersurface could be determined at the Mk-MRCCSD/cc-pCVTZ level of theory.

configurations $|\Phi_1\rangle = |(\operatorname{core})^2(11a_1)^2\rangle$ and $|\Phi_2\rangle = |(\operatorname{core})^2(7b_2)^2\rangle$. However, the S₀ state is dominated by $|\Phi_1\rangle$, whereas the S₁ state is dominated by $|\Phi_2\rangle$. Since the triplet state comes energetically close to the aforementioned singlets, three electronic states with almost coinciding energies are obtained. As there are no experimental data available, it is impossible to determine the ground state of 2,6-pyridyne without doubt. With respect to the triplet states, Table 3.8 shows almost the same pattern for the pyridynes as for the benzynes. CCSD and EOM-CCSD predict for 2,6-pyridyne a triplet ground state by 0.51 eV and 0.32 eV, respectively, while Mk-MRCCSD and CCSD(T) find a negligible energy difference of 0.04 eV with respect to the S_0 state and the MR-AQCC results fall in between. In contrast, only CCSD favors the triplet state for the 2,6-pyridynium cation. Deviations of similar magnitude are also found for the open-shell singlet states (S_2) of both pyridynes. Mk-MRCCSD and MR-AQCC are in good agreement for 2,6-pyridyne, but EOM-CCSD delivers an excitation energy, which is larger by about 0.6 eV. Concerning the 2.6-pyridynium cation, EOM-CCSD yields a value smaller by 0.8 eV compared to Mk-MRCCSD, whereas MR-AQCC calculations for this state suffer from the same problems that have been discussed above for the benzynes. Regarding the closed-shell states (S_0 and S_1), all methods except for CCSD assign a lower energy to the S_0 state with a maximum deviation of 0.20 eV. In consideration of the multireference character of these two states, this good match is rather unexpected.

 C_2C_6 distances computed at different levels of theory are presented in Table 3.10. As discussed for the benzynes, this parameter differs most noticeably between the electronic states under consideration and can thus be used as a measure to quantify the influence of the configurations $|\Phi_1\rangle$ and $|\Phi_2\rangle$. Complete optimized structures have been published in Ref. 137. As observed for the benzynes, the best agreement of all methods is obtained for the triplet states, for which C_2C_6 distances of ≈ 2.22 Å (2,6-pyridyne) and ≈ 2.30 Å (2,6-pyridynium cation) are calculated. In contrast, a qualitative mismatch occurs for the open-shell singlet state of the 2,6-pyridynium cation, where EOM-CCSD and Mk-MRCCSD yield C_2C_6 distances of 2.15 Å and 2.30 Å, respectively. Better agreement is observed for the corresponding state of 2,6-pyridyne, for which C_2C_6 distances deviate by less than 0.03 Å. Concerning the S₀ states, Mk-MRCCSD, MR-AQCC, and CCSD(T) agree within 0.03 Å on the C_2C_6 distance, while CCSD delivers considerably smaller values. The deviation of CCSD from the other methods is greater than 0.15 Å for 2,6-pyridyne and approximately equals 0.07 Å for the 2,6-pyridynium cation. Interestingly, the deviation of CCSD from the multireference methods is much smaller for the S₁ state (0.03 Å) albeit this state has noticeable multireference character. All methods attribute a longer C_2C_6 distance to this state than to the S₀ state, which is explained by the different weights of $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in conjunction with Figure 3.5.

4. Application of Linear-Response Theory to the Mk-MRCC Wave Function

In this chapter, the theoretical framework for the treatment of static and dynamic secondorder properties as well as excitation energies at the Mk-MRCC level of theory is presented. The quasienergy formalism [16] is applied to study the time evolution of the Mk-MRCC wave function in the presence of an oscillating perturbation. To determine the response of the wave function to the perturbation in first order, the Mk-MRCC linear-response equations are derived. An expression for the Mk-MRCC linear-response function is presented and applied to the calculation of the polarizability tensor.

Static and dynamic polarizabilities as well as vertical excitation energies have been implemented within the Mk-MRCCSD approximation into the quantum-chemical program package CFOUR [124]. This implementation has been used to carry out some illustrative calculations in order to demonstrate the impact of a multireference ansatz on the polarizability tensor and vertical excitation spectra. Moreover, the response treatment allows for the reassessment of Mk-MRCC theory from a new perspective as it provides further insight into the Mk-MRCC sufficiency conditions.

4.1. Theory

4.1.1. Time Evolution of the Mk-MRCC Wave Function

An appropriate ansatz for the time-dependent Mk-MRCC wave function is

$$|\widetilde{\Psi}(t)\rangle = e^{-iF(t)} |\Psi(t)\rangle = e^{-iF(t)} \sum_{\mu} e^{\widehat{T}_{\mu}(t)} |\Phi_{\mu}\rangle c_{\mu}(t)$$
(4.1)

with $e^{-iF(t)}$ as a time-dependent phase factor and $|\Psi(t)\rangle$ as the phase-isolated wave function, whose time dependence is parametrized in terms of the CI coefficients $c_{\mu}(t)$ and the cluster operators $\hat{T}_{\mu}(t) = \sum_{q \in Q(\mu)} t_{q}^{\mu}(t) \hat{\tau}_{q}^{\mu}$. The orbitals used to construct the reference determinants are chosen to be time-independent, which constitutes an orbital-unrelaxed approach. When aiming at dynamic properties, the exclusion of orbital relaxation is common in CC response theory [15, 16] as otherwise an additional set of unphysical poles appears in the response functions and deteriorates the results significantly [207, 208].

Inserting Eq. (4.1) into the time-dependent Schrödinger equation Eq. (2.79) leads to

$$e^{-iF}\left(\hat{H}(t)|\Psi(t)\rangle - i\frac{\partial}{\partial t}|\Psi(t)\rangle - \dot{F}|\Psi(t)\rangle\right) = 0.$$
(4.2)

The time-dependent quasienergy \dot{F} is obtained in a similar way as the energy in the timeindependent case. Projecting Eq. (4.2) onto the reference determinants gives rise to

$$\sum_{\nu} H^{\text{eff}}_{\mu\nu} c_{\nu} = \dot{F} c_{\mu} + i \dot{c}_{\mu} .$$
(4.3)

To determine the time evolution of the cluster amplitudes, the resolution of the identity in the form of Eq. (2.42), i.e., $1 = e^{\hat{T}_{\mu}}(\hat{P} + \hat{Q})e^{-\hat{T}_{\mu}}$, is inserted into Eq. (4.2), which yields after interchange of the indices μ and ν

$$\sum_{\mu} \left[\sum_{\nu} e^{\hat{T}_{\nu}} \left| \Phi_{\mu} \right\rangle H_{\mu\nu}^{\text{eff}} c_{\nu} + e^{\hat{T}_{\mu}} \hat{Q} \overline{H}_{\mu} \left| \Phi_{\mu} \right\rangle c_{\mu} - \dot{F} e^{\hat{T}_{\mu}} \left| \Phi_{\mu} \right\rangle c_{\mu} - i \frac{\partial}{\partial t} \left(c_{\mu} e^{\hat{T}_{\mu}} \left| \Phi_{\mu} \right\rangle \right) \right] = 0 . \quad (4.4)$$

In analogy to Eq. (2.46), individual terms in the summation over μ are set to zero, which represents the straightforward generalization of the Mk-MRCC sufficiency conditions to the time-dependent case. After multiplication with $e^{-\hat{T}_{\mu}}$ and projection onto $\langle \Phi_q^{\mu} \rangle$, the timedependent Mk-MRCC amplitude equations are obtained as

$$\left\langle \Phi_{q}^{\mu} \right| \overline{H}_{\mu} \left| \Phi_{\mu} \right\rangle c_{\mu} + \sum_{\nu \neq \mu} \left\langle \Phi_{q}^{\mu} \right| e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} \left| \Phi_{\mu} \right\rangle H_{\mu\nu}^{\text{eff}} c_{\nu} = i c_{\mu} \dot{t}_{q}^{\mu} .$$

$$\tag{4.5}$$

The Lagrangian technique [80, 112, 116] is used to ensure that Eqs. (4.3) and (4.5) remain fulfilled when propagating the wave function in time. Augmenting the quasienergy by suitable constraints with Lagrange multipliers $\bar{c}_{\mu}(t)$ and $\bar{c}_{\mu}(t) \lambda_{q}^{\mu}(t)$ yields the time-dependent Mk-MRCC Lagrangian

$$L(t) = \dot{F} + \sum_{\mu} \bar{c}_{\mu} \left[\sum_{\nu} H^{\text{eff}}_{\mu\nu} c_{\nu} - \dot{F} c_{\mu} - i\dot{c}_{\mu} \right] + \sum_{\mu} \sum_{q \in Q(\mu)} \bar{c}_{\mu} \lambda^{\mu}_{q} \left[\left\langle \Phi^{\mu}_{q} \right| \overline{H}_{\mu} \left| \Phi_{\mu} \right\rangle c_{\mu} \right] + \sum_{\nu \neq \mu} \left\langle \Phi^{\mu}_{q} \right| e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} \left| \Phi_{\mu} \right\rangle H^{\text{eff}}_{\mu\nu} c_{\nu} - ic_{\mu} \dot{t}^{\mu}_{q} \right].$$

$$(4.6)$$

To align L(t) as closely as possible with the time-independent Lagrangian from Eq. (2.63), $\bar{c}_{\mu}(t) \lambda_{q}^{\mu}(t)$ instead of $\lambda_{q}^{\mu}(t)$ is employed as Lagrange multiplier. Imposing the biorthonormality condition

$$\sum_{\mu} \bar{c}_{\mu}(t) c_{\mu}(t) = 1 \tag{4.7}$$

as a further constraint with corresponding Lagrange multiplier ϵ , the Lagrangian can be rewritten in a form independent of \dot{F} as

$$L(t) = \sum_{\mu} \left[\bar{c}_{\mu} c_{\mu} H_{\mu\mu}^{\text{eff}} + \sum_{q \in Q(\mu)} \bar{c}_{\mu} \lambda_{q}^{\mu} c_{\mu} \langle \Phi_{q}^{\mu} | \overline{H}_{\mu} | \Phi_{\mu} \rangle \right] + \sum_{\mu} \sum_{\nu \neq \mu} \left[\bar{c}_{\mu} c_{\nu} H_{\mu\nu}^{\text{eff}} \right]$$
(4.8)

$$+\sum_{q\in Q(\mu)} \bar{c}_{\mu}\lambda^{\mu}_{q}c_{\nu} \left\langle \Phi^{\mu}_{q}\right| e^{-\hat{T}_{\mu}}e^{\hat{T}_{\nu}} \left| \Phi_{\mu} \right\rangle H^{\text{eff}}_{\mu\nu} \bigg] - \epsilon \bigg[\sum_{\mu} \bar{c}_{\mu}c_{\mu} - 1\bigg] - i\sum_{\mu} \bar{c}_{\mu}\dot{c}_{\mu} - i\sum_{\mu} \sum_{q\in Q(\mu)} \bar{c}_{\mu}\lambda^{\mu}_{q}c_{\mu}\dot{t}^{\mu}_{q} \ .$$

The time evolution of the system is determined by expanding the time-dependent parameters t_q^{μ} , c_{μ} , λ_q^{μ} , \bar{c}_{μ} , and ϵ into Fourier series in terms of frequencies of the perturbation, for example

$$t_q^{\mu}(t) = t_q^{\mu}(0) + \sum_X \varepsilon_X(\omega_X) t_q^{\mu(X)}(\omega_X) e^{-i\omega_X t}$$

$$+ \frac{1}{2} \sum_{X,Y} \varepsilon_X(\omega_X) \varepsilon_Y(\omega_Y) t_q^{\mu(X,Y)}(\omega_X,\omega_Y) e^{-i(\omega_X + \omega_Y)t} + \dots$$

$$(4.9)$$

However, special attention has to be paid to the expansion of $\bar{c}_{\mu}(t)\lambda_{q}^{\mu}(t)$, which has to be treated as a single multiplier $\bar{\lambda}_{q}^{\mu}(t)$, whose first-order response parameters are given as

$$\bar{\lambda}_{q}^{\mu(X)}(\omega_{X}) = \bar{c}_{\mu}(0)\,\lambda_{q}^{\mu(X)}(\omega_{X}) + \bar{c}_{\mu}^{(X)}(\omega_{X})\,\lambda_{q}^{\mu}(0) \,. \tag{4.10}$$

In this way, a time-averaged representation $\{L\}_T$ of the Mk-MRCC Lagrangian can be formulated in analogy to Eq. (2.83). The time-dependent equations may then be solved in each order of perturbation separately by calculating the response parameters corresponding to t_q^{μ} , c_{μ} , $\bar{\lambda}_q^{\mu}$, and \bar{c}_{μ} .

4.1.2. Mk-MRCC Polarizability Tensor

According to Eqs. (2.81) and (2.85), an element $\alpha_{XY}(\omega_X, \omega_Y)$ of the dynamic polarizability tensor can be calculated by differentiating $\{L\}_T$ with respect to the strength parameters ε_X and ε_Y . Bearing in mind the (2n + 1) and (2n + 2) rules of response theory [16, 112], the expression for α_{XY} becomes

$$\alpha_{XY}(\omega_X, \omega_Y) = -P(XY) \left[\begin{pmatrix} \eta_{\nu}^{(X)} \\ \eta_{q}^{\nu(X)} \end{pmatrix}^{\top} \begin{pmatrix} c_{\nu}^{(Y)}(\omega_Y) \\ t_{q}^{\nu(Y)}(\omega_Y) \end{pmatrix}^{\top} \begin{pmatrix} F_{\mu\nu} & F_{\mu q_{\nu}} \\ F_{p_{\mu}\nu} & F_{p_{\mu}q_{\nu}} \end{pmatrix} \begin{pmatrix} c_{\nu}^{(X)}(\omega_X) \\ t_{q}^{\nu(X)}(\omega_X) \end{pmatrix} \right]$$
(4.11)

with $\omega_Y = -\omega_X$ and P(XY) as a permutation operator, whose action on an arbitrary function f is defined as P(XY) f(X,Y) = f(X,Y) + f(Y,X). The elements of the vector $\boldsymbol{\eta}^{(X)}$ are given as

$$\eta_{\nu}^{(X)} = \bar{c}_{\nu} \langle \Phi_{\nu} | \left(1 + \hat{\Lambda}_{\nu} \right) \overline{X}_{\nu} | \Phi_{\nu} \rangle - \bar{c}_{\nu} \langle X \rangle , \qquad (4.12)$$

$$\eta_q^{\nu(X)} = \bar{c}_{\nu} \langle \Phi_{\nu} | \left(1 + \hat{\Lambda}_{\nu} \right) \left[\overline{X}_{\nu}, \hat{\tau}_q^{\nu} \right] | \Phi_{\nu} \rangle c_{\nu} + \sum_{\mu} \bar{c}_{\mu} \langle \Phi_{\mu} | \frac{\partial \Lambda_{\mu}^{\text{int}}}{\partial t_q^{\nu}} \overline{X}_{\mu} | \Phi_{\mu} \rangle c_{\mu}$$
(4.13)

with $\overline{X}_{\nu} = e^{-\hat{T}_{\nu}} \hat{X} e^{\hat{T}_{\nu}}$ as similarity-transformed perturbation operator. $\langle X \rangle$ denotes the expectation value of the operator \hat{X} , while $\hat{\Lambda}$ and $\hat{\Lambda}^{\text{int}}$ represent the deexcitation operators introduced in Eqs. (2.64) and (2.66). The elements of the matrix **F** read

$$F_{\mu\nu} = 0 av{4.14}$$

$$F_{p_{\mu}\nu} = \delta_{\mu\nu} \left[\bar{c}_{\mu} \left\langle \Phi_{\mu} \right| \left(1 + \hat{\Lambda}_{\mu} \right) \left[\overline{H}_{\mu}, \hat{\tau}_{p}^{\mu} \right] \left| \Phi_{\mu} \right\rangle \right] + \bar{c}_{\nu} \left\langle \Phi_{\nu} \right| \frac{\partial \hat{\Lambda}_{\nu}^{\text{int}}}{\partial t_{p}^{\mu}} \overline{H}_{\nu} \left| \Phi_{\nu} \right\rangle + \delta_{\mu\nu} \bar{c}_{\mu} \lambda_{p}^{\mu} \omega_{X} , \quad (4.15)$$

$$F_{\mu q_{\nu}} = \delta_{\mu\nu} \left[\bar{c}_{\nu} \left\langle \Phi_{\nu} \right| \left(1 + \hat{\Lambda}_{\nu} \right) \left[\overline{H}_{\nu}, \hat{\tau}_{q}^{\nu} \right] \left| \Phi_{\nu} \right\rangle \right] + \bar{c}_{\mu} \left\langle \Phi_{\mu} \right| \frac{\partial \hat{\Lambda}_{\mu}^{\text{int}}}{\partial t_{q}^{\nu}} \overline{H}_{\mu} \left| \Phi_{\mu} \right\rangle + \delta_{\mu\nu} \bar{c}_{\nu} \lambda_{q}^{\nu} \omega_{X} , \quad (4.16)$$

$$F_{p_{\mu}q_{\nu}} = \delta_{\mu\nu} \left[\bar{c}_{\nu} \langle \Phi_{\nu} | \left(1 + \hat{\Lambda}_{\nu} \right) \left[[\overline{H}_{\nu}, \hat{\tau}_{p}^{\nu}], \hat{\tau}_{q}^{\nu} \right] | \Phi_{\nu} \rangle c_{\nu} \right] + \left[P_{pq}^{\mu\nu} \bar{c}_{\mu} \langle \Phi_{\mu} | \frac{\partial \hat{\Lambda}_{\mu}^{\text{int}}}{\partial t_{q}^{\nu}} [\overline{H}_{\mu}, \hat{\tau}_{p}^{\mu}] | \Phi_{\mu} \rangle c_{\mu} + \sum_{\lambda} \bar{c}_{\lambda} \langle \Phi_{\lambda} | \frac{\partial^{2} \hat{\Lambda}_{\lambda}^{\text{int}}}{\partial t_{p}^{\mu} \partial t_{q}^{\nu}} \overline{H}_{\lambda} | \Phi_{\lambda} \rangle c_{\lambda} \right] , \qquad (4.17)$$

where the operator $P_{pq}^{\mu\nu}$ acts on a general function f according to

$$P_{pq}^{\mu\nu}f(\mu,\nu,p_{\mu},q_{\nu}) = f(\mu,\nu,p_{\mu},q_{\nu}) + f(\nu,\mu,q_{\nu},p_{\mu}) .$$
(4.18)

It should be noted that the second line of Eq. (4.11) is formally equal to the expression for the polarizability obtained in single-reference CC response theory [14,16]. More precisely, the first terms in Eqs. (4.13) and (4.17) are also present in single-reference CC response theory, while the remaining terms in $\eta_q^{\nu(X)}$ and $F_{p_\mu q_\nu}$ result from the coupling between amplitudes belonging

to different reference determinants. In contrast, the first line in Eq. (4.11) represents the contribution of the CI coefficients' response to α_{XY} and is not present in single-reference CC response theory. The blocks $F_{p_{\mu}\nu}$ and $F_{\mu q_{\nu}}$ can be interpreted as coupling between amplitude-response parameters $(t^{(X)})$ and CI coefficient-response parameters $(c^{(X)})$. A further difference to single-reference CC is that the matrix **F** is frequency-dependent through its off-diagonal blocks $F_{\mu q_{\nu}}$ and $F_{p_{\mu}\nu}$. In addition, it is noteworthy that $F_{\mu\nu}$ vanishes due to the linear parametrization of the wave function with respect to c_{μ} . As a consequence, the Mk-MRCC Lagrangian in Eq. (4.8) contains no products of the CI coefficients.

The calculation of the polarizability tensor according to Eq. (4.11) requires the evaluation of the response parameters $t^{(X)}$, $c^{(X)}$, $t^{(Y)}$, and $c^{(Y)}$ corresponding to two distinct frequencies ω_X and ω_Y . However, the Mk-MRCC response equations (Eq. (4.25)) can be employed to recast Eq. (4.11) in an asymmetric form involving response parameters for one frequency only [16]. Yet, the resulting expression

$$\alpha_{XY}(\omega_X,\omega_Y) = -\begin{pmatrix} \eta_{\nu}^{(Y)} \\ \eta_{q}^{\nu(Y)} \end{pmatrix}^{\top} \begin{pmatrix} c_{\nu}^{(X)}(\omega_X) \\ t_{q}^{\nu(X)}(\omega_X) \end{pmatrix} - \begin{pmatrix} \bar{c}_{\mu}^{(X)}(\omega_X) \\ \bar{\lambda}_{p}^{\mu(X)}(\omega_X) \end{pmatrix}^{\top} \begin{pmatrix} \xi_{\mu}^{(Y)} \\ \xi_{p}^{\mu(Y)} \end{pmatrix} , \ \omega_Y = -\omega_X$$
(4.19)

contains the response of the Lagrange multipliers $\bar{\lambda}$ and \bar{c} as well. In this equation, the vector $\boldsymbol{\xi}^{(Y)}$ has been introduced as an additional intermediate quantity with its elements given as

$$\xi_{\mu}^{(Y)} = \sum_{\nu} \left(Y_{\mu\nu}^{\text{eff}} - \delta_{\mu\nu} \langle Y \rangle \right) c_{\nu} , \qquad (4.20)$$

$$\xi_p^{\mu(Y)} = \langle \Phi_p^{\mu} | \overline{Y}_{\mu} | \Phi_{\mu} \rangle c_{\mu} + \sum_{\nu \neq \mu} \langle \Phi_p^{\mu} | e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} | \Phi_{\mu} \rangle Y_{\mu\nu}^{\text{eff}} c_{\nu} , \qquad (4.21)$$

where \overline{Y}_{μ} is a similarity-transformed perturbation operator and $Y_{\mu\nu}^{\text{eff}}$ is defined in analogy to $H_{\mu\nu}^{\text{eff}}$ (cf. Eq. (2.40)). A particular advantage of Eq. (4.19) is that it can be rewritten in terms of the density matrices defined in Eq. (2.71), which greatly facilitates a practical implementation. This yields

$$\alpha_{XY}(\omega_X,\omega_Y) = -\sum_{\mu} \left[\bar{c}_{\mu} c_{\mu} \sum_{pq} \frac{\partial D_{pq}^{\mu}}{\partial \varepsilon_X(\omega_X)} h_{pq}^Y + \left(\bar{c}_{\mu}^{(X)} c_{\mu} + \bar{c}_{\mu} c_{\mu}^{(X)} \right) \sum_{pq} D_{pq}^{\mu} h_{pq}^Y \right]$$
(4.22)

with h_{pq}^{Y} denoting the derivative of the one-electron integrals with respect to the magnitude of the electric field ε_{Y} .

4.1.3. Mk-MRCC Linear-Response Equations

The calculation of the polarizability tensor according to Eq. (4.19) requires the first-order response to the wave-function parameters $t^{(X)}$ and $c^{(X)}$ and the Lagrange multipliers $\bar{\lambda}^{(X)}$ and $\bar{c}^{(X)}$. These quantities are obtained through stationarity conditions for $\{L\}_T^{(2)}$, i.e., the timeaveraged Lagrangian truncated at second order in perturbation. From the four conditions

$$\frac{\partial \{L\}_T^{(2)}}{\partial t_q^{\mu(X)}(\omega_X)} = 0 , \ \frac{\partial \{L\}_T^{(2)}}{\partial c_\mu^{(X)}(\omega_X)} = 0 , \ \frac{\partial \{L\}_T^{(2)}}{\partial \bar{\lambda}_q^{\mu(X)}(\omega_X)} = 0 , \\ \frac{\partial \{L\}_T^{(2)}}{\partial \bar{c}_\mu^{(X)}(\omega_X)} = 0 \ \forall \mu, q \in Q(\mu) , \ (4.23)$$

two systems of linear equations can be deduced, which read

$$\begin{bmatrix} \begin{pmatrix} A_{\mu\nu} & A_{\mu q_{\nu}} \\ A_{p\mu\nu} & A_{p\mu q_{\nu}} \end{pmatrix} - \omega_X \begin{pmatrix} \delta_{\mu\nu} & 0 \\ 0 & S_{p\mu q_{\nu}} \end{pmatrix} \end{bmatrix} \begin{pmatrix} c_{\nu}^{(X)}(\omega_X) \\ t_q^{\nu(X)}(\omega_X) \end{pmatrix} + \begin{pmatrix} \xi_{\mu}^{(X)} \\ \xi_{p}^{\mu(X)} \end{pmatrix} = 0 , \qquad (4.24)$$

$$\begin{pmatrix} \bar{c}^{(X)}_{\mu}(\omega_X) \\ \bar{\lambda}^{\mu(X)}_{p}(\omega_X) \end{pmatrix}^{\top} \begin{bmatrix} \begin{pmatrix} A_{\mu\nu} & A_{\mu q_{\nu}} \\ A_{p_{\mu}\nu} & A_{p_{\mu}q_{\nu}} \end{pmatrix} + \omega_X \begin{pmatrix} \delta_{\mu\nu} & 0 \\ 0 & S_{p_{\mu}q_{\nu}} \end{pmatrix} \end{bmatrix} + \begin{pmatrix} \eta^{(X)}_{\nu} \\ \eta^{\nu(X)}_{q} \end{pmatrix}^{\top} + \begin{pmatrix} c^{(X)}_{\mu}(\omega_X) \\ t^{\mu(X)}_{p}(\omega_X) \end{pmatrix}^{\top} \begin{pmatrix} F_{\mu\nu} & F_{\mu q_{\nu}} \\ F_{p_{\mu}\nu} & F_{p_{\mu}q_{\nu}} \end{pmatrix} = 0 .$$

$$(4.25)$$

 ${\bf A}$ denotes the perturbation-independent Mk-MRCC Jacobian matrix, whose elements are given as

$$A_{\mu\nu} = H^{\text{eff}}_{\mu\nu} - \delta_{\mu\nu}E , \qquad (4.26)$$

$$A_{\mu q_{\nu}} = \langle \Phi_{\mu} | \left[\overline{H}_{\nu}, \hat{\tau}_{q}^{\nu} \right] | \Phi_{\nu} \rangle c_{\nu} , \qquad (4.27)$$

$$A_{p_{\mu}\nu} = (1 - \delta_{\mu\nu}) \langle \Phi_p^{\mu} | e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} | \Phi_{\mu} \rangle H_{\mu\nu}^{\text{eff}} + \delta_{\mu\nu} \langle \Phi_p^{\mu} | \overline{H}_{\mu} | \Phi_{\mu} \rangle , \qquad (4.28)$$

$$A_{p_{\mu}q_{\nu}} = (1 - \delta_{\mu\nu}) \left[\left\langle \Phi_{p}^{\mu} \right| e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} \left| \Phi_{\mu} \right\rangle \left\langle \Phi_{\mu} \right| \left[\overline{H}_{\nu}, \hat{\tau}_{q}^{\nu} \right] \left| \Phi_{\nu} \right\rangle c_{\nu} + \left\langle \Phi_{p}^{\mu} \right| e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} \hat{\tau}_{q}^{\nu} \left| \Phi_{\mu} \right\rangle H_{\mu\nu}^{\text{eff}} c_{\nu} \right] \right.$$

$$\left. + \delta_{\mu\nu} \left[\left\langle \Phi_{p}^{\mu} \right| \left[\overline{H}_{\mu}, \hat{\tau}_{q}^{\mu} \right] \left| \Phi_{\mu} \right\rangle c_{\mu} - \sum_{\lambda \neq \mu} \left\langle \Phi_{p}^{\mu} \right| \hat{\tau}_{q}^{\mu} e^{-\hat{T}_{\mu}} e^{\hat{T}_{\lambda}} \left| \Phi_{\mu} \right\rangle H_{\mu\lambda}^{\text{eff}} c_{\lambda} \right] .$$

$$(4.29)$$

Explicit expressions for the coupling terms in the matrix **A** within the Mk-MRCCSD approximation will be derived in Section 4.1.6. The elements $S_{p_{\mu}q_{\nu}}$ of the metric matrix **S** are defined as

$$S_{p_{\mu}q_{\nu}} = \delta_{\mu\nu}\delta_{pq}c_{\mu} . \tag{4.30}$$

A two-component matrix representation has been chosen for the Mk-MRCC linear-response equations to emphasize that both equations determine two different sets of response parameters. The first line in Eqs. (4.24) and (4.25) accounts for the response of the CI coefficients c and corresponding Lagrange multipliers \bar{c} , while the second line refers to the response of the CC amplitudes t and Lagrange multipliers $\bar{\lambda}$. However, all equations are coupled through the off-diagonal blocks of the matrices **A** and **F**. Noteworthy is also the fact that the third term of Eq. (4.29) formally represents the single-reference CC Jacobian matrix. When solving Eqs. (4.24) and (4.25) in an actual calculation, a complication arises from the fact that the block $A_{\mu\nu}$ of the Mk-MRCC Jacobian is singular as it is identical to Eq. (2.39). This singularity is easily lifted by imposing

$$\sum_{\mu} c_{\mu} c_{\mu}^{(X)}(\omega_X) = 0 , \qquad (4.31)$$

$$\sum_{\mu} \left(\bar{c}_{\mu}^{(X)}(\omega_X) \, c_{\mu} + \bar{c}_{\mu} \, c_{\mu}^{(X)}(\omega_X) \right) = 0 \; . \tag{4.32}$$

The static limit ($\omega_X = 0$) of Eqs. (4.24) and (4.25) can be also derived within analyticderivative theory: Taking the derivative of Eqs. (2.39) and (2.47) with respect to a timeindependent perturbation yields Eq. (4.24) without the frequency-dependent term, whereas a corresponding analogue of Eq. (4.25) is obtained in the same way from the Mk-MRCC Λ equations [74].

4.1.4. Excitation Energies

The direct application of CC theory to excited states is possible, but hampered by the fact that different CC states are interacting and non-orthogonal. This complicates, for example,

the evaluation of transition properties. Furthermore, one is often confronted with a pronounced multireference character when going beyond the lowest state of a given spin and spatial symmetry and thus experiences problems in converging the CC equations [20]. These impediments are overcome when excitation energies are determined using CC linear-response (CC-LR) theory [11–14] or the equation-of-motion (EOM) CC approach [125, 209, 210]. Although conceptually different, these approaches can lead to identical working equations for excitation energies. In a CC-LR or EOM-CC calculation, excited states are mutually biorthogonal and all advantages of the CC description of the corresponding reference state are kept. In particular, excitation energies are size-intensive [119]. Hence, CC-LR theory and EOM-CC have evolved to the methods of choice for the treatment of excited states within the CC framework.

However, both CC-LR theory and EOM-CC share the limitations of the underlying CC calculation. Since low-order truncated CC schemes such as CCSD fail when strong static correlation is present, it is not recommendable to use states with multireference character as reference in a CCSD-LR calculation. A possible solution to this problem consists in using the Mk-MRCC wave function for the description of the reference state. The excited states can then be obtained from a linear-response treatment as in single-reference CC theory. It should be added that the direct application of Mk-MRCC theory to excited states is, in principle, also possible. However, since Mk-MRCC is a state-specific theory, different states do not possess a well-defined relation. As a consequence, the treatment of excited states via an EOM or LR ansatz should be preferred in Mk-MRCC theory for the same reasons as in single-reference CC theory.

In Mk-MRCC linear-response (Mk-MRCC-LR) theory, excitation energies can be determined as eigenvalues ω_j of the Mk-MRCC Jacobian. Hence, either the right-hand side or the lefthand side eigenvalue equation for this matrix has to be solved according to

$$\begin{pmatrix} A_{\mu\nu} & A_{\mu q_{\nu}} \\ A_{p_{\mu}\nu} & A_{p_{\mu}q_{\nu}} \end{pmatrix} \begin{pmatrix} r_{\nu}^{j} \\ r_{q_{\nu}}^{j} \end{pmatrix} = \omega_{j} \begin{pmatrix} \delta_{\mu\nu} & 0 \\ 0 & S_{p_{\mu}q_{\nu}} \end{pmatrix} \begin{pmatrix} r_{\nu}^{j} \\ r_{q_{\nu}}^{j} \end{pmatrix} , \qquad (4.33)$$

$$\begin{pmatrix} \ell_{\mu}^{j} \\ \ell_{p_{\mu}}^{j} \end{pmatrix}^{\top} \begin{pmatrix} A_{\mu\nu} & A_{\mu q_{\nu}} \\ A_{p_{\mu}\nu} & A_{p_{\mu}q_{\nu}} \end{pmatrix} = \omega_{j} \begin{pmatrix} \ell_{\mu}^{j} \\ \ell_{p_{\mu}}^{j} \end{pmatrix}^{\top} \begin{pmatrix} \delta_{\mu\nu} & 0 \\ 0 & S_{p_{\mu}q_{\nu}} \end{pmatrix} , \qquad (4.34)$$

where r_{ν}^{j} as well as $r_{q_{\nu}}^{j}$ and ℓ_{μ}^{j} as well as $\ell_{p_{\mu}}^{j}$ denote the elements of the *j*-th right-hand side and left-hand side eigenvector of **A**, respectively. $r_{q_{\nu}}^{j}$ and $\ell_{p_{\mu}}^{j}$ should be regarded as analogs to the r_{q}^{j} and ℓ_{p}^{j} parameters from single-reference CC-LR theory, while r_{ν}^{j} and ℓ_{μ}^{j} may be interpreted as rotation of the CI coefficients in the Mk-MRCC reference wave function and do not possess a single-reference CC counterpart.

Eqs. (4.33) and (4.34) can be alternatively derived in an EOM fashion as done by Mukherjee and coworkers [89], who also showed that Mk-MRCC-LR theory delivers rigorously sizeintensive excitation energies. In the EOM framework, the wave function for the excited state is constructed explicitly using the ansatz

$$|\Psi_{\rm exc}\rangle = \sum_{\mu} \hat{R}_{\mu} e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle c_{\mu} . \qquad (4.35)$$

In this equation, \hat{R}_{μ} is a reference-specific excitation operator defined via

$$\hat{R}_{\mu} = r_0^{\mu} + \sum_{q \in Q(\mu)} r_q^{\mu} \hat{\tau}_q^{\mu} .$$
(4.36)

Yet, the resulting expressions are fully compatible with those derived in Mk-MRCC-LR theory. Moreover, the discrepancy between single-reference CC-LR theory and EOM-CC for transition properties, which arises from the r_0 -term in the EOM-CC ansatz, is not present in the multireference case as the upper lines of Eqs. (4.33) and (4.34) account for the r_0 -term in Eq. (4.36).

Spin adaptation of the Mk-MRCC-LR eigenvectors is performed using the same formulas that apply to single-reference CC-LR theory, i.e.,

$$\hat{R}^{\text{sing}}_{\mu} = r_0^{\mu} + \sum_{ai} r_i^a(\mu) \left(\hat{a}^{\dagger}_{a\alpha} \hat{a}_{i\alpha} + \hat{a}^{\dagger}_{a\beta} \hat{a}_{i\beta} \right) + \dots$$
(4.37)

for singlet states and

$$\hat{R}^{\text{trip}}_{\mu} = r^{\mu}_{0} + \sum_{ai} r^{a}_{i}(\mu) \left(\hat{a}^{\dagger}_{a\alpha} \hat{a}_{i\alpha} - \hat{a}^{\dagger}_{a\beta} \hat{a}_{i\beta} \right) + \dots$$
(4.38)

for triplet states. When acting on a closed-shell reference of the form of Eq. (2.19), $\hat{R}_{\mu}^{\text{sing}}$ and $\hat{R}_{\mu}^{\text{trip}}$ generate properly spin-adapted singlet and $M_s=0$ triplet states. However, this does not hold any longer if open-shell reference determinants are involved just as it is the case in single-reference CC-LR theory [211].

One of the important assets of CC-LR theory is that the excited states are biorthogonal with respect to each other and the ground state as it is the case for the exact wave functions [20]. This condition can be formally fulfilled in Mk-MRCC-LR theory as well, however, the interpretation of the eigenvalues of the Mk-MRCC Jacobian matrix A as excitation energies becomes problematic. This can be realized by looking at the dimension of the block $A_{p_{\mu}q_{\nu}}$. The indices p_{μ} and q_{ν} run over all excited determinants that can be generated from references $|\Phi_{\mu}\rangle$ or $|\Phi_{\nu}\rangle$, respectively. However, since a generic excited determinant can be reached from more than one reference (cf. Figure 2.2), the basis spanned by the columns of the Mk-MRCC Jacobian \mathbf{A} is overcomplete [89]. If the excitation manifold is left untruncated, i.e., in the full CI limit, every excited determinant is within reach of every reference. Hence, every root of A is d-fold degenerate (with d as the number of reference determinants) and the eigenvectors belonging to the same root represent different but equally valid parametrizations of the same excited state. However, as soon as the excitation manifold is truncated, the different eigenvectors no longer lead to descriptions of the same quality for a certain excited state. As a consequence, the degeneracy is lifted and an artificial splitting arises, where all contributions from excited determinants that can be reached from n references are scattered over n components. Hence, not all eigenvalues of A describe different excited states and the meaning of the eigenvectors' formal biorthogonality becomes questionable. This problem is independent of the size of the reference space, yet one may anticipate that the identification of roots that actually describe the same state becomes increasingly difficult for larger reference spaces. It should be added that the upper lines of Eqs. (4.33) and (4.34) are not affected by the overcompleteness in $A_{p_{\mu}q_{\nu}}$, i.e., the contributions from determinants that lie in the reference space do not appear multiple times.

A discrimination between physically meaningful and spurious roots has been proposed [89] to deal with the overcompleteness in Mk-MRCC-LR theory. Yet, such a procedure can be carried out only for weak multireference cases since all but one component become unreliable upon approaching the single-reference limit. For strong multireference cases, the discrimination becomes pointless as more than one component of a certain excited state represents a valid parametrization. In addition, it is always impossible to exclude any roots when calculating the polarizability tensor.

4.1.5. Symmetry Considerations for Complete Active Space (2,2) as Reference Space

In this section, the Mk-MRCC linear-response equations (Eqs. (4.24) and (4.25)) as well as the equations for the determination of excitation energies (Eqs. (4.33) and (4.34)) are analyzed with respect to their dependence on molecular point-group symmetry. To simplify the discussion somewhat, all considerations refer to a model space with two electrons distributed in two active orbitals s and t as introduced in Figure 2.1. If the active orbitals transform under different irreducible representations Γ_s and Γ_t , the reference space may be limited to the closed-shell determinants $|\Phi_1^{cs}\rangle$ and $|\Phi_2^{cs}\rangle$ since the open-shell determinants $|\Phi_1^{os}\rangle$ and $|\Phi_2^{os}\rangle$ do not contribute to the energy due to symmetry reasons.

The situation changes if the system is studied in the presence of a perturbation X, which transforms under an irreducible representation $\Gamma_X = \Gamma_s \otimes \Gamma_t$. Under these circumstances, the open-shell determinants are coupled to the closed-shell determinants and deliver a contribution to the energy [212]. However, it is not straightforward to solve Eqs. (4.24) and (4.25) for such a perturbation: The CI coefficients for the open-shell determinants c_1^{os} and c_2^{os} are zero and the effective Hamiltonian has a block structure

$$\mathbf{H}^{\text{eff}} = \begin{pmatrix} H_{11}^{\text{cs}} & H_{12}^{\text{cs}} & 0 & 0 \\ H_{21}^{\text{cs}} & H_{22}^{\text{cs}} & 0 & 0 \\ 0 & 0 & H_{11}^{\text{cs}} & H_{12}^{\text{cs}} \\ 0 & 0 & H_{21}^{\text{cs}} & H_{22}^{\text{cs}} \end{pmatrix} .$$

$$(4.39)$$

Bearing this in mind, it can be seen from the expression for $A_{p_{\mu}q_{\nu}}$ (Eq. (4.29)) that there is no direct contribution of $t^{\text{os}(X)}$ to the equations for $t^{\text{cs}(X)}$ as all coupling terms vanish. Due to the block structure of \mathbf{H}^{eff} , there can be no contribution of $c^{\text{os}(X)}$ via the block $A_{p_{\mu}\nu}$ either so that the equations for $t^{\text{cs}(X)}$ are left unchanged in the presence of the perturbation. A similar result is obtained when looking at the equations for $c^{\text{cs}(X)}$: The block structure of \mathbf{H}^{eff} renders any coupling between $c^{\text{cs}(X)}$ and $c^{\text{os}(X)}$ impossible.

However, this does not mean that either $t^{os(X)}$ or $c^{os(X)}$ are equal to zero. In contrast, these quantities contribute to the polarizability via Eq. (4.11). Furthermore, the solution of Eq. (4.25) also requires $t^{os(X)}$ and $c^{os(X)}$ as the matrix element $\langle \Phi_{\mu} | [\overline{H}_{\nu}, \hat{\tau}_{q}^{\nu}] | \Phi_{\nu} \rangle$ conveys a contribution of $c^{os(X)}$ and $t^{os(X)}$ to the equation for $\overline{\lambda}^{cs(X)}$. Yet, this is the only coupling between open-shell and closed-shell determinants as there is no direct contribution of $|\Phi_{1}^{os}\rangle$ and $|\Phi_{2}^{os}\rangle$ to the polarizability when evaluating α_{XY} via Eq. (4.22). In principle, $t^{os(X)}$ and $c^{os(X)}$ are obtained by solving Eq. (4.24), but this involves the unperturbed amplitudes t^{os} , which are ill-defined in Eq. (2.47). The computation of t^{os} would thus require special techniques, e.g., Tikhonov regularization [111].

The situation is even worse when dealing with excitation energies, which refer to a state of symmetry Γ_X since closed-shell and open-shell determinants are completely decoupled in Eqs. (4.33) and (4.34). This means that it is impossible to take account of the open-shell determinants when calculating the excitation energy for such a state. As a substitute, internal excitations such as r_t^s , which corresponds to the generation of $|\Phi_1^{os}\rangle$ from $|\Phi_1^{cs}\rangle$, cannot be excluded from r_1^{cs} or r_2^{cs} . For the sake of consistency, internal excitations should also be included in the amplitude-response vectors $t_1^{cs(X)}$ and $t_2^{cs(X)}$ when evaluating polarizabilities. For these reasons, the model space is always limited to two closed-shell determinants in this work whenever the active orbitals are of different spatial symmetry. Yet, it should be mentioned that the inclusion of internal excitations may spoil the intermediate normalization of the wave function.

4.1.6. The Mk-MRCCSD Approximation

In the Mk-MRCCSD approximation, the cluster operators \hat{T}_{μ} are truncated according to

$$\hat{T}_{\mu} = \hat{T}_{1}(\mu) + \hat{T}_{2}(\mu) .$$
 (4.40)

Explicit expressions for all terms appearing in the Mk-MRCCSD amplitude or Λ equations have been presented in the literature [69,74]. Hence, the focus is here only on the evaluation of those coupling terms in the linear-response equations (Eqs. (4.24) and (4.25)) and the expression for the elements of the polarizability tensor (Eq. (4.19)), which do not appear in Refs. 69 and 74.

The corresponding terms in Eq. (4.24) may be evaluated as

$$\sum_{\nu \neq \mu} \left[\sum_{q \in Q_{\rm SD}(\nu)} \langle \Phi_i^a(\mu) | e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} \hat{\tau}_q^{\nu} | \Phi_{\mu} \rangle H_{\mu\nu}^{\rm eff} c_{\nu} t_q^{\nu(X)} - \sum_{q \in Q_{\rm SD}(\mu)} \langle \Phi_i^a(\mu) | \hat{\tau}_q^{\mu} e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} | \Phi_{\mu} \rangle H_{\mu\nu}^{\rm eff} c_{\nu} t_q^{\mu(X)} \right] \\
= \sum_{\nu \neq \mu} \left(t_i^{a(X)}(\nu/\mu) - t_i^{a(X)}(\mu) \right) H_{\mu\nu}^{\rm eff} c_{\nu} \tag{4.41}$$

for singles and

$$\sum_{\nu \neq \mu} \left[\sum_{q \in Q_{\rm SD}(\nu)} \langle \Phi_{ij}^{ab}(\mu) | e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} \hat{\tau}_{q}^{\nu} | \Phi_{\mu} \rangle H_{\mu\nu}^{\rm eff} c_{\nu} t_{q}^{\nu(X)} - \sum_{q \in Q_{\rm SD}(\mu)} \langle \Phi_{ij}^{ab}(\mu) | \hat{\tau}_{q}^{\mu} e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} | \Phi_{\mu} \rangle H_{\mu\nu}^{\rm eff} c_{\nu} t_{q}^{\mu(X)} \right]$$

$$= \sum_{\nu \neq \mu} \left(t_{ij}^{ab(X)}(\nu/\mu) - t_{ij}^{ab(X)}(\mu) \right) H_{\mu\nu}^{\rm eff} c_{\nu} + P(ij)P(ab) \left(t_{i}^{a(X)}(\nu/\mu) - t_{i}^{a(X)}(\mu) \right) \left(t_{j}^{b}(\nu/\mu) - t_{j}^{b}(\mu) \right) H_{\mu\nu}^{\rm eff} c_{\nu}$$

$$(4.42)$$

for doubles, where $Q_{\text{SD}}(\mu)$ denotes the excitation manifold of reference determinant $|\Phi_{\mu}\rangle$ within the Mk-MRCCSD approximation. The antisymmetric permutation operators P(ij) and P(ab) are defined as P(ij) f(i,j) = f(i,j) - f(j,i) and P(ab) f(a,b) = f(a,b) - f(b,a). The frequency dependence of $t_q^{\mu(X)}$ has been omitted in Eqs. (4.41) and (4.42) for the sake of brevity. The common amplitude-response parameters $t_i^{a(X)}(\nu/\mu)$ and $t_{ij}^{ab(X)}(\nu/\mu)$ are defined in accordance with

$$t_{ij\ldots}^{ab\ldots}(\nu/\mu) = \begin{cases} t_{ij\ldots}^{ab\ldots}(\nu) & \text{if } i, j \cdots \in \operatorname{occ}(\mu) \text{ and } \operatorname{occ}(\nu) \\ & \text{and } a, b, \ldots \in \operatorname{vir}(\mu) \text{ and } \operatorname{vir}(\nu) \\ 0 & \text{else } . \end{cases}$$
(4.43)

The analogous terms from Eq. (4.25) read

$$\sum_{\mu \neq \nu} \left[\sum_{p \in Q_{\rm SD}(\mu)} \lambda_p^{\mu(X)} \langle \Phi_p^{\mu} | e^{-\hat{T}_{\mu}} e^{\hat{T}_{\nu}} \hat{\tau}_i^a(\nu) | \Phi_{\mu} \rangle H_{\mu\nu}^{\rm eff} c_{\nu} - \sum_{p \in Q_{\rm SD}(\nu)} \lambda_p^{\nu(X)} \langle \Phi_p^{\nu} | \hat{\tau}_i^a(\nu) e^{-\hat{T}_{\nu}} e^{\hat{T}_{\mu}} | \Phi_{\nu} \rangle H_{\nu\mu}^{\rm eff} c_{\mu} \right] \\
= \sum_{\mu \neq \nu} \left[\lambda_a^{i(X)}(\mu/\nu) H_{\mu\nu}^{\rm eff} c_{\nu} - \lambda_a^{i(X)}(\nu) H_{\nu\mu}^{\rm eff} c_{\mu} + \sum_{bj} \left[\left(\lambda_{ab}^{ij(X)}(\mu/\nu) t_j^b(\nu/\mu) - \lambda_{ab}^{ij(X)}(\mu) t_j^b(\mu) \right) H_{\mu\nu}^{\rm eff} c_{\nu} \right] \\
+ \left(\lambda_{ab}^{ij(X)}(\nu) t_j^b(\mu) - \lambda_{ab}^{ij(X)}(\nu) t_j^b(\mu/\nu) \right) H_{\nu\mu}^{\rm eff} c_{\mu} \right] \right]$$
(4.44)

for singles and

$$\sum_{\mu\neq\nu}\left[\sum_{p\in Q_{\rm SD}(\mu)}\lambda_p^{\mu(X)}\left\langle\Phi_p^{\mu}\right|e^{-\hat{T}_{\mu}}e^{\hat{T}_{\nu}}\hat{\tau}_{ij}^{ab}(\nu)\left|\Phi_{\mu}\right\rangle H_{\mu\nu}^{\rm eff}c_{\nu}-\sum_{p\in Q_{\rm SD}(\nu)}\lambda_p^{\nu(X)}\left\langle\Phi_p^{\nu}\right|\hat{\tau}_i^a(\nu)e^{-\hat{T}_{\nu}}e^{\hat{T}_{\mu}}\left|\Phi_{\nu}\right\rangle H_{\nu\mu}^{\rm eff}c_{\mu}\right]$$

$$= \sum_{\mu \neq \nu} \left[\lambda_{ab}^{ij(X)}(\mu/\nu) H_{\mu\nu}^{\text{eff}} c_{\nu} - \lambda_{ab}^{ij(X)}(\nu) H_{\nu\mu}^{\text{eff}} c_{\mu} \right]$$
(4.45)

for doubles.

In addition, the matrix **F** in Eq. (4.25) contains a term that requires the evaluation of the second derivative of $\hat{\Lambda}^{\text{int}}$ with respect to the CC amplitudes. This yields

$$\sum_{\mu,\lambda} \bar{c}_{\lambda} \langle \Phi_{\lambda} | \frac{\partial^{2} \hat{\Lambda}_{\lambda}^{\text{int}}}{\partial t_{p}^{\mu} \partial t_{q}^{\nu}} \overline{H}_{\lambda} | \Phi_{\lambda} \rangle c_{\lambda} t_{p}^{\mu(X)} = \sum_{\mu \neq \nu} \left[\sum_{bj} \bar{c}_{\mu} \lambda_{ab}^{ij}(\mu) \left(t_{j}^{b(X)}(\nu/\mu) - t_{j}^{b(X)}(\mu) \right) H_{\mu\nu}^{\text{eff}} c_{\nu} + \bar{c}_{\nu} \lambda_{ab}^{ij}(\nu) \left(t_{j}^{b(X)}(\nu) - t_{j}^{b(X)}(\mu/\nu) \right) H_{\nu\mu}^{\text{eff}} c_{\mu} \right]$$

$$(4.46)$$

as the only non-vanishing contribution within the Mk-MRCCSD approximation stems from the case where $\hat{\tau}_p = \hat{\tau}_i^b$ is a single excitation and $\hat{\tau}_q = \hat{\tau}_{ij}^{ab}$ a double excitation.

4.2. Implementation

Based on the expressions presented in Section 4.1, orbital-unrelaxed static and dynamic polarizabilities as well as excitation energies have been implemented at the Mk-MRCCSD level of theory into the quantum-chemical program package CFOUR [124]. The implementation allows for the use of a reference space of two-closed shell determinants or the full CAS(2,2) comprising four determinants with no restrictions regarding spatial symmetry. It is based on the infrastructure of CFOUR for corresponding calculations at the single-reference CCSD level of theory. The course of the calculation is shown in Figure 4.1. As already mentioned in Section 3.1, the handling of the active space relies on the duplication of all active orbitals in such a manner that every active orbital appears once in the block of occupied orbitals and once in the block of virtual orbitals as this allows for the use of the single-reference infrastructure in CFOUR. However, the duplication gives rise to redundant elements in all tensors, which need to be set to zero explicitly. Further details on the orbital-duplication scheme in the context of the unperturbed Mk-MRCCSD amplitude and Λ equations are available from Ref. 73.

The computational cost for the calculation of polarizabilities or excitation energies at the Mk-MRCCSD level scales as $d \cdot n_o^2 \cdot n_v^4$, where d is the number of reference determinants and n_o and n_v denote the number of occupied and virtual orbitals. It thus equals d times the cost of a single-reference CCSD calculation. Verification of the implementation has been achieved as follows: The static polarizability tensor has been validated by numerical differentiation. A rigorous verification of the dynamic polarizability is not possible, however, the frequency-dependent terms in Eqs. (4.24) and (4.25) possess a very simple structure so that the verification of the static polarizability may be considered valid for the dynamic polarizability as well. In addition, $\alpha(\omega)$ has been tested for invariance with respect to sign change of the frequency ω . The implementation of excitation energies is finally verified through Eq. (2.86), i.e., excitation energies are compared to the position of poles in the dynamic polarizability. Moreover, Eqs. (4.33) and (4.34) must yield identical eigenvalues.

4.2.1. Static and Dynamic Polarizability

The calculation of the polarizability tensor $\boldsymbol{\alpha}$ at the Mk-MRCCSD level of theory includes all steps necessary for the determination of the dipole moment. Hence, the modules ecc and lcc are invoked to solve the Mk-MRCCSD amplitude and Λ equations. Thereafter, the density matrices D^{μ}_{pq} and Γ^{μ}_{pqrs} are set up for all reference determinants $|\Phi_{\mu}\rangle$ by module dens. Next,

CHAPTER 4. APPLICATION OF LINEAR-RESPONSE THEORY TO THE MK-MRCC WAVE FUNCTION



Figure 4.1.: Flowchart for the calculation of polarizabilities and excitation energies at the Mk-MRCCSD level of theory. Dashed lines refer to steps, which are necessary only for the calculation of polarizabilities, and dotted lines to steps, which are required for the calculation of excitation energies.

the dipole integrals $h_{\mu\nu}^{\varepsilon}$ are evaluated in the AO basis by module vdint and transformed to the MO basis by module cphf. For the latter step, the duplication of active orbitals needs to be taken into account, which is done in routine cphf/expdip.f. The main part of the calculation comprising the solution of the Mk-MRCCSD response equations (Eqs. (4.24) and (4.25)) and the subsequent formation of the polarizability tensor is then carried out by the module sdcc. For the actual implementation, both equations have been recast in terms of a single-reference part and additional coupling terms. In this way, all routines in sdcc required for the evaluation of α at the single-reference CCSD level of theory could be left unchanged. The solution of both, Eq. (4.24) and Eq. (4.25) is driven by the routine sdcc/dvcc.f. As first step towards solving Eq. (4.24), the inhomogeneous terms $\xi_p^{\mu(\varepsilon)}$ and $\xi_{\mu}^{(\varepsilon)}$ need to be set up. To this end, the routine sdcc/rightct.f is called for each reference determinant μ to compute the single-reference contribution to $\xi_p^{\mu(\varepsilon)}$, which is then scaled by c_{μ} in routine sdcc/scalect.f. The coupling term in $\xi_p^{\mu(\varepsilon)}$ is non-zero only if $\Gamma_{\varepsilon} = 1$. In contrast, $\xi_{\mu}^{(\varepsilon)}$ is always different from zero. Nevertheless, it needs to be formed only if $\Gamma_{\varepsilon} = 1$ since otherwise $c_{\mu}^{(\varepsilon)}$ and $t_{p}^{\mu(\varepsilon)}$ are decoupled in Eq. (4.24) and the former quantity vanishes. Hence, if $\Gamma_{\varepsilon} \neq 1$, the calculation of the inhomogeneous term in Eq. (4.24) is already complete after sdcc/rightct.f und sdcc/scalect.f have been called for each determinant apart from the fact that redundant elements arising from the orbital duplication need to be set to zero. The latter task is carried out by routine sdcc/maskmrcc.f. For totally symmetric perturbations, however, the effective dipole moment matrix $\boldsymbol{\mu}^{\text{eff}}$ (defined in analogy to \mathbf{H}^{eff}) is set up in sdcc/formheffx.f and used to form $\xi_{\mu}^{(\varepsilon)}$ and the coupling term in $\xi_{p}^{\mu(\varepsilon)}$, which is done in sdcc/cictr.f.

The actual solution of Eq. (4.24) is carried out using an algorithm that is applied in singlereference CCSD theory as well. It relies on the fact that the matrix **A** is diagonally dominant, which allows for an iterative solution according to

$$(t_p^{\mu(\varepsilon)})^{(n+1)} = (D_p^{\mu})^{-1} \cdot Z_p^{\mu(n)}$$

$$= (D_p^{\mu})^{-1} \cdot \left[\xi_p^{\mu(\varepsilon)} + \sum_{\nu} \sum_{q \in Q(\nu)} A'_{p_{\mu}q_{\nu}} \cdot (t_q^{\nu(\varepsilon)})^{(n)} + \sum_{\nu} A_{p_{\mu}\nu} \cdot (c_{\nu}^{(\varepsilon)})^{(n)} \right]$$

$$(4.47)$$

with $(t_p^{\mu(\varepsilon)})^{(0)} = 0 \ \forall \ \mu, p \in Q(\mu)$. The "denominator" D_p^{μ} is defined as

$$D_i^a(\mu) = f_{ii}^{\mu} - f_{aa}^{\mu} + E - H_{\mu\mu}^{\text{eff}}$$
 for singles and (4.48)

$$D_{ij}^{ab}(\mu) = f_{ii}^{\mu} + f_{jj}^{\mu} - f_{aa}^{\mu} - f_{bb}^{\mu} + E - H_{\mu\mu}^{\text{eff}} \quad \text{for doubles} , \qquad (4.49)$$

while the matrix **A'** arises from **A** by separating out **D**. In every iteration cycle, the residual Z_p^{μ} is formed for each reference determinant $|\Phi_{\mu}\rangle$ in a sequential fashion and subsequently used to generate a new set of amplitude-response parameters $t_p^{\mu(\varepsilon)}$ according to Eq. (4.47). In the latter step, the DIIS procedure [213] is employed to accelerate convergence.

The most time-consuming step in this procedure is the evaluation of the single-reference contribution to Z_p^{μ} , which is driven by the routine sdcc/righthx.f. Since this routine invokes the contraction $Z_p \leftarrow \langle \Phi_p | [\overline{H}, \hat{\tau}_q] | \Phi_0 \rangle \cdot t_q^{(\varepsilon)}$ in the single-reference case, whereas Mk-MRCCSD requires $Z_p^{\mu} \leftarrow \langle \Phi_p^{\mu} | [\overline{H}_{\mu}, \hat{\tau}_q^{\mu}] | \Phi_{\mu} \rangle \cdot t_q^{\mu(\varepsilon)} \cdot c_{\mu}$, Eq. (4.24) is technically solved for $c_{\mu} \cdot t_p^{\mu(\varepsilon)}$ instead of $t_p^{\mu(\varepsilon)}$. The frequency-dependent term in Eq. (4.24) is also handled by this routine. After sdcc/righthx.f has been called, all coupling terms are added to Z_p^{μ} , which is done in routines sdcc/addcoupr.f, sdcc/intcoupr.f, and sdcc/cirelaxr.f. The first of these routines treats the coupling terms shown in Eqs. (4.41) and (4.42), which arise from $A_{p_{\mu}q_{\nu}} \cdot t_q^{\nu(\varepsilon)}$ and contribute regardless of spatial symmetry. However, $t_i^{a(\varepsilon)}(\mu)$ in

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Eq. (4.41) and $t_{ij}^{ab(\varepsilon)}(\mu)$ in Eq. (4.42) are treated as zero in addcoupr.f as these quantities are included in the denominator D_p^{μ} , where they give rise to the shift $E - H_{\mu\mu}^{\text{eff}}$. The routines sdcc/intcoupr.f and sdcc/cirelaxr.f take care of the remaining coupling terms, which need to be considered only if $\Gamma_{\varepsilon} = 1$. In addition, the equation for $c_{\mu}^{(\varepsilon)}$, i.e., the upper line of Eq. (4.24) is also solved in sdcc/cirelaxr.f in every iteration cycle. The formation of Z_p^{μ} is completed by calling sdcc/maskmrcc.f in order to set redundant elements equal to zero.

Once Eq. (4.24) has been solved, the calculation proceeds with the solution of Eq. (4.25). This again requires at first to set up the inhomogeneous terms. The single-reference part is computed by routine sdcc/mkhxbar2.f, whereas the contributions of internal λ -amplitudes and the coupling terms from Eq. (4.46) are considered in routines sdcc/intcoupl.f and sdcc/addcoupct.f, respectively. For totally symmetric perturbations, additional terms need to be set up, which is done in routines sdcc/cictl1.f and sdcc/cictl2.f. Special care is necessary in all these routines as Eq. (4.25) is formulated in terms of $\bar{\lambda}_p^{\mu(\varepsilon)} = \lambda_p^{\mu(\varepsilon)} \bar{c}_\mu + \lambda_p^{\mu} \bar{c}_e^{(\varepsilon)}$, while the actual implementation relies on $\lambda_p^{\mu(\varepsilon)}$. In particular, the latter term in $\bar{\lambda}_p^{\mu(\varepsilon)}$, i.e., $\lambda_p^{\mu} \bar{c}_{\mu}^{(\varepsilon)}$ introduces a dependence of $\bar{c}_{\mu}^{(\varepsilon)}$ so that the matrix element $F_{\mu\nu}$ in Eq. (4.16) is also handled in sdcc/cictl2.f. As is the case for Eq. (4.24), the formation of the constant term is completed by calling sdcc/maskmrcc.f in order to set redundant elements equal to zero.

For the actual solution of Eq. (4.25), the scheme presented in Eq. (4.47) is applied again. This reads

$$(\lambda_q^{\nu(\varepsilon)})^{(n+1)} = (D_q^{\nu})^{-1} \cdot Z_q^{\nu(n)}$$

$$= (D_q^{\nu})^{-1} \cdot \left[\left[\eta + F \cdot t^{(\varepsilon)} + F \cdot c^{(\varepsilon)} \right]_q^{\nu(\varepsilon)} + \sum_{\mu} \sum_{p \in Q(\mu)} (\lambda_p^{\mu(\varepsilon)})^{(n)} \cdot A'_{p_\mu q_\nu} + \sum_{\mu} \left(\bar{c}_{\mu}^{(\varepsilon)} \right)^{(n)} \cdot A_{\mu q_\nu} \right],$$

$$(4.50)$$

where $(\lambda_q^{\nu(\varepsilon)})^{(0)} = 0 \ \forall \ \nu, q \in Q(\nu)$ and the "denominators" are the same that have been defined in Eqs. (4.48) and (4.49). In every iteration cycle, the residual Z_q^{ν} is formed for each reference determinant $|\Phi_{\nu}\rangle$ and used to create a new set of amplitude-response parameters $\lambda_q^{\nu(\varepsilon)}$. DIIS [213] is employed again to accelerate convergence. As discussed for Eq. (4.24), the most time-consuming step is the evaluation of the single-reference contribution to Z_q^{ν} , which is driven by sdcc/lefthx.f. For similar reasons as discussed above, Eq. (4.25) is technically solved for $\bar{c}_{\nu}\lambda_q^{\nu(\varepsilon)}$ instead of $\lambda_q^{\nu(\varepsilon)}$. The coupling terms from Eqs. (4.44) and (4.45) are added to the residual by sdcc/addcoupl.f. Again, certain contributions are separated out and included in D_q^{ν} instead. Redundant elements in Z_q^{ν} are set to zero by sdcc/maskmrcc.f. If a totally symmetric perturbation is treated, additional contributions to Z_q^{ν} need to be taken into account. This is done in routine sdcc/cirelaxl.f, which treats the equation for $\bar{c}_{\nu}^{(\varepsilon)}$ as well. The latter needs to be done only for totally symmetric perturbations.

When all response parameters are available for a certain perturbation ε_i , the perturbed density matrices $dD_{pq}^{\mu}/d\varepsilon_i$ are constructed and directly contracted with the dipole integrals $h_{pq}^{\varepsilon_j}$ to compute α_{ij} . This task is driven by routine sdcc/ddens.f. The adaptation to Mk-MRCCSD requires nothing but a loop over the single-reference code to ensure that $dD_{pq}^{\mu}/d\varepsilon_i$ is calculated for all reference determinants followed by scaling with $\overline{c}_{\mu}c_{\mu}$. For totally-symmetric perturbations, however, the contributions arising from $dc_{\mu}/d\varepsilon_i$ and $d\overline{c}_{\mu}/d\varepsilon_i$ need to be added, which is done in sdcc/dcxd.f.

4.2.2. Excitation Energies

Excitation energies can be calculated either from Eq. (4.33) or Eq. (4.34). The solution of both equations has been implemented, yet in a normal calculation, only Eq. (4.33) is solved, while Eq. (4.34) can be invoked for debugging purposes. After the Mk-MRCCSD amplitude equations have been solved, module lcc is called to construct all matrix elements of \overline{H}_{μ} necessary for the solution of Eq. (4.33). The solution of the latter equation is carried out in analogy to single-reference CCSD-LR theory using a modified Davidson algorithm [214]. Currently, only one root can be determined at a time. Hence, if several roots are requested, the calculation has to be performed in a sequential fashion. The solution is driven by routine sdcc/dvcc.f and closely follows the implementation of polarizabilities outlined in Section 4.2.1. Yet, the first step does not consist in constructing the inhomogeneous terms, instead, a guess for the linear-response eigenvector is made. This currently requires the specification of dominant excitations, i.e., an input by the user, which is processed by routine sdcc/newges2.f. The trial vector is then used to evaluate the single-reference contribution to the residual Z_p^{μ} for each reference determinant $|\Phi_{\mu}\rangle$ by sdcc/righthx.f. As for polarizabilities, this represents the most time-consuming step. The scaling factor c_{μ} mentioned in Section 4.2.1 has no impact on Eq. (4.33) as the normalization of the eigenvectors is, in principle, arbitrary. After sdcc/righthx.f has been called, sdcc/addcoupr.f adds the coupling terms from Eqs. (4.41) and (4.42) to the residual Z_p^{μ} . In contrast to polarizability calculations, the full expression is calculated as no terms are separated out as denominator. If the target state is of the same symmetry as the reference state, Z_{μ} as well as additional contributions to Z_p^{μ} need to be evaluated, which is done in sdcc/intcoupr.f and sdcc/cirelaxr.f. As last step, sdcc/maskmrcc.f is called to set redundant elements in Z_p^{μ} equal to zero. Once Z_p^{μ} and Z_{μ} have been evaluated for all μ , sdcc/newvec.f is called to generate new trial vectors using the Davidson algorithm. Z_p^{μ} and Z_{μ} are treated on an equal footing in this routine.

4.3. Applications

4.3.1. Preliminary Examples for Polarizability Calculations

As a first example, Table 4.1 contains static polarizability tensors for boron monohydride calculated at the CCSD, CCSD(T), Mk-MRCCSD, and full CI levels of theory. The comparison to full CI results allows for a rigorous assessment of the accuracy in the polarizability and the position of the poles at all approximate levels of theory. A basis set of triple-zeta quality [215] is used and all electrons are correlated. All calculations are carried out at twice the experimental equilibrium distance (R=2.4648 Å) [216] with the z-axis as the molecular axis. The ground-state wave function of boron monohydride can be correctly approximated by a single determinant at the equilibrium bond length, but displays increasing multireference character upon stretching the bond. Mk-MRCCSD calculations for this molecule rely on a CAS(2,2) comprising the four determinants $|\Phi_1\rangle = |(\operatorname{core})^2(3\sigma^+)^2\rangle$, $|\Phi_2\rangle = |(\operatorname{core})^2(4\sigma^+)^2\rangle$, $|\Phi_3\rangle = |(\operatorname{core})^2(3\sigma^+)(\overline{4\sigma^+})\rangle$, and $|\Phi_4\rangle = |(\operatorname{core})^2(\overline{3\sigma^+})(4\sigma^+)\rangle$, which arise from distributing two electrons in the bonding $3\sigma^+$ and the antibonding $4\sigma^+$ molecular orbital. The CI coefficients obtained in these calculations are $c_1 = 0.935$, $c_2 = -0.328$, and $c_3 = c_4 = -0.094$, which validates the multireference character of the system.

The results in Table 4.1 show that CCSD deviates from the full CI limit by $\approx 1\%$ for the elements α_{xx} and α_{yy} and by 6% for α_{zz} . The comparison to full CI also reveals that both CCSD(T) and Mk-MRCCSD represent an improvement over CCSD. The discrepancy between Mk-MRCCSD and full CI amounts to 0.5 % in the case of α_{xx} and α_{yy} and to 0.4% in the case of α_{zz} . However, Mk-MRCCSD leads to a slight overcorrection of all values.

Table 4.1.: Static polarizability in atomic units for the ${}^{1}\Sigma^{+}$ ground state of boron monohydride as computed at the CCSD, CCSD(T), Mk-MRCCSD, and full CI levels of theory using a TZP basis set, R(BH)=2.4648 Å.

Method	α_{xx}	α_{yy}	α_{zz}
CCSD	13.358	13.358	55.633
CCSD(T)	13.398	13.398	54.420
Mk-MRCCSD	13.588	13.588	52.362
Full CI	13.515	13.515	52.568

The frequency dependence of the element α_{zz} of the dynamic polarizability tensor for boron monohydride is shown in Figure 4.2a (see Table A.1 in Appendix A for the data used to generate the figure). From this figure it is clear that Mk-MRCCSD deviates significantly less from full CI than CCSD for low frequencies. This changes when approaching the first pole in the linear-response function, which is observed near 0.1859 a.u. in the full CI limit, but near 0.1877 a.u. and 0.1930 a.u. at the CCSD and Mk-MRCCSD levels of theory, respectively. Hence, the difference in the position of the first pole is larger between Mk-MRCCSD and full CI than between CCSD and full CI. A possible explanation for this deterioration consists in the wrong pole structure of the Mk-MRCCSD linear-response function, which has been explained in detail in Section 4.1.4.

As a second preliminary example, Figure 4.2b features the dynamic polarizability α_{uu} for the ¹A₁ ground state of methylene calculated at the CCSD and Mk-MRCCSD levels of theory using the cc-pCVTZ basis set (see Table A.2 in Appendix A for the data used to generate the figure). The molecule is oriented such that the y-axis is parallel to the connecting line of the two hydrogen atoms. Mk-MRCCSD calculations are based on a CAS(2,2) with active orbitals of a_1 and b_1 symmetry. The examined state displays only modest multireference character as seen from the CI coefficients obtained in Mk-MRCCSD calculations. Their values are -0.977 and 0.213. As a consequence, one may expect the CCSD and Mk-MRCCSD linearresponse functions to closely resemble each other. The curves shown in Figure 4.2b fulfill this expectation as the deviation between the two functions remains well below 1 a.u. until the CCSD linear-response function approaches its first pole near 0.349 a.u. Also beyond this pole, the two curves qualitatively show the same behavior. The poles in the CCSD linear-response function near 0.349 a.u. and 0.370 a.u. correspond to poles in the Mk-MRCCSD linearresponse function near 0.352 a.u. and 0.373 a.u. Despite this good match between CCSD and Mk-MRCCSD, Figure 4.2b spectacularly reveals the overcompleteness problem of Mk-MRCC response theory. The Mk-MRCCSD curve in Figure 4.2b possesses an additional pole near 0.294 a.u., which has a very thin shape and hardly affects its neighborhood. Moreover, the left-sided limit of the polarizability at this pole is minus infinity. Due to these features, it is easy to identify the pole as spurious as discussed in Section 4.1.4. However, the situation is less clear when studying systems with stronger multireference character.

4.3.2. Static and Dynamic Polarizability of Aryne Compounds

In this section, the results from calculations for the polarizability tensor of p-benzyne and 2,6-pyridyne are presented. The ground state of p-benzyne and the two lowest-lying singlet states of 2,6-pyridyne are well known for their quasidegeneracy (cf. Figure 3.4 for their molecular structure and Section 3.4 for more details on their electronic structure). While it is clear that this calls CCSD and CCSD(T) calculations into question, the corresponding results are reported anyway to quantify how the polarizability tensor changes when going



(a) α_{zz} for the ${}^{1}\Sigma^{+}$ ground state of boron monohydride as computed at the CCSD, Mk-MRCCSD, and full CI levels of theory using a TZP basis set, R(BH) = 2.4648 Å.



- Figure 4.2.: Dynamic polarizability of boron monohydride and methylene. Reprinted with permission from J. Chem. Phys. 137, 044115 (2012). Copyright 2012, American Institute of Physics.
- Table 4.2.: Static polarizability in atomic units for the ${}^{1}A_{g}$ ground state of *p*-benzyne as computed at the CCSD, CCSD(T), and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ and aug-cc-pCVTZ basis sets, structure optimized at the Mk-MRCCSD/cc-pCVTZ level of theory.

Method	Basis set	α_{xx}	α_{yy}	α_{zz}
CCSD CCSD(T) Mk-MRCCSD	aug-cc-pCVDZ aug-cc-pCVDZ aug-cc-pCVDZ	$79.661 \\ 77.910 \\ 79.552$	$85.359 \\ 64.840 \\ 73.113$	42.631 42.377 42.498
CCSD CCSD(T) Mk-MRCCSD	aug-cc-pCVTZ aug-cc-pCVTZ aug-cc-pCVTZ	$79.888 \\78.446 \\79.685$	$86.794 \\ 65.161 \\ 72.121$	$\begin{array}{c} 42.256 \\ 42.116 \\ 42.093 \end{array}$

from single-reference to multireference CC theory. Calculations for *p*-benzyne are carried out within D_{2h} symmetry, while C_{2v} symmetry is imposed for 2,6-pyridyne. All Mk-MRCCSD calculations are based on a CAS(2,2) with active orbitals of a_g and b_{3u} symmetry for *p*benzyne and active orbitals of a_1 and b_2 symmetry for 2,6-pyridyne. The two states of the latter molecule that are of interest here are both dominated by the same two configurations, but the weights of these configurations are different (cf. Section 3.4). Both molecules are always oriented such that the *z*-axis is perpendicular to the molecular plane. For *p*-benzyne the *x*-axis is parallel to the connecting line of the dehydrogenated carbon nuclei, while this holds true for the *y*-axis in the case of 2,6-pyridyne. The augmented correlation-consistent core-valence polarized basis sets aug-cc-pCVXZ(X=D,T) of Dunning and co-workers [130, 217,218] are employed in all calculations and all electrons are correlated.

Static polarizability tensors for the ${}^{1}A_{g}$ ground state of *p*-benzyne and the two lowest-lying closed-shell states of 2,6-pyridyne (1 ${}^{1}A_{1}$ and 2 ${}^{1}A_{1}$) are shown in Tables 4.2 and 4.3, while Table 4.4 summarizes the CI coefficients obtained from Mk-MRCCSD calculations, which can be used to quantify the multireference character of the states under examination. The computed values for all three states reveal that only the element α_{yy} of the polarizability tensor changes significantly when CCSD is replaced by either CCSD(T) or Mk-MRCCSD.

Table 4.3.: Static polarizability in atomic units for the 1 ${}^{1}A_{1}$ and 2 ${}^{1}A_{1}$ states of 2,6-pyridyne as computed at the CCSD, CCSD(T), and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ and aug-cc-pCVTZ basis sets, structures optimized at the Mk-MRCCSD/cc-pCVTZ level of theory.

Method	Basis set	α_{xx}	α_{yy}	α_{zz}	α_{xx}	$lpha_{yy}$	α_{zz}
		1	$^{1}A_{1}$ stat	e	:	$2 {}^{1}A_{1}$ state	
CCSD CCSD(T) Mk-MRCCSD	aug-cc-pCVDZ aug-cc-pCVDZ aug-cc-pCVDZ	$39.358 \\ 39.046 \\ 39.121$	77.578 69.048 72.529	70.998 70.107 70.839	39.753 39.624 39.514	100.807 98.342 95.975	67.143 66.334 66.727
CCSD CCSD(T) Mk-MRCCSD	aug-cc-pCVTZ aug-cc-pCVTZ aug-cc-pCVTZ	39.026 38.830 38.748	$78.057 \\ 69.439 \\ 72.063$	$70.735 \\ 70.142 \\ 70.535$	$39.386 \\ 39.370 \\ 39.134$	100.075 97.995 94.724	$66.960 \\ 66.435 \\ 66.518$

Table 4.4.: Coefficients c_1 and c_2 for *p*-benzyne and 2,6-pyridyne as computed at the Mk-MRCCSD level of theory using the aug-cc-pCVDZ and aug-cc-pCVTZ basis sets, structures optimized at the Mk-MRCCSD/cc-pCVTZ level of theory.

	aug-cc-j	pCVDZ	aug-cc-pCVTZ		
	c_1	c_2	c_1	c_2	
<i>p</i> -Benzyne	-0.520	0.855	-0.524	0.852	
2,6-Pyridyne $(1 {}^{1}A_{1})$	-0.915	0.403	-0.915	0.403	
2,6-Pyridyne $(2^{1}A_{1})$	-0.244	0.971	-0.247	0.970	

Regarding α_{xx} and α_{zz} , CCSD and Mk-MRCCSD agree within 0.4 a.u. for all states. At the CCSD(T) level of theory, α_{xx} and α_{zz} are computed to be slightly smaller, but the deviation to CCSD and Mk-MRCCSD does not exceed 1.7 a.u. ($\approx 2\%$). In contrast, the values for α_{yy} computed at the CCSD and Mk-MRCCSD levels of theory differ by 14 a.u. for *p*-benzyne, by 6 a.u. for the 1 ¹A₁ state of 2,6-pyridyne, and by 5 a.u. for the 2 ¹A₁ state of 2,6-pyridyne with the Mk-MRCCSD value always being smaller. This pattern nicely corresponds to the CI coefficients displayed in Table 4.4, which show that the multireference character decreases from *p*-benzyne via the 1 ¹A₁ state of 2,6-pyridyne to the 2 ¹A₁ state of this molecule. In the cases of *p*-benzyne and the 1 ¹A₁ state of 2,6-pyridyne, the CCSD(T) results for α_{yy} are even smaller than those obtained at the Mk-MRCCSD level of theory. Again, the deviation between CCSD(T) and CCSD reduces from 20 a.u. to 8 a.u. and 2.5 a.u. when going from *p*-benzyne to the 1 ¹A₁ and 2 ¹A₁ states of 2,6-pyridyne. From these results one may deduce that perturbative triples corrections overestimate the higher-order correction, which should by seen in conjunction with similar findings from Chapter 3.

The fact that the choice of method affects α_{yy} but hardly α_{xx} and α_{zz} can be related to the symmetry of the active orbitals in a Mk-MRCCSD calculation. The direct product of their irreducible representations transforms as the *y*-component of the electric field. Also of interest is the comparison of the two states of 2,6-pyridyne. While α_{xx} hardly differs between the 1 ${}^{1}A_{1}$ state and the 2 ${}^{1}A_{1}$ state and α_{zz} changes by less than 4 a.u., the crucial element α_{yy} increases by 30 a.u. when going from the 1 ${}^{1}A_{1}$ to the 2 ${}^{1}A_{1}$ state. All conclusions hold for both basis sets used and the changes observed when replacing the aug-cc-pCVDZ basis by the larger aug-cc-pCVTZ basis can be considered as a typical basis-set effect.

The expansion of the reference space as discussed in Section 4.1.5 affects only α_{yy} . Using four determinants one obtains for the element α_{yy} a value of 79.639 a.u. in the case of *p*-benzyne. This number should be compared to the value of 73.113 a.u. in Table 4.2, which



(a) α_{xx} for the ground state of *p*-benzyne. Convergence of the Mk-MRCCSD linear-response equations could not be achieved beyond $\omega = 0.197 \ E_h$.



(b) α_{yy} for the ground state of *p*-benzyne. Convergence of the Mk-MRCCSD linear-response equations could not be achieved between $\omega = 0.14 \ E_h$ and $\omega = 0.177 \ E_h$.









(e) α_{yy} for the lowest ¹A₁ state of 2,6-pyridyne. (f) α_{zz} for the lowest ¹A₁ state of 2,6-pyridyne.

Figure 4.3.: Dynamic polarizability of p-benzyne and 2,6-pyridyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ and aug-cc-pCVTZ basis sets, structures optimized at the Mk-MRCCSD/cc-pCVTZ level of theory. (a), (b), and (c) have been reprinted with permission from J. Chem. Phys. 137, 044115 (2012). Copyright 2012, American Institute of Physics.

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is based on two reference determinants. This shows that the choice of reference space is of significant numerical importance (10%) at least for *p*-benzyne. However, only the latter value is compatible with the results for the dynamic polarizability presented in the following.

Dynamic polarizabilities for the ground state of *p*-benzyne and the lowest singlet state of 2,6-pyridyne are shown in Figure 4.3 at the CCSD and Mk-MRCCSD levels of theory. As a reasonable compromise between reliability and computational cost, all curves are calculated using the aug-cc-pCVDZ basis set, but underpinned with exemplary values for the larger aug-cc-pCVTZ basis set. The values used to generate the figures are provided in Tables A.3 to A.14 in Appendix A. At first glance, it is obvious that there is no uniform change in the polarizability when going from CCSD to Mk-MRCCSD. On the contrary, some Mk-MRCCSD curves differ hardly from the corresponding CCSD curves as it is the case for α_{xx} of *p*-benzyne and 2,6-pyridyne (Figures 4.3a and 4.3d) as well as for α_{zz} of 2,6-pyridyne (Figure 4.3f), while a qualitatively different behavior is observed for the remaining curves.

Concerning the former three cases, the shifts of the poles in the Mk-MRCCSD linear-response function never exceed 15 m E_h . These shifts are positive with respect to the CCSD linearresponse function for α_{xx} of both molecules and negative for α_{zz} of 2,6-pyridyne. However, the comparison is hampered in the case of α_{xx} for *p*-benzyne as convergence of the Mk-MRCCSD linear-response equations could not be achieved beyond 0.197 a.u. for this example.

The remaining three cases (Figures 4.3b, 4.3c, and 4.3e) potentially suffer from the wrong pole structure as explained in Section 4.1.4 from a theoretical perspective. For α_{zz} of p-benzyne (Figure 4.3c), the two poles in the Mk-MRCCSD linear-response function near 0.178 a.u. and 0.229 a.u. are separated by a similar distance from the pole in the CCSD linear-response function near 0.208 a.u. Moreover, the shape of all three poles is similar so that it becomes impossible to declare one of the two poles in the Mk-MRCCSD linear-response function as spurious. This should be compared to Figure 4.2b, where it is possible to separate out the spurious pole. Since CCSD results are not reliable for p-benzyne due to the strong multireference character of this system, the possibility that both poles in the Mk-MRCCSD linear-response function are valid cannot be ruled out either. The two poles are, however, reconsidered in Section 4.3.4. For α_{yy} of p-benzyne (Figure 4.3b), the CCSD linear-response function has a pole near 0.151 a.u., while the corresponding Mk-MRCCSD curve exhibits two poles near 0.141 a.u. and 0.176 a.u. For α_{yy} of 2,6-pyridyne (Figure 4.3e), two poles in the CCSD linear-response function near 0.128 a.u. and 0.189 a.u. are observed, but three poles in the Mk-MRCCSD linear-response function, which approximately lie at 0.125 a.u., 0.174 a.u., and 0.197 a.u. Again, it is impossible to separate out spurious poles, one may only note that the first poles of the CCSD and the Mk-MRCCSD curve nearly coincide.

Another problem of Mk-MRCCSD linear-response theory shows up for α_{yy} of both molecules. There are frequency ranges, where the Mk-MRCCSD linear-response function does not increase monotonically. Such a behavior is observed for *p*-benzyne (Figure 4.3b) near the first pole, whereas it happens near the third pole for 2,6-pyridyne (Figure 4.3e). This should be contrasted with the exact linear-response function presented in Figure 2.3, which increases monotonically for all frequencies. One may relate the considerable differences between CCSD and Mk-MRCCSD for α_{yy} of both molecules to the fact that the *y*-component of the electric field transforms under the irreducible representation that corresponds to the direct product of the active orbitals in a Mk-MRCCSD calculation. However, the inclusion of internal amplitudes into the amplitude-response vectors as discussed in Section 4.1.5 cannot be the reason for the anomalous shape of the Mk-MRCCSD linear-response functions in Figures 4.3b and 4.3e as a similar behavior is also observed in Figure 4.2b, where internal amplitudes need not be considered due to symmetry reasons.

4.3.3. Vertical Excitation Spectrum of Ozone

Ozone represents one of the standard test systems for multireference methods. While most previous investigations have dealt with the ground state, its equilibrium structure, and especially its vibrational frequencies [37, 61, 69, 204, 219–221], this section focuses on the excited states of ozone, which have also often served for the assessment of methodological developments [222–229]. It has been a major hurdle for many multireference methods to correctly describe the interplay of static and dynamic electron correlation for ozone although its multireference character is only moderately pronounced. At the same time, highly accurate values for structural parameters and vibrational frequencies have been determined by means of single-reference CC calculations when including up to quadruple excitations into the cluster operator [230].

At the Mk-MRCCSD level of theory, the two dominant configurations $|\Phi_1\rangle = |(\operatorname{core})^2(1b_1)^2 (4b_2)^2(6a_1)^2(2b_1)^2\rangle$ and $|\Phi_2\rangle = |(\operatorname{core})^2(1b_1)^2(4b_2)^2(6a_1)^2(1a_2)^2\rangle$ deliver considerably different contributions of 24% and 76% to the wave function. Since the ground state, which is used as reference state in all Mk-MRCCSD-LR calculations, displays only modest multireference character, a valid comparison to results from CCSD-LR and CCSDT-LR calculations is possible in order to judge the performance of the Mk-MRCCSD-LR approach. Furthermore, the artificial splitting of certain excited states in Mk-MRCC-LR theory (cf. Section 4.1.4) is more easily recognized when one reference dominates the underlying Mk-MRCCSD wave function. A distinction between physically meaningful and artificial states can be made only for weak multireference cases as outlined in Section 4.1.4.

Table 4.5 comprises absolute energies and excitation energies with respect to the ground state for five singlet and five triplet states of ozone. All states have been targeted at the Mk-MRCCSD-LR, CCSD-LR, and CCSDT-LR levels of theory using the cc-pCVXZ (X=D,T,Q) basis sets with all electrons included in the correlation treatment, but as a reasonable compromise between computational cost and reliability, the CCSDT-LR method has only been applied in conjunction with the cc-pCVDZ and cc-pCVTZ basis sets. The ground state's equilibrium structure has been optimized at the Mk-MRCCSD/cc-pCVQZ level of theory (R(OO)=1.2569 Å, \angle =116.54°). The results in Table 4.5 show that the ground state is lowered by $\approx 16 \text{ m}E_h$ when replacing CCSD by Mk-MRCCSD, but a concurrent change does not occur for the excited states. Instead, they follow different patterns, which should be related to the structure of the CCSD-LR and Mk-MRCCSD-LR eigenvectors, whose dominant elements are listed in Table 4.6. Based on these data, the excited states can be classified into two groups plus three additional special cases, which will be discussed in the following. Group I comprises the lowest-lying ¹B₁, ¹A₂, ³A₁, ³B₁, and ³A₂ states, for which CCSD-LR

Croup Fcomprises the lowestrying D_1 , A_2 , A_1 , D_1 , and A_2 states, for which CCSD-LR and Mk-MRCCSD-LR energies nearly coincide. As a consequence, the relative excitation energies for all these states are ≈ 0.4 eV higher at the Mk-MRCCSD-LR level of theory. This should be contrasted with the change induced by the inclusion of triple excitations into the cluster operator. At the CCSDT-LR level of theory, the ground state lies almost 50 m E_h lower compared to the CCSD-LR result, but the energies of the excited states are also reduced, which in total causes the CCSDT-LR excitation energies to be smaller by 0.11 eV for the singlet states and to be larger by 0.03 eV for the triplet states. This matches the usual expectations for CCSDT-LR and is in line with CCSDT-LR values available from Ref. 227. Table 4.6 illustrates that states in group I are described very similarly at the CCSD-LR and Mk-MRCCSD-LR levels of theory. For all states in question, both eigenvectors are dominated by the same single excitations, all of which lift an electron from a core orbital to the $2b_1$ orbital. Since this orbital belongs to the reference space in the Mk-MRCCSD treatment, it is unoccupied in only one of the reference determinants so that the crucial single excitations cannot appear multiple times in the Mk-MRCCSD-LR eigenvector. Hence,

: Vertical excitation energies in eV and absolute energies in atomic units for the ground state and several excited states of ozone	ted at the CCSD-LR, CCSDT-LR, and Mk-MRCCSD-LR levels of theory using the cc-pCVDZ, cc-pCVTZ, and cc-pCVC	ate amound-etate structure antimized at the ML-MRCCSD/oc.nCVOZ lavel of theory
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	SD-LR Exp.	$\Delta E/eV$ $\Delta E/eV$	$\begin{array}{c c} - & - \\ 8.831 \\ 9.965 \end{array} & \begin{array}{c} - \\ - \\ - \end{array}$	$\begin{array}{c c} 2.800 & 2.1^c \\ 6.121 & - \end{array}$	$\begin{array}{c c} 5.751 \\ 6.582 \\ \hline - \\ \hline \end{array}$	$2.795 \left 1.92^c / 1.6^d \right $	8.555	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.365 1.80^{c}	D-LR or CCSDT-LF
	Mk-MRCC JVQZ	E/a.u.	-225.3488 -225.0242 -224.9826	-225.2458 -225.1238	-225.1374 -225.1069	-225.2460	-225.0344 -225.0240	-225.2683 -225.1309	-225.2785 -225.2659	-225.2619	t have CCS
)-LR cc-p($\Delta E/\mathrm{eV}$	9.636	2.391	5.576	2.367	8.149 8.779	1.779 —	1.402 —	1.959	ou op sr
eory.	CCSE	E/a.u.	-225.3326 -224.9785 	-225.2447 	-225.1277	-225.2455	-225.0331 -225.0099	-225.2672	-225.2810	-225.2605	em and thu
el of th	CSD-LR	$\Delta E/\mathrm{eV}$		$2.793 \\ 6.009$	5.822 6.612	2.790	$8.594 \\ 8.873$	$2.176 \\ 5.823$	1.908 2.242	2.357	ss proble
VUZ IEV	Mk-MRC	E/a.u.	-225.2724 -224.9469 -224.9166	-225.1698 -225.0515	-225.0585 -225.0294	-225.1699	-224.9566 -224.9463	-225.1925 -225.0584	-225.2023 -225.1900	-225.1858	ompletene L.R. level c
/cc-bC/	r-LR VTZ	$\Delta E/\mathrm{eV}$	5.290	2.275	5.549 —	2.219		1.813 —	1.737 —	2.070	ae overc
(decron	CCSD7 cc-pC7	E/a.u.	-225.3040 -225.1096	-225.2204	-225.1001	-225.225	e e 	-225.2374 	-225.2402	-225.2279	ise from tl ad at the (
MIK-M	-LR	$\Delta E/\mathrm{eV}$		2.388	5.664 —	2.366	8.200 8.813	1.769 —	1.398 —	1.954	2 ³ B ₂ ar
ed at the	CCSD	$E/\mathrm{a.u.}$	-225.2564 -224.9016 	-225.1687 	-225.0483 	-225.1695	-224.9551 -224.9325	-225.1914	-225.2050	-225.1846	$\frac{{}^{3}\mathrm{B}_{1}}{{}^{3}\mathrm{B}_{1}}$, and
ptimize	CSD-LR	$\Delta E/eV$	$\frac{-}{8.910}$ 8.503	2.756 5.528	5.957 6.682	2.761	8.732 8.910	$2.130 \\ 5.375$	$1.920 \\ 2.206$	2.334	$2^{1}B_{2}, 2$
ncture o	Mk-MRC0	E/a.u.	-225.0132 -224.6858 -224.7007	-224.9119 -224.8100	-224.7943 -224.7676	-224.9118	-224.6923 -224.6858	-224.9349 -224.8157	-224.9427 -224.9322	-224.9274	$A_1, 2^{1}B_1,$
cate su	r-LR /DZ	$\Delta E/\mathrm{eV}$	5.043	2.267	5.719	2.223		1.794 —	1.716 —	1.979	id as 3 ¹ . ate and
ground-st	CCSD7 cc-pCV	E/a.u.	-225.0311 -224.8457 	-224.9478 	-224.8209	-224.9494	e e 	-224.9651	-224.9680	-224.9583	oots labele e 1 ³ A ₁ st.
s sets, §	-LR	$\Delta E/\mathrm{eV}$	9.587	2.384	5.869 —	2.366	8.442 8.808	1.755 —	1.421	1.957	SD-LR r sons. th
Dast	CCSD	E/a.u.	-224.9981 -224.6458	-224.9105	-224.7824	-224.9111	-224.6879 -224.6744	-224.9336	-224.9459 	-224.9262	ht-MRCCS serparts. Ref. 222. Ref. 231. Ref. 232. shnical rea
	Root		$\left[\begin{array}{c} 1 & ^1{\rm A}_1 \\ 2 & ^1{\rm A}_1 \\ 3 & ^1{\rm A}_1 & ^a \end{array} \right]$	$\frac{1}{2} \frac{{}^1\mathrm{B}_1}{{}^1\mathrm{B}_1}{}^a$	${1 \atop 2 }{}^{1}{ m B}_{2}{}^{a}$	$1 \ ^1\mathrm{A_2}$	$\begin{bmatrix}1 & ^3\mathrm{A}_1\\ 2 & ^3\mathrm{A}_1\end{bmatrix}$	${1 \ }^{3}{ m B_{1}}{ m 2}{ m }_{3}{ m B_{1}}{ m a}{ m a}{ m b_{1}}{ m a}{ m b_{1}}{ m b_{1}}{ m a}{ m b_{1}}{ m b_{2}}{ m b$	${1 }^{3}{ m B}_{2}{}^{3}{ m B}_{2}{}^{a}$	$1^{3}A_{2}$	a The M count b From j $^{e} From j$ $^{d} From j$

CHAPTER 4. APPLICATION OF LINEAR-RESPONSE THEORY TO THE MK-MRCC WAVE FUNCTION

Root	CCSD-LR		CCSDT-LR		Mk-MRCCSD-LR	
$2 {}^{1}A_{1}$	$1b_1 \rightarrow 2b_1$	0.461	$6a_1/6a_1 \rightarrow 2b_1/2b_1$	0.746	r_0^1	0.887
	$1a_2/1a_2 \rightarrow 2b_1/2b_1$	-0.423	$4b_2/4b_2 \rightarrow 2b_1/2b_1$	-0.568	r_0^2	0.292
					$1b_1 \rightarrow 2b_1 \ (\Phi_2)$	-0.154
$3 {}^{1}A_{1}$	—	_	—		$4b_2/4b_2 \to 1a_2/1a_2 \ (\Phi_1)$	0.669
					$6a_1/6a_1 \to 1a_2/1a_2 \ (\Phi_1)$	-0.623
$1 {}^{1}B_{1}$	$6a_1 \rightarrow 2b_1$	0.672	$6a_1 \rightarrow 2b_1$	0.639	$6a_1 \rightarrow 2b_1 \ (\Phi_2)$	0.662
$2 {}^{1}B_{1}$	—	—	—		$4b_2 \rightarrow 1a_2 \ (\Phi_1)$	0.541
					$6a_1/2b_1 \to 1a_2/1a_2 \ (\Phi_1)$	0.404
					$2b_1/6a_1 \to 1a_2/1a_2 \ (\Phi_1)$	0.404
$1 \ {}^{1}B_{2}$	$1a_2 \rightarrow 2b_1$	0.617	$1a_2 \rightarrow 2b_1$	0.597	$1a_2 \rightarrow 2b_1 \ (\Phi_2)$	0.582
					$2b_1 \rightarrow 1a_2 \ (\Phi_1)$	-0.138
$2 {}^{1}B_{2}$		_	_	_	$2b_1 \rightarrow 1a_2 \ (\Phi_1)$	0.557
					$1b_1 \rightarrow 1a_2 \ (\Phi_1)$	0.339
					$1a_2 \rightarrow 2b_1 \ (\Phi_2)$	0.157
$1 {}^{1}A_{2}$	$4b_2 \rightarrow 2b_1$	0.668	$4b_2 \rightarrow 2b_1$	0.631	$4b_2 \rightarrow 2b_1 \ (\Phi_2)$	0.663
$1 {}^{3}A_{1}$	$1b_1 \rightarrow 2b_1$	0.676	b		$1b_1 \rightarrow 2b_1 \ (\Phi_2)$	0.653
$2 {}^{3}A_{1}$	$6a_1 \rightarrow 7a_1$	0.614	b		$6a_1 \rightarrow 7a_1 \ (\Phi_2)$	0.570
					$6a_1 \rightarrow 7a_1 \ (\Phi_1)$	-0.173
$1 {}^{3}B_{1}$	$6a_1 \rightarrow 2b_1$	0.678	$6a_1 \rightarrow 2b_1$	0.649	$6a_1 \rightarrow 2b_1 \ (\Phi_2)$	0.672
$2 {}^{3}B_{1}$	_				$4b_2 \rightarrow 1a_2 \ (\Phi_1)$	0.569
					$6a_1/2b_1 \to 1a_2/1a_2 \ (\Phi_1)$	0.371
					$2b_1/6a_1 \to 1a_2/1a_2 \ (\Phi_1)$	0.371
$1 {}^{3}B_{2}$	$1a_2 \rightarrow 2b_1$	0.688	$1a_2 \rightarrow 2b_1$	0.661	$1a_2 \rightarrow 2b_1 \ (\Phi_2)$	0.687
$2 {}^{3}B_{2}$					$2b_1 \rightarrow 1a_2 \ (\Phi_1)$	0.694
$1 {}^{3}A_{2}$	$4b_2 \rightarrow 2b_1$	0.674	$4b_2 \rightarrow 2b_1$	0.640	$4b_2 \rightarrow 2b_1 \ (\Phi_2)$	0.673

Table 4.6.: Dominant elements of the CCSD-LR, CCSDT-LR, and Mk-MRCCSD-LR eigenvectors for the excited states of ozone as computed using the cc-pCVTZ basis set.^a

^aThe wave function of the ground state is dominated by

 $|\Phi_1\rangle = |(\operatorname{core})^2 (1b_1)^2 (4b_2)^2 (6a_1)^2 (2b_1)^2\rangle$ and $|\Phi_2\rangle = |(\operatorname{core})^2 (1b_1)^2 (4b_2)^2 (6a_1)^2 (1a_2)^2\rangle$. The weights of $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in the Mk-MRCCSD wave function for the ground state are $c_1 \approx -0.30$ and $c_2 \approx 0.95$.

 b For technical reasons, the 1 $^{3}A_{1}$ state and the 2 $^{3}A_{1}$ state could not be targeted at the CCSDT-LR level of theory.

the almost coinciding absolute energies can be related to the fact that the Mk-MRCCSD-LR eigenvectors essentially are of single-reference character, i.e., dominated by excitations out of one reference determinant.

Group II only includes the 2 ${}^{3}A_{1}$ state for the given example. The Mk-MRCCSD-LR energy of this state is 14 m E_{h} lower than the corresponding CCSD-LR energy. Table 4.6 shows that the Mk-MRCCSD-LR eigenvector for this state is dominated by two elements, which describe the same excitation from the $6a_{1}$ to the $7a_{1}$ orbital, but refer to different reference determinants. The weights of these leading excitations are roughly in the same proportion as the CI coefficients for the ground state are. In general, a state mainly formed by corevirtual excitations can benefit from the multireference treatment as the Mk-MRCCSD-LR eigenvector may contain appreciable contributions from both references. Accordingly, such a state undergoes an energetic reduction when replacing CCSD-LR by Mk-MRCCSD-LR.

The change in energy observed for the 1 ${}^{1}B_{2}$ state (10 m E_{h}) is similar to that of the 2 ${}^{3}A_{1}$ state. However, it should rather be treated as a special case since the largest elements in the Mk-MRCCSD-LR eigenvector for this state are those internal excitations mentioned in Section 4.1.5 that lift an electron from one active orbital to another. CCSDT-LR results for the 1 ${}^{1}B_{2}$ state follow the same pattern as those for states in group I and are thus not affected by the special role of this state in the Mk-MRCCSD-LR description.

The corresponding triplet state $(1 \ {}^{3}B_{2})$ is the only state contained in Table 4.5, for which Mk-MRCCSD-LR delivers an absolute energy that is higher than the CCSD-LR value. As the

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Figure 4.4.: Qualitative change of the excitation spectrum induced by the replacement of the CCSD reference $|\Psi\rangle = e^{\hat{T}} |(\operatorname{core})^2 t^2\rangle$ by the Mk-MRCCSD reference $|\Psi\rangle = c_t e^{\hat{T}_t} |(\operatorname{core})^2 t^2\rangle + c_s e^{\hat{T}_s} |(\operatorname{core})^2 s^2\rangle$.

CCSDT-LR energy for this state is smaller than the CCSD-LR energy by only 22 m E_h , the change in relative excitation energy is similar when going from CCSD-LR to either CCSDT-LR or Mk-MRCCSD-LR. Further insight is provided by Table 4.6, which shows that the Mk-MRCCSD-LR eigenvector for the 1 ${}^{3}B_{2}$ state is dominated by a single element, namely the internal excitation from the $1a_2$ to the $2b_1$ orbital, while the eigenvector for the 1 ${}^{1}B_{2}$ state includes an appreciable contribution from the reverse excitation as well.

The most pronounced discrepancy between the three methods under consideration is observed for the first excited state of ${}^{1}A_{1}$ symmetry, whose Mk-MRCCSD-LR and CCSDT-LR energies are decreased by 45 m E_{h} and 200 m E_{h} , respectively, compared to CCSD-LR. As a consequence, the 2 ${}^{1}A_{1}$ state is the only state discussed here, for which Mk-MRCCSD-LR predicts a smaller relative excitation energy than CCSD-LR. Since CCSDT-LR yields an even smaller excitation energy, one may conclude that Mk-MRCCSD-LR describes this state significantly better than CCSD-LR. From Table 4.6, it can be seen that the CCSD-LR and CCSDT-LR eigenvectors for the 2 ${}^{1}A_{1}$ state qualitatively differ, which raises doubts about the validity of the CCSD-LR results. In the Mk-MRCCSD framework, the double excitation that dominates the CCSD-LR eigenvector converts one reference determinant into the other one. It is thus excluded from the Mk-MRCCSD-LR treatment. Instead, the Mk-MRCCSD-LR eigenvector for the 2 ${}^{1}A_{1}$ state is largely made up of contributions from the upper lines in Eqs. (4.33) and (4.34), which can be interpreted as rotation of the CI coefficients.

All remaining entries in Table 4.5 can be interpreted as additional components of the states discussed before. This is most obvious for the roots 2 ${}^{1}B_{2}$ and 2 ${}^{3}B_{2}$, which can easily

be identified as alternative representations of the states 1 ${}^{1}B_{2}$ and 1 ${}^{3}B_{2}$ with the reversed internal excitations as main contribution. The roots labeled as 3 ${}^{1}A_{1}$, 2 ${}^{1}B_{1}$, and 2 ${}^{3}B_{1}$ are, in principle, of the same character as the states collected in group I. Their Mk-MRCCSD-LR eigenvectors are all dominated by excitations from core orbitals to the 1*a*₂ orbital, which is unoccupied only in reference determinant $|\Phi_{1}\rangle$. Also noteworthy are the large contributions from double excitations to the roots 2 ${}^{1}B_{1}$ and 2 ${}^{3}B_{1}$. These create the same configurations that dominate the roots 1 ${}^{1}B_{1}$ and 1 ${}^{3}B_{1}$, however, the latter are mainly composed of single excitations, which explains that 2 ${}^{1}B_{1}$ and 2 ${}^{3}B_{1}$ are higher in energy than 1 ${}^{1}B_{1}$ and 1 ${}^{3}B_{1}$. Accordingly, the former two roots should be interpreted as inferior representations of the physical states 1 ${}^{1}B_{1}$ and 1 ${}^{3}B_{1}$.

All conclusions drawn in this section are summarized in Figure 4.4, which shows the energetic changes to be expected for a generic system when going from CCSD-LR to Mk-MRCCSD-LR. Also noteworthy is the fact that experimental values are available [222, 231, 232] for most of the excitation energies discussed here. The values are included in Table 4.5. Two general observations are that all CCSD-LR and Mk-MRCCSD-LR values are considerably larger than the corresponding experimental numbers and that Mk-MRCCSD-LR represents an improvement over CCSD-LR only for the 2 1A_1 state. In contrast, CCSDT-LR agrees with experiment within 0.3 eV for the B₁ and A₂ states, within 0.5 eV for the 2 1A_1 state, and within 0.65 eV for the 1B_2 state.

4.3.4. Vertical Excitation Spectra of Aryne Compounds

This section centers on the excitation spectra of the three isomers of benzyne (cf. Figure 3.4 for their molecular structure). Vertical and adiabatic singlet-triplet splittings have been of particular interest in previous studies [61, 69, 71, 190–192, 194, 196–199], while other excited states beyond the lowest-lying triplet are less well investigated [77, 193]. The multireference character of the closed-shell ground states of these compounds increases in the direction ortho < meta < para as seen from the CI coefficients obtained in Mk-MRCCSD calculations. Their values are 0.97 and -0.24 for *o*-benzyne, 0.96 and -0.28 for *m*-benzyne, and -0.53 and 0.85 for *p*-benzyne. The active space used in the present study comprises the 10 a_1 and $8b_2$, the 11 a_1 and $7b_2$, and the $6a_q$ and $5b_{3u}$ orbitals, respectively.

Tables 4.7, 4.8, and 4.9 comprise absolute energies and vertical excitation energies for a selection of electronic states computed at the CCSD-LR and Mk-MRCCSD-LR levels of theory. As experimental data on the excitation spectra of the benzynes are not available from the literature, the focus is only on the comparison of Mk-MRCCSD-LR to CCSD-LR in this section. Hence, results for only one basis set are presented. From Tables 4.7 to 4.9, it is seen that the ground states of all three molecules lie lower at the Mk-MRCCSD level of theory, but the magnitude of this energetic lowering with respect to CCSD increases from 5 m E_h for *o*-benzyne over 8 m E_h for *m*-benzyne to 25 m E_h for *p*-benzyne. While this pattern illustrates that the ground state's multireference character grows in the same direction, a similar energetic change is not observed for the excited states as it has been introduced in the previous section, is valid for the benzynes as well. Tables 4.7 to 4.9 thus contain the corresponding assignments as well as the dominant contributions to the Mk-MRCCSD-LR and CCSD-LR eigenvectors to underpin these claims.

States, whose Mk-MRCCSD-LR eigenvector is dominated by core-active or active-virtual excitations, hardly benefit from the multireference treatment. Almost coinciding absolute energies at the CCSD-LR and Mk-MRCCSD-LR levels of theory are observed for states in this group. As a consequence, the corresponding relative excitation energies are always larger when computed using the Mk-MRCCSD-LR method. The difference between CCSD-LR and

Table 4.7.: Absolute energies in atomic units, vertical excitation energies in eV, and dominant elements of the LR eigenvectors for selected excited singlet and triplet states of *o*-benzyne as computed at the CCSD-LR and Mk-MRCCSD-LR levels of theory using the cc-pCVTZ basis set, ground-state structure optimized at the Mk-MRCCSD/cc-pCVTZ level of theory.

Root	Type			CCSD-LR			Mk-1	MRCCSD-LR	
		E/a.u.	$\Delta E/\mathrm{eV}$	Eigenvector dominat	ed by	E/a.u.	$\Delta E/\mathrm{eV}$	Eigenvector domin	nated by
$1 {}^{1}A_{1}$	a	-230.7215	_			-230.7270	_		
$2 {}^{1}A_{1}$	core-	-230.5212	5.452	$2b_1 \rightarrow 3b_1$	0.553	-230.5261	5.467	$2b_1 \rightarrow 3b_1 \ (\Phi_1)$	0.536
	virtual			$1a_2 \rightarrow 2a_2$	-0.364			$1a_2 \rightarrow 2a_2 \ (\Phi_1)$	-0.354
$4 {}^{1}A_{1}$	CI	-230.3935	8.927	$10a_1 \rightarrow 11a_1$	0.539	-230.4105	8.613	r_{0}^{2}	0.881
	rotation			$7b_2 \rightarrow 8b_2$	0.302			r_0^1	0.226
				$10a_1/10a_1 \to 8b_2/8b_2$	0.193				
$1 \ ^{1}B_{1}$	core-	-230.5580	4.450	$1a_2 \rightarrow 8b_2$	0.661	-230.5600	4.545	$1a_2 \rightarrow 8b_2 \ (\Phi_1)$	0.651
	active								
$3 {}^{1}B_{1}$	core-	-230.4125	8.410	$2b_1 \rightarrow 11a_1$	0.651	-230.4173	8.429	$2b_1 \rightarrow 11a_1 \ (\Phi_1)$	0.628
	virtual							$2b_1 \rightarrow 11a_1 \ (\Phi_2)$	-0.153
$1 {}^{1}B_{2}$	active-	-230.5231	5.400	$10a_1 \rightarrow 8b_2$	0.602	-230.5345	5.240	$10a_1 \rightarrow 8b_2 \ (\Phi_1)$	0.544
	active			$2b_1 \rightarrow 2a_2$	-0.257			$2b_1 \rightarrow 2a_2 \ (\Phi_1)$	0.238
$2 {}^{1}B_{2}$	active-	—	_	—		-230.4841	6.610	$8b_2 \to 10a_1 \ (\Phi_2)$	0.623
	active								
$1 \ {}^{1}A_{2}$	core-	-230.5624	4.329	$2b_1 \rightarrow 8b_2$	0.659	-230.5650	4.409	$2b_1 \rightarrow 8b_2 \ (\Phi_1)$	0.652
	active								
$1 {}^{3}A_{1}$	core-	-230.5376	5.006	$2b_1 \rightarrow 3b_1$	0.623	-230.5426	5.017	$2b_1 \rightarrow 3b_1 \ (\Phi_1)$	0.604
	virtual			$1a_2 \rightarrow 2a_2$	0.250			$1a_2 \rightarrow 2a_2 \ (\Phi_1)$	0.244
$1 {}^{3}B_{1}$	core-	-230.5633	4.307	$1a_2 \rightarrow 8b_2$	0.664	-230.5652	4.403	$1a_2 \rightarrow 8b_2 \ (\Phi_1)$	0.653
	active								
$3 {}^{3}B_{1}$	core-	-230.4164	8.304	$2b_1 \rightarrow 11a_1$	0.638	-230.4213	8.319	$2b_1 \rightarrow 11a_1 \ (\Phi_1)$	0.613
	virtual							$2b_1 \rightarrow 11a_1 \ (\Phi_2)$	-0.150
$1 {}^{3}B_{2}$	active-	-230.6411	2.188	$10a_1 \rightarrow 8b_2$	0.664	-230.6388	2.400	$10a_1 \rightarrow 8b_2 \ (\Phi_1)$	0.662
	active								
$2 {}^{3}B_{2}$	active-		_	—		-230.6254	2.764	$8b_2 \to 10a_1 \ (\Phi_2)$	0.693
	active								
$1 {}^{3}A_{2}$	core-	-230.5836	3.752	$2b_1 \rightarrow 8b_2$	0.645	-230.5861	3.834	$2b_1 \rightarrow 8b_2 \ (\Phi_1)$	0.642
	active								

^aThe wave function of the ground state is dominated by $|\Phi_1\rangle = |(\operatorname{core})^2 (2b_1)^2 (1a_2)^2 (10a_1)^2\rangle$ and $|\Phi_2\rangle = |(\operatorname{core})^2 (2b_1)^2 (1a_2)^2 (8b_2)^2\rangle$. The weights of $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in the Mk-MRCCSD wave function for the ground state are $c_1 \approx 0.97$ and $c_2 \approx -0.24$.

Mk-MRCCSD-LR excitation energies does not exceed 0.2 eV in the cases of o-benzyne and m-benzyne, but reaches values of up to 0.7 eV for p-benzyne.

States, to which the most important contributions are delivered by core-virtual excitations, possess structurally similar Mk-MRCCSD-LR and CCSD-LR eigenvectors. Yet, all CCSD-LR contributions are split up into two subcontributions out of the two different reference determinants at the Mk-MRCCSD-LR level. The relative weights of these subcontributions are most often similar to the CI coefficients for the ground-state wave function. The absolute energies of states in this group undergo a significant reduction when replacing CCSD-LR by Mk-MRCCSD-LR. The differences approximately amount to 5 m E_h for o-benzyne, 8 m E_h for m-benzyne, and 20-30 m E_h for p-benzyne. As these changes roughly match those for the respective ground states, relative excitation energies for the states in question are almost identical when computed using CCSD-LR or Mk-MRCCSD-LR. Furthermore, it is noteworthy that the 2 ${}^1B_{2u}$ and 1 3A_g states of p-benzyne are the only examples, where a considerable mixing of core-virtual, core-active, and active-virtual excitations takes place. However, there is no formal reason for this to occur, the situation may be less clear for other molecules.

Active-active excitations are dominant for the 1 ${}^{1}B_{2}$ states of *o*-benzyne and *m*-benzyne

Table 4.8.: Absolute energies in atomic units, vertical excitation energies in eV, and dominant elements of the LR eigenvectors for selected excited singlet and triplet states of *m*-benzyne as computed at the CCSD-LR and Mk-MRCCSD-LR levels of theory using the cc-pCVTZ basis set, ground-state structure optimized at the Mk-MRCCSD/cc-pCVTZ level of theory.

Root	Type		(CCSD-LR		Mk-MRCCSD-LR				
		E/a.u.	$\Delta E/\mathrm{eV}$	Eigenvector	dominated by	E/a.u.	$\Delta E/\mathrm{eV}$	Eigenvector dominated	by	
$1 {}^{1}A_{1}$	a	-230.6941			`	-230.7020				
$2 {}^{1}A_{1}$	core-	-230.4420	6.858	$1a_2 \rightarrow 2a_2$	0.495	-230.4503	6.849	$1a_2 \rightarrow 2a_2 \ (\Phi_1)$	0.487	
	virtual			$2b_1 \rightarrow 3b_1$	0.454			$2b_1 \rightarrow 3b_1 \ (\Phi_1)$	0.420	
								$1a_2 \rightarrow 2a_2 \ (\Phi_2)$	-0.144	
$1 {}^{1}B_{1}$	core-	-230.5418	4.144	$1a_2 \rightarrow 7b_2$	0.639	-230.5441	4.299	$1a_2 \rightarrow 7b_2 \ (\Phi_1)$	0.638	
	active									
$3 {}^{1}B_{1}$	core-		_			-230.3946	8.365	$7b_2/1a_2 \to 11a_1/11a_1 \ (\Phi_2)$	0.495	
	active							$1a_2/7b_2 \to 11a_1/11a_1 \ (\Phi_2)$	0.495	
								$7b_2 \rightarrow 2a_2 \ (\Phi_2)$	0.283	
$1 \ {}^{1}B_{2}$	active-	-230.5227	4.663	$1a_2 \rightarrow 3b_1$	0.473	-230.5377	4.473	$11a_1 \rightarrow 7b_2 \ (\Phi_1)$	0.466	
	active			$11a_1 \rightarrow 7b_2$	-0.468			$1a_2 \rightarrow 3b_1 \ (\Phi_1)$	0.412	
$3 {}^{1}B_{2}$	active-		_	—	—	-230.4650	6.451	$7b_2 \rightarrow 11a_1 \ (\Phi_2)$	0.613	
	active									
$1 {}^{1}A_{2}$	core-	-230.5096	5.021	$2b_1 \rightarrow 7b_2$	0.632	-230.5121	5.169	$2b_1 \rightarrow 7b_2 \ (\Phi_1)$	0.631	
	active			$11a_1 \rightarrow 2a_2$	-0.206			$11a_1 \rightarrow 2a_2 \ (\Phi_1)$	0.186	
$1 {}^{3}A_{1}$	core-	-230.5349	4.331	$2b_1 \rightarrow 3b_1$	0.512	-230.5422	4.350	$2b_1 \rightarrow 3b_1 \ (\Phi_1)$	0.481	
	virtual			$1a_2 \rightarrow 2a_2$	0.430			$1a_2 \rightarrow 2a_2 \ (\Phi_1)$	0.423	
$1 {}^{3}B_{1}$	core-	-230.5515	3.879	$1a_2 \rightarrow 7b_2$	0.648	-230.5538	4.034	$1a_2 \rightarrow 7b_2 \ (\Phi_1)$	0.647	
	active									
$3 {}^{3}B_{1}$	core-		_	_	—	-230.3966	8.312	$7b_2/1a_2 \to 11a_1/11a_1 \ (\Phi_2)$	0.555	
	active							$1a_2/7b_2 \to 11a_1/11a_1 \ (\Phi_2)$	0.555	
								$7b_2 \rightarrow 2a_2 \ (\Phi_2)$	0.259	
$1 {}^{3}B_{2}$	active-	-230.6347	1.615	$11a_1 \rightarrow 7b_2$	0.675	-230.6317	1.913	$11a_1 \rightarrow 7b_2 \ (\Phi_1)$	0.675	
	active									
$2 {}^{3}B_{2}$	active-					$-230.61\overline{84}$	2.277	$7b_2 \rightarrow 11a_1 \ (\Phi_2)$	0.693	
	active									
$1 {}^{3}A_{2}$	active-	-230.5222	4.677	$11a_1 \rightarrow 2a_2$	0.595	-230.5239	4.849	$11a_1 \rightarrow 2a_2 \ (\Phi_1)$	0.561	
	virtual			$2b_1 \rightarrow 7b_2$	0.307			$2b_1 \rightarrow 7b_2 \ (\Phi_1)$	-0.341	

^aThe wave function of the ground state is dominated by $|\Phi_1\rangle = |(\operatorname{core})^2 (2b_1)^2 (1a_2)^2 (11a_1)^2\rangle$ and $|\Phi_2\rangle = |(\operatorname{core})^2 (2b_1)^2 (1a_2)^2 (7b_2)^2\rangle$. The weights of $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in the Mk-MRCCSD wave function for the ground state are $c_1 \approx 0.96$ and $c_2 \approx -0.28$.

as well as for the 1 ${}^{1}B_{3u}$ state of *p*-benzyne. The energy of these three states reduces more strongly than that of the respective ground state when going from CCSD-LR to Mk-MRCCSD-LR so that the latter method yields slightly lower excitation energies. This should be seen in contrast to the states discussed before, where Mk-MRCCSD-LR leads to either higher or nearly identical excitation energies. It should be added that the 2 ${}^{1}B_{2}$ root of *o*-benzyne, the 3 ${}^{1}B_{2}$ root of *m*-benzyne, and the 2 ${}^{1}B_{3u}$ root of *p*-benzyne represent additional components of the states in question. Especially in the case of *p*-benzyne, the roots 1 ${}^{1}B_{3u}$ and 2 ${}^{1}B_{3u}$ form a striking example for the overcompleteness in Mk-MRCC-LR theory. The eigenvectors for these roots are largely dominated by the same pair of internal excitations, which transfer an electron from the $5b_{3u}$ to the $6a_g$ orbital or vice versa. Both roots are reasonable descriptions of the same excited state and neither root can be discarded as spurious.

The corresponding triplet states (1 ${}^{3}B_{2}$ for *o*-benzyne and *m*-benzyne and 1 ${}^{3}B_{3u}$ for *p*-benzyne) are also dominated by active-active excitations. However, their energetic behavior is different from the singlet states as they represent the only states, for which Mk-MRCCSD-LR leads to higher absolute energies than CCSD-LR. The concurrent change in relative excitation

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Table 4.9.: Absolute energies in atomic units, vertical excitation energies in eV, and dominant elements of the LR eigenvectors for selected excited singlet and triplet states of *p*-benzyne as computed at the CCSD-LR and Mk-MRCCSD-LR levels of theory using the cc-pCVTZ basis set, ground-state structure optimized at the Mk-MRCCSD/cc-pCVTZ level of theory.

Root	Type		CCSD-LR		Mk-MRCCSD-LR				
		E /a.u. ΔE /eV Eigenvector dominated by			$E/a.u.$ $\Delta E/eV$ Eigenvector dominated by				
$1 {}^{1}A_{g}$	$\underline{}^{a}$	-230.6505	_			-230.6772	_		
$2 {}^{1}A_{g}$	CI	-230.4271	6.082	$5b_{3u}/5b_{3u} \rightarrow 6a_g/6a_g$	0.806	-230.4902	5.089	r_0^1	0.834
	rotation			$5a_g \to 6a_g$	0.294			r_{0}^{2}	0.521
$1 {}^{1}\mathrm{B}_{2u}$	core-	-230.4537	5.355	$1b_{2g} \rightarrow 1a_u$	0.558	-230.4782	5.417	$1b_{2g} \rightarrow 1a_u \ (\Phi_2)$	0.466
	virtual			$1b_{3g} \rightarrow 2b_{1u}$	-0.354			$1b_{3g} \rightarrow 2b_{1u} \ (\Phi_2)$	-0.322
								$1b_{2g} \rightarrow 1a_u \ (\Phi_1)$	-0.272
- 15			- 100	41 01				$\frac{1b_{3g} \to 2b_{1u} \ (\Phi_1)}{2b_{1u}}$	0.206
$2 {}^{1}\mathrm{B}_{2u}$	mixed	-230.3863	7.192	$1b_{3g} \rightarrow 2b_{1u}$	0.479	-230.4007	7.525	$1b_{3g} \rightarrow 2b_{1u} \ (\Phi_2)$	0.406
				$4b_{2u} \rightarrow ba_g$	0.366			$4b_{2u} \rightarrow ba_g (\Phi_2)$	0.306
				$10_{2g} \rightarrow 1a_u$	0.258			$10_{2g} \rightarrow 1a_u \ (\Psi_2)$	0.288
1 1 R.	activo	230 5010	4.046	5ha ba	0 568	220 5266	3 8 9 7	$\frac{103g \rightarrow 201u \ (\Psi_1)}{5b_0 \rightarrow 6g \ (\Phi_2)}$	0.487
$1 D_{3u}$	active-	-230.3019	4.040	$5b_{3u} \rightarrow 5b_{g}$	0.308	-230.3300	5.621	$5b_{3u} \rightarrow 5b_{2u} (\Phi_2)$	-0.272
	active			$102g \rightarrow 201u$	0.201			$bag \rightarrow bb3u \ (\Phi_1)$ $1b_2 \rightarrow 2b_1 \ (\Phi_2)$	-0.272
$2^{1}B_{2}$	active-				_	-230 4997	4 831	$\frac{102g}{6a_{\pm} \rightarrow 5b_{2u}} (\Phi_1)$	0.522
2 D ₃ <i>u</i>	active					200.1001	1.001	$5b_{3u} \rightarrow 6a_a (\Phi_2)$	0.309
$1 {}^{1}B_{1u}$	core-			_		-230,4995	4.836	$\frac{1b_{2g} \rightarrow 5b_{3y}}{1} (\Phi_1)$	0.666
14	active							2934 (-1)	
$2^{1}B_{1u}$	core-	-230.4400	5.728	$1b_{1u} \rightarrow 6a_a$	0.595	-230.4433	6.365	$1b_{1u} \rightarrow 6a_a \ (\Phi_2)$	0.595
10	active			$5b_{3u}/1b_{2g} \rightarrow 6a_g/6a_g$	0.311			$5b_{3u}/1b_{2g} \rightarrow 6a_g/6a_g \ (\Phi_2)$	0.304
				$1b_{2g}/5b_{3u} \rightarrow 6a_g/6a_g$	0.311			$1b_{2g}/5b_{3u} \rightarrow 6a_g/6a_g \ (\Phi_2)$	0.304
$1 {}^{1}\mathrm{B}_{2g}$	core-	-230.5425	2.941	$1b_{2g} \rightarrow 6a_g$	0.672	-230.5466	3.556	$1b_{2g} \rightarrow 6a_g \ (\Phi_2)$	0.671
	active								
$3 {}^{1}\mathrm{B}_{2g}$	core-	-		—		-230.4355	6.578	$6a_g/1b_{2g} \to 5b_{3u}/5b_{3u} \ (\Phi_1)$	0.498
	active							$1b_{2g}/6a_g \to 5b_{3u}/5b_{3u} \ (\Phi_1)$	0.498
								$1b_{1u} \to 5b_{3u} \ (\Phi_1)$	0.456
$1 \ ^{1}A_{u}$	core-	_		—		-230.4966	4.917	$1b_{3g} \to 5b_{3u} \ (\Phi_1)$	0.674
	active								
$3 {}^{1}A_{u}$	core-	-230.3414	8.413	$5b_{3u}/1b_{3g} \rightarrow 6a_g/6a_g$	0.657	-230.3413	9.142	$5b_{3u}/1b_{3g} \rightarrow 6a_g/6a_g \ (\Phi_2)$	0.609
1 3 4	active	000 0555	0.000	$1b_{3g}/5b_{3u} \rightarrow 6a_g/6a_g$	0.657	000 0700	0.001	$\frac{1b_{3g}/5b_{3u} \rightarrow 6a_g/6a_g}{11} (\Phi_2)$	0.609
$1 {}^{o}A_g$	mixed	-230.3555	8.029	$5b_{3u}/1b_{3g} \rightarrow 1a_u/ba_g$	0.428	-230.3729	8.281	$1b_{1u} \rightarrow 2b_{1u} \ (\Phi_2)$	0.422
				$10_{3g}/30_{3u} \rightarrow 0a_g/1a_u$	-0.428			$1b_{1u} \rightarrow 2b_{1u} \ (\Phi_1)$ $1b_{1u} \rightarrow 2b_{2u} \ (\Phi_2)$	-0.203
$1.3 P_{2}$	coro	230 4730	4 830	$\frac{10_{1u} \rightarrow 20_{1u}}{1b_{2u} \rightarrow 1a}$	0.333	230 4061	4 0 2 8	$\frac{102g \rightarrow 202g \ (\Psi_2)}{1b_2 \rightarrow 1g \ (\Phi_2)}$	0.201
$1 D_{2u}$	virtual	-230.4730	4.050	$10_{2g} \rightarrow 1u_u$ $1b_2 \rightarrow 2b_1$	0.037	-230.4901	4.920	$1b_{2g} \rightarrow 1a_u \ (\Psi_2)$ $1b_2 \rightarrow 1a_u \ (\Phi_1)$	-0.342
	VIItuai			$103g \rightarrow 201u$	0.210			$1b_{2g} \rightarrow 1a_u \ (\Psi_1)$ $1b_{2g} \rightarrow 2b_{1u} \ (\Phi_2)$	0 204
$1^{3}B_{2u}$	active-	-230.6688	-0.497	$5b_{2n} \rightarrow 6a_n$	0.684	-230.6630	0.387	$\frac{103g}{5b_{2u}} \rightarrow 6a_{a} (\Phi_{2})$	0.685
1 234	active		0.101	003u $000g$	0.001		0.001	\cos_{3u} $\cos_{y}(12)$	0.000
$2^{3}B_{3u}$	active-	-230.5009	4.073	$1b_{3a} \rightarrow 1a_{u}$	0.625	-230.5265	4.103	$1b_{3a} \rightarrow 1a_{u} \ (\Phi_2)$	0.534
	active			$1b_{2q} \rightarrow 2b_{1u}$	0.239			$1b_{3q} \rightarrow 1a_u \ (\Phi_1)$	-0.331
$1 {}^{3}B_{1u}$	core-					-230.5216	4.235	$1b_{2g} \rightarrow 5b_{3u} \ (\Phi_1)$	0.674
	active							5	
$2 {}^{3}B_{1u}$	core-	-230.4411	5.700	$1b_{1u} \rightarrow 6a_g$	0.596	-230.4441	6.344	$1b_{1u} \to 6a_g \ (\Phi_2)$	0.595
	active			$5b_{3u}/1b_{2g} \rightarrow 6a_g/6a_g$	0.310			$5b_{3u}/1b_{2g} \rightarrow 6a_g/6a_g \ (\Phi_2)$	0.302
				$1b_{2g}/5b_{3u} \rightarrow 6a_g/6a_g$	-0.310			$1b_{2g}/5b_{3u} \to 6a_g/6a_g \ (\Phi_2)$	-0.302
$1 {}^{3}\mathrm{B}_{2g}$	core-	-230.5625	2.395	$1b_{2g} \to 6a_g$	0.671	-230.5667	3.009	$1b_{2g} \to 6a_g \ (\Phi_2)$	0.672
	active								
$3 {}^{3}\mathrm{B}_{2g}$	core-	_		—		-230.4416	6.412	$6a_g/1b_{2g} \to 5b_{3u}/5b_{3u} \ (\Phi_1)$	0.544
	active							$1b_{2g}/6a_g \to 5b_{3u}/5b_{3u} \ (\Phi_1)$	-0.544
								$\frac{1b_{1u} \to 5b_{3u} \ (\Phi_1)}{2}$	0.391
$1 {}^{\circ}\mathrm{A}_{u}$	core-				_	-230.4971	4.902	$1b_{3g} \rightarrow 5b_{3u} \ (\Phi_1)$	0.674
2.3 4	active	020 2404	0.905	EL /1L C. /C	0.600	020 2421	0.000	11 /EL . C. /C. (X)	0 /01
$\mathfrak{Z} \mathcal{A}_u$	core-	-230.3424	8.385	$\frac{\partial v_{3u}}{\partial b_{3g}} \rightarrow \frac{\partial a_g}{\partial b_{3g}}$	0.060	-230.3431	9.092	$103g/303u \rightarrow ba_g/ba_g (\Phi_2)$	0.421
	active			$103g/303u \rightarrow 0ag/0ag$	-0.000			$503u/103g \rightarrow 0ag/0ag (\Psi_2)$	0.421
								$10_{2g} \rightarrow 50_{2u} \ (\Psi_2)$ $1b_2 \rightarrow 5b_2 \ (\Phi_2)$	0.000
		l						$10_{2g} \rightarrow 30_{2u} \ (\Psi_1)$	-0.210

^aThe wave function of the ground state is dominated by $|\Phi_1\rangle = |(\operatorname{core})^2 (4b_{2u})^2 (1b_{1u})^2 (1b_{2g})^2 (1b_{3g})^2 (6a_g)^2\rangle$ and $|\Phi_2\rangle = |(\operatorname{core})^2 (4b_{2u})^2 (1b_{1u})^2 (1b_{2g})^2 (1b_{3g})^2 (5b_{3u})^2\rangle$. The weights of $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in the Mk-MRCCSD wave function for the ground state are $c_1 \approx -0.53$ and $c_2 \approx 0.85$. energy increases from 0.2 eV for *o*-benzyne over 0.3 eV for *m*-benzyne to almost 0.9 eV for *p*-benzyne. Most important, Mk-MRCCSD-LR correctly predicts a positive excitation energy for the 1 ${}^{3}B_{3u}$ state of *p*-benzyne, whereas this state drops below the 1 ${}^{1}A_{g}$ state at the CCSD-LR level of theory. The energetic differences between singlet and triplet states can be related to the structure of the Mk-MRCCSD-LR eigenvectors. Tables 4.7 to 4.9 show that the eigenvectors for the triplet states are dominated by a single internal excitation, while a mixing of internal excitations occurs for the singlet states.

The 4 ${}^{1}A_{1}$ state of *o*-benzyne and the 2 ${}^{1}A_{g}$ state of *p*-benzyne are obtained 20 m E_{h} and 60 m E_{h} lower in energy, respectively, when computed at the Mk-MRCCSD-LR level of theory. As these values considerably surpass the energetic changes of the ground states, these two states represent the sole examples, for which the replacement of CCSD by Mk-MRCCSD causes a significant reduction of the relative excitation energy. Most prominently, the excitation energy for the 2 ${}^{1}A_{g}$ state of *p*-benzyne is lowered by nearly 1.0 eV. The LR eigenvectors in Tables 4.7 and 4.9 reveal that the states in question are treated conceptually differently at the CCSD-LR and Mk-MRCCSD-LR levels of theory. The latter method deals with both of them by means of rotating the CI coefficients, while the former method describes the 4 ${}^{1}A_{1}$ state of *o*-benzyne mainly by single excitations and the 2 ${}^{1}A_{g}$ state of *p*-benzyne by a double excitation, which is excluded as internal in the Mk-MRCCSD-LR treatment. Table 4.8 shows that such a state, mainly described via rotation of the CI coefficients, does not exist for *m*-benzyne.

All roots listed in Tables 4.7 to 4.9, for which the CCSD-LR column is left blank, should be interpreted as a result of the overcompleteness in Mk-MRCC-LR theory. They can be easily identified as second components of other roots based on the dominant contributions to their eigenvectors. At first glance, it seems that the number of spurious roots grows when going from o-benzyne to p-benzyne. However, this does not mean that the redundancy of Mk-MRCCSD-LR theory increases in the same direction, but rather that roots, which aim at describing the same physical state, are more clearly separated for weak multireference cases. Hence, the results presented in this work often cover only one component for obenzyne and m-benzyne. For p-benzyne, both components are covered more often, but the discrimination between physical and spurious roots becomes increasingly difficult for this molecule. For example, it is well possible to argue that, for the states of B_{1u} and A_u symmetry, the lower-lying Mk-MRCCSD-LR roots are more reliable as they are largely dominated by single excitations, while the higher-lying roots contain considerable contributions from double excitations. A parametrization in terms of single excitations should be regarded as superior based on standard arguments [119].

4.3.5. Ground and Excited States of Silicon Disulfide

In this section, the excited states of silicon disulfide are investigated. It is well established that there are two minima on the lowest potential hypersurface, which correspond to a linear and a cyclic isomer. The latter has recently been characterized experimentally for the first time [27], while the former has been known for long [233,234]. Still, the shape of the potential hypersurface between the two minima has been explored much less. Likewise, little is known about the excited states of silicon disulfide as only the lowest-lying triplet state has been investigated [235]. From an experimental point of view, a particularly intriguing question is whether the cyclic form can be synthesized photochemically from linear silicon disulfide. This would mean to lift the linear molecule to an excited state by means of irradiation followed by relaxation to the minimum on the hypersurface. However, such a reaction path would require the existence of an excited state, from which the cyclic minimum can be reached.

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Figure 4.5.: Energies for ground and excited states of silicon disulfide computed at the Mk-MRCCSD-LR level of theory using the cc-pCVTZ basis set.

Both isomers, the linear and the cyclic form of silicon disulfide, are accurately described by single-reference CC theory. The leading configurations are $|\Phi_1\rangle = |(\operatorname{core})^2(11a_1)^2\rangle$ for the cyclic form and $|\Phi_2\rangle = |(\operatorname{core})^2(8b_2)^2\rangle$ for the linear form in C_{2v} symmetry.¹ Between the two minima, both $|\Phi_1\rangle$ and $|\Phi_2\rangle$ deliver appreciable contributions to the wave function thereby giving rise to a distinct multireference character. Hence, the present investigation at the Mk-MRCCSD-LR level of theory is based on a reference space comprising $|\Phi_1\rangle$ and $|\Phi_2\rangle$. However, the aim here is not to make quantitative predictions about the excitation spectrum of silicon disulfide, but rather to test the reliability of the Mk-MRCCSD-LR approach. To this end, selected excited states are also studied at the MR-CISD level of theory including Pople's size-extensivity correction (MR-CISD+P) [105]. These calculations are based on a CAS(4,4), which comprises the orbitals $10a_1$, $11a_1$, $8b_2$, and $2a_2$.²

Figure 4.5 displays potential-energy curves for the ground state and the lowest-lying excited states of silicon disulfide in the range from $\measuredangle(SSiS) = 70^{\circ}$ to $\measuredangle(SSiS) = 170^{\circ}$. The excited states are targeted at the Mk-MRCCSD-LR level of theory, whereas the ground state is treated using the parent Mk-MRCCSD method. The potential-energy curve for the ground electronic state has been obtained by varying the angle $\measuredangle(SSiS)$ in steps of 5° while optimizing all bond lengths in every step. Starting from these structures, the vertical excitation spectrum has been recalculated for every angle to generate the potential-energy curves for the excited states. All structural parameters and the excitation energies used to generate Figure 4.5 are provided in Tables B.1 to B.4 in Appendix B. Dashed and continuous curves in Figure 4.5 refer to states, whose Mk-MRCCSD-LR eigenvector is dominated by excitations out of $|\Phi_1\rangle$ and $|\Phi_2\rangle$, respectively, while different colors are chosen to denote different spatial symmetry of the excited states. Without discussing in detail the electronic structure of the states displayed in Figure 4.5, it can be stated that the reliability of the results is potentially affected by the

¹The linear form actually has $D_{\infty h}$ symmetry. However, for the sake of comparability, it is characterized using C_{2v} symmetry.

²These calculations have been carried out by Leonie Mück using the COLUMBUS program package [205].


Figure 4.6.: Energies for ground and excited states of silicon disulfide computed at the Mk-MRCCSD-LR (\circ) and MR-CISD+P (\times) levels of theory using the cc-pCVTZ basis set. To allow for a better comparison, all MR-CISD+P values have been shifted by 44.36 m E_h so that Mk-MRCCSD and MR-CISD+P energies coincide for the linear equilibrium structure.

overcompleteness in Mk-MRCCSD-LR theory. This is obviously the case for the two lowest states of B_2 symmetry, which are represented in Figure 4.5 by the two lowest-lying green lines. These roots are mainly described in terms of active-active excitations between the $11a_1$ and $8b_2$ orbitals and aim at describing the same physical state. Regarding all further states, it is less clear whether any potential-energy curves should be discarded. Near the cyclic and the linear minimum, where the ground-state wave function is of single-reference character, a valid comparison to CCSD-LR calculations is possible. However, this is not the case in the region between the two minima, where genuine multireference methods need to be applied. In Figure 4.6, five potential-energy curves from Figure 4.5 are compared to the outcome of MR-CISD+P calculations.³ This shows that Mk-MRCCSD-LR and MR-CISD+P yield rather similar potential-energy curves for the states under investigation with the only larger deviation occurring for the ${}^{1}A_{1}$ state near the cyclic minimum. Hence, the redundancy of Mk-MRCCSD-LR does not hamper the accurate description of the low-lying excited states at least for the present example. With respect to the initial question whether the linear species can be converted photochemically into the cyclic form, Figure 4.6 shows that the vertical energy difference between the ground state and the lowest-lying symmetry-allowed excited state $({}^{1}B_{2})$ approximately amounts to 4.3 eV (290 nm), which is well within reach of photochemical irradiation techniques.⁴ Regarding the shape of the ¹B₂ state's hypersurface, it also seems plausible that an appreciable share of the excited molecules reaches a point on this hypersurface, where subsequent decay would yield the cyclic equilibrium structure. However, a confirmation of these predictions can be achieved only by experiment.

³All MR-CISD+P results are summarized in Table B.5 in Appendix B.

⁴The ¹B₂ state corresponds to the ¹ Π_g state in $D_{\infty h}$ symmetry, to which a transition is forbidden by symmetry. The proposed mechanism thus requires the simultaneous excitation of the bending vibrational mode.

5. Dipole Hessian Matrix for Correlated Levels of Theory

5.1. Theory

5.1.1. Third Derivative of the Hartree-Fock Energy

An expression for the third derivative of the HF energy can be obtained in a straightforward manner from Eq. (2.9), which reads

$$L = \sum_{i} 2h_{ii} + \sum_{ij} \left(2 \langle ij|ij \rangle - \langle ij|ji \rangle \right) - \sum_{ij} 2f_{ij} \left(\langle i|j \rangle - \delta_{ij} \right)$$
(5.1)

after RHF spin integration has been carried out. Differentiating this Lagrangian three times while taking account of the (2n + 1) and (2n + 2) rules of derivative theory [112] leads to [236, 237]

$$\begin{aligned} \frac{d^{3}E}{d\chi_{1}d\chi_{2}d\chi_{3}} &= \frac{\partial^{3}L}{\partial\chi_{1}\partial\chi_{2}\partial\chi_{3}} = \sum_{i} 2h_{ii}^{\chi_{1}\chi_{2}\chi_{3}} + \sum_{ij} \left(2 \langle ij|ij \rangle^{\chi_{1}\chi_{2}\chi_{3}} - \langle ij|ji \rangle^{\chi_{1}\chi_{2}\chi_{3}} \right) \\ &- \sum_{ij} 2f_{ij}S_{ij}^{\chi_{1}\chi_{2}\chi_{3}} + P_{123}^{3} \left[4 \sum_{ai} f_{ai}^{(\chi_{1},\chi_{2})}U_{ai}^{\chi_{3}} - 2 \sum_{ij} f_{ij}^{(\chi_{1},\chi_{2})}S_{ij}^{\chi_{3}} - 4 \sum_{aij} f_{ij}S_{ai}^{\chi_{1}\chi_{2}}U_{aj}^{\chi_{3}} \right. \\ &+ 2 \sum_{ijk} f_{ij}S_{jk}^{\chi_{1}\chi_{2}}S_{ik}^{\chi_{3}} - 2 \sum_{ij} \frac{df_{ij}}{d\chi_{1}}S_{ij}^{\chi_{2}\chi_{3}} + 4 \sum_{abij} A_{aibjj}^{\chi_{1}}U_{ai}^{\chi_{2}}U_{bj}^{\chi_{3}} - 2 \sum_{aijk} A_{aijk}^{\chi_{1}}U_{ai}^{\chi_{2}}S_{jk}^{\chi_{3}} \\ &- 2 \sum_{aijk} A_{aijk}^{\chi_{1}}U_{ai}^{\chi_{3}}S_{jk}^{\chi_{2}} + \sum_{ijkl} A_{ijkl}^{\chi_{1}}S_{ij}^{\chi_{2}}S_{kl}^{\chi_{3}} \right] \\ &+ P_{123}^{3} \left[4 \sum_{abi} U_{ai}^{\chi_{1}}U_{bi}^{\chi_{2}}\frac{df_{ab}}{d\chi_{3}} - 4 \sum_{aij} U_{ai}^{\chi_{1}}U_{aj}^{\chi_{2}}\frac{df_{ij}}{d\chi_{3}} - 4 \sum_{aij} U_{ai}^{\chi_{1}}S_{aj}^{\chi_{2}}\frac{df_{ij}}{d\chi_{3}} - 4 \sum_{aij} U_{ai}^{\chi_{1}}S_{aj}^{\chi_{2}}\frac{df_{ij}}{d\chi_{3}} - 4 \sum_{aij} U_{ai}^{\chi_{1}}S_{aj}^{\chi_{2}}S_{kl}^{\chi_{3}} \right] \\ &+ 4 \sum_{abci} U_{ai}^{\chi_{1}}U_{bi}^{\chi_{2}}S_{ac}^{\chi_{3}}f_{bc} + 4 \sum_{ijk} S_{ij}^{\chi_{1}}S_{ik}^{\chi_{2}}\frac{df_{jk}}{d\chi_{3}} - 4 \sum_{abij} U_{ai}^{\chi_{1}}U_{bj}^{\chi_{2}}S_{ab}^{\chi_{3}}f_{ij} + 2 \sum_{aijk} U_{ai}^{\chi_{1}}S_{aj}^{\chi_{2}}S_{jk}^{\chi_{3}}f_{ik} \right] \\ &- 2 \sum_{aijk} U_{ai}^{\chi_{1}}S_{aj}^{\chi_{2}}S_{ik}^{\chi_{3}}f_{jk} - 2 \sum_{aijk} U_{ai}^{\chi_{1}}S_{aj}^{\chi_{3}}S_{ik}^{\chi_{2}}f_{jk} \right]$$

$$(5.2)$$

with P_{123}^3 invoking a cyclic permutation of the perturbations χ_1 , χ_2 , and χ_3 . The derivatives of the Fock-matrix elements can be written as

$$\frac{\partial f_{pq}}{\partial \chi} = f_{pq}^{(\chi)} + \sum_{r} \left(U_{rq}^{\chi} f_{pr} + U_{rp}^{\chi} f_{qr} \right) + \sum_{rj} U_{rj}^{\chi} A_{pqrj} , \qquad (5.3)$$

where all appearing quantities have been defined in Section 2.3.2, while A_{pqrs}^{χ} is given by

$$A_{pqrs}^{\chi} = 4 \langle pr|qs \rangle^{\chi} - \langle pr|sq \rangle^{\chi} - \langle ps|rq \rangle^{\chi} \quad . \tag{5.4}$$

Eq. (5.2) holds regardless of the nature of the perturbations χ_1 , χ_2 , χ_3 . However, if the dipole Hessian matrix is under consideration, i.e., if χ_1 and χ_2 are nuclear displacements x and y and χ_3 is an electric-field component ε , all terms involving $\langle pq || rs \rangle^{\chi_3}$, $A_{pqrs}^{\chi_3}$, or $S_{pq}^{\chi_3}$ can be neglected.

5.1.2. Third Derivative of the MP2 and the CC Energy

In order to derive an expression for the third derivative of the MP2 and the CC energy, a suitable Lagrangian must be constructed first as both MP2 and CC theory do not rely on the variational principle. In the case of CC theory, an appropriate starting point is

$$L = \langle \Psi_0 | \left(1 + \hat{\Lambda} \right) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle \quad , \tag{5.5}$$

where the deexcitation operator $\hat{\Lambda} = \sum_{q} \lambda_{q} \hat{\tau}_{q}^{\dagger}$ ensures the stationarity of L with respect to the CC amplitudes t_{q} . Using the density matrices

$$D_{pq} = \langle \Psi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \{ \hat{a}_p^{\dagger} \hat{a}_q \} e^{\hat{T}} | \Psi_0 \rangle \quad , \tag{5.6}$$

$$\Gamma_{pqrs} = \frac{1}{4} \langle \Psi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \{ \hat{a}_p^{\dagger} \hat{a}_q^{\dagger} \hat{a}_s \hat{a}_r \} e^{\hat{T}} | \Psi_0 \rangle \quad , \tag{5.7}$$

Eq. (5.5) can be recast as

$$L = \sum_{pq} D_{pq} f_{pq} + \sum_{pqrs} \Gamma_{pqrs} \langle pq || rs \rangle \quad .$$
(5.8)

To allow for a concise discussion, it is advantageous to rewrite the MP2 energy expression from Eq. (2.31) in terms of Eq. (5.8). Introducing the MP2 amplitudes as

$$t_{ij}^{ab} = \frac{\langle ab||ij\rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}}$$
(5.9)

yields the MP2 Lagrangian

$$L_{\rm MP2} = \frac{1}{4} \sum_{ijab} t^{ab}_{ij} \langle ij||ab\rangle + \lambda^{ij}_{ab} \Big[\langle ab||ij\rangle - t^{ab}_{ij} \big(f_{ii} + f_{jj} - f_{aa} - f_{bb} \big) \Big]$$
(5.10)

$$=\sum_{ij} D_{ij} f_{ij} + \sum_{ab} D_{ab} f_{ab} + \sum_{ijab} \Gamma_{ijab} \langle ij || ab \rangle$$
(5.11)

with the Lagrange multipliers λ_{ab}^{ij} given as

$$\lambda_{ab}^{ij} = \frac{\langle ij||ab\rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}} = \left(t_{ij}^{ab}\right)^* \tag{5.12}$$

and the density matrices given as

$$D_{ij} = -\frac{1}{2} \sum_{mef} \lambda_{ef}^{im} t_{jm}^{ef} , \qquad (5.13)$$

$$D_{ab} = \frac{1}{2} \sum_{mne} \lambda_{ae}^{mn} t_{mn}^{be} , \qquad (5.14)$$

$$\Gamma_{ijab} = \frac{1}{4} \left((\lambda_{ab}^{ij})^* + t_{ij}^{ab} \right) \,. \tag{5.15}$$

In addition, the dependence of the MP2 or CC energy on the molecular orbitals must be considered if orbital-relaxed derivatives are requested. To this end, the Brillouin condition and the orthonormality of the orbitals are included as further constraints in Eq. (5.8), which leads to

$$\mathcal{L} = \sum_{pq} D_{pq} f_{pq} + \sum_{pqrs} \Gamma_{pqrs} \langle pq || rs \rangle + \sum_{ai} Z_{ai} f_{ai} + \sum_{pq} I_{pq} (\langle p | q \rangle - \delta_{pq}) .$$
(5.16)

The Lagrange multipliers Z_{ai} and I_{pq} can be obtained via stationarity conditions of \mathcal{L} with respect to the orbital-rotation parameters U_{pq} introduced in Eq. (2.10), i.e., from $(d\mathcal{L}/dU_{pq})_{\mathbf{U}=\mathbf{1}} = 0$. Explicit expressions for I_{pq} in the context of MP2 and CCSD are available from the literature [238], while Z_{ai} is determined by a system of linear equations as outlined in Section 2.3.4. Since \mathcal{L} is stationary with respect to all parameters involved, the (2n+1) and (2n+2) rules of derivative theory [112] can be fully exploited for its differentiation. The resulting expression reads

$$\frac{d^{3}E}{d\chi_{1}d\chi_{2}d\chi_{3}} = \frac{\partial^{3}\mathcal{L}}{\partial\chi_{1}\partial\chi_{2}\partial\chi_{3}} = \sum_{pq} D_{pq} \left(\frac{\partial^{3}f_{pq}}{\partial\chi_{1}\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} + \sum_{pqrs} \Gamma_{pqrs} \left(\frac{\partial^{3}\langle pq||rs\rangle}{\partial\chi_{1}\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} \\
+ \sum_{ai} Z_{ai} \left(\frac{\partial^{3}f_{ai}}{\partial\chi_{1}\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} + \sum_{pq} I_{pq} \left(\frac{\partial^{3}S_{pq}}{\partial\chi_{1}\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} \\
+ P_{123}^{3} \left[\sum_{pq} \frac{\partial D_{pq}}{\partial\chi_{1}} \left(\frac{\partial^{2}f_{pq}}{\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} + \sum_{pqrs} \frac{\partial \Gamma_{pqrs}}{\partial\chi_{1}} \left(\frac{\partial^{2}\langle pq||rs\rangle}{\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} \\
+ \sum_{ai} \frac{\partial Z_{ai}}{\partial\chi_{1}} \left(\frac{\partial^{2}f_{ai}}{\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} + \sum_{pq} \frac{\partial I_{pq}}{\partial\chi_{1}} \left(\frac{\partial^{2}S_{pq}}{\partial\chi_{2}\partial\chi_{3}}\right)^{(1)} \\
+ P_{123}^{3} \left[\sum_{pq} \left(\frac{\partial^{2}D_{pq}}{\partial\chi_{1}\partial\chi_{2}}\right)^{(1,1)} \frac{\partial f_{pq}}{\partial\chi_{3}} + \sum_{pqrs} \left(\frac{\partial^{2}\Gamma_{pqrs}}{\partial\chi_{1}\partial\chi_{2}}\right)^{(1,1)} \frac{\partial \langle pq||rs\rangle}{\partial\chi_{3}} \right] \\
+ \sum_{pqrs} \left(\frac{\partial^{3}\Gamma_{pqrs}}{\partial\chi_{1}\partial\chi_{2}\partial\chi_{3}}\right)^{(1,1)} \langle pq||rs\rangle ,$$
(5.17)

where χ_1, χ_2 , and χ_3 represent arbitrary perturbations and P_{123}^3 is the cyclic permutation operator. The explicit expressions for the derivatives of D_{pq} and Γ_{pqrs} depend on the underlying wave function. They can be obtained by straightforward differentiation of the unperturbed density matrices while bearing in mind that only first-order t and λ amplitudes are to be considered as indicated by the superscript (1, 1). In CC theory, the evaluation of the latter quantities, i.e., $dt/d\chi$ and $d\lambda/d\chi$ requires to solve the perturbed CC and Λ equations. Details on these systems of linear equations are available from the literature [239, 240]. For MP2, no equations need to be solved to obtain $dt/d\chi$ and $d\lambda/d\chi$. However, the determination of $dZ_{ai}/d\chi$ always involves the solution of an additional system of linear equations, which is derived by taking the derivative of Eq. (2.76). In contrast, $dI_{pq}/d\chi$ can be directly constructed from the derivatives of D_{pq} and Γ_{pqrs} . For MP2, further simplifications are possible as the two-particle density matrix does not contain any products of t and λ (cf. Eq. (5.15)). Hence, all terms in Eq. (5.17) that involve second or third derivatives of Γ_{pqrs} vanish.

Fock-matrix derivatives and two-electron integral derivatives of second and third order have been labeled by the superscript (1) in Eq. (5.17), which denotes that only first-order CPHF coefficients contribute to the respective quantity. The first derivative of the Fock matrix has been presented in Section 5.1.1, whereas the higher derivatives of f_{pq} are conveniently split up into an one-electron part and a two-electron part. This yields

$$\left(\frac{\partial^2 f_{pq}}{\partial \chi_1 \partial \chi_2}\right)^{(1)} = \left(\frac{\partial^2 h_{pq}}{\partial \chi_1 \partial \chi_2}\right)^{(1)} + \sum_{jrs} \delta_{rj} \delta_{sj} \left(\frac{\partial^2 \langle pr||qs\rangle}{\partial \chi_1 \partial \chi_2}\right)^{(1)}, \tag{5.18}$$

$$\left(\frac{\partial^3 f_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3}\right)^{(1)} = \left(\frac{\partial^3 h_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3}\right)^{(1)} + \sum_{jrs} \delta_{rj} \delta_{sj} \left(\frac{\partial^3 \langle pr||qs\rangle}{\partial \chi_1 \partial \chi_2 \partial \chi_3}\right)^{(1)} . \tag{5.19}$$

The required derivatives of the one-electron Hamiltonian are given as

$$\left(\frac{\partial^2 h_{pq}}{\partial \chi_1 \partial \chi_2}\right)^{(1)} = h_{pq}^{\chi_1 \chi_2} + P_{12} \left[\sum_r \left(U_{rq}^{\chi_1} h_{pr}^{\chi_2} + U_{rp}^{\chi_1} h_{rq}^{\chi_2} \right) + \sum_{rs} U_{rp}^{\chi_1} U_{sq}^{\chi_2} h_{rs} \right],$$
(5.20)

$$\left(\frac{\partial^3 h_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3}\right)^{(1)} = h_{pq}^{\chi_1 \chi_2 \chi_3} + P_{123}^3 \sum_r \left(U_{rq}^{\chi_1} h_{pr}^{\chi_2 \chi_3} + U_{rp}^{\chi_1} h_{rq}^{\chi_2 \chi_3} \right) + P_{123}^6 \sum_{rs} U_{rp}^{\chi_1} U_{sq}^{\chi_2} h_{rs}^{\chi_3} \tag{5.21}$$

with P_{123}^6 as the full permutation operator and P_{12} defined in analogy to P_{123}^3 . The derivatives of the two-electron integrals become

$$\frac{\partial \langle pq||rs\rangle}{\partial \chi} = \langle pq||rs\rangle^{\chi} + \sum_{t} \left(U_{tp}^{\chi} \langle tq||rs\rangle + U_{tq}^{\chi} \langle pt||rs\rangle + U_{tr}^{\chi} \langle pq||ts\rangle + U_{ts}^{\chi} \langle pq||rt\rangle \right) , \qquad (5.22)$$

$$\left(\frac{\partial^{-} \langle pq||rs \rangle}{\partial \chi_{1} \partial \chi_{2}}\right)^{\Gamma} = \langle pq||rs \rangle^{\chi_{1}\chi_{2}}
+ P_{12} \sum_{t} \left(U_{tp}^{\chi_{1}} \langle tq||rs \rangle^{\chi_{2}} + U_{tq}^{\chi_{1}} \langle pt||rs \rangle^{\chi_{2}} + U_{tr}^{\chi_{1}} \langle pq||ts \rangle^{\chi_{2}} + U_{ts}^{\chi_{1}} \langle pq||rt \rangle^{\chi_{2}} \right)
+ P_{12} \sum_{tu} \left(U_{tp}^{\chi_{1}} U_{uq}^{\chi_{2}} \langle tu||rs \rangle + U_{tp}^{\chi_{1}} U_{ur}^{\chi_{2}} \langle tq||us \rangle + U_{tp}^{\chi_{1}} U_{us}^{\chi_{2}} \langle tq||ru \rangle
+ U_{tq}^{\chi_{1}} U_{ur}^{\chi_{2}} \langle pt||us \rangle + U_{tq}^{\chi_{1}} U_{us}^{\chi_{2}} \langle pt||ru \rangle + U_{tr}^{\chi_{1}} U_{us}^{\chi_{2}} \langle pq||tu \rangle \right),$$
(5.23)

$$\begin{pmatrix} \frac{\partial^{3} \langle pq||rs \rangle}{\partial \chi_{1} \partial \chi_{2} \partial \chi_{3}} \end{pmatrix}^{(1)} = \langle pq||rs \rangle^{\chi_{1}\chi_{2}\chi_{3}} \\ + P_{123}^{3} \sum_{t} \left(U_{tp}^{\chi_{1}} \langle tq||rs \rangle^{\chi_{2}\chi_{3}} + U_{tq}^{\chi_{1}} \langle pt||rs \rangle^{\chi_{2}\chi_{3}} + U_{tr}^{\chi_{1}} \langle pq||ts \rangle^{\chi_{2}\chi_{3}} + U_{ts}^{\chi_{1}} \langle pq||rt \rangle^{\chi_{2}\chi_{3}} \right) \\ + P_{123}^{6} \sum_{tu} \left(U_{tp}^{\chi_{1}} U_{uq}^{\chi_{2}} \langle tu||rs \rangle^{\chi_{3}} + U_{tp}^{\chi_{1}} U_{ur}^{\chi_{2}} \langle tq||us \rangle^{\chi_{3}} + U_{tp}^{\chi_{1}} U_{us}^{\chi_{2}} \langle tq||ru \rangle^{\chi_{3}} \\ + U_{tq}^{\chi_{1}} U_{ur}^{\chi_{2}} \langle pt||us \rangle^{\chi_{3}} + U_{tq}^{\chi_{1}} U_{us}^{\chi_{2}} \langle pt||ru \rangle^{\chi_{3}} + U_{tr}^{\chi_{1}} U_{us}^{\chi_{2}} \langle pq||tu \rangle^{\chi_{3}} \right) \\ + P_{123}^{6} \sum_{tuv} \left(U_{tp}^{\chi_{1}} U_{uq}^{\chi_{2}} U_{vr}^{\chi_{3}} \langle tu||vs \rangle + U_{tp}^{\chi_{1}} U_{uq}^{\chi_{2}} U_{vs}^{\chi_{3}} \langle tu||rv \rangle \\ + U_{tp}^{\chi_{1}} U_{ur}^{\chi_{2}} U_{vs}^{\chi_{3}} \langle tq||uv \rangle + U_{tq}^{\chi_{1}} U_{ur}^{\chi_{2}} U_{vs}^{\chi_{3}} \langle pt||uv \rangle \right) ,$$

$$(5.24)$$

while the second and third derivatives of the overlap matrices appearing in Eq. (5.17) are defined as

$$\left(\frac{\partial^2 S_{pq}}{\partial \chi_1 \partial \chi_2}\right)^{(1)} = S_{pq}^{\chi_1 \chi_2} + P_{12} \left[\sum_r \left(U_{rq}^{\chi_1} S_{pr}^{\chi_2} + U_{rp}^{\chi_1} S_{rq}^{\chi_2} \right) + \sum_r U_{rp}^{\chi_1} U_{rq}^{\chi_2} \right],$$
(5.25)

$$\left(\frac{\partial^3 S_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3}\right)^{(1)} = S_{pq}^{\chi_1 \chi_2 \chi_3} + P_{123}^3 \sum_r \left(U_{rq}^{\chi_1} S_{pr}^{\chi_2 \chi_3} + U_{rp}^{\chi_1} S_{rq}^{\chi_2 \chi_3}\right) + P_{123}^6 \sum_{rs} U_{rp}^{\chi_1} U_{sq}^{\chi_2} S_{rs}^{\chi_3} .$$
(5.26)

All equations presented so far are valid for generic perturbations χ_1 , χ_2 , χ_3 . If χ_1 and χ_2 represent nuclear displacements x and y and χ_3 is an electric-field component ε as is the case for the dipole Hessian, some expressions can be further simplified as discussed in Section 5.1.1. The partial derivatives $\langle pq || rs \rangle^{\varepsilon}$ and S_{pq}^{ε} vanish as neither the two-electron integrals nor the overlap integrals depend on the electric field.

5.2. Implementation

Based on the expressions presented in Section 5.1, analytic dipole Hessians at the HF-SCF, MP2, and CCSD levels of theory have been implemented into the quantum-chemical program package CFOUR [124]. The implementation currently allows for the use of RHF reference wave functions only and in addition, spatial symmetry is not exploited so far, i.e., all calculations have to be carried out in C_1 symmetry. The implementation builds upon the infrastructure of CFOUR for orbital-unrelaxed first hyperpolarizabilities $(\beta_{ijk} = d^3 E/d\varepsilon_i d\varepsilon_j d\varepsilon_k)$ and polarizability gradients $(d\alpha_{ij}/dx = d^3 E/dx d\varepsilon_i d\varepsilon_j)$ at the CCSD level of theory, which has been described in the literature [33]. All newly implemented features have been validated by means of numerical differentiation.

The principal flow of a calculation is outlined in Figure 5.1. With the exception of the integrals $h^{xy\varepsilon}_{\mu\nu}$, all quantities necessary for the computation of the dipole Hessian matrix are also required for the evaluation of the second energy derivatives $d^2E/dxdy$ and $d^2E/dxd\varepsilon$. Hence, they are available from the CFOUR code for second derivatives. The integrals $h_{\mu\nu}^{xy\varepsilon}$, however, have been made available via interfacing the integral-derivative library GEN1INT [241] to CFOUR.

5.2.1. Dipole Hessian Matrix at the Hartree-Fock Level of Theory

For the computation of the dipole Hessian at the HF-SCF level of theory, the course of the calculation is at first similar to that of a second-derivative calculation, i.e., the firstorder integral derivatives are evaluated in the AO basis by module vdint and subsequently transformed to the MO basis by module cphf. The two-electron contributions are processed in a mean-field manner as $f_{pq}^{(x)}$ and $f_{pq}^{(\varepsilon)}$ with no need to transform two-electron integral derivatives to the MO basis. Next, cphf solves the CPHF equations for all electric and geometric perturbations and the resulting CPHF coefficients U_{pq}^{ε} and U_{pq}^{x} are stored to disk. In addition, the total derivatives of the Fock matrix $(df_{pq}/d\varepsilon)$ and df_{pq}/dx are constructed as convenient intermediates and stored to disk as well. Once U_{pq}^{χ} and $df_{pq}/d\chi$ are available for all perturbations, the first set of contributions to $d^3E/dxdyd\varepsilon$ is computed. This comprises all terms that appear in lines 5 to 8 of Eq. (5.2), i.e., all terms that involve only $df_{pq}/d\chi$ or S_{pq}^{χ} as integral derivatives. The calculation is carried out in routine cphf/scfelanh.f and is based directly on Eq. (5.2) with the only further simplification resulting from the Fock matrix being diagonal $(f_{pq} = \delta_{pq} f_{pp})$. The use of spatial symmetry has been implemented for all expressions calculated by this routine.

The calculation of the remaining contributions to $d^3E/dxdyd\varepsilon$ is preferably carried out in the AO basis as the transformation of the higher-order integral derivatives to the MO basis can be circumvented in this way. Hence, the perturbed SCF density matrices $dD_{pq}^{\text{SCF}}/d\chi$ and intermediates $dI_{pq}^{\text{SCF}}/d\chi$ are set up¹ and transformed to the AO basis according to²

$$\frac{dD'_{\mu\nu}}{dx} = \sum_{pq} C_{\mu p} \frac{dD_{pq}^{\text{SCF}}}{dx} C_{\nu q} = \sum_{pq} C_{\mu p} C_{\nu q} \begin{cases} -S_{pq}^{x} & \text{if } p, q \in \text{occ} \\ U_{qp}^{x} & \text{if } p \in \text{occ}, q \in \text{vir} \\ U_{pq}^{x} & \text{if } q \in \text{occ}, p \in \text{vir} \\ 0 & \text{else} \end{cases}$$

$$(5.27)$$

¹Only $dI_{\mu\nu}^{\rm SCF}/d\varepsilon$ but not $dI_{\mu\nu}^{\rm SCF}/dx$ is required for the calculation of $d^3E/dxdyd\varepsilon$. ²The primed quantities dD'_{pq}/dx , $dD'_{pq}/d\varepsilon$, and $dI'_{pq}/d\varepsilon$ are identical to $dD_{pq}^{\rm SCF}/dx$, $dD_{pq}^{\rm SCF}/d\varepsilon$, and $dI_{pq}^{\rm SCF}/d\varepsilon$ for a HF-SCF calculation. They are, however, introduced here for the sake of consistency.



Figure 5.1.: Flowchart for the calculation of the dipole Hessian at the HF-SCF, MP2, and CCSD levels of theory. Dashed lines refer to steps that are required only for correlated wave functions.

$$\frac{dD'_{\mu\nu}}{d\varepsilon} = \sum_{pq} C_{\mu p} \frac{dD_{pq}^{\rm SCF}}{d\varepsilon} C_{\nu q} = \sum_{pq} C_{\mu p} C_{\nu q} \begin{cases} U_{qp}^{\varepsilon} & \text{if } p \in \operatorname{occ}, q \in \operatorname{vir} \\ U_{pq}^{\varepsilon} & \text{if } q \in \operatorname{occ}, p \in \operatorname{vir} \\ 0 & \text{else} \end{cases}$$
(5.28)

$$\frac{dI'_{\mu\nu}}{d\varepsilon} = \sum_{pq} C_{\mu p} \frac{dI^{\rm SCF}_{pq}}{d\varepsilon} C_{\nu q} = \sum_{pq} C_{\mu p} C_{\nu q} \begin{cases} df_{pq}/d\varepsilon & \text{if } p, q \in \text{occ} \\ U^{\varepsilon}_{qp} f_{pp} & \text{if } p \in \text{occ}, q \in \text{vir} \\ U^{\varepsilon}_{pq} f_{qq} & \text{if } q \in \text{occ}, p \in \text{vir} \\ 0 & \text{else} \end{cases}$$
(5.29)

The calculation in the MO basis is done in routines cphf/mkpertd.f, cphf/mkpertd2.f, and cphf/mkpertw.f, which were already available prior to the present implementation. The subsequent transformation of the perturbed densities and intermediates to the AO basis is carried out in module vdint. In this module, the calculation proceeds as follows: The driver for oneelectron integrals vdint/onedrv.f invokes first the evaluation of the integrals $h^{y\varepsilon}_{\mu\nu}$, $h^{xy}_{\mu\nu}$, and $S^{xy}_{\mu\nu}$, which are then contracted on the fly with the perturbed densities and intermediates as shown in Figure 5.1. The latter task is carried out by the routines vdint/elaavrx.f (x=1-4), which were created either by adapting routines for the calculation of the polarizability gradient $(dD'_{\mu\nu}/d\varepsilon_i \cdot h^{x\varepsilon_j}_{\mu\nu} \rightarrow dD'_{\mu\nu}/dx \cdot h^{y\varepsilon}_{\mu\nu})$ or starting from routines for the calculation of $d^2E/dxdy$ (all remaining terms) and replacing the unperturbed densities and intermediates by the perturbed ones. vdint/onedrv.f also drives the computation of the contribution $D_{\mu\nu} \cdot h^{xy\varepsilon}_{\mu\nu}$. The necessary integrals are evaluated by the routine contr_cgto_carmom.f from the library GEN1INT [241], which is called in vdint/inig1i.f. Since GEN1INT has been originally developed for use with the DALTON suite of programs [242] and since the basis functions are ordered differently in DALTON and CFOUR, the output of contr_cgto_carmom.f needs to be reordered before it is contracted with $D_{\mu\nu}$. This has been implemented for basis functions with angular quantum number up to $\ell = 6$ (i-functions).

The evaluation of all terms involving two-electron integrals is driven by routines vdint/ twoexp.f and vdint/twoint.f. The two-electron contribution to $f_{\mu\nu}^{(xy)}$ is formed and contracted with a mean-field two-particle density in routines vdint/intexpe.f and vdint/ deroutx.f, which were created from routines for the calculation of $d^2E/dxdy$ by replacing unperturbed densities by perturbed ones. The evaluation of $dD_{\mu\nu}^{\rm SCF}/d\varepsilon \cdot dD_{\sigma\rho}^{\rm SCF}/dx \cdot \langle \mu\sigma | \nu\rho \rangle^y$ is carried out in vdint/dfock.f and vdint/twoelanh.f, where the first routine performs the contraction of $dD_{\sigma\rho}^{\rm SCF}/dx$ and $\langle \mu\sigma | \nu\rho \rangle^y$ and the second routine that of the resulting intermediate with $dD_{\mu\nu}^{\rm SCF}/d\varepsilon$.

5.2.2. Dipole Hessian Matrix at the MP2 and CCSD Levels of Theory

As shown in Figure 5.1, all steps required for the dipole Hessian matrix at the HF-SCF level of theory have to be passed as well when $d^3E/dxdyd\varepsilon$ is calculated at the MP2 or CCSD level. The course of the calculation is similar to that of a second-derivative calculation for correlated methods. After the CC and Λ equations have been solved (or in the case of MP2: after t_{ij}^{ab} has been calculated according to Eq. (5.9)), the one-particle and two-particle density matrices D_{pq} and Γ_{pqrs} as well as the one-particle intermediate I_{pq} are formed and stored to disk in module dens. In addition, the Z-vector equations (Eq. (2.76)) are solved and Z_{ai} is also stored to disk.⁴ Thereafter, the modules vdint and cphf are invoked as discussed in Section 5.2.1.

 $^{{}^{3}}f^{(xy)}_{\mu\nu}$ is never constructed explicitly. Instead, the one-particle part and the two-particle part are computed separately and directly contracted with the density matrices.

⁴The following modules treat Z_{ai} as D_{ai} . The same applies to $dZ_{ai}/d\varepsilon$ and dZ_{ai}/dx .

Routine	Term
d3gamdrv.f	$\left(rac{\partial^3\Gamma_{pqrs}}{\partial x\partial y\partial arepsilon} ight)^{(1,1)}\!\langle pq rs angle$
d2densxy.f	$\left(rac{\partial^2 D_{pq}}{\partial x \partial y} ight)^{(1,1)} rac{\partial f_{pq}}{\partial arepsilon}$
d2densyz.f	$\left(\frac{\partial^2 D_{pq}}{\partial x \partial \varepsilon}\right)^{(1,1)} \frac{\partial f_{pq}}{\partial y} + \left(\frac{\partial^2 D_{pq}}{\partial y \partial \varepsilon}\right)^{(1,1)} \frac{\partial f_{pq}}{\partial x}$
d2densyz.f	$\left(\frac{\partial^2 \Gamma_{pqrs}}{\partial x \partial y}\right)^{(1,1)} \frac{\partial \langle pq rs \rangle}{\partial \varepsilon} + \left(\frac{\partial^2 \Gamma_{pqrs}}{\partial x \partial \varepsilon}\right)^{(1,1)} \frac{\partial \langle pq rs \rangle}{\partial y} + \left(\frac{\partial^2 \Gamma_{pqrs}}{\partial y \partial \varepsilon}\right)^{(1,1)} \frac{\partial \langle pq rs \rangle}{\partial x}$
densd3i.f	$D_{pq} \left(\frac{\partial^3 f_{pq}}{\partial x \partial y \partial \varepsilon}\right)^{(1)} + \Gamma_{pqrs} \left(\frac{\partial^3 \langle pq rs \rangle}{\partial x \partial y \partial \varepsilon}\right)^{(1)}$
ddensd2i.f	$\frac{\partial D_{pq}}{\partial x} \left(\frac{\partial^2 f_{pq}}{\partial y \partial \varepsilon}\right)^{(1)} + \frac{\partial \Gamma_{pqrs}}{\partial x} \left(\frac{\partial^2 \langle pq rs \rangle}{\partial y \partial \varepsilon}\right)^{(1)}$
d1d2f.f	$\frac{\partial D_{pq}}{\partial y} \left(\frac{\partial^2 f_{pq}}{\partial x \partial \varepsilon}\right)^{(1)} + \frac{\partial \Gamma_{pqrs}}{\partial y} \left(\frac{\partial^2 \langle pq rs \rangle}{\partial x \partial \varepsilon}\right)^{(1)}$
d1d2f2.f	$\frac{\partial D_{pq}}{\partial \varepsilon} \left(\frac{\partial^2 f_{pq}}{\partial x \partial y} \right)^{(1)} + \frac{\partial \Gamma_{pqrs}}{\partial \varepsilon} \left(\frac{\partial^2 \langle pq rs \rangle}{\partial x \partial y} \right)^{(1)}$
did2s.f	$rac{\partial I_{pq}}{\partial x} \left(rac{\partial^2 S_{pq}}{\partial y \partial \varepsilon} ight)^{(1)}$
did2s2.f	$\frac{\partial I_{pq}}{\partial y} \left(\frac{\partial^2 S_{pq}}{\partial x \partial \varepsilon}\right)^{(1)} + \frac{\partial I_{pq}}{\partial \varepsilon} \left(\frac{\partial^2 S_{pq}}{\partial x \partial y}\right)^{(1)}$
iind3s.f	$I_{pq} \left(\frac{\partial^3 S_{pq}}{\partial x \partial y \partial \varepsilon}\right)^{(1)}$

Table 5.1.: Implementation of Eq. (5.17) into the module sdcc of the CFOUR program system.^{*a*}

^aContributions arising from second-order or third-order integral derivatives are not considered in sdcc (compare text). x refers to the perturbation, for which the perturbed wave function has been calculated directly before and $y \leq x$.

Next, the module sdcc is called to evaluate the perturbed amplitudes $dt/d\varepsilon$ and $d\lambda/d\varepsilon$, which are then used to form the derivatives of the density matrices $dD_{pq}/d\varepsilon$ and $d\Gamma_{pqrs}/d\varepsilon$. In addition, sdcc solves the perturbed Z-vector equations for $dZ_{ai}/d\varepsilon$ and sets up the perturbed intermediate $dI_{pq}/d\varepsilon$. $dt/d\varepsilon$ and $d\lambda/d\varepsilon$ as well as $dZ_{ai}/d\varepsilon$ and $dI_{pq}/d\varepsilon$ are subsequently stored to disk by routines sdcc/writdt.f and sdcc/writd1.f. For later use in module vdint, $dD_{pq}/d\varepsilon$, $d\Gamma_{pqrs}/d\varepsilon$, and $dI_{pq}/d\varepsilon$ are expanded by CPHF contributions to the corresponding primed quantities according to

$$\frac{dD'_{pq}}{d\varepsilon} = \frac{dD_{pq}}{d\varepsilon} + \frac{dD^{\rm SCF}_{pq}}{d\varepsilon} + \sum_{r} \left(U^{\varepsilon}_{rp} D_{rq} + U^{\varepsilon}_{rq} D_{pr} \right) \,, \tag{5.30}$$

$$\frac{dI'_{pq}}{d\varepsilon} = \frac{dI_{pq}}{d\varepsilon} + \frac{dI^{\rm SCF}_{pq}}{d\varepsilon} + \sum_{r} \left(U^{\varepsilon}_{rp} I_{rq} + U^{\varepsilon}_{rq} I_{pr} \right) \,, \tag{5.31}$$

$$\frac{d\Gamma'_{pqrs}}{d\varepsilon} = \frac{d\Gamma_{pqrs}}{d\varepsilon} + \sum_{t} \left(U_{tp}^{\varepsilon} \Gamma_{tqrs} + U_{tq}^{\varepsilon} \Gamma_{ptrs} + U_{tr}^{\varepsilon} \Gamma_{pqts} + U_{ts}^{\varepsilon} \Gamma_{pqrt} \right) \,. \tag{5.32}$$

 $d\Gamma_{pqrs}/d\varepsilon$ is then reordered and transformed to the AO basis. This is done by modules anti and bcktrn and requires no modifications to the code as the same steps are also performed with $d\Gamma_{pqrs}/dx$ for correlated second derivatives. Next, module vdint evaluates the integrals $\langle \mu\sigma | \nu\rho \rangle^{xy}$, which are then contracted on the fly with $d\Gamma_{pqrs}/d\varepsilon$ in routine vdint/deroutx.f. Again, the course of the calculation is similar to that of a second-derivative calculation with $d\Gamma_{\mu\nu\sigma\rho}/dx$ and $\langle \mu\sigma | \nu\rho \rangle^y$ replaced by $d\Gamma_{\mu\nu\sigma\rho}/d\varepsilon$ and $\langle \mu\sigma | \nu\rho \rangle^{xy}$, respectively. However, as CFOUR cannot handle more than one perturbed two-particle density matrix at the same time, the components of the electric field need to be treated in a sequential fashion as shown in Figure 5.1.

Once all electric-field components have been treated, the derivatives of the wave function with respect to nuclear displacements are computed. This task is also carried out in a sequential fashion by module sdcc, but vdint needs to be invoked for each perturbation before sdcc runs as the derivatives of the two-electron integrals $d\langle pq|rs\rangle/dx$ are required to calculate dt/dx and $d\lambda/dx$. From the latter quantities, the derivatives of D_{pq} , Γ_{pqrs} , I_{pq} , and Z_{ai} are constructed. Thereafter, all contributions to $d^3E/dxdyd\varepsilon$ from Eq. (5.17), which do not involve second-order or third-order integral derivatives, are calculated. This is driven by the routines sdcc/tdcc.f and sdcc/tdcc2.f, the details are summarized in Table 5.1. For all contributions, the computation is carried out in a "triangular" fashion, i.e., after the perturbed densities and intermediates for a certain geometric perturbation x have been calculated, contributions to all elements of $d^3E/dxdyd\varepsilon$ with $y \leq x$ are evaluated. The code is directly based on the expressions presented in Eqs. (5.17) to (5.26) with one minor modification: The CPHF contributions to the second and third derivatives of the two-electron integrals in Eqs. (5.23) and (5.24) are computed by contracting the CPHF coefficients with the MO coefficients followed by the transformation of the two-electron integrals to the MO basis using these perturbed coefficients.

The next step then consists in the formation of dD'_{pq}/dx , which is defined similar to $dD'_{pq}/d\varepsilon$ (cf. Eq. (5.30)). All remaining contributions are evaluated in the AO basis by module vdint as discussed in Section 5.2.1 for the HF-SCF level of theory. No modifications to the implementation presented there are required for the adaptation to correlated methods, it is only necessary to pass into vdint the correlated density matrices and intermediates.

5.3. Pilot Application: Analytical vs. Numerical Differentiation

In this section, numerical and analytical differentiation techniques are compared with respect to their accuracy. In particular, it is examined how repeated numerical differentiation impairs the accuracy of a target quantity. When calculated analytically, the accuracy of a derivative quantity is, in principle, equal to that of the undifferentiated parent quantity. A strict upper bound to the accuracy is given by the intrinsic machine precision of the computer system, on which a calculation is carried out. If the data are processed in double-precision floating-point format, 16 significant digits should be within reach. However, the accuracy achievable in actual computations is always lower than that due to rounding errors and numerical instabilities. With respect to quantum chemistry, the thresholds and convergence criteria, which are applied during the course of a calculation, play a pivotal role. This starts with the fact that all integrals are computed with finite precision and that all integrals, whose absolute values do not exceed a certain threshold, are neglected. Furthermore, all equations involved in a quantum-chemical calculation such as, for example, the HF-SCF or CC equations are solved only with finite precision. The impact of the various thresholds and convergence criteria on the results is not uniform, but rather requires a more detailed discussion. For the present investigation, however, it is only necessary to have at hand an estimate for the overall uncertainty in the analytically evaluated quantities.

In numerical differentiation schemes, two errors are present [111]. The first is the discretization error resulting from approximating derivatives by finite differences. When using doublesided numerical differentiation, i.e., when evaluating the derivatives of a function f according to^5

$$\left(\frac{df}{dx}\right)_{x=x_0} \approx \frac{f(x_0+h) - f(x_0-h)}{2h} ,$$
 (5.33)

$$\left(\frac{d^2f}{dx^2}\right)_{x=x_0} \approx \frac{f(x_0+h) - 2f(x_0) + f(x_0-h)}{h^2} , \qquad (5.34)$$

$$\left(\frac{d^3f}{dx^3}\right)_{x=0} \approx \frac{f(x_0+2h) - 2f(x_0+h) + 2f(x_0-h) - f(x_0-2h)}{2h^3} , \qquad (5.35)$$

$$\left(\frac{d^4f}{dx^4}\right)_{x=x_0} \approx \frac{f(x_0+2h) - 4f(x_0+h) + 6f(x_0) - 4f(x_0-h) + f(x_0-2h)}{h^4} , \qquad (5.36)$$

the discretization error is always of order h^2 with h as step size regardless of how many differentiation steps are carried out. It is, however, possible to reduce the discretization error by taking more points into consideration. The second error stems from the uncertainty η in the undifferentiated parent quantity and is thus largely governed by the applied convergence criteria. In contrast to the discretization error, this error is different for numerical first, second, etc. derivatives, but it can be estimated by means of error propagation. This yields⁶ that the error is proportional to η/h^n for the *n*-th numerical derivative. When choosing the step size h, one hence has to balance two effects: Minimizing the discretization error requires a small step size while minimizing the second error demands a large step size. However, it is possible to determine a critical value for h, where both errors make an impact of the same order of magnitude. This is the case for $h \approx \frac{n+2}{\eta}$.

To validate these predictions, the geometrical derivatives of the dipole moment $(d^n \mu_z/dR^n)$ with $n = 1, \ldots, 5$ have been studied for hydrogen fluoride and hydrogen chloride at the CCSD level of theory using the cc-pCVDZ basis set [130]. All calculations have been carried out at the corresponding equilibrium bond length $(R_{eq}(\text{HF}) = 0.918485821936 \text{ Å} \text{ and } R_{eq}(\text{HC}) =$ 1.286686571469 Å). The derivatives $d^n \mu_z/dR^n$ have been calculated three times, i.e., starting from the analytically evaluated dipole moment μ_z , dipole gradient $d\mu_z/dR$, or dipole Hessian $d^2\mu_z/dR^2$. In addition, the displacement ΔR used for the numerical differentiation procedure has been varied. In all analytic-derivative calculations, integrals with a value of less than 10^{-13} a.u. were neglected. The HF-SCF equations were considered converged when the maximum absolute change in the density-matrix elements fell below a value of 10^{-12} a.u. The CC and Λ equations as well as the equations for the first derivatives of the CC and Λ amplitudes were considered converged when the maximum absolute change in the amplitudes fell below a value of 10^{-12} a.u. For the present example, these criteria allow for an accuracy of 12 significant digits in the values for the dipole moment and 11 significant digits in the values for the dipole gradient and the dipole Hessian.

All results are summarized in Table 5.2. In the case of $d\mu_z/dR$ and $d^2\mu_z/dR^2$, a comparison to the fully analytic values is possible, whereas for the higher derivatives, one can only compare results that involve a different number of numerical differentiation steps. For all entries in Table 5.2, only significant digits are reported. The number of the latter has been estimated from the uncertainty in the analytically evaluated values for μ_z , $d\mu_z/dR$, and $d^2\mu_z/dR^2$ as discussed above. This already illustrates the main drawbacks of numerical differentiation: The number of significant digits inevitably shrinks when seeking higher derivatives or using smaller step sizes. Moreover, it is seen that the use of too large step sizes, for example 10^{-2} Å for numerical first derivatives, leads to results that are significantly contaminated by

⁵These formulas hold provided that f is often enough continuously differentiable in the intervals $x_0 - h < x < x_0 + h$ or $x_0 - 2h < x < x_0 + 2h$, respectively.

⁶Assuming that the error stems exclusively from the evaluation of the function f, i.e., if $x, x + h, \ldots$ can be exactly represented.

Table 5.2.: Geometrical derivatives of the dipole moment for hydrogen fluoride and hydrogen chloride at the CCSD/cc-pCVDZ level of theory in atomic units as obtained via numerical differentiation, bond lengths optimized at the same level of theory $(R_{eq}(\text{HF}) = 0.918485821936 \text{ Å} \text{ and } R_{eq}(\text{HCl}) = 1.286686571469 \text{ Å}).$

Target quantity		$\left(\frac{d\mu_z}{dR}\right)_{R=R_{eq}}$	$\left(\frac{d^2\mu_z}{dR^2}\right)_{R=R_{eq}}$	$\left(\frac{d^3\mu_z}{dR^3}\right)_{R=R_{eq}}$	$\left(\frac{d^4\mu_z}{dR^4}\right)_{R=R_{eq}}$	$\left(\frac{d^5\mu_z}{dR^5}\right)_{R=R_{eq}}$
a.e.q. ^a	$\Delta R/{ m \AA}$		Hyd	rogen fluoride		
$\mu_z \ \mu_z \ \mu_z \ \mu_z \ \mu_z$	$ \begin{array}{r} 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} \\ \end{array} $	$\begin{array}{c} -0.3173676440^{b} \\ -0.317412644 \\ -0.31741309 \\ -0.3174131 \end{array}$	0.17871386 0.178712 0.1787 0.18	0.763567 0.764 	0.0750 	
$\frac{d\mu_z/dR}{d\mu_z/dR}$ $\frac{d\mu_z/dR}{d\mu_z/dR}$ $\frac{d\mu_z/dR}{d\mu_z/dR}$	$ \begin{array}{r} 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} \end{array} $	 	$\begin{array}{c} 0.1787160589^c \\ 0.178711645 \\ 0.17871157 \\ 0.1787139 \end{array}$	0.76369291 0.763745 0.7656 0.77	0.0748442 0.0714 	2.112
$d^2 \mu_z/dR^2 \ d^2 \mu_z/dR^2 \ d^2 \mu_z/dR^2 \ d^2 \mu_z/dR^2 \ d^2 \mu_z/dR^2$	$ \begin{array}{r} 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} \end{array} $			$\begin{array}{c} 0.7636297628\\ 0.763754290\\ 0.76375554\\ 0.7637555\end{array}$	0.075009981 0.0750835 0.07509 0.075	2.11131 2.11 — —
Fully analytic value -0.3		-0.317413033924	0.178711554063	_	—	—
a.e.q. ^a	$\Delta R/{ m \AA}$		Hyd	rogen chloride		
$\mu_z \ \mu_z \ \mu_z \ \mu_z \ \mu_z$	$ \begin{array}{r} 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} \\ \end{array} $	-0.1507211853 ^d -0.150732066 -0.15073218 -0.1507322	0.11561607 0.115618 0.1156 0.12	0.184709 0.185 —	-0.0275 	
$\frac{d\mu_z/dR}{d\mu_z/dR}$ $\frac{d\mu_z/dR}{d\mu_z/dR}$ $\frac{d\mu_z/dR}{d\mu_z/dR}$	$ 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} $		$\begin{array}{c} 0.1156151970^e \\ 0.115616751 \\ 0.11561680 \\ 0.1156147 \end{array}$	0.18467527 0.184667 0.1892 0.28	-0.0270382 -0.025 	0.5630
$\frac{d^2 \mu_z/dR^2}{d^2 \mu_z/dR^2} \\ \frac{d^2 \mu_z/dR^2}{d^2 \mu_z/dR^2} \\ \frac{d^2 \mu_z/dR^2}{d^2 \mu_z/dR^2}$	$ \begin{array}{r} 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} \end{array} $ tic value	 		0.1846917369 0.184658421 0.18465809 0.1846581	-0.026850362 -0.0267575 -0.02676 -0.027	0.566667 0.563 — —

^aa.e.q. = analytically evaluated quantity.

 b Taking into account the correction from Eq. (5.37) leads to an improved value of -0.3174157536.

 $^c\mathrm{Taking}$ into account the correction from Eq. (5.37) leads to an improved value of 0.1787113294.

^dTaking into account the correction from Eq. (5.37) leads to an improved value of -0.1507328171.

^eTaking into account the correction from Eq. (5.37) leads to an improved value of 0.1156168825.

higher derivatives. It is, however, possible to calculate correction terms such as

$$\frac{f(x_0+h) - f(x_0-h)}{2h} - \left(\frac{df}{dx}\right)_{x=x_0} \approx \frac{h^2}{3} \left(\frac{d^3f}{dx^3}\right)_{x=x_0}$$
(5.37)

for first derivatives. Taking this term into account yields substantially better results as exemplified for some values of $d\mu_z/dR$ and $d^2\mu_z/dR^2$ in Table 5.2. It should be added that a similar study on electrical properties is available from Ref. [243].

From the theoretical considerations presented above, one can deduce that the best results for numerical first derivatives⁷ should be obtained with a step size of $10^{-4} = \sqrt[3]{10^{-12}}$. The

⁷This strictly holds for the derivatives of μ_z only, while the best step size for first derivatives of $d\mu_z/dR$ and

corresponding values for $d\mu_z/dR$ and $d^2\mu_z/dR^2$ in Table 5.2 show that this is indeed the case. When using such a step size, the resulting values agree within 7 digits with their analytical counterparts for the present example. Regarding numerical second derivatives, theoretical arguments recommend a step size of 10^{-3} Å, which should allow for 6 significant digits. Table 5.2 shows that numerical results for $d^2\mu_z/dR^2$ computed from μ_z agree within 10^{-6} a.u. with the fully analytic value. However, significantly worse performance is observed with respect to the computation of $d^3\mu_z/dR^3$ from $d\mu_z/dR$. For both molecules, the results only agree within 4 digits with those calculated from $d^2\mu_z/dR^2$. This is most likely related to the lower accuracy of $d\mu_z/dR$ as compared to μ_z . For numerical third derivatives, the optimal step size should roughly equal⁸ 10^{-2} Å and allow for 4 significant digits, which is already less than what is commonly desired in quantum chemistry. The comparison of the calculation of $d^3\mu_z/dR^4$ from $d\mu_z/dR$ shows that better results are obtained in the first case. Again, this is most likely due to the different accuracy of the parent quantity.

Somewhat surprisingly, the results obtained for $d^{4}\mu_{z}/dR^{4}$ via four numerical differentiation steps agree very well with those obtained when starting from $d^{2}\mu_{z}/dR^{2}$ in the case of hydrogen fluoride. This should be considered as a coincidence, whereas a more representative performance is probably observed in the case of hydrogen chloride. Values for $d^{5}\mu_{z}/dR^{5}$ are only reported for the sake of completeness. Yet, the analysis of the results for lower derivatives indicates that values for $d^{5}\mu_{z}/dR^{5}$ computed from $d^{2}\mu/dR^{2}$ are at least not completely unreliable. Rather, they provide a qualitatively correct approximation to this quantity.

It should be added as a final remark that an accuracy of 11 or 12 significant digits for the dipole moment and its analytic derivatives is rarely achievable in calculations for systems that are larger than the ones considered here. As a consequence, numerical differentiation may perform considerably worse for such cases than observed in this study.

 $d^2 \mu_z / dR^2$ is $\sqrt[3]{10^{-11}}$.

⁸Actually, a step size of the order of $(\sqrt[5]{10^{-12}})$ would be optimal for third derivatives.

6. Conclusions

Coupled-cluster (CC) theory is one of the most successful approaches in high-accuracy quantum chemistry. An important contribution to its success is made by complementary techniques for the treatment of molecular properties and excitation energies. In this regard, CC analytic-derivative theory and CC response theory represent the two approaches that have been used most often. The present work deals with both of these methodologies. Firstorder and second-order properties as well as excitation energies have been studied starting from the multireference CC method proposed by Mukherjee and coworkers (Mk-MRCC). The performance of Mk-MRCC in the determination of molecular equilibrium structures has been benchmarked. Moreover, a scheme for the calculation of second-order properties and excitation energies within Mk-MRCC theory has been developed. In the single-reference CC framework, an implementation for the analytic evaluation of the dipole Hessian matrix, a third-order quantity relevant to anharmonic effects in infrared spectroscopy, has been presented. A detailed summary of the results together with an outlook on possible future developments is given in the following.

Structure Optimizations Using Mk-MRCC Calculations

A comprehensive benchmark study on equilibrium structures and adiabatic excitation energies at the Mk-MRCCSD level of theory has been presented in Chapter 3. By means of analytic-gradient techniques, the Mk-MRCCSD method has been applied to molecules as large as naphthalene. Hence, the performance of Mk-MRCCSD could be examined for medium-sized molecules of chemical interest, while most previous studies were confined to small model systems of mainly theoretical interest.

Negligible discrepancies have been observed between Mk-MRCCSD calculations for the lowspin components of triplet states and CCSD calculations for the corresponding high-spin components. For open-shell states of molecules that possess a single-reference closed-shell ground state (cf. Chapters 3.2 and 3.3), Mk-MRCCSD results have been compared to those obtained using the equation-of-motion (EOM) CCSD approach. Again, marginal differences have been observed so that Mk-MRCCSD can be considered as a reasonable alternative to EOM-CCSD for the characterization of such states. Calculations on aryne compounds in Chapter 3.4 have confirmed the increasing multireference character of the closed-shell ground state when going from o- to m- and p-benzyne. In the same direction, the agreement between Mk-MRCCSD results and CCSD results deteriorates. Most prominently, p-benzyne is assigned a triplet ground state at the CCSD level of theory, while multireference methods agree on a singlet ground state. The use of CCSD(T) instead of CCSD sometimes leads to a substantial improvement, but in general the impact of the perturbative triples correction is not uniform. These shortcomings make it obvious that single-reference CC methods fail for states with multireference character such as they occur in biradical systems. The same applies to EOM-CC calculations that are based on reference states with multireference character. In contrast, Mk-MRCCSD can provide reliable results for the equilibrium structures of mul-

tireference systems. For such cases, it is clearly superior to the single-reference CCSD scheme. However, it is also clear that Mk-MRCC theory still suffers from a number of problems that prevent it from being used in a routine manner. Noteworthy formal deficiencies include the lack of invariance of the energy with respect to rotations among active orbitals [69, 78, 79] as well as an unfavorable scaling of the computational cost with respect to the size of the reference space [69]. For symmetry reasons, the former problem does not make an impact on the cases covered by the present investigation, however, its importance has been demonstrated in other studies [69, 78, 79]. In particular, the inclusion of selected higher excitations has been shown to mitigate the dependence of the energy on the choice of orbitals [79] and the use of localized orbitals has been recommended in order to improve the results [109]. The latter problem, i.e., the fact that the computational cost is proportional to the size of the reference space, would, for example, become more visible when targeting higher-lying states of the molecules considered in this work as some of these states require the use of a larger reference space. This should be contrasted with internally contracted MRCC methods [60,61] and EOM-based CC methods [44, 45, 125], whose computational cost is nearly independent of the electronic structure of the target state.

Calculations from Chapter 3.4 illustrate that Mk-MRCCSD results often agree very well with results obtained from multireference averaged-quadratic CC (MR-AQCC) calculations. However, the results also show that Mk-MRCCSD is, in general, not superior to MR-AQCC. At best, the use of smaller reference spaces is sometimes possible when using Mk-MRCCSD. This finding is in line with other investigations [34,35], which reached similar conclusions regarding the performance of Mk-MRCCSD in comparison to MR-AQCC and other approaches formulated within the framework of multireference configuration-interaction theory. Higher accuracy than that provided by the Mk-MRCCSD approach can be achieved in the context of Mk-MRCCSDT scheme, where triple excitations are fully considered, has been shown to yield significantly more accurate results [73, 75]. In addition, schemes for the perturbative treatment of triple excitations have been proposed [204, 244]. However, these improvements come at the price of increased computational cost.

In total, the present study shows that the Mk-MRCC method is a valuable tool for the determination of equilibrium structures as it yields reliable descriptions for a variety of multireference cases, where single-reference CC methods fail. Moreover, the present study demonstrates for the first time that this conclusion holds not only for small model systems, but also for medium-sized molecules. At the same time, Mk-MRCC cannot be considered as the final solution to the problem of generalizing CC theory to the multireference case as it is subject to a number of theoretical problems and often gives rise to results of unsatisfactory accuracy. Nevertheless, Mk-MRCC theory represents an important step towards a convincing solution and one can assume that future developments will benefit from the insights gained in the context of Mk-MRCC theory.

Application of Linear-Response Theory to the Mk-MRCC Wave Function

The Mk-MRCC linear-response function and the Mk-MRCC linear-response equations have been derived in Chapter 4.1 starting from an appropriate time-dependent wave function. In addition, an implementation suitable for the calculation of static and dynamic polarizabilities as well as excitation energies within the Mk-MRCCSD approximation has been presented in Chapter 4.2. Based on calculations for systems as large as 2,6-pyridyne, the impact of a MRCC ansatz on the polarizability tensor could be quantified for the first time (cf. Chapter 4.3). The present work shows that when aiming at second-order properties of systems such as biradicals, single-reference CC methods face the same problems that have been described earlier for energy and energy-gradient calculations [34,35]. This demonstrates that multireference methods are needed for the treatment of second-order properties as well. A comparison to the full configuration-interaction limit shows that Mk-MRCCSD accurately recovers the static polarizability of multireference systems. Hence, the implementation presented in this work should be considered as the first step towards the derivation and implementation of general higher-order properties for MRCC wave functions. With respect to the calculation of further static second-order properties such as nuclear magnetic shielding tensors, the present work indicates that Mk-MRCC theory is able provide accurate and reliable results.

Yet, the applicability of Mk-MRCC to the treatment of dynamic properties and excitation energies is severely limited by its inherent redundancy. The theoretical analysis of the linearresponse equations carried out in Chapter 4.1.4 reveals that the Mk-MRCC Jacobian matrix is defined in an overcomplete basis independent of the choice of reference space. For truncated Mk-MRCC schemes, this overcompleteness leads to an artificial splitting of some excited states. In the linear-response function, this shows up in the form of a wrong pole structure as exemplary calculations for the dynamic polarizability in Chapters 4.3.1 and 4.3.2 illustrate.

These conclusions are also underpinned by studies on the vertical excitation spectra of ozone and the three isomers of benzyne (cf. Chapters 4.3.3 and 4.3.4, respectively). Moreover, it is seen that a uniform energetic change does not take place for the excited states when going from CCSD to Mk-MRCCSD. A scheme for classifying the excited states has been proposed based on the structure of the respective linear-response eigenvectors. It seems likely that Mk-MRCCSD linear-response calculations become more problematic with growing multireference character or if the reference space is enlarged. However, in spite of these drawbacks, it is possible to obtain meaningful results from Mk-MRCCSD linear-response theory as the investigation of the excited states of silicon disulfide in Chapter 4.3.5 shows. For this example, a rather accurate match between Mk-MRCCSD calculations and size-extensivity corrected multireference configuration-interaction calculations has been achieved.

From a general perspective, the present investigation has demonstrated that the comprehensive assessment of a quantum-chemical method requires to take into account not only the theory necessary for the evaluation of the total energy. Rather, schemes for the treatment of molecular properties and excitation energies need to be considered as well. With respect to MRCC theory, all assessment criteria discussed in the previous section such as, for example, the scaling of the computational cost remain valid. Yet, an additional new criterion can be established: A convincing MRCC method should allow for the reliable determination of dynamic properties and excitation energies.

Concerning future prospects of Mk-MRCC, mixed conclusions should be drawn from the present investigation. While reliable and encouraging results could be obtained for the static polarizability tensor, Mk-MRCC linear-response theory faces severe problems with respect to dynamic properties and excitation energies. Since its problems are rooted directly in the Mk-MRCC sufficiency conditions, a solution within the Mk-MRCC framework seems unlikely. Furthermore, other MRCC methods, which also make use of sufficiency conditions, may potentially suffer from similar problems. It might be well worth the effort to review them in this regard. Judging from the knowledge gained in this work, a reliable scheme for the treatment of dynamic properties in state-specific MRCC theory seems to be within reach when starting from a wave function that does not make use of sufficiency conditions, but rather employs the correct number of parameters from the beginning. Promising in this respect are the MRexpT method [57] as well as internally contracted MRCC approaches [60, 61]. The present work may serve as basis for the development of corresponding linear-response techniques.

Dipole Hessian Matrix for Correlated Levels of Theory

An expression for the third derivative of the MP2 energy and the CC energy has been derived in Chapter 5.1 and subsequently applied to implement analytic dipole Hessians at the MP2 and CCSD levels of theory as presented in Chapter 5.2. In some pilot applications in Chapter 5.3, the accuracy of analytical and numerical differentiation schemes has been explored. It has been shown that numerical schemes are, in principle, able to provide valid results if one, two, or sometimes even three differentiation steps are carried out numerically. Special attention has to be paid to the step size used as the reliability of the results strongly depends on this parameter. In particular, numerical second or third derivatives demand larger step sizes than numerical first derivatives. This should be contrasted with analytic-derivative techniques, which can always be used in a black-box manner. In addition, the accuracy within reach of numerical differentiation is often not sufficient for quantum-chemical applications.

The present work reports the first implementation of fully analytic dipole Hessians for correlated levels of theory. Complementary developments for cubic force constants are currently under way. Put together, these two pieces of work will greatly facilitate the routine evaluation of anharmonic effects at correlated levels of theory and thus allow for a more efficient high-accuracy treatment of infrared spectra in quantum chemistry. Moreover, the work presented here is worthwhile to be extended in two directions. First, the reformulation of the theory for general CC schemes is straightforward. Such an extension would, for example, enable the efficient investigation of anharmonic effects at even higher levels of theory. Second, the present work may serve as starting point for the further exploration of the realm of higher-order properties [4]. This includes the fully analytic calculation of other third-order quantities, but also the determination of fourth-order or fifth-order quantities via numerical differentiation starting from analytical third derivatives. In addition, schemes for the calculation of vibrationally averaged properties will benefit from the availability of higher analytic derivatives. The implementation of such facilities at the CC level of theory will certainly reinforce the interplay of quantum chemistry with experimental disciplines.

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A. Dynamic Polarizability of Boron Monohydride, Methylene, p-Benzyne, and 2,6-Pyridyne

Table A.1.: Element α_{zz} of the polarizability tensor at various frequencies ω for the ${}^{1}\Sigma^{+}$ ground state of boron monohydride as computed at the CCSD, Mk-MRCCSD, and full CI levels of theory using a TZP basis set. All values in atomic units.

ω	α_{zz}	ω	α_{zz}	ω	α_{zz}	
CCSD		Mk-M	RCCSD	Full CI		
0.000	55.633	0.000	52.362	0.000	52.568	
0.020	56.184	0.020	52.686	0.020	53.081	
0.040	57.912	0.040	54.023	0.040	54.691	
0.060	61.067	0.060	56.552	0.060	57.631	
0.080	66.184	0.080	60.657	0.080	62.401	
0.100	74.350	0.100	67.089	0.100	70.022	
0.110	80.237	0.110	71.625	0.110	75.562	
0.120	87.994	0.120	77.430	0.120	82.794	
0.130	98.553	0.130	85.024	0.130	92.729	
0.140	113.630	0.140	97.379	0.140	107.010	
0.150	136.750	0.150	114.883	0.150	129.175	
0.160	176.513	0.160	152.008	0.160	168.192	

ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	ω	α_{yy}
\mathbf{C}	CSD	CCSD		Mk-MRCCSD		Mk-MRCCSD		Mk-MRCCSD	
0.000	15.183	0.352	-92.254	0.000	15.094	0.2939	28.151	0.384	6.969
0.020	15.209	0.354	-39.466	0.020	15.120	0.296	27.419	0.386	10.337
0.040	15.288	0.356	-16.201	0.040	15.198	0.300	28.264	0.388	13.142
0.060	15.422	0.358	-2.161	0.060	15.330	0.310	30.984	0.390	15.586
0.080	15.615	0.360	8.269	0.080	15.519	0.320	34.997	0.392	17.789
0.100	15.873	0.362	17.654	0.100	15.773	0.330	41.857	0.394	19.833
0.120	16.203	0.364	28.173	0.120	16.097	0.340	58.181	0.396	21.775
0.140	16.618	0.366	43.954	0.140	16.505	0.342	65.030	0.398	23.657
0.160	17.134	0.368	82.520	0.160	17.010	0.344	75.186	0.400	25.515
0.180	17.773	0.374	-26.708	0.180	17.635	0.346	92.067		
0.200	18.569	0.376	-11.104	0.200	18.413	0.348	126.410		
0.220	19.574	0.378	-2.748	0.220	19.391	0.356	-49.602		
0.240	20.870	0.380	2.725	0.240	20.647	0.358	-21.207		
0.260	22.600	0.382	6.753	0.260	22.313	0.360	-5.358		
0.280	25.050	0.384	9.952	0.280	24.645	0.362	5.739		
0.300	28.898	0.386	12.635	0.290	26.203	0.364	15.150		
0.310	31.894	0.388	14.979	0.2938	21.469	0.366	24.978		
0.320	36.446	0.390	17.094	0.29381	15.927	0.368	38.375		
0.330	44.728	0.392	19.055	0.293815	7.732	0.370	65.902		
0.340	68.012	0.394	20.914	0.293817	-0.831	0.376	-31.789		
0.342	79.834	0.396	22.711	0.29382	-27.241	0.378	-12.715		
0.344	100.482	0.398	24.478	0.293855	85.835	0.380	-3.276		
0.346	146.862	0.400	26.241	0.29386	42.194	0.382	2.678		

Table A.2.: Element α_{yy} of the polarizability tensor at various frequencies ω for the ¹A₁ ground state of methylene as computed at the CCSD and Mk-MRCCSD levels of theory using the cc-pCVTZ basis set. All values in atomic units.

Table A.3.: Element α_{xx} of the polarizability tensor at various frequencies ω for the ${}^{1}A_{g}$ ground state of *p*-benzyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ basis set. All values in atomic units.

ω	α_{xx}	ω	α_{xx}	ω	α_{xx}	ω	α_{xx}
CCSD		CCSD		Mk-M	Mk-MRCCSD		RCCSD
0.000	79.661	0.198	55.667	0.000	79.552	0.176	103.797
0.020	79.859	0.200	83.194	0.020	79.752	0.180	106.041
0.040	80.463	0.204	99.058	0.040	80.360	0.186	110.462
0.060	81.503	0.210	109.017	0.060	81.408	0.189	113.654
0.080	83.039	0.220	121.103	0.080	82.952	0.192	118.475
0.100	85.167	0.226	129.090	0.090	83.938	0.194	123.619
0.120	88.052	0.232	138.972	0.100	85.087	0.196	129.854
0.140	91.995	0.236	147.373	0.110	86.422	0.197	136.857
0.160	97.675	0.240	158.176	0.120	87.968	0.1975	140.318
0.170	101.745	0.242	164.931	0.130	89.765		
0.180	107.830	0.244	172.991	0.140	91.864		
0.185	112.938	0.246	182.853	0.149	94.073		
0.190	123.523	0.248	195.310	0.158	96.673		
0.193	143.660			0.167	99.813		

ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	
CCSD		CCSD		Mk-N	Mk-MRCCSD		Mk-MRCCSD	
0.000	85.359	0.175	95.375	0.000	73.113	0.178	91.573	
0.020	85.667	0.180	100.654	0.020	73.203	0.179	98.196	
0.040	86.620	0.185	105.612	0.040	73.455	0.180	101.601	
0.060	88.322	0.190	110.639	0.060	73.791	0.183	106.423	
0.080	91.011	0.197	118.414	0.080	73.981	0.186	108.954	
0.100	95.242	0.204	128.104	0.090	73.825	0.189	110.903	
0.110	98.367	0.209	137.460	0.100	73.225	0.192	112.698	
0.120	102.795	0.220	192.363	0.105	72.604	0.196	115.121	
0.125	105.886	0.222	237.869	0.110	71.605	0.200	117.738	
0.130	110.056			0.115	69.980	0.203	119.901	
0.135	116.240			0.120	67.236	0.206	122.280	
0.140	127.056			0.125	62.241	0.209	124.929	
0.147	181.812			0.130	51.704	0.212	127.902	
0.155	14.706			0.133	38.121	0.215	131.280	
0.160	64.808			0.136	6.157	0.218	135.166	
0.165	80.453			0.139	-152.519	0.220	138.111	
0.170	89.124			0.177	71.865			

Table A.4.: Element α_{yy} of the polarizability tensor at various frequencies ω for the ${}^{1}A_{g}$ ground state of *p*-benzyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ basis set. All values in atomic units.

Table A.5.: Element α_{zz} of the polarizability tensor at various frequencies ω for the ${}^{1}A_{g}$ ground state of *p*-benzyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ basis set. All values in atomic units.

ω	α_{zz}	ω	α_{zz}	ω	α_{zz}	ω	α_{zz}
CC	$^{\circ}SD$	CCSD		Mk-M	RCCSD	Mk-M	RCCSD
0.000	42.631	0.228	56.100	0.000	42.498	0.183	46.076
0.020	42.701	0.236	59.156	0.020	42.567	0.186	48.002
0.040	42.912	0.242	61.858	0.040	42.779	0.192	49.864
0.060	43.272	0.248	65.290	0.060	43.141	0.197	50.980
0.080	43.797	0.252	68.279	0.080	43.670	0.203	52.253
0.100	44.511	0.258	74.814	0.100	44.393	0.209	53.628
0.120	45.450	0.262	82.062	0.110	44.841	0.215	55.288
0.140	46.681	0.265	91.179	0.120	45.358	0.220	57.202
0.160	48.324	0.268	108.888	0.130	45.958	0.223	58.992
0.180	50.689	0.270	135.987	0.140	46.665	0.225	60.984
0.190	52.490			0.149	47.429	0.227	65.266
0.195	53.821			0.158	48.400	0.228	70.893
0.200	56.014			0.164	49.286	0.229	93.903
0.204	60.264			0.170	50.747	0.231	41.493
0.206	67.046			0.173	52.245	0.232	48.650
0.207	77.630			0.176	56.749	0.234	53.635
0.208	200.00			0.1765	58.787	0.238	57.570
0.2088	-10.0			0.177	62.243	0.243	60.794
0.210	33.817			0.1775	69.478	0.248	64.078
0.213	47.210			0.178	94.663	0.253	68.175
0.216	50.582			0.1787	-15.951	0.258	74.134
0.220	52.926			0.179	19.382	0.262	81.870
0.224	54.605			0.180	38.346	0.266	96.913

ω ω α_{xx} ω α_{xx} ω α_{xx} α_{xx} CCSD CCSD Mk-MRCCSD Mk-MRCCSD 0.000 106.447 79.888 0.180108.5630.000 79.6850.180 0.04080.6950.190126.1370.04080.498 0.190115.7920.08083.291 0.200 86.701 0.08083.108 0.12088.347 0.210 109.881 0.12088.1640.14092.3310.220122.0720.14092.0950.230 97.609 0.16098.092136.9270.160

Table A.6.: Element α_{xx} of the polarizability tensor at various frequencies ω for the ${}^{1}A_{g}$ ground state of *p*-benzyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVTZ basis set. All values in atomic units.

Table A.7.: Element α_{yy} of the polarizability tensor at various frequencies ω for the ${}^{1}A_{g}$ ground state of *p*-benzyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVTZ basis set. All values in atomic units.

ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	
CCSD		CCSD		Mk-M	Mk-MRCCSD		Mk-MRCCSD	
0.000	86.794	0.160	74.883	0.000	72.121	0.210	125.168	
0.040	88.170	0.170	90.793	0.040	72.368	0.220	137.200	
0.080	93.100	0.180	100.933	0.080	72.457			
0.120	108.288	0.190	110.457	0.120	62.324			
0.130	120.405	0.200	121.700	0.180	104.856			
0.140	168.129	0.210	138.344	0.190	111.687			
0.150	5.214	0.220	181.792	0.200	117.386			

Table A.8.: Element α_{zz} of the polarizability tensor at various frequencies ω for the ${}^{1}A_{g}$ ground state of *p*-benzyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVTZ basis set. All values in atomic units.

$\omega \qquad \alpha_{zz}$ CCSD	$\begin{array}{ c c c } \omega & \alpha_{zz} \\ & \text{CCSD} \end{array}$	$ \begin{array}{c c} \omega & \alpha_{zz} \\ Mk-MRCCSD \end{array} $	$\omega \qquad \alpha_{zz}$ Mk-MRCCSD
$\begin{array}{c ccccc} 0.000 & 42.256 \\ 0.040 & 42.533 \\ 0.080 & 43.407 \\ 0.120 & 45.033 \\ 0.160 & 47.830 \\ 0.180 & 50.079 \\ 0.200 & 54.603 \\ 0.210 & -35.545 \\ \end{array}$	$\begin{array}{ccccc} 0.220 & 52.246 \\ 0.230 & 56.081 \\ 0.240 & 59.800 \\ 0.250 & 64.763 \\ 0.260 & 73.136 \\ 0.270 & 96.426 \end{array}$	$\begin{array}{ccccc} 0.000 & 42.093 \\ 0.040 & 42.371 \\ 0.080 & 43.250 \\ 0.120 & 44.912 \\ 0.140 & 46.201 \\ 0.160 & 48.216 \\ 0.170 & 50.672 \\ 0.180 & 44.061 \end{array}$	$\begin{array}{cccc} 0.190 & 49.012 \\ 0.200 & 51.003 \\ 0.210 & 53.038 \\ 0.220 & 52.246 \\ 0.230 & 63.391 \\ 0.240 & 56.777 \\ 0.250 & 63.290 \end{array}$

ω	α_{xx}	ω	α_{xx}	ω	α_{xx}	ω	α_{xx}	
C	CSD	CCSD		Mk-M	Mk-MRCCSD		Mk-MRCCSD	
0.000	39.358	0.155	34.413	0.000	39.121	0.148	50.026	
0.020	39.448	0.160	36.656	0.020	39.201	0.150	56.693	
0.040	39.731	0.170	39.146	0.040	39.447	0.153	107.925	
0.060	40.255	0.180	40.792	0.060	39.889	0.157	14.889	
0.080	41.151	0.190	42.196	0.080	40.595	0.160	28.084	
0.100	42.891	0.200	43.573	0.090	41.095	0.162	31.481	
0.105	43.659	0.210	45.050	0.100	41.753	0.165	34.390	
0.110	44.765	0.220	46.753	0.110	42.677	0.170	37.049	
0.115	46.619	0.228	48.403	0.118	43.789	0.180	39.844	
0.120	51.055	0.234	49.931	0.122	44.597	0.190	41.662	
0.122	55.979	0.240	51.909	0.126	45.747	0.200	43.233	
0.124	74.376	0.248	56.461	0.130	47.650	0.206	44.167	
0.126	-18.138	0.252	62.716	0.133	50.461	0.212	45.140	
0.127	20.434			0.135	54.619	0.218	46.185	
0.130	37.628			0.136	59.080	0.224	47.342	
0.135	46.131			0.137	68.754	0.230	48.666	
0.140	65.189			0.140	28.005	0.236	50.249	
0.142	137.934			0.142	37.901	0.242	52.293	
0.144	-19.854			0.144	42.502	0.246	54.211	
0.150	29.700			0.145	44.267	0.250	57.810	

Table A.9.: Element α_{xx} of the polarizability tensor at various frequencies ω for the lowest singlet state of 2,6-pyridyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ basis set. All values in atomic units.

Table A.10.: Element α_{yy} of the polarizability tensor at various frequencies ω for the lowest singlet state of 2,6-pyridyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ basis set. All values in atomic units.

ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	ω	α_{yy}
C	CSD	C	CSD	Mk-MRCCSD		Mk-M	RCCSD
0.000	77.578	0.170	98.466	0.000	72.529	0.168	84.018
0.020	77.880	0.176	109.864	0.020	72.761	0.170	88.271
0.040	78.834	0.180	124.386	0.040	73.492	0.172	98.183
0.060	80.619	0.184	161.028	0.060	74.861	0.173	111.328
0.080	83.725	0.195	32.438	0.080	77.267	0.1735	125.494
0.090	86.188	0.200	59.940	0.090	79.228	0.180	14.129
0.100	89.918	0.203	68.109	0.100	82.348	0.1815	55.408
0.105	92.699	0.205	72.253	0.110	88.714	0.182	71.548
0.110	96.702	0.207	75.782	0.115	96.027	0.184	72.688
0.115	103.235	0.210	80.358	0.118	105.046	0.187	73.031
0.120	116.723	0.215	87.049	0.120	116.784	0.190	71.450
0.122	127.707	0.220	93.688	0.122	143.446	0.193	65.182
0.124	148.468	0.224	100.042	0.134	54.745	0.195	52.009
0.126	203.971	0.228	110.189	0.135	57.151	0.196	28.490
0.130	-84.626	0.232	159.865	0.138	62.436	0.198	127.201
0.135	44.175	0.234	-1.520	0.141	65.928	0.199	108.724
0.140	63.678	0.236	76.561	0.145	69.227	0.200	101.586
0.142	67.823	0.238	90.746	0.150	72.292	0.201	118.540
0.144	71.103	0.240	98.138	0.153	73.862	0.202	150.926
0.150	78.302	0.244	108.365	0.157	75.859		
0.155	83.001	0.248	118.023	0.160	77.418		
0.160	87.482	0.252	131.149	0.165	80.707		

Table A.11.: Element α_{zz} of the polarizability tensor at various frequencies ω for the lowest singlet state of 2,6-pyridyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVDZ basis set. All values in atomic units.

ω	α_{zz}	ω	α_{zz}	ω	α_{zz}	ω	α_{zz}
CCSD		CCSD		Mk-M	Mk-MRCCSD		IRCCSD
0.000	70.998	0.195	103.443	0.000	70.839	0.190	97.321
0.020	71.171	0.200	112.005	0.020	71.009	0.192	100.133
0.040	71.701	0.203	126.578	0.040	71.530	0.194	108.404
0.060	72.613	0.205	171.843	0.060	72.427	0.195	125.277
0.080	73.956	0.207	-11.593	0.080	73.744	0.200	33.766
0.100	75.810	0.210	80.223	0.090	74.583	0.201	52.043
0.120	78.306	0.215	96.739	0.100	75.559	0.202	69.831
0.130	79.857	0.220	104.164	0.110	76.687	0.204	75.502
0.140	81.663	0.224	109.118	0.120	77.989	0.207	83.460
0.150	83.782	0.228	114.147	0.135	80.331	0.209	92.766
0.160	86.304	0.232	119.940	0.150	83.261	0.211	103.943
0.170	89.379			0.160	85.646	0.213	115.474
0.180	93.310			0.170	88.501	0.216	136.890
0.190	98.964			0.180	92.049		

Table A.12.: Element α_{xx} of the polarizability tensor at various frequencies ω for the lowest singlet state of 2,6-pyridyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVTZ basis set. All values in atomic units.

ω	α_{xx}	ω	α_{xx}	$ \omega$	α_{xx}	ω	α_{xx}
CCSD		CCSD		Mk-MRCCSD		Mk-MRCCSD	
0.000	39.026	0.150	32.033	0.000	38.748	0.160	29.616
0.040	39.402	0.170	39.080	0.040	39.069	0.180	39.610
0.080	40.858	0.190	41.879	0.080	40.202	0.200	42.785
0.100	42.752	0.210	44.578	0.100	41.357	0.220	45.897
0.120	59.048	0.230	48.231	0.120	43.846	0.240	50.378
0.130	41.049	0.240	51.314	0.130	47.919		
0.140	122.593			0.150	58.496		

Table A.13.: Element α_{yy} of the polarizability tensor at various frequencies ω for the lowest singlet state of 2,6-pyridyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVTZ basis set. All values in atomic units.

ω	α_{yy}	ω	α_{yy}	ω	α_{yy}	ω	α_{yy}
CCSD		CCSD		Mk-MRCCSD		Mk-MRCCSD	
0.000	78.057	0.150	78.861	0.000	72.063	0.160	80.334
0.040	79.363	0.160	87.886	0.040	72.985	0.170	95.963
0.080	84.531	0.170	99.068	0.080	76.542	0.190	61.334
0.100	91.358	0.180	126.408	0.100	81.204		
0.120	126.985	0.200	59.791	0.120	112.149		
0.130	-7.206	0.220	92.103	0.140	67.422		
0.140	65.639			0.150	74.415		

Table A.14.: Element α_{zz} of the polarizability tensor at various frequencies ω for the lowest singlet state of 2,6-pyridyne as computed at the CCSD and Mk-MRCCSD levels of theory using the aug-cc-pCVTZ basis set. All values in atomic units.

ω	α_{zz}	$\begin{bmatrix} \omega \\ 0 \end{bmatrix}$	α_{zz}	ω Mk-M	α_{zz} RCCSD	ω Mk-M	α_{zz} RCCSD
0.000 0.040 0.080	70.735 71.432 73.667	0.160 0.180 0.190	85.801 92.447 97.403	0.000	$ \begin{array}{r} 10003D \\ \hline 70.535 \\ 71.221 \\ 73.414 \end{array} $	0.160 0.180 0.190	85.140 91.317 95 927
$0.120 \\ 0.140$	77.966 81.270	0.150	51.405	$0.000 \\ 0.120 \\ 0.140$	77.612 80.811	$0.205 \\ 0.210$	55.031 91.960

B. Excitation Energies and Structural Parameters for Silicon Disulfide

Table B.1.: Absolute energies for the 1 ${}^{1}A_{1}$ ground state and the low-lying excited states of ${}^{1}A_{1}$ symmetry of silicon disulfide as computed for various molecular structures at the Mk-MRCCSD-LR level of theory using the cc-pCVTZ basis set.

∠(SSiS)/°	$ m R(SiS)/ m \AA$	$E(1 \ ^{1}A_{1})/a.u.$	$E(2 \ ^{1}A_{1})/a.u.$	$E(3 \ ^{1}A_{1})/a.u.$	$E(4 \ ^{1}A_{1})/a.u.$
70.0	2.06558	-1085.493660	_	_	_
75.0	2.05512	-1085.481937	-1085.278159	—	
80.0	2.05378	-1085.468910	-1085.319044	—	
85.0	2.05938	-1085.455945	-1085.360291	-1085.257216	—
90.0	2.06957	-1085.445548	-1085.382725	-1085.284081	—
95.0	2.07439	-1085.439349	-1085.395988	-1085.304352	-1085.235485
100.0	2.05136	-1085.441137	-1085.399236	-1085.317029	-1085.240914
105.0	2.01830	-1085.450046	-1085.391696	-1085.326526	-1085.246491
110.0	1.99571	-1085.460874	-1085.379253	-1085.333645	-1085.251632
115.0	1.97959	-1085.471343	-1085.365432	-1085.339280	-1085.256202
120.0	1.96716	-1085.480960	-1085.350828	-1085.343781	-1085.259878
125.0	1.95718	-1085.489657	_	-1085.345369	_
130.0	1.94899	-1085.497469	-1085.322655	-1085.347082	-1085.263100
135.0	1.94219	-1085.504441	-1085.307927	-1085.347268	-1085.265852
140.0	1.93652	-1085.510617	-1085.293088	-1085.346242	-1085.268294
145.0	1.93180	-1085.516026	-1085.277950	-1085.344105	-1085.270766
150.0	1.92790	-1085.520689	—	-1085.340940	-1085.272521
155.0	1.92474	-1085.524618	_	-1085.336840	-1085.275436
160.0	1.92223	-1085.527821	—	-1085.331920	-1085.279019
165.0	1.92033	-1085.530300	—	-1085.326350	-1085.283704
170.0	1.91900	-1085.532055	—	-1085.320462	-1085.289422

Table B.2.: Absolute energies for the low-lying excited states of ${}^{1}B_{1}$ symmetry of silicon disulfide as computed for various molecular structures at the Mk-MRCCSD-LR level of theory using the cc-pCVTZ basis set.

$\measuredangle(\rm SSiS)/^\circ$	$\rm R(SiS)/\rm \AA$	$E(1 \ ^{1}B_{1})/a.u.$	$E(2 \ ^{1}B_{1})/a.u.$	$E(3 \ ^{1}B_{1})/a.u.$	$E(4 \ ^{1}B_{1})/a.u.$	$E(5 \ ^{1}B_{1})/a.u.$
70.0	2.06558	-1085.409964	_	_	_	-1085.340140
75.0	2.05512	-1085.414291	-1085.196138	—	—	-1085.332443
80.0	2.05378	-1085.414553	-1085.272007	—	—	-1085.323090
85.0	2.05938	-1085.411995	-1085.302406	—	—	-1085.313275
90.0	2.06957	-1085.407365	-1085.326890	—	—	-1085.303534
95.0	2.07439	-1085.400669	-1085.344451	-1085.225832	—	-1085.293779
100.0	2.05136	-1085.390498	-1085.354902	-1085.235816	—	-1085.282732
105.0	2.01830	-1085.376441	-1085.360827	-1085.243362	—	-1085.269283
110.0	1.99571	—	-1085.365274	_	—	-1085.257823
115.0	1.97959	-1085.346898	-1085.368443	-1085.260664	—	-1085.240610
120.0	1.96716	-1085.332139	-1085.370363	-1085.267116	—	-1085.228736
125.0	1.95718	-1085.317302	-1085.371048	-1085.273110	—	-1085.217334
130.0	1.94899	-1085.302338	-1085.370546	-1085.278431	—	-1085.206957
135.0	1.94219	-1085.287217	-1085.368904	—	-1085.188910	—
140.0	1.93652	-1085.271920	-1085.366164	-1085.287114	-1085.202036	—
145.0	1.93180	-1085.256467	-1085.362363	-1085.290560	-1085.215962	—
150.0	1.92790	-1085.240894	-1085.357534	-1085.293467	-1085.230108	—
155.0	1.92474	-1085.225253	-1085.351711	-1085.295871	-1085.244135	—
160.0	1.92223	_	-1085.344934	-1085.297806	-1085.257797	—
165.0	1.92033	—	-1085.337259	-1085.299307	-1085.270908	—
170.0	1.91900	—	-1085.328794	-1085.300437	-1085.283207	—

Table B.3.: Absolute energies for the low-lying excited states of ¹B₂ symmetry of silicon disulfide as computed for various molecular structures at the Mk-MRCCSD-LR level of theory using the cc-pCVTZ basis set.

$\measuredangle(\mathrm{SSiS})/^\circ$	$\rm R(SiS)/\rm \AA$	$E(1 \ ^{1}B_{2})/a.u.$	${\rm E}(2\ ^1{\rm B}_2)/{\rm a.u.}$	$\mathrm{E}(3\ ^{1}\mathrm{B}_{2})/\mathrm{a.u.}$	$E(4 \ ^1B_2)/a.u.$	$E(5 \ ^{1}B_{2})/a.u.$	$\mathrm{E}(6\ ^{1}\mathrm{B}_{2})/\mathrm{a.u.}$
70.0	2.06558	-1085.378235	-1085.352848	_	_	_	_
75.0	2.05512	-1085.398972	-1085.378876	_	_	-1085.324958	-1085.265596
80.0	2.05378	-1085.413469	-1085.397665	-1085.237925	—	-1085.309545	-1085.260802
85.0	2.05938	-1085.422428	-1085.410668	-1085.267596	—	-1085.300041	-1085.249761
90.0	2.06957	-1085.426960	-1085.419142	-1085.298545	-1085.246769	-1085.281242	—
95.0	2.07439	-1085.428864	-1085.424751	-1085.307917	-1085.252026	-1085.279142	-1085.223238
100.0	2.05136	-1085.431322	-1085.430134	-1085.317086	-1085.257366	-1085.271384	-1085.216593
105.0	2.01830	-1085.432213	-1085.433633	-1085.323644	-1085.270790	-1085.250146	-1085.206045
110.0	1.99571	-1085.430887	-1085.434678	-1085.328649	-1085.275388	-1085.236579	-1085.195109
115.0	1.97959	-1085.428310	-1085.434299	-1085.332452	-1085.280187	-1085.222502	—
120.0	1.96716	-1085.424846	-1085.432864	-1085.335146	-1085.284696	-1085.208471	-1085.172525
125.0	1.95718	-1085.420629	-1085.430541	-1085.336824	-1085.288904	-1085.194103	—
130.0	1.94899	-1085.415719	-1085.427430	-1085.337587	-1085.292883		—
135.0	1.94219	-1085.410151	-1085.423595	-1085.337553	-1085.296727	—	—
140.0	1.93652	-1085.403949	-1085.419089	-1085.336872	-1085.300522	—	—
145.0	1.93180	-1085.397133	-1085.413958	-1085.335767	-1085.304308	—	—
150.0	1.92790	-1085.389733	-1085.408255	-1085.334623	-1085.307986		—
155.0	1.92474	-1085.381798	-1085.402047	-1085.334135	-1085.311137	—	—
160.0	1.92223	-1085.373421	-1085.395433	-1085.335319	-1085.312977	—	—
165.0	1.92033	-1085.364806	-1085.388578	-1085.338737	-1085.313086	—	—
170.0	1.91900	-1085.356490	-1085.381813	-1085.343700	-1085.312113	—	—
∡(SSiS)/°	$ m R(SiS)/ m \AA$	$E(1 \ ^{1}A_{2})/a.u.$	$E(2 \ ^{1}A_{2})/a.u.$	$E(3 \ ^{1}A_{2})/a.u.$	$E(4 \ ^{1}A_{2})/a.u.$		
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70.0	2.06558	-1085.269220	-1085.319118	_			
75.0	2.05512	-1085.312421	-1085.337051	-1085.261840	—		
80.0	2.05378	-1085.345889	—	-1085.284956			
85.0	2.05938	-1085.371290	-1085.357344	-1085.303098			
90.0	2.06957	-1085.389958	-1085.361573	-1085.316395			
95.0	2.07439	-1085.403225	-1085.361488	-1085.325844			
100.0	2.05136	-1085.413120	-1085.354508	-1085.332748	—		
105.0	2.01830	-1085.419753	—	-1085.337035	—		
110.0	1.99571	-1085.423966	—	-1085.339880	—		
115.0	1.97959	-1085.426548	-1085.317927	-1085.342060	—		
120.0	1.96716	-1085.427766	-1085.306125	-1085.343807			
125.0	1.95718	-1085.427765	-1085.294706	-1085.345241			
130.0	1.94899	-1085.426641	-1085.283952	-1085.346437			
135.0	1.94219	-1085.424467	-1085.274157	-1085.347446			
140.0	1.93652	-1085.421298	-1085.265410	-1085.348302	—		
145.0	1.93180	-1085.417182	-1085.257181	-1085.349028	-1085.275744		
150.0	1.92790	-1085.412163	-1085.249204	-1085.349639	-1085.288708		
155.0	1.92474	-1085.406291	—	-1085.350144	-1085.301613		
160.0	1.92223	-1085.399629	—	-1085.350551	-1085.314204		
165.0	1.92033	-1085.392289		-1085.350863	-1085.326250		
170.0	1.91900	-1085.384518	—	-1085.351084	-1085.337411		

Table B.4.: Absolute energies for the low-lying excited states of ${}^{1}A_{2}$ symmetry of silicon disulfide as computed for various molecular structures at the Mk-MRCCSD-LR level of theory using the cc-pCVTZ basis set.

Table B.5.: Absolute energies for the 1 ${}^{1}A_{1}$ ground state and several low-lying excited states of silicon disulfide as computed for various molecular structures at the MR-CISD+P level of theory using the cc-pCVTZ basis set.

∠(SSiS)/°	$E(1 \ ^{1}A_{1})/a.u.$	$E(2 \ ^{1}A_{1})/a.u.$	$E(1 \ ^{1}B_{2})/a.u.$	$E(1 \ ^{1}A_{2})/a.u.$	$E(2 \ ^{1}A_{2})/a.u.$
70.0	-1085.452874	-1085.265895	-1085.325232	-1085.239436	-1085.225225
80.0	-1085.426411	-1085.300713	-1085.357368	-1085.309051	-1085.250222
90.0	-1085.397933	-1085.328702	-1085.372427	-1085.347452	-1085.275665
100.0	-1085.384766	-1085.353454	-1085.384210	-1085.368668	-1085.288540
110.0	-1085.405857	-1085.343716	-1085.391183	-1085.380950	-1085.295915
120.0	-1085.428548	-1085.304504	-1085.390349	-1085.385366	-1085.300015
130.0	-1085.456990	-1085.284685	-1085.385219	-1085.384384	-1085.302743
140.0	-1085.462472	-1085.244760	-1085.376820	-1085.378853	-1085.304719
150.0	-1085.474229	-1085.215133	-1085.365696	-1085.369242	-1085.306141
160.0	-1085.482617	-1085.187042	-1085.352622	-1085.356055	-1085.307272
170.0	-1085.487692	-1085.161982	-1085.338338	-1085.339201	-1085.307949

C. List of Publications

Publications Resulting from this Work

- T.-C. Jagau and J. Gauss, Ground and excited state geometries via Mukherjee's multireference coupled-cluster method, *Chem. Phys.* **401**, 73-87 (2012).
- T.-C. Jagau and J. Gauss, Linear-response theory for Mukherjee's multireference coupledcluster method: Static and dynamic polarizabilities, *J. Chem. Phys.* **137**, 044115/1-14 (2012).
- T.-C. Jagau and J. Gauss, Linear-response theory for Mukherjee's multireference coupledcluster method: Excitation energies, J. Chem. Phys. 137, 044116/1-16 (2012).
- A. Köhn, M. Hanauer, L. A. Mück, T.-C. Jagau, and J. Gauss, State-specific multireference coupled-cluster theory, *WIRES Comput. Mol. Sci.* **3**, 176-197 (2013).

Further Publications

- I. P. Roof, T.-C. Jagau, W. G. Zeier, M. D. Smith, and H.-C. zur Loye, Crystal growth of a new series of complex niobates, LnKNaNbO₅ (Ln=La, Pr, Nd, Sm, Eu, Gd, and Tb): structural properties and photoluminescence, *Chem. Mater.* **21**, 1955-1961 (2009).
- T.-C. Jagau, I. P. Roof, M. D. Smith, and H.-C. zur Loye, Crystal growth, structural properties, and photophysical characterization of Ln₄Na₂K₂M₂O₁₃ (M=Nb, Ta; Ln=Nd, Sm, Eu, Gd), *Inorg. Chem.* 48, 8220-8226 (2009).
- T.-C. Jagau, E. Prochnow, F. A. Evangelista, and J. Gauss, Analytic gradients for Mukherjee's multireference coupled-cluster method using two-configurational self-consistent-field orbitals, J. Chem. Phys. 132, 144110/1-9 (2010).