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Development and Benchmarking of Novel Electronic Structure Methods based on the Algebraic Diagrammatic Construction and Unitary Coupled Cluster Schemes

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Diese Arbeit wrde durchgeführt am
Institut für wissenschaftliches Rechenen (IWR)
in Heidelberg unter der Aufsicht von

Prof. Dr. Andreas Dreuw (IWR)

Zweitgutachter:
Prof. Dr. Oriol Vendrell (Institut für Theoretische Chemie)

Meiner Familie

"Ich glaub' ich Spin!"

- Der Autor

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Abstract

During the last three decades, the field of theoretical and computational chemistry has evolved rapidly, promoted by the increasing availability of computational power inherent in modern CPUs and cluster structures. This development has expressed itself in a particular manner in the formulation of modern state-of-the-art electronic structure methods in the frameworks of, for instance, the Algebraic Diagrammatic Construction scheme or Coupled Cluster. Application of these methods to the calculation of molecular excitation energies and properties that describe the most fundamental processes of light-matter interaction, has been established as a profound and reliable tool for experimentalists within chemistry and molecular sciences.

This work, which is spilt into three main parts, presents the implementation as well as benchmarking of novel electronic structure methods for the Algebraic Diagrammatic Construction scheme (ADC) as well as Unitary Coupled Cluster (UCC).

In the first part, an implementation and benchmark study for the calculation doubly-ionized as well as double electronically-attached states for ADC, termed DIP-ADC and DEA-ADC, respectively, up to third order is presented. The implementation was executed in the `Q-Chem` program package, benchmark studies included the comparison of states to Full CI data for DIP as well as EOMDIP-CCSD and EOMDEA-CCSD. For both schemes, the third-order methods DIP-ADC(3) as well as DEA-ADC(3) proved to produce results which are in a remarkable good agreement to the corresponding EOM-CCSD method.

As for the second part, a benchmark study on core excitation energies in the framework of Unitary Coupled Cluster was presented. To this end, the Core-valence separation approximation was applied to the second-and third-order UCC schemes for electron excitations. It was shown that CVS-UCC is very suitable in the computation of X-ray spectra, similar to CVS-ADC, which has been studied before by Wenzel et al. and that it provides reliable data for the description and simulation of energetically high-lying core excitations.

The last part of this work features an implementation of an automated code generator for

Unitary Coupled Cluster as it was realized by Leitner et al. for the computation of electronically excited states on a ADC(4) level. Working equations for a UCC3-x scheme (in similarity to UCC2-x with an extended description of the doubles/doubles block of the secular matrix) as well as a full UCC4 for the calculation of electronically-excited states and properties are presented, together with an improved ground-state description, termed UCC4+5[s,t] that includes fifth-order terms.

At the end of this work, all results for the three presented topics are summarized in detail, accompanied by a short outlook of what could include future work and development.

Zusammenfassung

Die Numerische Chemie erlebte in den letzten drei Jahrzehnten, befördert von ständig wachsender Rechenleistung der verfügbaren Prozessoren und Rechenclustern, einen wahren Wachstumsschub. Diese Entwicklung manifestiert sich in besonderem Maße in der Formulierung von modernen Elektronenstrukturmethoden, wie sie zum Beispiel in den Formalismen des Algebraisch-diagrammatischen Konstruktionsverfahrens und Coupled Cluster zu finden sind. Die Anwendung dieser Methoden zur Beschreibung der fundamintalsten Eigenschaften von Molekülen, z. B. Anregungsenergien oder Wellenfunktionseigenschaften, haben sich zu einem zuverlässigem Werkzeug entwickelt, dass die Arbeit von Experimentatoren in allen Fachgebieten der Chemie ergänzt und vorantreibt.

Diese Arbeit, die sich in drei Themen aufteilt, präsentiert die Implementierung und statistische Auswertung von neuartigen Elektronenstrukturmethoden für das Algebraisch-diagrammatische Konstruktionsverfahren (ADC) sowie unitärem Coupled Cluster (UCC).

Im ersten Teil werden ADC-Schemata für die Berechnung von Doppelionisationspotentialen (DIP-ADC) sowie Doppelelektronaffinitäten (DEA-ADC) bis zur dritten Ordnung vorgestellt. Dies beinhaltet sowohl die Implementierung, welche im `Q-Chem` vorgenommen wurde, als auch die statistische Auswertung im Vergleich zu Full CI (für DIP) und EOMDIP-/EOMDEA-CCSD Daten. In beiden Fällen zeigte sich, dass DIP-ADC(3) sowie DEA-ADC(3) in sehr guter Übereinstimmung mit den entsprechenden EOM-CCSD Daten sind.

Der zweite Teil dieser Arbeit beschäftigte sich mit der Berechnung von hochenergetischen Kernelektronenanregungen für unitäre Coupled Cluster Methoden bis einschließlich dritter Ordnung. Zu diesem Zweck wurde die sogenannte Core-valence separation-Näherung auf die unterliegenden UCC-Schemata für die Berechnung elektronisch angeregter Zustände angewandt. Die statistische Auswertung erfolgte mit den Sets an Molekülen, die bereits zuvor von Jan Wenzel et al. für CVS-ADC Schemata verwendet wurden. Es konnte festgestellt werden, dass CVS-UCC und CVS-ADC vergleichbar gute Ergebnisse für die Berechnung von Röntgenspektren liefern.

Eine automatisierte Generierung von Gleichungen für die Berechnung von elektronisch angeregten Zuständen in UCC4 wurde im letzten Teil dieser Arbeit vorgestellt. Ein ähnlicher Ansatz wurde bereits zuvor von Jonas Leitner et al. für ADC(4) realisiert. Neben der vollen UCC4-Säkularmatrix wird ein verbessertes Grundzustandsschema, welches Beiträge in fünfter Ordnung enthält (UCC4+5[s,t]) vorgestellt.

Das letzte Kapitel dieser Arbeit dient der ausführlichen Zusammenfassung der Ergebnisse aus allen drei oben genannten Teilen und beinhaltet darüber hinaus auch einen kleinen Ausblick auf möglich zukünftige Entwicklungen zu den hier präsentierten Ergebnissen.

Contents

1. Theoretical Background

1.1. A brief historical introduction

"A physicist is just an atom's way of looking at itself."

- Niels Bohr

This famous quote, without a doubt ambiguous, gives a good idea of how profound yet strange the emergence of modern chemistry and physics, especially quantum mechanics, must have been for scientists at the end of the 19th and the beginning of the 20th century. Evidence of the quantum nature of atoms date back to the late 19th century, for instance, when Kirchhoff and Bunsen introduced the spectral analysis in Heidelberg (1859). But it was not until the early 20th century that theory and experiment could deduce profound models of "the indivisible" - the atom itself. It was Niels Bohr who in 1913[8,39] introduced the first atomic model to include elements of a novel theory, quantum mechanics, even before its postulates were formulated (see figure 1.1), introducing a breakthrough to modern chemistry. Bohr's atomic model, albeit revolutionary, showed significant weaknesses, such as an inconsistency with the laws of electrodynamics. The model was expanded by Sommerfeld in 1915[29], but it was not until 1926[86] when Schrödinger introduced the equation-of-motion, so to speak, for the scales of atoms and molecules where classical mechanic breaks down. Electrons, previously seen as particles, inherit properties of waves, an electron is now described by a wavefunction and delocalized in space. The application of this equation to the hydrogen atom[13,57] was the birth hour of atomic and molecular physics and, along with it, modern chemistry. Since this point, theoretical chemists and, especially in the early days of quantum mechanics in the 1920s and 1930s, theoretical physicists established a frame-

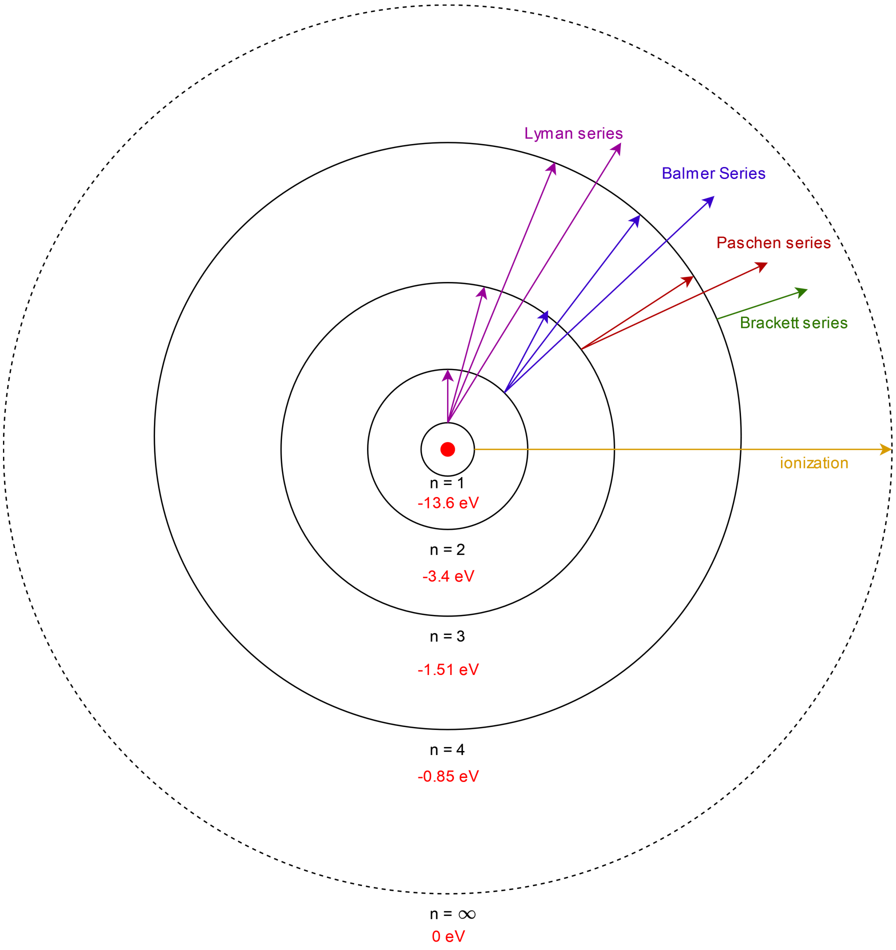

Figure 1.1.: The Bohr model for hydrogen. Depicted in different colours are the sets of spectral lines for each main shell.

work for the calculation of molecular properties that has made modern quantum chemistry become the theoretical foundation of all contemporary chemistry. Since then, experimental progress (i. e. in laser physics) as well as the ability to use machines to compute equations has led to the development of highly accurate theoretical models for the description of atoms and molecules. Modern state-of-the-art methods, such as Møller-Plesset[69] perturbation theory for the ground state and Coupled Cluster[15] or the Algebraic Diagrammatic Construction scheme[25] for excited states and molecular properties enable high-precision calculations that are in an extraordinary accordance with experimental results. The component of steadily increasing computational power (Moore's law[70]) fuels the process of development for highly-accurate, although computationally costly, methods in quantum chemistry. Modern quantum chemistry has become a discipline where all professions, chemistry, physics, mathematics and informatics meet and complement each other perfectly.

1.2. The wavefunction

As briefly mentioned in the previous chapter, modern quantum chemistry aims to deduce the solution of the Schrödinger equation[86], in its most general form given as

$$\hat{H}\,\Psi(\vec{r}) \;=\; E\,\Psi(\vec{r}), \tag{1.1}$$

for atomic and molecular systems with energy E and a wavefunction Ψ . The formulation of the atomic and molecular version of this equation in its most general form can be written using the full Hamiltonian function[13,57] $\hat{H} = \hat{T} + \hat{V}$ as

$$\begin{aligned} \hat{H}(\hat{r}) \;=& -\sum_{i=1}^{N}\frac{1}{2m_e}\,\hat{\nabla}_i^2 - \sum_{a=1}^{X}\frac{1}{2m_a}\,\hat{\nabla}_a^2 \\ &+ \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{\hat{r}_{ij}} + \sum_{a=1}^{X}\sum_{b>a}^{X}\frac{Z_a Z_b}{\hat{r}_{ab}} + \sum_{i=1}^{N}\sum_{a=1}^{X}\frac{Z_a}{\hat{r}_{ia}} \end{aligned} \tag{1.2}$$

where the first two terms in the first line give the the kinetic energy of the N electrons and X atomic nuclei in the system, respectively. In the second line, the potential (electronic) terms are given, namely the electron-electron repulsion (first term), the nuclei repulsion (second term) and the electron-nucleus repulsion (third term). Summation indices are restricted to avoid a double-counting of terms. m_e and m_a constitute electron and nucleus masses, Z_a the nuclear charges and the $\hat{r}$ represent the distance operators.

Born-Oppenheimer approximation

One of the most fundamental assumptions for the solution of the molecular Schrödinger equation is the Born-Oppenheimer approximation[9]. It states that the motion of the electrons around the nuclei and the nuclei motion itself happen each on different time scales ($\frac{m_{electron}}{m_{proton}} \approx \frac{1}{1836}$), assuming that the electron motion adapts almost instantaneously to that of the nuclei.

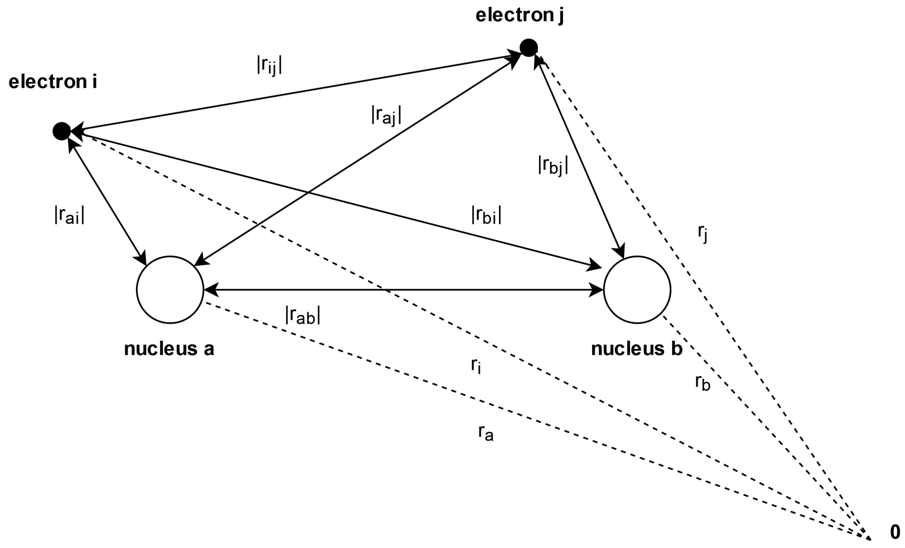

Figure 1.2.: Coordinate system for the Hamiltonian. The coordinate origin is given as 0.

This leads to a product ansatz,

$$\Psi(\vec{r}_a, \vec{r}_i) = \Psi_a(\vec{r}_a) \cdot \Psi_i(\vec{r}_i), \tag{1.3}$$

that reformulates the full wavefunction in equation 1.1 as a product of a nuclear (Ψ_a) and electronic (Ψ_i) wavefunction. The corresponding eigenvalue problems then become

$$\begin{aligned} \hat{H}_i \Psi_i(\vec{r}_i) &= E_i \Psi_i(\vec{r}_i), \\ \hat{H}_a \Psi_a(\vec{r}_a) &= E_a \Psi_a(\vec{r}_a). \end{aligned} \tag{1.4}$$

The (electronic) Hamiltonian, representing the most fundamental operator in quantum chemistry, then reduces to the electronic terms

$$\hat{H}_i(\hat{r}_i) = -\sum_{i=1}^{N} \frac{1}{2m_e} \hat{\nabla}_i^2 + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{\hat{r}_{ij}} + \sum_{i=1}^{N} \sum_{a=1}^{X} \frac{Z_a}{\hat{r}_{ia}}. \tag{1.5}$$

This Hamiltonian constitutes the starting point for all types of electronic structure calculations.

Within this work, **atomic units** ($\hbar = e = m_e = \frac{1}{4\pi\epsilon_0} \equiv 1$) are used.

LCAO-Ansatz and basis functions

Until now, the formulation of the Hamiltonian and the wavefunction is kept in an general manner, i. e. applicable to both atoms and molecules. This means that an algebraically consistent ansatz is needed to formulate a multi-electron wavefunction. John Lennard-Jones introduced the LCAO (Linear combination of atomic orbitals[54,14]) ansatz as early as 1929, establishing the connection between the solution of the one-electron Schrödinger equation (atomic orbitals) and a multi-electronic wavefunction (molecular orbitals),

$$\phi_i = \sum_{i}^{N} c_{i\nu}\, \psi_\nu . \tag{1.6}$$

The vector space of the so-called molecular orbitals ϕ_i is thus spanned by the atomic orbitals ψ_ν, $c_{i\nu}$ represent the expansion coefficients of the atomic orbitals to form the molecular orbitals. A set of N atomic orbitals spans a vector space of exactly N molecular orbitals. The set of atomic orbitals $\{\psi_\nu\}$ represents the basis set of the system. Each basis function ψ_ν itself is a linear combination of functions depending on the coordinates of that system. To model physically correct Slater-type orbitals[91] (STO) that possess a radial part of the form $\sim e^{-r}$, generally a series of Gaussian-type orbitals[36] (GTO) that behave like $\sim e^{-r^2}$ is combined. The reason is the much easier mathematical manipulation of these type of expression, which is important for the computation. Examples for commonly used basis sets for benchmarking are the Pople bases[24], the correlation-consistent Dunning bases[28] or the Karlsruhe basis sets[47], with the second and third presenting state-of-the-art sets for precise calculations. A major collection of basis sets for computational chemistry is provided at the Basis set exchange[75].

A perfect basis, that is, a basis that physically represents the electronic structure of an atom correctly, would have to be of infinite size. This is of course not a feasible task, but procedures to approach this completeness in a limit, called the complete basis set limit[54,14] (CBS) may be employed. This is done by using a series of basis sets increasing in size and thus precision (but also computational cost) for a fixed system. The series of (converging) generated data points may then be fitted, understanding the result as the CBS limit.

Spin and the fermionic wavefunction

Electrons possess an intrinsic spin[39,12] which can take two quantum numbers, $m_s = \pm\frac{1}{2}$, a property that was discovered in 1922 by Walther Stern and Otto Gerlach[35]. It was one of the first experiments to reveal the quantum nature of electrons. However, this finding leads to a specific implication for the wavefunction of an electron: Each spatial orbital may be populated by exactly two electrons with opposite spin.

Spin may be introduced in a mathematical sense with $\alpha(\omega)$ and $\beta(\omega)$ representing the functions for spin-up ($m_s = +\frac{1}{2}$) and spin-down ($m_s = -\frac{1}{2}$), respectively[94]. ω is an auxiliary spin variable. The spin functions feature the properties

$$\int_\omega \alpha(\omega)\beta(\omega)\, d\omega \; = \; \int_\omega \beta(\omega)\alpha(\omega)\, d\omega \; = 0 \tag{1.7}$$

as well as

$$\int_\omega \alpha(\omega)\alpha(\omega)\, d\omega \; = \; \int_\omega \beta(\omega)\beta(\omega)\, d\omega \; = \; 1. \tag{1.8}$$

Every spatial (molecular) orbital $\phi(\vec{r})$ may thus be expanded to two spin orbitals by multiplying the respective spin functions as

$$\phi(\vec{r}) \begin{cases} \phi_\alpha(\vec{r},\omega) & = \; \phi(\vec{r}) \cdot \alpha(\omega) \\ \phi_\beta(\vec{r},\omega) & = \; \phi(\vec{r}) \cdot \beta(\omega) \end{cases} \tag{1.9}$$

with the spin orbitals ϕ_α, ϕ_β (also denoted as χ in the literature) depending on both, position ($\vec{r}$) and spin (ω). For notational brevity, the subscripts α and β will be skipped through this work, understanding the wavefunction ϕ as a spin orbital from now on.

An arbitrary composed wavefunction Ψ of electrons (being fermions) needs to suffice the Fermi-Dirac statistics[32,23]. As "indistinguishable" particles, the total wavefunction needs to be antisymmetric for each permutation of fermions (Pauli principle[89]), or formulated alternatively, two fermions can not possess the same set of quantum numbers,

$$\Psi(\vec{r}_1,\omega_1;\vec{r}_2\omega_2;...;\vec{r}_n,\omega_n) \; = \; -\Psi(\vec{r}_2,\omega_2;\vec{r}_1\omega_1;...;\vec{r}_n,\omega_n). \tag{1.10}$$

The antisymmetry of the electronic wavefunction is thus a purely quantum-mechanical feature and has no classical interpretation to it.

1.3. Second quantization and the particle/hole formalism

When working with multi-particle states that are constructed using (orthonormal) single-particle states, the formalism of second quantization[88] is a very helpful and straightforward tool for the formulation of operators and wavefunctions. In particular, for fermionic systems as for electrons, this formalism introduces the ability to evaluate mathematical expressions efficiently and also enables the use of automatic code generation, as will be represented later in chapter 4.

An arbitrary fermionic wavefunction that has been constructed from a set of single-particle wavefunctions may be written as a determinant

$$|\Psi\rangle = |1_p, ..., 1_q\rangle , \tag{1.11}$$

where the subscript denotes the respective single-particle wavefunction and the number the occupation number for this particular one. It is quite intuitive to understand that this number is either 1 or 0, or in other words, an election exactly possesses all quantum numbers of this wavefunction ("occupies this orbital") or does not. If no other electron does so for this wavefunction, it is called an "unoccupied" or "virtual" orbital. While occupied orbitals have the occupation number 1, virtuals do have the occupation number 0. A completely unpopulated state (a state that contains no electrons), also referred to as the vacuum state, is thus represented as

$$|\Psi_{vac}\rangle = |0_p, ..., 0_q\rangle \equiv |0\rangle . \tag{1.12}$$

At this point, the so-called creation and annihilation operators, denoted as $\hat{a}^\dagger$ and $\hat{a}$, respectively, may be introduced by their action onto a state as

$$\hat{a}_p^\dagger |0_p\rangle = |1_p\rangle \qquad \hat{a}_p |1_p\rangle = |0_p\rangle . \tag{1.13}$$

In a general way, the action of these operators onto a multi-particle wavefunction is

$$\begin{aligned}\hat{a}_q^\dagger \,|\zeta_p, ..., 0_q, ..., \zeta_r\rangle &= \Gamma_q \; \delta_{0,\zeta_q} \,|\zeta_p, ..., 1_q, ..., \zeta_r\rangle \\ \hat{a}_q^\dagger \,|\zeta_p, ..., 1_q, ..., \zeta_r\rangle &= \Gamma_q \; \delta_{1,\zeta_q} \,|\zeta_p, ..., 0_q, ..., \zeta_r\rangle\end{aligned} \tag{1.14}$$

where $\zeta = \{0, 1\}$ denotes the occupation number and Γ being the phase factor

$$\Gamma_p = \prod_{n=1}^{p-1} -1^{\zeta_n}. \tag{1.15}$$

The phase factor may be understood by permuting the corresponding orbital to the leftmost position of the Ket-state (the rightmost for a Bra-state) and then acting on it. For an even number of electron permutations, $\Gamma = 1$ holds, while for an odd number, $\Gamma = -1$ holds. Also, as equation 1.14 demonstrates, the creation and annihilation operators will only yield a non-zero result if the respective orbital acted on is virtual (for creators, $\delta_{0,\zeta_p} = 1$) or occupied (for annihilators, $\delta_{1,\zeta_p} = 1$), respectively.

It should be noted that the common nomenclature, as also used throughout this work, is labelling orbitals $i, j, k, l, ...$ when referring to them as occupied, $a, b, c, d, ...$ when virtual as well as $p, q, r, s, ...$ when referring to them in a general sense.

Anticommutation relations and Normal ordering

Due to their definition (eqs. 1.13, 1.14), second-quantized operators posses an anti-commutator relation amongst each other, that is

$$\begin{aligned}[\hat{a}_p^\dagger \hat{a}_q^\dagger] &= \hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = 0 \\ [\hat{a}_p \hat{a}_q] &= \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0 \\ [\hat{a}_p^\dagger \hat{a}_q] &= \hat{a}_p^\dagger \hat{a}_q + \hat{a}_q \hat{a}_p^\dagger = \delta_{pq},\end{aligned} \tag{1.16}$$

or, formulated differently,

$$\hat{a}_p^\dagger \hat{a}_q^\dagger = -\hat{a}_q^\dagger \hat{a}_p^\dagger \qquad \hat{a}_p \hat{a}_q = -\hat{a}_q \hat{a}_p \qquad \hat{a}_p^\dagger \hat{a}_q = \delta_{pq} - \hat{a}_q \hat{a}_p^\dagger. \tag{1.17}$$

A normal-ordered string of second-quantized operators may now be defined as a string where all annihilation operators stand on the right of all creation operators[15], or equivalently, where all creation operators stand on the left of all annihilation operators. Introducing normal-ordering facilitates the evaluation of strings of creation and annihilation operators, for example, by identifying combinations that yield zero. By definition of the normal-ordering, the expectation value of a normal-ordered string $\{\hat{S}\}$ (commonly denoted by curly brackets or colons in the literature) with respect to the vacuum state must vanish,

$$\langle 0|\{\hat{S}\}|0\rangle = 0. \tag{1.18}$$

Taking, as examples, the two simple strings

$$\hat{S} = \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \qquad \hat{T} = \hat{a}_p^\dagger \hat{a}_q \hat{a}_r^\dagger \tag{1.19}$$

it it obvious that $\hat{S}$ is already in normal order ($\hat{S} \equiv \{\hat{S}\}$) while $\hat{T}$ may be brought into normal order by using the anti-commutation relations presented above:

$$\{\hat{T}\} = \delta_{qr}\hat{a}_p^\dagger - \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r. \tag{1.20}$$

An arbitrary string of creation and annihilation operators may be therefore translated into a set of normal-ordered strings in an iterative manner by re-applying these rules. Defining the contraction of two arbitrary second-quantized operators $\hat{\alpha}$ and $\hat{\beta}$ as

$$\hat{\alpha}^\bullet \hat{\beta}^\bullet = \hat{\alpha}\hat{\beta} - \{\hat{\alpha}\hat{\beta}\} \tag{1.21}$$

enables the reformulation of the anti-commutator relations (eqs. 1.16, 1.17) in a more elegant way as

$$\hat{a}_p^{\dagger\bullet} \hat{a}_q^{\dagger\bullet} = \hat{a}_p^\bullet \hat{a}_q^\bullet = \hat{a}_p^{\dagger\bullet} \hat{a}_q^\bullet = 0 \qquad \hat{a}_p^\bullet \hat{a}_q^{\dagger\bullet} = \delta_{pq}, \tag{1.22}$$

where only the non-normal-ordered combination $\hat{a}_p \hat{a}_q^\dagger$ will yield a non-zero result.

Wick's theorem

The reformulation of a string of second-quantized operators is, of course in general, a much more tedious task as the easy example of a three-operators string given above. A generalized way to compute the linear combination of normal-ordered strings arising from an arbitrary string of creation and annihilation operators is introduced by Wick's theorem[109]. It states that an arbitrary string of creation and annihilation operators $\hat{\alpha}\hat{\beta}\hat{\gamma}...\hat{\delta}\hat{\epsilon}\hat{\zeta}$ may be reformulated as a linear combination of normal-ordered strings according to

$$\begin{aligned} \hat{\alpha}\hat{\beta}\hat{\gamma}...\hat{\delta}\hat{\epsilon}\hat{\zeta} &= \{\hat{\alpha}\hat{\beta}\hat{\gamma}...\hat{\delta}\hat{\epsilon}\hat{\zeta}\} \\ &+ \sum_{\substack{single\\contractions}} \{\hat{\alpha}^{\bullet}\hat{\beta}^{\bullet}\hat{\gamma}...\hat{\delta}\hat{\epsilon}\hat{\zeta}\} \\ &+ \sum_{\substack{double\\contractions}} \{\hat{\alpha}^{\bullet}\hat{\beta}^{\bullet}\hat{\gamma}^{\bullet\bullet}...\hat{\delta}^{\bullet\bullet}\hat{\epsilon}\hat{\zeta}\} \\ &+ ... \\ &+ \sum_{\substack{full\\contraction}} \{\hat{\alpha}^{\bullet}\hat{\beta}^{\bullet}\hat{\gamma}^{\bullet\bullet}...\hat{\delta}^{\bullet\bullet}\hat{\epsilon}^{\bullet\bullet\bullet}\hat{\zeta}^{\bullet\bullet\bullet}\}. \end{aligned} \tag{1.23}$$

This means that the string can be rewritten by applying all pairwise operator contractions in the manifold of a single contraction, two contractions etc. up to a fully contracted scheme that includes all operators. For the expectation value with respect to the vacuum state (eq. 1.18),

$$\langle 0|\hat{\alpha}\hat{\beta}\hat{\gamma}...\hat{\delta}\hat{\epsilon}\hat{\zeta}|0\rangle\,, \tag{1.24}$$

only the fully contracted scheme, i. e. where every operator is paired up with another one via contraction and no uncontracted operators remain, may produce a result that differs from zero.

For notation brevity, the curly brackets to denote normal-ordered strings are omitted through the rest of this work, understanding all second-quantized strings as normal-ordered.

General operators in second quantization

Using the formalism introduced in the previous section, general one- and two-electron operators take the form

$$\hat{O}_1 = P_1 \sum_{pq} O_{pq} \hat{a}_p^\dagger \hat{a}_q \tag{1.25}$$

and

$$\hat{O}_2 = P_2 \sum_{pqrs} O_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r, \tag{1.26}$$

respectively. O_{pq} and O_{pqrs} represent the matrix elements for the operator in the underlying basis. P_1 and P_2 represent the, in a general formulation, complex prefactors which are often restricted to the real number space.

1.4. Hartree-Fock theory

Introduced as early as 1935, the Hartree-Fock method[43,34,44,94] represents the most fundamental method for modern quantum chemical calculations. It has been established as the starting point for most wavefunction-based state-of-the-art methods. The Hartree-Fock method seeks to find the best possible description of the atomic or molecular ground state in a variational way for a single ground-state wavefunction. To this end, a product ansatz, the so-called Hartree product, is chosen to parametrize the total wavefunction,

$$|\Phi(\vec{r}_1 ... \vec{r}_N)\rangle = |\phi_1(\vec{r}_1).....\phi_N(\vec{r}_N)\rangle \equiv |\phi_1 ... \phi_N\rangle . \tag{1.27}$$

In this ansatz, Φ is formed as a product of single-electron molecular orbitals ϕ_i. The molecular Hamiltonian is now acting on each molecular orbital individually,

$$\hat{H}\,|\Phi\rangle = \left(\hat{H}_i + ... + \hat{H}_N\right)\, \phi_i(\vec{r}_i)...\phi_N(\vec{r}_N) = E\,|\Phi\rangle . \tag{1.28}$$

assuming that the single electronic wavefunctions are uncorrelated, yielding the total energy E of the system as a sum of the single-electron energies ϵ_i. To form a fermionic wavefunction, the Hartree product is now antisymmetrized with respect to all orbitals and coordinates (see eq. 1.10),

$$|\Phi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \cdots & \phi_N(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_N) & \cdots & \phi_N(\vec{r}_N) \end{vmatrix} \tag{1.29}$$

which gives the so-called Slater determinant[90,94]. This fully antisymmetrized and normalized wavefunction is able to parametrize spin-pure eigenstates of a given electronic system, i. e. in a proper linear combination for singlet or triplet states as configuration state fucntions[46]. It is important to note that the short hand notation for the Hartree product is in general used in the literature to describe the fully antisymmetrized Slater determinant of the form 1.29.
The Hartree-Fock Hamiltonian acting on a single molecular orbital is divided into two parts, the one-electron part

$$\hat{h}_i(\vec{r}_1) = -\frac{1}{2}\,\hat{\nabla}(\vec{r}_1) - \sum_{k=1}^{X} \frac{Z_k}{|\vec{r}_k - \vec{r}_1|} \tag{1.30}$$

including kinetic energy of the electron and the electron-nuclei attraction as well as the part to describe the electron-electron interaction,

$$\hat{J}_i(\vec{r}_1) = \int d^3\vec{r}_2\, \frac{\phi_j^\star(\vec{r}_2)\,\phi_j(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\,, \quad \hat{K}_i(\vec{r}_1) = \int d^3\vec{r}_2\, \frac{\phi_j^\star(\vec{r}_2)\,\phi_i(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}. \tag{1.31}$$

The first term in equation 1.31, $\hat{J}$ can be interpreted classically as the Coulomb term that describes the electrostatic potential arising from a charge distribution at $\vec{r}_2$. For the second term $\hat{K}$, on the other hand, no classical interpretation exists, making this term a purely quantum mechanical effect. As such, the so-called exchange term is due to the fermionic nature of the wavefunction.
Summarizing the operators in equation 1.30 and 1.31 gives the Fock operator

$$\hat{f} = \hat{h}_i + \sum_j \hat{J}_j - \sum_j \hat{K}_j \tag{1.32}$$

At this pont, it is now straightforward to define the two-electron integrals for the Coulomb and exchange operator as

$$\langle \phi_i(\vec{r}_1)|\, \hat{J}_j(\vec{r}_1)\, |\phi_i(\vec{r}_1)\rangle \equiv \langle ij|ij\rangle \tag{1.33}$$

and

$$\langle\phi_i(\vec{r}_1)|\,\hat{K}_j(\vec{r}_1)\,|\phi_i(\vec{r}_1)\rangle \;\equiv\; \langle ij|ji\rangle\,. \tag{1.34}$$

as well as the antisymmetrized two-electron integral, also called electron repulsion integral (ERI) as

$$\langle ij||ij\rangle \;\equiv \langle ij|ij\rangle - \langle ij|ji\rangle\,. \tag{1.35}$$

Using the short-hand notation of equation 1.35, the Fock operator in equation 1.32 acting on a single orbital may be evaluated as

$$\hat{f}\phi_i \;=\; f_i\phi_i \;=\; \left(h_{ii} + \sum_{j\neq i}\langle ij||ij\rangle\right)\phi_i \;=\; \epsilon_i\phi_i, \tag{1.36}$$

where canonical orbitals (orbitals that diagonalize the Fock operator, $f_{ij} = \delta_{ij}f_i$) have been assumed. For the atomic or molecular ground state, the Hartree-Fock energy is now given as the expectation value of the full Hamiltonian (eq. 1.28) with respect to the Hartree-Fock ground state wavefunction $|\Phi_0\rangle$,

$$E_{HF} \;=\; \langle\Phi_0|\hat{H}|\Phi_0\rangle \;=\; \sum_i h_{ii} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \;=\; \sum_i \epsilon_i - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle\,. \tag{1.37}$$

In the formalism of second quantization, the Hartree-Fock Hamiltonian (usually denoted as $\hat{F}$) takes the general form

$$\hat{F} \;=\; \sum_{pq} f_{pq}\hat{a}_p^\dagger\hat{a}_q \;=\; \sum_{pq} h_{pq}\hat{a}_p^\dagger\hat{a}_q + \sum_{i,pq}\langle pi||qi\rangle\,\hat{a}_p^\dagger\hat{a}_q \tag{1.38}$$

The Hartree-Fock energy is a suited and computationally cheap method to recover about 95%[76] of the atomic or molecular ground state energy, however, the lack of explicit electron-electron correlation makes it unsuitable for highly accurate calculations. More elaborate electronic structure methods, the so-called Post-Hartree-Fock methods therefore aim to recover the correlation energy,

$$E_{corr} \;=\; E_{tot} - E_{HF}, \tag{1.39}$$

that constitutes the energy difference between the total (exact) energy of the electronic system and the Hartree-Fock energy.

Roothaan-Hall equations and the self-consistent filed procedure

The introduction of a suited basis set of atomic orbitals to parametrize the molecular orbitals (LCAO ansatz, see eq. 1.6) allows to rewrite the Hartree-Fock eigenvalue equation in 1.36 as

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} \;=\; \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \;\text{ or in matrix notation }\; \mathbf{FC} \;=\; \epsilon\, \mathbf{SC}. \tag{1.40}$$

This equation, the so-called Roothaan-Hall equation[77,40], introduces the Fock matrix $F_{\mu\nu}$ as

$$F_{\mu\nu} = \langle \phi_\mu | \hat{f} | \phi_\nu \rangle \tag{1.41}$$

as well as the overlap matrix of the (generally not orthogonal) basis functions $S_{\mu\nu}$ as

$$S_{\mu\nu} \;=\; \langle \phi_\mu | \phi_\nu \rangle \,. \tag{1.42}$$

The matrix of coefficients $C_{\mu i}$ stem from the LCAO ansatz.

A practical way to solve the Hartree-Fock equations is now achieved by the so-called self-consistent field approach (SCF or HF-SCF)[94]. The idea is to use an iterative rule that is reapplied to equation 1.40 until the computed eigenvalue does not differ more than a certain threshold in two consecutive iteration steps, and thus, has reached self-consistency. This is done by starting off with an initial guess for the electron density of the system (for **C**), calculating and diagonalizing **F** and forming new coefficients in **C**. The solution of the Hartree-Fock self-consistent field method is the starting point for more elaborate methods, as the eigenvalue of a converged Hartree-Fock wavefunction always presents a lower bound to the exact energy of the system (see equation 1.39),

$$E_{HF}(\Phi_0) \;=\; \frac{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} \;\leq\; E_{tot}. \tag{1.43}$$

Brillouin's theorem and the Slater-Condon rules

An important feature of a converged Hartree-Fock wavefunction is formulated by Brillouin's theorem[94,46]. It states that the matrix element of the electronic Hamiltonian between a singly excited determinant and the converged Hartee-Fock ground state wavefunction is zero,

$$\langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = 0. \tag{1.44}$$

Additionally, in a general sense, the Slater-Condon rules[90,94,46] state that the matrix element for an arbitrary one-electron operator $\hat{O}_1$ vanishes if the Bra and Ket for an arbitrary determinant $|\Psi\rangle$ differ in more than one spin orbital. Analogously, for an arbitrary two-electron operator $\hat{O}_2$, both may only differ by at maximum two spin orbitals:

$$\begin{aligned} \langle \Psi_{rs}^{pq} | \hat{O}_1 | \Psi \rangle &= 0, \\ \langle \Psi_{stu}^{pqr} | \hat{O}_2 | \Psi \rangle &= 0. \end{aligned} \tag{1.45}$$

The Slater-Condon rules constitute fundamental principles in the application of electron correlation methods, as their implications are used throughout this work.

Fermi vacuum and particle-hole formalism

Although the true vacuum state $|0\rangle$ may be used to generate any physically allowed population of electrons, it is more useful and intuitive to utilize the so-called Fermi vacuum when working with second-quantized operators, instead. The Fermi vacuum is represented by the underlying reference state $|\Phi_0\rangle$, all one-electron states populated (occupied with indices $i, j, k, ...$) in $|\Phi_0\rangle$ are denoted as hole states, while unpopulated (virtual with indices $a, b, c, ...$) states are denoted as particle states. The particle-hole formalism[15,46] is intuitively understood by the application of creation and annihilation operators: The process

$$\hat{a}_a^\dagger \hat{a}_i \, |\Phi_0\rangle = |\Phi_i^a\rangle \tag{1.46}$$

promotes an electron from an occupied to a virtual orbital creating both, a hole ($\hat{a}_i$) in the occupied space as well as a particle ($\hat{a}_a^\dagger$) in the virtual space. De-excitation would then annihilate a particle ($\hat{a}_a$) in the virtual space and by putting it back into the occupied space also annihilate a hole ($\hat{a}_i^\dagger$) in there,

$$\hat{a}_i^\dagger \hat{a}_a \, |\Phi_i^a\rangle = |\Phi_0\rangle \, . \tag{1.47}$$

These so-called quasi-particle operators, often abbreviated as q-creators and q-annihilators, establish a very useful framework for the application of Wick's theorem or a diagrammatic approach to quantum chemistry[15,46]. Using the above definitions, the fundamental contraction rules of second-quantized operators in equation 1.22 may now be reformulated for q-creators and q-annihilators according to

$$\begin{aligned} \hat{a}_p^{\dagger\bullet}\hat{a}_q^{\dagger\bullet} &= \hat{a}_p^{\bullet}\hat{a}_q^{\bullet} = 0 \\ \hat{a}_i^{\dagger\bullet}\hat{a}_a^{\bullet} = \hat{a}_a^{\bullet}\hat{a}_i^{\dagger\bullet} &= \hat{a}_a^{\dagger\bullet}\hat{a}_b^{\bullet} = \hat{a}_i^{\bullet}\hat{a}_j^{\dagger\bullet} = 0 \\ \hat{a}_i^{\dagger\bullet}\hat{a}_j^{\bullet} &= \delta_{ij} \\ \hat{a}_a^{\bullet}\hat{a}_b^{\dagger\bullet} &= \delta_{ab}. \end{aligned} \tag{1.48}$$

1.5. Perturbation theory

The need for a mathematical formalism of treating small deviations to an otherwise well-described eigenvalue problem, i. e. a small perturbation to an operator, emerged as early as the formulation of quantum mechanics itself. The most common approach, the Rayleigh-Schrödinger perturbation theory[87,89], assumes that the complete spectrum of the eigenvalue equation for a Hamiltonian $\hat{H}_0$ is known,

$$\hat{H}_0 \, |\Psi_i^{(0)}\rangle = E_i^{(0)} \, |\Psi_i^{(0)}\rangle \, . \tag{1.49}$$

As a requirement, the set of eigenfunctions to the unperturbed Hamiltonian $\{|\Psi_i^{(0)}\rangle\}$ is orthonormal. A small perturbation $\hat{H}_P$ is now introduced to the Hamiltonian,

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_P, \tag{1.50}$$

which is assumed to change the spectrum of the Hamiltonian only on small scales. The new eigenvalue equation for the perturbed Hamiltonian $\hat{H}$ reads then

$$\hat{H} \, |\Psi_i\rangle = (\hat{H}_0 + \lambda \hat{H}_P) \, |\Psi_i\rangle = E_i \, |\Psi_i\rangle \tag{1.51}$$

where λ is introduced as an ordering parameter. The eigenfunctions and eigenstates of the perturbed system are parametrized using an infinite series for the wavefunction

$$|\Psi_i\rangle \;=\; |\Psi_i^{(0)}\rangle \;+\; \lambda\,|\Psi_i^{(1)}\rangle \;+\; \lambda^2\,|\Psi_i^{(2)}\rangle \;+\; ... \;=\; \sum_{n=1}^{\infty} \lambda^n\,|\Psi_i^{(n)}\rangle \tag{1.52}$$

and for the energy

$$E_i \;=\; E_i^{(0)} \;+\; \lambda E_i^{(1)} \;+\; \lambda^2 E_i^{(2)} \;+\; ... \;=\; \sum_{n=1}^{\infty} \lambda^n E_i^{(n)}. \tag{1.53}$$

Inserting the expressions for the perturbed wavefunction (equation 1.52) and the perturbed energy (equation 1.53) into equation 1.51 and using the order parameter λ to regroup terms yields

$$\begin{aligned} \hat{H}_0\,|\Psi_i^{(0)}\rangle \;&=\; E_i^{(0)}\,|\Psi_i^{(0)}\rangle \\ \lambda\hat{H}_0\,|\Psi_i^{(1)}\rangle \;+\; \lambda\hat{H}_P\,|\Psi_i^{(0)}\rangle \;&=\; \lambda E_i^{(0)}\,|\Psi_i^{(1)}\rangle \;+\; \lambda E_i^{(1)}\,|\Psi_i^{(0)}\rangle \\ \lambda^2\hat{H}_0\,|\Psi_i^{(2)}\rangle \;+\; \lambda^2\hat{H}_P\,|\Psi_i^{(1)}\rangle \;&=\; \lambda^2 E_i^{(0)}\,|\Psi_i^{(2)}\rangle \;+\; \lambda^2 E_i^{(1)}\,|\Psi_i^{(1)}\rangle \;+\; \lambda^2 E_i^{(2)}\,|\Psi_i^{(0)}\rangle \\ \cdots \;&=\cdots \end{aligned} \tag{1.54}$$

or, in the general form,

$$\left\{\left(\hat{H}_0 + \lambda\hat{H}_P\right)\sum_{n=1}^{\infty}\lambda^n\,|\Psi_i^{(n)}\rangle\right\}_{\Pi(\lambda)=C} \;=\; \left\{\left(\sum_{n=1}^{\infty}\lambda^n E_i^{(n)}\right)\left(\sum_{n=1}^{\infty}\lambda^n\,|\Psi_i^{(n)}\rangle\right)\right\}_{\Pi(\lambda)=C} \tag{1.55}$$

where the curly brackets indicate that all terms with the same perturbation order, i. e. the same power of λ (as the factor C equals $1, \lambda, \lambda^2, \lambda^3, ...$) are grouped together. The parameter λ thus is an artificial one to switch the perturbation on and off and order the terms of the perturbation series, for the solution of the eigenvalue problem itself it has no meaning and can be omitted. Choosing the wavefunction correction of 1.52 to be orthogonal to $|\Psi_i^{(0)}\rangle$ introduces the so-called intermediate normalization

$$\langle\Psi_i^{(0)}|\Psi_i\rangle \;=\; \langle\Psi_i^{(0)}|\Psi_i^{(0)}\rangle \;=\; 1 \tag{1.56}$$

and allows to reformulate the expansion of equation 1.54 as

$$\begin{aligned}\langle\Psi_i^{(0)}|\ \hat{H}_0\ |\Psi_i^{(0)}\rangle &= E_i^{(0)}\\ \langle\Psi_i^{(0)}|\ \hat{H}_P\ |\Psi_i^{(0)}\rangle &= E_i^{(1)}\\ \langle\Psi_i^{(0)}|\ \hat{H}_P\ |\Psi_i^{(1)}\rangle &= E_i^{(2)}.\end{aligned} \tag{1.57}$$

Wave-function corrections may be obtained in a similar way by projecting the zeroth-order expression $\langle\Psi_i^{(0)}|$ from the left onto the expansion in equation 1.54. As the eigenfunctions of $\hat{H}_0$ constitute an orthonormal basis ($\langle\Psi_i^{(0)}|\Psi_j^{(0)}\rangle = \delta_{ij}$), the expansion coefficients for $i \neq j$ are obtained as

$$C_{ij}^{(n)} = \langle\Psi_j^{(0)}|\Psi_i^{(n)}\rangle\,, \tag{1.58}$$

which, as an example, would be in first-order

$$C_{ij}^{(n)} = \frac{\langle\Psi_j^{(0)}|\hat{H}_P|\Psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}. \tag{1.59}$$

Møller-Plesset perturbation theory

The lack of explicit electron-electron correlation within the Hartree-Fock framework introduces a new manifold of electronic structure methods, the Post-Hartree-Fock methods. As an application of quantum-mechanical perturbation theory, the Møller-Plesset perturbation theory[69,94,54] is presented in the following.

Starting with the full electronic Hamiltonian $\hat{H}$ containing a one- as well as two-electron part,

$$\hat{H} = \sum_{pq} h_{pq}\hat{a}_p^\dagger\hat{a}_q + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\,\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r, \tag{1.60}$$

and recalling the Hartree-Fock Hamiltonian from equation 1.38,

$$\hat{F} = \sum_{pq} h_{pq}\hat{a}_p^\dagger\hat{a}_q + \sum_{i,pq}\langle pi||qi\rangle\,\hat{a}_p^\dagger\hat{a}_q,$$

all explicit electron-electron correlation effects may now be parametrized in the two-electron part with the so-called fluctuation potential $\hat{V}$ defined as

$$\hat{V} = -\sum_{i,pq} \langle pi||qi\rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r. \tag{1.61}$$

The sum of both, $\hat{F}$ and $\hat{V}$ as defined above, is reproducing the full electronic Hamiltonian of equation 1.60 exactly. Starting from a converged Hartree-Fock ground state solution, $\hat{F}$ may be simplified as

$$\hat{F} = \sum_p \epsilon_p \hat{a}_p^\dagger \hat{a}_p.$$

In the framework of Rayleigh-Schrödinger perturbation theory, $\hat{V}$ is now introduced as the perturbation in analogy to $\hat{H}_P$ in equation 1.50, while $\hat{F}$ constitutes the unperturbed Hamiltonian $\hat{H}_0$. This partitioning, called the Møller -Plesset partitioning[48] of the electronic Hamiltonian, enables the effective computation of perturbative energy and wavefunction corrections for a well-described unperturbed system, which constitutes the premise of Rayleigh-Schrödinger perturbation theory. The Møller-Plesset Hamiltonian can now be formulated as:

$$\hat{H}_{MP} = \hat{F} + \lambda\hat{V} = \sum_p \epsilon_p \hat{a}_p^\dagger \hat{a}_p + \lambda\Big(-\sum_{i,pq} \langle pi||qi\rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\Big). \tag{1.62}$$

Applying the generating formula (eq. 1.55) to the Møller-Plesset Hamiltonian $\hat{H}_{MP}$ of 1.62 allows for the formulation of the MP energy and wavefunction corrections. The zeroth-order wavefunction is then given as the Hartree-Fock ground state wavefunction, $|\Psi_0^{(0)}\rangle = |\Phi_0\rangle$. The wavefunction corrections are formulated in a CI-like ansatz[94] of excited determinants (which constitute eigenfunctions of the Fock operator $\hat{F}$),

$$|\Psi_0^{(n)}\rangle = \sum_{i,a} t_i^{a(n)} |\Phi_i^a\rangle + \sum_{i,a} t_{ij}^{ab^{(n)}} |\Phi_{ij}^{ab}\rangle + ... \tag{1.63}$$

where the so-called t-amplitudes in the Møller-Plesset formulation represent the expansion coefficients C from equation 1.58 in the Rayleigh-Schrödinger formulation. For a first-order treatment (MP1), the exact Hartree-Fock energy is recovered[94]. A first improvement of the HF ground state is introduced by the second-order MP2 scheme, where the corresponding energy correction (see 1.57) is given as

$$E_0^{(2)} = \frac{1}{4}\sum_{ij,ab} t_{ij}^{ab(1)} \langle ij||ab\rangle = \frac{1}{4}\sum_{ij,ab} \frac{\langle ab||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \langle ij||ab\rangle \tag{1.64}$$

along with the first-order wave-function correction (see 1.59) for the ground state

$$|\Psi_0^{(1)}\rangle = \frac{1}{4}\sum_{ij,ab} t_{ij}^{ab(1)} |\Phi_{ij}^{ab}\rangle = \frac{1}{4}\sum_{ij,ab} \frac{\langle ab||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} |\Phi_{ij}^{ab}\rangle\,. \tag{1.65}$$

Higher-order expressions as well as a diagrammatic approach to determine Møller-Plesset working equations are presented in the literature[46,94].

1.6. Configuration Interaction

Among the Post-Hartree-Fock methods, the most straightforward and simplest is the so-called Configuration Interaction[46,54]. It expands the Hartree-Fock ground state by including virtual orbitals, that is, exciting electrons from occupied orbitals and populating previously unoccupied ones. This may be done for one, two, n electrons simultaneously, leading to different excitation classes. In a second-quantized form, these excitation operators may be written as

$$\hat{C}_{CI} = 1 + \hat{C}_{CI,S} + \hat{C}_{CI,D} + \ldots = 1 + \sum_{ia} c_S\, \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4}\sum_{ijab} c_D\, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \ldots \tag{1.66}$$

where the coefficients c are the amplitude coefficients of the corresponding excitation. The CI wavefunction ansatz then simply reads

$$\begin{aligned} |\Psi_{CI}\rangle &= \hat{C}_{CI}\, |\Phi_0\rangle\,, \\ |\Psi_{CI}\rangle &= |\Phi_0\rangle + \sum_{ia} c_S\, |\Phi_i^a\rangle + \frac{1}{4}\sum_{ijab} c_D\, |\Phi_{ij}^{ab}\rangle + \ldots \end{aligned} \tag{1.67}$$

where the lower line of equation 1.67 is the fully expanded form including excited determinants. The CI eigenvalue equation

$$\hat{H}\,|\Psi_{CI}\rangle = E_{CI}\,|\Psi_{CI}\rangle \tag{1.68}$$

may be solved in an iterative manner using the variational principle. To this end, it is common to choose intermediate normalization $\langle \Psi_{CI} | \Phi_0 \rangle = 1$. A truncation of the full CI scheme is labelled respectively, i. e. the truncation of the full scheme to singles and doubles excitations is labelled as CISD (Configuration Interaction for Singles and Doubles). The FCI (full CI) scheme without truncations for an N-electron system goes up to the N-th excitation class and represents an exact parametrization of the electronic Schrödinger equation. However, the treatment of molecules with FCI is limited to small systems due to the computational cost of the full CI expansion.

1.7. Coupled Cluster

The Coupled Cluster[15,7,5,46] formalism represents one of the most commonly used methods in quantum chemistry. Its wavefunction is an exponential ansatz of the so-called cluster operator $\hat{T}$,

$$|\Psi_{CC}\rangle \;=\; exp(\hat{T}) \cdot |\Phi_0\rangle\,, \tag{1.69}$$

where, just as in Configuration Interaction, the different excitation classes and their respective amplitudes t are represented as

$$\hat{T} \;=\; \hat{T}_1 + \hat{T}_2 + ... \;=\; \sum_{ia} t_i^a \; \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \; \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + ... \tag{1.70}$$

with a general prefactor of $(n!)^{-2}$ for the n-th excitation class. Truncating the cluster operator after the singly (S), doubly (D) etc. excitation class leads to the respective scheme, for instance with singles and doubles labelled CCSD. The Taylor expansion for the exponential function,

$$e^{\hat{T}} \;=\; 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + ..., \tag{1.71}$$

represents a power series of the cluster operator. As a difference to the linear CI ansatz (equation 1.67), the CC ansatz gives a product form of the cluster operators (e. g. $\hat{T}^2 = \hat{T}_1^2 + 2\hat{T}_1\hat{T}_2 + \hat{T}_2^2$ for CCSD), introducing size consistency as a fundamental property of Coupled Cluster.

Using the CC wavefunction (equation 1.69), the Coupled cluster working equations are formulated as

$$\begin{aligned}\langle\Phi_0|\,\hat{H}e^{\hat{T}}\,|\Phi_0\rangle &= E_{CC}\\ \langle\Phi_I|\,\hat{H}e^{\hat{T}}\,|\Phi_0\rangle &= E_{CC}\,\langle\Phi_I|\,e^{\hat{T}}\,|\Phi_0\rangle\end{aligned} \tag{1.72}$$

with the upper equation representing the CC energy equation and the lower equation representing the CC amplitude equations, with the example of CCSD, the working equations for the calculation of singles and doubles amplitudes. As before for Configuration Interaction, intermediate normalization was chosen, $\langle\Psi_{CC}|\Phi_0\rangle = 1$. By introducing the so-called similarity-transformed Hamiltonian $\bar{H}$ [15] as

$$\bar{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}, \tag{1.73}$$

the equations 1.72 may be decoupled and solved individually, yielding the common CC working equations

$$\begin{aligned}\langle\Phi_0|\,\bar{H}\,|\Phi_0\rangle &= E_{CC},\\ \langle\Phi_I|\,\bar{H}\,|\Phi_0\rangle &= 0\end{aligned} \tag{1.74}$$

for the CC amplitudes and energy, respectively. Amplitude equations are solved iteratively and coupled (e. g. in the singles and doubles space for CCSD) until a self-consistency is reached, the converged amplitudes are then plugged into the energy equation to yield the corresponding value.

Baker-Campbell-Hausdorff formula

Including an exponential ansatz in the similarity-transformed Hamiltonian, the approach to solve the CC working equations 1.74 is the so-called Baker-Campbell-Hausdorff (BCH) identity,

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + ... \tag{1.75}$$

which reformulates the exponential ansatz in a power series of nested commutators (remember that $[\hat{H},\hat{T}]$ simply means $\hat{H}\hat{T} - \hat{T}\hat{H}$). The solution of the CC working equations is now issue to the solution of the BCH expansion for the Hamiltonian.

Diagrams in Coupled Cluster theory

The application of diagrams in quantum chemistry has become a common and useful task[84,66] and facilitates the work with strings of second-quantized operators, as will be shortly presented in the following.

Computation of the Coupled Cluster working equations (1.74) applying the BCH expansion (1.75) may be executed in several ways, the most straightforward being the application of Wick's theorem. The strings of creation and annihilation operators that arise from the different fragments in the BCH expansion, namely the Hamiltonian fragments $\hat{F}$ and $\hat{V}$ as well as the amplitude fragments $\hat{T}$, are combined and then contracted. However, this is a very tedious task when executed by hand, and the applicability of a certain class of diagrams (Feynmnan diagrams) may be utilized to represent the terms in the CC working equations. At this point, a brief introduction to Coupled Cluster diagrams shall be given, as they are not only a suited tool to generate CC equations but also give a great framework for a better understanding of the Coupled Cluster (and later Unitary Coupled Cluster) formalism. A more detailed description can be found in the literature[15,48].

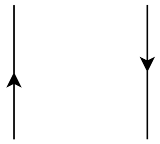

Figure 1.3.: Free particle line and free hole line.

As a starting point, consider the lines that represent the second-quantized operators. Lines that are directed upwards are particle lines acting on virtual orbitals $a, b, c, ...$ while downward directed ones are hole lines acting on occupied orbitals $i, j, k, ...$. These lines meet at the interaction vertices, at each of these exactly one line enters and one line leaves the vertex. Lines above the vertex correspond to creators, lines underneath to annihilators. For the one-particle operators, $\hat{F}$ and $\hat{D}$ (see eq. 1.25, $\hat{O}_1$), the diagrams are represented as

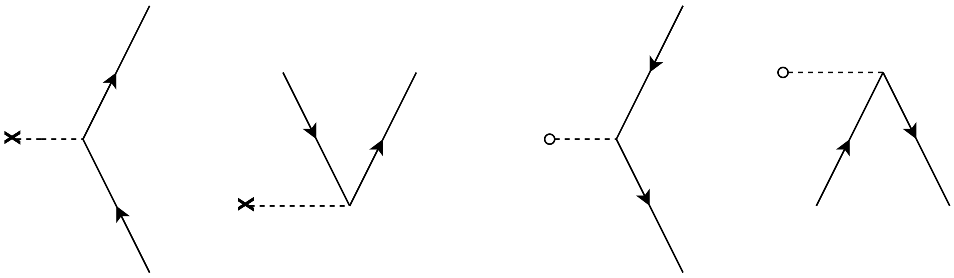

Figure 1.4.: Examples of diagram fragments for one-particle operators.

where the "X" represents the Fock matrix element and the circle the matrix element of an arbitrary one-particle operator. The diagrams in figure 1.4 thus represent the terms

$$\sum_{ab} f_{ab}\, \hat{a}_a^\dagger \hat{a}_b \qquad \sum_{ia} f_{ai}\, \hat{a}_a^\dagger \hat{a}_i \qquad \sum_{ij} d_{ij}\, \hat{a}_i^\dagger \hat{a}_j \qquad \sum_{ia} d_{ia}\, \hat{a}_i^\dagger \hat{a}_a. \tag{1.76}$$

Upon constructing the diagrams, general orbital indices are replaced by occupied and virtual orbital indices to produce all possible combinations. The direction of the lines in a diagram determines its so-called excitation number, that is, the number of electrons that are promoted from the occupied to the virtual space. Consider the two fragments of $\hat{F}$ in figure 1.4: The left one has two particle lines (both pointing upwards), one underneath the vertex and one above, therefore annihilating and creating a particle. This means that the electrons are shifted around within the virtual space, thus not exciting an electron and giving an excitation class of 0. The right one has two lines above the vertex, two creators, one acting on the hole and one on the particle space, promoting an electron and yielding an overall excitation number of $+1$. Similarly, the other two diagrams in figure 1.4 have the excitation classes 0 and -1, respectively. In general, the excitation class of a diagram may be calculated as:

$$\begin{aligned} \text{Excitation class} &= \frac{1}{2} \cdot (\text{Number of open creator lines} \\ &\qquad - \text{Number of open annihilator lines}). \end{aligned}$$

For the two-electron part $\hat{V}$, the diagrams take the form

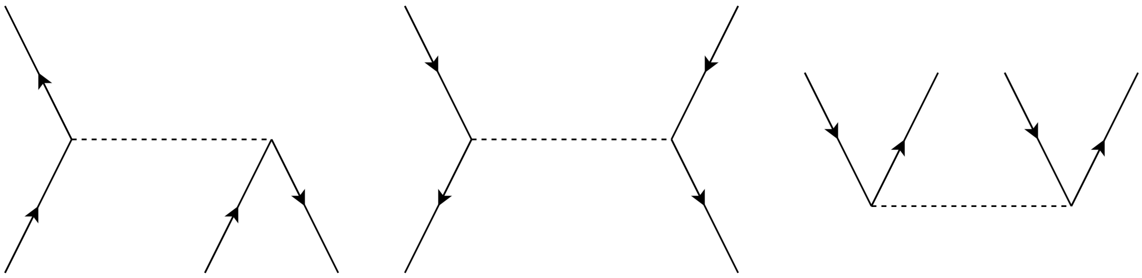

Figure 1.5.: Examples of diagram fragments for $\hat{V}$.

The corresponding terms are

$$\frac{1}{2}\sum_{iabc}\langle ai||bc\rangle\ \hat{a}_a^\dagger\hat{a}_i^\dagger\hat{a}_c\hat{a}_b \qquad \frac{1}{4}\sum_{ijkl}\langle ij||kl\rangle\ \hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k \qquad \frac{1}{4}\sum_{ijab}\langle ab||ij\rangle\ \hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_j\hat{a}_i \tag{1.77}$$

The two-electron part of the Hamiltonian includes nine individual contributions[15] (of which three are depicted above, excitation classes are from left to right: -1, 0, +2), three with excitation class 0, two with +1 and -1, respectively as well as one with +2 and one with -2. As a final diagram class, the amplitude fragments represent one-, two- or *n*-electron fragments and are given as

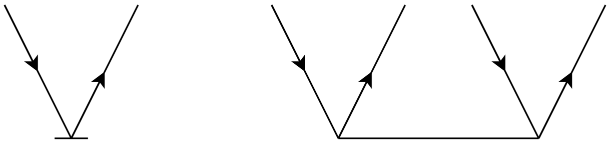

Figure 1.6.: Examples of diagram fragments for $\hat{T}$.

with the corresponding analytical expressions

$$\sum_{ia} t_i^a\ \hat{a}_a^\dagger\hat{a}_i \qquad \frac{1}{4}\sum_{ijab} t_{ij}^{ab}\ \hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_j\hat{a}_i \tag{1.78}$$

Amplitude fragments connect their vertices with a solid line in contrast to the dashed line for the $\hat{V}$ fragments. For Coupled Cluster, $\hat{T}$ diagram fragments always have a positive excitation number (+1 for the singles part $\hat{T}_1$, +2 for the doubles part $\hat{T}_2$ etc.).

Full Coupled Cluster diagrams are now obtained by combining the different fragments for $\hat{F}$, $\hat{V}$ and $\hat{T}$. As an example for the second term of the BCH expansion (the single commutator), the following diagrams may be constructed:

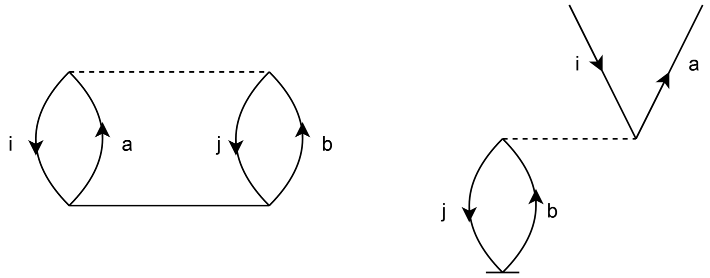

Figure 1.7.: Examples of two connected fragments, $\hat{V}$ and $\hat{T}_2$ on the left, $\hat{V}$ and $\hat{T}_1$ on the right.

Indices that start and end at a vertex are summation indices, i. e. they occur in a sum of the corresponding algebraic expression, while indices connected to only one vertex (open lines) are the target indices of the term. For the left diagram in figure 1.7, the type and algebraic expression are

$$\langle\Phi_0|\hat{H}|\Phi_0\rangle \leftarrow \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle\, t_{ij}^{ab}. \tag{1.79}$$

Indices are distributed for each fragment by using the rule left out, right out - left in, right in ("loro-liri"). If no open lines leave the diagram, either at the top or at the bottom, this gives rise to the ground-state determinant $|\Phi_0\rangle$. Therefore, this diagram is part of the CC ground state energy expression. A factor of $\frac{1}{4}$ needs to be added since the pair of internal lines begin and end at the same vertex, respectively. The prefactor is determined by $-1^{(h+l)}$ with h being the hole lines in a diagram and l being the closed loops, thus we find here $-1^4 = 1$. For the right diagram in figure 1.7, one finds

$$\langle\Phi_i^a|\hat{H}|\Phi_0\rangle \leftarrow \sum_{jb}\langle ja||bi\rangle\, t_j^b, \tag{1.80}$$

giving now rise to an amplitude diagram with the ground-state determinant on the right of the expression (on the bottom of the diagram) and the singly-excited determinant on the left (on top of the diagram, on open hole and particle line). The excitation level of the diagram is +1, therefore contributing to the singles amplitudes equation, for +2 it would be doubles and so on. A detailed set of construction rules can be found in the literature[15,48].

The Baker-Campbell-Hausdorff expansion (eq. 1.75) for the derivation of Coupled Cluster equations naturally truncates, as an example, for CCSD after the quadruply nested commutator. This becomes obvious when looking at the excitation levels of the diagrams: In the CCSD working equations, the highest excitation level that occurs is +2 for the doubles amplitudes part. Singles amplitudes have an excitation class of +1, meaning that the corresponding part for the fluctuation potential $\hat{V}$ with an excitation class of -2 may be combined with four singles amplitudes to yield an overall +2. For the doubles amplitudes, it is only the doubly nested commutator, since doubles amplitudes possess an excitation class of +2. As will be discussed later, in an Unitary Coupled Cluster[61,62] scheme, this very handy property of the BCH expansion is not valid any more, urging the introduction of a suitable truncation scheme.

A fundamental rule for the construction of CC diagrams is the so-called connectedness. The algebraic expressions of connected diagrams represent the only terms that do not vanish when evaluating the Baker-Campbell-Hausdorff expansion of nested commutators. Their definition is embedded in the following statement:

> *The only nonzero terms in the Hausdorff expansion are those in which the Hamiltonian has at least one contraction with every cluster operator on its right.*[15]

Connected diagrams may thus be immediately recognized by their form as they constitute a conjoined structure in a topological sense, while disconnected ones form separate structures that are not connected by any contraction (see figure 1.8).

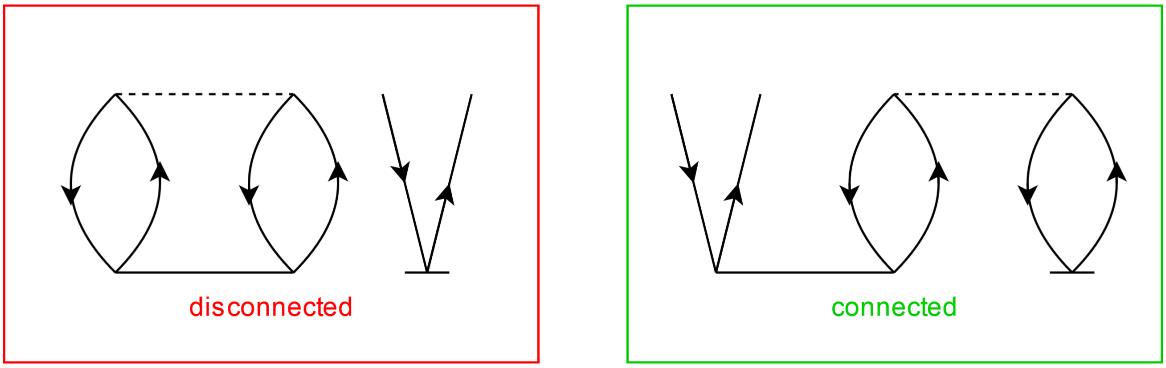

Figure 1.8.: Examples of a connected and an unconnected diagram.

Referring to the definition above, it is important to note that diagrams of the form in figure 1.9 do also count as connected diagrams, as the open fermion lines may be interpreted as "connected in infinity"[84]. However, this is only possible if the diagrammatic fragments contain open fermion lines and not, as the fragment on the left in figure 1.8, represent fully contracted expressions without open lines. These kind of diagrams arise, for instance, in the construction of the Unitary Coupled Cluster secular matrix.

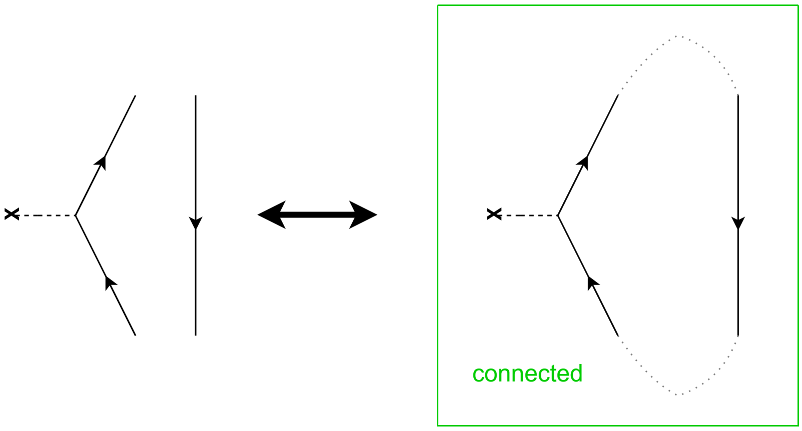

Figure 1.9.: Example of a connected diagram with open fermion lines.

As an example, the diagram above constitutes a part of the zeroth-order energy contribution,

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle^{(0)} \leftarrow f_{ab} \delta_{ij}, \tag{1.81}$$

as present in the singles/singles block for PP-UCC.

Equation-of-motion Coupled Cluster

To make Coupled Cluster also applicable to excited states, the so-called equation-of-motion ansatz for Coupled Cluster (EOM-CC)[5,46] is applied to the CC ground state $|\Psi_{CC}\rangle$,

$$|\Psi_{EOM}\rangle = \hat{\mathcal{R}} \, |\Psi_{CC}\rangle \,, \tag{1.82}$$

with $\hat{\mathcal{R}}$ being an excitation operator, just like $\hat{T}$ for the ground state, of the form

$$\hat{\mathcal{R}} = \hat{\mathcal{R}}_1 + \hat{\mathcal{R}}_2 + \ldots = \sum_{ia} r_i^a \, \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4} \sum_{ijab} r_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \ldots \tag{1.83}$$

where r represent the excitation amplitudes. Plugging the EOM wavefunction ansatz into the Schrödinger equation 1.1 and using the CC ground-state wavefunction parametrization 1.69, the EOM-CC eigenvalue equation is obtained,

$$\hat{H}\hat{\mathcal{R}}\,|\Psi_{CC}\rangle \;=\; E^{e}_{CC}\hat{\mathcal{R}}\,|\Psi_{CC}\rangle\,. \tag{1.84}$$

E^{e}_{CC} represents the excited state energy. Applying now the excitation operator of equation 1.83 to the CC ground state,

$$\hat{\mathcal{R}}\hat{H}\,|\Psi_{CC}\rangle \;=\; E_{CC}\hat{\mathcal{R}}\,|\Psi_{CC}\rangle\,, \tag{1.85}$$

and subtracting 1.85 from 1.84, the commutator expression

$$[\hat{H},\hat{\mathcal{R}}]\,|\Psi_{CC}\rangle \;=\; \Delta E^{e}_{CC}\hat{\mathcal{R}}\,|\Psi_{CC}\rangle \tag{1.86}$$

is obtained. This is where the name, equation-of-motion Coupled Cluser, comes from: The similarity to the equations of motion in quantum mechanics[89,12], which contain the commutator of the position with the momentum operator. ΔE^{e}_{CC} represents now the excitation energy as the difference of the total excited state energy and the ground-state energy, $\Delta E^{e}_{CC} \;=\; E^{e}_{CC} - E_{CC}$.

Inserting now the CC parametrization of the ground-state wavefunction (eq. 1.69) into the EOM ansatz (eq. 1.84),

$$\hat{H}\hat{\mathcal{R}}e^{\hat{T}}\,|\Phi_0\rangle \;=\; E^{e}_{CC}\hat{\mathcal{R}}e^{\hat{T}}\,|\Phi_0\rangle\,, \tag{1.87}$$

the EOM-CC working equation[5] may be reformulated using the similarity-transformed Hamiltonian to yield excited state energies as

$$[\bar{H},\hat{\mathcal{R}}]\,|\Phi_0\rangle \;=\; \Delta E^{e}_{CC}\,\hat{\mathcal{R}}\,|\Phi_0\rangle\,. \tag{1.88}$$

A similar equation may be established for a de-excitation operator,

$$\hat{\mathcal{L}} \;=\; \hat{\mathcal{L}}_1 + \hat{\mathcal{L}}_2 + \ldots \;=\; \sum_{ia} l^{a}_{i}\,\hat{a}^{\dagger}_{i}\hat{a}_{a} + \frac{1}{4}\sum_{ijab} l^{ab}_{ij}\,\hat{a}^{\dagger}_{i}\hat{a}^{\dagger}_{j}\hat{a}_{b}\hat{a}_{a} + \ldots, \tag{1.89}$$

as

$$\langle \Phi_0 | \, [\hat{\mathcal{L}}, \bar{H}] \; = \; \langle \Phi_0 | \, \hat{\mathcal{L}} \; \Delta E^e_{CC} \tag{1.90}$$

with the same eigenvalues as the right-hand side eigenvalue problem. Combining both leads to the EOM-CC energy equation

$$E^e_{CC} \; = \; \langle \Phi_0 | \hat{\mathcal{L}} \bar{H} \hat{\mathcal{R}} | \Phi_0 \rangle \, . \tag{1.91}$$

An important property of EOM-CC is the so-called bi-orthogonality

$$\langle \Phi_0 | \hat{\mathcal{L}}_I \hat{\mathcal{R}}_J | \Phi_0 \rangle \; = \delta_{IJ} \; \neq \; \langle \Phi_0 | \hat{\mathcal{R}}^\dagger_I \hat{\mathcal{R}}_J | \Phi_0 \rangle \, , \tag{1.92}$$

with I and J labelling CC state functions. The EOM-CC secular matrix may now be constructed by expanding the Hamiltonian with the full set of excited state functions for both, the right and the left hand side,

$$\bar{H}_{IJ} \; = \; \langle \Phi_I | \bar{H} | \Phi_J \rangle \quad l_I \; = \; \langle \Phi_0 | \hat{\mathcal{L}} | \Phi_I \rangle \quad r_J \; = \; \langle \Phi_J | \hat{\mathcal{R}} | \Phi_0 \rangle \, , \tag{1.93}$$

and the energy equation for excited states reads

$$(l_I)^T \; \bar{H} \; r_J \; = \; E^e_{CC} \tag{1.94}$$

where the left-hand side eigenvector is transposed, bi-orthogonality is enclosed as $(l_I)^T \; r_J = \delta_{IJ}$. Depending on the set of excitation operators $\hat{\mathcal{R}}$ and $\hat{\mathcal{L}}$ that are chosen for the computation, EOM-CC can be also applied to excitation schemes that do not preserve the electron number, in particular (doubly-) ionized as well as (double-) electronically attached states.

1.8. Algebraic Diagrammatic Construction scheme

The Algebraic Diagrammatic Construction scheme[25,26,27,84,111], developed by Jochen Schirmer et al.[82,99], is a versatile tool to precisely describe electronically-excited states for atomic and molecular species. It is based on many body Green's functions theory[33,84] for a specific set of electronic propagators, as Green's functions represent a robust tool for the solution to inhomogeneous differential equations. The versatility of the ADC formalism enables the description of all kinds of excited states, be it electronically excited states where the number of electrons in the system N is kept constant[82], (doubly-) ionized states with less electrons than the ground state or (doubly-) electronically attached sates with more electrons[79,78]. As a starting point, the spectral (or Lehmann[25]) representation of the corresponding Green's function for a specific propagator is considered,

$$\begin{aligned}\Pi_{I,J}(\omega) \;=\; & \sum_{n\in N^+} \frac{\langle\Psi_0^N|\,\hat{C}_I\,|\Psi_n^{N^+}\rangle\;\langle\Psi_n^{N^+}|\,\hat{C}_J\,|\Psi_0^N\rangle}{\omega + E_0^N - E_n^{N^+} + i\eta} \\ & - \sum_{n\in N^-} \frac{\langle\Psi_0^N|\,\hat{C}_J^\dagger\,|\Psi_n^{N^-}\rangle\;\langle\Psi_n^{N^-}|\,\hat{C}_I^\dagger\,|\Psi_0^N\rangle}{\omega - E_0^N + E_n^{N^-} - i\eta}\end{aligned} \tag{1.95}$$

where the N-electron ground-state energy is denoted as E_0^N and the energies of the corresponding excited state as E^{N^+} and E^{N^-}, respectively. The poles of the spectral function thus represent the excitation energies $\omega_n = -(E_0^N - E_n^{N^+})$ as well as $\omega_n = E_0^N + E_n^{N^-}$.
For the particle-hole propagator $\hat{C} = \hat{a}_p^\dagger \hat{a}_q$, equation 1.95 describes electronically excited states which conserve the total number of electrons in the system, $N = N^+ = N^-$, thus both sums contain the same information. Similarly, for the hole propagator $\hat{a}_q$ together with its conjugate operator, the particle operator $\hat{a}_p^\dagger$, ionized as well as electronically attached states are represented by the two sums in equation 1.95, one with $N+1$ and $N-1$ electron states, respectively. The same accounts for doubly ionized and doubly attached states.
Equation 1.95 may be rewritten as[82,25]

$$\Pi(\omega) \;=\; \mathbf{x}^\dagger(\omega\mathbb{1} - \mathbf{\Omega})^{-1}\mathbf{x}, \tag{1.96}$$

with $\mathbf{x}$ being the matrix of transition (or spectroscopic) amplitudes and $\mathbf{\Omega}$ being the diagonal matrix of excitation energies ω_n. $\mathbb{1}$ represents the unitary matrix. As a fundamental assumption of ADC, this so-called diagonal form of the spectroscopic function may be reformulated in a non-diagonal way,

$$\Pi(\omega) \;=\; \mathbf{F}^\dagger(\omega\mathbb{1} - \mathbf{M})^{-1}\mathbf{F}, \tag{1.97}$$

where $\mathbf{F}$ are now the modified (or effective) transition moments and $\mathbf{M}$ represents an non-diagonal form of the "effective" Hamiltonian. M may now be further split into a diagonal part $\mathbf{K}$ (the zeroth-order Hartree-Fock energies) as well as the non-diagonal part $\mathbf{C}$ that describes the electron correlation,

$$\mathbf{M} = \mathbf{K} + \mathbf{C}. \tag{1.98}$$

This form allows now for a diagrammatic treatment of the spectral Green's function in terms of Feynman-Goldstone diagrams[84], which enables an expansion of the quantities $\mathbf{F}$ and $\mathbf{C}$ in a perturbative manner using the Møller-Plesset partitioning of the Hamiltonian (eq. 1.62). The corresponding expressions may be evaluated up to an arbitrary order in perturbation theory,

$$\mathbf{F} = \sum_{n}^{\infty} \mathbf{F}^{(n)} \qquad \mathbf{C} = \sum_{n}^{\infty} \mathbf{C}^{(n)}, \tag{1.99}$$

and plugged into equation 1.97 to yield the corresponding contributions to an n-th order ADC scheme:

$$\begin{aligned}
\mathbf{\Pi}^{(0)}(\omega) &= \mathbf{F}^{(0)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{F}^{(0)} \\
\mathbf{\Pi}^{(1)}(\omega) &= \mathbf{F}^{(0)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{C}^{(1)}\,\mathbf{F}^{(0)} + \mathbf{F}^{(1)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{F}^{(0)} \\
&\quad + \mathbf{F}^{(0)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{F}^{(1)} \\
\mathbf{\Pi}^{(2)}(\omega) &= \mathbf{F}^{(0)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{C}^{(2)}\mathbf{F}^{(0)} + \mathbf{F}^{(1)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{C}^{(1)}\,\mathbf{F}^{(0)} \\
&\quad + \mathbf{F}^{(0)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{C}^{(1)}\mathbf{F}^{(1)} + \mathbf{F}^{(1)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{C}^{(0)}\,\mathbf{F}^{(1)} \\
\mathbf{\Pi}^{(3)}(\omega) &= \mathbf{F}^{(0)\dagger}\,(\omega\mathbb{1} - \mathbf{K})^{-1}\,\mathbf{C}^{(3)}\mathbf{F}^{(0)} + \ldots
\end{aligned} \tag{1.100}$$

In an ADC(n) scheme, all expressions to describe $\Pi(\omega)$ consistent through n-th order in perturbation theory are included[84]. The solution of the ADC equations is thus issue to the eigenvalue problem

$$\mathbf{MY} = \mathbf{Y\Omega}, \tag{1.101}$$

where the matrix $\mathbf{Y}$ is composed of the ADC eigenvectors $\mathbf{y}$. The matrix of ADC eigenvectors suffices the relations

$$\mathbf{Y}^{\dagger}\mathbf{Y} = \mathbb{1} \tag{1.102}$$

and the eigenvectors are related to the spectral amplitudes via

$$\mathbf{x} = \mathbf{y}^{\dagger}\mathbf{F}. \tag{1.103}$$

The algebraic approach to determine the ADC working equations was, as the name implies, the first one applied. A different approach is represented by the so-called Intermediate state representation (ISR) which shall be introduced briefly in the following.

Intermediate state representation for ADC

The Intermediate state representation[83,80,25] for ADC seeks to represent the electronically excited state wavefunctions in a correlated basis of excited determinants, that is, the eigenfunctions of the matrix representation of the shifted electronic Hamiltonian as

$$M_{IJ} = \langle\tilde{\Psi}_I|\hat{H} - E_0|\tilde{\Psi}_J\rangle = \langle\tilde{\Psi}_I|\hat{H}|\tilde{\Psi}_J\rangle - \delta_{IJ}E_0, \tag{1.104}$$

where the exact solution of the excited state wavefunction $|\Psi_n\rangle$ can be represented in the basis of these intermediate states $\{|\tilde{\Psi}_I\rangle\}$,

$$|\Psi_n\rangle = \sum_I y_{nI}\,|\tilde{\Psi}_I\rangle\,. \tag{1.105}$$

Capital indices $(I, J, ...)$ are referring to the intermediate states here. To this end, a CI-like ansatz is used to construct the excited state determinants by acting on the correlated (Møller-Plesset) ground state determinant as $\hat{C}_I\,|\Psi_0\rangle$. Depending on the ADC scheme, these sets of excitation operators $\{\hat{C}_I\}$ form manifolds of excited states (for a constant number of elections in the system N), ionized or electronically attached states (for states with $N-1$ or $N+1$ electrons), doubly ionized and attached states ($N \pm 2$) and so on. As an example,

$$\begin{aligned}
\{\hat{C}_I^{PP}\} &= \{\hat{a}_a^{\dagger}\hat{a}_i, \hat{a}_a^{\dagger}\hat{a}_b^{\dagger}\hat{a}_j\hat{a}_i, \ldots\,; a < b, i < j\} \\
\{\hat{C}_I^{EA}\} &= \{\hat{a}_a^{\dagger}, \hat{a}_a^{\dagger}\hat{a}_b^{\dagger}\hat{a}_i, \ldots\,; a < b\} \\
\{\hat{C}_I^{DIP}\} &= \{\hat{a}_j\hat{a}_i, \hat{a}_a^{\dagger}\hat{a}_k\hat{a}_j\hat{a}_i, \ldots\,; i < j < k\}
\end{aligned} \tag{1.106}$$

represent the excitation operators for electronically excited states (particle-hole, two particle-two hole configurations etc.), electronically attached states (particle, two particle-hole configurations etc.) and doubly-ionized states (two hole, particle-three hole configurations etc.), respectively.

To construct the full set of orthogonal intermediate states $|\tilde{\Psi}_I\rangle$, in a first step, the so-called precursor states $|\Psi^{\#}_I\rangle$ are constructed using the excitation operators $\hat{C}_I$ in 1.106 and the ground state determinant $|\Psi_0\rangle$,

$$|\Psi^{\#}_I\rangle \; = \; \hat{C}_I \, |\Psi_0\rangle - |\Psi_0\rangle \, \langle\Psi_0|\hat{C}_I|\Psi_0\rangle \tag{1.107}$$

which then need to be orthonormalized. This is done by employing a Gram-Schmidt[25] scheme. States of the different excitation classes (e. g. two hole, two-particle two-hole for electronically excited states) are orthogonalized with respect to each other successively by employing the so-called excitation class orthogonalization (ECO). The overlap matrix between two states I and J is then constructed as

$$S_{IJ} \; = \; \langle\Psi^{\#}_I|\Psi^{\#}_J\rangle \; = \; \langle\Psi_0|\hat{C}^{\dagger}_I\hat{C}_J|\Psi_0\rangle - \langle\Psi_0|\hat{C}^{\dagger}_I|\Psi_0\rangle \, \langle\Psi_0|\hat{C}_J|\Psi_0\rangle \tag{1.108}$$

to produce the set of orthonormalized excited state determinants, the basis of the intermediate state representation,

$$|\tilde{\Psi}_I\rangle \; = \; \sum_J S^{-\frac{1}{2}}_{IJ} \; |\Psi^{\#}_J\rangle \, . \tag{1.109}$$

By inserting the expressions of the ISR (eq. 1.109) into the general form of the ADC secular matrix (eq. 1.104), the ADC matrix of the effective Hamiltonian spanned by the intermediate states is obtained,

$$M_{IJ} \; = \; \sum_{KL} S^{-\frac{1}{2}}_{IK} \, \langle\Psi^{\#}_K|\hat{H} - E_0|\Psi^{\#}_L\rangle \, S^{-\frac{1}{2}}_{LJ} . \tag{1.110}$$

However, a direct evaluation of this expression is neither desirable nor feasible. This is why the individual components of 1.110 are evaluated, just as in 1.55 , in a perturbative manner,

$$\lambda^{\alpha+\beta+\gamma} \; M^{(\alpha+\beta+\gamma)}_{IJ} \; = \; \sum_{KL} \lambda^{\alpha}\Big(S^{-\frac{1}{2}}_{IK}\Big)^{(\alpha)} \, \lambda^{\beta}\Big(\langle\Psi^{\#}_K|\hat{H} - E_0|\Psi^{\#}_L\rangle \Big)^{\beta} \, \lambda^{\gamma}\Big(S^{-\frac{1}{2}}_{LJ}\Big)^{(\gamma)} . \tag{1.111}$$

The auxiliary indices α, β and γ are, as for the derivation of the Møller-Plesset working equations, needed to group terms of a certain perturbation order together: The sum of perturbation orders of the individual constituents equals the one of the matrix element M_{IJ}. The inverse square root of the overlap matrix, S_{IJ}, is constructed using a Taylor series and employing the order relations of perturbation theory to it.
For a general one-particle operator $\hat{D}$ of the form 1.25, e. g. the dipole operator, the formalism of the intermediate state representation may be applied to set up the corresponding matrix representation as[112,25]

$$F_I = \langle \tilde{\Psi}_I | \hat{D} | \Psi_0 \rangle \tag{1.112}$$

for the ground-to excited state expectation values and

$$B_{IJ} = \langle \tilde{\Psi}_I | \hat{D} - D_0 | \tilde{\Psi}_J \rangle \,. \tag{1.113}$$

for the state-to-state expectation values with $D_0 = \langle \Psi_0 | \hat{D} | \Psi_0 \rangle$ being the ground-state contribution for the operator. Using the above, ground-to excited state moments may be computed as

$$\langle \Psi_n | \hat{D} | \Psi_0 \rangle = \mathbf{y}_n^\dagger \mathbf{F} \tag{1.114}$$

and excited state properties ($m = n$) as well as state-to-state moments ($m \neq n$) as

$$\langle \Psi_m | \hat{D} | \Psi_n \rangle = \mathbf{y}_m^\dagger \mathbf{B} \mathbf{y}_n \tag{1.115}$$

with $\mathbf{y}_n$ being the ADC eigenvectors formed by the coefficients of 1.105.

1.9. Unitary Coupled Cluster

Unitary Coupled Cluster[6,96,61], or abbreviated UCC, modifies the ordinary (bi-orthogonal) Coupled Cluster scheme by introducing a hermitian matrix representation for the calculation of excited states, making it very similar to the previously introduces Algebraic Diagrammatic Construction scheme. The starting point, just as in ordinary Coupled Cluster, is the wavefunction ansatz,

$$|\Psi_{UCC}\rangle = exp(\hat{\sigma}) \cdot |\Phi_0\rangle \,. \tag{1.116}$$

As a difference to the CC cluster operators $\hat{T}$, the UCC cluster operators $\hat{\sigma}$ are composed of an excitation part (as in $\hat{T}$) as well as a de-excitation part,

$$\begin{aligned}\hat{\sigma} \;=\; \hat{\sigma}_1 + \hat{\sigma}_2 + ... \;=\; & \sum_{ia} \sigma_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{ia} \sigma_a^i \, \hat{a}_i^\dagger \hat{a}_a \\ & + \frac{1}{4} \sum_{ijab} \sigma_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \frac{1}{4} \sum_{ijab} \sigma_{ab}^{ij} \, \hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_a \hat{a}_b \\ & + ... \end{aligned} \tag{1.117}$$

Nomenclature is the same as in CC, for instance, the scheme to include singles and doubles is called UCCSD. The above definition of the UCC cluster operator $\hat{\sigma}$ introduces it as anti-hermitian, meaning that

$$\hat{\sigma}^\dagger \;=\; -\hat{\sigma} \tag{1.118}$$

holds true and the cluster amplitudes in equation 1.117 fulfill the relations

$$\sigma_{a...}^{i...} \;=\; -\,(\sigma_{i...}^{a...})^* \tag{1.119}$$

for the manifolds of singles, doubles and so on cluster amplitudes. Restricting the wavefunction to real values therefore establishes the straightforward relation between excitation and de-excitation amplitudes in an UCCSD scheme, for example, as

$$\sigma_a^i \;=\; -\,\sigma_i^a \qquad \sigma_{ab}^{ij} \;=\; -\,\sigma_{ij}^{ab}. \tag{1.120}$$

Introducing the UCC version of the similarity-transformed Hamiltonian (see eq. 1.73) as

$$\bar{H} \;=\; e^{\hat{\sigma}^\dagger} \hat{H} e^{\hat{\sigma}} \;=\; e^{-\hat{\sigma}} \hat{H} e^{\hat{\sigma}} \tag{1.121}$$

allows to formulate the UCC working equations in the same way as the traditional CC ones of equation 1.74,

$$\begin{aligned} \langle \Phi_0 | \, \bar{H} \, | \Phi_0 \rangle \;&=\; E_0^{UCC} \\ \langle \Phi_I | \, \bar{H} \, | \Phi_0 \rangle \;&=\; 0 \end{aligned} \tag{1.122}$$

with $|\Phi_I\rangle$ representing the manifolds of excited states. As for ordinary Coupled Cluster, $\bar{H}$ may be evaluated using the BCH expansion,

$$\bar{H} = \hat{H} + [\hat{H},\hat{\sigma}] + \frac{1}{2}[[\hat{H},\hat{\sigma}],\hat{\sigma}] + \frac{1}{6}[[[\hat{H},\hat{\sigma}],\hat{\sigma}],\hat{\sigma}] + ... \qquad (1.123)$$

However, due to the de-excitation operators in the cluster amplitudes, valid contributions (connected diagrams) as shown in figure 1.10 lead to a non-terminating expansion of $\bar{H}$.

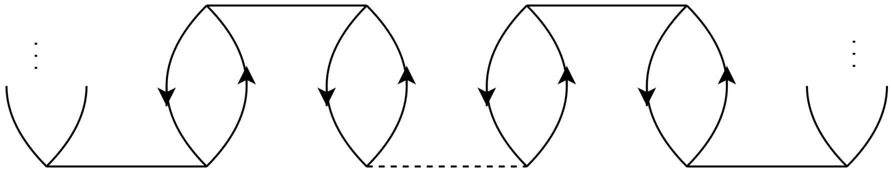

Figure 1.10.: Schematic example of the non-terminating BCH expansion using diagrams. Note the indirect connection of fragments to $\hat{V}$ via other fragments.

This introduces the necessity for a proper termination scheme for the similarity-transformed Hamiltonian for Unitary Coupled Cluster.

1.10. Bernoulli expansion for UCC

An alternative to the BCH expansion in equation 1.123 is the parametrization of the similarity-transformed UCC Hamiltonian $\bar{H}$ using Bernoulli numbers. Introduced by Liu et al.[61,62], the Bernoulli-UCC scheme (referred to as simply UCC in this work) includes the Fock part of the Hamiltonian $\hat{F}$ only in the ordinary commutator and not in the nested expressions, unlike the normal BCH-UCC[48]. Furthermore, an iterative rule to generate $\bar{H}$ using Bernoulli numbers is introduced. A short overview of Bernoulli-UCC is given in the following.

At first, the definition of the so-called superoperator (denoted with a double hat) is useful. It is defined by its effect on an arbitrary operator,

$$\hat{\hat{\beta}}\hat{\alpha} = [\hat{\alpha},\hat{\beta}], \qquad (1.124)$$

which simply acts as the commutator when applied to another operator. Following definition 1.124, $\bar{H}$ of equation 1.121 is alternatively formulated as

$$\bar{H} = e^{\hat{\hat{\sigma}}}\hat{H}, \tag{1.125}$$

which is equal to the BCH formulation of equation 1.123. The Hamiltonian can now be separated using the superoperator,

$$\bar{H} = e^{\hat{\hat{\sigma}}}\hat{F} + e^{\hat{\hat{\sigma}}}\hat{V} = \hat{F} + \hat{X}(\hat{\hat{\sigma}})\hat{\hat{\sigma}}\hat{F} + e^{\hat{\hat{\sigma}}}\hat{V}, \tag{1.126}$$

with the polynomial function $\hat{X}$ being the exponential Taylor series where the power of the argument is lowered by one order,

$$\hat{X}(\hat{\hat{\sigma}}) = 1 + \frac{1}{2}\hat{\hat{\sigma}} + \frac{1}{6}\hat{\hat{\sigma}}^2 + \ldots . \tag{1.127}$$

The inverse of this function, $\hat{X}^{-1}(\hat{\hat{\sigma}})$, is represented as[61]

$$\hat{X}^{-1}(\hat{\hat{\sigma}}) = 1 + \sum_{n>0} B_n \hat{\hat{\sigma}}^n \tag{1.128}$$

where B_n constitute the Bernoulli numbers

$$B_1 = -\frac{1}{2}, \; B_2 = \frac{1}{12}, \; B_3 = 0, \; B_4 = -\frac{1}{720}, \; \ldots . \tag{1.129}$$

Plugging in the inverse function $\hat{X}^{-1}(\hat{\hat{\sigma}})$ into the separated Hamiltonian of equation 1.126 leads to the expression

$$\hat{X}^{-1}(\hat{\hat{\sigma}})[\bar{H} - \hat{F}] = \hat{\hat{\sigma}}\hat{F} + \hat{X}^{-1}(\hat{\hat{\sigma}})e^{\hat{\hat{\sigma}}}\hat{V}. \tag{1.130}$$

Inserting the definition of $\hat{X}^{-1}(\hat{\hat{\sigma}})$ from equation 1.128 yields the iterative rule for the generation of the UCC similarity-transformed Hamiltonian using Bernoulli numbers as expansion coefficients[48],

$$\begin{aligned} \bar{H} &= \hat{F} + \bar{V} \\ \bar{V} &= \hat{\hat{\sigma}}\hat{F} + \hat{X}^{-1}(\hat{\hat{\sigma}})e^{\hat{\hat{\sigma}}}\hat{V} - \sum_{n>0} B_n \hat{\hat{\sigma}}^n \bar{V}. \end{aligned} \tag{1.131}$$

As equation 1.131 shows, the iterative generation of $\bar{H}$ includes $\hat{F}$ only in the very first term which is a singly nested commutator.

Non-diagonal and Rest part of an operator

To be able to apply the iterative rule to generate $\bar{H}$, it is necessary to introduce a characterization scheme for the operators that are involved in the expansion of the Hamiltonian. Consider a general operator $\hat{\alpha}$ which can be split into two parts[61],

$$\hat{\alpha} \equiv \hat{\alpha}_O = \hat{\alpha}_N + \hat{\alpha}_R, \tag{1.132}$$

where the subscript "O" refers to the ordinary (full) expression of the operator, "N" refers to the non-diagonal part of the operator which includes all excitations and de-excitations and "R" represents the rest part that remains when excluding the non-diagonal part from the full operator. Using diagrams, this partition can be directly understood: The non-diagonal part of an operator or a product of operators always constitutes a diagram with only creators or only annihilators, that is, only open fermion lines above or below the vertices. Since in a UCCSD scheme (UCC2 and UCC3) the amplitude equations (1.122) have to be fulfilled for singles and doubles, non-diagonal contributions may have the excitation levels -2, -1, 1 or 2. For a UCCSDT scheme such as UCC4, however, the additional triples amplitudes introduce contributions with an excitation level of -3 and 3 in the non-diagonal part (see figure 1.11). All other contributions, that is, products of operators whose diagrammatic representation include both, creators and annihilators, or do exceed the demanded excitation level, are collected in the rest part. With this definition, the generating function for the UCC amplitude equations may now be rewritten as

$$\langle \Phi_I | \bar{H} | \Phi_0 \rangle = \langle \Phi_I | \bar{V}_N | \Phi_0 \rangle , \tag{1.133}$$

assuming a block-diagonal Fock operator,

$$\langle \Phi_I | \hat{F}_N | \Phi_0 \rangle = 0. \tag{1.134}$$

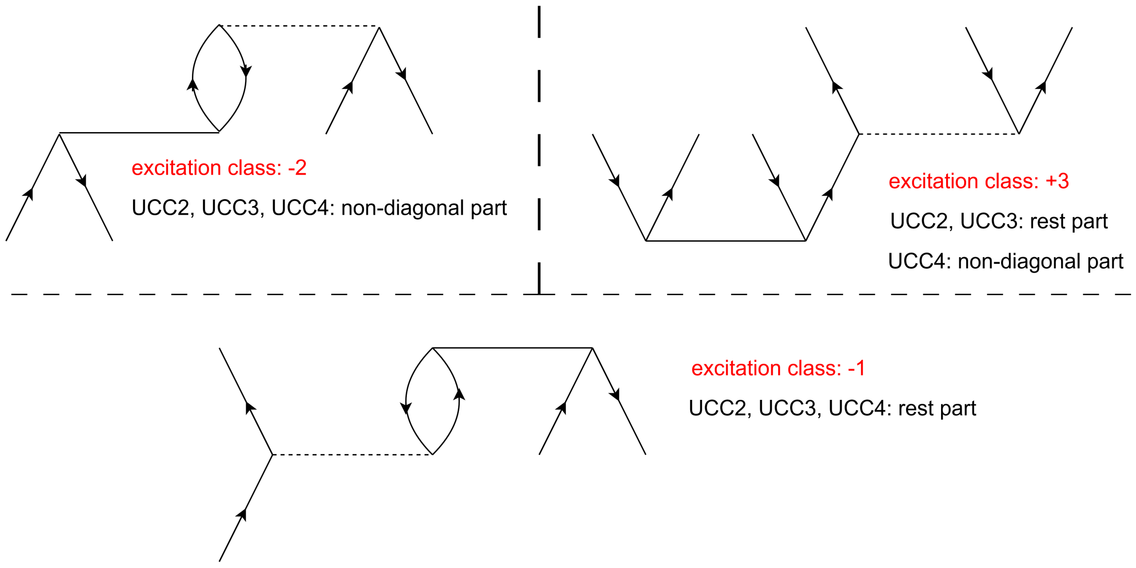

Figure 1.11.: Examples for the "N" and "R" parts in different UCC*n* schemes.

Equations 1.133 and 1.134 may now be applied to the iterative rule to generate the fluctuation potential $\bar{V}$ in equation 1.131,

$$\bar{V}^{(k+1)} = \hat{\hat{\sigma}}\hat{F} + \hat{X}^{-1}(\hat{\hat{\sigma}})e^{\hat{\hat{\sigma}}}\hat{V} - \sum_{n>0} B_n \hat{\hat{\sigma}}^n \bar{V}_R^{(k)}, \tag{1.135}$$

which allows to construct $\bar{H}$ by including only the rest part of the fluctuation potential $\bar{V}_R$ with an initial statement of $\bar{V}_R^{(0)} = \hat{V}_R$[61]. The full expressions up to the quadruply nested commutator for $\bar{H}$ are thus evaluated as[62,63]

$$
\begin{aligned}
\bar{H} &= \sum_i \bar{H}_i \\
\bar{H}_0 &= \hat{F} + \hat{V} \\
\bar{H}_1 &= [\hat{F}, \hat{\sigma}] + \frac{1}{2}[\hat{V}, \hat{\sigma}] + \frac{1}{2}[\hat{V}_R, \hat{\sigma}] \\
\bar{H}_2 &= \frac{1}{12}[[\hat{V}_N, \hat{\sigma}], \hat{\sigma}] + \frac{1}{4}[[\hat{V}, \hat{\sigma}]_r, \hat{\sigma}] + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}]_R, \hat{\sigma}] \\
\bar{H}_3 &= \frac{1}{24}[[[\hat{V}_N, \hat{\sigma}], \hat{\sigma}]_R, \hat{\sigma}_2] + \frac{1}{8}[[[\hat{V}_R, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}] + \frac{1}{8}[[[\hat{V}, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}_2] \\
&\quad - \frac{1}{24}[[[\hat{V}, \hat{\sigma}]_R, \hat{\sigma}], \hat{\sigma}] - \frac{1}{24}[[[\hat{V}_R, \hat{\sigma}]_R, \hat{\sigma}], \hat{\sigma}] \\
\bar{H}_4 &= \frac{1}{16}[[[[\hat{V}_R, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}] + \frac{1}{16}[[[[\hat{V}, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma} a] + \frac{1}{48}[[[[\hat{V}_N, \hat{\sigma}], \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}] \\
&\quad - \frac{1}{48}[[[[\hat{V}, \hat{\sigma}]_R, \hat{\sigma}], \hat{\sigma}]_R, \hat{\sigma}] - \frac{1}{48}[[[[\hat{V}_R, \hat{\sigma}]_R, \hat{\sigma}], \hat{\sigma}]_R, \hat{\sigma}] - \frac{1}{144}[[[[\hat{V}_N, \hat{\sigma}], \hat{\sigma}]_R, \hat{\sigma}], \hat{\sigma}] \\
&\quad - \frac{1}{48}[[[[\hat{V}, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}], \hat{\sigma}] - \frac{1}{48}[[[[\hat{V}_R, \hat{\sigma}]_R, \hat{\sigma}]_R, \hat{\sigma}], \hat{\sigma}] - \frac{1}{720}[[[[\hat{V}_N, \hat{\sigma}], \hat{\sigma}], \hat{\sigma}], \hat{\sigma}]
\end{aligned}
\tag{1.136}
$$

where the subscript gives the level of commutator nesting. These nested commutator expressions may now be used together with a suited truncation scheme for the generation of UCC working equations.

Throughout this work, the common truncation scheme that is applied to the similarity- transformed UCC Hamiltonian is labelled as UCC*n*. In such a UCC*n* scheme, in similarity to an ADC(*n*) scheme, the UCC working equations are truncated after a certain order in perturbation theory *n*. To this end, UCC amplitudes are attributed with the perturbation order of the corresponding MP expressions: σ_2 being a first order property, σ_1 and σ_3 being second order properties etc., $\hat{F}$ and $\hat{D}$ fragments constitute zeroth-order properties and $\hat{V}$ fragments constitute a first-order property. Another example for a practical truncation scheme would be the evaluation of a certain number of nested commutators, as it is done for qUCCSD[62,63].

Intermediate state representation for UCC

As for ADC, an intermediate state approach can be applied to UCC[50,51] to establish a formalism to describe excited-state wavefunctions. In this ISR-UCC formulation, excitation operators as given in 1.106 are applied to the UCC ground state wavefunction of 1.116,

$$|\tilde{\tilde{\Psi}}_I\rangle \;=\; e^{\sigma}\hat{C}_I\,|\Phi_0\rangle \tag{1.137}$$

Secular matrix expressions can then be directly evaluated as

$$\langle\tilde{\tilde{\Psi}}_I|\hat{H}|\tilde{\tilde{\Psi}}_J\rangle \;=\; \langle\Phi_0|\hat{C}_I^{\dagger}e^{-\hat{\sigma}}\hat{H}e^{\hat{\sigma}}\hat{C}_J|\Phi_0\rangle \;=\; \langle\Phi_I|\bar{H}|\Phi_J\rangle\,. \tag{1.138}$$

Since both, ADC and UCC follow a CI-like parametrization for the construction of excited states, the sets of intermediate states for both methods $\{|\tilde{\tilde{\Psi}}_I\rangle\}$ and $\{|\tilde{\Psi}\rangle_J\}$ are connected via a unitary transformation $\mathbf{U}$[61,50] as

$$\langle\tilde{\tilde{\Psi}}_I|\tilde{\Psi}_J\rangle \;=\; U_{IJ}. \tag{1.139}$$

This establishes the same order relations in UCC*n* secular matrices as in the corresponding ADC(*n*) scheme. Applying the Baker-Campbell-Hausdorff expansion to the similarity-transformed expression of an arbitrary one-particle operator $\hat{D}$ as

$$\bar{D} \;\equiv\; e^{-\hat{\sigma}}\hat{D}e^{\hat{\sigma}} \;=\; \hat{D} + [\hat{D},\hat{\sigma}] + \frac{1}{2!}[[\hat{D},\hat{\sigma}],\hat{\sigma}] + \;... \tag{1.140}$$

allows for the calculation of the UCC ground state density as

$$D_0 \;=\; \langle\Phi_0|\bar{D}|\Phi_0\rangle\,, \tag{1.141}$$

ground- to excited states moments as

$$F_I \;=\; \langle\Phi_I|\bar{D}|\Phi_0\rangle\,, \tag{1.142}$$

and state-to-state moments as well as excited state properties as

$$B_{IJ} + \delta_{IJ}D_0 \;=\; \langle\Phi_I|\bar{D}|\Phi_J\rangle\,. \tag{1.143}$$

Section C in the appendix includes UCC equations that were computed and used in the scope of this work.

1.11. CC, ADC and UCC: A short comparison

This last section of the theory part gives a short comparison of the electronic structure methods used throughout this work, namely Coupled Cluster, the Algebraic Diagrammatic Construction scheme and Unitary Coupled Cluster.

Starting with the underlying ground state: For CC, the iterated amplitudes also introduce an iterated description of the ground state. For CCSD, the ground state furthermore includes explicit singles contributions of the form $\langle ij||ab\rangle\, t_i^a t_j^b$[15]. These are not present in the non-iterative ground-state descriptions of Møller-Plesset up to the fifth order, as for an ADC*n* calculation, the MP*n* ground state is used as a starting point. Unitary Coupled Cluster, on the other hand, combines the iterative nature of cluster amplitudes with the perturbative order relations for the energy expression: The UCC ground-state energy corresponds to the MP expression up to third order, additionally including the advantage of an iterative amplitude description as in ordinary CC.

For the calculation of excited states and properties, however, the non-Hermitian formulation of the similarity-transformed CC Hamiltonian (eq. 1.73) leads to a significant drawback: The bi-orthogonality of the EOM-CC secular matrix with separate left- and right-hand-side eigenvalue problems that need to be solved (see eq. 1.144 to the left). This is not the case for Hermitian ADC and UCC matrices (see eq. 1.144 to the right), facilitating the evaluation of secular matrices of any kind. Again, the similarity between ADC and UCC (eq. 1.139) shall be noted, for the calculation of electronically excited states, the secular matrices of the second- and third-order schemes show the same term structure[61], with the difference of an iterative nature for UCC amplitudes.

$$\mathbf{M}_{CC} = \begin{pmatrix} E_0 & \mathbf{H}_{0S} & \mathbf{H}_{0D} \\ 0 & \mathbf{H}_{SS} & \mathbf{H}_{SD} \\ 0 & \mathbf{H}_{DS} & \mathbf{H}_{DD} \end{pmatrix} \qquad \mathbf{M}_{ADC/UCC} = \begin{pmatrix} E_0 & 0 & 0 \\ 0 & \mathbf{M}_{SS} & \mathbf{M}_{SD} \\ 0 & \mathbf{M}_{DS} & \mathbf{M}_{DD} \end{pmatrix} \tag{1.144}$$

The computational cost for the second-order schemes ADC(2) and UCC2 is identical with $\mathcal{O}(N^5)$, N being the number of basis functions. For the third-order schemes ADC(3) and UCC3 as well as the extended second-order schemes ADC(2)-x and UCC2-x this is, as for CCSD schemes, $\mathcal{O}(N^6)$. Notably, UCC calculations are slightly more expensive due to the additional iteration of the amplitudes.

As a summary, UCC may be characterized as a suitable mélange of both CC and ADC, inheriting the iterative amplitude description from CC as well as the Hermiticity from ADC as big advantages to be combined in one single method.

2. The Algebraic Diagrammatic Construction scheme for the two-hole and two-particle propagators

Ionizations and electron attachments are among the most investigated processes in a whole variety of fields of physics, chemistry and biology. For instance, the ionization of electrons from a species constitutes one of the most fundamental light-matter interactions. A prominent example for the ionization of two electrons is represented by the Auger effect[4] (figure 2.1): Upon high-energy radiation, a first ionization is followed by a recombination and second ionization, both of lower energy as the initial electron to be removed. A theoretical approach would enable the prediction of this kind of spectra.

In this section, an implementation and benchmark of the Algebraic Diagrammatic Construction scheme for the two-hole propagator[78,95] is presented. As has been already shown before, the application of the ADC scheme for the calculation of electronically excited (PP) states[111,112,41,65] as well as ionized (IP)[22,20,21] and attached (EA) states[18] has proven to be very successfully and is competitive to EOM-CC or other state-of-the-art electronic structure methods. An efficient implementation for the two-hole propagator in the ADC framework does not only complement this family of methods, but further introduces a novel method for the calculation of doubly-ionized and double electronically-attached states within the quantum chemistry software `Q-Chem`[30].

- **Parts of this chapter were already explicated briefly in**:
  S. M. Thielen. Implementation of the Algebraic Diagrammatic Construction scheme for the two-hole propagator to study double ionization, master thesis, Hiedelberg, 2018. ([97])

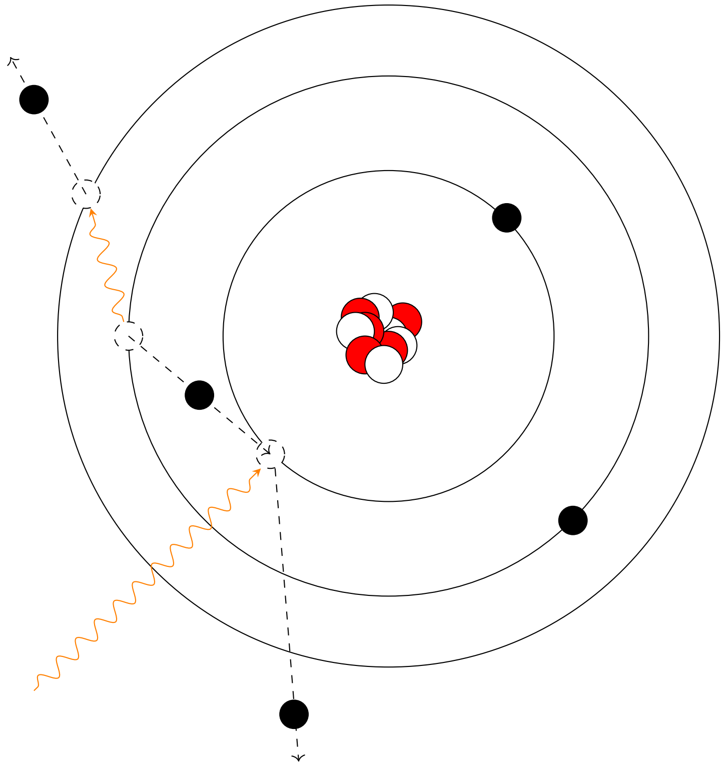

Figure 2.1.: Schematic depiction of the Auger Effect. Taken from[97].

2.1. Theory

As has been already outlined in the theory chapter for the Algebraic Diagrammatic Construction scheme, the starting point for the calculation of doubly-ionized as well as double electronically-attached states is the spectral (or Lehmann[78]) representation of the Green's function of the two-hole propagator (see eq. 1.95),

$$\begin{aligned}\Pi_{ij,kl}(\omega) &= \sum_{n\in N+2} \frac{\langle\Psi_0^N|\, \hat{a}_i\hat{a}_j\, |\Psi_n^{N+2}\rangle\ \langle\Psi_n^{N+2}|\, \hat{a}_k^\dagger\hat{a}_l^\dagger\, |\Psi_0^N\rangle}{\omega + E_0^N - E_n^{N+2} + i\eta} \\ &- \sum_{n\in N-2} \frac{\langle\Psi_0^N|\, \hat{a}_l^\dagger\hat{a}_k^\dagger\, |\Psi_n^{N-2}\rangle\ \langle\Psi_n^{N-2}|\, \hat{a}_j\hat{a}_i\, |\Psi_0^N\rangle}{\omega - E_0^N + E_n^{N-2} - i\eta},\end{aligned} \tag{2.1}$$

where the upper line of equation 2.1 corresponds to the double electron attachment spanned by states with a surplus of two electrons $|\Psi_n^{N+2}\rangle$ and the lower line to doubly-ionized states spanned by states with two less electrons $|\Psi_n^{N-2}\rangle$. The corresponding set of second-quantized operators which create the intermediate states in an ISR approach are thus

$$\{\hat{C}_I^{DIP}\} = \{\hat{a}_j\hat{a}_i, \hat{a}_a^\dagger\hat{a}_k\hat{a}_j\hat{a}_i, \ldots ; i < j < k\} \tag{2.2}$$

for double ionization (DIP) as well as

$$\{\hat{C}_I^{DEA}\} = \{\hat{a}_a^\dagger \hat{a}_b^\dagger, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i, \ldots ; a < b < c\} \tag{2.3}$$

for double electron attachment (DEA), respectively. Figure 2.2 gives a qualitative understanding of these excitation classes using the example of double ionization: While the "singles" configuration (two hole-configuration) represents the actual double ionization, the "doubles" configuration (particle/three hole-configuration) may be understood as an additional excitation after the double ionization. This is the case for all ADC schemes, after the base propagator (2h for DIP, 2p for DEA), higher-order configurations are created by additional electron excitations. Therefore, in a fourth-order DIP scheme, the "triples" configurations would be represented by a 2p/4h space.

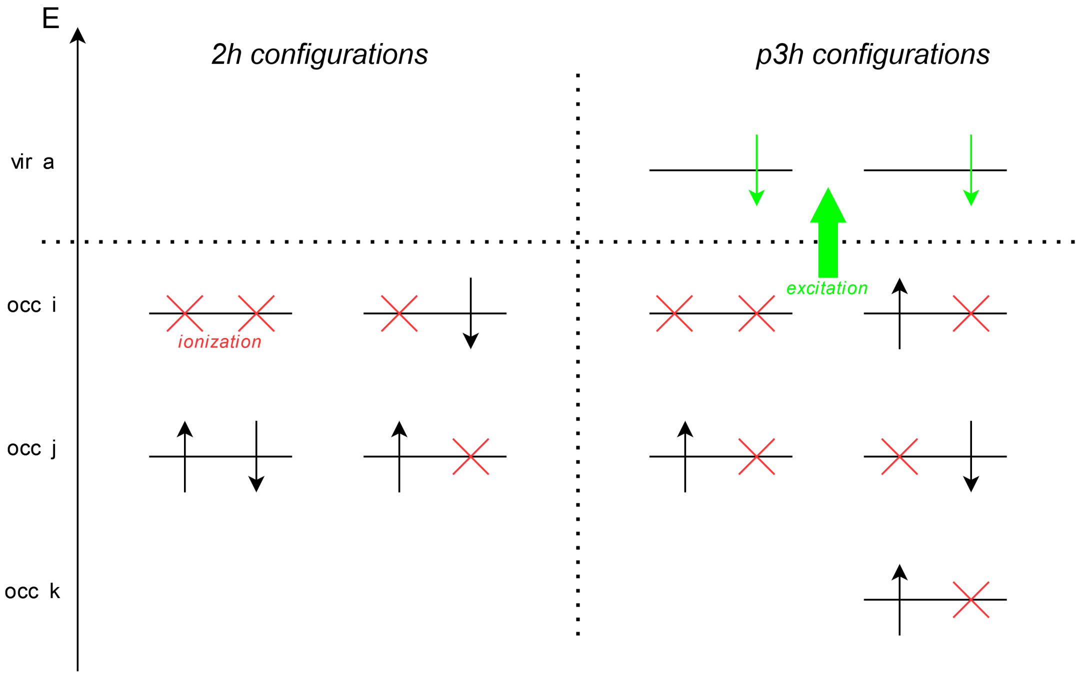

Figure 2.2.: Molecular orbital diagrams to illustrate double ionization: The 2h propagator removes two electrons from the occupied space, the p3h propagator includes an additional electron excitation.

Although it seems to be obvious that DIP/DEA-ADC are closely related to IP/EA-ADC due to the same physical processes happening (namely electron removal as well as electron attachment for a given system), the algebraic structure of DIP-ADC as well as DEA-ADC is very closely related to the electron number preserving PP-ADC scheme for excited states.

This can be explained by the same number of second-quantized operators used to create the manifolds of excited states. For PP as well as DIP and DEA, the number of creation and annihilation operators is even, i. e. two for the singles space, four for the doubles space and so on. This is also the reason why spin-pure configurations for DIP and DEA, just like for PP, have singlet, triplet, quintet etc. character. For IP and EA, the number of creators and annihilators is odd: One for the singles part, three for the doubles part and so on. This, on the other hand, leads to doublet, quartet etc. spin-pure configurations. Furthermore, DIP and DEA schemes for ADC do include, just as PP-ADC, a first-order description, which is not present in IP/EA-ADC[84].

This work features DIP-ADC and DEA-ADC schemes up to third order in perturbation theory. Figure 2.3 gives, with the example of DIP-ADC, an overview of the five distinct matrices that constitute each of the individual schemes. Thereby, the ADC(0) scheme is also included, although the eigenenergies of this scheme are simply the differences of the Hartree-Fock orbital energies ϵ, the reason being that this particular scheme is also called Delta-Hartree-Fock (ΔHF). The first, second and third order schemes follow the strict order relations for the perturbative treatment of the ADC matrix blocks[78]. As an ad-hoc extension of the second-order scheme, ADC(2)-x introduces a first-order treatment to the doubles/doubles block.

A very elegant way to determine the order relations of the different ADC blocks is achieved by re-writing the general ADC eigenvalue problem,

$$\begin{pmatrix} \mathbf{M}_{SS} & \mathbf{M}_{SD} \\ \mathbf{M}_{DS} & \mathbf{M}_{DD} \end{pmatrix} \begin{pmatrix} v_S \\ v_D \end{pmatrix} = \omega \begin{pmatrix} v_S \\ v_D \end{pmatrix}, \tag{2.4}$$

in a way to substitute the contribution of the doubles part of the ADC vector into the singles part[48],

$$\left[\mathbf{M}_{SS} + \mathbf{M}_{SD}\left(\omega\mathbf{1} - \mathbf{M}_{DD}\right)^{-1}\mathbf{M}_{DS}\right] v_S = \omega\, v_S. \tag{2.5}$$

Lowest contributions to the diagonal blocks $\mathbf{M}_{SS}$ and $\mathbf{M}_{DD}$ are of zeroth order, while for the coupling blocks $\mathbf{M}_{SD}$ and $\mathbf{M}_{DS}$, they are of first order. Taking ADC(2) as an example, the $\mathbf{M}_{SS}$ block has to be evaluated in second order to account for an overall second order scheme.

For DIP-ADC, the general form of the secular matrix of equation 2.4 with the corresponding

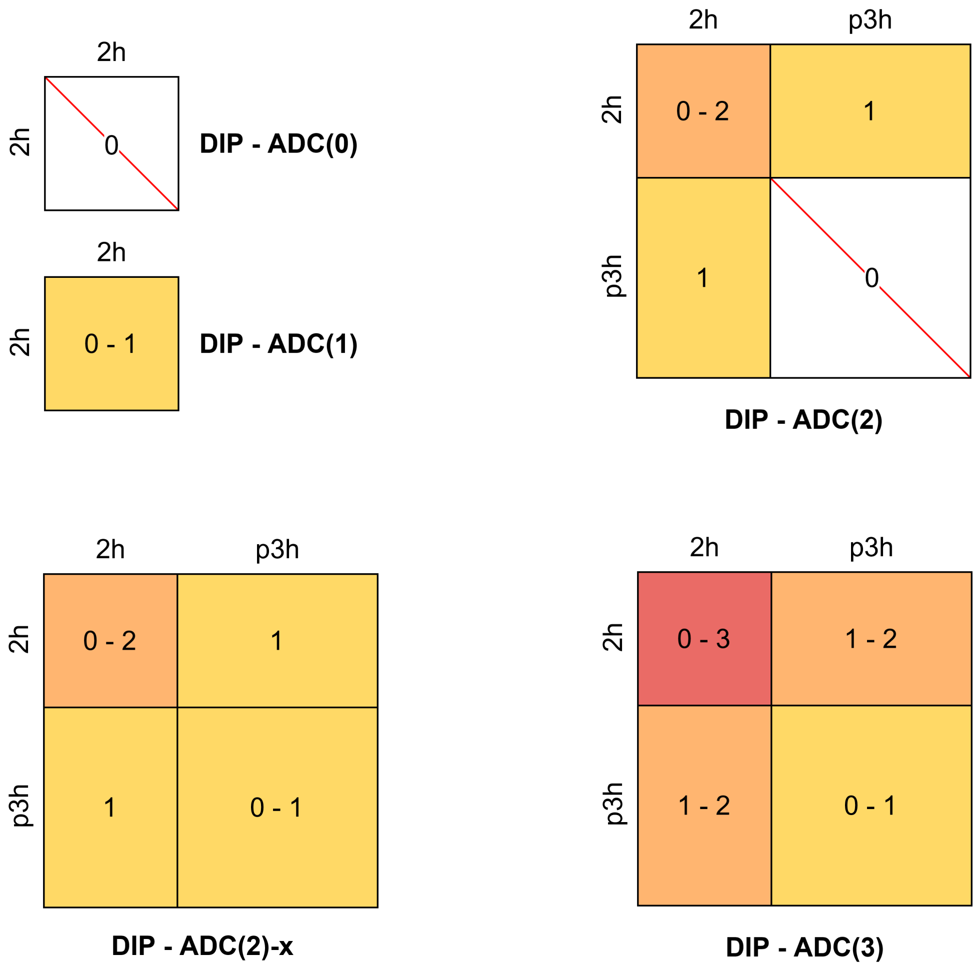

Figure 2.3.: DIP-ADC matrices from zeroth order (ΔHF) up to third order with the second-order ad-hoc expansion scheme (2)-x.

labellings is given as

$$\begin{pmatrix} \mathbf{M}_{ij,kl} & \mathbf{M}_{ij,klma} \\ \mathbf{M}_{ijka,lm} & \mathbf{M}_{ijka,lmnb} \end{pmatrix} = \begin{pmatrix} \{\langle\Psi_{ij}|\,\hat{H}-E_0\,|\Psi_{kl}\rangle\} & \{\langle\Psi_{ij}|\,\hat{H}-E_0\,|\Psi_{klma}\rangle\} \\ \{\langle\Psi_{ijka}|\,\hat{H}-E_0\,|\Psi_{lm}\rangle\} & \{\langle\Psi_{ijka}|\,\hat{H}-E_0\,|\Psi_{lmnb}\rangle\} \end{pmatrix} \tag{2.6}$$

and for DEA-ADC as

$$\begin{pmatrix} \mathbf{M}_{ab,cd} & \mathbf{M}_{ab,icde} \\ \mathbf{M}_{iabc,de} & \mathbf{M}_{iabc,jdef} \end{pmatrix} = \begin{pmatrix} \{\langle\Psi_{ab}|\,\hat{H}-E_0\,|\Psi_{cd}\rangle\} & \{\langle\Psi_{ab}|\,\hat{H}-E_0\,|\Psi_{icde}\rangle\} \\ \{\langle\Psi_{iabc}|\,\hat{H}-E_0\,|\Psi_{de}\rangle\} & \{\langle\Psi_{iabc}|\,\hat{H}-E_0\,|\Psi_{jdef}\rangle\}. \end{pmatrix} \tag{2.7}$$

The DIP-ADC as well as DEA-ADC working equations will be presented in the following chapters. Furthermore, the configuration state functions (CSF) for doubly-ionized and double electronically-attached states, which are necessary for the computation, are introduced.

2.2. General considerations for the matrix-vector products

To enable an iterative treatment for the eigenvalue problem of the ADC matrix, the individual matrix contributions are rewritten as matrix-vector products with the corresponding ADC vectors. For example, the matrix-vector product of the 2h-2h part of the DIP-ADC matrix with the 2h part of the ADC vector reads

$$r_{ij} = \sum_{\substack{k,l \\ k<l}} M_{ij,kl}\, \tilde{v}_{kl}. \tag{2.8}$$

Sum restrictions are needed here to make sure that all contributions are only included uniquely, that is, not faulty more terms than physically correct are included. However, the mathematical treatment imposes some issues regarding the index restrictions which occur for all occupied indices (as in eq. 2.8, $i < j < k...$) as well as for all virtual indices ($a < b < c...$). Lifting of these sum restrictions is a requirement to use computationally efficient tensor algebra for the calculations[60]:

$$\sum_{\substack{ij \\ i\leq j}} \rightarrow \frac{1}{2}\sum_{ij}\ ,\ \sum_{\substack{ijab \\ i\leq j, a\leq b}} \rightarrow \frac{1}{4}\sum_{ijab}\ ,\ \cdots \tag{2.9}$$

As can be seen in equation 2.9, the overcounting of matrix elements needs to be compensated by a suited prefactor, which is for the lifting of n_o occupied as well as n_v virtual restrictions equal to $(n_o! \cdot n_v!)$.

Furthermore, the antisymmetric character of the ADC vector (which is a fermionic wavefunction, see eq. 1.10) needs to be considered, this is also inherited by the ADC matrix. The 2h vector, for example, suffices the antisymmetric relation $v_{ij} = -v_{ji}$. Applying this now to the 2h as well as the p3h vector leads to the fully antisymmetrized forms

$$v_{ij} = \frac{1}{\sqrt{2}}\left(\tilde{v}_{ij} - \tilde{v}_{ji}\right)\ ,\ v_{ijka} = \frac{1}{\sqrt{6}}\left(\tilde{v}_{ijka} - \tilde{v}_{jika} + \tilde{v}_{jkia} - \tilde{v}_{kjia} + \tilde{v}_{kija} - \tilde{v}_{ikja}\right). \tag{2.10}$$

where a prefactor was introduced to ensure that the vector norm is conserved. This relates now the unsymmetrized form of the vector $\tilde{v}$ and its fully antisymmetrized counterpart v as[60]

$$\sum_{ij} |v_{ij}|^2 = 2 \sum_{ij} |\tilde{v}_{ij}|^2 \,, \quad \sum_{ijka} |v_{ijka}|^2 = 6 \sum_{ijka} |\tilde{v}_{ijka}|^2 \tag{2.11}$$

and balances the overcounting due to the sum restriction lifting. For a general ADC vector, this full antisymmetrization takes the form

$$v_{IA} = \frac{1}{\sqrt{N_o! \cdot N_v!}} \sum_{\mathcal{P}(I),\mathcal{P}(A)} \varepsilon_I \cdot \varepsilon_A \cdot \tilde{v}_{IA} \tag{2.12}$$

where $I = \{i, j, k, ...\}$, $|I| = N_o$ and $A = \{a, b, c, ...\}$, $|A| = N_v$ are the sets and numbers of occupied and virtual indices in the ADC vector, respectively. $\mathcal{P}$ produces all permutations for the underlying set of indices. ε represents the N-dimensional Levi-Civita symbol.

The antisymmetrizaion of the ADC vectors has another very helpful aspect: It avoids the introduction of redundant vector elements, as they would occur due to the lifted sum restrictions, for example the $i = j$ case for the 2h vector. As can be readily seen in equation 2.10, for this particular case $v_{ii} = \tilde{v}_{ii} - \tilde{v}_{ii} = 0$ and thus vanishes, which is true for all antisymmetrized ADC vectors in every ADC scheme.

2.3. DIP-ADC working equations

2.3.1. Matrix equations

In the following, the equations for the DIP-ADC secular matrix up to extended second order are given. Equations were taken from the original publication of Jochen Schirmer et al.[78] and reformulated in the common formalism used in this work.

- Diagonal matrices of orbital energies for the singles/singles (2h/2h) and doubles/doubles (p3h/p3h) blocks:

$$\begin{aligned} K_{ij,ij} &= \epsilon_i + \epsilon_j \\ K_{ijka,ijka} &= \epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a \end{aligned} \tag{2.13}$$

- Interaction matrices for the singles/singles block in first and second order:

$$\begin{aligned} C^{(1)}_{ij,kl} &= -\left\langle ij||kl\right\rangle \\ C^{(2)}_{ij,kl} &= -\frac{1}{4}\sum_{abm}\delta_{jl}\left(\frac{\left\langle ab||km\right\rangle\left\langle ab||im\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_m}+\frac{\left\langle ab||km\right\rangle\left\langle ab||im\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_k-\epsilon_m}\right) \\ &+\frac{1}{4}\sum_{abm}\delta_{il}\left(\frac{\left\langle ab||km\right\rangle\left\langle ab||jm\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_j-\epsilon_m}+\frac{\left\langle ab||km\right\rangle\left\langle ab||jm\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_k-\epsilon_m}\right) \\ &+\frac{1}{4}\sum_{abm}\delta_{jk}\left(\frac{\left\langle ab||lm\right\rangle\left\langle ab||im\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_m}+\frac{\left\langle ab||lm\right\rangle\left\langle ab||im\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_l-\epsilon_m}\right) \\ &-\frac{1}{4}\sum_{abm}\delta_{ik}\left(\frac{\left\langle ab||lm\right\rangle\left\langle ab||jm\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_j-\epsilon_m}+\frac{\left\langle ab||lm\right\rangle\left\langle ab||jm\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_l-\epsilon_m}\right) \\ &+\frac{1}{4}\sum_{ab}\left(\frac{\left\langle ab||kl\right\rangle\left\langle ab||ij\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j}+\frac{\left\langle ab||kl\right\rangle\left\langle ab||ij\right\rangle}{\epsilon_a+\epsilon_b-\epsilon_k-\epsilon_l}\right) \end{aligned} \tag{2.14}$$

- Interaction matrices for the singles/doubles (2h/p3h) as well as the doubles/singles (p3h/2h) coupling blocks in first order:

$$\begin{aligned} C^{(1)}_{ij,klma} &= -\delta_{ik}\left\langle ja||lm\right\rangle - \delta_{im}\left\langle ja||kl\right\rangle - \delta_{il}\left\langle ja||mk\right\rangle \\ &+\delta_{jk}\left\langle ia||lm\right\rangle + \delta_{jm}\left\langle ia||kl\right\rangle + \delta_{jl}\left\langle ia||mk\right\rangle \\ C^{(1)}_{ijka,lm} &= -\delta_{li}\left\langle ma||jk\right\rangle - \delta_{lk}\left\langle ma||ij\right\rangle - \delta_{lj}\left\langle ma||ki\right\rangle \\ &+\delta_{mi}\left\langle la||jk\right\rangle + \delta_{mk}\left\langle la||ij\right\rangle + \delta_{mj}\left\langle la||ki\right\rangle \end{aligned} \tag{2.15}$$

- Interaction matrix for the doubles/doubles block in first order:

$$\begin{aligned}
C^{(1)}_{ijka,lmnb} = &- \delta_{ab}\delta_{il}\langle jk||mn\rangle - \delta_{ab}\delta_{im}\langle jk||nl\rangle - \delta_{ab}\delta_{in}\langle jk||lm\rangle \\
&- \delta_{ab}\delta_{kl}\langle ji||mn\rangle - \delta_{ab}\delta_{jm}\langle ki||nl\rangle - \delta_{ab}\delta_{jn}\langle ki||lm\rangle \\
&- \delta_{ab}\delta_{kl}\langle ij||mn\rangle - \delta_{ab}\delta_{km}\langle ij||nl\rangle - \delta_{ab}\delta_{kn}\langle ij||lm\rangle \\
&+ \delta_{jm}\delta_{kn}\langle bi||al\rangle + \delta_{jl}\delta_{km}\langle bi||an\rangle + \delta_{jl}\delta_{kn}\langle bi||am\rangle \\
&+ \delta_{im}\delta_{jn}\langle bk||al\rangle + \delta_{il}\delta_{jm}\langle bk||an\rangle + \delta_{il}\delta_{jn}\langle bk||am\rangle \\
&- \delta_{im}\delta_{kn}\langle bj||al\rangle - \delta_{il}\delta_{km}\langle bj||an\rangle - \delta_{il}\delta_{kn}\langle bj||am\rangle
\end{aligned} \tag{2.16}$$

2.3.2. DIP-ADC matrix vector products

This section introduces the matrix-vector products for DIP-ADC up to third order as implemented in `Q-Chem`[30]. All third-order equations were generated using an automated code generator developed by J. Leitner et al. which was previously applied to the formulation of PP-ADC(4) equations[60].

MVP for the singles (2h) part

- General form:

$$\begin{aligned}
r_{ij} &= \sum_{kl} M_{ij,kl}\, v_{kl} + \sum_{klm,a} M_{ij,klma}\, v_{klma} \\
&= r^{SS(0)}_{ij} + r^{SS(1)}_{ij} + r^{SS(2)}_{ij} + r^{SS(3)}_{ij} + r^{SD(1)}_{ij} + r^{SD(2)}_{ij}
\end{aligned} \tag{2.17}$$

- Zeroth-order singles-singles (2h/2h) block:

$$r^{SS(0)}_{ij} = \frac{1}{2}\mathcal{P}^{-}_{ij}\Big[- \sum_{k} f_{ik} v_{kj} - \sum_{k} f_{jk} v_{ik}\Big] \tag{2.18}$$

- First order singles-singles block:

$$r^{SS(1)}_{ij} = \frac{1}{2}\mathcal{P}^{-}_{ij}\Big[\frac{1}{2}\sum_{kl}\langle ij||kl\rangle\, v_{kl}\Big] \tag{2.19}$$

- Second order singles-singles block:

$$\begin{aligned} r_{ij}^{SS(2)} &= \frac{1}{2}\mathcal{P}_{ij}^{-}\Big[-2\sum_{k} I_{ik}v_{jk} - \frac{1}{8}\sum_{ab} t_{ij}^{ab}\sum_{kl}\langle kl||ab\rangle\, v_{kl} \\ &\quad - \frac{1}{8}\sum_{ab}\langle ij||ab\rangle\sum_{kl} t_{kl}^{ab}v_{kl}\Big] \end{aligned} \tag{2.20}$$

with the intermediate I_{ij} defined as

$$I_{ij} = \frac{1}{4}\mathcal{P}_{ij}^{+}\Big[\sum_{k,ab} t_{ik}^{ab}\,\langle jk||ab\rangle\Big] \tag{2.21}$$

- Third order singles-singles block:

$$r_{ij}^{SS(3)} = \frac{1}{2}\mathcal{P}_{ij}^{-}\Big[\frac{1}{2}\sum_{kl} M_{ij,kl}^{(3)}v_{kl}\Big] \tag{2.22}$$

with the intermediate $M_{ij,kl}^{(3)}$ as given in the appendix (eq. A.1).

- First order singles-doubles (2h/p3h) block:

$$r_{ij}^{SD(1)} = \frac{1}{2}\mathcal{P}_{ij}^{-}\Big[\sqrt{3}\sum_{kl,a}\langle kl||ia\rangle\;\, v_{jkla}\Big] \tag{2.23}$$

- Second order singles-doubles block:

$$\begin{aligned} r_{ij}^{SD(2)} &= \frac{1}{2}\mathcal{P}_{ij}^{-}\Big[\frac{\sqrt{3}}{2}\sum_{k,b}\langle ij||kb\rangle\sum_{lm,a} t_{lm}^{ab}\, v_{klma} \\ &\quad + 2\sqrt{3}\sum_{lm,b}\langle im||lb\rangle\sum_{k,a} t_{km}^{ab}v_{jkla} - \frac{\sqrt{3}}{2}\sum_{abc}\langle ia||bc\rangle\sum_{kl} t_{kl}^{bc}v_{jkla}\Big] \end{aligned} \tag{2.24}$$

MVP for the doubles (p3h) part

- General form:

$$\begin{aligned} r_{ijka} &= \sum_{lm} M_{ijka,lm}\, v_{lm} + \sum_{lmn,b} M_{ijka,lmnb}\, v_{imnb} \\ &= r_{ijka}^{DS(1)} + r_{ijka}^{DS(2)} + r_{ijka}^{DD(0)} + r_{ijka}^{DD(1)} \end{aligned} \tag{2.25}$$

- First order doubles-singles (p3h/2h) block:

$$r^{DS(1)}_{ijka} = \frac{1}{6}\mathcal{P}^{-}_{ijk}\Big[-\sqrt{3}\sum_{l} \langle ij||la\rangle\, v_{kl}\Big] \tag{2.26}$$

- Second order doubles-singles block:

$$\begin{aligned} r^{SD(2)}_{ijka} = \frac{1}{6}\mathcal{P}^{-}_{ijk}\Big[&\frac{\sqrt{3}}{2}\sum_{bc} t^{bc}_{ij}\sum_{l}\langle la||bc\rangle\, v_{kl} \\ &+ \frac{\sqrt{3}}{2}\sum_{b} t^{ab}_{ij}\sum_{lm}\langle lm||kb\rangle\, v_{lm} - 2\sqrt{3}\sum_{m,b} t^{ab}_{im}\sum_{l}\langle lm||jb\rangle\, v_{kl}\Big] \end{aligned} \tag{2.27}$$

- Zeroth-order doubles-doubles (p3h/p3h) block:

$$r^{DD(0)}_{ijka} = \frac{1}{6}\mathcal{P}^{-}_{ijk}\Big[\sum_{b} f_{ab}v_{ijkb} - \sum_{l} f_{il}v_{ljka} - \sum_{l} f_{jl}v_{ilka} - \sum_{l} f_{kl}v_{ijla}\Big] \tag{2.28}$$

- First order doubles-doubles block:

$$r^{DD(1)}_{ijka} = \frac{1}{6}\mathcal{P}^{-}_{ijk}\Big[\frac{3}{2}\sum_{lm}\langle jk||lm\rangle\, v_{ilma} - 3\sum_{l,b}\langle ib||la\rangle\, v_{jklb}\Big] \tag{2.29}$$

2.4. DEA-ADC working equations

2.4.1. Matrix equations

The matrix equations for DEA-ADC may be generated using the DIP-ADC ones by exchanging the occupied and virtual configuration spaces and adjusting the prefactor[78]. Both sets of equations are linked by the transformation relations compiled in table 2.1.

Table 2.1.: Connection of DIP and DEA equations for ADC[78].

DEA-ADC	↔	DIP-ADC
$\mathbf{K}_{ab,ab}$	$\leftrightarrow$	$-\mathbf{K}_{ij,ij}$
$\mathbf{K}_{abci,abci}$	$\leftrightarrow$	$-\mathbf{K}_{ijka,ijka}$
$\mathbf{C}_{ab,cd}$	$\leftrightarrow$	$-\mathbf{C}^{(1)}_{ij,ka} + \mathbf{C}^{(2)}_{ij,ka}$
$\mathbf{C}_{ab,cdei}$	$\leftrightarrow$	$\mathbf{C}^{(1)}_{ij,klma}$
$\mathbf{C}_{abci,defj}$	$\leftrightarrow$	$-\mathbf{C}^{(1)}_{ijka,lmnb}$

2.4.2. DEA-ADC matrix vector product

This section introduces the matrix-vector products for DEA-ADC up to third order as implemented in `Q-Chem`[30]. All third-order equations were generated using an automated code generator developed by J. Leitner et al. which was previously applied to the formulation of PP-ADC(4) equations[60].

MVP for the singles (2p) part

- General form:

$$\begin{aligned} r_{ab} &= \sum_{cd} M_{ab,cd}\, v_{cd} + \sum_{i,cde} M_{ab,icde}\, v_{icde} \\ &= r_{ab}^{SS(0)} + r_{ab}^{SS(1)} + r_{ab}^{SS(2)} + r_{ab}^{SS(3)} + r_{ab}^{SD(1)} + r_{ab}^{SD(2)} \end{aligned} \tag{2.30}$$

- Zeroth-order singles-singles (2p/2p) block:

$$r_{ab}^{SS(0)} = \frac{1}{2}\mathcal{P}_{ab}^{-}\Big[\sum_{c} f_{ac} v_{cb} + \sum_{c} f_{bc} v_{ac}\Big] \tag{2.31}$$

- First order singles-singles block:

$$r_{ab}^{SS(1)} = \frac{1}{2}\mathcal{P}_{ab}^{-}\Big[\frac{1}{2}\sum_{cd} \langle ab||cd\rangle\, v_{cd}\Big] \tag{2.32}$$

- Second order singles-singles block:

$$\begin{aligned} r_{ab}^{SS(2)} = \frac{1}{2}\mathcal{P}_{ab}^{-}\Big[&-2\sum_{c} I_{cb} v_{ac} - \frac{1}{8}\sum_{ij} t_{ij}^{ab} \sum_{cd} \langle ij||cd\rangle\, v_{cd} \\ &-\frac{1}{8}\sum_{ij} \langle ij||ab\rangle \sum_{cd} t_{ij}^{cd} v_{cd}\Big] \end{aligned} \tag{2.33}$$

with the intermediate I_{ab} defined as

$$I_{ab} = \frac{1}{4}\mathcal{P}_{ab}^{+}\Big[\sum_{ij,c} t_{ij}^{ac}\, \langle ij||bc\rangle\Big] \tag{2.34}$$

- Third order singles-singles block:

$$r_{ab}^{SS(3)} \;=\; \frac{1}{2}\mathcal{P}_{ab}^{-}\Big[\frac{1}{2}\sum_{cd} M_{ab,cd}^{(3)} v_{cd}\Big] \tag{2.35}$$

with the intermediate $M_{ab,cd}^{(3)}$ as given in the appendix (equation A.2).

- First order singles-doubles (2p/3ph) block:

$$r_{ab}^{SD(1)} \;=\; \frac{1}{2}\mathcal{P}_{ab}^{-}\Big[\sqrt{3}\sum_{i,cd} \langle ia||cd\rangle \; v_{ibcd}\Big] \tag{2.36}$$

- Second order singles-doubles block:

$$\begin{aligned} r_{ab}^{SD(2)} \;=\; & \frac{1}{2}\mathcal{P}_{ab}^{-}\Big[-\frac{\sqrt{3}}{2}\sum_{j,d}\langle jd||ab\rangle \sum_{i,ce} t_{ij}^{ce}\, v_{icde} \\ & + 2\sqrt{3}\sum_{i,cd} v_{iacd}\sum_{j,e}\langle jc||be\rangle\, t_{ij}^{de} - \frac{\sqrt{3}}{2}\sum_{ijk}\langle jk||ia\rangle \sum_{cd} t_{jk}^{cd} v_{ibcd}\Big] \end{aligned} \tag{2.37}$$

MVP for the doubles (3ph) part

- General form:

$$\begin{aligned} r_{iabc} \;&=\; \sum_{de} M_{iabc,de}\, v_{de} + \sum_{j,def} M_{iabc,jdef}\, v_{jdef} \\ &= r_{iabc}^{DS(1)} + r_{iabc}^{DS(2)} + r_{iabc}^{DD(0)} + r_{iabc}^{DD(1)} \end{aligned} \tag{2.38}$$

- First order doubles-singles (3ph/2p) block:

$$r_{iabc}^{DS(1)} \;=\; \frac{1}{6}\mathcal{P}_{abc}^{-}\Big[-\sqrt{3}\sum_{d}\langle id||ab\rangle\, v_{cd}\Big] \tag{2.39}$$

- Second order doubles-singles block:

$$\begin{aligned} r_{iabc}^{SD(2)} \;=\; & \frac{1}{6}\mathcal{P}_{abc}^{-}\Big[\frac{-\sqrt{3}}{2}\sum_{jk} t_{jk}^{ac}\sum_{d}\langle jk||id\rangle\, v_{bd} \\ & - \frac{\sqrt{3}}{2}\sum_{j} t_{ij}^{ac}\sum_{de}\langle jb||de\rangle\, v_{de} - 2\sqrt{3}\sum_{j,e} t_{ij}^{ce}\sum_{d}\langle ja||de\rangle\, v_{bd}\Big] \end{aligned} \tag{2.40}$$

- Zeroth-order doubles-doubles (3ph/3ph) block:

$$r_{iabc}^{DD(0)} = \frac{1}{6}\mathcal{P}_{abc}^{-}\Big[\sum_{d} f_{ad} v_{idbc} + \sum_{d} f_{bd} v_{iadc} + \sum_{d} f_{cd} v_{iabd} - \sum_{j} f_{ij} v_{jabc}\Big] \tag{2.41}$$

- First order doubles-doubles block:

$$r_{iabc}^{DD(1)} = \frac{1}{6}\mathcal{P}_{abc}^{-}\Big[\frac{3}{2}\sum_{de} \langle bc||de\rangle\, v_{iade} - 3\sum_{j,d} \langle id||ja\rangle\, v_{jbcd}\Big] \tag{2.42}$$

2.5. Configuration state functions for $N \pm 2$ determinants

The proper setup for the calculation of doubly-ionized as well as double electronically-attached states includes the formulation of the corresponding configuration state functions (CSF). These functions represent a proper linear combination of single Slater determinants, which then form spin-pure eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ for singlet states, triplet states etc. (in the case of IP and EA, doublets, quartets etc.). Coefficients in the linear expansion of these CSF are the so-called Clebsch-Gordan coefficients[89,12] which can be utilized to couple different systems with angular momenta in quantum mechanics. A general approach to formulate these CSF is presented, for example, in Helgaker's Molecular Electronic-Structure Theory book with the so-called genealogical coupling scheme[46]. This scheme uses the fundamental doublet operators $\{\hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger\}$ and $\{\hat{a}_\alpha, -\hat{a}_\beta\}$ (which arise from the commutator relations for creators and annihilators) to iteratively construct a CSF by successively coupling these together. This allows for the construction of arbitrary n-electron configurations starting from a closed-shell ground state wavefunction. However, this work will introduce a slightly different approach to form the CSF.

As has been depicted in figure 2.2, the p3h propagator may be understood as a double ionization in combination with an electron excitation (the same holds for the 3ph propagator in double attachment). Therefore, the underlying CSF for the 2h (2p) part as well as the ph part from PP-ADC may be used as a basis to construct p3h (3ph) states by forming the suited linear combinations as tensor products[71]. In the following, these are given and combined to spin-pure CSF for singlet and triplet p3h (3ph) state functions.

For the setup of restricted calculations, only singlet and triplet states with $m_S = 0$ are considered and are presented in the following. The necessary $m_S \neq 0$ triplet functions that are needed to construct these are also given. A short-hand notation for the action of the creation and annihilation operators onto the closed-shell ground state is introduced. Take as an example the following expression:

$$\hat{a}^\dagger_{a,\alpha}\hat{a}_{i,\beta}\,|\Phi_0\rangle \;\equiv\; |\alpha_a\beta_i\rangle \tag{2.43}$$

which would create an α (spin-up) electron in the virtual spin orbital a and remove a β (spin-down) electron in the occupied spin orbital i. The red highlighted functions represent those needed for restricted calculations of singlet and triplet states.

It should be noted at this point that changing the total sign of a CSF does not alter the calculation outcome since the overall factor of -1 introduced in the wavefunction does not have an impact on the computed eigenvalues whatsoever. However, the relative signs between the different spin configurations (spin blocks) is of crucial importance since they determine whether a state is of singlet or triplet (quintet etc.) character.

Particle-hole functions

Needed in the construction of p3h (DIP) as well as 3ph (DEA) configuration state functions.

- Singlet configuration:

$$|S_{ia}\rangle \;=\; \frac{1}{\sqrt{2}}\left(|\alpha_i\alpha_a\rangle + |\beta_i\beta_a\rangle\right) \tag{2.44}$$

- Triplet configurations:

$$\begin{aligned} |T^1_{ia}\rangle &= -\,|\beta_i\alpha_a\rangle \\ |T^0_{ia}\rangle &= \frac{1}{\sqrt{2}}\left(|\alpha_i\alpha_a\rangle - |\beta_i\beta_a\rangle\right) \\ |T^{-1}_{ia}\rangle &= |\alpha_i\beta_a\rangle \end{aligned} \tag{2.45}$$

2.5.1. $N-2$ configuration state functions for double ionization

Two-hole functions

- Singlet configurations, the first one represents double ionization from the same orbital:

$$\begin{aligned} |S_{ii}\rangle &= |\alpha_i \beta_i\rangle \\ |S_{ij}\rangle &= \frac{1}{\sqrt{2}}\Big(|\beta_i \alpha_j\rangle - |\alpha_i \beta_j\rangle \Big) \end{aligned} \tag{2.46}$$

- Triplet configurations:

$$\begin{aligned} |T^{1}_{ij}\rangle &= |\beta_i \beta_j\rangle \\ |T^{0}_{ij}\rangle &= \frac{1}{\sqrt{2}}\Big(|\alpha_i \beta_j\rangle + |\beta_i \alpha_j\rangle \Big) \\ |T^{-1}_{ij}\rangle &= |\alpha_i \alpha_j\rangle \end{aligned} \tag{2.47}$$

Particle-three hole functions

- Singlet configurations, the first one includes double ionization from the same orbital:

$$\begin{aligned} |S_{iija}\rangle &= |S_{ii}\rangle \otimes |S_{ja}\rangle \\ &= \frac{1}{\sqrt{2}}\Big(|\alpha_i \beta_i \beta_j \beta_a\rangle - |\beta_i \alpha_i \alpha_j \alpha_a\rangle \Big) \\ |S^{(I)}_{ijka}\rangle &= |S_{ij}\rangle \otimes |S_{ka}\rangle \\ &= \frac{1}{2}\Big(|\beta_i \alpha_j \alpha_k \alpha_a\rangle + |\beta_i \alpha_j \beta_k \beta_a\rangle + |\alpha_i \beta_j \alpha_k \alpha_a\rangle + |\alpha_i \beta_j \beta_k \beta_a\rangle \Big) \\ |S^{(II)}_{ijka}\rangle &= \frac{1}{\sqrt{3}}\Big(|T^{1}_{ij}\rangle \otimes |T^{-1}_{ka}\rangle - |T^{0}_{ij}\rangle \otimes |T^{0}_{ka}\rangle + |T^{-1}_{ij}\rangle \otimes |T^{1}_{ka}\rangle \Big) \\ &= \frac{1}{2\sqrt{3}}\Big(2\,|\beta_i \beta_j \alpha_k \beta_a\rangle - 2\,|\alpha_i \alpha_j \beta_k \alpha_a\rangle \\ &\quad - |\alpha_i \beta_j \alpha_k \alpha_a\rangle + |\alpha_i \beta_j \beta_k \beta_a\rangle - |\beta_i \alpha_j \alpha_k \alpha_a\rangle + |\beta_i \alpha_j \beta_k \beta_a\rangle \Big) \end{aligned} \tag{2.48}$$

- Triplet configurations, the first one includes double ionization from the same orbital:

$$\begin{aligned}
|T^{0}_{iija}\rangle &= |S_{ii}\rangle \otimes |T^{0}_{ja}\rangle \\
&= \frac{1}{\sqrt{2}}\Big(|\alpha_i\beta_i\alpha_j\alpha_a\rangle + |\beta_i\alpha_i\beta_j\beta_a\rangle \Big) \\
|T^{0(I)}_{ijka}\rangle &= |S_{ij}\rangle \otimes |T^{0}_{ka}\rangle \\
&= \frac{1}{2}\Big(|\beta_i\alpha_j\alpha_k\alpha_a\rangle - |\beta_i\alpha_j\beta_k\beta_a\rangle - |\alpha_i\beta_j\alpha_k\alpha_a\rangle + |\alpha_i\beta_j\beta_k\beta_a\rangle \Big) \\
|T^{0(II)}_{ijka}\rangle &= |T^{0}_{ij}\rangle \otimes |S_{ka}\rangle \\
&= \frac{1}{2}\Big(|\alpha_i\beta_j\alpha_k\alpha_a\rangle + |\alpha_i\beta_j\beta_k\beta_a\rangle + |\beta_i\alpha_j\alpha_k\alpha_a\rangle + |\beta_i\alpha_j\beta_k\beta_a\rangle \Big) \\
|T^{0(III)}_{ijka}\rangle &= \frac{1}{\sqrt{2}}\Big(|T^{1}_{ij}\rangle \otimes |T^{-1}_{ka}\rangle - |T^{-1}_{ij}\rangle \otimes |T^{1}_{ka}\rangle \Big) \\
&= \frac{1}{\sqrt{2}}\Big(|\beta_i\beta_j\alpha_k\beta_a\rangle + |\alpha_i\alpha_j\beta_k\alpha_a\rangle \Big)
\end{aligned} \tag{2.49}$$

- Quintet configuration:

$$\begin{aligned}
|Q^{0}_{ijka}\rangle &= \frac{1}{\sqrt{6}}\Big(|T^{1}_{ij}\rangle \otimes |T^{-1}_{ka}\rangle + 2\,|T^{0}_{ij}\rangle \otimes |T^{0}_{ka}\rangle + |T^{-1}_{ij}\rangle \otimes |T^{1}_{ka}\rangle \Big) \\
&= \sqrt{\frac{2}{3}}\,\Big(\frac{1}{2}\,|\beta_i\beta_j\alpha_k\beta_a\rangle - \frac{1}{2}\,|\alpha_i\alpha_j\beta_k\alpha_a\rangle \\
&\qquad + |\alpha_i\beta_j\alpha_k\alpha_a\rangle - |\alpha_i\beta_j\beta_k\beta_a\rangle + |\beta_i\alpha_j\alpha_k\alpha_a\rangle - |\beta_i\alpha_j\beta_k\beta_a\rangle \Big)
\end{aligned} \tag{2.50}$$

2.5.2. $N+2$ configuration state functions for double attachment

Two-particle functions

- Singlet configurations, the first one represents double attachment in the same orbital:

$$\begin{aligned}
|S_{aa}\rangle &= |\alpha_a\beta_a\rangle \\
|S_{ab}\rangle &= \frac{1}{\sqrt{2}}\Big(|\beta_a\alpha_b\rangle - |\alpha_a\beta_b\rangle \Big)
\end{aligned} \tag{2.51}$$

- Triplet configurations:

$$\begin{aligned}
|T^{1}_{ab}\rangle &= |\alpha_a \alpha_b\rangle \\
|T^{0}_{ab}\rangle &= \frac{1}{\sqrt{2}}\Big(|\alpha_a \beta_b\rangle + |\beta_a \alpha_b\rangle \Big) \\
|T^{-1}_{ab}\rangle &= |\beta_a \beta_b\rangle
\end{aligned} \tag{2.52}$$

Three particle-hole functions

- Singlet configurations, the first one includes double attachment in the same orbital:

$$\begin{aligned}
|S_{iabb}\rangle &= |S_{ia}\rangle \otimes |S_{bb}\rangle \\
&= \frac{1}{\sqrt{2}}\Big(|\alpha_i \alpha_a \alpha_b \beta_b\rangle - |\beta_i \beta_a \beta_b \alpha_b\rangle \Big) \\
|S^{(I)}_{iabc}\rangle &= |S_{ia}\rangle \otimes |S_{bc}\rangle \\
&= \frac{1}{2}\Big(|\alpha_i \alpha_a \beta_b \alpha_c\rangle - |\alpha_i \alpha_a \alpha_b \beta_c\rangle + |\beta_i \beta_a \beta_b \alpha_c\rangle - |\beta_i \beta_a \alpha_b \beta_c\rangle \Big) \\
|S^{(II)}_{iabc}\rangle &= \frac{1}{\sqrt{3}}\Big(|T^{1}_{ia}\rangle \otimes |T^{-1}_{bc}\rangle - |T^{0}_{ia}\rangle \otimes |T^{0}_{bc}\rangle + |T^{-1}_{ia}\rangle \otimes |T^{1}_{bc}\rangle \Big) \\
&= \frac{1}{2\sqrt{3}}\Big(2\,|\alpha_i \beta_a \alpha_b \alpha_c\rangle - 2\,|\beta_i \alpha_a \beta_b \beta_c\rangle \\
&\qquad - |\alpha_i \alpha_a \alpha_b \beta_c\rangle + |\alpha_i \alpha_a \beta_b \alpha_c\rangle - |\beta_i \beta_a \alpha_b \beta_c\rangle + |\beta_i \beta_a \beta_b \alpha_c\rangle \Big)
\end{aligned} \tag{2.53}$$

- Triplet configurations, the first one includes double attachment in the same orbital:

$$\begin{aligned}
|T^{0}_{iabb}\rangle &= |T^{0}_{ia}\rangle \otimes |S_{bb}\rangle \\
&= \frac{1}{\sqrt{2}}\Big(|\alpha_i \alpha_a \alpha_b \beta_b\rangle + |\beta_i \beta_a \beta_b \alpha_b\rangle \Big) \\
|T^{0(I)}_{iabc}\rangle &= |T^{0}_{ia}\rangle \otimes |S_{bc}\rangle \\
&= \frac{1}{2}\Big(|\alpha_i \alpha_a \beta_b \alpha_c\rangle - |\alpha_i \alpha_a \alpha_b \beta_c\rangle - |\beta_i \beta_a \beta_b \alpha_c\rangle + |\beta_i \beta_a \alpha_b \beta_c\rangle \Big) \\
|T^{0(II)}_{iabc}\rangle &= |S_{ia}\rangle \otimes |T^{0}_{bc}\rangle \\
&= \frac{1}{2}\Big(|\alpha_i \alpha_a \alpha_b \beta_c\rangle + |\alpha_i \alpha_a \beta_b \alpha_c\rangle + |\beta_i \beta_a \alpha_b \beta_c\rangle + |\beta_i \beta_a \beta_b \alpha_c\rangle \Big) \\
|T^{0(III)}_{iabc}\rangle &= \frac{1}{\sqrt{2}}\Big(|T^{1}_{ia}\rangle \otimes |T^{-1}_{bc}\rangle - |T^{-1}_{ia}\rangle \otimes |T^{1}_{bc}\rangle \Big) \\
&= \frac{1}{\sqrt{2}}\Big(- |\beta_i \alpha_a \beta_b \beta_c\rangle - |\alpha_i \beta_a \alpha_b \alpha_c\rangle \Big)
\end{aligned} \tag{2.54}$$

- Quintet configuration:

$$\begin{aligned}
|Q^0_{iabc}\rangle &= \frac{1}{\sqrt{6}}\Big(|T^1_{ia}\rangle \otimes |T^{-1}_{bc}\rangle + 2\,|T^0_{ia}\rangle \otimes |T^0_{bc}\rangle + |T^{-1}_{ia}\rangle \otimes |T^1_{bc}\rangle \Big) \\
&= \sqrt{\frac{2}{3}}\,\Big(\frac{1}{2}\,|\alpha_i\beta_a\alpha_b\alpha_c\rangle - \frac{1}{2}\,|\beta_i\alpha_a\beta_b\beta_c\rangle \\
&\quad + |\alpha_i\alpha_a\alpha_b\beta_c\rangle + |\alpha_i\alpha_a\beta_b\alpha_c\rangle - |\beta_i\beta_a\alpha_b\beta_c\rangle - |\beta_i\beta_a\beta_b\alpha_c\rangle \Big)
\end{aligned} \tag{2.55}$$

2.6. Implementation

The implementation of DIP/DEA-ADC has been executed in the `adcman` program package of `Q-Chem` 5.2[30], originally developed by M. Wormit et al. for excited state calculations in the ADC framework[111]. Already existing infrastructure for PP-ADC and IP-ADC has been used. All working equations, i. e. matrix-vector products, computational intermediates and diagonals have been implemented in the `libadc` program package, which has been developed together with `adcman` to perform highly-efficient tensor algebra calculations. Therefore, the syntax of the open-source `C++` tensor library `libtensor`[31] is applied for these computations. All ADC calculations (also PP and IP) follow the same progression of steps. In general, the four most important steps during an ADC calculation are in the order of their execution:

1. Loading of all prerequisites for the calculation
2. Setting up the correct symmetry for the tensor objects
3. Setting up the guess vectors and diagonals
4. Running the Davidson solver

In the following, each of the four steps will be explained in brevity.

Loading of prerequisites

Before the ADC calculation starts, the corresponding MP ground state calculation is performed and used as a reference, that is, for ADC(2) and ADC(2)-x the MP2 ground state and for ADC(3) the MP3 ground state. For the calculation of the ADC matrix-vector products and diagonals, tensor objects from the Møller-Plesset (and Hartree-Fock) calculations are needed, such as for example the antisymmetrized electron-repulsion integrals and the MP amplitudes. Furthermore, for computational efficiency, intermediates have been precomputed and need to be loaded for the calculation.

Symmetry setup

A correct setup of the spin and permutational symmetry for the tensor objects is crucial for a proper calculation. As for the spin, the configuration spaces of the 2h (2p) and p3h (3ph) tensors may be split in different spin blocks. There are four spin blocks for the 2h (2p) case and 16 for the p3h (3ph) case. For restricted calculations, only spin-pure singlet ($S = 0$) and triplet ($S = 1$) states with a projected spin quantum number of $m_S = 0$ are considered, meaning that the number of spin-up (α) and spin-down (β) states needs to be kept equal. All allowed spin blocks are summarized in table 2.2. The six allowed spin blocks are then mapped onto each other pairwise (as shown in eq. 2.56), depending on the calculation type: For a singlet calculation, the mapping coefficient is -1, whereas for a triplet calculation it is +1. These mappings and their respective coefficients are important for the correct processing of singlet and triplet calculations. The mapping coefficients equal the prefactors of the respective spin blocks in the singlet and triplet configuration state functions (guess vectors) for DIP-ADC and DEA-ADC, respectively (see in the previous section).

$$
\begin{array}{cc}
\text{DIP spin block mappings:} & \text{DEA spin block mappings:} \\
\alpha\beta \overset{+1/-1}{\Longleftrightarrow} \beta\alpha & \alpha\beta \overset{+1/-1}{\Longleftrightarrow} \beta\alpha \\
\alpha\alpha\beta\alpha \overset{+1/-1}{\Longleftrightarrow} \beta\beta\alpha\beta & \alpha\alpha\alpha\beta \overset{+1/-1}{\Longleftrightarrow} \beta\beta\beta\alpha \\
\alpha\beta\alpha\alpha \overset{+1/-1}{\Longleftrightarrow} \beta\alpha\beta\beta & \alpha\alpha\beta\alpha \overset{+1/-1}{\Longleftrightarrow} \beta\beta\alpha\beta \\
\beta\alpha\alpha\alpha \overset{+1/-1}{\Longleftrightarrow} \alpha\beta\beta\beta & \alpha\beta\alpha\alpha \overset{+1/-1}{\Longleftrightarrow} \beta\alpha\beta\beta
\end{array}
\tag{2.56}
$$

Besides the spin symmetry, the correct permutational symmetry for tensor objects must be further established. As mentioned before, the ADC vectors are antisymmetrized with respect to index permutations to ensure an efficient computation.

Table 2.2.: All spin blocks for the 2h and p3h configuration spaces of DIP-ADC (left) as well as all spin blocks for the 2p and 3ph configuration spaces of DEA-ADC (right). Note that occupied indices are before virtual ones.

2h configurations

spin block	m_S	allowed?
$\alpha\alpha$	-1	no
$\alpha\beta$	0	yes
$\beta\alpha$	0	yes
$\beta\beta$	1	no

2p configurations

spin block	m_S	allowed?
$\alpha\alpha$	1	no
$\alpha\beta$	0	yes
$\beta\alpha$	0	yes
$\beta\beta$	-1	no

p3h configurations

spin block	m_S	allowed?
$\alpha\alpha\alpha\alpha$	-1	no
$\alpha\alpha\alpha\beta$	-2	no
$\alpha\alpha\beta\alpha$	0	yes
$\alpha\beta\alpha\alpha$	0	yes
$\beta\alpha\alpha\alpha$	0	yes
$\alpha\alpha\beta\beta$	-1	no
$\alpha\beta\alpha\beta$	-1	no
$\alpha\beta\beta\alpha$	1	no
$\beta\alpha\alpha\beta$	-1	no
$\beta\alpha\beta\alpha$	1	no
$\beta\beta\alpha\alpha$	1	no
$\alpha\beta\beta\beta$	0	yes
$\beta\alpha\beta\beta$	0	yes
$\beta\beta\alpha\beta$	0	yes
$\beta\beta\beta\alpha$	2	no
$\beta\beta\beta\beta$	1	no

3ph configurations

spin block	m_S	allowed?
$\alpha\alpha\alpha\alpha$	1	no
$\alpha\alpha\alpha\beta$	0	yes
$\alpha\alpha\beta\alpha$	0	yes
$\alpha\beta\alpha\alpha$	0	yes
$\beta\alpha\alpha\alpha$	2	no
$\alpha\alpha\beta\beta$	-1	no
$\alpha\beta\alpha\beta$	-1	no
$\alpha\beta\beta\alpha$	-1	no
$\beta\alpha\alpha\beta$	1	no
$\beta\alpha\beta\alpha$	1	no
$\beta\beta\alpha\alpha$	1	no
$\alpha\beta\beta\beta$	-2	no
$\beta\alpha\beta\beta$	0	yes
$\beta\beta\alpha\beta$	0	yes
$\beta\beta\beta\alpha$	0	yes
$\beta\beta\beta\beta$	-1	no

Guess vectors and diagonals

As a preliminary step to the calculation of double ionization/double electron attachment energies, an estimated ADC vector (guess vector) needs to be set up for the solver. This vector is constructed using the CSF for singlet or triplet states introduced in the previous chapter, depending on the calculation. As a first guess on the energy, the diagonals of the corresponding ADC matrix are computed as (with the example of DIP):

$$\begin{aligned} \mathbf{D}_{ij,ij} &= \delta_{ik}\delta_{jl}\,\mathbf{M}_{ij,kl}, \\ \mathbf{D}_{ijka,ijka} &= \delta_{il}\delta_{jm}\delta_{kn}\delta_{ab}\,\mathbf{M}_{ijka,lmnb}. \end{aligned} \tag{2.57}$$

Singles (2h, 2p) guess vectors lie energetically lower than doubles (p3h, 3ph). If not specified explicitly, the lowest-lying guess vectors are always chosen for a calculation. Therefore, the guess vector setup is usually dominated by singles vectors that are expected to approach the converged states the most.

Davidson solver

The Davidson solver[16] is an iterative solver designed to determine the lowest-lying eigenstates and eigenvalues of a diagonally-dominated matrix. This is done by diagonalizing not the whole matrix at once, but rather subspaces at a time to build up a solution for the full expression. Matrix-vector products (see in the previous section) are computed in every step of the procedure. If, in two consecutive iteration steps, a certain threshold (for vector amplitudes as well as energies) is undercut, the ADC vector is seen as converged and returned with the corresponding energy. Figure 2.4 schematically demonstrates this process. Although the Davidson procedure is very efficient in computing the lowest-lying eigenstates, it may get difficult when asking for higher-lying states. A possible solution is, for example, introduced by altering the matrix to be evaluated: For example by restricting the orbital spaces as it is the case in the core-valence separation approach[10] (see in chapter 3).

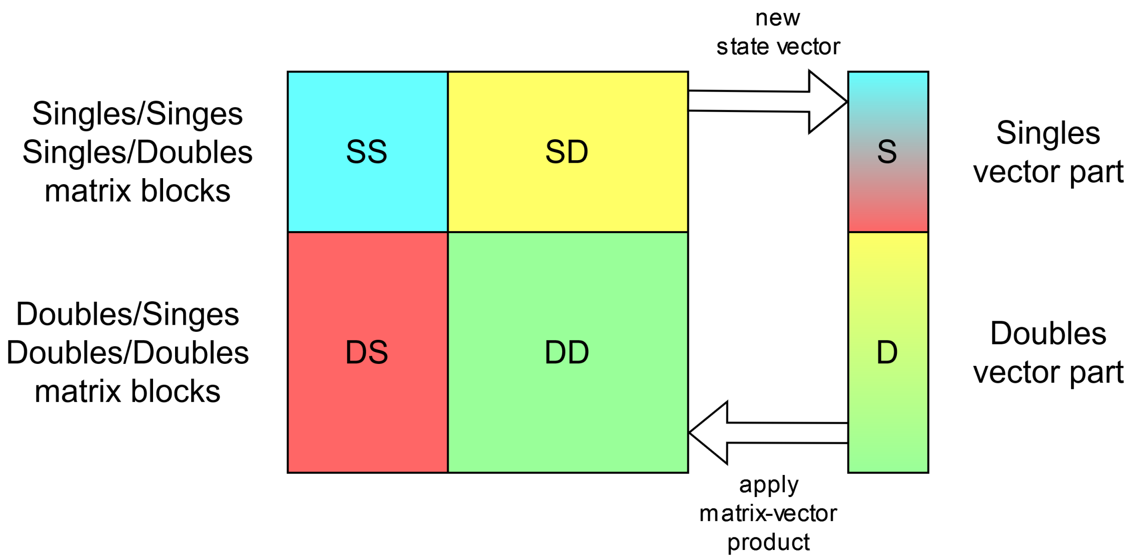

Figure 2.4.: Conceptional scheme for the eigenvalue solver. Applicable to all ADC schemes (PP, IP, EA, DIP, DEA).

2.7. Benchmarking / Calculations for doubly-ionized states

In this section, a benchmark study of DIP-ADC is presented. Benchmark data has been generated for DIP-ADC(2), DIP-ADC(2)-x as well as DIP-ADC(3) and has been compared to EOMDIP-CCSD[58,59] as well as FCI data. For DIP-ADC(0) as well as DIP-ADC(1), single values are shown as well and presented in the context of higher-order DIP-ADC(n) methods. Calculations for DIP-ADC and EOMDIP-CCSD were performed using `Q-Chem` 5.2[30].

2.7.1. Doubly-ionized states on a Full CI level

The first small benchmark set includes singlet and triplet calculations for H_2O, LiH and HF. Geometries used for the calculations can be found in the appendix (section A.2), the 3-21G basis set[24] was used to calculate doubly-ionized states. This set was applied by Velkov et al.[101] to compare DIP-ADC(2)-x data to FCI values. It has been expanded to second- as well as third-order DIP-ADC values. Benchmark data is collected in table 2.4 and the energy landscape for the hierarchy of DIP-ADC methods as well as EOMDIP-CCSD and FCI is presented in figure 2.5 for the lowest-lying singlet and triplet states of the included species.
As figure 2.5 depicts, the hierarchy of ADC(n) methods shows a clear pattern for the calculation of double-ionization energies: ADC(0), which only includes the diagonal of orbital energies, underestimates the energy in a very stark manner, ADC(1) clearly overestimates it. Although the second-order scheme ADC(2) with its zeroth-order doubles/doubles diagonal is still too low with respect to the FCI values, the extended scheme ADC(2)-x is capable of approaching FCI values well, although with an underestimation. ADC(3) reproduces FCI data pretty good and tends to lie slightly above the corresponding energies. The iterative ground-state of EOM-CCSD as well as the higher-order terms[15,5] lets this method perform best with respect to FCI data.
This observation may be amended by the amount of doubles (p3h) wavefunction contributions for the different methods. While the zeroth- and first order scheme completely lack a doubles description, the second order scheme ADC(2) includes only a zeoth-order parametrization of doubles amplitudes. The energetically lower-lying zeroth-order contribu-

tions influence the energy eigenvalues, resulting in comparatively high amounts of doubles amplitudes, lying about 30% or even higher. For the extended second-order scheme inheriting a first-order description of the doubles/doubles space, the amount of doubles amplitudes diminishes significantly to ≤ 15%, for ADC(3) and EOM-CCSD even reducing further to about 10%. An explanation for this trend may be in similarity to CVS-ADC for core excitations[104]: The double ionization introduces a strong lack of electron density to the equilibrated ground state, which produces a physically unfavourable configuration of the remaining dication. As a result, orbital relaxation processes arise to counteract this. As the first-order doubles/doubles block enables a proper description of these effects, the ADC(2)-x scheme is the first to reproduce reasonable double-ionization energies. Interestingly, for the low-lying $^1\Sigma^+$ state of LiH which represents a pure singles excitation (doubles amp. >1%), ADC(1) already delivers a valid description (see figure 2.5).

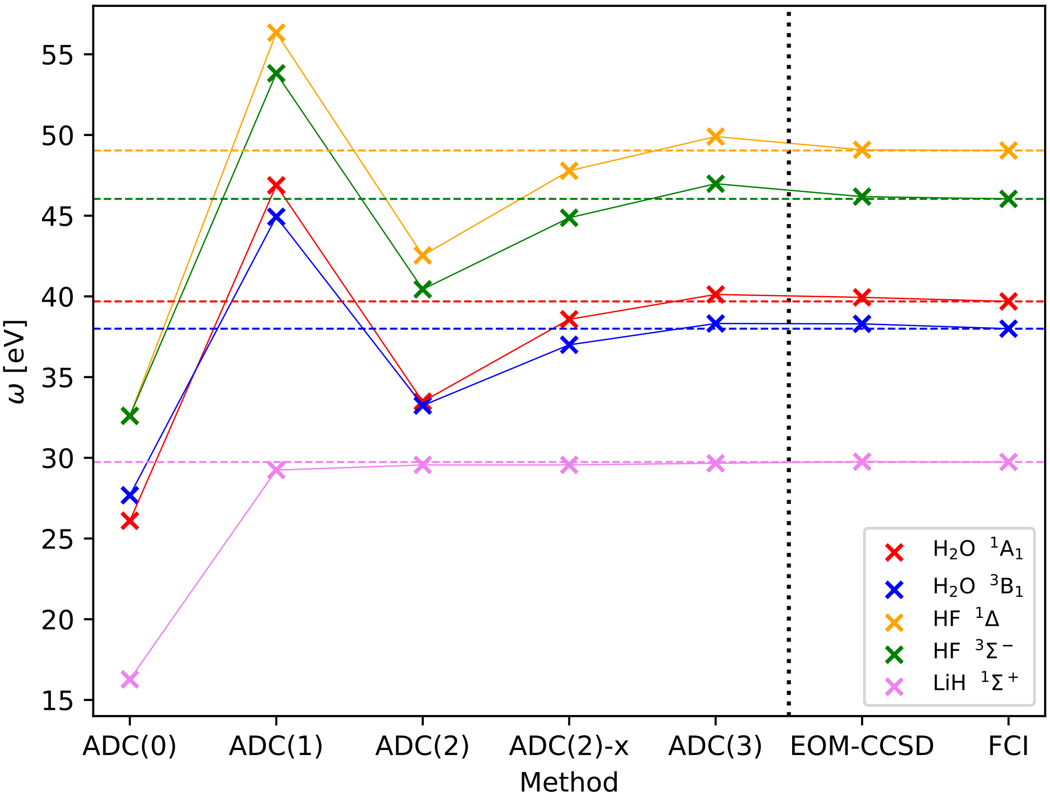

Figure 2.5.: Double-ionization energies for the lowest-lying singlet and triplet states of table 2.4, given in the hierarchy of DIP-ADC methods.

Table 2.4.: Double-ionization energies for singlet and triplet states for DIP-ADC(2), DIP-ADC(2)-x , DIP-ADC(3) as well as EOMDIP-CCSD compared to FCI. FCI value taken from[101].

		Double e-attachment energy [eV]					Doubles contribution				ω_X - ω_{FCI} [eV] X =			
		ADC			EOM-		ADC			EOM-	ADC			EOM-
Mole-cule	Exci-tation	(2)	(2)-x	(3)	CCSD	FCI	(2)	(2)-x	(3)	CCSD	(2)	(2)-x	(3)	CCSD
H_2O	1 A1	33.48	38.58	40.72	39.94	39.69	0.36	0.16	0.13	0.12	-6.21	-1.11	1.03	0.25
	1 B1	35.34	39.96	41.84	41.22	40.99	0.33	0.15	0.12	0.11	-5.65	-1.03	0.85	0.23
	1 A1	38.73	42.89	44.47	44.00	43.9	0.30	0.13	0.11	0.10	-5.17	-1.01	0.57	0.10
	1 A2	40.49	43.85	45.25	44.87	44.79	0.27	0.12	0.10	0.09	-4.30	-0.94	0.46	0.08
	1 B2	42.90	45.99	47.33	46.95	46.98	0.26	0.11	0.09	0.08	-4.08	-0.99	0.35	-0.03
	1 A1	49.16	51.37	52.31	52.10	52.13	0.40	0.08	0.07	0.06	-2.97	-0.76	0.18	-0.03
	1 A1	59.08	64.87	66.68	66.22	66.31	0.61	0.19	0.26	0.15	-7.23	-1.44	0.37	-0.09
	1 B1	-	64.14	65.78	65.65	66.90	-	0.27	0.43	0.18	-	-2.76	-1.12	-1.25
LiH	1 Σ+	29.56	29.56	29.66	29.76	29.74	0.0005	0.0003	0.0003	0	-0.18	-0.18	-0.08	0.02
	1 Σ+	80.14	82.39	82.51	-	82.57	0.44	0.08	0.08	-	-2.43	-0.18	-0.06	-
HF	1 Δ	42.54	47.78	49.90	49.08	49.04	0.33	0.13	0.11	0.10	-6.50	-1.26	0.86	0.04
	1 Δ	43.65	49.16	51.24	50.43	50.41	0.35	0.13	0.11	0.10	-6.76	-1.25	0.83	0.02
	1 Π	47.55	51.18	52.59	52.12	52.18	0.25	0.10	0.08	0.08	-4.63	-1.00	0.41	-0.06
	1 Σ+	54.01	55.94	57.03	56.66	56.87	0.12	0.07	0.05	0.05	-2.86	-0.93	0.16	-0.21
	1 Σ+	76.22	80.54	82.19	81.61	82.2	0.29	0.11	0.10	0.09	-5.98	-1.66	-0.01	-0.59
H_2O	3 B1	33.24	37.00	38.96	38.30	38.00	0.30	0.16	0.13	0.12	-4.76	-1.00	0.96	0.30
	3 A2	39.04	42.04	43.49	43.09	42.98	0.26	0.13	0.10	0.10	-3.94	-0.94	0.51	0.11
	3 B2	41.05	43.59	44.87	44.55	44.48	0.23	0.12	0.10	0.09	-3.43	-0.89	0.39	0.07
	3 B1	53.04	56.78	58.75	58.11	57.61	0.37	0.17	0.15	0.13	-4.57	-0.83	1.14	0.50
	3 B2	61.36	63.46	64.53	64.48	64.81	0.23	0.18	0.28	0.14	-3.45	-1.36	-0.28	-0.33
LiH	3 Σ-	79.97	82.09	82.21	-	82.27	0.39	0.07	0.07	-	-2.30	-0.18	-0.06	-
HF	3 Σ-	40.44	44.87	46.98	46.18	46.04	0.29	0.14	0.11	0.11	-5.60	-1.17	0.94	0.14
	3 Π	45.13	48.24	49.76	49.23	49.25	0.23	0.11	0.09	0.09	-4.12	-1.01	0.51	-0.02
	3 Π	64.99	68.44	70.53	69.71	69.43	0.30	0.13	0.11	0.10	-4.44	-0.99	1.10	0.28
	3 Σ-	69.64	71.96	73.39	72.95	72.65	0.20	0.12	0.12	0.10	-3.01	-0.69	0.74	0.30

For the eight (seven for DIP-ADC(2)) singlet states in table 2.4, DIP-ADC(2) has an average deviation of -5.09 eV from the corresponding FCI value, DIP-ADC(2)-x deviates in average -1.25 eV, DIP-ADC(3) 0.34 eV and EOMDIP-CCSD -0.09 eV; as for the five triplet states, the average deviation for DIP-ADC(2) is -7.12 eV to FCI, for DIP-ADC(2)-x -2.01 eV, for DIP-ADC(3) 0.54 eV and for EOMDIP-CCSD -0.15 eV; proving that the pure second-order scheme does not deliver quantitatively exact results. DIP-ADC(3) values are in very good agreement with EOMDIP-CCSD and FCI values. Generally, they tend to exceed the corresponding FCI values slightly, an exception to this constitutes the last singlet state for water (B1), which shows a remarkably high amount of doubles amplitudes and lies under the corresponding FCI value. DIP-ADC(2)-x values, on the other hand, are also located in a reasonable scope around these values, but tend to underestimate the double-ionization energies.

Taking the findings above, the next section presents a larger benchmark set of small and medium-sized molecules for an extensive study of second-and third-order DIP-ADC methods in comparison to EOMDIP-CCSD. A detailed statistical analysis is provided for both, doubly-ionized singlet as well as triplet states.

2.7.2. Benchmark study on doubly-ionized states for small- to medium-sized molecules

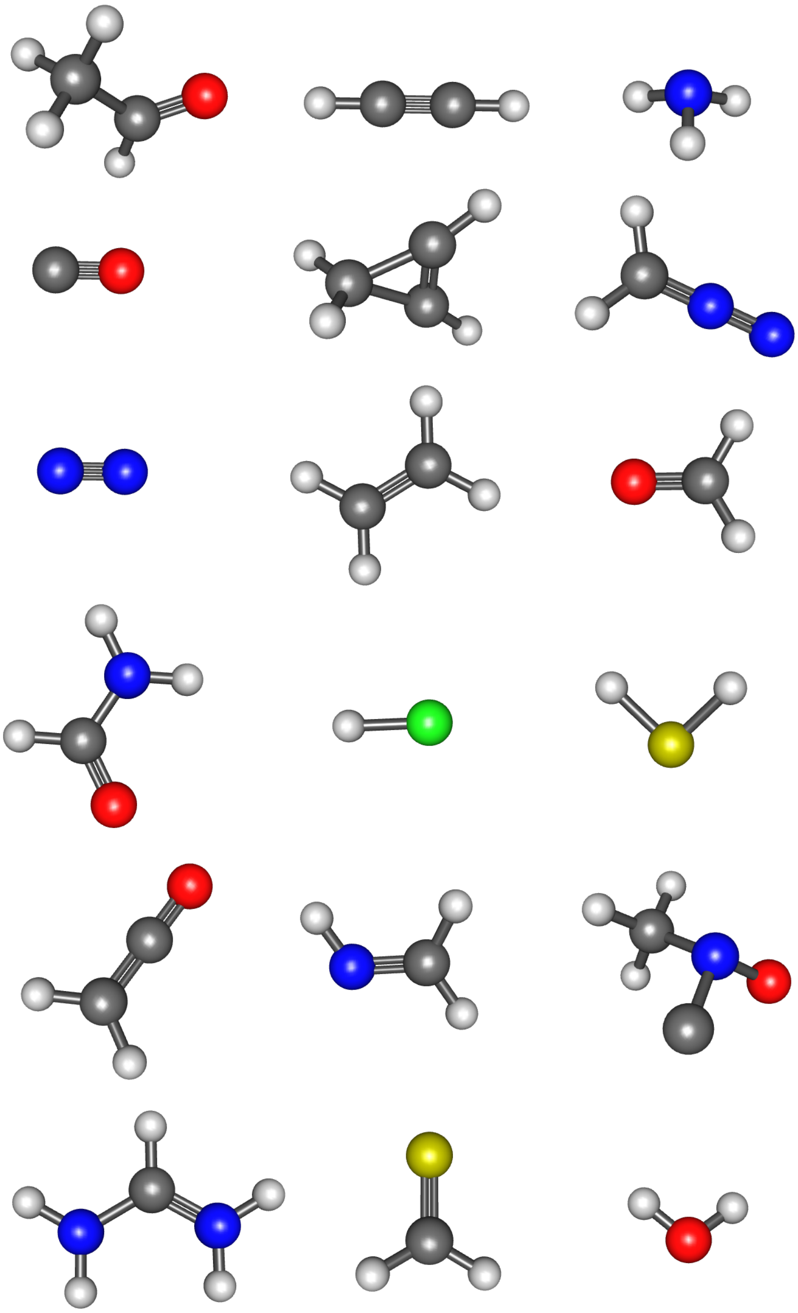

Figure 2.6.: Jacquemins benchmark set[64]. From top to bottom, left to right: Acetaldehyde, acetylene, ammonia, carbonmonoxide, cyclopropene, diazomethane, dinitrogen, ethylene, formaldehyde, formamide, hydrogen chloride, hydrogen sulfide, ketene, methanamine, nitrosomethane, streprocyanine, thioformaldehyde, water.

The second benchmark set used for the calculation of doubly-ionized states is the set of small to medium-sized compounds introduced by Jacquemin et al.[64]. It features 18 molecular species that are shown in figure 2.6, the corresponding geometries that were used in the calculations (which are optimized on a CC3/aug-cc-pVTZ level) can be found in the appendix (section A.3). Calculations were performed for DIP-ADC(2), DIP-ADC(2)-x and DIP-ADC(3) as well as EOMDIP-CCSD[58,59] using `Q-Chem` 5.2. All doubly-ionized singlet and triplet states were calculated using the aug-cc-pVTZ basis set[28,55].

Doubly-ionized singlet states

All benchmark data for the calculation of doubly-ionized singlet states for the set of Jacquemin et al.[64] is collected in the appendix A.4, including a statistical evaluation for each molecule and method used. Table 2.5 gives a statistical summary for the full benchmark set. Figure 2.7 represents a spread-plot of all doubly-ionized singlet states that were computed. In figure 2.8, as before, the trend of double ionization energies within the hierarchy of DIP-ADC(*n*) methods is presented, featuring six examples. Figures 2.9 and 2.11 visualize the distribution of double-ionization energies relative to EOMDIP-CCSD and DIP-ADC(3), respectively. In connection to these plots, figures 2.10 and 2.12 represent the corresponding histograms for the energy deviations. Table 2.6 collects the mean amounts of doubles amplitudes for doubly-ionized states of the different methods.

Table 2.5.: Statistical analysis for the doubly-ionized singlet states of Jacquemins benchmark set. EOMDIP-CCSD and DIP-ADC(3) are chosen as reference.

EOMDIP-CCSD as reference

vs. DIP-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(3)	72	0.75	-0.99	-0.23 ± 0.35	-0.7 ± 0.9	0.34 ± 0.24	0.9 ± 0.6
(2)-x	72	-0.7	-2.22	-1.31 ± 0.29	-3.6 ± 0.9	1.31 ± 0.29	3.6 ± 0.9
(2)	72	-2.52	-7.84	-4.02 ± 1.31	-10.8 ± 2.9	4.02 ± 1.31	10.8 ± 2.9

DIP-ADC(3) as reference

vs. DIP-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(2)-x	72	0.14	-2.57	-1.08 ± 0.55	-2.9 ± 1.4	1.08 ± 0.54	2.9 ± 1.3
(2)	72	-1.93	-8.59	-3.79 ± 1.57	-10.2 ± 3.5	3.79 ± 1.57	10.2 ± 3.5

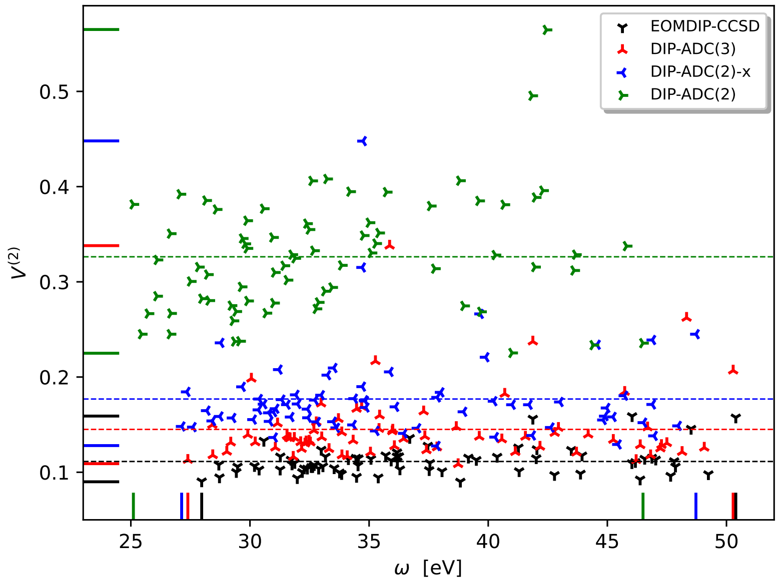

Figure 2.7.: Spreadplot (energy ω vs. amount of doubles amplitudes $V^{(2)}$) of all doubly-ionized singlet states from tables A.10, A.11 and A.12. Ticks at both axes give the range of the corresponding values. Horizontal lines give the mean $V^{(2)}$ values for each set of data points.

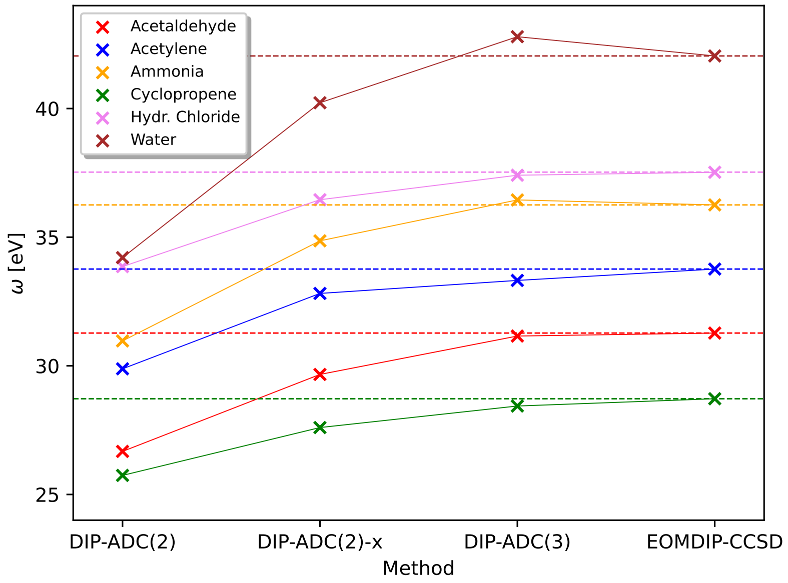

Figure 2.8.: Double ionization energies for the lowest lying singlet states of tables A.10, A.11 and A.12 for some selected molecules, given in the hierarchy of DIP-ADC methods.

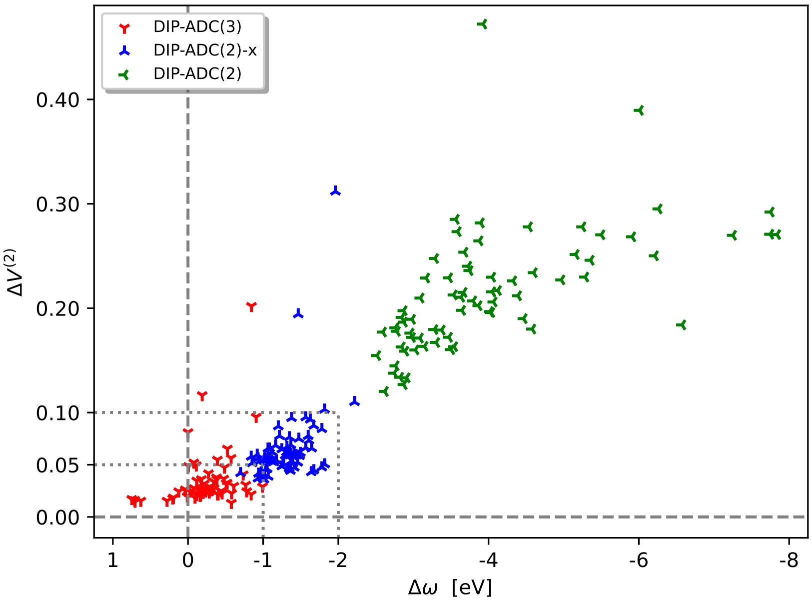

Figure 2.9.: Spreadplot (energy difference $\Delta\omega$ vs. difference in the amount of doubles amplitudes $\Delta V^{(2)}$) of all doubly-ionized singlet states from tables A.10, A.11 and A.12, relative to EOMDIP-CCSD.

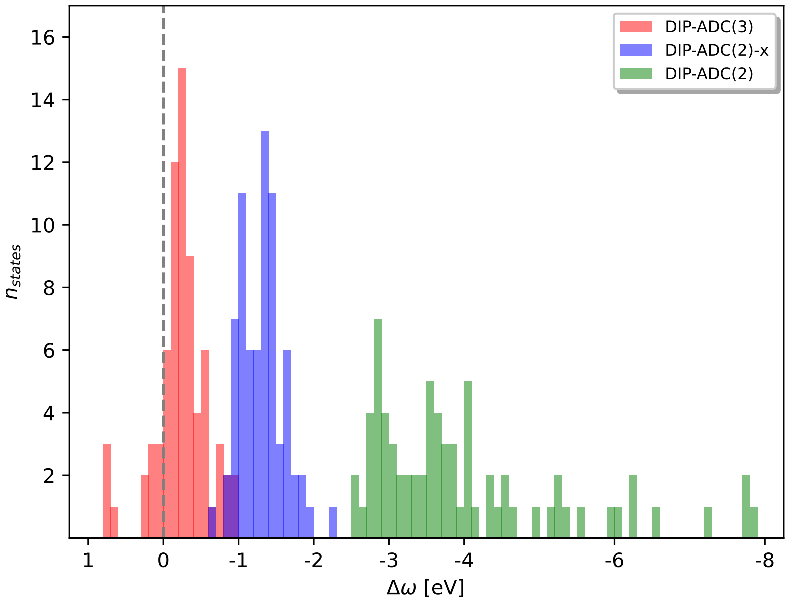

Figure 2.10.: Histogram for the energies of doubly-ionized singlet states from tables A.10, A.11 and A.12, relative to EOMDIP-CCSD.

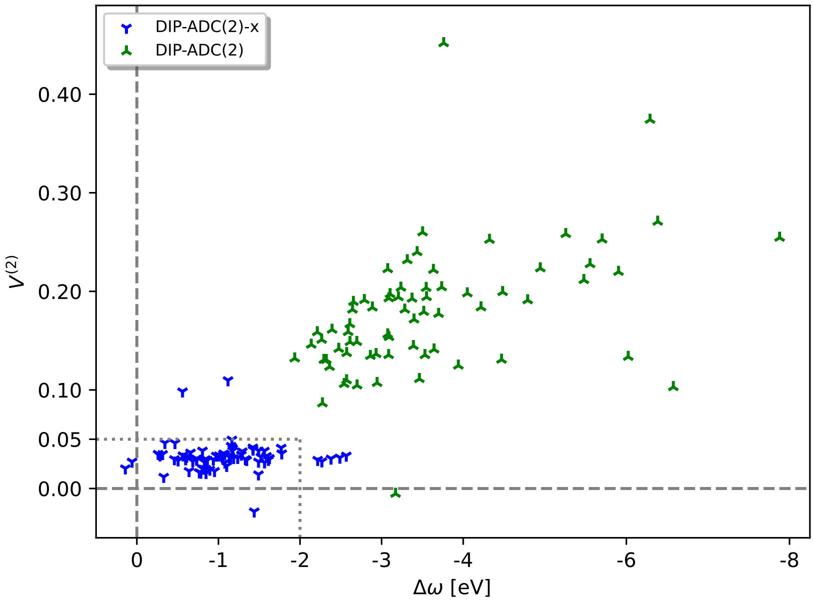

Figure 2.11.: Spreadplot (energy difference $\Delta\omega$ vs. difference in the amount of doubles amplitudes $\Delta V^{(2)}$) of all doubly-ionized singlet states from tables A.10, A.11 and A.12, relative to DIP-ADC(3).

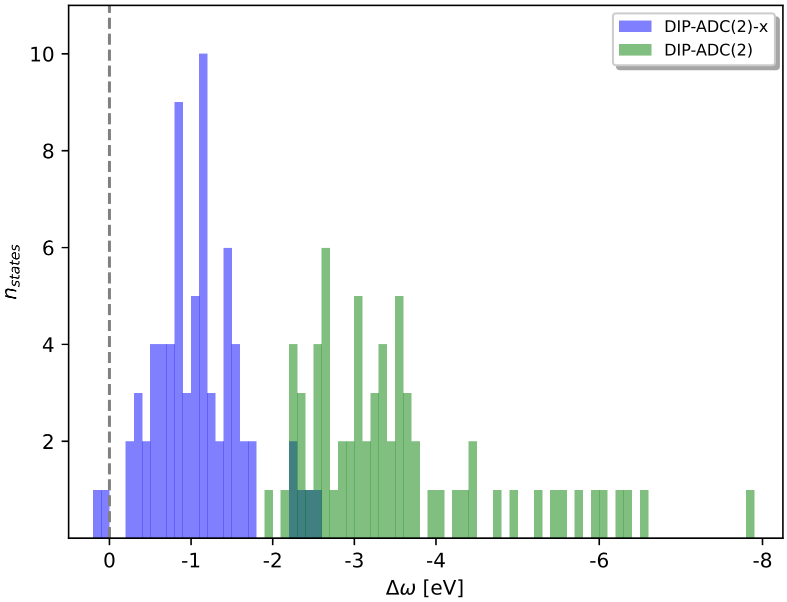

Figure 2.12.: Histogram for the energies of doubly-ionized singlet states from tables A.10, A.11 and A.12, relative to DIP-ADC(3).

Table 2.6.: Mean amount of doubles amplitudes $V^{(2)}$ for all doubly-ionized singlet states in the benchmark set.

Method	EOMDIP-CCSD	DIP-ADC(3)	DIP-ADC(2)-x	DIP-ADC(2)
$V^{(2)}$	0.11	0.15	0.18	0.33

The spreadplot 2.7 as well as the deviation plots 2.9 and 2.11 show the clear trend that has already been mentioned in the previous section: Double-ionization energies increase for the second- to third-order methods consecutively, while the doubles contribution to the wavefunction reduces with higher order (see table 2.6). DIP-ADC(3) double-ionization energies lie remarkably close to EOMDIP-CCSD ones, deviating by only -0.23 ± 0.35 eV or (-0.7%) in average. In contrast to that, for DIP-ADC(2), the range of relative deviation towards the more precise methods is tremendous, as the mean deviations turn out to be -4.02 ± 1.31 eV (-10.8%) relative to EOMDIP-CCSD and -3.79 ± 1.57 eV (-10.2%) relative to DIP-ADC(3). This may be, as discussed before, due to the lack of a proper description of orbital relaxation effects after the species is left in an unrelaxed doubly-ionized state. The extended second order scheme DIP-ADC(2)-x proves to be consistent with the more precise third order and CC method by presenting a narrow distribution in figures 2.9 and 2.11, however, underestimating double-ionization energies in average by -1.31 ± 0.29 eV (-3.6%) in the case of EOMDIP-CCSD and -1.08 ± 0.55 eV (-2.9%) in the case of DIP-ADC(3).

A direct comparison of DIP-ADC(3) and EOMDIP-CCSD values for individual species (table A.13) shows that the latter are lower in the vast majority of cases. Only for acetaldehyde, ammonia, formaldehyde, formamide and water, the maximum deviations take positive values. In the particular case of water, however, DIP-ADC(3) values do always exceed EOMDIP-CCSD ones, making this a unique observation in the case of doubly-ionized states of the underlying benchmark set. This is directly seen in the MAE value which is increased by a factor of roughly 1.5, while the standard deviation is simultaneously decreased by the same factor. Comparison of MSE and MAE values for the second- and extended second-order schemes show that they always, with very few exceptions, lie under the corresponding third-order and CC values.

Doubly-ionized triplet states

As for the singlet states, all benchmark data for the calculation of doubly-ionized triplet states for Jacquemins benchmark set is collected in the appendix, section A.5, including a statistical evaluation for each molecule and method used. Table 2.7 gives a statistical summary for the full benchmark set. Figure 2.13 represents a spread-plot of all doubly-ionized triplet states that were computed. In figure 2.14, as before, the trend of double-ionization energies within the hierarchy of DIP-ADC(n) methods is presented, featuring six examples. Figures 2.15 and 2.17 visualize the distribution of double-ionization energies relative to EOMDIP-CCSD and DIP-ADC(3), respectively. In connection to these plots, figures 2.16 and 2.18 represent the corresponding histograms for the energy deviations. Table 2.8 collects the mean amounts of doubles amplitudes for doubly-ionized states of the different methods.

Table 2.7.: Statistical analysis for the doubly-ionized triplet states of Jacquemins benchmark set. EOMDIP-CCSD and DIP-ADC(3) are chosen as reference.

EOMDIP-CCSD as reference

vs. DIP-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(3)	72	0.88	-2.05	-0.33 ± 0.45	-0.9 ± 1.0	0.45 ± 0.34	1.1 ± 0.8
(2)-x	72	-0.69	-2.55	-1.47 ± 0.36	-3.9 ± 0.9	1.47 ± 0.36	3.9 ± 0.9
(2)	68	-1.95	-7.23	-3.70 ± 1.19	-9.8 ± 2.7	3.70 ± 1.19	9.8 ± 2.7

DIP-ADC(3) as reference

vs. DIP-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(2)-x	72	0.26	-3.08	-1.14 ± 0.60	3.0 ± 1.4	1.15 ± 0.58	3.0 ± 1.3
(2)	68	-0.96	-7.96	-3.37 ± 1.46	-9.0 ± 3.3	3.37 ± 1.46	9.0 ± 3.3

Table 2.8.: Mean amount of doubles amplitudes $V^{(2)}$ for all doubly-ionized triplet states in the benchmark set.

Method	EOMDIP-CCSD	DIP-ADC(3)	DIP-ADC(2)-x	DIP-ADC(2)
$V^{(2)}$	0.12	0.20	0.21	0.31

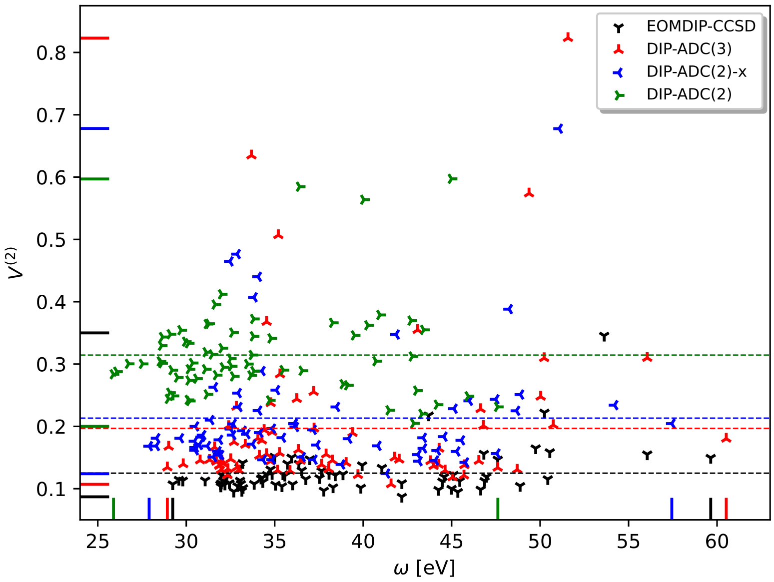

Figure 2.13.: Spreadplot (energy ω vs. amount of doubles amplitudes $V^{(2)}$) of all doubly-ionized triplet states from tables A.18, A.19 and A.20. Ticks at both axes give the range of the corresponding values. Horizontal lines give the mean $V^{(2)}$ values for each set of data points.

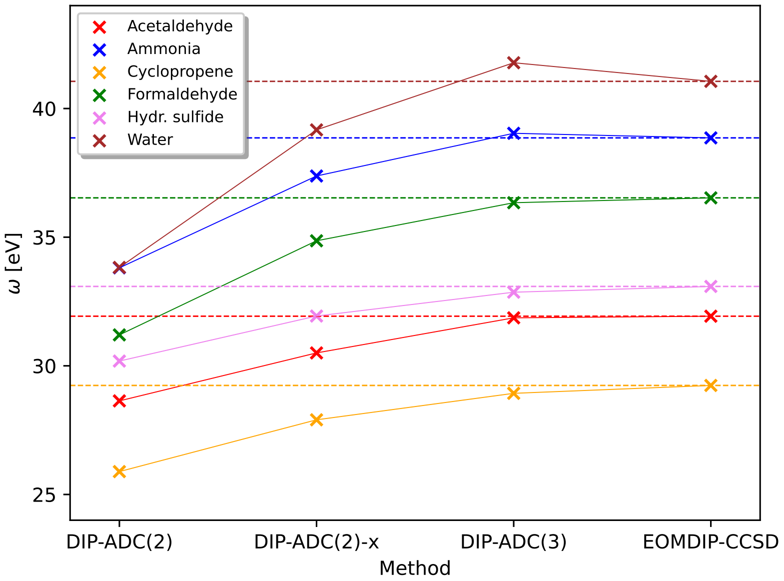

Figure 2.14.: Double ionization energies for the lowest lying triplet states of tables A.18, A.19 and A.20 for some selected molecules, given in the hierarchy of DIP-ADC methods.

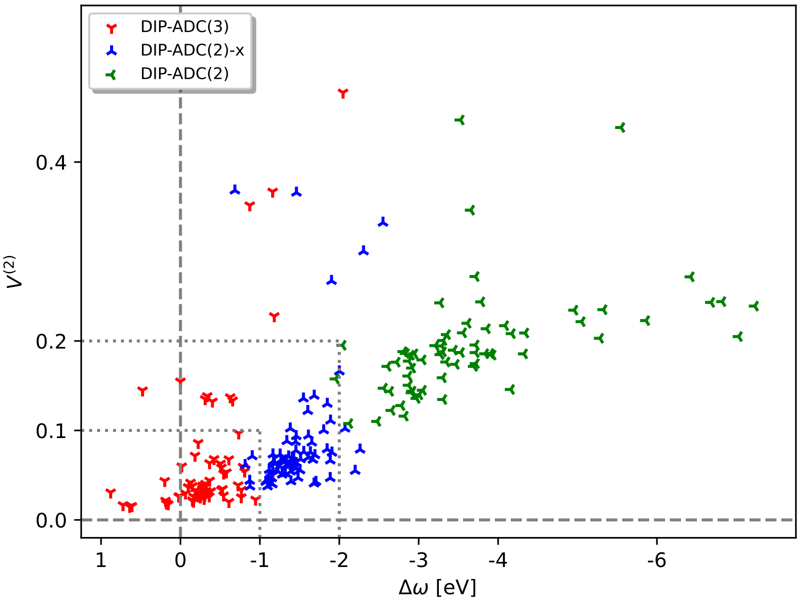

Figure 2.15.: Spreadplot (energy difference $\Delta\omega$ vs. difference in the amount of doubles amplitudes $\Delta V^{(2)}$) of all doubly-ionized triplet states from tables A.18, A.19 and A.20, relative to EOMDIP-CCSD.

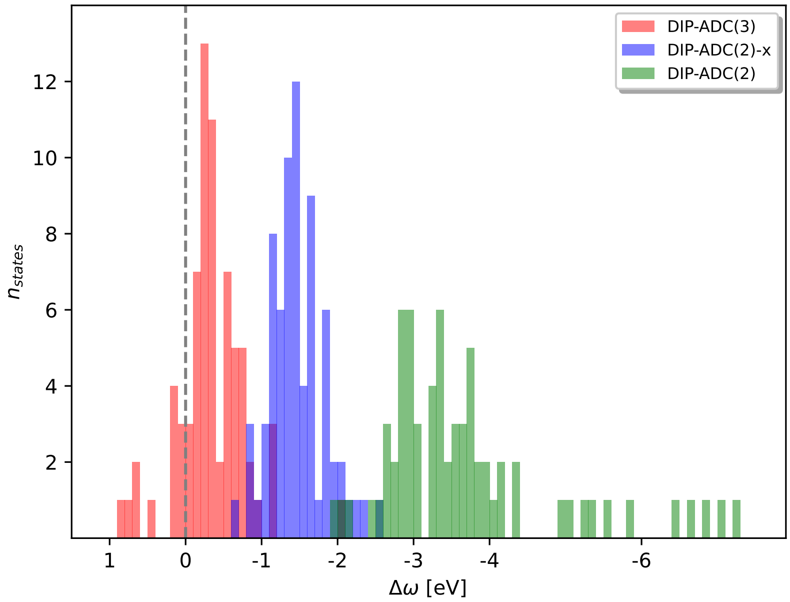

Figure 2.16.: Histogram for the energies of doubly-iononized triplet states from tables A.18, A.19 and A.20, relative to EOMDIP-CCSD.

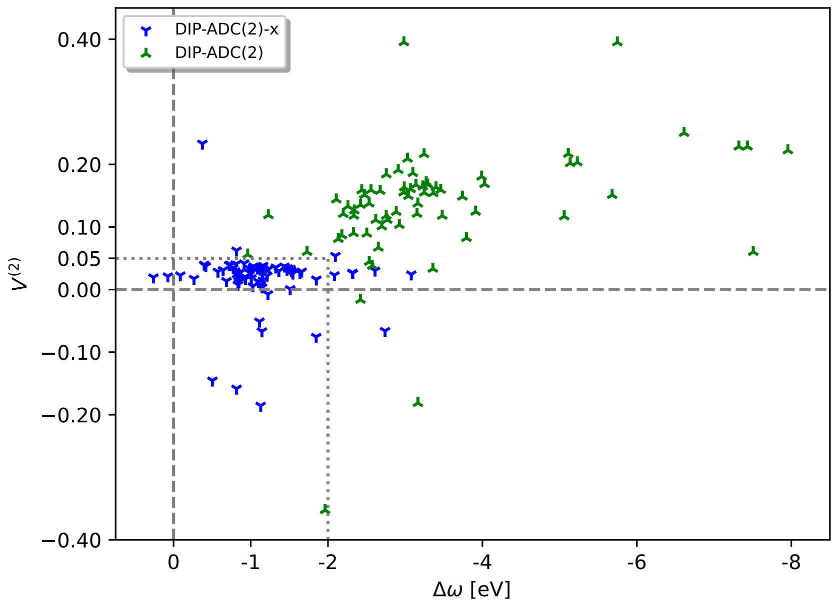

Figure 2.17.: Spreadplot (energy difference $\Delta\omega$ vs. difference in the amount of doubles amplitudes $\Delta V^{(2)}$) of all doubly-iononized triplet states from tables A.18, A.19 and A.20, relative to DIP-ADC(3).

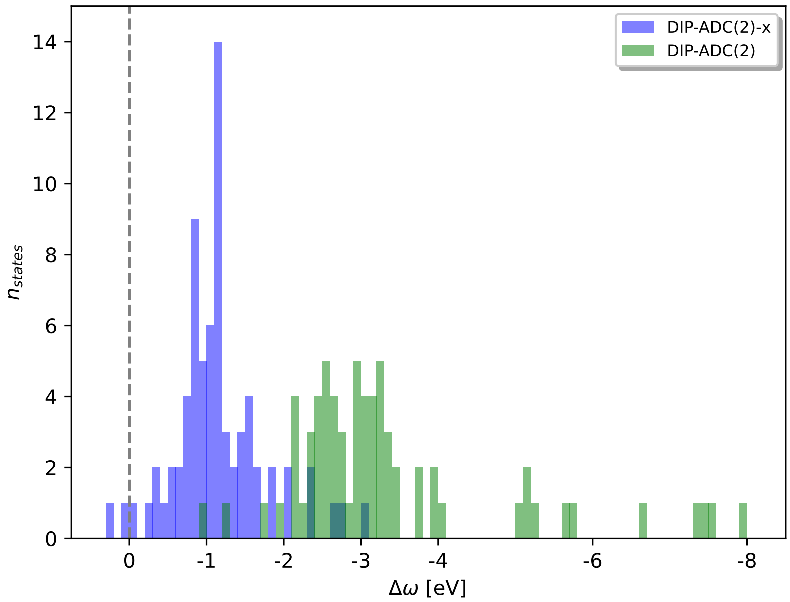

Figure 2.18.: Histogram for the energies of doubly-iononized triplet states from tables A.18, A.19 and A.20, relative to DIP-ADC(3).

For doubly-ionized triplet states the same principal observations as for the singlet states can be made, that is, an ascending of double ionization energies for higher-order methods in combination with a decline of doubles amplitudes in the excited state wave-function. However, the spread within the sets of DIP-ADC energy values tends to be slightly bigger as for the singlet states, as can be seen in figures 2.15 and 2.17. The average deviation for DIP-ADC(3) double-ionization energies with respect to EOMDIP-CCSD amounts -0.33 ± 0.45 eV (-0.9%), putting again the third-order ADC scheme remarkably close to the EOM-CCSD scheme. For DIP-ADC(2)-x, the relative deviations turn out to be -1.47 ± 0.36 eV (-3.9%) towards EOMDIP-CCSD and -1.14 ± 0.60 eV (3.0%) towards DIP-ADC(3), respectively. For the second order scheme, again, deviations reach up to an average of -3.70 ± 1.19 eV (-9.8%) and -3.37 ± 1.46 eV (-9.0%) towards EOMDIP-CCSD and DIP-ADC(3), respectively. As an interesting observation, the average deviations towards the EOM-CCSD scheme slightly increase for doubly-ionized triplet states in ADC(3) and ADC(2)-x, from -0.7% to -0.9% and -3.6% to -3.9%, respectively. For ADC(2), the exact opposite is observed: a decrease for the average deviation of triplet states from -10.8% to -9.8%, yet still the pure second-order ADC scheme is not capable to correctly describe doubly-ionized triplet states due to the lack of a sufficient parametrization of the doubles/doubles part of the secular matrix.

2.8. Benchmarking / Calculations for double electronically-attached states

In this section, the benchmark of double electronically-attached states is presented. As for doubly-ionized states, Jacquemins benchmark set of small compounds has been chosen. Calculations have been performed for eight of the 18 molecules in the set, ammonia, dinitrogen, ethylene, formaldehyde, hydrogen chloride, hydrogen sulfide, methanimine and water. The used geometries (same as for DIP) can be found in the appendix, section A.3. Calculations were performed for DEA-ADC(1), DEA-ADC(2), DEA-ADC(2)-x and DEA-ADC(3) as well as EOMDEA-CCSD[58,59] using `Q-Chem` 5.2. All double attachment calculations were performed using the aug-cc-pVTZ basis set[28,55].

Doubly-attached singlet states

Benchmark data for the calculation of doubly-attached singlet states for Jacquemins benchmark set is collected in the appendix, section A.6, including a statistical evaluation for each molecule and method used. Table 2.9 gives a statistical summary for all molecules used in the benchmark set. Figure 2.19 represents a spread-plot of all doubly-attached singlet states that were computed. In figure 2.20, as before, the trend of double attachment energies within the hierarchy of DEA-ADC(n) methods is presented, featuring four examples. Figures 2.21 and 2.22 visualize the distribution of double attachment energies relative to EOMDEA-CCSD. Table 2.10 collects the mean amounts of doubles amplitudes for doubly-attached states of the different methods.

Table 2.9 as well as figure 2.20 show precisely how doubly-attached states for the different ADC(n) methods behave compared to EOM-CCSD: The energies for the second- and third-order ADC schemes fall below corresponding data, for DEA-ADC(2) the mean deviation with respect to EOMDEA-CCSD is found to be -0.17 ± 0.11 eV (-3.1%), for DEA-ADC(2)-x this is -0.19 ± 0.11 eV (-3.4%) and for DEA-ADC(3) -0.10 ± 0.09 (-1.9%). In similarity to doubly-ionized states, the full third-order treatment approaches the reference value in the best way, although the overall deviation for all these three ADC schemes is found to be very small. However, it is worth noting that the extended second-order scheme DEA-ADC(2)-x performs

Table 2.9.: Statistical analysis for the doubly attached singlet states of all eight computed species in the benchmark set. EOMDEA-CCSD and DEA-ADC(3) are chosen as reference.

EOMDEA-CCSD as reference

vs. DEA-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(3)	27	0.07	-0.37	-0.10 ± 0.09	-1.9 ± 1.2	0.11 ± 0.08	2.0 ± 1.1
(2)-x	27	-0.08	-0.61	-0.19 ± 0.11	-3.4 ± 1.6	0.19 ± 0.11	3.4 ± 1.6
(2)	27	-0.07	-0.55	-0.17 ± 0.11	-3.1 ± 1.5	0.17 ± 0.11	3.1 ± 1.5
(1)	32	0.76	0.11	0.29 ± 0.18	5.2 ± 2.7	0.29 ± 0.18	5.2 ± 2.7

DEA-ADC(3) as reference

vs. DEA-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(2)-x	27	0.01	-0.24	-0.08 ± 0.06	-1.5 ± 0.9	0.08 ± 0.06	1.6 ± 0.9
(2)	27	0.01	-0.25	-0.06 ± 0.06	-1.2 ± 0.9	0.07 ± 0.06	1.2 ± 0.8
(1)	27	0.76	0.16	0.33 ± 0.14	6.3 ± 2.1	0.33 ± 0.14	6.3 ± 2.1

Table 2.10.: Mean amount of doubles amplitudes $V^{(2)}$ for all doubly attached singlet states in the benchmark set.

Method	EOMDEA-CCSD	DEA-ADC(3)	DEA-ADC(2)-x	DEA-ADC(2)
R^2 [% / 100]	0.014	0.014	0.018	0.014

slightly worse than the pure second-order scheme, as may be observed in figures 2.21 and 2.22. For these calculations, the extension of the doubles/doubles (3ph/3ph) block to first order seems, unlike as for DIP, to introduce no improvement. As a difference to the double-ionization calculations, the benchmark of doubly-attached states also includes DEA-ADC(1) values. This is justified by the fact that doubly-attached states constitute almost pure singlet (2p) states in general (see table 2.10). DEA-ADC(1) tends to exceed EOMDEA-CCSD data by an average of 0.29 ± 0.18 eV (5.2%).

An interesting observation can be made in the matching of ADC and EOM-CC states: For EOMDEA-CCSD states that contain a high amount of doubles amplitude in the wavefunction, a unique and distinct matching with the corresponding second- or third-order ADC state was not possible. As table A.44 shows with the example of formaldehyde, states that could be possibly matched due to the similar amplitude composition of the wavefunction tend to either exceed or underestimate the corresponding values. For DEA-ADC(1), however, the relative ordering of states and energy gaps in between consecutive ones was preserved in all times with respect to EOMDEA-CCSD, enabling a proper state matching in all cases.

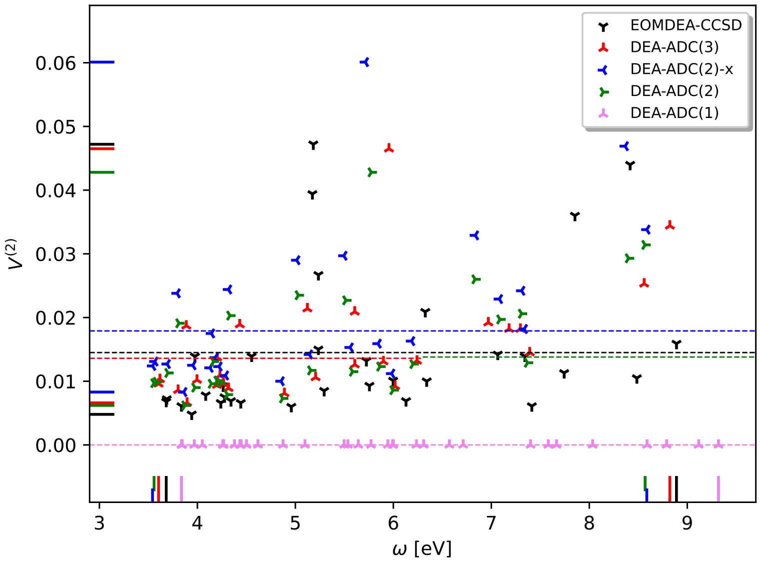

Figure 2.19.: Spreadplot (energy ω vs. amount of doubles amplitudes $V^{(2)}$) of all double electronically attached singlet states from tables A.26 and A.27. Ticks at both axes give the range of the corresponding values. Horizontal lines give the mean $V^{(2)}$ values for each set of data points.

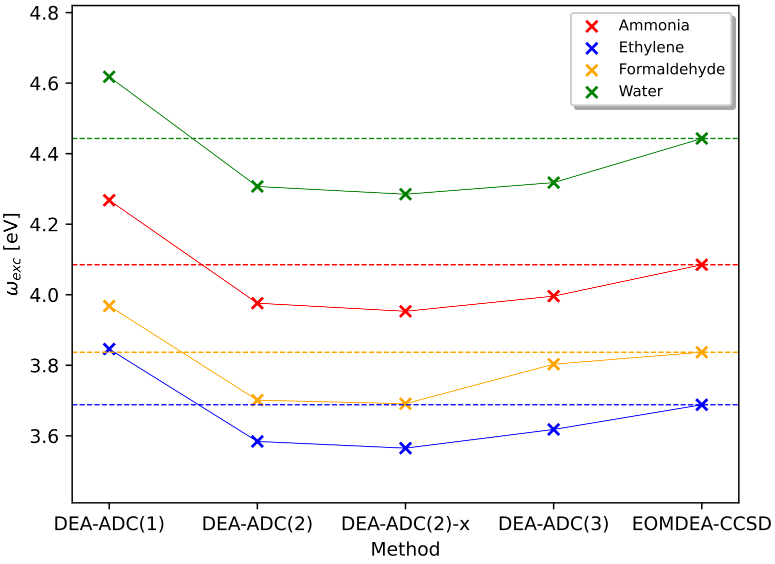

Figure 2.20.: Double attachment energies for the lowest lying singlet states of tables A.26 and A.27 for some selected molecules, given in the hierarchy of DIP-ADC methods.

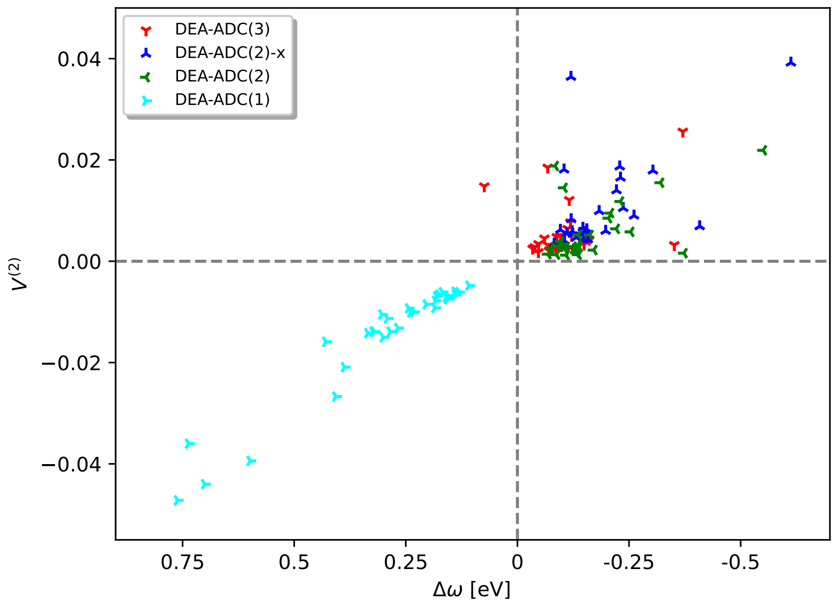

Figure 2.21.: Spreadplot (energy difference $\Delta\omega$ vs. difference in the amount of doubles amplitudes $\Delta V^{(2)}$) of all double electronically attached singlet states from tables A.26 and A.27, relative to EOMDEA-CCSD.

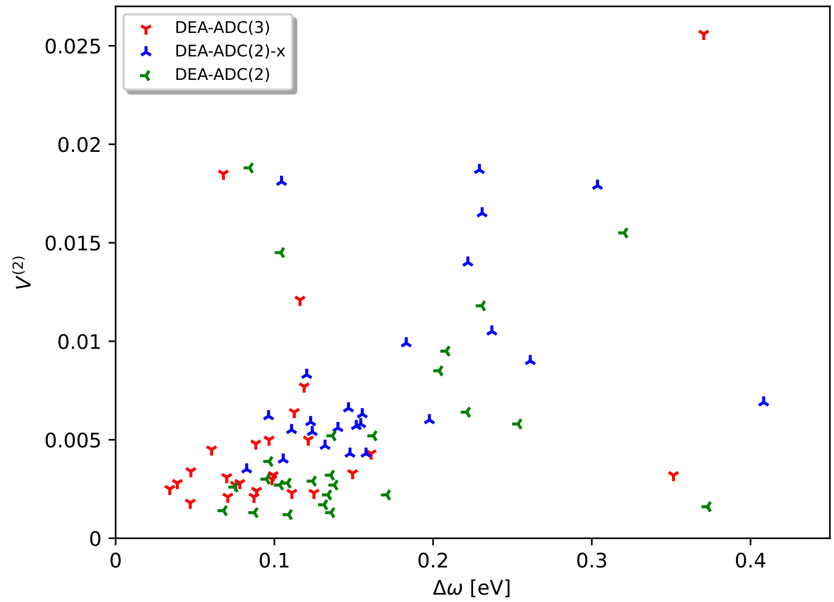

Figure 2.22.: Zoom-in of figure 2.21

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For the here presented set of small compounds, the process of double electron attachment may be characterized as a "singles process", that is, the wavefunction is dominated by singles (2p) amplitudes and possesses only a very small ($\sim 1\%$) amount of doubles (3ph) amplitudes. Therefore, the first-order treatment of the double attachment process in ADC(1), which completely lacks the description of doubles amplitudes, is already capable to deliver qualitatively good results. Due to an overestimation of doubles excitations in DEA-ADC(2)-x, the pure second-order scheme tends to be, if only slightly, closer to DEA-ADC(3) and EOMDEA-CCSD, which on their side yield values that are located remarkably close to one another. In a physical sense this may be understood intuitively, as the attachment of two electrons onto a small system introduces an additional negative charge density in the virtual orbital space. An additional electron excitation into this space thus represents an unfavourable process. Nevertheless, the small doubles contribution may still be characterized as an important attribute of the wave-function to describe orbital relaxation, as is shown by the mean deviations of DEA-ADC(1) values (no doubles contributions) to DEA-ADC(3) and EOMDEA-CCSD values (doubles contributions $\sim 1.4\%$), which lies at 6.3% and 5.2%, respectively.

Doubly-attached triplet states

In similarity to the singlet states, all benchmark data for the calculation of doubly attached triplet states is collected in the appendix, section A.7, including a statistical evaluation for each molecule and method used. Table 2.11 gives a statistical summary for all molecules used in the benchmark set. Figure 2.23 represents a spread-plot of all doubly attached triplet states that were computed. In figure 2.24, as before, the trend of double attachment energies within the hierarchy of DEA-ADC(n) methods is presented, featuring four examples. Figures 2.25 and 2.26 visualize the distribution of double attachment energies relative to EOMDEA-CCSD. Table 2.12 collects the mean amounts of doubles amplitudes for doubly attached states of the different methods.

Observations that can be made for the benchmark of doubly-attached triplet states are identical as for singlet states, which were discussed in detail previously. Figure 2.26 presents the small-scale layering of DEA-ADC(2) and DEA-ADC(3) values in contrast to DEA-ADC(2)-x in a more distinct way, precisely showing how the sets of energies for the different meth-

Table 2.11.: Statistical analysis for the doubly attached triplet states of all eight computed species in the benchmark set. EOMDEA-CCSD and DEA-ADC(3) are chosen as reference.

EOMDEA-CCSD as reference

vs. DEA-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(3)	26	-0.01	-0.39	-0.12 ± 0.10	-2.0 ± 1.3	0.12 ± 0.10	2.0 ± 1.3
(2)-x	26	-0.08	-0.47	-0.18 ± 0.10	-3.1 ± 1.1	0.18 ± 0.10	3.1 ± 1.1
(2)	26	-0.06	-0.42	-0.17 ± 0.10	-2.8 ± 1.1	0.17 ± 0.10	-2.8 ± 1.1
(1)	32	0.85	0.10	0.28 ± 0.18	4.7 ± 2.3	0.28 ± 0.18	4.7 ± 2.3

DEA-ADC(3) as reference

vs. DEA-ADC	States	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
(2)-x	26	-0.01	-0.18	-0.06 ± 0.03	-1.2 ± 0.5	0.06 ± 0.03	1.2 ± 0.5
(2)	26	0.01	-0.17	-0.05 ± 0.04	-0.8 ± 0.6	0.05 ± 0.04	0.8 ± 0.5
(1)	26	0.74	0.12	0.33 ± 0.15	5.8 ± 1.7	0.33 ± 0.15	5.8 ± 1.7

Table 2.12.: Mean amount of doubles amplitudes $V^{(2)}$ for all doubly attached triplet states in the benchmark set.

Method	EOMDEA-CCSD	DEA-ADC(3)	DEA-ADC(2)-x	DEA-ADC(2)
R^2 [% / 100]	0.013	0.010	0.014	0.010

ods are separated. With EOMDEA-CCSD as a reference, the second- and third-order ADC schemes underestimate double attachment energies slightly, with DEA-ADC(2)-x inheriting the lowest average deviation of -0.18 ± 0.10 eV (-3.1%) followed closely by DEA-ADC(2) with -0.17 ± 0.10 eV (-2.8%). DEA-ADC(3) remains the closest method, showing an average deviation of only -0.12 ± 0.10 eV (-2.0%) from the corresponding EOMDEA-CCSD value. As for DEA-ADC(1), the energy values are again found to exceed the corresponding CC ones by averagely 0.28 ± 0.18 eV (4.7%).

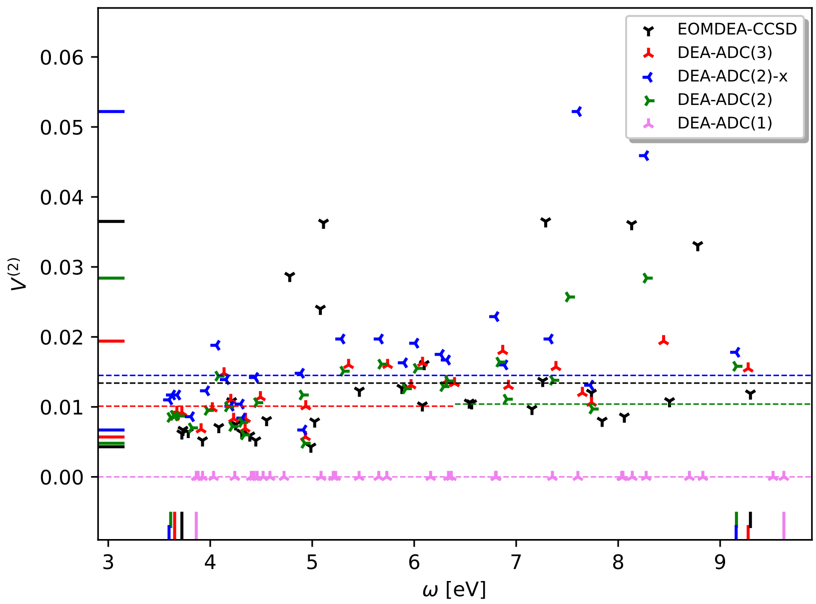

Figure 2.23.: Spreadplot (energy ω vs. amount of doubles amplitudes $V^{(2)}$) of all double electronically attached triplet states from tables A.35 and A.36. Ticks at both axes give the range of the corresponding values. Horizontal lines give the mean $V^{(2)}$ values for each set of data points.

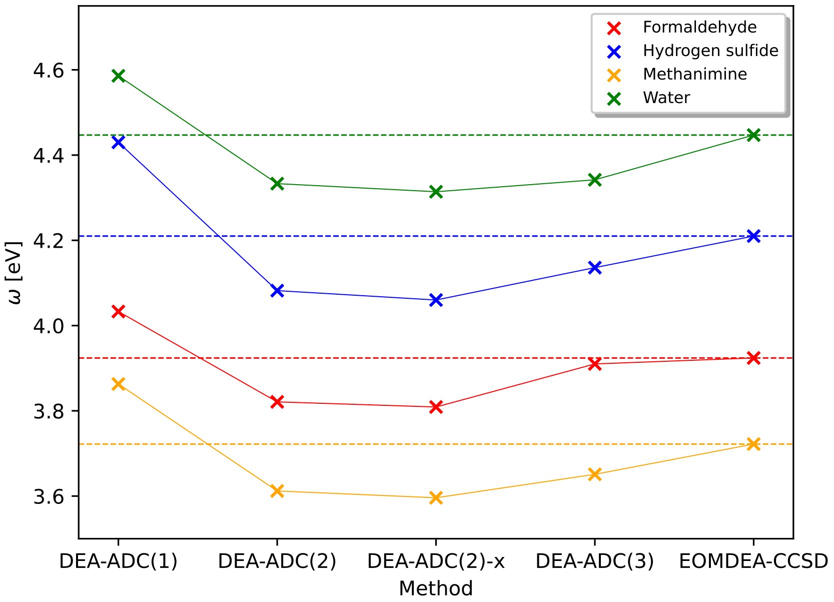

Figure 2.24.: Double attachment energies for the lowest lying triplet states of tables A.35 and A.36 for some selected molecules, given in the hierarchy of DIP-ADC methods.

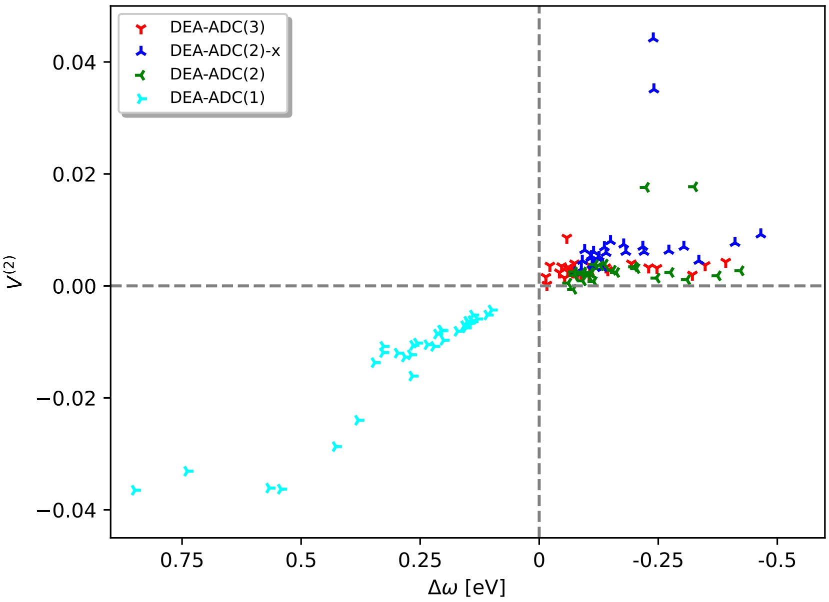

Figure 2.25.: Spreadplot (energy difference $\Delta\omega$ vs. difference in the amount of doubles amplitudes $\Delta V^{(2)}$) of all double electronically attached triplet states from tables A.35 and A.36, relative to EOMDEA-CCSD.

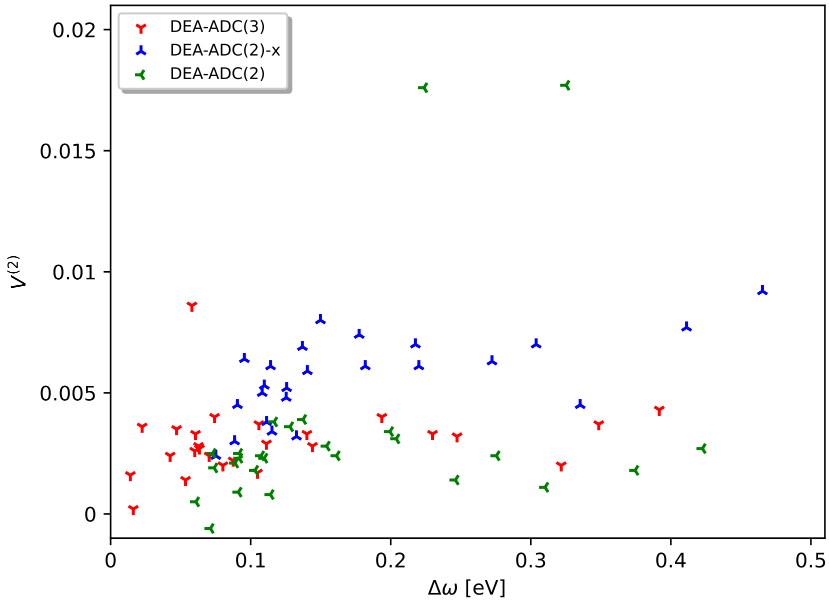

Figure 2.26.: Zoom-in of figure 2.25

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2.9. Summary

This chapter presented the implementation and benchmark study of doubly-ionized as well as double electronically-attached states within the framework of the Algebraic Diagrammatic Construction scheme up to third order. Data was compared to EOM-CCSD values, for DIP also to FCI values. Calculations were executed for both, singlet and triplet states.

At first, the observations that were made for the doubly-ionized states will be recapitulated. For the small set of FCI data by Velkov et al.[101] which featured H_2O, LiH and HF, DIP-ADC(3) values as well as EOMDIP-CCSD values were able to approach the corresponding FCI data remarkably well, with the CC scheme being superior with an average deviation of only -0.09 eV for eight singlet states (in comparison to 0.34 eV for DIP-ADC(3)) and -0.15 eV for five triplet states (in comparison to 0.54 eV for DIP-ADC(3)).

For the bigger second benchmark set (Jacquemins set of 18 small to medium-sized compounds[64]), an extended study on 72 states for DIP-ADC(3) and DIP-ADC(2)-x as well as 68 states for DIP-ADC(2) triplets in comparison to EOMDIP-CCSD was carried out and presented. It was shown that a sufficient description of the doubles/doubles (p3h/p3h) part of the secular matrix is needed to adequately describe double-ionization processes, thereby illustrating DIP-ADC(2)-x as the first method in the ADC hierarchy to deliver qualitatively correct results with deviations of -1.31 ± 0.29 eV (-3.6%) for singlet states and -1.47 ± 0.36 eV (-3.9%) for triplet states. However, this still presents a significant underestimation. The third-order method DIP-ADC(3) excels the other methods by far, presenting a remarkably congruence with EOMDIP-CCSD data, differing only by -0.23 ± 0.35 eV (-0.7%) for singlet states and -0.33 ± 0.45 eV (-0.9%) for triplet states to EOMDIP-CCSD results. For the pure second-order scheme, the description of doubly-ionized states is due to the zeroth-order singles/singles block insufficient with deviations reaching up to -4.02 ± 1.31 eV (-10.8%) for singlet states and -3.70 ± 1.19 eV (-9.8%) for triplet states. This may be seen by the particular high amount of doubles (p3h) amplitudes in DIP-ADC(2) states, implying an insufficient physical description of the doubles (p3h) space. DIP-ADC(1), lacking a doubles (p3h) description, is not suited at all to describe double ionization processes. Along with an increase of double-ionization energies for higher-order DIP-ADC methods, it was further observed that the amount of doubles amplitudes (p3h amplitudes) to constitute the doubly-ionized wavefunction decreases, supporting the findings mentioned above.

The benchmark study of double electronically-attached states has been carried out on eight molecules of Jacquemins benchmark set, ammonia, dinitrogen, ethylene, formaldehyde, hydrogen chloride, hydrogen sulfide, methanimine and water. For DEA-ADC(2), DEA-ADC(2)-x and DEA-ADC(3), 27 (singlets) and 26 (triplet) states were computed, for DEA-ADC(1), 32 states were computed. It was observed that for all second- and third-order methods, double attachment energies lie very close together, with again DEA-ADC(3) being the best method in comparison to EOMDEA-CCSD with a deviation of only -0.10 ± 0.09 eV (-1.9%) for singlet states and -0.12 ± 0.10 eV (-2.0%) for triplet states. Interestingly, DEA-ADC(2)-x seems to perform slightly worse than DEA-ADC(2) which may be due to an overestimation of the doubles/doubles part of the secular matrix. Compared to EOMDEA-CCSD data, DEA-ADC(2) deviates -0.17 ± 0.11 eV (-3.1%) for singlet states and -0.17 ± 0.10 eV (-2.8%) for triplet states. For DEA-ADC(2)-x, this is found to be -0.19 ± 0.11 eV (-3.4%) for singlet states and -0.18 ± 0.10 eV (-3.1%) for triplet states, respectively. Since double-attachment processes constitute almost pure singlet (2p) processes, DEA-ADC(1) was also included in this benchmark study, showing deviations of 0.29 ± 0.18 eV (5.2%) for singlet states and 0.28 ± 0.18 eV (4.7%) for triplet states. In contrast to the second- and third-order methods, DEA-ADC(1) data is always exceeding corresponding EOMDEA-CCSD data.

It is remarkable that for the frame of small compounds as present in this benchmark set, the first-order DEA-ADC(1) scheme has proven to be a more precise tool to describe double electron attachment processes as the second-order DIP-ADC(2) is for the description of double ionizations. In the case of the third-order ADC(3) scheme which provides for both, DIP and DEA states the best results in comparison to EOM-CCSD data, the deviations are with only -0.7% (singlet states) and -0.9% (triplet states) remarkably smaller for DIP as for DEA, where the corresponding values are -1.9% (singlet states) and -2.0% (triplet states). In absolute, however, the values for double attachment energies are significantly smaller than those for double ionization energies, amounting only about $\frac{1}{10}$th of their magnitude. As a general remark, the third-order ADC scheme can be employed as a valid alternative and/or supplement to EOM-CCSD for the calculation of doubly-ionized as well as double electronically-attached states.

3. Core-valence separation for Unitary Coupled cluster

In modern experimental setups, X-ray absorption spectra have become a reliable and precise tool for the characterization of atomic and molecular species and their properties[92]. This leads to the necessity of an accurate theoretical description of simulations[72]. Energetically, the electron excitations that arise from X-radiation exceed the typically studied HOMO-LUMO excitations by far, involving scales of $10^2 - 10^3$ eV instead of the usually studied ranges of $\sim 10^1$ eV. These energies are element-specific and, since the excitations happen form the lowest-lying orbitals (K-edge), increase with the atomic number. A reliable theoretical model to be applied to high-energy core excitations needs to include an adequate description of electron relaxation processes. This has been discussed in detail by J. Wenzel et al. for the application of the PP-ADC framework to calculate core-excited states[108,107,106,105,104] using the so-called Core-valence separation ansatz[10]. An Unitary Coupled Cluster scheme for the computation of electronically excited states up to third order[61] has been previously implemented and benchmarked successfully by Hodecker et al.[50,51]. In the following chapter, the application of the so-called Core-valence separation to Unitary Coupled Cluster, including the implementation in the `Q-Chem`[30] program package and benchmarking, will be presented.

- **Parts of this chapter (Core-valence separation for Unitary Coupled cluster) were already published in**:
  Sebastian M. Thielen, Manuel Hodecker, Julia Piazolo, Dirk R. Rehn, and Andreas Dreuw. Unitary coupled-cluster approach for the calculation of core-excited states and X-ray absorption spectra. The Journal of Chemical Physics, 154(15):154108, 04 2021 ([98])

3.1. Theory

The computation of high-lying excitation energies, as they occur for X-ray absorption spectra, is problematic for the common eigenvalue solvers, such as the Davidson algorithm[16] as used in ordinary ADC and UCC schemes. These algorithms return the eigenvalues of a given secular matrix ordered by their magnitude, i. e., to get to a high energy regime, one would have to solve for all lower-lying states, too. To circumvent this issue, Cederbaum, Domcke and Schirmer introduced the decoupling of the energetically well-separated core and valence excitations as early as in 1980[10]. This so-called Core-valence separation (CVS) approach applied to the secular matrix of excited states for ADC or UCC results in an effective reduction of its size as depicted in figure 3.1. In a numerical sense, this separation is established by

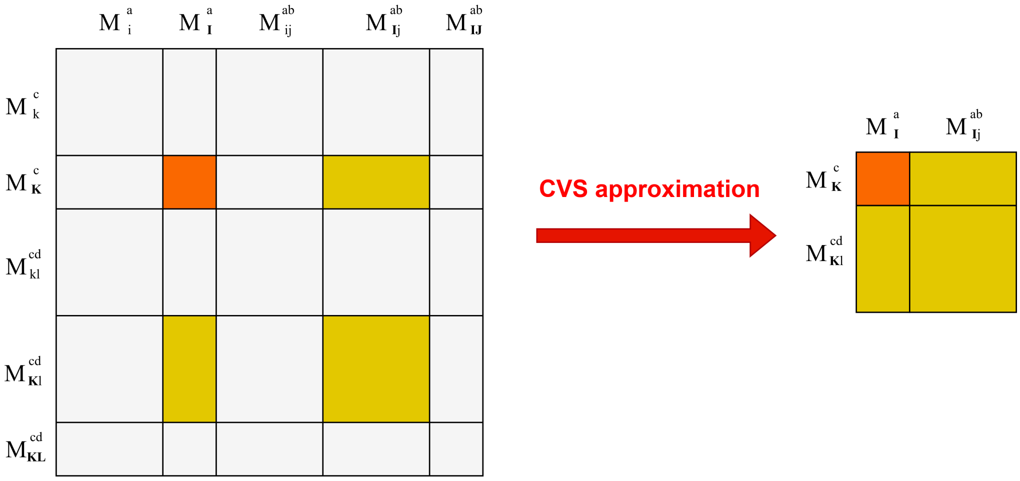

Figure 3.1.: CVS approximation applied to a full ADC matrix.

setting the two-electron Coulomb integrals that include a core index I, J, K to zero,

$$\begin{aligned} \langle Ip|qr\rangle = \langle pI|qr\rangle = \langle pq|Ir\rangle = \langle pq|rI\rangle &= 0 \\ \langle IJ|pq\rangle = \langle pq|IJ\rangle &= 0 \\ \langle IJ|Kp\rangle = \langle IJ|pK\rangle = \langle Ip|JK\rangle = \langle pI|JK\rangle &= 0. \end{aligned} \tag{3.1}$$

For the calculation of electronically excited states using the CVS approximation in UCC (CVS-UCC), the two-electron integral identities of equation 3.1 were inserted into the UCC working equations to produce the CVS-UCC secular matrix. The full set of working equations for the second-and third-order Unitary Coupled Cluster schemes can be found in the appendix, section C.1.

Applying the integrals in 3.1 is equivalent to employing the frozen-core (fc) approximation to the MP*n* ground state energy which constitutes the starting point for an ADC*n* calculation[25]. In the underlying implementation, however, this approximation is not made and the MP ground state energy is evaluated fully for second- and third- order CVS-ADC calculations. For the UCC approach, on the other hand, the frozen-core approximation is also applied to the singles and doubles ground-state amplitudes, resulting in a fc-CVS-UCC scheme which stands in similarity to the fc-CVS-EOM-CCSD approach[102].

3.2. Implementation and Benchmarking

CVS-UCC2, CVS-UCC2-x and CVS-UCC3 have been implemented in the `adcman` program package of `Q-Chem` 5.2[30], exploiting the existing code infrastructure of UCC for electronically-excited states as well as for the CVS-ADC schemes up to third order. Tensor operations were implemented in the `libadc` package, which uses the open-source `C++` tensor library `libtensor`[31] for computation.

Benchmark calculations have been performed on a set of small to medium-sized molecules that has been previously used for CVS-ADC by Wenzel et al.[108,107,106]. For the second- and extended second-order scheme, calculations were performed with acenaphthenequinone (ANQ), bithiophene (BT), porphine, 3,4,9,10-perylentetracarboxylicacidianhydride (PTCDA), thymine and anthracene (depicted in figure 3.2). Furthermore, five small open-shell species were included: the CH_3, OH and allyl radicals, the O_2 diradical and the anthracene cation for both, the optimized neutral as well as the optimized cationic ground-state structures.

For the third-order scheme, calculations were performed for CO, NH_3 and the CH_3 radical. All molecular geometries used for calculations can be found in the appendix, sections B.1 and B.2. A detailed summary on geometry optimizations of all employed molecules can be found in the original publication[98]. Calculation of core-excited states for CVS-UCC2 and CVS-UCC2-x were executed using the 6-311++G** basis set[56,67]; for porphine the 6-31++G**[45,42,11] and PTCDA the 6-31G**[45,42] basis sets were used. For the third-order CVS-UCC scheme, calculations were performed with the series of correlation-consistent polarized valence (cc-pVXZ) basis sets[28] as well as their augmented (aug)[55] and doubly-augmented (d-aug)[55,110] versions. X as the cardinal number ranges from double-ζ to quintuple-ζ for the cc- and aug-cc series and up to quadruple-ζ for the d-aug-cc series. In all cases, the Cartesian 6d/10f versions of the respective basis sets have been used.

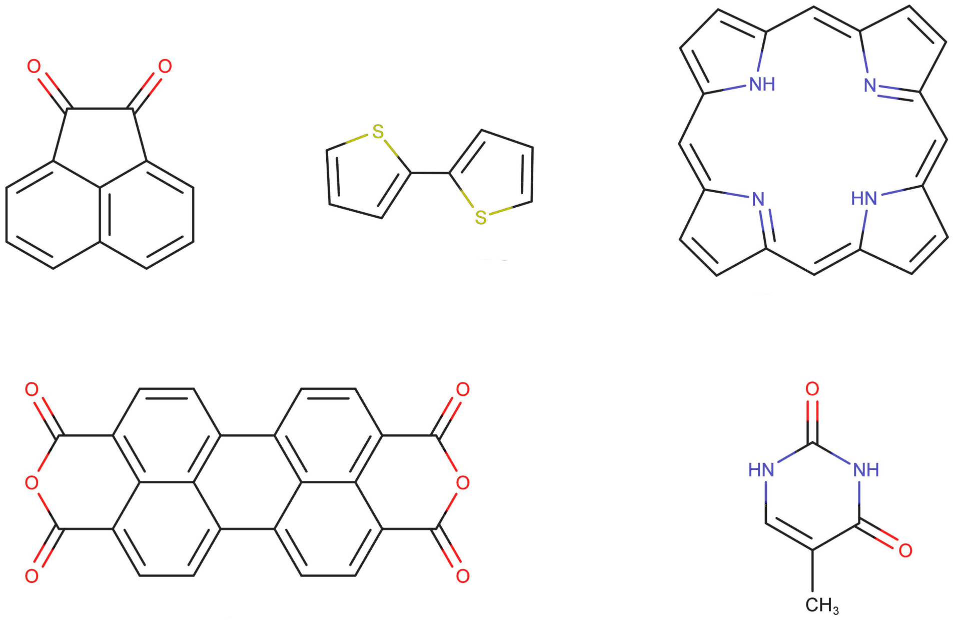

Figure 3.2.: Benchmark molecules for CVS-UCC. Top row from left to right: ANQ, bithiophene, porphine; bottom row left and right: PTCDA, thymine.

3.3. Results and discussion

In the following section, CVS-UCC benchmark results in comparison to CVS-ADC are presented. Excitation energies are given for the second- as well as the extended second-order scheme CVS-UCC2 and CVS-UCC2-x. For the third-order scheme CVS-UCC3, excitation energies and oscillator strengths in the CBS limit are given.

CVS-UCC2

Table 3.1 presents the statistical analysis of the CVS-UCC2 benchmark with respect to CVS-ADC(2) data. The full datasets for each molecule can be found in the appendix, section B.3. Relative deviations for CVS-UCC2 in comparison to CVS-ADC(2) are presented in figure 3.3 on the left side. As table 3.1 shows, CVS-UCC2 energies tend to slightly exceed CVS-ADC(2) ones (except for thymine and porphine). The relative deviation between both methods, however, turns out to be very small with a maximum of 0,04% for PTCDA. For this molecule, the largest deviation of 0.18 eV is observed. For porphine, the relative deviation of 0.001% for five computed states turns out to be the smallest, aslo showing a remarkable small variation of 0.005 eV. Furthermore, it is interesting to see that the relative deviations between the CVS-UCC2 and CVS-ADC(2) core excitation energies become smaller as the absolute value increases. Thymine represents a good example for this behaviour: For C 1s core excitations (around 290 eV), the relative deviation amounts 0.02%, for N 1s core excitations (around 404 eV) 0.01% and for O 1s core excitations (around 533 eV) 0.004%. The comparison to experimental data shows that both methods lie close to the reference values, again with CVS-UCC2 slightly exceeding CVS-ADC(2) values.

Table 3.1.: CVS-UCC2 in comparison to CVS-ADC(2): Number of states, minimal and maximal deviation [eV], mean signed and mean absolute error [eV] as well as the standard deviation [eV] as well as the mean relative deviation [%]. All data sets are included in the appendix, section B.3.

CVS-UCC2

Molecule	States	Min	Max	MSE	MAE	Std. dev.	Rel. dev.
ANQ (C 1s)	9	0.04	0.11	0.07	0.07	0.02	0.03
ANQ (O 1s)	8	0.06	0.09	0.08	0.08	0.01	0.01
BT (C 1s)	12	0.01	0.1	0.08	0.08	0.03	0.03
BT (S 1s)	6	0.01	0.1	0.06	0.06	0.04	0.002
PTCDA (C 1s)	9	0.04	0.18	0.1	0.1	0.05	0.04
Thymine (C 1s)	5	-0.01	0.11	0.04	0.05	0.05	0.02
Thymine (N 1s)	6	-0.02	0.08	0.02	0.03	0.03	0.01
Thymine (O 1s)	2	0.01	0.03	0.02	0.02	-	0.004
Porphine (N 1s)	5	0	0.01	0.006	0.006	0.005	0.001

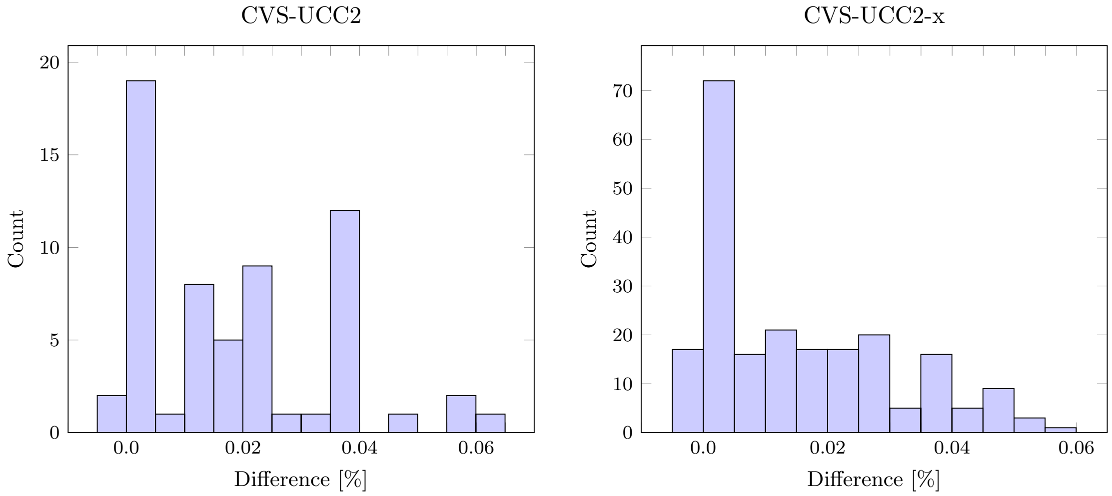

Figure 3.3.: Relative energy deviations of the second- and extended second-order CVS-UCC scheme compared to the corresponding CVS-ADC scheme for the molecules presented above.

CVS-UCC2-x

In table 3.2, the statistical analysis of the CVS-UCC2-x benchmarks with respect to CVS-ADC(2)-x data for the closed- and open-shell species are presented. The full datasets for each molecule can be found in the appendix, section B.3. Relative deviations for CVS-UCC2-x in comparison to CVS-ADC(2)-x are presented in figure 3.3 on the right side.

For the closed-shell molecules, similarly to the second-order scheme, CVS-UCC2-x energies exceed CVS-ADC(2)-x energies with only few exceptions found for thymine and porphine. Relative deviations are very small with a maximum of 0.03% for ANQ and PTCDA. Again, PTCDA shows the maximum deviation of 0.15 eV. Porphine presents with 0.001% the smallest relative deviation together with a variation of 0.01 eV for ten states. The extended second-order scheme shows, as the second-order scheme before, smaller relative deviations for core excitation energies for larger absolute values.

As for the open-shell molecules, the same trends may be observed, with a maximum deviation for anthracene at 0.13 eV. Particularly for the O_2 diradical, the relative deviation is remarkably small with 0.002 eV. For the experimental values, CVS-UCC2-x tends to deviate slightly more than CVS-ADC(2)-x if the experimental value exceeds both. In the opposite case, the CVS-UCC2-x energies are closer to the experimental ones.

Table 3.2.: CVS-UCC2-x in comparison to CVS-ADC(2)-x: Number of states, minimal and maximal deviation [eV], mean signed and mean absolute error [eV] as well as the standard deviation [eV] as well as the mean relative deviation [%]. All data sets are included in the appendix, section B.3.

CVS-UCC2-x

Molecule	States	Min	Max	MSE	MAE	Std. dev.	Rel. dev.
ANQ (C 1s)	18	0.05	0.1	0.08	0.08	0.02	0.03
ANQ (O 1s)	8	0.06	0.09	0.07	0.07	0.01	0.01
BT (C 1s)	14	0.01	0.1	0.06	0.06	0.03	0.02
BT (S 1s)	6	0.02	0.08	0.06	0.06	0.03	0.002
PTCDA (C 1s)	8	0.03	0.15	0.1	0.1	0.05	0.03
Thymine (C 1s)	15	0	0.1	0.03	0.03	0.03	0.01
Thymine (N 1s)	7	-0.02	0.08	0.02	0.03	0.03	0.01
Thymine (O 1s)	15	-0.02	0.05	0.01	0.01	0.02	0.002
Porphine (N 1s)	10	-0.01	0.02	0.004	0.005	0.01	0.001
Anthracene (C 1s)	10	0.01	0.13	0.07	0.07	0.05	0.02

CVS-UCC2-x

Molecule	States	Min	Max	MSE	MAE	Std. dev.	Rel. dev.
CH_3 radical (C 1s)	5	0.01	0.07	0.03	0.03	0.02	0.01
OH radical (O 1s)	5	0	0.09	0.04	0.04	0.03	0.01
Allyl radical (C 1s)	8	0.02	0.16	0.08	0.08	0.05	0.03
O_2 diradical (O 1s)	25	-0.02	0.01	-0.004	0.01	0.01	0.002
Anthracene cation ONS (C 1s)	35	0.01	0.08	0.04	0.04	0.02	0.02
Anthracene cation OCS (C 1s)	30	0.01	0.15	0.08	0.08	0.04	0.03

The applicability of CVS-UCC2-x for the computation of X-ray absorption spectra is furthermore presented in figures 3.4 and 3.5. These spectra feature the soft X-ray region between 281 and 289 eV for the anthracene cation. Figure 3.4 represents a calculation on an optimized neutral structure, while figure 3.5 is calcluclted using the optimized cationic structure. In each figure, the corresponding CVS-ADC spectrum is given for comparison at the top. All data for the CVS-UCC spectra is summarized in tables B.45 and B.46 in the appendix, section B.3.

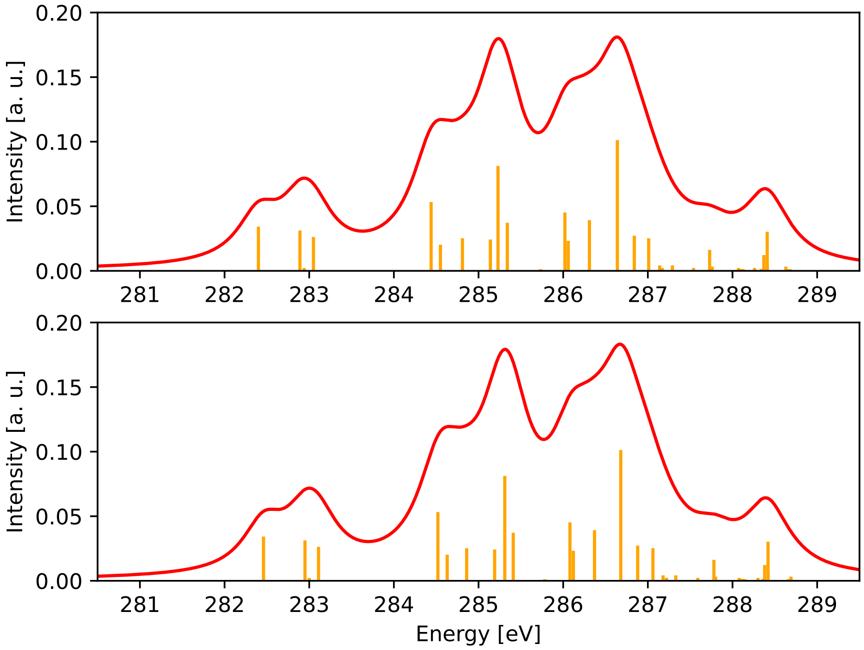

Figure 3.4.: Comparison of CVS-ADC(2)-x (top) and CVS-UCC2-x (bottom): Spectrum of the anthracene cation (optimized neutral structure) in the soft X-ray region between 281 and 289 eV. Fitted with a Lorentzian of 0.6 eV at fwhm.

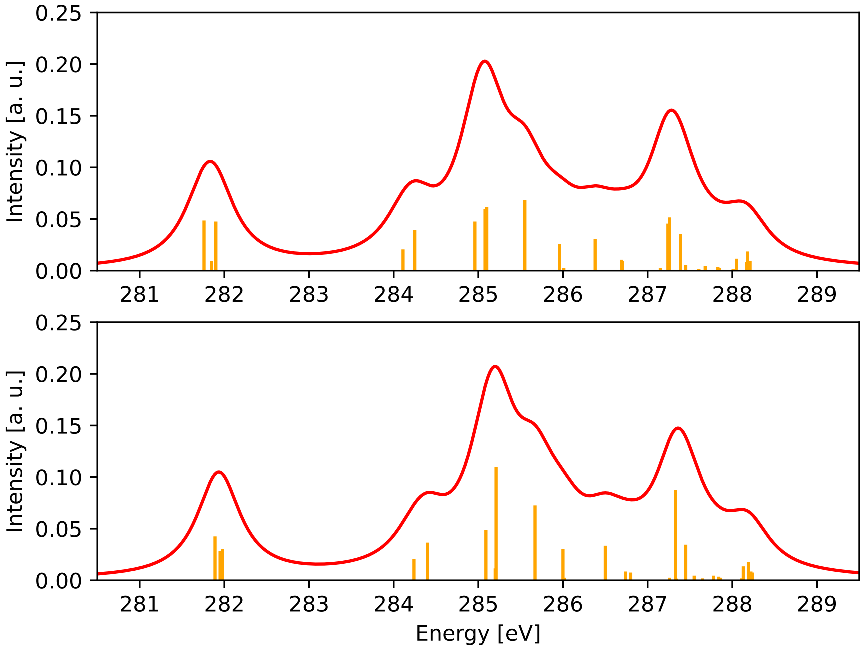

Figure 3.5.: Comparison of CVS-ADC(2)-x (top) and CVS-UCC2-x (bottom): Spectrum of the anthracene cation (optimized cationic structure) in the soft X-ray region between 281 and 289 eV. Fitted with a Lorentzian of 0.6 eV at fwhm.

CVS-UCC3

For the third-order UCC scheme, calculations have been performed for the small compounds CO, NH_3 and CH_3 using (augmented-) Dunning basis sets. A complete basis set limit has been extrapolated by using a second-order exponential fitting function,

$$\omega_X = \omega_{CBS} + Ae^{-(X-1)} + Be^{-(X-1)^2}, \tag{3.2}$$

with X being the cardinal number of the respecting basis set, X=2 for D, X=3 for T and so on. Table 3.3 gives a comparison to the respective CVS-ADC(3) energies.

Table 3.3.: CVS-UCC3 in comparison to CVS-ADC(3): K-edge excitation energies ω [eV] of the CBS limit for the different basis sets. The difference with respect to the corresponding CVS-ADC(3) values is given as Δ [eV]. All data sets are included in the appendix, section B.4.

	State	cc series		aug-cc series		d-aug-cc series	
		ω	Δ	ω	Δ	ω	Δ
CO C	1	288.14	0.45	288.16	0.46	288.15	0.46
	2			294.15	0.48	294.13	0.48
	3			295.22	0.51	295.19	0.52
CO O	1	537.08	-1.11	537.11	-1.12	537.13	-1.11
	2			542.91	-1.26	542.92	-1.25
	3			544.27	-1.35	544.22	-1.35
NH_3 N	1	403.63	0.09	403.57	0.1	403.58	0.1
	2	405.28	0.13	405.15	0.12	405.14	0.08
	3			406.06	0.09	405.98	0.08
CH_3 C	1	282.0	0.17	282.01	0.17	282.01	0.16

In table 3.4, the comparison of CVS-UCC3 as well as CVS-ADC(3) core-excitation energies with experimental data is presented. As before, CVS-UCC3 values tend to exceed the corresponding CVS-ADC(3) ones, ranging from only about 0.02% for NH_3 to about 0.16% for CO C 1s. Remarkably, however, is the circumstance that for CO O 1s, core-excitation energies in the UCC framework lie significantly lower (about 0.23%) as the corresponding ADC ones.

Table 3.4.: CVS-UCC3 in comparison to CVS-ADC(3): K-edge excitation energies in the CBS limit for the different basis sets, the difference to experimental data[81,100,3] Δ_{ADC}, Δ_{UCC} [eV] is presented. All data sets are included in the appendix, section B.4.

	State	cc series		aug-cc series		d-aug-cc series		Expt.
		Δ_{ADC}	Δ_{UCC}	Δ_{ADC}	Δ_{UCC}	Δ_{ADC}	Δ_{UCC}	[eV]
CO C	1	0.29	0.74	0.3	0.76	0.29	0.75	287.4
	2			1.17	1.65	1.15	1.63	292.5
	3			1.31	1.82	1.27	1.79	293.4
CO O	1	4.09	2.98	4.13	3.01	4.14	3.03	534.1
	2			5.37	4.11	5.37	4.12	538.8
	3			5.82	4.47	5.77	4.42	539.8
NH_3 N	1	2.88	2.97	2.81	2.91	2.82	2.92	400.66
	2	2.82	2.95	2.7	2.82	2.7	2.81	402.33
	3			3.11	3.2	3.04	3.12	402.86
CH_3 C	1	0.48	0.65	0.49	0.66	0.5	0.66	281.35

Oscillator strengths

All computed oscillator strengths for the second- and third-order UCC schemes are compiled in the appendix, sections B.3 and B.4. As can be observed, oscillator strengths for both, CVS-UCC and CVS-ADC, are remarkably similar in most cases, if not, identical. This is the case for all applied schemes, CVS-UCC2, CVS-UCC2-x as well as CVS-UCC(3/2). As was shown in figures 3.4 and 3.5, the capability of reproducing proper oscillator strengths enables the CVS-UCC methods (example spectra for CVS-UCC2 and CVS-UCC2-x) to generate spectra that are in very good agreement with CVS-ADC ones.

3.4. Summary

This section summarizes a benchmark study on the application of the Core-valence separation approach to Unitary Coupled Cluster for the CVS-UCC2, CVS-UCC2-x and CVS-UCC3 schemes. Core-excitation energies are located in the high-energy or X-ray region of optical spectra, meaning that a description of these excitations enables the computation of X-ray spectra for molecular species. For this purpose, the work on corresponding CVS-ADC methods executed by Wenzel et al.[108,107,106] was used as a reference. CVS-UCC data was computed using the same molecular species as for the CVS-ADC approach.

For CVS-UCC2 and CVS-UCC2-x, core excitation energies lie remarkably close to the corresponding CVS-ADC ones, ranging from 0.001% to 0.04% for the second-order scheme and 0.001% to 0.03% for the extended second-order scheme, respectively. As may be observed in both cases, CVS-UCC values tend to exceed the corresponding CVS-ADC ones, albeit only slightly.

The study on third-order core excitation energies included CO, NH_3 and CH_3. A complete basis set limit has been extrapolated using computations on the cc- aug-cc- as well as d-aug-cc-pVXZ basis set series. As before, the corresponding CVS-UCC and CVS-ADC values are located closely together. In all cases except for CO O 1s, CVS-UCC3 values exceed the corresponding CVS-ADC(3) ones, up to about 0.16% for CO C 1s. For CO O 1s, the opposite is the case, with CVS-UCC3 values lying about 0.23% under the corresponding CVS-ADC(3) ones. Compared to experimental data, CVS-ADC(3) tends to lie closer in all cases except for CO O 1s, where CVS-UCC3 excels. Oscillator strengths for all levels of computation (CVS-UCC2, CVS-UCC2-x and CVS-UCC(3/2)) are in good congruence with the corresponding CVS-ADC ones with only few exceptions.

This benchmark study on core excited states in the frameworks of ADC and UCC showed that both, CVS-ADC as well as CVS-UCC, are similarly well suited in the description of these kind of excitations. Interestingly, the iterative description of the ground state for UCC (that is similar to CVS-CC methods and in contrast to the non-iterative MP ground state for ADC) does not seem to change the performance of the calculations, as the improvements may be regarded as negligible around the ground-state geometry.

4. Automated generation of Unitary Coupled Cluster working equations

In this chapter, an implementation to automate the code generation for Unitary Coupled Cluster working equations shall be presented. Additionally, the full UCC4 equations including triples amplitudes will be introduced for the ground state as well as the ISR, including both, excitation energies for electronically excited states (PP-UCC) and properties. The automated code generation for highly accurate electronic structure methods has been previously applied very successfully to ADC[60] by introducing a full fourth-order scheme for the computation of electronically-excited states in this framework. This may be seen as an inspiration to do the same in the UCC framework.

4.1. Preliminary

It has been already mentioned shortly in the historical introduction, the permanently increasing computational power is a true sake for theoretical chemists, does it not only increase the system size to be studied but also the precision, that is, the level of theory to be applied in a calculation. The reason for that is very simple: the underlying working equations become bigger and bigger for more accurate methods and therefore, the number of floating point operations that need to be executed increases. For a long time, however, this did not impose any restriction on the deduction of these working equations. But what if, at some point, the sheer amount and size of terms has grown to magnitudes that make it neither desirable nor possible to deduce these equations in a reasonable time "by hand"? An approach for an automated generation of working equations needs to be considered. In fact, the theoretical feasibility of such an approach is given without a doubt. All electronic structure methods have in common that they are developed by applying a fixed set of rules iteratively - an algorithm so to say - to a pre-defined set of algebraic quantities. However, the implementation of such an algorithm may impose significant conditions on the code, such as reliability and, of course, correctness in a mathematical sense.

The biggest advantage of a successful (correct) implementation is, however, the guarantee of proper equations. Casually speaking, a correctly implemented algorithm will never generate a wrong sign, prefactor, or forget a term. This may easily happen when deducing equations by hand and is certainly known infamously to most theoretical chemists. Searching for that one small error is not only tedious but may sometimes even be really frustrating, especially when energy differences on a scale of 0.1 eV or smaller matter. As an addition, an existing code base for a method may easily be applied to different schemes derived from this method, a feature that is not included in a manual derivation.

In the following, an approach to automatically generate Unitary Coupled Cluster working equations is presented. It includes a general introduction of the implemented code as well as the results, that is, the equations for a full UCC4 scheme. Included are the UCC4 ground-state energy and density (UCC amplitude equations for singles, doubles and triples), the UCC4 secular matrix for electronically excited states, the ground-to-excited state transition moments as well as the state-to-state transition matrix. In addition, an extension to the already existing UCC3 scheme is presented, UCC3-x, which is in analogy to UCC2-x an ad-hoc extension. Furthermore, an UCC4+5[s,t] scheme for an improved ground state that includes fifth-order terms will be presented.

4.2. Implementation

4.2.1. Theory

The fourth-order Unitary Coupled Cluster scheme for the polarization propagator (PP-UCC4) includes all terms up to fourth order in the energy and amplitudes equations, furthermore it introduces the full computation of triples amplitudes,

$$\hat{\sigma}_3 = \frac{1}{36}\sum_{ijkabc} \sigma_{ijk}^{abc}\, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_k \hat{a}_j \hat{a}_i + \frac{1}{36}\sum_{ijkabc} \sigma_{abc}^{ijk}\, \hat{a}_k^\dagger \hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_a \hat{a}_b \hat{a}_c . \tag{4.1}$$

This means that, for UCC4, the set of amplitude working equations

$$\begin{aligned} \langle \Phi_i^a | \bar{H} | \Phi_0 \rangle &= 0 \\ \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle &= 0 \\ \langle \Phi_{ijk}^{abc} | \bar{H} | \Phi_0 \rangle &= 0 \end{aligned} \tag{4.2}$$

must be converged iteratively and coupled including all terms up to fourth order in perturbation theory. As for the PP-UCC4 secular matrix, the similarity to PP-ADC(4)[60] introduces the ordering relations for the matrix blocks as depicted in figure 4.1. Also shown is the PP-UCC3-x matrix, which includes a second order treatment to the doubles/doubles block.

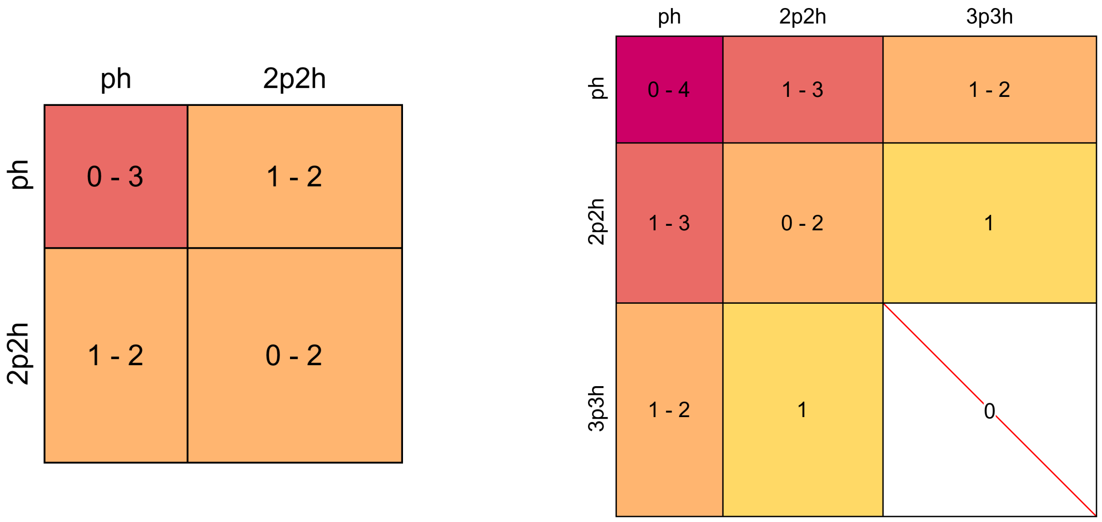

Figure 4.1.: Schematic structure and order relations for the PP-UCC3-x matrix (left) as well as the PP-UCC4 matrix (right).

As a preliminary step to the actual implementation, the full UCC Hamiltonian (eq. 1.136) may be rearranged. For a fourth-order treatment, terms of the Hamiltonian up to $\bar{H}_3$ are needed, however, not the full set of terms up to $\bar{H}_3$ contributes in a strict fourth-order formalism. Using the linearity of the commutator,

$$[\alpha, \beta + \gamma] = [\alpha, \beta] + [\alpha, \gamma], \tag{4.3}$$

the UCC4 Hamiltonian may be rewritten to contain exactly all necessary terms for a fourth order scheme. For $\bar{H}_0$ and $\bar{H}_1$, no restrictions occur, since the terms do not exceed third order. With $\hat{\sigma}_{123} = \hat{\sigma}_1 + \hat{\sigma}_2 + \hat{\sigma}_3$, it can be rewritten as

$$\bar{H}_{0,1} = \hat{F} + \hat{V} + [\hat{F}, \hat{\sigma}_{123}] + \frac{1}{2}[\hat{V}, \hat{\sigma}_{123}] + \frac{1}{2}[\hat{V}_R, \hat{\sigma}_{123}]. \tag{4.4}$$

For $\bar{H}_2$, the nested commutator may only contain the second order properties σ_1 and σ_3 once to not exceed the perturbation order. With $\hat{\sigma}_{13} = \hat{\sigma}_1 + \hat{\sigma}_3$, $\bar{H}_2$ can be rewritten as

$$\begin{aligned}\bar{H}_2 = & \frac{1}{12}[[\hat{V}_N, \hat{\sigma}_{13}], \hat{\sigma}_2] + \frac{1}{12}[[\hat{V}_N, \hat{\sigma}_2], \hat{\sigma}_2] + \frac{1}{12}[[\hat{V}_N, \hat{\sigma}_2], \hat{\sigma}_{13}] \\ & + \frac{1}{4}[[\hat{V}, \hat{\sigma}_{13}], \hat{\sigma}_2] + \frac{1}{4}[[\hat{V}, \hat{\sigma}_2], \hat{\sigma}_2] + \frac{1}{4}[[\hat{V}, \hat{\sigma}_2], \hat{\sigma}_{13}] \\ & + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}_{13}], \hat{\sigma}_2] + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}_2], \hat{\sigma}_2] + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}_2], \hat{\sigma}_{13}].\end{aligned} \tag{4.5}$$

The only contribution from the triply nested commutator not exceeding fourth order is with the first order propertyσ_2, thus leaving the terms

$$\begin{aligned}\bar{H}_3 = & \frac{1}{24}[[[\hat{V}_N, \hat{\sigma}_2], \hat{\sigma}_2]_R, \hat{\sigma}_2] + \frac{1}{8}[[[\hat{V}_R, \hat{\sigma}_2]_R, \hat{\sigma}_2]_R, \hat{\sigma}_2] + \frac{1}{8}[[[\hat{V}, \hat{\sigma}_2]_R, \hat{\sigma}_2]_R, \hat{\sigma}_2] \\ & - \frac{1}{24}[[[\hat{V}, \hat{\sigma}_2]_R, \hat{\sigma}_2], \hat{\sigma}_2] - \frac{1}{24}[[[\hat{V}_R, \hat{\sigma}_2]_R, \hat{\sigma}_2], \hat{\sigma}_2].\end{aligned} \tag{4.6}$$

As an addition, for the UCC4+5[s,t] scheme, the singly nested commutator in fifth order $\bar{H}_2^{(5)}$ with singles and doubles is included in the ground-state energy and amplitude description,

$$\begin{aligned}\bar{H}_2^{(5)} = & \frac{1}{12}[[\hat{V}_N, \hat{\sigma}_1], \hat{\sigma}_1] + \frac{1}{12}[[\hat{V}_N, \hat{\sigma}_1], \hat{\sigma}_3] + \frac{1}{12}[[\hat{V}_N, \hat{\sigma}_3], \hat{\sigma}_1] + \frac{1}{12}[[\hat{V}_N, \hat{\sigma}_3], \hat{\sigma}_3] \\ & + \frac{1}{4}[[\hat{V}, \hat{\sigma}_1], \hat{\sigma}_1] + \frac{1}{4}[[\hat{V}, \hat{\sigma}_1], \hat{\sigma}_3] + \frac{1}{4}[[\hat{V}, \hat{\sigma}_3], \hat{\sigma}_1] + \frac{1}{4}[[\hat{V}, \hat{\sigma}_3], \hat{\sigma}_3] \\ & + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}_1], \hat{\sigma}_1] + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}_1], \hat{\sigma}_3] + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}_3], \hat{\sigma}_1] + \frac{1}{4}[[\hat{V}_R, \hat{\sigma}_3], \hat{\sigma}_3].\end{aligned} \tag{4.7}$$

Including these terms does not increase the scaling (cost) of the amplitude and energy equations, thus enabling to add additional precision to the ground-state description.

The most "expensive" step in a computational sense is the evaluation of Wick's theorem, which scales exponentially with the number of second-quantized operators in a string. Particularly for the triples amplitudes, it is therefore very desirable to exclude all contributions that should not be considered in a certain scheme. As an example, the Hamiltonian part $\bar{H}_3$

with triples amplitudes would represent a seventh order contribution not present in the desired equation.

For the computation of the fourth-order ground-state density $\langle \Phi_0 | \bar{D} | \Phi_0 \rangle$ as well as the fourth-order ground-to excited state moments $\langle \Phi_I | \hat{D} | \Phi_0 \rangle$ and the matrix of state-to-state moments $\langle \Phi_I | \bar{D} | \Phi_J \rangle$ for the fourth-order UCC scheme, the Baker-Campbell-Hausdorff expansion for $\bar{D}$ needs to be expanded to the quadruply-nested commutator, however, only including the doubles amplitudes,

$$\bar{D}^{(4)} \leftarrow [[[[\hat{D}, \hat{\sigma}_2], \hat{\sigma}_2], \hat{\sigma}_2], \hat{\sigma}_2]. \tag{4.8}$$

Just as for the similarity-transformed Hamiltonian $\bar{H}$, the linearity of the commutator may be applied to reformulate the full expression of $\bar{D}$ (eq. 1.140) with the objective of only generating terms of the desired perturbation order in the computation.

4.2.2. Structure of the equation generator

Implementation of the UCC code generator has been done using `SymPy`[68], the example given on the `SymPy` GitHub page for the generation of CCSD ground-state equations[1] was used as an orientation. The `secondquant` library of `SymPy` gives the ability to efficiently evaluate expressions in second quantization, in particular for the application of Wick's theorem to the nested commutators in the Baker-Campbell-Hausdorff expansion. In figure 4.2, the general structure of the code is presented.

In the following, a short explanation of the different parts of the code and its structure along with some examples are given.

The `base` folder

This folder contains the basic routines and classes that are needed for a computation. These are the files:

- `evaluate.py`: This file contains all routines to compute the raw UCC equations by applying Wick's theorem.
- `hamiltonian.py`: In this file, the Hamiltonian to be computed and all classes to ini-

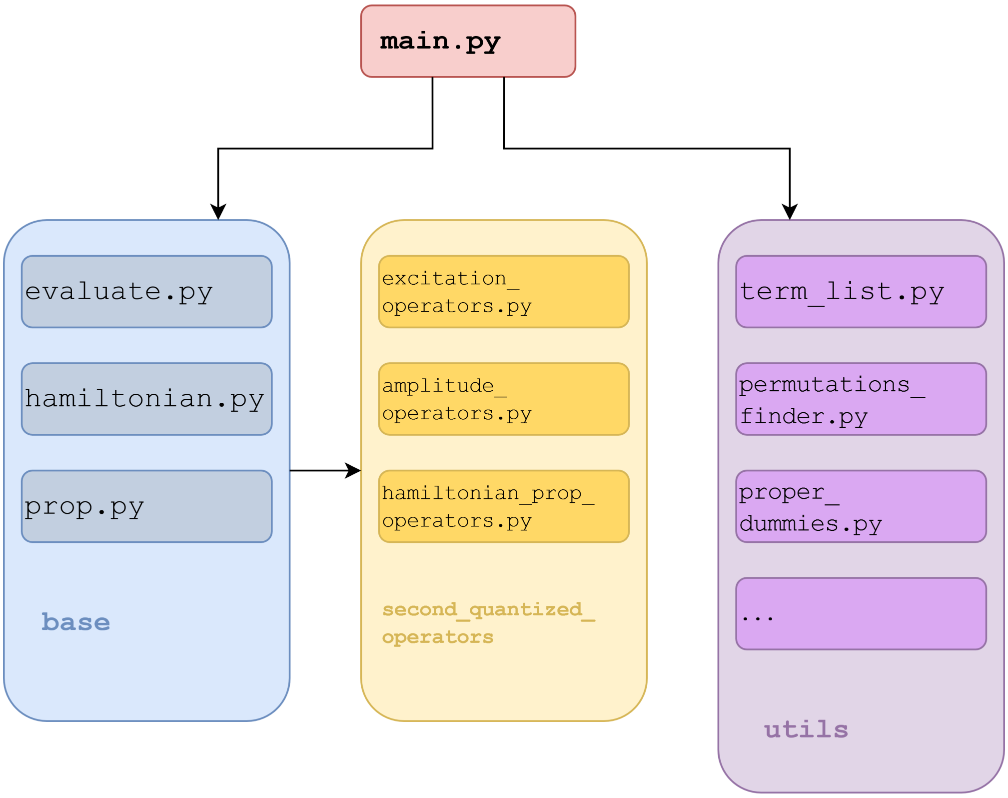

Figure 4.2.: Schematic structure of the implemented UCC code generator. The dependencies of the different instances are indicated by arrows.

tialize it are included.

- `prop.py`: As for the Hamiltonian, this file contains the expressions to calculate densities and transition moments.

To illustrate how the Hamiltonian is initialized, the code example in figure 4.3 shows how the UCC3 Hamiltonian as well as the full third-order properties objects are set up. The class `hamiltonian_ucc3` contains as members the Boolean `only_real`, set in the main routine, to determine whether complex amplitudes are allowed in the calculation. Otherwise, only real amplitudes are included (as given in eq. 1.119). The `domain` string is needed to evaluate expressions according to their non-diagonal and rest part correctly, as explained in the theory chapter on UCC (see figure 1.11). No terms that exceed the integer `order` are included in the result.

For the initialization of the Hamiltonian (or property) object, a list of individual objects to be evaluated is set up, the `comm_list`. The constituents of this list represent one of the following three objects:

- `no_comm`: Class fo expressions without a commutator, that is, the pure fragments of the Hamiltonian $\hat{F}$ and $\hat{V}$.
- `comm`: Class for the single commutator of two expressions, always $\hat{V}$ with an amplitude fragment.
- `nested_comm`: Class for the nested commutator of $\hat{V}$ and a specific (nested) list of amplitude fragments.

All of these classes are initialized with a rational, the prefactor of the respective expression, as well as the tensor objects to be evaluated: This is one for no commutator and two for the standard commutator. For the nested commutator, a list of all tensor objects together with a list of the respective operation to be applied is given to either determine the rest (R) part of a commutator result or not. Take as an example the line

```
self.comm_list.append(nested_comm(['vo', 's12', 's12'], ['rest'], 0.25))
```

which would correspond to

$$\frac{1}{4}[[\hat{V},(\sigma_1+\sigma_2)]_R,(\sigma_1+\sigma_2)]. \tag{4.9}$$

The string `'ord'` will leave the result as it is while the `'rest'` operation will only return the rest part. Note that only these two operations occur in the nested UCC Hamiltonians up to $\bar{H}_4$[62,63]; furthermore, up to this level, the last nesting does always contain the `'ord'` operation. This means that the array of operations has always two entries less than the array of tensors.

```
class hamiltonian_ucc3():
"""
Full UCC3 Hamiltonian
-only_real: Boolean, decide if cluster amplitudes are only real
-domain: Define domain of calculation (i. e. uccsd, uccsdt)
-order: Perturbation order not to be exceeded (optional)
"""
def __init__(self, only_real):
self.only_real = only_real
self.domain = ’uccsd’
self.order = 3
self.comm_list = []

#UCC Hbar_0 Terms F + V
self.comm_list.append(no_comm(’fv’, 1.))
#UCC Hbar_1 first term [F, Sigma]
self.comm_list.append(comm(’f’, ’s12’, 1.))
#UCC Hbar_1 second term 0.5*[V, Sigma]
self.comm_list.append(comm(’vo’, ’s12’, 0.5))
#UCC Hbar_1 third term 0.5*[V_R, Sigma]
self.comm_list.append(comm(’vr’, ’s12’, 0.5))
#UCC Hbar_2 first term 1./12.*[[V_N, Sigma], Sigma]
self.comm_list.append(nested_comm([’vn’, ’s12’, ’s12’],
        [’ord’], 1./12.))
#UCC Hbar_2 second term 1./4.*[[V, Sigma]_R, Sigma]
self.comm_list.append(nested_comm([’vo’, ’s12’, ’s12’],
        [’rest’], 0.25))
#UCC Hbar_2 third term 1./4.*[[V_R, Sigma]_R, Sigma]
self.comm_list.append(nested_comm([’vr’, ’s12’, ’s12’],
        [’rest’], 0.25))


class prop_ucc3():
"""
UCC3 ISR for the calculation of properties
"""
def __init__(self, only_real):
self.only_real = only_real
self.domain = ’uccsd’
self.order = 3
self.comm_list = []

#ISR zeroth-order D
self.comm_list.append(no_comm(’d’, 1.))
#ISR first-order [D, Sigma]
self.comm_list.append(comm(’d’, ’s12’, 1.))
#ISR second-order 0.5*[[D, Sigma], Sigma]
self.comm_list.append(nested_comm([’d’, ’s12’, ’s12’],
        [’ord’], 0.5))
#ISR third-order 1/6*[[[D, Sigma], Sigma], Sigma]
self.comm_list.append(nested_comm([’d’, ’s2’, ’s2’, ’s2’],
        [’ord’, ’ord’], 1./6.))
```

Figure 4.3.: Set-up of the full UCC3 Hamiltonian $\bar{H}$, as well as $\bar{D}$ for the calculation of properties.

```
def sigma3(is_ucc, only_real):
"""
Triples amplitude operator
- is_ucc: UCC t3 amplitude operator if True, normal CC one if
                               False
- only_real: relevant for UCC, if True only real cluster
                               amplitudes
"""
i, j, k = symbols(’i,j,k’, below_fermi=True, cls=Dummy)
a, b, c = symbols(’a,b,c’, above_fermi=True, cls=Dummy)
sigma_abcijk = AntiSymmetricTensor(’sigma3’, (a, b, c),
        (i, j, k))
sigma_ijkabc = AntiSymmetricTensor(’sigma3c’, (a, b, c),
        (i, j, k))
abckji = NO(Fd(a)*Fd(b)*Fd(c)*F(k)*F(j)*F(i))
ijkcba = NO(Fd(i)*Fd(j)*Fd(k)*F(c)*F(b)*F(a))

if is_ucc:
    if only_real:
        Sigma3 = Rational(1, 36)*sigma_abcijk*abckji
                - Rational(1, 36)*sigma_abcijk*ijkcba
    else:
        Sigma3 = Rational(1, 36)*sigma_abcijk*abckji
                - Rational(1, 36)*sigma_ijkabc*ijkcba
else:
    Sigma3 = Rational(1, 36)*sigma_abcijk*abckji

return Sigma3
```

Figure 4.4.: UCC triples amplitudes set-up. Note the differentiation to ordinary CC triples as well as the option of only real cluster amplitudes.

The `second_quantized_objects` folder

In this folder, all objects that contain strings of second-quantized operators are included:

- `excitation_operators`: Includes all normal-ordered strings to be applied to the ground-state $|\Phi_0\rangle$ to form excited determinants $|\Phi_I\rangle$.
- `amplitude_operators`: Includes all amplitude operators $\hat{\sigma}$ for singles, doubles and triples.
- `hamiltonian_prop_operators`: Includes all operators that occur in the Hamiltonian and for the properties, $\hat{F}$, $\hat{V}$ and $\hat{D}$.

The formalism contains the boolean `is_ucc` which, if set false, simply reproduces the ordinary CC energy and amplitude expressions (see figure 4.4). As already mentioned earlier, it is also possible to enable only real amplitudes by setting the boolean `only_real` to true, transforming all amplitudes according to 1.119. The fluctuation potential $\hat{V}$ needs to be introduced not only in its full form, but also as a pure non-diagonal or rest fragment which is needed for the composition of the UCC Hamiltonian.

The `utils` folder

Finally, the `utils` folder is containing all additional routines and functions that may be used to further manipulate the solution, be it by simplification, symmetrization or other operations. The set-up for proper dummy (summation) indices is, for example, located in this folder. Also, the print-out routines, for example to a LaTeX format, are found in this folder. It can be further extended to introduce additional features to the code generator.

4.3. Running the code generator

The implementation of the UCC code generator enables for a set-up of individual expressions (e. g. the Hamiltonian) to be computed. An example for a computation is shown in figure 4.5. This particular example includes the computation of the UCC3 ground-state energy (specified with ’0’) as well as the UCC3 amplitude equations (singles and doubles specified with ’s’ and ’d’).

All tuples that are specified in `expr_list` are computed successively according to the specified expression and calculation type. The available calculation types that may be employed are listed in table 4.1 together with the perturbation order that corresponds to the set of generated equations for a certain UCC scheme. These calculation types correspond, as listed, to the different expectation values for $\hat{H}$ and $\hat{D}$ with respect to the ground- and/or excited-state determinants.

Table 4.1.: Available input keys for the UCC code generator as well as the corresponding expressions and perturbation orders of these expressions in different UCC schemes.

[a] Fifth-order terms from the singles-triples commutator are included.

[b] Additional terms in UCC4+5[s,t] only evaluated for the ground state energy and amplitude.

calculation type	evaluated expression	method			
	$\bar{O} = \bar{H}$ or $\bar{D}$	UCC3	UCC3-x	UCC4	UCC4+5[s,t]
0	$\langle \Phi_0 \vert \, \bar{O} \, \vert \Phi_0 \rangle$	3	3	4	4 (+5)[a]
s	$\langle \Phi_i^a \vert \, \bar{O} \, \vert \Phi_0 \rangle$	3	3	4	4 (+5)[a]
d	$\langle \Phi_{ij}^{ab} \vert \, \bar{O} \, \vert \Phi_0 \rangle$	3	3	4	4 (+5)[a]
t	$\langle \Phi_{ijk}^{abc} \vert \, \bar{O} \, \vert \Phi_0 \rangle$	-	-	4	4 (+5)[a]
ss	$\langle \Phi_i^a \vert \, \bar{O} \, \vert \Phi_j^b \rangle$	3	3	4	-[b]
sd	$\langle \Phi_i^a \vert \, \bar{O} \, \vert \Phi_{jk}^{bc} \rangle$	2	2	3	
st	$\langle \Phi_i^a \vert \, \bar{O} \, \vert \Phi_{jkl}^{bcd} \rangle$	-	-	2	
ds	$\langle \Phi_{ij}^{ab} \vert \, \bar{O} \, \vert \Phi_k^c \rangle$	2	2	3	
dd	$\langle \Phi_{ij}^{ab} \vert \, \bar{O} \, \vert \Phi_{kl}^{cd} \rangle$	1	2	2	
dt	$\langle \Phi_{ij}^{ab} \vert \, \bar{O} \, \vert \Phi_{klm}^{cde} \rangle$	-	-	1	
ts	$\langle \Phi_{ijk}^{abc} \vert \, \bar{O} \, \vert \Phi_l^d \rangle$	-	-	2	
td	$\langle \Phi_{ijk}^{abc} \vert \, \bar{O} \, \vert \Phi_{lm}^{de} \rangle$	-	-	1	
tt	$\langle \Phi_{ijk}^{abc} \vert \, \bar{O} \, \vert \Phi_{lmn}^{def} \rangle$	-	-	0	

```
from base.hamiltonian import *
from base.evaluate import *
from utils.proper_dummies import *
from utils.permutations_finder import *
from utils.term_list import *

#define here the expression to be evaluated and the
#calculation type as a tuple
expr_list = [(hamiltonian_ucc3(False), ’0’),
        (hamiltonian_ucc3(False), ’s’),
        (hamiltonian_ucc3(False), ’d’)]

def main():
    for expr in expr_list:

        #Main calculation
        #eq: Sympy equation (result of Wick’s theorem)
        #lit, rti: left and rght targets
        #dummies: dictionnary of dummies for the calculation
        eq, lti, rti, dummies = evaluate_expr(expr[0], expr[1])

        #Defining target indices to be checked for permutation
        perms_o = lti[0]
        perms_v = lti[1]

        #Searching permutations
        perms = find_perms(eq, perms_o, perms_v, dummies)

        #Saving the result
        term_list = build_term_list(eq, perms)
        write_latex(expr[0], expr[1], term_list)

if __name__ == "__main__":
    main()
```

Figure 4.5.: Set-up for the generation of equations in the `main.py` file. In this example, the equations for the UCC3 ground-state energy as well as singles and doubles amplitudes are computed.

4.4. Generated UCC schemes

A short overview of all generated equations is given in the following. All generated equations can be found in the appendix, section C.

UCC3-x scheme for the calculation of electronically-excited states

As a straightforward extension to the already existing UCC schemes, the PP-UCC3-x scheme with a second-order doubles/doubles block for the secular matrix is presented. In section C.1, included are:

- The UCC3 ground-state scheme with the third-order energy expression as well as third-order equations for singles and doubles amplitudes, section C.1.1.
- The PP-UCC3-x secular matrix (figure 4.1 on the left), section C.1.2.
- The third-order UCC ground-state density as well as third-order ground- to excited state moments for singles and doubles, section C.1.3.
- State-to-state moments for PP-UCC3-x states, following the order relations in figure 4.1, section C.1.4.

UCC4 scheme for electronically-excited states with an improved ucc4+5[s,t] ground state

Furthermore, the PP-UCC4 scheme including full triples is presented. The ground-state description is improved by the application of the doubly-nested commutators including $\hat{\sigma}_1$ and $\hat{\sigma}_3$ in $\bar{H}_2$, which is referred to as UCC4+5[s,t]. The resulting fifth-order terms do not increase the scaling of a full UCC4 scheme, thus making it computationally feasible, and include explicit singlet/triplet contractions which are not present in an ordinary UCC4 scheme. The full sets of working equations presented in section C.2 are:

- The UCC4+5[s,t] ground state scheme with the corresponding energy expression and singles, doubles and triples amplitudes, section C.2.1.
- The PP-UCC4 secular matrix (figure 4.1 on the right), section C.2.2.

- The fourth-order UCC ground-state density as well as fourth-order ground-to excited state moments for singles, doubles and triples, section C.2.3
- State-to-state moments for PP-UCC4 states, following the order relations in figure 4.1, section C.2.4.

4.4.1. Complexity and scaling

In a short final section, the increasing complexity of UCC working equations is discussed as a showcase example for a general circumstance in quantum chemistry. To give a sense of this, figure 4.6 shows the number of terms that are included in the iterative formulae for the ground-state energy and amplitudes in different UCC schemes.

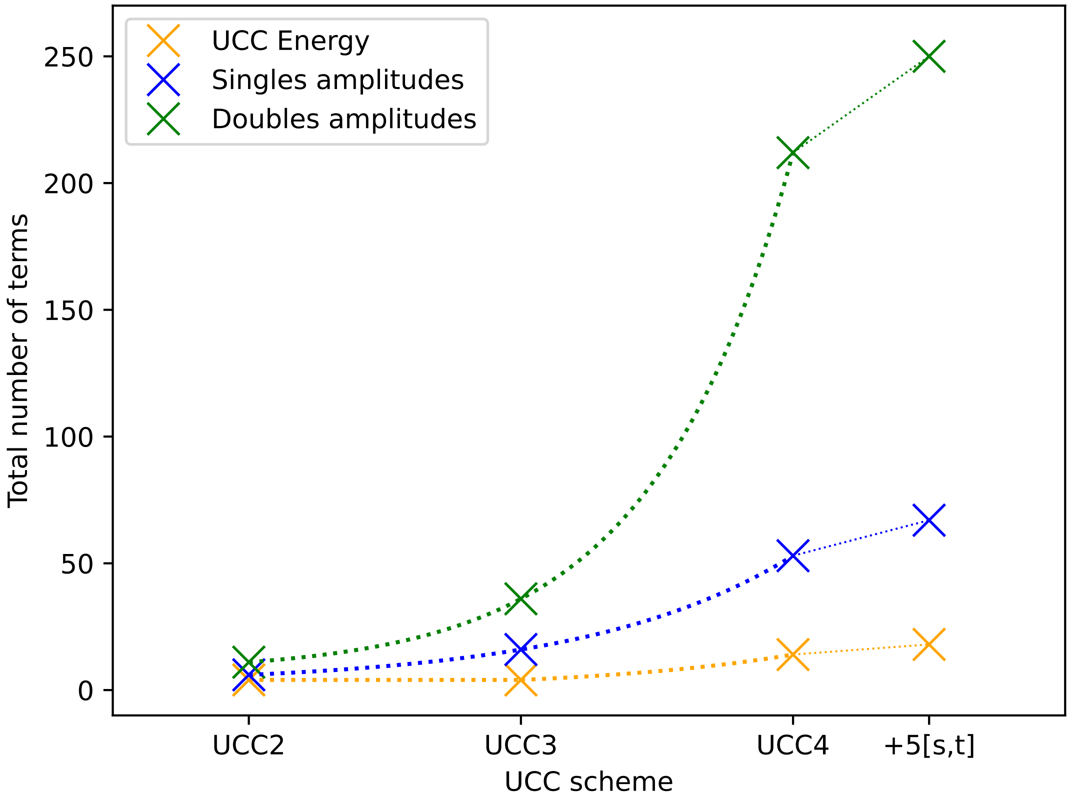

Figure 4.6.: Number of terms present in the UCC energy and amplitude equations for different schemes. An exponential fitting has been applied to the strict UCCn schemes.

As may be directly understood, the complexity and thus computational cost of the methods scale exponentially with the applied order of perturbation theory, including a remarkable step from UCC3 to UCC4 for doubles amplitudes (from 53 to 212 terms). For UCC4 and UCC4+5[s,t] the triples equations consist of even 657 and 741 terms, respectively.

The computational cost for the raw, that is, unoptimized PP-UCC4 matrix equations amounts to $\mathcal{O}(N^{10})$, however, before any optimization. This is the same as for PP-ADC(4)[60], which possesses an identical raw scaling without the introduction of intermediates for computational purposes. In an optimized scheme, the scaling may be reduced by two orders of magnitude to $\mathcal{O}(N^{8})$ for PP-ADC(4). Therefore, it is to be expected that an optimized PP-UCC4 scheme will sustain the same scaling behaviour. For the amplitudes, on the other hand, the most expensive terms occurring in the iterative formula for the fourth-order triples show a raw scaling which is as high as $\mathcal{O}(N^{11})$, an example for such a term is

$$\langle \Phi_{ijk}^{abc} | \bar{H} | \Phi_0 \rangle^{(4)} \leftarrow \frac{1}{6} \mathcal{P}^{-}_{(abc)} \sum_{lm,def} \langle ae || id \rangle \, \sigma_{jk}^{bf} \sigma_{lm}^{cd} \sigma_{lm}^{ef*} . \tag{4.10}$$

An appropriate splitting of these kind of expressions may lead to a reduction of at least two orders of magnitudes (to $\mathcal{O}(N^{9})$) for the scaling of these terms, however, a suited scheme for the computation of the here presented equations in an optimized matrix-vector product formulation is yet to be established. Note that this only includes the computation of the cluster amplitudes which, already in the case for small molecules as presented in the benchmarks above, only remain to be a fraction in the full computational cost. In the improved ground-state scheme UCC4+5[s,t] this scaling is not exceeded, thus offering the opportunity to include these additional explicit singlet-triplet commutator terms (which are of fifth order) in the computation.

The applicability of a full fourth-order scheme including explicit triples amplitudes in the UCC framework imposes a computationally costly task, however, the application may deliver highly-accurate and reliable values. Furthermore, an expansion of the above presented schemes to the computation of ionized or electronically attached states or other models in the UCC framework[49,19] is a simple and straightforward task that may be realized expeditiously.

5. Summary

The development and application of highly-accurate electronic structure methods has become a fundamental task of modern theoretical and computational chemistry. Availability of increasing computational power has enabled theoreticians to push the limits to ever higher precisions, being able to establish a solid model framework to complement the work of experimentalists in all disciplines of chemistry and molecular sciences.

In this work, the implementation and benchmarking of modern state-of-the-art methods for the computation of excited states in the frameworks of the Algebraic Diagrammatic Construction scheme as well as Unitary Coupled Cluster were presented. To this end, the work was divided into three parts: In the first part, **The Algebraic Diagrammatic Construction scheme for the two-hole and two-particle propagators (chapter 2)**, an implementation of DIP-ADC as well as DEA-ADC for the calculation of doubly-ionized as well as double electronically-attached states has been introduced along with benchmark data. The second part, **Core-valence separation for Unitary Coupled Cluster (chapter 3)**, includes an investigation of core excited states in the UCC framework. Finally, the third part, **Automated generation of Unitary Coupled Cluster working equations (chapter 4)**, introduces the implementation of a code generator for the computation of UCC working equations.

Chapter 2 presents an implementation along with a benchmark study for the calculation of doubly-ionized as well as double electronically-attached states in the framework of the Algebraic Diagrammatic Construction scheme up to third order. This implementation was realized in the `adcman` and `libadc` folders of the `Q-Chem` program package, exploiting the high-performance tensor library `libtensor` for calculations. Benchmark calculations for double ionizations were executed using two benchmark sets, a small one previously applied by Velkov et al. (containing H_2O, LiH and HF) for the computation of doubly-ionized states on a FCI level as well as a set introduced by Jacquemin et al. consisting of 18 small to medium-sized compounds for both, DIP and DEA.

A direct comparison to FCI values shows that both, DIP-ADC(3) as well as EOMDIP-CCSD, are able to generate precise results, however, the latter being superior with deviations of only -0.09 eV for eight singlet states (in comparison to 0.34 eV for DIP-ADC(3)) and -0.15 eV for five triplet states (in comparison to 0.54 eV for DIP-ADC(3)). For the extended study of 18 species in the second benchmark set, 72 states for DIP-ADC(2)-x and DIP-ADC(3) as well as 68 states for DIP-ADC(2) triplets were compared to the corresponding EOMDIP-CCSD values. The main finding is that a proper description of doubly-ionized states explicitly demands for an adequate parametrization of the doubles/doubles (p3h/p3h) block of the secular matrix, possibly relating to relaxation processes that occur upon double ionization to the equilibrated ground state. Due to this circumstance, DIP-ADC(2)-x with its first-order doubles/doubles block is as first method within the hierarchy of DIP-ADC methods able to yield double-ionization energies which are at least roughly comparable to EOMDIP-CCSD values with deviations of -1.31 ± 0.29 eV (-3.6%) for the singlet states and -1.47 ± 0.36 eV (-3.9%) for the triplet states; however, still inheriting a huge underestimation. For DIP-ADC(3), on the other hand, an excellent agreement to EOMDIP-CCSD was observed, with deviations of only -0.23 ± 0.35 eV (-0.7%) for singlet states and -0.33 ± 0.45 eV (-0.9%) for triplet states, respectively. As explained above, the pure second-order scheme fails in a proper description of doubly-ionized states due to an only zeroth-order diagonal present in the doubles/doubles block of the secular matrix, showing deviations as high as -4.02 ± 1.31 eV (-10.8%) for singlet states and -3.70 ± 1.19 eV (-9.8%) for triplet states when compared to EOMDIP-CCSD data. The particular high amounts of doubles (p3h) amplitudes in DIP-ADC(2) states here imply an insufficient physical description of the doubles (p3h) space. Not suited at all is the pure first-order scheme DIP-ADC(1), which does not include a description of the doubles (p3h) space. Furthermore, an increase of double-ionization energies for higher-order DIP-ADC methods, together with a decrease in the amount of doubles amplitudes (p3h amplitudes) in the doubly-ionized wavefunction is observed, supporting the findings mentioned above.

For the benchmark of doubly-attached states, eight out of 18 molecules of Jacquemins set (ammonia, dinitrogen, ethylene, formaldehyde, hydrogen chloride, hydrogen sulfide, methanimine and water) were used. The calculations include 27 (singlet) and 26 (triplet) states for DEA-ADC(2), DEA-ADC(2)-x and DEA-ADC(3), respectively as well as 32 states for DEA-ADC(1). As the key finding, all second- and third-order methods lie very closely together in the description of double attachment energies, again, the third-order method DEA-ADC(3) excels here with a deviation of only 0.10 ± 0.09 eV (-1.9%) for singlet states and -0.12 ± 0.10 eV (-2.0%) for triplet states. As for the other methods compared to EOMDEA-CCSD, DEA-ADC(2) shows a deviation of -0.17 ± 0.11 eV (-3.1%) for the singlet states and -0.17 ± 0.10 eV (-2.8%) for the triplet states, this is found to be -0.19 ± 0.11 eV (-3.4%) for the singlet states and -0.18 ± 0.10 eV (-3.1%) for the triplet states in the case of DEA-ADC(2)-x. This means that, unlike to DIP-ADC, the pure second-order scheme for DEA-ADC constitutes a better method than the extended second-order scheme which at this part introduces a slightly worse description with its first-order doubles/doubles block. As a difference to DIP-ADC, a benchmark of the first-order method DEA-ADC(1) was also included, stemming from the fact that double attachment processes may be characterized as almost purely of singles (2p) character with very little amounts of doubles amplitudes in the excited state wavefunction. Deviations of DIP-ADC(1) were found to be 0.29 ± 0.18 eV (5.2%) for singlet states and 0.28 ± 0.18 eV (4.7%) for triplet states. Therefore, in contrast to the second- and third-order methods, DEA-ADC(1) is always exceeding double attachment energies.

Recognizing the findings above, it is particularly interesting to see that DEA-ADC(1) constitutes a better method to describe the process of double attachment than DIP-ADC(2) does in the case of double ionization. For both processes, the third-order ADC scheme delivers the best results compared to EOM-CCSD, however, results are closer in the case of DIP (deviating by only -0.7% for singlet states and -0.9% for triplet states) as in the case of DEA (deviating by -1.9% for singlet states and -2.0% for triplet states). The third-order methods DIP-ADC(3) and DEA-ADC(3) thus constitute valid alternatives as well as supplements to the corresponding EOM-CCSD schemes.

Chapter 3 (previously published[98]) presents the application of the Core-valence separation (CVS) approach to Unitary Coupled Cluster. The CVS formalism enables the computation of core-excitation energies which exceed with 10^2 - 10^3 eV the usual studied HOMO-LUMO excitations of $\sim 10^1$ eV by far. These excitations are located in the high-energy or X-ray region of optic spectra, thus giving access to the computation of X-ray spectra for molecular species. Benchmark studies were executed on the same set of closed-and open-shell species that was previously used by Wenzel et al. to study the CVS approach for the Algebraic Diagrammatic Construction scheme. As for CVS-ADC, calculations were performed for CVS-UCC2, CVS-UCC2-x as well as CVS-UCC3 using `Q-Chem` 5.2.

It was shown that CVS-UCC and CVS-ADC core-excitation energies are located remarkably close to one another, with the deviations for the different systems investigated ranging from 0.001% to 0.04% for CVS-UCC2 (relative to CVS-ADC(2)) and 0.001% to 0.03% for CVS-UCC2-x (relative to CVS-ADC(2)-x). For the third-order scheme, the investigation of core-excitation energies on the three small molecular species CO, NH_3 and CH_3 including a complete basis set extrapolation on the cc- aug-cc- and d-aug-cc-pVXZ basis set series showed that also for this scheme, CVS-UCC and CVS-ADC are in a very good accordance. CVS-UCC3 values exceeded the corresponding CVS-ADC(3) values (up to about 0.16% for CO C 1s) except for CO O 1s, where they are located about 0.23% under the CVS-ADC values. Also for the calculations on CO O 1s, CVS-UCC3 values lie closer to experimental data, in all other cases CVS-ADC(3) values are found to be closer. With only few exceptions, computed oscillator strengths on the different levels (CVS-UCC2, CVS-UCC2-x and CVS-UCC(3/2)) are in good agreement, if not identical, to the corresponding CVS-ADC ones. An extended example, featuring the spectrum of cationic anthracene in the region between 281 and 289 eV, shows the capability of CVS-UCC2-x to produce X-ray spectra in comparison to CVS-ADC(2)-x.

As a summary, CVS-UCC as well as CVS-ADC methods up to third order are similarly well suited for the computation of core-excitation energies. However, the iterative ground-state description for UCC, in contrast to the non-iterative MP ground state for ADC, seems to not change the performance of the calculations, as it may be regarded as negligible around the ground-state geometries.

Chapter 4 introduces the implementation of an automated code generator for Unitary Coupled Cluster working equations. A detailed description of the code and implemented features is provided, along with code snippets that serve as comprehensive examples. The applicability of the code generator has been shown by the generation of the full sets of UCC3-x as well as UCC4 working equations for the calculation of electronically-excited states (PP-UCC). The sets of generated equations further include the description of properties such as ground-state densities, ground-to excited state as well as state-to-state densities. UCC3-x in this context represents an ad-hoc extension of UCC3, expanding the doubles/doubles block of the UCC secular matrix in second order. The UCC4 scheme includes full triples, furthermore, an improved ground-state scheme, named UCC4+5[s,t] is introduced. This scheme includes fifth-order terms that explicitly contract singles and triples amplitudes without increasing the principal scaling (cost) of the scheme. As for PP-UCC4, the raw equations show a scaling of $\mathcal{O}(N^{10})$ just as for PP-ADC(4), implying that an optimized implementation would also be able to reach the $\mathcal{O}(N^{8})$ of PP-ADC(4). For the amplitudes, on the other hand, the scaling reaches a $\mathcal{O}(N^{11})$, which may be reduced to at least $\mathcal{O}(N^{9})$. However, a suitable implementation for the computation of PP-UCC(4) needs yet to be realized.

5.1. Outlook

As the concluding part of this work, a short outlook on possible applications to be further made for the here introduced developments shall be made.

For doubly-ionized as well as double electronically-attached states in the DIP-ADC and DEA-ADC frameworks, an extended benchmark of bigger molecules could be a desirable task. Furthermore, the calculation of excited-state properties for DIP-ADC and DEA-ADC as for PP-ADC[65] or IP/EA-ADC[20,21,18] could be included. To enable this, the existing code structure in `adcman` as well as `libadc` can be straightforwardly used. In similarity to PP-ADC[60], the application of a fourth-order DIP/DEA-ADC scheme could be considered. The same holds true for the CVS-UCC scheme: A higher-order application, namely CVS-UCC4, could be established, along with the calculation of properties on a high level of theory.

This would be, as the UCC4 scheme for the calculation of excited states, an extension to the hierarchy of UCC methods by fourth order. However, as this work "only" presents the fourth-order UCC ground-state and secular matrix equations, an efficient implementation of the working equations in the form of matrix-vector products would be the next step towards this. Also, the application of the UCC code generator to different excitation schemes, such as the (double-) ionization[19,49] as well as the (double-) attachment to formulate fourth-order UCC schemes for these processes may be an interesting endeavour.

A. Algebraic-Diagrammatic construction scheme for doubly-ionized/double electronically attached states

A.1. Intermediates for computation

Generated automatically using a code generator for ADC introduced by J. Leitner et al.[60].

$$
\begin{aligned}
M^{(3)}_{ij,kl} \;=\; & P^{+}_{ij}\, P^{+}_{kl} \Big[\frac{1}{2} P^{-}_{ij}\, P^{-}_{kl} \Big(\sum_{ab} \langle ia||kb\rangle\, t^{(2sq)}_{jalb} + \frac{1}{2} \sum_{mn} \langle in||lm\rangle \sum_{ab} t^{ab}_{jm} \sum_{ab} t^{ab}_{kn} \Big) \\
& \qquad + P^{-}_{kl} \Big(\sum_{a} \langle ij||ka\rangle\, \rho_{la} + \frac{1}{2} \sum_{m} \langle ij||km\rangle\, \rho_{lm} + \frac{1}{2} \sum_{ab} t^{ab}_{ij} Z^{(4)}_{klab} \Big) \\
& \qquad - \frac{1}{4} \sum_{ab} \langle ij||ab\rangle\, t^{(d2)}_{klab} \\
& + P^{-}_{ij}\, P^{-}_{kl} \Big[\delta_{ik} \cdot \Big(\frac{1}{2} \sum_{m,ab} t^{ab}_{jm} Z^{(4)}_{lmba} - \sum_{m,a} \langle jm||la\rangle\, \rho_{ma} - \frac{1}{8} \sum_{m,ab} t^{ab}_{jm} Z^{(3)}_{lmab} \\
& \qquad + \frac{1}{4} \sum_{m,ab} \langle jm||ab\rangle\, t^{(d2)}_{lmab} - \frac{1}{2} \sum_{ab} \langle ja||lb\rangle\, \rho_{ab} - \frac{1}{2} \sum_{mn} \langle jn||lm\rangle\, \rho_{mn} \Big) \Big] \Big]
\end{aligned}
\tag{A.1}
$$

and

$$
\begin{aligned}
M^{(3)}_{ab,cd} \;=\; P^{+}_{ab}\,P^{+}_{cd}\,\Bigg[& \frac{1}{2} P^{-}_{ab}\,P^{-}_{cd} \Big(\sum_{ij} \langle ia||jc\rangle\, t^{(2sq)}_{ibjd} + \frac{1}{2} \sum_{ef} \langle af||de\rangle \sum_{ij} t^{be}_{ij} \sum_{ij} t^{cf}_{ij} \Big) \\
& + P^{-}_{cd} \Big(\sum_{i} \langle ia||cd\rangle\, \rho_{ib} + \frac{1}{2} \sum_{e} \langle ab||de\rangle\, \rho_{ce} + \frac{1}{2} \sum_{ij} t^{ab}_{ij} Z^{(4)}_{ijcd} \Big) \\
& - \frac{1}{4} \sum_{ij} \langle ij||ab\rangle\, t^{(d2)}_{ijcd} \\
+ P^{-}_{ab}\,P^{-}_{cd} \Bigg[& \delta_{ac} \cdot \Big(\frac{1}{2} \sum_{ij,e} t^{be}_{ij} Z^{(4)}_{ijed} - \sum_{i,e} \langle ib||de\rangle\, \rho_{ie} - \frac{1}{8} \sum_{ij,e} t^{be}_{ij} Z^{(5)}_{ijde} \\
& + \frac{1}{4} \sum_{ij,e} \langle ij||be\rangle\, t^{(d2)}_{ijde} + \frac{1}{2} \sum_{ef} \langle bf||de\rangle\, \rho_{ef} + \frac{1}{2} \sum_{ij} \langle ib||jd\rangle\, \rho_{ij} \Big) \Bigg] \Bigg]
\end{aligned}
\tag{A.2}
$$

with ρ being the MP ground-state densities,

$$
t^{(2sq)}_{iajb} \;=\; \sum_{k,c} t^{ac}_{ik} t^{bc}_{jk} \tag{A.3}
$$

and

$$
t^{(d2)}_{ijab} \;=\; 2\Big[P^{-}_{ij} P^{-}_{ab} (Z^{(4)}_{jiab}) - 0.5 (Z^{(5)}_{ijab} + Z^{(3)}_{ijab}) \Big] \cdot \Big[P^{+}_{ij} (f_{ia} + f_{jb}) \Big]^{-1} \tag{A.4}
$$

with f being the Delta-Fock matrix and

$$
\begin{aligned}
Z^{(3)}_{ijab} &= \sum_{kl} t^{ab}_{kl} \langle ij||kl\rangle \\
Z^{(4)}_{ijab} &= \sum_{k,c} t^{ac}_{jk} \langle kb||ic\rangle \\
Z^{(5)}_{ijab} &= \sum_{cd} t^{cd}_{ij} \langle ab||cd\rangle
\end{aligned}
\tag{A.5}
$$

the n^6 intermediates[17].

A.2. Geometries for the Full CI set

The first number in brackets gives the absolute charge, the second the multiplicity of the species.

Water (0 1)

O	0.00000	0.00000	0.00000
H	0.95700	0.00000	0.00000
H	-0.23961	0.92652	0.00000

Lithium hydride (0 1)

Li	0.0000000	0.0000000	0.0000000
H	1.5950000	0.0000000	0.0000000

Hydrogen fluoride (0 1)

F	0.0000000	0.0000000	0.0000000
H	0.9170000	0.0000000	0.0000000

A.3. Geometries for Jacquemins benchmark set

The first number in brackets gives the absolute charge, the second the multiplicity of the species.

Acetaldehyde (0 1)

C	-0.00234503	0.00000000	0.87125063
C	-1.75847785	0.00000000	-1.34973671
O	2.27947397	0.00000000	0.71968028
H	-0.92904537	0.00000000	2.73929404
H	-2.97955463	1.66046488	-1.25209463
H	-2.97955463	-1.66046488	-1.25209463
H	-0.70043433	0.00000000	-3.11066412

Acetylene (0 1)

C	0.00000000	0.00000000	1.14048351
C	0.00000000	0.00000000	-1.14048351
H	0.00000000	0.00000000	3.14009043
H	0.00000000	0.00000000	-3.14009043

Ammonia (0 1)

N	0.12804615	-0.00000000	0.00000000
H	-0.59303935	0.88580079	-1.53425197
H	-0.59303935	-1.77160157	-0.00000000
H	-0.59303935	0.88580079	1.53425197

Carbonmonoxide (0 1)

C	0.00000000	0.00000000	-1.24942055
O	0.00000000	0.00000000	0.89266692

Cyclopropene (0 1)

C	0.00000000	0.00000000	-1.66820880
C	0.00000000	1.22523906	0.90681419
C	0.00000000	-1.22523906	0.90681419
H	1.72255446	0.00000000	-2.77881149
H	-1.72255446	0.00000000	-2.77881149
H	0.00000000	2.97844519	1.92076771
H	0.00000000	-2.97844519	1.92076771

Diazomethane (0 1)

C	0.00000000	0.00000000	-2.30830005
N	0.00000000	0.00000000	0.14457890
N	0.00000000	0.00000000	2.29923216
H	0.00000000	1.79875201	-3.24272317
H	0.00000000	-1.79875201	-3.24272317

Dinitrogene (0 1)

N	0.00000000	0.00000000	1.04008632
N	0.00000000	0.00000000	-1.04008632

Formaldehyde (0 1)

C	0.00000000	0.00000000	-1.13947666
O	0.00000000	0.00000000	1.14402883
H	0.00000000	1.76627623	-2.23398653
H	0.00000000	-1.76627623	-2.23398653

Hydrogen chloride (0 1)

Cl	0.00000000	0.00000000	-0.02489783
H	0.00000000	0.00000000	2.38483140

Ketene (0 1)

C	0.00000000	0.00000000	-2.44810151
C	0.00000000	0.00000000	0.03498545
O	0.00000000	0.00000000	2.23663914
H	0.00000000	1.77432079	-3.43705988
H	0.00000000	-1.77432079	-3.43705988

Nitrosomethane (0 1)

C	-1.78426612	0.00000000	-1.07224050
N	-0.00541753	0.00000000	1.08060391
O	2.18814985	0.00000000	0.43452135
H	-0.77343975	0.00000000	-2.86415606
H	-2.97471478	1.66801808	-0.86424584
H	-2.97471478	-1.66801808	-0.86424584

Thioformaldehyde (0 1)

C	0.00000000	0.00000000	-2.08677304
S	0.00000000	0.00000000	0.97251194
H	0.00000000	1.73657773	-3.17013507
H	0.00000000	-1.73657773	-3.17013507

Ethylene (0 1)

C	0.00000000	1.26026583	0.00000000
C	0.00000000	-1.26026583	0.00000000
H	0.00000000	2.32345976	1.74287672
H	0.00000000	-2.32345976	1.74287672
H	0.00000000	2.32345976	-1.74287672
H	0.00000000	-2.32345976	-1.74287672

Formamide (0 1)

C	0.00183118	0.00000000	0.79313299
O	2.26817156	0.00000000	0.43918824
N	-1.76886033	0.00000000	-1.06219243
H	-0.84133459	0.00000000	2.68872485
H	-1.21254414	0.00000000	-2.87596907
H	-3.61627502	0.00000000	-0.65031317

Hydrogen sulfide (0 1)

S	0.00000000	0.00000000	-0.50365086
H	0.00000000	1.81828105	1.25212288
H	0.00000000	-1.81828105	1.25212288

Methanimine (0 1)

C	0.10696646	0.00000000	1.11091130
N	0.10764012	0.00000000	-1.29677742
H	-1.59140953	0.00000000	2.27296652
H	1.90475160	0.00000000	2.09393982
H	-1.69956184	0.00000000	-1.96217482

Streptocyanine (1 1)

C	0.00000000	0.00000000	0.80488833
N	0.00000000	2.19423463	-0.33580561
N	0.00000000	-2.19423463	-0.33580561
H	0.00000000	0.00000000	2.84436959
H	0.00000000	2.36978315	-2.23371976
H	0.00000000	-2.36978315	-2.23371976
H	0.00000000	3.79412648	0.69399206
H	0.00000000	-3.79412648	0.69399206

Water (0 1)

O	0.00000000	0.00000000	-0.13209669
H	0.00000000	1.43152878	0.97970006
H	0.00000000	-1.43152878	0.97970006

A.4. Benchmark of doubly-ionized singlet states

This section collects all data that was computed for the benchmark study of doubly-ionized singlet states. Besides the full data set, an individual statistical analysis for each molecular species in comparison to EOMDIP-CCSD as well as DIP-ADC(3) is provided.

Table A.10.: Benchmark data for doubly-ionized singlet states for the set of Jacquemin et al.[64] I.

Molecule	Excitation	Double ionization energy [eV]				Doubles contribution [%/100]			
		ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Acetaldehyde	1 A’	26.674	29.665	31.158	31.274	0.35	0.19	0.15	0.12
	1 A”	29.307	30.823	32.170	32.197	0.26	0.15	0.12	0.10
	1 A’	29.367	30.790	32.311	32.275	0.24	0.16	0.13	0.10
	1 A”	31.045	33.512	34.688	35.079	0.31	0.21	0.17	0.11
Acetylene	1 Ag	29.884	32.814	33.319	33.761	0.36	0.15	0.12	0.10
	1 Ag	30.579	33.621	34.082	34.474	0.38	0.15	0.12	0.10
	1 B2u	35.423	38.002	38.660	39.168	0.35	0.18	0.15	0.12
	1 B2g	37.590	39.889	40.693	41.267	0.38	0.22	0.18	0.13
Ammonia	1 A’	30.968	34.858	36.447	36.254	0.35	0.17	0.14	0.12
	1 A’	35.018	38.960	40.573	40.375	0.36	0.16	0.13	0.12
	1 A’	40.677	44.815	46.380	46.177	0.38	0.15	0.13	0.11
	1 A’	41.848	46.512	48.138	47.859	0.50	0.15	0.12	0.11
Carbonmonoxide	1 Σ^+	38.989	40.996	41.561	42.015	0.27	0.17	0.14	0.11
	1 Π	39.698	41.843	42.172	42.782	0.27	0.14	0.13	0.10
	1 Σ^+	41.992	44.564	45.729	46.039	0.39	0.23	0.18	0.16
	1 Δ	42.303	46.887	48.326	48.515	0.40	0.24	0.26	0.15
Cyclopropene	1 A1	25.742	27.601	28.438	28.720	0.27	0.15	0.12	0.09
	1 A2	26.103	28.184	29.194	29.478	0.28	0.16	0.13	0.11
	1 A1	27.856	30.381	31.555	31.722	0.32	0.18	0.14	0.11
	1 B2	28.235	30.570	31.632	31.880	0.31	0.17	0.14	0.11
Diazomethane	1 A1	25.457	27.132	27.392	27.974	0.25	0.15	0.11	0.09
	1 A2	29.650	31.546	31.862	32.630	0.29	0.17	0.14	0.11
	1 B2	31.576	33.246	33.714	34.448	0.30	0.20	0.16	0.12
	1 A2	32.612	34.707	35.266	36.174	0.41	0.32	0.22	0.12

Table A.11.: Benchmark data for doubly-ionized singlet states for the set of Jacquemin et al.[64] II.

Molecule	Excitation	Double ionization energy [eV]				Doubles contribution [%/100]			
		ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Dinitrogene	1 Σ_g^+	40.304	43.006	42.947	43.938	0.33	0.17	0.15	0.12
	1 Π_u	41.966	44.967	45.250	46.031	0.32	0.17	0.13	0.11
	1 Σ_g^+	43.609	46.957	46.816	47.657	0.31	0.14	0.12	0.10
	1 Δ_g	43.681	46.883	47.227	47.804	0.33	0.17	0.13	0.11
Ethylene	1 Ag	27.990	30.128	31.065	31.267	0.28	0.16	0.13	0.10
	1 Au	29.923	31.707	32.535	32.883	0.28	0.16	0.13	0.10
	1 Ag	32.791	34.323	35.057	35.384	0.27	0.15	0.12	0.09
	1 B1u	31.901	34.371	35.418	35.695	0.32	0.18	0.15	0.12
Formaldehyde	1 A1	28.602	32.435	33.859	33.849	0.38	0.16	0.12	0.10
	1 A2	32.395	36.104	37.340	37.553	0.36	0.17	0.14	0.11
	1 B1	33.240	37.855	39.624	39.501	0.41	0.18	0.14	0.11
	1 A1	35.297	39.657	41.873	41.873	0.34	0.27	0.24	0.16
Formamide	1 A”	26.690	28.730	30.221	30.191	0.27	0.16	0.13	0.11
	1 A’	28.294	30.354	31.684	31.765	0.28	0.17	0.14	0.11
	1 A’	27.081	31.209	32.985	32.991	0.39	0.21	0.17	0.12
	1 A”	31.011	32.983	34.474	34.552	0.28	0.18	0.17	0.11
Hydrogen chloride	1 Δ	33.857	36.455	37.408	37.523	0.32	0.14	0.12	0.10
	1 Σ^+	35.102	37.842	38.737	38.830	0.33	0.13	0.11	0.09
	1 Π	37.763	40.288	41.136	41.298	0.31	0.14	0.12	0.10
	1 Σ^+	42.448	45.444	46.209	46.376	0.56	0.13	0.11	0.09
Hydrogen sulfide	1 A1	29.226	31.011	31.816	31.986	0.28	0.14	0.12	0.09
	1 B2	31.443	33.483	34.330	34.537	0.32	0.15	0.13	0.11
	1 A2	33.451	35.278	36.062	36.294	0.29	0.14	0.13	0.10
	1 A1	34.775	37.028	37.850	38.061	0.35	0.15	0.13	0.10

Table A.12.: Benchmark data for doubly-ionized singlet states for the set of Jacquemin et al.[64] III.

Molecule	Excitation	Double ionization energy [eV]				Doubles contribution [%/100]			
		ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Ketene	1 A1	26.666	28.416	29.028	29.428	0.25	0.15	0.12	0.10
	1 A2	30.690	32.415	33.012	33.534	0.27	0.17	0.14	0.10
	1 A2	33.149	34.710	35.441	35.927	0.29	0.19	0.16	0.11
	1 B2	32.886	34.837	35.972	36.188	0.28	0.17	0.14	0.11
Methanimine	1 A’	28.161	31.327	32.483	32.696	0.39	0.18	0.13	0.11
	1 A”	29.804	32.720	33.855	34.131	0.34	0.18	0.14	0.11
	1 A’	31.776	34.809	35.995	36.167	0.33	0.18	0.14	0.12
	1 A’	32.499	35.868	37.290	37.467	0.35	0.21	0.16	0.13
Nitrosomethane	1 A’	26.118	28.767	30.059	30.583	0.32	0.24	0.20	0.13
	1 A”	29.586	30.980	32.127	32.408	0.24	0.16	0.13	0.10
	1 A’	29.425	31.076	32.357	32.572	0.27	0.17	0.13	0.11
	1 A”	32.690	34.743	35.861	36.706	0.33	0.45	0.34	0.14
Streptocyanine	1 A1	41.005	42.624	43.704	43.874	0.23	0.15	0.12	0.10
	1 A2	44.413	45.715	46.688	47.031	0.23	0.18	0.15	0.11
	1 B2	46.497	47.967	49.068	49.241	0.24	0.15	0.13	0.10
	1 B1	45.811	48.718	50.281	50.392	0.34	0.25	0.21	0.16
Thioformaldehyde	1 A1	25.106	27.344	28.421	28.694	0.38	0.18	0.15	0.11
	1 A2	27.515	29.268	29.908	30.384	0.30	0.16	0.14	0.10
	1 A1	29.894	31.998	32.683	33.063	0.34	0.17	0.14	0.11
	1 B1	29.696	31.920	32.785	33.169	0.35	0.18	0.15	0.12
Water	1 A1	34.205	40.224	42.791	42.044	0.39	0.17	0.14	0.12
	1 B2	35.740	41.706	44.195	43.487	0.39	0.17	0.14	0.12
	1 A1	38.815	44.892	47.272	46.567	0.41	0.16	0.13	0.11
	1 A2	39.620	45.231	47.498	46.871	0.39	0.16	0.13	0.12

Table A.13.: Doubly-ionized singlet state statistics for the four lowest-lying states: DIP-ADC(3) compared to EOMDIP-CCSD.

DIP-ADC(3) vs. EOMDIP-CCSD Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	0.036	-0.391	-0.125	-0.4	0.143	0.4
Acetylene	-0.393	-0.574	-0.479	-1.3	0.479	1.3
Ammonia	0.279	0.193	0.218	0.5	0.218	0.5
Carbonmonoxide	-0.189	-0.610	-0.391	-0.9	0.391	0.9
Cyclopropene	-0.167	-0.284	-0.245	-0.8	0.245	0.8
Diazomethane	-0.581	-0.907	-0.748	-2.3	0.748	2.3
Dinitrogene	-0.577	-0.991	-0.798	-1.7	0.798	1.7
Ethylene	-0.203	-0.348	-0.289	-0.9	0.289	0.9
Formaldehyde	0.123	-0.213	-0.020	-0.1	0.087	0.2
Formamide	0.031	-0.082	-0.034	-0.1	0.049	0.2
Hydrogen chloride	-0.093	-0.167	-0.134	-0.3	0.134	0.3
Hydrogen sulfide	-0.170	-0.232	-0.205	-0.6	0.205	0.6
Ketene	-0.216	-0.521	-0.406	-1.2	0.406	1.2
Methanimine	-0.172	-0.276	-0.210	-0.6	0.210	0.6
Nitrosomethane	-0.215	-0.845	-0.466	-1.4	0.466	1.4
Streptocyanine-c1	-0.110	-0.343	-0.199	-0.4	0.199	0.4
Thioformaldehyde	-0.272	-0.475	-0.378	-1.2	0.378	1.2
Water	0.748	0.628	0.697	1.6	0.697	1.6
Total	**0.75**	**-0.99**	**-0.23 ± 0.35**	**-0.7 ± 0.9**	**0.34 ± 0.24**	**0.9 ± 0.6**

Table A.14.: Doubly-ionized singlet state statistics for the four lowest-lying states: DIP-ADC(2)-x compared to EOMDIP-CCSD.

DIP-ADC(2)-x vs. EOMDIP-CCSD Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-1.374	-1.609	-1.508	-4.6	1.508	4.6
Acetylene	-0.853	-1.378	-1.086	-2.9	1.086	2.9
Ammonia	-1.346	-1.415	-1.380	-3.3	1.380	3.3
Carbonmonoxide	-0.939	-1.627	-1.265	-2.8	1.265	2.8
Cyclopropene	-1.119	-1.341	-1.266	-4.2	1.266	4.2
Diazomethane	-0.841	-1.467	-1.149	-3.5	1.149	3.5
Dinitrogene	-0.700	-1.065	-0.905	-2.0	0.905	2.0
Ethylene	-1.061	-1.324	-1.175	-3.5	1.175	3.5
Formaldehyde	-1.414	-2.216	-1.682	-4.4	1.682	4.4
Formamide	-1.411	-1.782	-1.556	-4.8	1.556	4.8
Hydrogen chloride	-0.932	-1.067	-0.999	-2.5	0.999	2.5
Hydrogen sulfide	-0.974	-1.053	-1.019	-2.9	1.019	2.9
Ketene	-1.012	-1.351	-1.175	-3.5	1.175	3.5
Methanimine	-1.358	-1.599	-1.434	-4.1	1.434	4.1
Nitrosomethane	-1.428	-1.962	-1.676	-5.1	1.676	5.1
Streptocyanine-c1	-1.249	-1.674	-1.379	-2.9	1.379	2.9
Thioformaldehyde	-1.065	-1.349	-1.195	-3.8	1.195	3.8
Water	-1.640	-1.820	-1.729	-3.9	1.729	3.9
Total	**-0.7**	**-2.22**	**-1.31 ± 0.29**	**-3.6 ± 0.9**	**1.31 ± 0.29**	**3.6 ± 0.9**

Table A.15.: Doubly-ionized singlet state statistics for the four lowest-lying states: DIP-ADC(2) compared to EOMDIP-CCSD.

DIP-ADC(2) vs. EOMDIP-CCSD Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-2.890	-4.600	-3.608	-11.0	3.608	11.0
Acetylene	-3.678	-3.895	-3.799	-10.3	3.799	10.3
Ammonia	-5.286	-6.011	-5.539	-13.1	5.539	13.1
Carbonmonoxide	-3.026	-6.212	-4.092	-9.0	4.092	9.0
Cyclopropene	-2.979	-3.865	-3.466	-11.4	3.466	11.4
Diazomethane	-2.516	-3.562	-2.982	-9.1	2.982	9.1
Dinitrogene	-3.634	-4.123	-3.967	-8.6	3.967	8.6
Ethylene	-2.593	-3.794	-3.156	-9.4	3.156	9.4
Formaldehyde	-5.158	-6.576	-5.810	-15.2	5.810	15.2
Formamide	-3.471	-5.910	-4.106	-12.7	4.106	12.7
Hydrogen chloride	-3.535	-3.927	-3.714	-9.1	3.714	9.1
Hydrogen sulfide	-2.760	-3.287	-2.996	-8.5	2.996	8.5
Ketene	-2.761	-3.302	-2.921	-8.7	2.921	8.7
Methanimine	-4.327	-4.968	-4.555	-13.0	4.555	13.0
Nitrosomethane	-2.822	-4.465	-3.612	-11.0	3.612	11.0
Streptocyanine-c1	-2.618	-4.580	-3.203	-6.7	3.203	6.7
Thioformaldehyde	-2.868	-3.587	-3.274	-10.5	3.274	10.5
Water	-7.251	-7.839	-7.647	-17.1	7.647	17.1
Total	**-2.52**	**-7.84**	**-4.02 ± 1.31**	**-10.8 ± 2.9**	**4.02 ± 1.31**	**10.8 ± 2.9**

Table A.16.: Doubly-ionized singlet state statistics for the four lowest-lying states: DIP-ADC(2)-x compared to DIP-ADC(3).

DIP-ADC(2)-x vs. DIP-ADC(3) Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-1.175	-1.521	-1.384	-4.3	1.384	4.3
Acetylene	-0.460	-0.804	-0.607	-1.6	0.607	1.6
Ammonia	-1.565	-1.625	-1.598	-3.8	1.598	3.8
Carbonmonoxide	-0.329	-1.438	-0.874	-1.9	0.874	1.9
Cyclopropene	-0.837	-1.174	-1.021	-3.4	1.021	3.4
Diazomethane	-0.260	-0.560	-0.401	-1.2	0.401	1.2
Dinitrogene	0.141	-0.344	-0.107	-0.2	0.207	0.4
Ethylene	-0.733	-1.047	-0.886	-2.7	0.886	2.7
Formaldehyde	-1.236	-2.216	-1.662	-4.3	1.662	4.3
Formamide	-1.330	-1.776	-1.522	-4.7	1.522	4.7
Hydrogen chloride	-0.766	-0.952	-0.865	-2.1	0.865	2.1
Hydrogen sulfide	-0.784	-0.847	-0.814	-2.3	0.814	2.3
Ketene	-0.598	-1.135	-0.769	-2.3	0.769	2.3
Methanimine	-1.135	-1.422	-1.225	-3.5	1.225	3.5
Nitrosomethane	-1.118	-1.292	-1.210	-3.7	1.210	3.7
Streptocyanine-c1	-0.974	-1.563	-1.180	-2.5	1.180	2.5
Thioformaldehyde	-0.640	-1.077	-0.817	-2.7	0.817	2.7
Water	-2.268	-2.567	-2.426	-5.4	2.426	5.4
Total	**0.14**	**-2.57**	**-1.08 ± 0.55**	**-2.9 ± 1.4**	**1.08 ± 0.54**	**2.9 ± 1.3**

Table A.17.: Doubly-ionized singlet state statistics for the four lowest-lying states: DIP-ADC(2) compared to DIP-ADC(3).

DIP-ADC(2) vs. DIP-ADC(3) Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-2.863	-4.484	-3.483	-10.7	3.483	10.7
Acetylene	-3.104	-3.502	-3.320	-9.1	3.320	9.1
Ammonia	-5.479	-6.290	-5.757	-13.5	5.757	13.5
Carbonmonoxide	-2.475	-6.023	-3.701	-8.2	3.701	8.2
Cyclopropene	-2.696	-3.699	-3.221	-10.6	3.221	10.6
Diazomethane	-1.935	-2.654	-2.235	-7.0	2.235	7.0
Dinitrogene	-2.643	-3.546	-3.170	-6.9	3.170	6.9
Ethylene	-2.265	-3.517	-2.867	-8.6	2.867	8.6
Formaldehyde	-4.945	-6.576	-5.791	-15.1	5.791	15.1
Formamide	-3.390	-5.904	-4.072	-12.6	4.072	12.6
Hydrogen chloride	-3.373	-3.761	-3.580	-8.8	3.580	8.8
Hydrogen sulfide	-2.590	-3.075	-2.791	-8.0	2.791	8.0
Ketene	-2.293	-3.086	-2.516	-7.6	2.516	7.6
Methanimine	-4.051	-4.790	-4.346	-12.5	4.346	12.5
Nitrosomethane	-2.541	-3.941	-3.146	-9.7	3.146	9.7
Streptocyanine-c1	-2.275	-4.470	-3.004	-6.3	3.004	6.3
Thioformaldehyde	-2.393	-3.315	-2.896	-9.4	2.896	9.4
Water	-7.879	-8.586	-8.344	-18.4	8.344	18.4
Total	**-1.93**	**-8.59**	**-3.79 ± 1.57**	**-10.2 ± 3.5**	**3.79 ± 1.57**	**10.2 ± 3.5**

A.5. Benchmark of doubly-ionized triplet states

This section collects all data that was computed for the benchmark study of doubly-ionized singlet states. Besides the full data set, an individual statistical analysis for each molecular species in comparison to EOMDIP-CCSD as well as DIP-ADC(3) is provided.

Table A.18.: Benchmark data for doubly-ionized triplet states for the set of Jacquemin et al.[64] I.

Molecule	Excitation	Double ionization energy [eV]				Doubles contribution [%/100]			
		ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Acetaldehyde	3 A”	28.637	30.502	31.865	31.929	0.30	0.17	0.14	0.11
	3 A’	29.081	30.496	31.965	31.956	0.25	0.16	0.13	0.10
	3 A’	30.141	32.617	34.131	34.229	0.33	0.19	0.15	0.12
	3 A”	30.608	32.964	34.402	34.768	0.28	0.23	0.19	0.13
Acetylene	3 B1g	29.110	31.780	32.355	32.898	0.35	0.16	0.13	0.10
	3 B2u	34.806	37.165	37.904	38.420	0.34	0.19	0.16	0.12
	3 B2g	36.413	38.482	39.396	39.940	0.58	0.23	0.19	0.14
	3 B1u	43.041	44.181	44.269	44.996	0.26	0.16	0.14	0.10
Ammonia	3 A’	33.808	37.378	39.038	38.859	0.34	0.17	0.14	0.12
	3 A”	39.519	43.086	44.631	44.478	0.35	0.15	0.13	0.11
	3 A’	44.997	48.660	50.744	50.546	0.60	0.23	0.20	0.16
	3 A’		54.206	56.053	56.053		0.23	0.31	0.16
Carbonmonoxide	3 Π	39.138	41.310	41.575	42.185	0.27	0.12	0.11	0.09
	3 Σ^+	41.477	43.145	43.980	44.259	0.23	0.14	0.14	0.10
	3 Σ^-	40.956	45.125	46.636	46.819	0.38	0.23	0.23	0.16
	3 Π	42.720	47.488	50.227	49.750	0.37	0.24	0.31	0.16
Cyclopropene	3 A2	25.889	27.902	28.931	29.237	0.28	0.17	0.13	0.11
	3 B2	27.537	29.660	30.783	31.068	0.30	0.18	0.15	0.11
	3 B1	28.546	30.846	32.007	32.263	0.30	0.18	0.14	0.12
	3 A1	30.129	31.527	32.326	32.689	0.24	0.15	0.12	0.10
Diazomethane	3 A2	29.210	30.921	31.318	32.086	0.29	0.19	0.15	0.11
	3 B2	29.978	31.584	32.400	33.188	0.34	0.26	0.20	0.14
	3 A1	31.722	32.869	33.685	34.329	0.28	0.48	0.63	0.11
	3 A2	32.007	33.821	34.541	35.723	0.41	0.41	0.37	0.14

Table A.19.: Benchmark data for doubly-ionized triplet states for the set of Jacquemin et al.[64] II.

Molecule	Excitation	Double ionization energy [eV]				Doubles contribution [%/100]			
		ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Dinitrogen	3 Π_u	40.736	43.388	43.805	44.572	0.30	0.18	0.14	0.12
	3 Σ_u^+	43.334	44.554	44.294	45.459	0.22	0.18	0.16	0.11
	3 Σ_g^-	42.786	45.770	45.696	46.642	0.31	0.14	0.12	0.10
	3 Π_g	43.433	45.993	46.796	47.604	0.35	0.24	0.20	0.15
Ethylene	3 Au	29.523	31.190	32.056	32.439	0.28	0.17	0.14	0.11
	3 B1u	31.138	33.414	34.537	34.854	0.32	0.19	0.16	0.12
	3 B3g	32.643	34.268	35.295	35.953	0.35	0.29	0.28	0.15
	3 B1g	33.484	35.429	36.464	36.759	0.30	0.18	0.14	0.12
Formaldehyde	3 A2	31.202	34.860	36.339	36.528	0.36	0.20	0.16	0.13
	3 A1	34.724	36.548	37.649	37.776	0.24	0.15	0.14	0.10
	3 B1	31.647	36.163	38.258	38.071	0.40	0.20	0.15	0.12
	3 B1	38.883	40.822	42.036	42.185	0.27	0.17	0.15	0.11
Formamide	3 A”	26.088	28.300	29.829	29.806	0.29	0.17	0.14	0.11
	3 A’	30.203	31.822	32.971	33.210	0.24	0.16	0.13	0.10
	3 A”	30.366	32.640	34.278	34.294	0.30	0.20	0.18	0.12
	3 A”	29.714	32.924	34.773	34.996	0.35	0.25	0.24	0.15
Hydrogen chloride	3 Σ^-	32.570	34.854	35.861	36.012	0.30	0.15	0.13	0.11
	3 Π	36.564	38.771	39.703	39.868	0.29	0.14	0.12	0.10
	3 Π		48.245	49.373	50.246		0.39	0.57	0.22
	3 Σ^+		51.071	51.574	53.622		0.68	0.82	0.35
Hydrogen sulfide	3 B2	30.185	31.935	32.862	33.086	0.29	0.15	0.13	0.11
	3 A2	32.689	34.336	35.160	35.410	0.28	0.15	0.13	0.10
	3 B1	35.491	37.208	38.048	38.299	0.29	0.15	0.13	0.10
	3 B2	40.046	41.853	43.076	43.703	0.56	0.35	0.35	0.22

Table A.20.: Benchmark data for doubly-ionized triplet states for the set of Jacquemin et al.[64] III.

Molecule	Excitation	Double ionization energy [eV]				Doubles contribution [%/100]			
		ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Ketene	3 A2	30.173	31.871	32.513	33.043	0.27	0.18	0.15	0.11
	3 A1	31.202	32.501	33.336	33.840	0.25	0.20	0.17	0.11
	3 A2	32.519	34.082	34.855	35.465	0.31	0.23	0.19	0.12
	3 B2	32.108	34.147	35.271	35.574	0.29	0.19	0.16	0.12
Methanimine	3 A”	28.670	31.374	32.697	33.011	0.34	0.21	0.17	0.13
	3 A’	31.487	33.747	34.758	35.044	0.32	0.17	0.14	0.11
	3 A’	33.840	36.085	37.198	37.535	0.29	0.20	0.26	0.12
	3 A”	33.746	36.095	37.225	37.648	0.31	0.20	0.20	0.13
Nitrosomethane	3 A’	29.003	30.463	31.700	31.976	0.24	0.18	0.14	0.11
	3 A”	29.277	30.728	31.895	32.188	0.25	0.17	0.14	0.11
	3 A”	32.040	34.060	35.205	36.366	0.33	0.44	0.51	0.14
	3 A”	33.671	35.090	36.246	36.980	0.28	0.26	0.24	0.15
Streptocyanine	3 B1	42.871	44.068	45.051	45.349	0.20	0.15	0.12	0.09
	3 A2	44.205	45.545	46.535	46.862	0.23	0.18	0.14	0.11
	3 B2	45.949	47.548	48.704	48.869	0.25	0.16	0.13	0.10
	3 B2	47.610	48.885	50.031	50.434	0.23	0.25	0.25	0.12
Thioformaldehyde	3 A2	26.748	28.320	29.006	29.585	0.30	0.18	0.17	0.11
	3 B1	28.615	30.516	31.603	31.970	0.33	0.20	0.17	0.12
	3 A1	31.105	32.460	32.834	33.146	0.29	0.46	0.23	0.10
	3 B2	31.293	33.201	34.049	34.564	0.36	0.19	0.18	0.12
Water	3 B2	33.824	39.170	41.779	41.056	0.37	0.18	0.15	0.13
	3 A2	38.285	43.401	45.718	45.107	0.37	0.16	0.14	0.12
	3 B1	40.279	45.278	47.600	46.961	0.36	0.16	0.13	0.12
	3 B2		57.442	60.521	59.642		0.20	0.18	0.15

Table A.21.: Doubly-ionized triplet state statistics for the four lowest-lying states: DIP-ADC(3) compared to EOMDIP-CCSD.

DIP-ADC(3) vs. EOMDIP-CCSD Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	0.010	-0.367	-0.129	-0.4	0.134	0.4
Acetylene	-0.516	-0.727	-0.582	-1.5	0.582	1.5
Ammonia	0.198	0.001	0.132	0.3	0.132	0.3
Carbonmonoxide	0.477	-0.610	-0.149	-0.4	0.387	0.9
Cyclopropene	-0.256	-0.363	-0.302	-1.0	0.302	1.0
Diazomethane	-0.645	-1.182	-0.846	-2.5	0.846	2.5
Dinitrogene	-0.766	-1.165	-0.921	-2.0	0.921	2.0
Ethylene	-0.295	-0.657	-0.413	-1.2	0.413	1.2
Formaldehyde	0.188	-0.189	-0.069	-0.2	0.163	0.4
Formamide	0.022	-0.239	-0.114	-0.3	0.125	0.4
Hydrogen chloride	-0.150	-2.047	-0.809	-1.6	0.809	1.6
Hydrogen sulfide	-0.224	-0.627	-0.338	-0.9	0.338	0.9
Ketene	-0.303	-0.610	-0.487	-1.4	0.487	1.4
Methanimine	-0.286	-0.423	-0.340	-0.9	0.340	0.9
Nitrosomethane	-0.276	-1.161	-0.616	-1.7	0.616	1.7
Streptocyanine-c1	-0.165	-0.403	-0.298	-0.6	0.298	0.6
Thioformaldehyde	-0.311	-0.579	-0.443	-1.4	0.443	1.4
Water	0.879	0.611	0.713	1.5	0.713	1.5
Total	**0.88**	**-2.05**	**-0.33 ± 0.45**	**-0.9 ± 1.0**	**0.45 ± 0.34**	**1.1 ± 0.8**

Table A.22.: Doubly-ionized triplet state statistics for the four lowest-lying states: DIP-ADC(2)-x compared to EOMDIP-CCSD.

DIP-ADC(2)-x vs. EOMDIP-CCSD Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-1.427	-1.804	-1.576	-4.7	1.576	4.7
Acetylene	-0.815	-1.458	-1.161	-3.0	1.161	3.0
Ammonia	-1.392	-1.887	-1.652	-3.5	1.652	3.5
Carbonmonoxide	-0.876	-2.262	-1.486	-3.2	1.486	3.2
Cyclopropene	-1.162	-1.417	-1.330	-4.3	1.330	4.3
Diazomethane	-1.165	-1.902	-1.533	-4.5	1.533	4.5
Dinitrogene	-0.872	-1.611	-1.143	-2.5	1.143	2.5
Ethylene	-1.249	-1.684	-1.426	-4.1	1.426	4.1
Formaldehyde	-1.228	-1.908	-1.542	-4.0	1.542	4.0
Formamide	-1.388	-2.073	-1.655	-5.0	1.655	5.0
Hydrogen chloride	-1.097	-2.550	-1.702	-3.7	1.702	3.7
Hydrogen sulfide	-1.074	-1.850	-1.291	-3.4	1.291	3.4
Ketene	-1.171	-1.427	-1.330	-3.9	1.330	3.9
Methanimine	-1.297	-1.637	-1.484	-4.2	1.484	4.2
Nitrosomethane	-1.460	-2.306	-1.792	-5.2	1.792	5.2
Streptocyanine-c1	-1.281	-1.549	-1.367	-2.9	1.367	2.9
Thioformaldehyde	-0.686	-1.454	-1.192	-3.7	1.192	3.7
Water	-1.682	-2.200	-1.869	-3.9	1.869	3.9
Total	**-0.69**	**-2.55**	**-1.47 ± 0.36**	**-3.9 ± 0.9**	**1.47 ± 0.36**	**3.9 ± 0.9**

Table A.23.: Doubly-ionized triplet state statistics for the four lowest-lying states: DIP-ADC(2) compared to EOMDIP-CCSD.
[a] Three states; [b] two states.

DIP-ADC(2) vs. EOMDIP-CCSD Triplets						
Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-2.874	-4.160	-3.603	-10.8	3.603	10.8
Acetylene	-1.954	-3.787	-3.221	-8.5	3.221	8.5
Ammonia[a]	-4.959	-5.549	-5.186	-11.7	5.186	11.7
Carbonmonoxide	-2.781	-7.030	-4.681	-10.0	4.681	10.0
Cyclopropene	-2.560	-3.717	-3.289	-10.5	3.289	10.5
Diazomethane	-2.608	-3.716	-3.102	-9.2	3.102	9.2
Dinitrogene	-2.125	-4.172	-3.497	-7.6	3.497	7.6
Ethylene	-2.916	-3.716	-3.304	-9.4	3.304	9.4
Formaldehyde	-3.052	-6.424	-4.526	-11.8	4.526	11.8
Formamide	-3.007	-5.282	-3.984	-12.0	3.984	12.0
Hydrogen chloride[b]	-3.303	-3.442	-3.373	-8.9	3.373	8.9
Hydrogen sulfide	-2.722	-3.657	-3.022	-8.0	3.022	8.0
Ketene	-2.639	-3.466	-2.980	-8.6	2.980	8.6
Methanimine	-3.557	-4.341	-3.874	-10.9	3.874	10.9
Nitrosomethane	-2.911	-4.325	-3.380	-9.8	3.380	9.8
Streptocyanine-c1	-2.478	-2.920	-2.720	-5.7	2.720	5.7
Thioformaldehyde	-2.041	-3.355	-2.876	-8.9	2.876	8.9
Water[a]	-6.682	-7.233	-6.912	-15.7	6.912	15.7
Total	**-1.95**	**-7.23**	**-3.70 ± 1.19**	**-9.8 ± 2.7**	**3.70 ± 1.19**	**9.8 ± 2.7**

Table A.24.: Doubly-ionized triplet state statistics for the four lowest-lying states: DIP-ADC(2)-x compared to DIP-ADC(3).

DIP-ADC(2)-x vs. DIP-ADC(3) Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-1.364	-1.515	-1.446	-4.4	1.446	4.4
Acetylene	-0.088	-0.914	-0.579	-1.6	0.579	1.6
Ammonia	-1.545	-2.085	-1.784	-3.8	1.784	3.8
Carbonmonoxide	-0.265	-2.739	-1.337	-2.8	1.337	2.8
Cyclopropene	-0.799	-1.161	-1.028	-3.3	1.028	3.3
Diazomethane	-0.397	-0.816	-0.687	-2.1	0.687	2.1
Dinitrogene	0.261	-0.803	-0.222	-0.5	0.389	0.9
Ethylene	-0.866	-1.123	-1.013	-2.9	1.013	2.9
Formaldehyde	-1.101	-2.096	-1.472	-3.8	1.472	3.8
Formamide	-1.149	-1.849	-1.541	-4.7	1.541	4.7
Hydrogen chloride	-0.503	-1.129	-0.893	-2.1	0.893	2.1
Hydrogen sulfide	-0.823	-1.223	-0.953	-2.6	0.953	2.6
Ketene	-0.642	-1.124	-0.844	-2.5	0.844	2.5
Methanimine	-1.011	-1.323	-1.144	-3.2	1.144	3.2
Nitrosomethane	-1.145	-1.237	-1.176	-3.5	1.176	3.5
Streptocyanine-c1	-0.983	-1.156	-1.069	-2.2	1.069	2.2
Thioformaldehyde	-0.374	-1.086	-0.748	-2.4	0.748	2.4
Water	-2.317	-3.079	-2.582	-5.3	2.582	5.3
Total	**0.26**	**-3.08**	**-1.14 ± 0.60**	**-3.0 ± 1.4**	**1.15 ± 0.58**	**3.0 ± 1.3**

Table A.25.: Doubly-ionized triplet state statistics for the four lowest-lying states: DIP-ADC(2) compared to DIP-ADC(3).
^{a} Three states; ^{b} two states.

DIP-ADC(2) vs. DIP-ADC(3) Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Acetaldehyde	-2.884	-3.990	-3.474	-10.5	3.474	10.5
Acetylene	-1.228	-3.245	-2.639	-7.1	2.639	7.1
Ammonia^a	-5.112	-5.747	-5.363	-12.1	5.363	12.1
Carbonmonoxide	-2.437	-7.507	-4.532	-9.7	4.532	9.7
Cyclopropene	-2.198	-3.461	-2.986	-9.7	2.986	9.7
Diazomethane	-1.963	-2.534	-2.257	-6.8	2.257	6.8
Dinitrogene	-0.960	-3.363	-2.576	-5.7	2.576	5.7
Ethylene	-2.534	-3.399	-2.891	-8.4	2.891	8.4
Formaldehyde	-2.925	-6.611	-4.456	-11.7	4.456	11.7
Formamide	-2.768	-5.059	-3.870	-11.7	3.870	11.7
Hydrogen chloride^b	-3.139	-3.291	-3.215	-8.5	3.215	8.5
Hydrogen sulfide	-2.471	-3.030	-2.684	-7.2	2.684	7.2
Ketene	-2.135	-3.163	-2.493	-7.3	2.493	7.3
Methanimine	-3.272	-4.027	-3.534	-10.0	3.534	10.0
Nitrosomethane	-2.574	-3.165	-2.763	-8.2	2.763	8.2
Streptocyanine-c1	-2.179	-2.754	-2.421	-5.1	2.421	5.1
Thioformaldehyde	-1.729	-2.988	-2.433	-7.6	2.433	7.6
Water^a	-7.320	-7.956	-7.570	-16.9	7.570	16.9
Total	**-0.96**	**-7.96**	**-3.37 ± 1.46**	**-9.0 ± 3.3**	**3.37 ± 1.46**	**9.0 ± 3.3**

A.6. Benchmark of doubly-attached singlet states

This section collects all data that was computed for the benchmark study of doubly-attached singlet states. Besides the full data set, an individual statistical analysis for each molecular species in comparison to EOMDEA-CCSD as well as DEA-ADC(3) is provided.

Table A.26.: Benchmark data for double electronically-attached singlet states for the set of Jacquemin et al.[64] I.

Molecule	Excitation	Double e-attachement energy [eV]					Doubles contribution [%/100]			
		ADC(1)	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Ammonia	1 A’	4.268	3.976	3.953	3.996	4.085	0.009	0.013	0.010	0.008
	1 A’	5.098	4.871	4.853	4.888	4.959	0.007	0.010	0.008	0.006
	1 A’	6.236	5.864	5.843	5.899	5.998	0.012	0.016	0.013	0.010
	1 A’	6.572	6.203	6.185	6.241	6.341	0.013	0.016	0.013	0.010
Dinitrogen	1 Σ_g^+	7.581	7.310	7.309	7.298	7.414	0.021	0.024	0.018	0.006
	1 Π_u	9.117	-	-	-	8.417	-	-	-	0.044
	1 Π_g	8.789	8.401	8.366	8.560	8.486	0.029	0.047	0.025	0.011
	1 Σ_u^+	9.319	8.570	8.587	8.822	8.890	0.031	0.034	0.034	0.016
Ethylene	1 Ag	3.846	3.584	3.565	3.618	3.688	0.010	0.013	0.010	0.007
	1 B1g	4.051	3.874	3.860	3.895	3.942	0.006	0.008	0.007	0.005
	1 B3u	4.447	4.166	4.143	4.202	4.263	0.013	0.018	0.014	0.009
	1 Ag	4.434	4.203	4.181	4.230	4.278	0.010	0.014	0.011	0.008
Form-aldehyde	1 A1	3.968	3.701	3.691	3.803	3.837	0.011	0.013	0.009	0.006
	1 A2	5.772	-	-	-	5.174	-	-	-	0.039
	1 B2	5.944	-	-	-	5.183	-	-	-	0.047
	1 B1	5.498	5.158	5.142	5.207	5.294	0.012	0.014	0.011	0.009
Hydrogen Chloride	1 Σ^+	4.874	4.333	4.317	4.433	4.554	0.020	0.024	0.019	0.014
	1 Σ^+	7.401	6.835	6.837	6.969	7.066	0.026	0.033	0.019	0.014
	1 Π	7.666	7.089	7.081	7.181	7.342	0.020	0.023	0.018	0.014
	1 Σ^+	8.590	-	-	-	7.854	-	-	-	0.036
Hydrogen Sulfide	1 A1	4.259	3.813	3.792	3.887	3.975	0.019	0.024	0.019	0.014
	1 B1	5.536	5.031	5.013	5.123	5.235	0.024	0.029	0.021	0.015
	1 A1	5.993	5.517	5.494	5.606	5.725	0.023	0.030	0.021	0.013
	1 B1	6.713	5.776	5.714	5.956	6.326	0.043	0.060	0.047	0.021

Table A.27.: Benchmark data for double electronically-attached singlet states for the set of Jacquemin et al.[64] II.

Molecule	Excitation	Double e-attachement energy [eV]					Doubles contribution [%/100]			
		ADC(1)	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Methan-imine	1 A’	3.837	3.558	3.542	3.604	3.682	0.010	0.012	0.010	0.007
	1 A’	4.378	4.144	4.128	4.200	4.239	0.010	0.012	0.009	0.007
	1 A’	4.501	4.235	4.219	4.268	4.343	0.010	0.012	0.010	0.007
	1 A”	5.642	-	-	-	5.236	-	-	-	0.027
Water	1 A1	4.618	4.307	4.285	4.318	4.443	0.008	0.011	0.009	0.007
	1 B1	5.999	5.585	5.558	5.607	5.756	0.012	0.015	0.013	0.009
	1 A1	6.310	5.998	5.982	6.018	6.130	0.009	0.011	0.009	0.007
	1 B1	8.034	7.371	7.335	7.392	7.744	0.013	0.018	0.015	0.011

Table A.28.: Double electronically-attached singlet state statistics for the four lowest-lying states: DEA-ADC(3) compared to EOMDEA-CCSD.
[a] Three states; [b] two states.

DEA-ADC(3) vs. EOMDEA-CCSD Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.071	-0.099	-0.089	-1.7	0.089	1.7
Dinitrogen[a]	0.074	-0.116	-0.037	-0.5	0.086	1.1
Ethylene	-0.047	-0.070	-0.056	-1.4	0.056	1.4
Formaldehyde[b]	-0.034	-0.087	-0.061	-1.3	0.061	1.3
Hydrogen Chloride[a]	-0.097	-0.161	-0.126	-2.1	0.126	2.1
Hydrogen Sulfide	-0.088	-0.371	-0.173	-3.1	0.173	3.1
Methanimine[a]	-0.039	-0.078	-0.064	-1.6	0.064	1.6
Water	-0.111	-0.351	-0.184	-2.9	0.184	2.9
Total	**0.07**	**-0.37**	**-0.10 ± 0.09**	**-1.9 ± 1.2**	**0.11 ± 0.08**	**2.0 ± 1.1**

Table A.29.: Double electronically-attached singlet state statistics for the four lowest-lying states: DEA-ADC(2)-x compared to EOMDEA-CCSD.
[a] Three states; [b] two states.

DEA-ADC(2)-x vs. EOMDEA-CCSD Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.106	-0.155	-0.137	-2.6	0.137	2.6
Dinitrogen[a]	-0.105	-0.304	-0.176	-2.1	0.176	2.1
Ethylene	-0.083	-0.123	-0.106	-2.6	0.106	2.6
Formaldehyde[b]	-0.147	-0.152	-0.149	-3.3	0.149	3.3
Hydrogen Chloride[a]	-0.229	-0.261	-0.242	-4.0	0.242	4.0
Hydrogen Sulfide	-0.183	-0.613	-0.312	-5.6	0.312	5.6
Methanimine[a]	-0.111	-0.140	-0.125	-3.1	0.125	3.1
Water	-0.148	-0.408	-0.228	-3.7	0.228	3.7
Total	**-0.08**	**-0.61**	**-0.19 ± 0.11**	**-3.4 ± 1.6**	**0.19 ± 0.11**	**3.4 ± 1.6**

Table A.30.: Double electronically-attached singlet state statistics for the four lowest-lying states: DEA-ADC(2) compared to EOMDEA-CCSD.
[a] Three states; [b] two states.

DEA-ADC(2) vs. EOMDEA-CCSD Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.087	-0.138	-0.117	-2.2	0.117	2.2
Dinitrogen[a]	-0.084	-0.320	-0.170	-2.0	0.170	2.0
Ethylene	-0.068	-0.103	-0.086	-2.1	0.086	2.1
Formaldehyde[b]	-0.136	-0.137	-0.136	-3.1	0.136	3.1
Hydrogen Chloride[a]	-0.221	-0.254	-0.235	-3.9	0.235	3.9
Hydrogen Sulfide	-0.162	-0.551	-0.281	-5.1	0.281	5.1
Methanimine[a]	-0.095	-0.124	-0.109	-2.7	0.109	2.7
Water	-0.131	-0.373	-0.203	-3.2	0.203	3.2
Total	**-0.07**	**-0.55**	**-0.17 ± 0.11**	**-3.1 ± 1.5**	**0.17 ± 0.11**	**3.1 ± 1.5**

Table A.31.: Double electronically-attached singlet state statistics for the four lowest-lying states: DEA-ADC(1) compared to EOMDEA-CCSD.

DEA-ADC(1) vs. EOMDEA-CCSD Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	0.239	0.139	0.198	3.7	0.198	3.7
Dinitrogen	0.700	0.168	0.400	4.7	0.400	4.7
Ethylene	0.185	0.108	0.152	3.8	0.152	3.8
Formaldehyde	0.761	0.131	0.424	8.4	0.424	8.4
Hydrogen Chloride	0.736	0.320	0.429	6.4	0.429	6.4
Hydrogen Sulfide	0.387	0.268	0.310	5.9	0.310	5.9
Methanimine	0.406	0.139	0.215	4.7	0.215	4.7
Water	0.291	0.176	0.223	3.7	0.223	3.7
Total	**0.76**	**0.11**	**0.29 ± 0.18**	**5.2 ± 2.7**	**0.29 ± 0.18**	**5.2 ± 2.7**

Table A.32.: Double electronically-attached singlet state statistics for the four lowest-lying states: DEA-ADC(2)-x compared to DEA-ADC(3).
[a] Three states; [b] two states.

DEA-ADC(2)-x vs. DEA-ADC(3) Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.035	-0.056	-0.048	-0.9	0.048	0.9
Dinitrogen[a]	0.012	-0.236	-0.139	-1.6	0.147	1.7
Ethylene	-0.036	-0.060	-0.049	-1.2	0.049	1.2
Formaldehyde[b]	-0.064	-0.113	-0.088	-2.1	0.088	2.1
Hydrogen Chloride[a]	-0.100	-0.133	-0.116	-2.0	0.116	2.0
Hydrogen Sulfide	-0.095	-0.242	-0.140	-2.7	0.140	2.7
Methanimine[a]	-0.048	-0.072	-0.061	-1.5	0.061	1.5
Water	-0.033	-0.057	-0.044	-0.8	0.044	0.8
Total	**0.01**	**-0.24**	**-0.08 ± 0.06**	**-1.5 ± 0.9**	**0.08 ± 0.06**	**1.6 ± 0.9**

Table A.33.: Double electronically-attached singlet state statistics for the four lowest-lying states: DEA-ADC(2) compared to DEA-ADC(3).
[a] Three states; [b] two states.

DEA-ADC(2) vs. DEA-ADC(3) Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.017	-0.039	-0.028	-0.5	0.028	0.5
Dinitrogen[a]	0.012	-0.252	-0.133	-1.5	0.141	1.6
Ethylene	-0.021	-0.036	-0.030	-0.7	0.030	0.7
Formaldehyde[b]	-0.048	-0.102	-0.075	-1.8	0.075	1.8
Hydrogen Chloride[a]	-0.093	-0.134	-0.109	-1.8	0.109	1.8
Hydrogen Sulfide	-0.074	-0.180	-0.109	-2.1	0.109	2.1
Methanimine[a]	-0.033	-0.056	-0.045	-1.1	0.045	1.1
Water	-0.011	-0.022	-0.019	-0.3	0.019	0.3
Total	**0.01**	**-0.25**	**-0.06 ± 0.06**	**-1.2 ± 0.9**	**0.07 ± 0.06**	**1.2 ± 0.8**

Table A.34.: Double electronically-attached singlet state statistics for the four lowest-lying states: DEA-ADC(1) compared to DEA-ADC(3).
[a] Three states; [b] two states.

DEA-ADC(1) vs. DEA-ADC(3) Singlets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	0.337	0.210	0.287	5.5	0.287	5.5
Dinitrogen[a]	0.497	0.229	0.337	4.1	0.337	4.1
Ethylene	0.245	0.155	0.208	5.2	0.208	5.2
Formaldehyde[b]	0.291	0.165	0.228	5.0	0.228	5.0
Hydrogen Chloride[a]	0.484	0.431	0.452	7.6	0.452	7.6
Hydrogen Sulfide	0.758	0.373	0.482	9.3	0.482	9.3
Methanimine[a]	0.234	0.178	0.215	5.4	0.215	5.4
Water	0.642	0.292	0.407	6.9	0.407	6.9
Total	**0.76**	**0.16**	**0.33 ± 0.14**	**6.3 ± 2.1**	**0.33 ± 0.14**	**6.3 ± 2.1**

A.7. Benchmark of doubly-attached triplet states

This section collects all data that was computed for the benchmark study of doubly-attached triplet states. Besides the full data set, an individual statistical analysis for each molecular species in comparison to EOMDEA-CCSD as well as DEA-ADC(3) is provided.

Table A.35.: Benchmark data for double electronically-attached triplet states for the set of Jacquemin et al.[64] I.

Molecule	Excitation	Double e-attachement energy [eV]					Doubles contribution [%/100]			
		ADC(1)	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Ammonia	3 A’	4.460	4.218	4.198	4.229	4.309	0.007	0.010	0.008	0.006
	3 A”	5.087	4.926	4.912	4.934	4.987	0.005	0.007	0.006	0.004
	3 A’	6.798	6.288	6.260	6.316	6.564	0.013	0.018	0.014	0.011
	3 A”	7.355	6.909	6.883	6.925	7.155	0.011	0.016	0.013	0.010
Dinitrogen	3 Σ_u^+	8.047	7.518	7.603	7.649	7.843	0.026	0.052	0.012	0.008
	3 Π_u	8.699	-	-	-	8.133	-	-	-	0.036
	3 Π_g	8.831	8.280	8.263	8.446	8.504	0.028	0.046	0.019	0.011
	3 Σ_u^+	9.625	9.160	9.157	9.275	9.297	0.016	0.018	0.016	0.012
Ethylene	3 B3u	3.881	3.644	3.625	3.673	3.733	0.009	0.012	0.009	0.007
	3 B2u	3.925	3.693	3.675	3.722	3.784	0.009	0.012	0.009	0.006
	3 B1g	4.403	4.176	4.153	4.202	4.249	0.010	0.014	0.011	0.008
	3 B1g	4.724	4.461	4.438	4.492	4.553	0.011	0.014	0.011	0.008
Formaldehyde	3 B1	4.033	3.821	3.809	3.910	3.924	0.007	0.009	0.007	0.005
	3 B2	5.206	-	-	-	4.780	-	-	-	0.029
	3 A1	5.230	4.907	4.887	4.936	5.024	0.012	0.015	0.010	0.008
	3 A2	5.653	-	-	-	5.111	-	-	-	0.036
Hydrogen chloride	3 Σ^+	6.336	5.919	5.898	5.969	6.080	0.013	0.016	0.013	0.010
	3 Π	6.804	6.336	6.320	6.396	6.540	0.014	0.017	0.013	0.011
	3 Σ^+	8.138	-	-	-	7.290	-	-	-	0.037
	3 Σ^+	9.519	-	-	-	8.781	-	-	-	0.033
Hydrogen sulfide	3 B1	4.430	4.082	4.060	4.136	4.210	0.014	0.019	0.015	0.011
	3 A1	5.731	5.308	5.285	5.357	5.463	0.015	0.020	0.016	0.012
	3 B2	6.161	5.680	5.662	5.739	5.879	0.016	0.020	0.016	0.013
	3 B1	6.364	6.027	6.009	6.082	6.098	0.016	0.019	0.016	0.016

Table A.36.: Benchmark data for double electronically-attached triplet states for the set of Jacquemin et al.[64] II.

Molecule	Excitation	Double e-attachement energy [eV]					Doubles contribution [%/100]			
		ADC(1)	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
Methan-imine	3 A’	3.863	3.612	3.596	3.651	3.722	0.009	0.011	0.009	0.006
	3 A’	4.241	3.976	3.958	4.020	4.084	0.010	0.012	0.010	0.007
	3 A’	4.519	4.314	4.298	4.346	4.388	0.008	0.010	0.008	0.006
	3 A”	5.460	-	-	-	5.080	-	-	-	0.024
Water	3 B1	4.586	4.333	4.314	4.342	4.447	0.006	0.008	0.007	0.005
	3 A1	7.605	6.837	6.795	6.868	7.260	0.016	0.023	0.018	0.014
	3 B1	8.035	7.364	7.327	7.390	7.738	0.014	0.020	0.016	0.012
	3 B2	8.275	7.750	7.725	7.739	8.061	0.010	0.013	0.011	0.009

Table A.37.: Double electronically-attached triplet state statistics for the four lowest-lying states: DEA-ADC(3) compared to EOMDEA-CCSD.
^{a} Three states; ^{b} two states.

DEA-ADC(3) vs. EOMDEA-CCSD Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.053	-0.247	-0.153	-2.5	0.153	2.5
Dinitrogen^a	-0.022	-0.194	-0.091	-1.1	0.091	1.1
Ethylene	-0.047	-0.063	-0.058	-1.4	0.058	1.4
Formaldehyde^b	-0.014	-0.088	-0.051	-1.1	0.051	1.1
Hydrogen Chloride^b	-0.111	-0.144	-0.128	-2.0	0.128	2.0
Hydrogen Sulfide	-0.016	-0.140	-0.084	-1.6	0.084	1.6
Methanimine^a	-0.042	-0.070	-0.059	-1.5	0.059	1.5
Water	-0.105	-0.392	-0.292	-4.1	0.292	4.1
Total	**-0.01**	**-0.39**	**-0.12 ± 0.10**	**-2.0 ± 1.3**	**0.12 ± 0.10**	**2.0 ± 1.3**

Table A.38.: Double electronically-attached triplet state statistics for the four lowest-lying states: DEA-ADC(2)-x compared to EOMDEA-CCSD.
^{a} Three states; ^{b} two states.

DEA-ADC(2)-x vs. EOMDEA-CCSD Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.075	-0.304	-0.191	-3.1	0.191	3.1
Dinitrogen^a	-0.140	-0.241	-0.207	-2.5	0.207	2.5
Ethylene	-0.095	-0.114	-0.107	-2.6	0.107	2.6
Formaldehyde^b	-0.115	-0.137	-0.126	-2.8	0.126	2.8
Hydrogen Chloride^b	-0.182	-0.220	-0.201	-3.2	0.201	3.2
Hydrogen Sulfide	-0.089	-0.218	-0.158	-3.0	0.158	3.0
Methanimine^a	-0.091	-0.126	-0.114	-2.8	0.114	2.8
Water	-0.133	-0.465	-0.336	-4.7	0.336	4.7
Total	**-0.08**	**-0.47**	**-0.18 ± 0.10**	**-3.1 ± 1.1**	**0.18 ± 0.10**	**3.1 ± 1.1**

Table A.39.: Double electronically-attached triplet state statistics for the four lowest-lying states: DEA-ADC(2) compared to EOMDEA-CCSD.
^{a} Three states; ^{b} two states.

DEA-ADC(2) vs. EOMDEA-CCSD Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.061	-0.275	-0.168	-2.7	0.168	2.7
Dinitrogen^a	-0.137	-0.325	-0.229	-2.8	0.229	2.8
Ethylene	-0.073	-0.092	-0.086	-2.1	0.086	2.1
Formaldehyde^b	-0.103	-0.117	-0.110	-2.5	0.110	2.5
Hydrogen Chloride^b	-0.161	-0.204	-0.183	-2.9	0.183	2.9
Hydrogen Sulfide	-0.071	-0.199	-0.138	-2.6	0.138	2.6
Methanimine^a	-0.074	-0.110	-0.097	-2.4	0.097	2.4
Water	-0.114	-0.423	-0.305	-4.3	0.305	4.3
Total	**-0.06**	**-0.42**	**-0.17 ± 0.10**	**-2.8 ± 1.1**	**0.17 ± 0.10**	**-2.8 ± 1.1**

Table A.40.: Double electronically-attached triplet state statistics for the four lowest-lying states: DEA-ADC(1) compared to EOMDEA-CCSD.

DEA-ADC(1) vs. EOMDEA-CCSD Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	0.234	0.100	0.171	3.0	0.171	3.0
Dinitrogen	0.566	0.203	0.356	4.2	0.356	4.2
Ethylene	0.171	0.140	0.153	3.8	0.153	3.8
Formaldehyde	0.542	0.108	0.321	6.6	0.321	6.6
Hydrogen Chloride	0.849	0.256	0.527	7.1	0.527	7.1
Hydrogen Sulfide	0.282	0.220	0.259	4.8	0.259	4.8
Methanimine	0.380	0.130	0.202	4.5	0.202	4.5
Water	0.345	0.139	0.249	3.6	0.249	3.6
Total	**0.85**	**0.10**	**0.28 ± 0.18**	**4.7 ± 2.3**	**0.28 ± 0.18**	**4.7 ± 2.3**

Table A.41.: Double electronically-attached triplet state statistics for the four lowest-lying states: DEA-ADC(2)-x compared to DEA-ADC(3).
[a] Three states; [b] two states.

DEA-ADC(2)-x vs. DEA-ADC(3) Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.022	-0.056	-0.038	-0.7	0.038	0.7
Dinitrogen[a]	-0.046	-0.183	-0.116	-1.3	0.116	1.3
Ethylene	-0.047	-0.101	-0.049	-1.2	0.049	1.2
Formaldehyde[b]	-0.049	-0.101	-0.075	-1.8	0.075	1.8
Hydrogen Chloride[b]	-0.071	-0.076	-0.073	-1.2	0.073	1.2
Hydrogen Sulfide	-0.072	-0.077	-0.074	-1.4	0.074	1.4
Methanimine[a]	-0.048	-0.062	-0.055	-1.4	0.055	1.4
Water	-0.014	-0.074	-0.044	-0.7	0.044	0.7
Total	**-0.01**	**-0.18**	**-0.06 ± 0.03**	**-1.2 ± 0.5**	**0.06 ± 0.03**	**1.2 ± 0.5**

Table A.42.: Double electronically-attached triplet state statistics for the four lowest-lying states: DEA-ADC(2) compared to DEA-ADC(3).
[a] Three states; [b] two states.

DEA-ADC(2) vs. DEA-ADC(3) Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	-0.007	-0.028	-0.016	-0.3	0.016	0.3
Dinitrogen[a]	-0.115	-0.166	-0.137	-1.6	0.137	1.6
Ethylene	-0.026	-0.031	-0.029	-0.7	0.029	0.7
Formaldehyde[b]	-0.029	-0.089	-0.059	-1.4	0.059	1.4
Hydrogen Chloride[b]	-0.050	-0.060	-0.055	-0.9	0.055	0.9
Hydrogen Sulfide	-0.048	-0.059	-0.054	-1.0	0.054	1.0
Methanimine[a]	-0.031	-0.044	-0.038	-1.0	0.038	1.0
Water	0.012	-0.031	-0.014	-0.2	0.019	0.3
Total	**0.01**	**-0.17**	**-0.05 ± 0.04**	**-0.8 ± 0.6**	**0.05 ± 0.04**	**0.8 ± 0.5**

Table A.43.: Double electronically-attached triplet state statistics for the four lowest-lying states: DEA-ADC(1) compared to DEA-ADC(3).
[a] Three states; [b] two states.

DEA-ADC(1) vs. DEA-ADC(3) Triplets

Molecule	Max [eV]	Min [eV]	MSE [eV]	MSE [%]	MAE [eV]	MAE [%]
Ammonia	0.481	0.153	0.324	5.6	0.324	5.6
Dinitrogen[a]	0.397	0.350	0.377	4.5	0.377	4.5
Ethylene	0.232	0.201	0.211	5.3	0.211	5.3
Formaldehyde[b]	0.293	0.123	0.208	4.5	0.208	4.5
Hydrogen Chloride[b]	0.408	0.367	0.388	6.3	0.388	6.3
Hydrogen Sulfide	0.422	0.282	0.343	6.5	0.343	6.5
Methanimine[a]	0.221	0.173	0.202	5.1	0.202	5.1
Water	0.737	0.244	0.540	8.0	0.540	8.0
Total	**0.74**	**0.12**	**0.33 ± 0.15**	**5.8 ± 1.7**	**0.33 ± 0.15**	**5.8 ± 1.7**

Table A.44.: Matching comparison for DEA singlet and triplet states at the example of formaldehyde.

Excitation	Double e-attachement energy [eV]					Doubles contribution			
	ADC(1)	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD	ADC(2)	ADC(2)-x	ADC(3)	EOM-CCSD
1 A2	5.772	2.704 6.090	2.629 6.071	3.089 6.150	5.174	0.062 0.036	0.080 0.042	0.063 0.017	0.039
1 B2	5.944	2.601 6.157	2.531 6.142	3.001 6.300	5.183	0.064 0.017	0.084 0.022	0.066 0.018	0.047
3 B2	5.206	2.548 5.335	2.480 5.313	2.937 5.496	4.780	0.063 0.018	0.082 0.023	0.064 0.020	0.029
3 A2	5.653	2.697 5.852	2.622 5.823	3.079 6.002	5.111	0.062 0.027	0.080 0.037	0.063 0.018	0.036

B. Core-valence separation for Unitary Coupled Cluster

B.1. Geometries for CVS-UCC2 and CVS-UCC2-x calculations

The first number in brackets gives the absolute charge, the second the multiplicity of the species.

ANQ (0 1)

C	-5.259698	-1.211946	-0.000001
C	-5.138437	0.194071	0.000001
C	-3.910009	0.835109	-0.000002
H	-6.035824	0.794218	-0.000001
C	-2.711492	0.085372	0.000002
H	-3.868573	1.914930	-0.000002
C	-2.853654	-1.316583	0.000007
C	-4.105930	-1.961123	0.000005
H	-6.229220	-1.686643	-0.000001
C	-1.386836	0.579225	-0.000002
C	-0.312134	-0.295376	0.000001
H	-1.210653	1.645384	-0.000002
C	-0.475591	-1.697114	-0.000001
H	0.687480	0.112390	-0.000001
C	-1.756307	-2.199407	0.000004
H	0.378874	-2.356786	-0.000001
C	-3.855048	-3.419391	0.000003
C	-2.294822	-3.577621	0.000003
O	-4.644987	-4.335939	-0.000006
O	-1.704980	-4.634093	-0.000006

bithiophene (0 1)

C	0.095254	-3.167054	0.227935
C	-1.181628	-2.777672	-0.110515
H	-2.216041	-0.864492	-0.483764
C	-1.310276	-1.379780	-0.207263
C	-0.127625	-0.711100	0.061883
S	1.119221	-1.824717	0.442074
C	0.127625	0.711100	0.061883
S	-1.119221	1.824717	0.442074
C	-0.095254	3.167054	0.227935
C	1.310276	1.379780	-0.207263
H	2.216041	0.864492	-0.483764
C	1.181628	2.777672	-0.110515
H	1.981762	3.476230	-0.289356
H	0.474334	-4.164330	0.359006
H	-1.981762	-3.476230	-0.289356
H	-0.474334	4.164330	0.359006

PTCDA (0 1)

H	3.375519	-3.388099	0.000000
C	2.824586	-2.460024	0.000000
C	1.398071	0.000000	0.000000
C	1.465500	-2.460357	0.000000
C	3.529370	-1.235962	0.000000
C	2.862972	0.000000	0.000000
C	0.718988	-1.244445	0.000000
H	0.959709	-3.411115	0.000000
C	3.529370	1.235962	0.000000
C	2.824586	2.460024	0.000000
H	3.375519	3.388099	0.000000
C	1.465500	2.460357	0.000000
H	0.959709	3.411115	0.000000
C	0.718988	1.244445	0.000000
C	-0.718988	-1.244445	0.000000
C	-0.718988	1.244445	0.000000
C	-1.398071	0.000000	0.000000
C	-1.465500	-2.460357	0.000000
H	-0.959709	-3.411115	0.000000
H	-3.375519	-3.388099	0.000000
C	-2.824586	-2.460024	0.000000
C	-3.529370	-1.235962	0.000000
C	-2.862972	0.000000	0.000000
C	-1.465500	2.460357	0.000000
H	-0.959709	3.411115	0.000000
C	-2.824586	2.460024	0.000000
H	-3.375519	3.388099	0.000000
C	-3.529370	1.235962	0.000000
C	4.972056	-1.210210	0.000000
C	4.972056	1.210210	0.000000
O	5.663957	2.226198	0.000000
O	5.663957	-2.226198	0.000000
O	5.597564	0.000000	0.000000
C	-4.972056	1.210210	0.000000
O	-5.663957	2.226198	0.000000
O	-5.597564	0.000000	0.000000
C	-4.972056	-1.210210	0.000000
O	-5.663957	-2.226198	0.000000

Porphine (0 1)

C	-4.231112	-0.679984	0.000000
C	-4.231112	0.679984	0.000000
C	-2.836994	1.081008	0.000000
C	-2.836994	-1.081008	0.000000
N	-2.001840	0.000000	0.000000
C	-2.432129	-2.416786	0.000000
C	-1.122875	-2.887735	0.000000
N	0.000000	-2.108424	0.000000
C	1.122875	-2.887735	0.000000
C	-0.686747	-4.247762	0.000000
C	0.686747	-4.247762	0.000000
C	2.432129	-2.416786	0.000000
C	2.836994	-1.081008	0.000000
N	2.001840	0.000000	0.000000
C	4.231112	0.679984	0.000000
C	4.231112	-0.679984	0.000000
C	1.122875	2.887735	0.000000
N	0.000000	2.108424	0.000000
C	-1.122875	2.887735	0.000000
C	-0.686747	4.247762	0.000000
C	0.686747	4.247762	0.000000
C	-2.432129	2.416786	0.000000
C	2.432129	2.416786	0.000000
C	2.836994	1.081008	0.000000
H	-5.076656	-1.351334	0.000000
H	-5.076656	1.351334	0.000000
H	-3.210392	-3.170599	0.000000
H	0.000000	-1.092811	0.000000
H	-1.347795	-5.099560	0.000000
H	1.347795	-5.099560	0.000000
H	3.210392	-3.170599	0.000000
H	5.076656	1.351334	0.000000
H	5.076656	-1.351334	0.000000
H	0.000000	1.092811	0.000000
H	-1.347795	5.099560	0.000000
H	1.347795	5.099560	0.000000
H	-3.210392	3.170599	0.000000
H	3.210392	3.170599	0.000000

Thymine (0 1)

C	0.702140	0.245308	-0.043970
C	0.465503	-1.081136	0.004181
N	-0.800394	-1.604574	0.085601
C	-1.945158	-0.838705	0.126119
N	-1.678910	0.512670	0.075775
C	-0.439264	1.149159	-0.007372
O	-3.062431	-1.308144	0.198221
C	2.065614	0.840407	-0.132604
O	-0.366528	2.365475	-0.043847
H	1.264606	-1.805083	-0.018912
H	-0.948867	-2.597935	0.120100
H	-2.488231	1.115588	0.102765
H	2.824705	0.064196	-0.150563
H	2.249422	1.496087	0.714089
H	2.157803	1.446667	-1.029584

Anthracene (0 1)

C	3.643404	0.708052	0.000000
C	3.643404	-0.708052	0.000000
C	2.462211	-1.402668	0.000000
C	1.218089	-0.719187	0.000000
C	2.462211	1.402668	0.000000
C	1.218089	0.719187	0.000000
C	0.000000	-1.401880	0.000000
C	-1.218089	-0.719187	0.000000
C	0.000000	1.401880	0.000000
C	-1.218089	0.719187	0.000000
C	-2.462211	-1.402668	0.000000
C	-3.643404	-0.708052	0.000000
C	-3.643404	0.708052	0.000000
C	-2.462211	1.402668	0.000000
H	4.581477	1.241783	0.000000
H	4.581477	-1.241783	0.000000
H	2.461759	-2.483603	0.000000
H	2.461759	2.483603	0.000000
H	0.000000	-2.484440	0.000000
H	0.000000	2.484440	0.000000
H	-2.461759	-2.483603	0.000000
H	-4.581477	-1.241783	0.000000
H	-4.581477	1.241783	0.000000
H	-2.461759	2.483603	0.000000

CH_3 (0 2)

C	2.714471	-3.773340	-0.489629
H	3.725593	-3.906814	-0.159156
H	2.209034	-4.567371	-1.002897
H	2.209012	-2.845596	-0.307428

OH (0 2)

O	-0.192179	0.000000	0.000000
H	0.774274	0.000000	0.000000

Allyl (0 2)

H	1.841479	-0.115634	1.450810
C	1.286614	-0.014964	0.535476
H	1.839759	0.153023	-0.373697
C	-0.081508	-0.096270	0.514435
H	-0.591994	-0.265842	1.451535
C	-0.844336	0.023372	-0.618335
H	-0.380549	0.193199	-1.575849
H	-1.916493	-0.048134	-0.583926

O_2 (0 3)

O	-5.995344	4.376461	0.048131
O	-6.402687	5.429850	-0.418601

Anthracene, opt. neutr. str. (1 2)

C	3.643404	0.708052	0.000000
C	3.643404	-0.708052	0.000000
C	2.462211	-1.402668	0.000000
C	1.218089	-0.719187	0.000000
C	2.462211	1.402668	0.000000
C	1.218089	0.719187	0.000000
C	0.000000	-1.401880	0.000000
C	-1.218089	-0.719187	0.000000
C	0.000000	1.401880	0.000000
C	-1.218089	0.719187	0.000000
C	-2.462211	-1.402668	0.000000
C	-3.643404	-0.708052	0.000000
C	-3.643404	0.708052	0.000000
C	-2.462211	1.402668	0.000000
H	4.581477	1.241783	0.000000
H	4.581477	-1.241783	0.000000
H	2.461759	-2.483603	0.000000
H	2.461759	2.483603	0.000000
H	0.000000	-2.484440	0.000000
H	0.000000	2.484440	0.000000
H	-2.461759	-2.483603	0.000000
H	-4.581477	-1.241783	0.000000
H	-4.581477	1.241783	0.000000
H	-2.461759	2.483603	0.000000

Anthracene, opt. cation. str. (1 2)

C	3.588973	0.694860	0.000000
C	3.588973	-0.694860	0.000000
C	2.427247	-1.439763	0.000000
C	1.198089	-0.710673	0.000000
C	2.427247	1.439763	0.000000
C	1.198089	0.710673	0.000000
C	0.000000	-1.441646	0.000000
C	-1.198089	-0.710673	0.000000
C	0.000000	1.441646	0.000000
C	-1.198089	0.710673	0.000000
C	-2.427247	-1.439763	0.000000
C	-3.588973	-0.694860	0.000000
C	-3.588973	0.694860	0.000000
C	-2.427247	1.439763	0.000000
H	4.520027	1.258525	0.000000
H	4.520027	-1.258525	0.000000
H	2.427900	-2.517859	0.000000
H	2.427900	2.517859	0.000000
H	0.000000	-2.521458	0.000000
H	0.000000	2.521458	0.000000
H	-2.427900	-2.517859	0.000000
H	-4.520027	-1.258525	0.000000
H	-4.520027	1.258525	0.000000
H	-2.427900	2.517859	0.000000

B.2. Geometries for CVS-UCC3 calculations

The first number in brackets gives the absolute charge, the second the multiplicity of the species.

CO (0 1)

C	0.000000	0.000000	-0.642568
O	0.000000	0.000000	0.479857

NH_3 (0 1)

N	-0.161851	0.000001	0.000000
H	0.213047	-0.467784	0.810229
H	0.213047	-0.467784	-0.810229
H	0.213044	0.935574	0.000000

CH_3 (0 2)

C	0.000000	0.000000	-0.000058
H	1.074635	0.000000	0.000145
H	-0.537317	0.930661	0.000145
H	-0.537317	-0.930661	0.000145

B.3. CVS-UCC2 and CVS-UCC2-x results

In this section of the appendix, CVS-UCC2 and CVS-UCC2-x excitation energies and oscillator strengths as well as the corresponding CVS-ADC(2) and CVS-ADC(2)-x data[107,108] are compiled. Experimental data is given as a reference to the computed data.

If multiple excitations have been assigned to one experimental value, they have been averaged and weighted by their corresponding oscillator strengths. These values are then presented in an extra table.

- **Data of this chapter (CVS-UCC2 and CVS-UCC2-x results) was already published in the Supporting Information of**:
  Sebastian M. Thielen, Manuel Hodecker, Julia Piazolo, Dirk R. Rehn, and Andreas Dreuw. Unitary coupled-cluster approach for the calculation of core-excited states and x-ray absorption spectra. The Journal of Chemical Physics, 154(15):154108, 04 2021 ([98])

ANQ C 1s

Table B.7.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of ANQ (C 1s) together with experimental data[52].

	CVS-ADC(2)		CVS-UCC2		
State	ω	f	ω	f	ω(Exp.)
1	287.76	0.051	287.86	0.049	284.1
2	288.1	0.155	288.21	0.108	284.45
3	288.33	0.029	288.38	0.031	284.8
4	288.36	0.06	288.47	0.057	
5	288.63	0.011	288.7	0.012	285
6	288.71	0.03	288.77	0.03	
7	289.1	0.029	289.17	0.029	285.6
8	289.3	0.015	289.34	0.014	
9	289.45	0.112	289.51	0.11	

Table B.8.: Comparison of CVS-UCC2 and CVS-ADC(2) excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2	
ω(Exp.)	ω	δ	ω	δ
284.1	287.76	1.29	287.86	1.32
284.45	288.1	1.28	288.21	1.32
284.8	288.35	1.25	288.44	1.28
285	288.69	1.29	288.75	1.32
285.6	289.37	1.32	289.43	1.34

Table B.9.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of ANQ (C 1s) together with experimental data[52].

	CVS-ADC(2)-x			CVS-UCC2-x			
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)
1 1A2	284.4	0	26	284.48	0	26	284.1
1 1B2	284.4	0.038	26	284.48	0.037	26	
2 1A2	284.78	0	25	284.86	0	25	
2 1B2	284.78	0.041	25	284.86	0.044	25	284.45
3 1A2	284.81	0	25	284.91	0	25	
3 1B2	284.81	0.086	25	284.91	0.082	25	
4 1A2	284.96	0	26	285.05	0	27	
4 1B2	284.96	0.036	26	285.05	0.035	27	284.8
5 1B2	285.27	0.024	24	285.33	0.025	24	285
5 1A2	285.42	0	28	285.52	0	28	
6 1A2	285.47	0	28	285.57	0	28	
7 1A2	285.6	0	27	285.67	0	27	
6 1B2	285.6	0.014	27	285.67	0.014	27	285.6
7 1B2	285.74	0.028	25	285.8	0.029	25	
8 1A2	285.9	0	23	285.95	0	24	
9 1A2	285.92	0	26	285.97	0	26	
8 1B2	285.92	0.034	26	285.97	0.032	26	
9 1B2	285.92	0.089	24	285.98	0.09	24	

Table B.10.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
284.1	284.4	0.11	284.48	0.13
284.45	284.8	0.12	284.89	0.16
284.8	284.96	0.06	285.05	0.09
285	285.27	0.09	285.33	0.12
285.6	285.86	0.09	285.92	0.11

ANQ O 1s

Table B.11.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of ANQ (O 1s) together with experimental data[85].

	CVS-ADC(2)		CVS-UCC2		
State	ω	f	ω	f	ω(Exp.)
T1	531.58		531.64		
T2	531.58		531.64		
S1	532.17	0.0002	532.24	0.0002	
S2	532.17	0.064	532.24	0.0628	529.2-531.4
T3	534.21		534.3		
T4	534.21		534.3		
S3	534.21	0.0001	534.3	0.0001	
S4	534.21	0.0006	534.3	0.0006	

Table B.12.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of ANQ (O 1s) together with experimental data[85].

	CVS-ADC(2)			CVS-UCC2			
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)
T1	528.99		21	529.05		21	
T2	528.99		21	529.05		21	
S1	529.45	0.0002	23	529.51	0.0002	23	
S2	529.45	0.0689	23	529.51	0.0686	23	529.2-531.4
S3	533.08	0	27	533.17	0	27	
S4	533.08	0.0003	27	533.17	0.0003	27	
T3	533.09		27	533.17		27	
T4	533.09		27	533.17		27	

BT C 1s

Table B.13.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of BT (C 1s) together with experimental data[103].

	CVS-ADC(2)		CVS-UCC2		
State	ω	f	ω	f	ω(Exp.)
1	288.58	0.005	288.68	0.005	285.7
2	288.58	0.053	288.68	0.052	
3	288.83	0.007	288.93	0.007	
4	288.83	0.095	288.93	0.093	
5	288.93	0.003	289.03	0.003	
6	288.93	0.043	289.03	0.042	
7	289.02	0.004	289.11	0.004	
8	289.05	0.067	289.15	0.066	
9	290.21	0.004	290.28	0.004	286.7
10	290.21	0.046	290.28	0.045	
11	290.28	0.006	290.29	0.006	
12	290.28	0.001	290.29	0.001	

Table B.14.: Comparison of CVS-UCC2 and CVS-ADC(2) excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2	
ω(Exp.)	ω	δ	ω	δ
285.7	288.85	1.1	288.95	1.14
286.7	290.22	1.23	290.28	1.25

Table B.15.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of BT (C 1s) together with experimental data[103].

	CVS-ADC(2)-x			CVS-UCC2-x			
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)
1 1B	285.19	0.004	26	285.27	0.004	26	285.7
1 1A	285.19	0.041	26	285.27	0.041	26	
2 1B	285.42	0.008	26	285.51	0.008	26	
2 1A	285.42	0.115	26	285.51	0.114	26	
3 1A	285.44	0	26	285.54	0.0002	26	
3 1B	285.44	0	26	285.54	0	26	
4 1B	285.67	0.003	25	285.75	0.003	25	
4 1A	285.7	0.056	25	285.78	0.056	26	
5 1B	287.08	0.001	25	287.12	0.003	26	286.7
5 1A	287.08	0.038	25	287.12	0.014	26	
6 1B	287.14	0.008	26	287.17	0.005	25	
6 1A	287.14	0.003	26	287.17	0.027	25	
7 1A	287.19	0	26	287.2	0	26	
7 1B	287.19	0.01	26	287.2	0.01	26	

Table B.16.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
285.7	285.45	-0.09	285.53	-0.06
286.7	287.11	0.14	287.16	0.16

BT S 1s

Table B.17.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of BT (S 1s) together with experimental data[53].

	CVS-ADC(2)		CVS-UCC2		
State	ω	f	ω	f	ω(Exp.)
1	2469.8	0.0039	2469.9	0.0035	2474
2	2469.8	0.0017	2469.9	0.002	
3	2470.08	0.0085	2470.14	0.008	
4	2470.08	0.001	2470.14	0.0011	
5	2471.28	0	2471.29	0	
6	2471.28	0.0003	2471.29	0.0004	

Table B.18.: Comparison of CVS-UCC2 and CVS-ADC(2) excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2	
ω(Exp.)	ω	δ	ω	δ
2474	2469.98	-0.16	2470.05	-0.16

Table B.19.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of BT (S 1s) together with experimental data[53].

	CVS-ADC(2)-x			CVS-UCC2-x			
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)
1 1B	2468.83	0.0057	15	2468.91	0.007	15	2474
1 1A	2468.83	0.0023	15	2468.91	0.0015	15	
2 1B	2468.97	0.0057	15	2469.05	0.0042	15	
2 1A	2468.97	0.0031	15	2469.05	0.0037	15	
3 1A	2470.69	0.0001	15	2470.71	0	15	
3 1B	2470.69	0.0006	15	2470.71	0.0004	15	

Table B.20.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
2474	2468.9	-0.21	2468.98	-0.2

PTCDA C 1s

Table B.21.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of PTCDA (C 1s) together with experimental data[52].

	CVS-ADC(2)		CVS-UCC2		
State	ω	f	ω	f	ω(Exp.)
1	287.87	0.069	288.03	0.063	284.4
2	288.01	0.06	288.19	0.053	
3	288.32	0.072	288.49	0.065	
4	288.41	0.091	288.55	0.09	
5	289.71	0.069	289.75	0.069	285.6
6	289.87	0.094	289.91	0.098	
7	289.92	0.203	290	0.198	
8	289.95	0.019	290.02	0.008	
9	290.01	0.02	290.07	0.015	

Table B.22.: Comparison of CVS-UCC2 and CVS-ADC(2) excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2	
ω(Exp.)	ω	δ	ω	δ
284.4	288.18	1.33	288.34	1.39
285.6	289.88	1.5	289.94	1.52

Table B.23.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of PTCDA (C 1s) together with experimental data[52].

	CVS-ADC(2)-x			CVS-UCC2-x			
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)
1 1B1u	285.36	0.072	26	285.5	0.069	26	284.4
2 1B1u	285.44	0.058	27	285.59	0.052	27	
3 1B1u	285.72	0.073	26	285.87	0.061	26	
4 1B1u	285.75	0.09	26	285.88	0.096	26	
5 1B1u	287.11	0.061	23	287.14	0.063	23	285.6
6 1B1u	287.19	0.09	25	287.25	0.078	25	
7 1B1u	287.23	0.095	22	287.26	0.103	22	
8 1B1u	287.3	0.076	26	287.38	0.074	26	

Table B.24.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
284.4	285.59	0.42	285.73	0.47
285.6	287.21	0.56	287.26	0.58

Thymine C 1s

Table B.25.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of Thymine (C 1s). The difference with respect to experimental data[73] is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2				
State	ω	f	ω	f	ω(Exp.)	$\delta_{\text{ADC(2)}}$	δ_{UCC2}
1	288.45	0.032	288.56	0.031	284.9	1.25	1.28
2	289.83	0.058	289.94	0.057	285.9	1.37	1.41
3	291.21	0.012	291.2	0.012	287.3	1.36	1.36
4	291.31	0.013	291.31	0.012	287.8	1.22	1.22
5	291.42	0.072	291.43	0.072	288.4	1.05	1.05

Table B.26.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV] and oscillator strengths f of Thymine (C 1s). The difference with respect to experimental data[73] is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x				
State	ω	f	ω	f	ω(Exp.)	$\delta_{\text{ADC(2)-x}}$	$\delta_{\text{UCC2-x}}$
1	284.84	0.024	284.94	0.023	284.9	-0.02	0.01
2	286.36	0.045	286.45	0.045	285.9	0.16	0.19
3	286.9	0	286.98	0.0001			
4	287.11	0.003	287.12	0.003			
5	287.29	0	287.3	0			
6	287.95	0.015	287.95	0.015	287.3	0.23	0.23
7	288.03	0.007	288.04	0.007			
8	288.07	0.002	288.08	0.002			
9	288.24	0.053	288.25	0.053	287.8	0.15	0.16
10	288.34	0	288.35	0			
11	288.39	0.004	288.4	0.004			
12	288.45	0.013	288.46	0.012	288.4	0.02	0.02
13	288.63	0	288.63	0.0001			
14	288.88	0.008	288.9	0.008			
15	289.11	0.002	289.11	0.002			

Thymine N 1s

Table B.27.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of Thymine (N 1s) together with experimental data[73].

	CVS-ADC(2)		CVS-UCC2		
State	ω	f	ω	f	ω(Exp.)
1	404.2	0.0098	404.25	0.0096	401.7
2	404.49	0.0069	404.57	0.0067	
3	404.59	0.0056	404.6	0.0055	
4	404.91	0.0026	404.92	0.0026	402.7
5	405.35	0.0041	405.35	0.004	
6	405.46	0.0027	405.44	0.0029	

Table B.28.: Comparison of CVS-UCC2 and CVS-ADC(2) excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2	
ω(Exp.)	ω	δ	ω	δ
401.7	404.39	0.67	404.44	0.68
402.7	405.26	0.64	405.26	0.64

Table B.29.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV] and oscillator strengths f of Thymine (C 1s) together with experimental data[73].

	CVS-ADC(2)-x		CVS-UCC2-x		
State	ω	f	ω	f	ω(Exp.)
1	401.5	0.0111	401.54	0.0109	401.7
2	401.82	0.007	401.9	0.0068	
3	402.21	0.0078	402.23	0.0078	
4	402.54	0.0035	402.52	0.0038	402.7
5	402.6	0.0066	402.61	0.0065	
6	403.03	0.0106	403.01	0.0105	
7	403.42	0.005	403.42	0.0049	

Table B.30.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value[73] is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
401.7	401.8	0.02	401.85	0.04
402.7	402.93	0.06	402.91	0.05

Thymine O 1s

Table B.31.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of Thymine (O 1s). The difference with respect to experimental data[73] is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2				
State	ω	f	ω	f	ω(Exp.)	$\delta_{\mathrm{ADC(2)}}$	δ_{UCC2}
1	532.95	0.024	532.98	0.0241	531.4	0.29	0.3
2	534.01	0.0218	534.02	0.0224	532.3	0.32	0.32

Table B.32.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV] and oscillator strengths f of Thymine (O 1s) together with experimental data[73].

	CVS-ADC(2)-x		CVS-UCC2-x		
State	ω	f	ω	f	ω(Exp.)
1	530.52	0.0282	530.53	0.0282	531.4
2	531.54	0.0268	531.52	0.0266	532.3
3	533.3	0.0001	533.3	0.0001	
4	533.43	0.0003	533.43	0.0003	
5	533.73	0.0003	533.78	0.0002	
6	534.1	0.0012	534.1	0.0012	535.7
7	534.14	0.0027	534.18	0.0025	
8	534.2	0.0002	534.2	0.0002	
9	534.37	0.0013	534.38	0.0012	
10	534.56	0.0006	534.57	0.0006	
11	534.71	0.0019	534.71	0.0019	
12	534.77	0.0007	534.77	0.0006	
13	534.9	0.0009	534.9	0.0009	
14	534.94	0.0018	534.94	0.0018	
15	535.26	0.0001	535.26	0.0001	

Table B.33.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
531.4	530.52	-0.17	530.53	-0.16
532.3	531.54	-0.14	531.52	-0.15
535.7	534.51	-0.22	534.52	-0.22

Porphine N 1s

Table B.34.: CVS-UCC2 and CVS-ADC(2) excitation energies ω[eV] and oscillator strengths f of Porphine (N 1s) together with experimental data[74].

	CVS-ADC(2)		CVS-UCC2		
State	ω	f	ω	f	ω(Exp.)
1	401.5	0.0212	401.51	0.0208	398.2
2	403.63	0.0169	403.64	0.0161	400.3
3	404.56	0.005	404.56	0.0046	402.3
4	404.9	0.0317	404.91	0.0311	
5	405.81	0.0056	405.81	0.0054	403.9

Table B.35.: Comparison of CVS-UCC2 and CVS-ADC(2) excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)		CVS-UCC2	
ω(Exp.)	ω	δ	ω	δ
398.2	401.5	0.83	401.51	0.83
400.3	403.63	0.83	403.64	0.83
402.3	404.85	0.63	404.86	0.64
403.9	405.81	0.47	405.81	0.47

Table B.36.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV] and oscillator strengths f of Porphine (N 1s) together with experimental data[74].

	CVS-ADC(2)-x		CVS-UCC2-x		
State	ω	f	ω	f	ω(Exp.)
1 1B1u	399.89	0.0338	399.89	0.0337	398.2
2 1B1u	402.12	0.0268	402.12	0.0258	400.3
3 1B1u	403.03	0.0263	403.05	0.0252	402.3
4 1B1u	403.59	0.0079	403.59	0.0084	
5 1B1u	404.29	0.0012	404.29	0.0011	
6 1B1u	404.82	0.0019	404.81	0.0019	
7 1B1u	404.9	0.0008	404.9	0.0007	
8 1B1u	405.18	0.0187	405.2	0.0178	403.9
9 1B1u	405.37	0.0001	405.38	0.0001	
10 1B1u	405.74	0.0085	405.74	0.0088	

Table B.37.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
398.2	399.89	0.42	399.89	0.42
400.3	402.12	0.45	402.12	0.45
402.3	403.16	0.21	403.19	0.22
403.9	405.18	0.32	405.2	0.32

CH_3 C 1s

Table B.38.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of CH_3 (C 1s). The difference with respect to experimental data[3] is denoted by δ[%].

	CVS-ADC(2)-x			CVS-UCC2-x					
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)	$\delta_{\text{ADC(2)-x}}$	$\delta_{\text{UCC2-x}}$
1	281.42	0.036	14	281.49	0.035	14	281.35	0.02	0.05
2	286.83	0	22	286.85	0	22			
3	287.72	0	23	287.75	0	23			
4	288.23	0.005	22	288.24	0.004	22			
5	288.23	0.005	22	288.24	0.004	22			

OH O 1s

Table B.39.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of OH (O 1s). The difference with respect to experimental data[93] is denoted by δ[%].

	CVS-ADC(2)-x			CVS-UCC2-x					
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)	$\delta_{\text{ADC(2)-x}}$	$\delta_{\text{UCC2-x}}$
1	525.17	0.0449	11	525.26	0.0446	11	525.85	-0.13	-0.11
2	534.86	0.0041	19	534.9	0.0041	19			
3	536.19	0.0115	20	536.23	0.0112	20			
4	538.81	0.0077	19	538.83	0.0077	19			
5	539.77	0.007	19	539.77	0.0069	19			

Allyl C 1s

Table B.40.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of Allyl (C 1s). The difference with respect to experimental data[2] is denoted by δ[%].

	CVS-ADC(2)-x			CVS-UCC2-x					
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)	$\delta_{\text{ADC(2)-x}}$	$\delta_{\text{UCC2-x}}$
1	282.37	0.001	16	282.5	0.002	16			
2	282.37	0.056	16	282.5	0.054	16	281.99	0.13	0.18
3	284.4	0	29	284.51	0	29			
4	284.78	0.022	16	284.94	0.021	16	285.27	-0.17	-0.12
5	286.7	0	24	286.72	0.0005	24			
6	286.7	0.001	24	286.72	0.001	24			
7	286.9	0.026	27	286.98	0.028	27	287.5	-0.21	-0.18
8	286.93	0.002	23	286.95	0.002	23			

O_2 O 1s

Table B.41.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of O_2 (O 1s) together with experimental data[37].

	CVS-ADC(2)-x			CVS-UCC2-x			
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)
1	529.82	0.0531	21	529.81	0.0532	21	530.7
2	529.82	0.0531	21	529.81	0.0532	21	
3	529.85	0	21	529.84	0	21	
4	529.85	0	21	529.84	0	21	
5	536.85	0	26	536.83	0	26	
6	536.87	0.0017	26	536.86	0.0016	26	
7	538.68	0	26	538.68	0	26	538.8
8	538.69	0.0706	26	538.68	0.0713	26	
9	539.17	0.0003	24	539.16	0.0003	24	
10	539.21	0	24	539.2	0	24	
11	540.27	0.0002	27	540.28	0.0002	27	
12	540.29	0	27	540.3	0	27	
13	540.71	0	24	540.72	0	24	
14	540.71	0	24	540.72	0	24	
15	540.75	0.005	24	540.76	0.005	24	
16	540.75	0.005	24	540.76	0.005	24	
17	541.52	0	26	541.5	0	26	
18	541.55	0.0185	26	541.53	0.0185	26	541.7
19	541.78	0	27	541.78	0	27	
20	541.78	0	27	541.78	0	27	
21	541.8	0.0056	27	541.8	0.0057	27	
22	541.8	0.0056	27	541.8	0.0057	27	
23	542.51	0	27	542.49	0	27	
24	542.51	0.0209	27	542.5	0.0215	27	
25	542.6	0.009	25	542.6	0.0077	25	

Table B.42.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
530.7	529.82	-0.17	529.81	-0.17
538.8	538.69	-0.02	538.68	-0.02
541.7	542.09	0.07	542.07	0.07

Anthracene C 1s

Table B.43.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of Anthracene (C 1s) together with experimental data[38].

	CVS-ADC(2)-x			CVS-UCC2-x			
State	ω	f	$R2$	ω	f	$R2$	ω(Exp.)
1 1B1u	284.63	0.058	26	284.75	0.057	26	284.5
2 1B1u	284.76	0.139	25	284.89	0.137	26	
3 1B1u	284.93	0.092	26	285.05	0.091	26	
4 1B1u	285.34	0.029	27	285.47	0.033	27	
5 1B1u	286.21	0.125	24	286.24	0.119	25	285.9
6 1B1u	286.57	0.048	27	286.63	0.044	27	
7 1B1u	286.79	0.003	29	286.82	0.003	29	
1 1B2u	286.91	0	26	286.92	0.0002	26	
1 1B3u	286.93	0.011	26	286.94	0.01	26	
2 1B2u	286.97	0.024	26	286.98	0.024	26	

Table B.44.: Comparison of CVS-UCC2-x and CVS-ADC(2)-x excitation energies to experimental data. The difference with respect to the experimental value is denoted by δ[%].

	CVS-ADC(2)-x		CVS-UCC2-x	
ω(Exp.)	ω	δ	ω	δ
284.5	284.79	0.1	284.91	0.15
285.9	286.31	0.14	286.35	0.16

Anthracene cation (optimized neutral structure) C 1s

Table B.45.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of the Anthracene cation with optimized neutral structure (C 1s). The column 'Symmetry' and 'State' refer to the irreducible representation of the transition and the term symbol of the excited state, respectively.

		CVS-ADC(2)-x			CVS-UCC2-x		
State	Symmetry	ω	f	$R2$	ω	f	$R2$
1 B2u	B1u	282.4	0.034	20	282.46	0.033	20
2 B2u	B1u	282.89	0.031	24	282.95	0.03	25
3 B2u	B1u	282.94	0.001	27	283	0.001	27
4 B2u	B1u	283.05	0.025	26	283.11	0.025	26
5 B2u	B1u	284.44	0.054	24	284.52	0.052	24
6 B2u	B1u	284.55	0.02	25	284.63	0.019	25
7 B2u	B1u	284.81	0.023	25	284.86	0.024	25
8 B2u	B1u	285.14	0.023	26	285.19	0.023	26
9 B2u	B1u	285.23	0.081	26	285.31	0.08	26
10 B2u	B1u	285.34	0.036	26	285.41	0.036	26
11 B2u	B1u	285.73	0	24	285.78	0	24
12 B2u	B1u	286.02	0.044	28	286.08	0.044	28
13 B2u	B1u	286.06	0.02	27	286.12	0.022	27
14 B2u	B1u	286.31	0.038	28	286.37	0.038	28
15 B2u	B1u	286.64	0.102	25	286.68	0.1	25
16 B2u	B1u	286.84	0.026	29	286.88	0.026	29
17 B2u	B1u	287.01	0.024	29	287.06	0.024	29
18 B2u	B1u	287.14	0.003	29	287.18	0.003	30
19 B2u	B1u	287.17	0.001	28	287.22	0.001	27
20 B2u	B1u	287.29	0.003	29	287.33	0.003	29
21 B2u	B1u	287.54	0.001	30	287.59	0.001	30
22 B2u	B1u	287.73	0.015	28	287.78	0.015	28
23 B2u	B1u	287.76	0.002	29	287.8	0.002	29
1 B1u	B2u	288.07	0.001	25	288.08	0.001	25
1 Au	B3u	288.07	0	25	288.09	0	25
2 B1u	B2u	288.1	0	25	288.12	0.0002	25
2 Au	B3u	288.12	0	25	288.14	0	25
24 B2u	B1u	288.26	0.001	31	288.3	0.001	31
3 B1u	B2u	288.34	0	26	288.36	0.0002	26
3 Au	B3u	288.37	0.011	26	288.38	0.011	26
4 B1u	B2u	288.41	0.029	26	288.42	0.029	26
4 Au	B3u	288.41	0.005	26	288.42	0.005	26
25 B2u	B1u	288.63	0.002	32	288.69	0.002	32

Table B.45.: (*Continued.*)

State	Symmetry	ω	f	$R2$	ω	f	$R2$
5 B1u	B2u	288.65	0	26	288.66	0.0001	26
5 Au	B3u	288.68	0	26	288.69	0	26

Anthracene cation (optimized cationic structure) C 1s

Table B.46.: CVS-UCC2-x and CVS-ADC(2)-x excitation energies ω[eV], oscillator strengths f and amounts of doubles amplitudes $R2$[%] of the Anthracene cation with optimized cationic structure (C 1s). The column ‘Symmetry’ and ‘State’ refer to the irreducible representation of the transition and the term symbol of the excited state, respectively.

		CVS-ADC(2)-x			CVS-UCC2-x		
State	Symmetry	ω	f	$R2$	ω	f	$R2$
1 B3u	B1u	281.76	0.047	23	281.89	0.041	24
2 B3u	B1u	281.85	0.008	28	281.95	0.027	26
3 B3u	B1u	281.9	0.046	23	281.98	0.029	25
4 B3u	B1u	284.11	0.019	20	284.24	0.019	20
5 B3u	B1u	284.25	0.038	20	284.4	0.035	21
6 B3u	B1u	284.96	0.046	27	285.09	0.047	27
7 B3u	B1u	285.08	0.058	26	285.2	0.01	26
8 B3u	B1u	285.1	0.06	26	285.21	0.108	26
9 B3u	B1u	285.55	0.067	28	285.67	0.071	28
10 B3u	B1u	285.96	0.024	24	286	0.029	25
11 B3u	B1u	286.01	0.001	28	286.02	0.001	27
12 B3u	B1u	286.38	0.029	29	286.5	0.032	29
13 B3u	B1u	286.69	0.009	29	286.74	0.007	30
14 B3u	B1u	286.7	0.008	29	286.8	0.006	29
15 B3u	B1u	287.15	0.001	28	287.26	0.001	28
16 B3u	B1u	287.24	0.044	28	287.34	0.0001	28
17 B3u	B1u	287.26	0.05	26	287.33	0.086	26
18 B3u	B1u	287.39	0.034	27	287.45	0.033	27
19 B3u	B1u	287.45	0.004	28	287.55	0.003	28
20 B3u	B1u	287.6	0	30	287.65	0.0003	30
21 B3u	B1u	287.68	0.003	30	287.78	0.003	30
1 B1u	B3u	287.83	0	25	287.84	0	25
1 Au	B2u	287.83	0.002	25	287.84	0.002	25
2 Au	B2u	287.85	0.001	25	287.86	0.001	25
22 B3u	B1u	288.01	0	31	288.11	0.0003	31
23 B3u	B1u	288.05	0.01	29	288.13	0.012	30

Table B.46.: (*Continued.*)

State	Symmetry	ω	f	$\boldsymbol{R}2$	ω	f	$\boldsymbol{R}2$
24 B3u	B1u	288.17	0.007	28	288.24	0.006	28
3 Au	B2u	288.18	0.017	26	288.19	0.016	26
2 B1u	B3u	288.18	0	26	288.19	0	26
4 Au	B2u	288.21	0.008	26	288.22	0.007	27

B.4. CVS-UCC3 results

In this section of the appendix, CVS-UCC3 excitation energies and oscillator strengths as well as the corresponding CVS-ADC(3) data[106] are compiled.
Experimental data[81,100,3] is given as a reference to the computed data.

Excitation energies

Table B.47.: CVS-UCC3 and CVS-ADC(3) excitation energies in eV for the first three excited states with different basis sets and the corresponding complete basis set limit for CO C 1s.

	CVS-ADC(3)			CVS-UCC3		
Basis	State 1	State 2	State 3	State 1	State 2	State 3
cc-pVDZ	289.96			290.48		
cc-pVTZ	288.11	296.3		288.6	297.71	
cc-pVQZ	287.82	295.12		288.28	295.6	
cc-pV5Z	287.74	294.49	295.74	288.2	294.96	296.25
CBS	287.69			288.14		
aug-cc-pVDZ	289.45	295.33	296.45	290.01		297.05
aug-cc-pVTZ	288.02	293.95	295.04	288.5	294.44	295.58
aug-cc-pVQZ	287.8	293.75	294.83	288.26	294.23	295.35
aug-cc-pV5Z	287.74	293.7	294.74	288.2	294.18	295.26
CBS	287.7	293.67	294.71	288.16	294.15	295.22
d-aug-cc-pVDZ	289.35	295.01	296.04	289.91	295.58	296.66
d-aug-cc-pVTZ	288.01	293.84	294.86	288.49	294.34	295.4
d-aug-cc-pVQZ	287.79	293.7	294.72	288.26	294.19	295.25
CBS	287.69	293.65	294.67	288.15	294.13	295.19
Exp.	287.4	292.5	293.4	287.4	292.5	293.4

- **Data of this chapter (CVS-UCC3 results) was already published in the Supporting Information of**: Sebastian M. Thielen, Manuel Hodecker, Julia Piazolo, Dirk R. Rehn, and Andreas Dreuw. Unitary coupled-cluster approach for the calculation of core-excited states and x-ray absorption spectra. The Journal of Chemical Physics, 154(15):154108, 04 2021 (98)

Table B.48.: CVS-UCC3 and CVS-ADC(3) excitation energies in eV for the first three excited states with different basis sets and the corresponding complete basis set limit for CO O 1s.

	CVS-ADC(3)			CVS-UCC3		
Basis	State 1	State 2	State 3	State 1	State 2	State 3
cc-pVDZ	541.38			540.21	550.25	552.18
cc-pVTZ	538.82	547.04		537.73	545.86	549.21
cc-pVQZ	538.37	545.62		537.27	544.44	547.09
cc-pV5Z	538.28	544.91	546.99	537.17	543.71	545.64
CBS	538.19			537.08		
aug-cc-pVDZ	541.32	547.33	549.15	540.02		547.59
aug-cc-pVTZ	538.74	544.66	546.29	537.61	543.41	544.93
aug-cc-pVQZ	538.38	544.32	545.86	537.26	543.07	544.51
aug-cc-pV5Z	538.28	544.22	545.68	537.17	542.97	544.33
CBS	538.23	544.17	545.62	537.11	542.91	544.27
d-aug-cc-pVDZ	541.26	547.13	548.57	539.96	545.68	547.02
d-aug-cc-pVTZ	538.72	544.57	545.97	537.58	543.31	544.61
d-aug-cc-pVQZ	538.38	544.28	545.68	537.26	543.03	544.33
CBS	538.24	544.17	545.57	537.13	542.92	544.22
Exp.	534.1	538.8	539.8	534.1	538.8	539.8

Table B.49.: CVS-UCC3 and CVS-ADC(3) excitation energies in eV for the first three excited states with different basis sets and the corresponding complete basis set limit for NH_3 N 1s.

	CVS-ADC(3)			CVS-UCC3		
Basis	State 1	State 2	State 3	State 1	State 2	State 3
cc-pVDZ	406.27	407.9		406.35	407.99	
cc-pVTZ	404.09	405.73		404.18	405.85	
cc-pVQZ	403.73	405.36		403.82	405.49	
cc-pV5Z	403.6	405.21	407.64	403.69	405.34	407.73
CBS	403.54	405.15		403.63	405.28	
aug-cc-pVDZ	405.95	407.55	408.89	405.87	407.5	408.78
aug-cc-pVTZ	403.92	405.48	406.59	403.94	405.55	406.6
aug-cc-pVQZ	403.61	405.17	406.17	403.68	405.27	406.23
CBS	403.47	405.03	405.97	403.57	405.15	406.06

Table B.49.: (*Continued.*)

Basis	State 1	State 2	State 3	State 1	State 2	State 3
d-aug-cc-pVDZ	405.91	407.49	408.35	405.82	407.44	408.25
d-aug-cc-pVTZ	403.9	405.46	406.31	403.93	405.53	406.33
d-aug-cc-pVQZ	403.61	405.16	406.02	403.68	405.26	406.08
CBS	403.48	405.03	405.9	403.58	405.14	405.98
Exp.	400.66	402.33	402.86	400.66	402.33	402.86

Table B.50.: CVS-UCC3 and CVS-ADC(3) excitation energies in eV for the first excited state with different basis sets and the corresponding complete basis set limit for CH_3 C 1s.

	CVS-ADC(3)	CVS-UCC3
Basis	State 1	State 1
cc-pVDZ	284.4	284.54
cc-pVTZ	282.33	282.48
cc-pVQZ	281.98	282.14
cc-pV5Z	281.9	282.06
CBS	281.83	282
aug-cc-pVDZ	284.09	284.21
aug-cc-pVTZ	282.24	282.38
aug-cc-pVQZ	281.96	282.12
CBS	281.84	282.01
d-aug-cc-pVDZ	284.04	284.16
d-aug-cc-pVTZ	282.22	282.37
d-aug-cc-pVQZ	281.96	282.12
CBS	281.85	282.01
Exp.	281.35	281.35

Table B.51.: Comparison of K-edge experimental energy values and CVS-UCC3 as well as CVS-ADC(3) excitation energy values in the CBS limit for the first three singlet excited states of CO, NH_3 and the first singlet excited state of CH_3. Differences with respect ot experimental data[81,100,3] (in %) are denoted by δ_{UCC} and δ_{ADC}, respectively. Different basis set series are denoted by cc, aug-cc and d-aug-cc, respectively.

	State	cc series		aug-cc series		d-aug-cc series		Expt.
		δ_{ADC}	δ_{UCC}	δ_{ADC}	δ_{UCC}	δ_{ADC}	δ_{UCC}	
CO C	1	0.1	0.26	0.1	0.26	0.1	0.26	287.4
	2			0.4	0.56	0.39	0.56	292.5
	3			0.45	0.62	0.43	0.61	293.4
CO O	1	0.77	0.56	0.77	0.56	0.78	0.57	534.1
	2			1	0.76	1	0.76	538.8
	3			1.08	0.83	1.07	0.82	539.8
NH_3 N	1	0.72	0.74	0.7	0.73	0.7	0.73	400.66
	2	0.7	0.73	0.67	0.7	0.67	0.7	402.33
	3			0.77	0.79	0.75	0.77	402.86
CH_3 C	1	0.17	0.23	0.17	0.23	0.18	0.23	281.35

Oscillator strengths

Table B.52.: CVS-UCC3 and CVS-ADC(3) oscillator strengths for the first three excited states with the aug-cc-series for CO C 1s.

	CVS-ADC(3)			CVS-UCC3		
Basis	State 1	State 2	State 3	State 1	State 2	State 3
aug-cc-pVDZ	0.0748		0.0083	0.0749		0.0084
aug-cc-pVTZ	0.0787	0.0048	0.0075	0.0787	0.0054	0.0077
aug-cc-pVQZ	0.0793	0.0046	0.0066	0.0793	0.0052	0.0067
aug-cc-pV5Z	0.0795	0.0045	0.0059	0.0795	0.0051	0.006

Table B.53.: CVS-UCC3 and CVS-ADC(3) oscillator strengths for the first three excited states with the aug-cc-series for CO O 1s.

	CVS-ADC(3)			CVS-UCC3		
Basis	State 1	State 2	State 3	State 1	State 2	State 3
aug-cc-pVDZ	0.0472		0.0007	0.044		0.0007
aug-cc-pVTZ	0.0478	0.0021	0.0008	0.0448	0.0019	0.0007
aug-cc-pVQZ	0.0479	0.002	0.0008	0.0448	0.0018	0.0007
aug-cc-pV5Z	0.048	0.002	0.0007	0.0448	0.0017	0.0007

Table B.54.: CVS-UCC3 and CVS-ADC(3) oscillator strengths for the first three excited states with the aug-cc-series for NH_3 N 1s.

	CVS-ADC(3)			CVS-UCC3		
Basis	State 1	State 2	State 3	State 1	State 2	State 3
aug-cc-pVDZ	0.0081	0.0307	0.0177	0.0083	0.0298	0.0178
aug-cc-pVTZ	0.008	0.0305	0.0144	0.0082	0.0297	0.0145
aug-cc-pVQZ	0.008	0.0307	0.0128	0.0082	0.0299	0.0128

Table B.55.: CVS-UCC3 and CVS-ADC(3) oscillator strengths for the first excited state with the aug-cc-series for CH_3 C 1s.

	CVS-ADC(3)	CVS-UCC3
Basis	State 1	State 1
aug-cc-pVDZ	0.0381	0.0382
aug-cc-pVTZ	0.0401	0.0402
aug-cc-pVQZ	0.0404	0.0405

C. Unitary Coupled Cluster code generator

Note that **Einstein's sum convention** is used in the following, that is, doubly occuring indices in an expression are summed over while single indices represent target indices.

All equations are automatically generated and formated. Products of an identical set of tensors are always put in an individual line.

C.1. Third-order Unitary Coupled Cluster

C.1.1. UCC3 ground state equations

UCC3 ground state energy:

$$
\begin{aligned}
&\langle \Phi_0 | \bar{H} | \Phi_0 \rangle \ = \\
&\frac{1}{8} \langle ab || ij \rangle \, \sigma_{ij}^{ab*} \\
&+ \frac{1}{8} \langle ij || ab \rangle \, \sigma_{ij}^{ab} \\
&+ f_{ai} \sigma_{i}^{a*} \\
&+ f_{ia} \sigma_{i}^{a}
\end{aligned}
$$

UCC3 singles amplitudes:

$$
\begin{aligned}
&\langle \Phi_i^a | \bar{H} | \Phi_0 \rangle \; = \\
&f_{ai} \\
&+ \frac{1}{2} \langle ab||ij\rangle \, \sigma_j^{b*} \\
&+ \frac{1}{2} \langle aj||bc\rangle \, \sigma_{ij}^{bc} - \frac{1}{2} \langle jk||ib\rangle \, \sigma_{jk}^{ab} \\
&+ f_{ab} \sigma_i^b - f_{ji} \sigma_j^a \\
&+ f_{jb} \sigma_{ij}^{ab} \\
&+ \langle aj||ib\rangle \, \sigma_j^b \\
&+ \frac{1}{4} \langle aj||kl\rangle \, \sigma_{ij}^{bc} \sigma_{kl}^{bc*} + \frac{1}{2} \langle ac||ib\rangle \, \sigma_{jk}^{bd} \sigma_{jk}^{cd*} + \langle ac||bj\rangle \, \sigma_{ik}^{bd} \sigma_{jk}^{cd*} + \langle bj||ik\rangle \, \sigma_{jl}^{ac} \sigma_{kl}^{bc*} \\
&\; - \frac{1}{4} \langle bj||kl\rangle \, \sigma_{ij}^{ac} \sigma_{kl}^{bc*} - \frac{1}{4} \langle cd||ib\rangle \, \sigma_{jk}^{ab} \sigma_{jk}^{cd*} - \frac{1}{4} \langle cd||bj\rangle \, \sigma_{ik}^{ab} \sigma_{jk}^{cd*} - \frac{1}{2} \langle aj||ik\rangle \, \sigma_{jl}^{bc} \sigma_{kl}^{bc*} \\
&= \; 0
\end{aligned}
$$

UCC3 doubles amplitudes:

$$
\begin{aligned}
&\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle \; = \\
&\langle ab||ij\rangle \\
&+ \frac{1}{2} \langle ab||cd\rangle \, \sigma_{ij}^{cd} + \frac{1}{2} \langle kl||ij\rangle \, \sigma_{kl}^{ab} + \mathcal{P}^-_{(ijab)} \langle ak||ic\rangle \, \sigma_{jk}^{bc} \\
&+ \mathcal{P}^-_{(ab)} f_{bc} \sigma_{ij}^{ac} + \mathcal{P}^-_{(ij)} f_{ki} \sigma_{jk}^{ab} \\
&+ \mathcal{P}^-_{(ij)} \langle ab||ic\rangle \, \sigma_j^c + \mathcal{P}^-_{(ab)} \langle bk||ij\rangle \, \sigma_k^a \\
&+ \frac{1}{6} \mathcal{P}^-_{(ab)} \langle bc||ij\rangle \, \sigma_{kl}^{ad} \sigma_{kl}^{cd*} + \frac{1}{6} \mathcal{P}^-_{(ab)} \langle bc||kl\rangle \, \sigma_{ij}^{ad} \sigma_{kl}^{cd*} + \frac{1}{3} \mathcal{P}^-_{(ijab)} \langle ac||ik\rangle \, \sigma_{jl}^{bd} \sigma_{kl}^{cd*} \\
&\; + \frac{1}{12} \langle ab||kl\rangle \, \sigma_{ij}^{cd} \sigma_{kl}^{cd*} + \frac{1}{12} \langle cd||ij\rangle \, \sigma_{kl}^{ab} \sigma_{kl}^{cd*} + \frac{1}{6} \mathcal{P}^-_{(ij)} \langle ab||jk\rangle \, \sigma_{il}^{cd} \sigma_{kl}^{cd*} \\
&\; + \frac{1}{6} \mathcal{P}^-_{(ij)} \langle cd||jk\rangle \, \sigma_{il}^{ab} \sigma_{kl}^{cd*} \\
&+ \frac{1}{6} \langle kl||cd\rangle \, \sigma_{kl}^{ab} \sigma_{ij}^{cd} + \frac{1}{3} \mathcal{P}^-_{(ij)} \langle kl||cd\rangle \, \sigma_{il}^{ab} \sigma_{jk}^{cd} + \frac{2}{3} \mathcal{P}^-_{(ij)} \langle kl||cd\rangle \, \sigma_{ik}^{ac} \sigma_{jl}^{bd} \\
&\; - \frac{1}{3} \mathcal{P}^-_{(ab)} \langle kl||cd\rangle \, \sigma_{ij}^{ac} \sigma_{kl}^{bd} \\
&= \; 0
\end{aligned}
$$

C.1.2. PP-UCC3-x secular matrix

PP-UCC3 singles/singles block:

$$\langle \Phi_i^a | \bar{H} - E_0 | \Phi_j^b \rangle \; =$$

$$- \langle aj || bi \rangle$$

$$+ \frac{1}{2} \langle ac || ik \rangle \, \sigma_{jk}^{bc*}$$

$$+ \frac{1}{2} \langle jk || bc \rangle \, \sigma_{ik}^{ac}$$

$$+ f_{ab} \delta_{ij} - f_{ji} \delta_{ab}$$

$$- \langle aj || bc \rangle \, \sigma_i^c - \langle jk || bi \rangle \, \sigma_k^a$$

$$- \langle aj || ik \rangle \, \sigma_k^{b*} - \langle ac || bi \rangle \, \sigma_j^{c*}$$

$$+ \frac{1}{4} \langle aj || bk \rangle \, \sigma_{il}^{cd} \sigma_{kl}^{cd*} + \frac{1}{4} \langle ae || cd \rangle \, \sigma_{ik}^{cd} \sigma_{jk}^{be*} + \frac{1}{4} \langle ak || bi \rangle \, \sigma_{kl}^{cd} \sigma_{jl}^{cd*} + \frac{1}{4} \langle jk || lm \rangle \, \sigma_{ik}^{ac} \sigma_{lm}^{bc*}$$

$$+ \frac{1}{4} \langle de || bc \rangle \, \sigma_{ik}^{ac} \sigma_{jk}^{de*} + \frac{1}{4} \langle kl || im \rangle \, \sigma_{kl}^{ac} \sigma_{jm}^{bc*} + \frac{1}{2} \langle ak || bl \rangle \, \sigma_{ik}^{cd} \sigma_{jl}^{cd*} + \frac{1}{2} \langle jd || ic \rangle \, \sigma_{kl}^{ac} \sigma_{kl}^{bd*}$$

$$+ \frac{1}{2} \langle jd || ck \rangle \, \sigma_{il}^{ac} \sigma_{kl}^{bd*} + \frac{1}{2} \langle dk || ic \rangle \, \sigma_{kl}^{ac} \sigma_{jl}^{bd*} - \frac{1}{4} \langle aj || ic \rangle \, \sigma_{kl}^{cd} \sigma_{kl}^{bd*} - \frac{1}{4} \langle jc || bi \rangle \, \sigma_{kl}^{ad} \sigma_{kl}^{cd*}$$

$$- \frac{1}{2} \langle ak || cl \rangle \, \sigma_{ik}^{cd} \sigma_{jl}^{bd*} - \frac{1}{2} \langle ck || bl \rangle \, \sigma_{ik}^{ad} \sigma_{jl}^{cd*} - \langle aj || ck \rangle \, \sigma_{il}^{cd} \sigma_{kl}^{bd*} - \langle ad || bc \rangle \, \sigma_{ik}^{ce} \sigma_{jk}^{de*}$$

$$- \langle jk || il \rangle \, \sigma_{km}^{ac} \sigma_{lm}^{bc*} - \langle ck || bi \rangle \, \sigma_{kl}^{ad} \sigma_{jl}^{cd*}$$

$$+ \langle ac || bk \rangle \, \sigma_k^{c*} \delta_{ij} - \langle jc || ik \rangle \, \sigma_k^{c*} \delta_{ab}$$

$$+ \langle ak || bc \rangle \, \sigma_k^c \delta_{ij} - \langle jk || ic \rangle \, \sigma_k^c \delta_{ab}$$

$$- \frac{1}{4} \langle ac || kl \rangle \, \sigma_{kl}^{bc*} \delta_{ij} - \frac{1}{4} \langle cd || ik \rangle \, \sigma_{jk}^{cd*} \delta_{ab}$$

$$- \frac{1}{4} \langle jk || cd \rangle \, \sigma_{ik}^{cd} \delta_{ab} - \frac{1}{4} \langle kl || bc \rangle \, \sigma_{kl}^{ac} \delta_{ij}$$

$$- f_{ak} \sigma_k^{b*} \delta_{ij} - f_{ci} \sigma_j^{c*} \delta_{ab}$$

$$- f_{jc} \sigma_i^c \delta_{ab} - f_{kb} \sigma_k^a \delta_{ij}$$

$$+ \frac{1}{2} \langle ad || bc \rangle \, \sigma_{kl}^{ce} \sigma_{kl}^{de*} \delta_{ij} + \frac{1}{2} \langle ak || cl \rangle \, \sigma_{km}^{cd} \sigma_{lm}^{bd*} \delta_{ij} + \frac{1}{2} \langle jk || il \rangle \, \sigma_{km}^{cd} \sigma_{lm}^{cd*} \delta_{ab} + \frac{1}{2} \langle ck || bl \rangle \, \sigma_{km}^{ad} \sigma_{lm}^{cd*} \delta_{ij}$$

$$- \frac{1}{8} \langle ae || cd \rangle \, \sigma_{kl}^{cd} \sigma_{kl}^{be*} \delta_{ij} - \frac{1}{8} \langle jk || lm \rangle \, \sigma_{ik}^{cd} \sigma_{lm}^{cd*} \delta_{ab} - \frac{1}{8} \langle de || bc \rangle \, \sigma_{kl}^{ac} \sigma_{kl}^{de*} \delta_{ij} - \frac{1}{8} \langle kl || im \rangle \, \sigma_{kl}^{cd} \sigma_{jm}^{cd*} \delta_{ab}$$

$$- \frac{1}{2} \langle ak || bl \rangle \, \sigma_{km}^{cd} \sigma_{lm}^{cd*} \delta_{ij} - \frac{1}{2} \langle jd || ic \rangle \, \sigma_{kl}^{ce} \sigma_{kl}^{de*} \delta_{ab} - \frac{1}{2} \langle jd || ck \rangle \, \sigma_{il}^{ce} \sigma_{kl}^{de*} \delta_{ab} - \frac{1}{2} \langle dk || ic \rangle \, \sigma_{kl}^{ce} \sigma_{jl}^{de*} \delta_{ab}$$

PP-UCC3 singles/doubles block:

$$
\begin{aligned}
&\langle \Phi_i^a | \bar{H} | \Phi_{jk}^{bc} \rangle \;= \\
&\mathcal{P}^-_{(jk)} \langle aj||il \rangle \, \sigma_{kl}^{bc*} + \mathcal{P}^-_{(bc)} \langle ad||bi \rangle \, \sigma_{jk}^{cd*} \\
&+ \mathcal{P}^-_{(jk)} \langle ak||bc \rangle \, \delta_{ij} + \mathcal{P}^-_{(bc)} \langle jk||ci \rangle \, \delta_{ab} \\
&+ \frac{1}{2}\mathcal{P}^-_{(jk)} \langle ak||lm \rangle \, \sigma_{lm}^{bc*} \delta_{ij} + \frac{1}{2}\mathcal{P}^-_{(bc)} \langle de||ci \rangle \, \sigma_{jk}^{de*} \delta_{ab} + \mathcal{P}^-_{(jkbc)} \langle ad||bl \rangle \, \sigma_{kl}^{cd*} \delta_{ij} + \mathcal{P}^-_{(jkbc)} \langle jd||il \rangle \, \sigma_{kl}^{bd*} \delta_{ac} \\
&+ \mathcal{P}^-_{(jk)} f_{al} \sigma_{kl}^{bc*} \delta_{ij} + \mathcal{P}^-_{(bc)} f_{di} \sigma_{jk}^{cd*} \delta_{ab} \\
&+ \mathcal{P}^-_{(jkbc)} f_{jb} \delta_{ac} \delta_{ik} \\
&+ \frac{1}{2}\mathcal{P}^-_{(jkbc)} \langle jd||lm \rangle \, \sigma_{lm}^{cd*} \delta_{ab} \delta_{ik} + \frac{1}{2}\mathcal{P}^-_{(jkbc)} \langle de||bl \rangle \, \sigma_{jl}^{de*} \delta_{ac} \delta_{ik} \\
&+ \mathcal{P}^-_{(jkbc)} f_{jl} \sigma_l^{c*} \delta_{ab} \delta_{ik} + \mathcal{P}^-_{(jkbc)} f_{db} \sigma_j^{d*} \delta_{ac} \delta_{ik} \\
&+ \mathcal{P}^-_{(jkbc)} f_{dl} \sigma_{jl}^{bd*} \delta_{ac} \delta_{ik}
\end{aligned}
$$

PP-UCC3 doubles/singles block:

$$
\begin{aligned}
&\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_k^c \rangle \;= \\
&\mathcal{P}^-_{(ij)} \langle ab||cj \rangle \, \delta_{ik} + \mathcal{P}^-_{(ab)} \langle bk||ij \rangle \, \delta_{ac} \\
&+ \mathcal{P}^-_{(ab)} \langle ak||cd \rangle \, \sigma_{ij}^{bd} + \mathcal{P}^-_{(ij)} \langle kl||ci \rangle \, \sigma_{jl}^{ab} \\
&+ \frac{1}{2}\mathcal{P}^-_{(ab)} \langle bk||de \rangle \, \sigma_{ij}^{de} \delta_{ac} + \frac{1}{2}\mathcal{P}^-_{(ij)} \langle lm||cj \rangle \, \sigma_{lm}^{ab} \delta_{ik} + \mathcal{P}^-_{(ijab)} \langle al||cd \rangle \, \sigma_{jl}^{bd} \delta_{ik} + \mathcal{P}^-_{(ijab)} \langle kl||id \rangle \, \sigma_{jl}^{ad} \delta_{bc} \\
&+ \mathcal{P}^-_{(ijab)} f_{ai} \delta_{bc} \delta_{jk} \\
&+ \mathcal{P}^-_{(ab)} f_{kd} \sigma_{ij}^{bd} \delta_{ac} + \mathcal{P}^-_{(ij)} f_{lc} \sigma_{jl}^{ab} \delta_{ik} \\
&+ \frac{1}{2}\mathcal{P}^-_{(ijab)} \langle al||de \rangle \, \sigma_{il}^{de} \delta_{bc} \delta_{jk} + \frac{1}{2}\mathcal{P}^-_{(ijab)} \langle lm||id \rangle \, \sigma_{lm}^{bd} \delta_{ac} \delta_{jk} \\
&+ \mathcal{P}^-_{(ijab)} f_{ad} \sigma_i^{d} \delta_{bc} \delta_{jk} + \mathcal{P}^-_{(ijab)} f_{li} \sigma_l^{b} \delta_{ac} \delta_{jk} \\
&+ \mathcal{P}^-_{(ijab)} f_{ld} \sigma_{il}^{ad} \delta_{bc} \delta_{jk}
\end{aligned}
$$

PP-UCC3-x doubles/doubles block:

$$\langle \Phi_{ij}^{ab} | \bar{H} - E_0 | \Phi_{kl}^{cd} \rangle \; =$$

$$\frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle ab||im \rangle \, \sigma_{lm}^{cd*} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle ab||jm \rangle \, \sigma_{km}^{cd*} \delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle ae||ij \rangle \, \sigma_{kl}^{de*} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle be||ij \rangle \, \sigma_{kl}^{ce*} \delta_{ad}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle kl||ce \rangle \, \sigma_{ij}^{be} \delta_{ad} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle kl||de \rangle \, \sigma_{ij}^{ae} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle km||cd \rangle \, \sigma_{jm}^{ab} \delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle lm||cd \rangle \, \sigma_{im}^{ab} \delta_{jk}$$

$$+ \mathcal{P}^{-}_{(ij)} \langle ab||cd \rangle \, \delta_{ik} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} \langle ak||cj \rangle \, \delta_{bd} \delta_{il} + \mathcal{P}^{-}_{(ijab)} \langle ak||di \rangle \, \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} \langle al||ci \rangle \, \delta_{bd} \delta_{jk}$$

$$+ \mathcal{P}^{-}_{(ijab)} \langle al||dj \rangle \, \delta_{bc} \delta_{ik} + \mathcal{P}^{-}_{(ab)} \langle kl||ij \rangle \, \delta_{ac} \delta_{bd}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ij)} \langle ab||mn \rangle \, \sigma_{mn}^{cd*} \delta_{ik} \delta_{jl} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} \langle ef||ij \rangle \, \sigma_{kl}^{ef*} \delta_{ac} \delta_{bd} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ae||im \rangle \, \sigma_{km}^{ce*} \delta_{bd} \delta_{jl}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ae||im \rangle \, \sigma_{lm}^{de*} \delta_{bc} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ae||jm \rangle \, \sigma_{lm}^{ce*} \delta_{bd} \delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ae||jm \rangle \, \sigma_{km}^{de*} \delta_{bc} \delta_{il}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ab)} \langle kl||ef \rangle \, \sigma_{ij}^{ef} \delta_{ac} \delta_{bd} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} \langle mn||cd \rangle \, \sigma_{mn}^{ab} \delta_{ik} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle km||ce \rangle \, \sigma_{im}^{ae} \delta_{bd} \delta_{jl}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle km||de \rangle \, \sigma_{jm}^{ae} \delta_{bc} \delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle lm||ce \rangle \, \sigma_{jm}^{ae} \delta_{bd} \delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle lm||de \rangle \, \sigma_{im}^{ae} \delta_{bc} \delta_{jk}$$

$$+ \mathcal{P}^{-}_{(ijab)} f_{ac} \delta_{bd} \delta_{ik} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} f_{ad} \delta_{bc} \delta_{il} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} f_{ki} \delta_{ad} \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} f_{li} \delta_{ac} \delta_{bd} \delta_{jk}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ae||mn \rangle \, \sigma_{mn}^{ce*} \delta_{bd} \delta_{il} \delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ae||mn \rangle \, \sigma_{mn}^{de*} \delta_{bc} \delta_{ik} \delta_{jl} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ef||im \rangle \, \sigma_{km}^{ef*} \delta_{ad} \delta_{bc} \delta_{jl}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ef||im \rangle \, \sigma_{lm}^{ef*} \delta_{ac} \delta_{bd} \delta_{jk}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle km||ef \rangle \, \sigma_{im}^{ef} \delta_{ad} \delta_{bc} \delta_{jl} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle lm||ef \rangle \, \sigma_{im}^{ef} \delta_{ac} \delta_{bd} \delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle mn||ce \rangle \, \sigma_{mn}^{ae} \delta_{bd} \delta_{il} \delta_{jk}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle mn||de \rangle \, \sigma_{mn}^{ae} \delta_{bc} \delta_{ik} \delta_{jl}$$

$$+ \mathcal{P}^{-}_{(ijab)} f_{am} \sigma_{m}^{c*} \delta_{bd} \delta_{il} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} f_{am} \sigma_{m}^{d*} \delta_{bc} \delta_{ik} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} f_{ei} \sigma_{k}^{e*} \delta_{ad} \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} f_{ei} \sigma_{l}^{e*} \delta_{ac} \delta_{bd} \delta_{jk}$$

$$+ \mathcal{P}^{-}_{(ijab)} f_{ke} \sigma_{i}^{e} \delta_{ad} \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} f_{le} \sigma_{i}^{e} \delta_{ac} \delta_{bd} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} f_{mc} \sigma_{m}^{a} \delta_{bd} \delta_{il} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} f_{md} \sigma_{m}^{a} \delta_{bc} \delta_{ik} \delta_{jl}$$

C.1.3. PP-UCC3 ground state and ground- to excited state densities

PP-UCC3 ground state density:

$$
\begin{aligned}
&\langle \Phi_0 | \bar{D} | \Phi_0 \rangle \; = \\
&d_{ai}\sigma_i^{a*} \\
&+ d_{ia}\sigma_i^{a} \\
&+ \frac{1}{2} d_{ai}\sigma_j^{b}\sigma_{ij}^{ab*} \\
&+ \frac{1}{2} d_{ba}\sigma_{ij}^{ac}\sigma_{ij}^{bc*} - \frac{1}{2} d_{ij}\sigma_{ik}^{ab}\sigma_{jk}^{ab*} \\
&+ \frac{1}{2} d_{ia}\sigma_{ij}^{ab}\sigma_j^{b*}
\end{aligned}
$$

PP-UCC3 ground- to excited-state density, singles:

$$
\begin{aligned}
&\langle \Phi_i^a | \bar{D} | \Phi_0 \rangle \; = \\
&d_{ai} \\
&+ d_{ab}\sigma_i^{b} - d_{ji}\sigma_j^{a} \\
&+ d_{jb}\sigma_{ij}^{ab} \\
&+ \frac{1}{2} d_{ab}\sigma_{ij}^{bc}\sigma_j^{c*} + d_{cb}\sigma_{ij}^{ab}\sigma_j^{c*} - \frac{1}{2} d_{ji}\sigma_{jk}^{ab}\sigma_k^{b*} - d_{jk}\sigma_{ij}^{ab}\sigma_k^{b*}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{1}{2} d_{bj}\sigma_{ik}^{ac}\sigma_{jk}^{bc*} - \frac{1}{4} d_{aj}\sigma_{ik}^{bc}\sigma_{jk}^{bc*} - \frac{1}{4} d_{bi}\sigma_{jk}^{ac}\sigma_{jk}^{bc*} \\
&+ \frac{1}{12} d_{jb}\sigma_{kl}^{ad}\sigma_{ij}^{bc}\sigma_{kl}^{cd*} + \frac{1}{6} d_{jb}\sigma_{kl}^{ab}\sigma_{ij}^{cd}\sigma_{kl}^{cd*} + \frac{1}{6} d_{jb}\sigma_{il}^{ad}\sigma_{jk}^{bc}\sigma_{kl}^{cd*} + \frac{1}{3} d_{jb}\sigma_{il}^{ab}\sigma_{jk}^{cd}\sigma_{kl}^{cd*} \\
&\;\; + \frac{1}{3} d_{jb}\sigma_{ij}^{ad}\sigma_{kl}^{bc}\sigma_{kl}^{cd*} - \frac{1}{12} d_{jb}\sigma_{jl}^{ab}\sigma_{ik}^{cd}\sigma_{kl}^{cd*} - \frac{2}{3} d_{jb}\sigma_{jl}^{ad}\sigma_{ik}^{bc}\sigma_{kl}^{cd*}
\end{aligned}
$$

PP-UCC3 ground- to excited-state density, doubles:

$$
\begin{aligned}
&\langle\Phi_{ij}^{ab}|\bar{D}|\Phi_0\rangle \;= \\
&\mathcal{P}^{-}_{(ab)} d_{bc}\sigma_{ij}^{ac} + \mathcal{P}^{-}_{(ij)} d_{ki}\sigma_{jk}^{ab} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ak}\sigma_{ij}^{bc}\sigma_{k}^{c*} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ci}\sigma_{jk}^{ab}\sigma_{k}^{c*} \\
&\quad + \mathcal{P}^{-}_{(ab)} d_{kc}\sigma_{k}^{a}\sigma_{ij}^{bc} + \mathcal{P}^{-}_{(ij)} d_{kc}\sigma_{i}^{c}\sigma_{jk}^{ab} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{kl}\sigma_{ik}^{ab}\sigma_{jm}^{cd}\sigma_{lm}^{cd*} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{kl}\sigma_{jm}^{ab}\sigma_{ik}^{cd}\sigma_{lm}^{cd*} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{dc}\sigma_{il}^{ab}\sigma_{jk}^{ce}\sigma_{kl}^{de*} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{dc}\sigma_{ik}^{ac}\sigma_{jl}^{be}\sigma_{kl}^{de*} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{kl}\sigma_{ij}^{ac}\sigma_{km}^{bd}\sigma_{lm}^{cd*} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{kl}\sigma_{jk}^{ac}\sigma_{im}^{bd}\sigma_{lm}^{cd*} \\
&\quad + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{kj}\sigma_{ik}^{ac}\sigma_{lm}^{bd}\sigma_{lm}^{cd*} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ac}\sigma_{jl}^{bc}\sigma_{ik}^{de}\sigma_{kl}^{de*} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{ki}\sigma_{jm}^{ab}\sigma_{kl}^{cd}\sigma_{lm}^{cd*} \\
&\quad + \frac{1}{24}\mathcal{P}^{-}_{(ab)} d_{bc}\sigma_{kl}^{ac}\sigma_{ij}^{de}\sigma_{kl}^{de*} + \frac{1}{24}\mathcal{P}^{-}_{(ij)} d_{ki}\sigma_{lm}^{ab}\sigma_{jk}^{cd}\sigma_{lm}^{cd*} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{bc}\sigma_{ij}^{ae}\sigma_{kl}^{cd}\sigma_{kl}^{de*} \\
&\quad + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{bc}\sigma_{kl}^{ae}\sigma_{ij}^{cd}\sigma_{kl}^{de*} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{kj}\sigma_{km}^{ab}\sigma_{il}^{cd}\sigma_{lm}^{cd*} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ac}\sigma_{jl}^{be}\sigma_{ik}^{cd}\sigma_{kl}^{de*} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ki}\sigma_{jl}^{ac}\sigma_{km}^{bd}\sigma_{lm}^{cd*} + \frac{1}{4} d_{dc}\sigma_{kl}^{ab}\sigma_{ij}^{ce}\sigma_{kl}^{de*} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{dc}\sigma_{ij}^{ae}\sigma_{kl}^{bc}\sigma_{kl}^{de*} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{dc}\sigma_{kl}^{ae}\sigma_{ij}^{bc}\sigma_{kl}^{de*} - \frac{1}{4} d_{kl}\sigma_{km}^{ab}\sigma_{ij}^{cd}\sigma_{lm}^{cd*}
\end{aligned}
$$

C.1.4. PP-UCC3 state-to-state densities

PP-UCC3 state-to-state density, singles/singles:

$$
\begin{aligned}
&\langle\Phi_i^a|\bar{D}|\Phi_j^b\rangle \;= \\
&d_{ab}\delta_{ij} - d_{ji}\delta_{ab} \\
&+ \frac{1}{2}d_{ac}\sigma_{ik}^{cd}\sigma_{jk}^{bd*} + \frac{1}{2}d_{cb}\sigma_{ik}^{ad}\sigma_{jk}^{cd*} + d_{dc}\sigma_{ik}^{ac}\sigma_{jk}^{bd*} - \frac{1}{2}d_{jk}\sigma_{il}^{ac}\sigma_{kl}^{bc*} \\
&\;- \frac{1}{2}d_{ki}\sigma_{kl}^{ac}\sigma_{jl}^{bc*} - d_{kl}\sigma_{ik}^{ac}\sigma_{jl}^{bc*} \\
&- \frac{1}{2}d_{ak}\sigma_{i}^{c}\sigma_{jk}^{bc*} - \frac{1}{2}d_{ci}\sigma_{k}^{a}\sigma_{jk}^{bc*} \\
&- \frac{1}{2}d_{jc}\sigma_{ik}^{ac}\sigma_{k}^{b*} - \frac{1}{2}d_{kb}\sigma_{ik}^{ac}\sigma_{j}^{c*} \\
&- d_{ak}\sigma_{k}^{b*}\delta_{ij} - d_{ci}\sigma_{j}^{c*}\delta_{ab} \\
&- d_{jc}\sigma_{i}^{c}\delta_{ab} - d_{kb}\sigma_{k}^{a}\delta_{ij} \\
&+ \frac{1}{4}d_{jk}\sigma_{il}^{cd}\sigma_{kl}^{cd*}\delta_{ab} + \frac{1}{4}d_{ki}\sigma_{kl}^{cd}\sigma_{jl}^{cd*}\delta_{ab} + \frac{1}{2}d_{kl}\sigma_{ik}^{cd}\sigma_{jl}^{cd*}\delta_{ab} + d_{kl}\sigma_{km}^{ac}\sigma_{lm}^{bc*}\delta_{ij} \\
&\;- \frac{1}{4}d_{ac}\sigma_{kl}^{cd}\sigma_{kl}^{bd*}\delta_{ij} - \frac{1}{4}d_{cb}\sigma_{kl}^{ad}\sigma_{kl}^{cd*}\delta_{ij} - \frac{1}{2}d_{dc}\sigma_{kl}^{ac}\sigma_{kl}^{bd*}\delta_{ij} - d_{dc}\sigma_{ik}^{ce}\sigma_{jk}^{de*}\delta_{ab} \\
&+ \frac{1}{2}d_{ck}\sigma_{l}^{a}\sigma_{kl}^{bc*}\delta_{ij} + \frac{1}{2}d_{ck}\sigma_{i}^{d}\sigma_{jk}^{cd*}\delta_{ab} - \frac{1}{2}d_{ak}\sigma_{l}^{c}\sigma_{kl}^{bc*}\delta_{ij} - \frac{1}{2}d_{ci}\sigma_{k}^{d}\sigma_{jk}^{cd*}\delta_{ab} \\
&+ \frac{1}{2}d_{kc}\sigma_{kl}^{ac}\sigma_{l}^{b*}\delta_{ij} + \frac{1}{2}d_{kc}\sigma_{ik}^{cd}\sigma_{j}^{d*}\delta_{ab} - \frac{1}{2}d_{jc}\sigma_{ik}^{cd}\sigma_{k}^{d*}\delta_{ab} - \frac{1}{2}d_{kb}\sigma_{kl}^{ac}\sigma_{l}^{c*}\delta_{ij} \\
&+ d_{ck}\sigma_{k}^{c*}\delta_{ab}\delta_{ij} \\
&+ d_{kc}\sigma_{k}^{c}\delta_{ab}\delta_{ij} \\
&+ \frac{1}{2}d_{ck}\sigma_{l}^{d}\sigma_{kl}^{cd*}\delta_{ab}\delta_{ij} \\
&+ \frac{1}{2}d_{dc}\sigma_{kl}^{ce}\sigma_{kl}^{de*}\delta_{ab}\delta_{ij} - \frac{1}{2}d_{kl}\sigma_{km}^{cd}\sigma_{lm}^{cd*}\delta_{ab}\delta_{ij} \\
&+ \frac{1}{2}d_{kc}\sigma_{kl}^{cd}\sigma_{l}^{d*}\delta_{ab}\delta_{ij}
\end{aligned}
$$

PP-UCC3 state-to-state density, singles/doubles:

$$
\begin{aligned}
&\langle \Phi_i^a | \bar{D} | \Phi_{jk}^{bc} \rangle \;= \\
&\frac{1}{2}\mathcal{P}^-_{(jk)} d_{jd} \sigma_{il}^{ad} \sigma_{kl}^{bc*} + \frac{1}{2}\mathcal{P}^-_{(bc)} d_{lb} \sigma_{il}^{ad} \sigma_{jk}^{cd*} \\
&+ \mathcal{P}^-_{(jk)} d_{al} \sigma_{kl}^{bc*} \delta_{ij} + \mathcal{P}^-_{(bc)} d_{di} \sigma_{jk}^{cd*} \delta_{ab} \\
&+ \mathcal{P}^-_{(jkbc)} d_{jb} \delta_{ac} \delta_{ik} \\
&+ \frac{1}{4}\mathcal{P}^-_{(jk)} d_{kd} \sigma_{lm}^{ad} \sigma_{lm}^{bc*} \delta_{ij} + \frac{1}{4}\mathcal{P}^-_{(bc)} d_{lc} \sigma_{il}^{de} \sigma_{jk}^{de*} \delta_{ab} + \frac{1}{2}\mathcal{P}^-_{(jkbc)} d_{jd} \sigma_{il}^{de} \sigma_{kl}^{be*} \delta_{ac} + \frac{1}{2}\mathcal{P}^-_{(jkbc)} d_{lb} \sigma_{lm}^{ad} \sigma_{jm}^{cd*} \delta_{ik} \\
&\quad + \frac{1}{2}\mathcal{P}^-_{(jk)} d_{ld} \sigma_{lm}^{ad} \sigma_{jm}^{bc*} \delta_{ik} + \frac{1}{2}\mathcal{P}^-_{(bc)} d_{ld} \sigma_{il}^{de} \sigma_{jk}^{be*} \delta_{ac} \\
&+ \mathcal{P}^-_{(jkbc)} d_{jl} \sigma_{l}^{c*} \delta_{ab} \delta_{ik} + \mathcal{P}^-_{(jkbc)} d_{db} \sigma_{j}^{d*} \delta_{ac} \delta_{ik} \\
&+ \mathcal{P}^-_{(jkbc)} d_{dl} \sigma_{jl}^{bd*} \delta_{ac} \delta_{ik} \\
&+ \frac{1}{4}\mathcal{P}^-_{(jkbc)} d_{jd} \sigma_{lm}^{de} \sigma_{lm}^{ce*} \delta_{ab} \delta_{ik} + \frac{1}{4}\mathcal{P}^-_{(jkbc)} d_{lb} \sigma_{lm}^{de} \sigma_{km}^{de*} \delta_{ac} \delta_{ij} + \frac{1}{2}\mathcal{P}^-_{(jkbc)} d_{ld} \sigma_{lm}^{de} \sigma_{jm}^{be*} \delta_{ac} \delta_{ik}
\end{aligned}
$$

PP-UCC3 state-to-state density, doubles/singles:

$$
\begin{aligned}
&\langle \Phi_{ij}^{ab} | \bar{D} | \Phi_k^c \rangle \;= \\
&\frac{1}{2}\mathcal{P}^-_{(ab)} d_{al} \sigma_{ij}^{bd} \sigma_{kl}^{cd*} + \frac{1}{2}\mathcal{P}^-_{(ij)} d_{di} \sigma_{jl}^{ab} \sigma_{kl}^{cd*} \\
&+ \mathcal{P}^-_{(ijab)} d_{ai} \delta_{bc} \delta_{jk} \\
&+ \mathcal{P}^-_{(ab)} d_{kd} \sigma_{ij}^{bd} \delta_{ac} + \mathcal{P}^-_{(ij)} d_{lc} \sigma_{jl}^{ab} \delta_{ik} \\
&+ \frac{1}{4}\mathcal{P}^-_{(ab)} d_{bl} \sigma_{ij}^{de} \sigma_{kl}^{de*} \delta_{ac} + \frac{1}{4}\mathcal{P}^-_{(ij)} d_{dj} \sigma_{lm}^{ab} \sigma_{lm}^{cd*} \delta_{ik} + \frac{1}{2}\mathcal{P}^-_{(ijab)} d_{al} \sigma_{im}^{bd} \sigma_{lm}^{cd*} \delta_{jk} + \frac{1}{2}\mathcal{P}^-_{(ijab)} d_{di} \sigma_{jl}^{ae} \sigma_{kl}^{de*} \delta_{bc} \\
&\quad + \frac{1}{2}\mathcal{P}^-_{(ij)} d_{dl} \sigma_{im}^{ab} \sigma_{lm}^{cd*} \delta_{jk} + \frac{1}{2}\mathcal{P}^-_{(ab)} d_{dl} \sigma_{ij}^{ae} \sigma_{kl}^{de*} \delta_{bc} \\
&+ \mathcal{P}^-_{(ijab)} d_{ad} \sigma_{i}^{d} \delta_{bc} \delta_{jk} + \mathcal{P}^-_{(ijab)} d_{li} \sigma_{l}^{b} \delta_{ac} \delta_{jk} \\
&+ \mathcal{P}^-_{(ijab)} d_{ld} \sigma_{il}^{ad} \delta_{bc} \delta_{jk} \\
&+ \frac{1}{4}\mathcal{P}^-_{(ijab)} d_{al} \sigma_{jm}^{de} \sigma_{lm}^{de*} \delta_{bc} \delta_{ik} + \frac{1}{4}\mathcal{P}^-_{(ijab)} d_{di} \sigma_{lm}^{be} \sigma_{lm}^{de*} \delta_{ac} \delta_{jk} + \frac{1}{2}\mathcal{P}^-_{(ijab)} d_{dl} \sigma_{im}^{ae} \sigma_{lm}^{de*} \delta_{bc} \delta_{jk}
\end{aligned}
$$

PP-UCC3 state-to-state density, doubles/doubles:

$$
\begin{aligned}
&\langle \Phi_{ij}^{ab} | \bar{D} | \Phi_{kl}^{cd} \rangle \; = \\
&\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae} \sigma_{im}^{be} \sigma_{km}^{cd*} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae} \sigma_{jm}^{be} \sigma_{lm}^{cd*} \delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ae} \sigma_{ij}^{ef} \sigma_{kl}^{df*} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{be} \sigma_{ij}^{ef} \sigma_{kl}^{cf*} \delta_{ad} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{km} \sigma_{in}^{ab} \sigma_{mn}^{cd*} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{km} \sigma_{ij}^{ae} \sigma_{lm}^{de*} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{km} \sigma_{ij}^{be} \sigma_{lm}^{ce*} \delta_{ad} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{lm} \sigma_{jn}^{ab} \sigma_{mn}^{cd*} \delta_{ik} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm} \sigma_{ij}^{ae} \sigma_{km}^{ce*} \delta_{bd} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm} \sigma_{ij}^{be} \sigma_{km}^{de*} \delta_{ac} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ec} \sigma_{im}^{ab} \sigma_{km}^{de*} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ec} \sigma_{jm}^{ab} \sigma_{lm}^{de*} \delta_{ik} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ec} \sigma_{ij}^{bf} \sigma_{kl}^{ef*} \delta_{ad} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ed} \sigma_{im}^{ab} \sigma_{lm}^{ce*} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ed} \sigma_{jm}^{ab} \sigma_{km}^{ce*} \delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ed} \sigma_{ij}^{af} \sigma_{kl}^{ef*} \delta_{bc} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{mi} \sigma_{mn}^{ab} \sigma_{kn}^{cd*} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi} \sigma_{jm}^{ae} \sigma_{kl}^{de*} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi} \sigma_{jm}^{be} \sigma_{kl}^{ce*} \delta_{ad} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{mj} \sigma_{mn}^{ab} \sigma_{ln}^{cd*} \delta_{ik} \\
&\quad + \mathcal{P}^{-}_{(ab)} d_{fe} \sigma_{ij}^{ae} \sigma_{kl}^{df*} \delta_{bc} + \mathcal{P}^{-}_{(ab)} d_{fe} \sigma_{ij}^{be} \sigma_{kl}^{cf*} \delta_{ad} + \mathcal{P}^{-}_{(ij)} d_{mn} \sigma_{im}^{ab} \sigma_{kn}^{cd*} \delta_{jl} + \mathcal{P}^{-}_{(ij)} d_{mn} \sigma_{jm}^{ab} \sigma_{ln}^{cd*} \delta_{ik} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{ac} \delta_{bd} \delta_{ik} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{ad} \delta_{bc} \delta_{il} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{ki} \delta_{ad} \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{li} \delta_{ac} \delta_{bd} \delta_{jk} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{ae} \sigma_{mn}^{be} \sigma_{mn}^{cd*} \delta_{il} \delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{km} \sigma_{ij}^{ef} \sigma_{lm}^{ef*} \delta_{ac} \delta_{bd} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{lm} \sigma_{ij}^{ef} \sigma_{km}^{ef*} \delta_{ad} \delta_{bc} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ec} \sigma_{mn}^{ab} \sigma_{mn}^{de*} \delta_{il} \delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ed} \sigma_{mn}^{ab} \sigma_{mn}^{ce*} \delta_{ik} \delta_{jl} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{mi} \sigma_{jm}^{ef} \sigma_{kl}^{ef*} \delta_{ac} \delta_{bd} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae} \sigma_{im}^{ef} \sigma_{km}^{cf*} \delta_{bd} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae} \sigma_{im}^{ef} \sigma_{lm}^{df*} \delta_{bc} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae} \sigma_{jm}^{ef} \sigma_{lm}^{cf*} \delta_{bd} \delta_{ik} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae} \sigma_{jm}^{ef} \sigma_{km}^{df*} \delta_{bc} \delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{km} \sigma_{in}^{ae} \sigma_{mn}^{de*} \delta_{bc} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{km} \sigma_{jn}^{ae} \sigma_{mn}^{ce*} \delta_{bd} \delta_{il} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{lm} \sigma_{in}^{ae} \sigma_{mn}^{ce*} \delta_{bd} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{lm} \sigma_{jn}^{ae} \sigma_{mn}^{de*} \delta_{bc} \delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ec} \sigma_{im}^{af} \sigma_{km}^{ef*} \delta_{bd} \delta_{jl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ec} \sigma_{jm}^{af} \sigma_{lm}^{ef*} \delta_{bd} \delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ed} \sigma_{im}^{af} \sigma_{lm}^{ef*} \delta_{bc} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ed} \sigma_{jm}^{af} \sigma_{km}^{ef*} \delta_{bc} \delta_{il} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi} \sigma_{mn}^{ae} \sigma_{ln}^{ce*} \delta_{bd} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi} \sigma_{mn}^{ae} \sigma_{kn}^{de*} \delta_{bc} \delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi} \sigma_{mn}^{be} \sigma_{kn}^{ce*} \delta_{ad} \delta_{jl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi} \sigma_{mn}^{be} \sigma_{ln}^{de*} \delta_{ac} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{fe} \sigma_{im}^{ae} \sigma_{km}^{cf*} \delta_{bd} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{fe} \sigma_{im}^{ae} \sigma_{lm}^{df*} \delta_{bc} \delta_{jk} \\
&\quad + \mathcal{P}^{-}_{(ijab)} d_{fe} \sigma_{jm}^{ae} \sigma_{lm}^{cf*} \delta_{bd} \delta_{ik} + \mathcal{P}^{-}_{(ijab)} d_{fe} \sigma_{jm}^{ae} \sigma_{km}^{df*} \delta_{bc} \delta_{il} + \mathcal{P}^{-}_{(ab)} d_{fe} \sigma_{ij}^{eg} \sigma_{kl}^{fg*} \delta_{ac} \delta_{bd} \\
&\quad + \mathcal{P}^{-}_{(ij)} d_{mn} \sigma_{mo}^{ab} \sigma_{no}^{cd*} \delta_{il} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{mn} \sigma_{im}^{ae} \sigma_{ln}^{ce*} \delta_{bd} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{mn} \sigma_{im}^{ae} \sigma_{kn}^{de*} \delta_{bc} \delta_{jl} \\
&\quad + \mathcal{P}^{-}_{(ijab)} d_{mn} \sigma_{jm}^{ae} \sigma_{kn}^{ce*} \delta_{bd} \delta_{il} + \mathcal{P}^{-}_{(ijab)} d_{mn} \sigma_{jm}^{ae} \sigma_{ln}^{de*} \delta_{bc} \delta_{ik} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{am} \sigma_{m}^{c*} \delta_{bd} \delta_{il} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{am} \sigma_{m}^{d*} \delta_{bc} \delta_{ik} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{ei} \sigma_{k}^{e*} \delta_{ad} \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{ei} \sigma_{l}^{e*} \delta_{ac} \delta_{bd} \delta_{jk} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{ke} \sigma_{i}^{e} \delta_{ad} \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{le} \sigma_{i}^{e} \delta_{ac} \delta_{bd} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{mc} \sigma_{m}^{a} \delta_{bd} \delta_{il} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{md} \sigma_{m}^{a} \delta_{bc} \delta_{ik} \delta_{jl}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{ae}\sigma^{ef}_{mn}\sigma^{cf*}_{mn}\delta_{bd}\delta_{il}\delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{ae}\sigma^{ef}_{mn}\sigma^{df*}_{mn}\delta_{bc}\delta_{ik}\delta_{jl} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{km}\sigma^{ef}_{in}\sigma^{ef*}_{mn}\delta_{ac}\delta_{bd}\delta_{jl} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{lm}\sigma^{ef}_{in}\sigma^{ef*}_{mn}\delta_{ad}\delta_{bc}\delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{ec}\sigma^{af}_{mn}\sigma^{ef*}_{mn}\delta_{bd}\delta_{il}\delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{ed}\sigma^{af}_{mn}\sigma^{ef*}_{mn}\delta_{bc}\delta_{ik}\delta_{jl} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{mi}\sigma^{ef}_{mn}\sigma^{ef*}_{kn}\delta_{ac}\delta_{bd}\delta_{jl} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{mi}\sigma^{ef}_{mn}\sigma^{ef*}_{ln}\delta_{ad}\delta_{bc}\delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{fe}\sigma^{ae}_{mn}\sigma^{cf*}_{mn}\delta_{bd}\delta_{il}\delta_{jk} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{fe}\sigma^{ae}_{mn}\sigma^{df*}_{mn}\delta_{bc}\delta_{ik}\delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mn}\sigma^{ef}_{im}\sigma^{ef*}_{kn}\delta_{ac}\delta_{bd}\delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mn}\sigma^{ef}_{im}\sigma^{ef*}_{ln}\delta_{ad}\delta_{bc}\delta_{jk} \\
&\quad + \mathcal{P}^{-}_{(ijab)} d_{fe}\sigma^{eg}_{im}\sigma^{fg*}_{km}\delta_{ad}\delta_{bc}\delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{fe}\sigma^{eg}_{im}\sigma^{fg*}_{lm}\delta_{ac}\delta_{bd}\delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{mn}\sigma^{ae}_{mo}\sigma^{ce*}_{no}\delta_{bd}\delta_{ik}\delta_{jl} \\
&\quad + \mathcal{P}^{-}_{(ijab)} d_{mn}\sigma^{ae}_{mo}\sigma^{de*}_{no}\delta_{bc}\delta_{il}\delta_{jk} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{em}\sigma^{e*}_{m}\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{me}\sigma^{e}_{m}\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{fe}\sigma^{eg}_{mn}\sigma^{fg*}_{mn}\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mn}\sigma^{ef}_{mo}\sigma^{ef*}_{no}\delta_{ac}\delta_{bd}\delta_{il}\delta_{jk}
\end{aligned}
$$

C.2. Fourth-order Unitary coupled Cluster

C.2.1. UCC4+5[s,t] ground state equations

UCC4+5[s,t] ground state enrgy:

$$
\begin{aligned}
&\langle \Phi_0 | \bar{H} | \Phi_0 \rangle \; = \\
&\frac{1}{8} \langle ab||ij \rangle \, \sigma_{ij}^{ab*} \\
&+ \frac{1}{8} \langle ij||ab \rangle \, \sigma_{ij}^{ab} \\
&+ f_{ai} \sigma_{i}^{a*} \\
&+ f_{ia} \sigma_{i}^{a} \\
&+ \frac{1}{12} \langle ab||ij \rangle \, \sigma_{kl}^{cd} \sigma_{jk}^{ac*} \sigma_{il}^{bd*} + \frac{1}{24} \langle ab||ij \rangle \, \sigma_{kl}^{cd} \sigma_{kl}^{ac*} \sigma_{ij}^{bd*} - \frac{1}{48} \langle ab||ij \rangle \, \sigma_{kl}^{cd} \sigma_{jk}^{ab*} \sigma_{il}^{cd*} \\
&\;\; - \frac{1}{96} \langle ab||ij \rangle \, \sigma_{kl}^{cd} \sigma_{kl}^{ab*} \sigma_{ij}^{cd*} - \frac{1}{48} \langle ab||ij \rangle \, \sigma_{kl}^{cd} \sigma_{il}^{ab*} \sigma_{jk}^{cd*} \\
&+ \frac{1}{12} \langle ij||ab \rangle \, \sigma_{jk}^{ac} \sigma_{il}^{bd} \sigma_{kl}^{cd*} + \frac{1}{24} \langle ij||ab \rangle \, \sigma_{kl}^{ac} \sigma_{ij}^{bd} \sigma_{kl}^{cd*} - \frac{1}{96} \langle ij||ab \rangle \, \sigma_{kl}^{ab} \sigma_{ij}^{cd} \sigma_{kl}^{cd*} \\
&\;\; - \frac{1}{48} \langle ij||ab \rangle \, \sigma_{il}^{ab} \sigma_{jk}^{cd} \sigma_{kl}^{cd*} - \frac{1}{48} \langle ij||ab \rangle \, \sigma_{jk}^{ab} \sigma_{il}^{cd} \sigma_{kl}^{cd*} \\
&+ \frac{1}{48} \langle ab||ij \rangle \, \sigma_{k}^{c} \sigma_{ijk}^{abc*} \\
&+ \frac{1}{48} \langle ij||ab \rangle \, \sigma_{ijk}^{abc} \sigma_{k}^{c*} \\
&- \frac{1}{12} \langle ab||ij \rangle \, \sigma_{j}^{a*} \sigma_{i}^{b*} \\
&- \frac{1}{12} \langle ij||ab \rangle \, \sigma_{j}^{a} \sigma_{i}^{b}
\end{aligned}
$$

UCC4+5[s,t] singles amplitudes:

$$
\begin{aligned}
&\langle \Phi_i^a | \bar{H} | \Phi_0 \rangle \;= \\
&f_{ai} \\
&+ \frac{1}{2} \langle ab||ij \rangle \, \sigma_j^{b*} \\
&+ \frac{1}{2} \langle aj||bc \rangle \, \sigma_{ij}^{bc} - \frac{1}{2} \langle jk||ib \rangle \, \sigma_{jk}^{ab} \\
&+ f_{ab} \sigma_i^b - f_{ji} \sigma_j^a \\
&+ f_{jb} \sigma_{ij}^{ab} \\
&+ \langle aj||ib \rangle \, \sigma_j^b \\
&+ \frac{1}{8} \langle jk||bc \rangle \, \sigma_{ijk}^{abc} \\
&+ \frac{1}{8} \langle ad||bc \rangle \, \sigma_{ijk}^{bce} \sigma_{jk}^{de*} + \frac{1}{8} \langle jk||il \rangle \, \sigma_{jkm}^{abc} \sigma_{lm}^{bc*} + \frac{1}{4} \langle cj||ib \rangle \, \sigma_{jkl}^{abd} \sigma_{kl}^{cd*} \\
&\quad - \frac{1}{4} \langle aj||bk \rangle \, \sigma_{ijl}^{bcd} \sigma_{kl}^{cd*} \\
&+ \frac{1}{8} \langle aj||kl \rangle \, \sigma_{ij}^{bc} \sigma_{kl}^{bc*} + \frac{1}{4} \langle ac||ib \rangle \, \sigma_{jk}^{bd} \sigma_{jk}^{cd*} + \frac{1}{2} \langle ac||bj \rangle \, \sigma_{ik}^{bd} \sigma_{jk}^{cd*} \\
&\quad + \frac{1}{2} \langle bj||ik \rangle \, \sigma_{jl}^{ac} \sigma_{kl}^{bc*} - \frac{1}{8} \langle cd||ib \rangle \, \sigma_{jk}^{ab} \sigma_{jk}^{cd*} - \frac{1}{4} \langle aj||ik \rangle \, \sigma_{jl}^{bc} \sigma_{kl}^{bc*} \\
&+ \frac{1}{4} \langle ad||bc \rangle \, \sigma_{ij}^{bc} \sigma_j^{d*} + \frac{1}{4} \langle jk||il \rangle \, \sigma_{jk}^{ab} \sigma_l^{b*} + \frac{1}{2} \langle cj||ib \rangle \, \sigma_{jk}^{ab} \sigma_k^{c*} \\
&\quad - \frac{1}{2} \langle aj||bk \rangle \, \sigma_{ij}^{bc} \sigma_k^{c*} \\
&+ \frac{1}{12} \langle ab||ij \rangle \, \sigma_{kl}^{cd} \sigma_{jkl}^{bcd*} + \frac{1}{12} \langle ab||jk \rangle \, \sigma_{il}^{cd} \sigma_{jkl}^{bcd*} + \frac{1}{12} \langle bc||ij \rangle \, \sigma_{kl}^{ad} \sigma_{jkl}^{bcd*} \\
&\quad + \frac{1}{48} \langle bc||jk \rangle \, \sigma_{il}^{ad} \sigma_{jkl}^{bcd*} \\
&+ \frac{5}{12} \langle jk||bc \rangle \, \sigma_j^b \sigma_{ik}^{ac} - \frac{1}{3} \langle jk||bc \rangle \, \sigma_j^a \sigma_{ik}^{bc} - \frac{1}{3} \langle jk||bc \rangle \, \sigma_i^b \sigma_{jk}^{ac} \\
&+ \frac{1}{6} \langle ab||jk \rangle \, \sigma_i^c \sigma_{jk}^{bc*} + \frac{1}{6} \langle bc||ij \rangle \, \sigma_k^a \sigma_{jk}^{bc*} + \frac{1}{3} \langle ab||ij \rangle \, \sigma_k^c \sigma_{jk}^{bc*} \\
&+ \frac{1}{48} \langle jk||bl \rangle \, \sigma_{im}^{ab} \sigma_{jk}^{cd} \sigma_{lm}^{cd*} + \frac{1}{12} \langle dj||bc \rangle \, \sigma_{jl}^{ae} \sigma_{ik}^{bc} \sigma_{kl}^{de*} + \frac{1}{48} \langle dj||bc \rangle \, \sigma_{ij}^{ae} \sigma_{kl}^{bc} \sigma_{kl}^{de*} \\
&\quad + \frac{1}{6} \langle jk||ib \rangle \, \sigma_{km}^{ad} \sigma_{jl}^{bc} \sigma_{lm}^{cd*} + \frac{1}{24} \langle aj||bc \rangle \, \sigma_{il}^{bc} \sigma_{jk}^{de} \sigma_{kl}^{de*} + \frac{1}{12} \langle jk||ib \rangle \, \sigma_{km}^{ab} \sigma_{jl}^{cd} \sigma_{lm}^{cd*}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{48}\langle aj||bc\rangle\,\sigma^{bc}_{kl}\sigma^{de}_{ij}\sigma^{de*}_{kl}+\frac{1}{12}\langle dj||bc\rangle\,\sigma^{ac}_{kl}\sigma^{be}_{ij}\sigma^{de*}_{kl}-\frac{1}{12}\langle jk||bl\rangle\,\sigma^{ab}_{km}\sigma^{cd}_{ij}\sigma^{cd*}_{lm}\\
&-\frac{1}{12}\langle aj||bc\rangle\,\sigma^{bd}_{kl}\sigma^{ce}_{ij}\sigma^{de*}_{kl}-\frac{1}{6}\langle jk||bl\rangle\,\sigma^{ad}_{km}\sigma^{bc}_{ij}\sigma^{cd*}_{lm}-\frac{1}{6}\langle aj||bc\rangle\,\sigma^{bd}_{jk}\sigma^{ce}_{il}\sigma^{de*}_{kl}\\
&-\frac{1}{12}\langle jk||bl\rangle\,\sigma^{ad}_{jk}\sigma^{bc}_{im}\sigma^{cd*}_{lm}-\frac{1}{12}\langle dj||bc\rangle\,\sigma^{ac}_{il}\sigma^{be}_{jk}\sigma^{de*}_{kl}-\frac{1}{12}\langle jk||bl\rangle\,\sigma^{ad}_{ik}\sigma^{bc}_{jm}\sigma^{cd*}_{lm}\\
&-\frac{1}{24}\langle dj||bc\rangle\,\sigma^{ac}_{ij}\sigma^{be}_{kl}\sigma^{de*}_{kl}-\frac{1}{6}\langle dj||bc\rangle\,\sigma^{ac}_{jl}\sigma^{be}_{ik}\sigma^{de*}_{kl}-\frac{1}{48}\langle jk||ib\rangle\,\sigma^{ab}_{lm}\sigma^{cd}_{jk}\sigma^{cd*}_{lm}\\
&-\frac{1}{24}\langle jk||ib\rangle\,\sigma^{ad}_{jk}\sigma^{bc}_{lm}\sigma^{cd*}_{lm}-\frac{1}{24}\langle jk||bl\rangle\,\sigma^{ab}_{ik}\sigma^{cd}_{jm}\sigma^{cd*}_{lm}\\
&+\frac{1}{2}\langle ac||ib\rangle\,\sigma^{b}_{j}\sigma^{c*}_{j}+\frac{1}{2}\langle ac||bj\rangle\,\sigma^{b}_{i}\sigma^{c*}_{j}+\frac{1}{2}\langle bj||ik\rangle\,\sigma^{a}_{j}\sigma^{b*}_{k}\\
&-\frac{1}{2}\langle aj||ik\rangle\,\sigma^{b}_{j}\sigma^{b*}_{k}\\
&+\langle jk||ib\rangle\,\sigma^{a}_{k}\sigma^{b}_{j}-\langle aj||bc\rangle\,\sigma^{b}_{j}\sigma^{c}_{i}\\
&+\frac{1}{4}\langle bj||ik\rangle\,\sigma^{acd}_{jlm}\sigma^{bcd*}_{klm}+\frac{1}{4}\langle ac||bj\rangle\,\sigma^{bde}_{ikl}\sigma^{cde*}_{jkl}+\frac{1}{12}\langle aj||kl\rangle\,\sigma^{bcd}_{ijm}\sigma^{bcd*}_{klm}\\
&+\frac{1}{12}\langle ac||ib\rangle\,\sigma^{bde}_{jkl}\sigma^{cde*}_{jkl}-\frac{1}{12}\langle aj||ik\rangle\,\sigma^{bcd}_{jlm}\sigma^{bcd*}_{klm}-\frac{1}{12}\langle cd||ib\rangle\,\sigma^{abe}_{jkl}\sigma^{cde*}_{jkl}\\
&-\frac{1}{8}\langle bj||kl\rangle\,\sigma^{acd}_{ijm}\sigma^{bcd*}_{klm}-\frac{1}{8}\langle cd||bj\rangle\,\sigma^{abe}_{ikl}\sigma^{cde*}_{jkl}\\
=\;& 0
\end{aligned}
$$

UCC4+5[s,t] doubles amplitudes:

$$
\begin{aligned}
&\langle\Phi^{ab}_{ij}|\bar{H}|\Phi_0\rangle \;=\\
&\langle ab||ij\rangle\\
&+\frac{1}{2}\langle ab||cd\rangle\,\sigma^{cd}_{ij}+\frac{1}{2}\langle kl||ij\rangle\,\sigma^{ab}_{kl}+\mathcal{P}^{-}_{(ijab)}\langle ak||ic\rangle\,\sigma^{bc}_{jk}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle bk||cd\rangle\,\sigma^{acd}_{ijk}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle kl||ic\rangle\,\sigma^{abc}_{jkl}\\
&+\mathcal{P}^{-}_{(ab)}f_{bc}\sigma^{ac}_{ij}+\mathcal{P}^{-}_{(ij)}f_{ki}\sigma^{ab}_{jk}\\
&+f_{kc}\sigma^{abc}_{ijk}\\
&+\mathcal{P}^{-}_{(ij)}\langle ab||ic\rangle\,\sigma^{c}_{j}+\mathcal{P}^{-}_{(ab)}\langle bk||ij\rangle\,\sigma^{a}_{k}\\
&\frac{1}{8}\mathcal{P}^{-}_{(ij)}\langle ab||ic\rangle\,\sigma^{cde}_{jkl}\sigma^{de*}_{kl}+\frac{1}{4}\mathcal{P}^{-}_{(ab)}\langle bk||lm\rangle\,\sigma^{acd}_{ijk}\sigma^{cd*}_{lm}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle ad||ic\rangle\,\sigma^{bce}_{jkl}\sigma^{de*}_{kl}
\end{aligned}
$$

$$+\mathcal{P}^{-}_{(ij)}\left\langle ck||jl\right\rangle\sigma^{abd}_{ikm}\sigma^{cd*}_{lm}+\frac{1}{8}\mathcal{P}^{-}_{(ab)}\left\langle bk||ij\right\rangle\sigma^{acd}_{klm}\sigma^{cd*}_{lm}+\frac{1}{4}\mathcal{P}^{-}_{(ij)}\left\langle de||ic\right\rangle\sigma^{abc}_{jkl}\sigma^{de*}_{kl}$$
$$+\mathcal{P}^{-}_{(ab)}\left\langle bd||ck\right\rangle\sigma^{ace}_{ijl}\sigma^{de*}_{kl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\left\langle ak||jl\right\rangle\sigma^{bcd}_{ikm}\sigma^{cd*}_{lm}-\frac{1}{4}\left\langle ck||lm\right\rangle\sigma^{abd}_{ijk}\sigma^{cd*}_{lm}$$
$$-\frac{1}{2}\left\langle ck||ij\right\rangle\sigma^{abd}_{klm}\sigma^{cd*}_{lm}-\frac{1}{4}\left\langle de||ck\right\rangle\sigma^{abc}_{ijl}\sigma^{de*}_{kl}-\frac{1}{2}\left\langle ab||ck\right\rangle\sigma^{cde}_{ijl}\sigma^{de*}_{kl}$$
$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\left\langle ad||ic\right\rangle\sigma^{bc}_{jk}\sigma^{d*}_{k}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\left\langle ak||jl\right\rangle\sigma^{bc}_{ik}\sigma^{c*}_{l}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\left\langle bd||ck\right\rangle\sigma^{ac}_{ij}\sigma^{d*}_{k}$$
$$+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\left\langle ck||jl\right\rangle\sigma^{ab}_{ik}\sigma^{c*}_{l}-\frac{1}{2}\left\langle ab||ck\right\rangle\sigma^{cd}_{ij}\sigma^{d*}_{k}-\frac{1}{2}\left\langle ck||ij\right\rangle\sigma^{ab}_{kl}\sigma^{c*}_{l}$$
$$+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\left\langle bk||cd\right\rangle\sigma^{a}_{k}\sigma^{cd}_{ij}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\left\langle kl||ic\right\rangle\sigma^{c}_{j}\sigma^{ab}_{kl}+\mathcal{P}^{-}_{(ijab)}\left\langle ak||cd\right\rangle\sigma^{c}_{i}\sigma^{bd}_{jk}$$
$$+\mathcal{P}^{-}_{(ab)}\left\langle ak||cd\right\rangle\sigma^{c}_{k}\sigma^{bd}_{ij}+\mathcal{P}^{-}_{(ijab)}\left\langle kl||ic\right\rangle\sigma^{b}_{k}\sigma^{ac}_{jl}+\mathcal{P}^{-}_{(ij)}\left\langle kl||jc\right\rangle\sigma^{c}_{k}\sigma^{ab}_{il}$$
$$+\frac{1}{6}\mathcal{P}^{-}_{(ab)}\left\langle bc||ij\right\rangle\sigma^{ad}_{kl}\sigma^{cd*}_{kl}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}\left\langle bc||kl\right\rangle\sigma^{ad}_{ij}\sigma^{cd*}_{kl}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\left\langle ac||ik\right\rangle\sigma^{bd}_{jl}\sigma^{cd*}_{kl}$$
$$+\frac{1}{12}\left\langle ab||kl\right\rangle\sigma^{cd}_{ij}\sigma^{cd*}_{kl}+\frac{1}{12}\left\langle cd||ij\right\rangle\sigma^{ab}_{kl}\sigma^{cd*}_{kl}+\frac{1}{6}\mathcal{P}^{-}_{(ij)}\left\langle ab||jk\right\rangle\sigma^{cd}_{il}\sigma^{cd*}_{kl}$$
$$+\frac{1}{6}\mathcal{P}^{-}_{(ij)}\left\langle cd||jk\right\rangle\sigma^{ab}_{il}\sigma^{cd*}_{kl}$$
$$+\frac{1}{6}\left\langle kl||cd\right\rangle\sigma^{ab}_{kl}\sigma^{cd}_{ij}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\left\langle kl||cd\right\rangle\sigma^{ab}_{il}\sigma^{cd}_{jk}+\frac{2}{3}\mathcal{P}^{-}_{(ij)}\left\langle kl||cd\right\rangle\sigma^{ac}_{ik}\sigma^{bd}_{jl}$$
$$-\frac{1}{3}\mathcal{P}^{-}_{(ab)}\left\langle kl||cd\right\rangle\sigma^{ac}_{ij}\sigma^{bd}_{kl}$$

$$\mathcal{P}^{-}_{(ijab)}\left\langle kl||im\right\rangle\sigma^{ac}_{jk}\sigma^{bd}_{ln}\sigma^{cd*}_{mn}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\left\langle ak||cl\right\rangle\sigma^{bc}_{im}\sigma^{de}_{jk}\sigma^{de*}_{lm}+\frac{1}{12}\mathcal{P}^{-}_{(ij)}\left\langle kl||jm\right\rangle\sigma^{ab}_{in}\sigma^{cd}_{kl}\sigma^{cd*}_{mn}$$
$$+\frac{1}{12}\mathcal{P}^{-}_{(ij)}\left\langle kl||jm\right\rangle\sigma^{ab}_{kl}\sigma^{cd}_{in}\sigma^{cd*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\left\langle ae||cd\right\rangle\sigma^{bf}_{jl}\sigma^{cd}_{ik}\sigma^{ef*}_{kl}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\left\langle ak||ic\right\rangle\sigma^{bc}_{lm}\sigma^{de}_{jk}\sigma^{de*}_{lm}$$
$$+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\left\langle dk||ic\right\rangle\sigma^{ac}_{jk}\sigma^{be}_{lm}\sigma^{de*}_{lm}+\frac{2}{3}\mathcal{P}^{-}_{(ijab)}\left\langle dk||cl\right\rangle\sigma^{ac}_{im}\sigma^{be}_{jk}\sigma^{de*}_{lm}+\mathcal{P}^{-}_{(ab)}\left\langle ak||cl\right\rangle\sigma^{be}_{km}\sigma^{cd}_{ij}\sigma^{de*}_{lm}$$
$$+\frac{2}{3}\mathcal{P}^{-}_{(ijab)}\left\langle ak||jc\right\rangle\sigma^{be}_{km}\sigma^{cd}_{il}\sigma^{de*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\left\langle ak||cl\right\rangle\sigma^{bc}_{jk}\sigma^{de}_{im}\sigma^{de*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ij)}\left\langle kl||mn\right\rangle\sigma^{ab}_{il}\sigma^{cd}_{jk}\sigma^{cd*}_{mn}$$
$$+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\left\langle ak||ic\right\rangle\sigma^{bc}_{jm}\sigma^{de}_{kl}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\left\langle dk||ic\right\rangle\sigma^{ac}_{kl}\sigma^{be}_{jm}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\left\langle dk||jc\right\rangle\sigma^{ab}_{im}\sigma^{ce}_{kl}\sigma^{de*}_{lm}$$
$$+\frac{2}{3}\mathcal{P}^{-}_{(ij)}\left\langle dk||cl\right\rangle\sigma^{ab}_{ik}\sigma^{ce}_{jm}\sigma^{de*}_{lm}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\left\langle ae||cd\right\rangle\sigma^{bd}_{kl}\sigma^{cf}_{ij}\sigma^{ef*}_{kl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\left\langle dk||ic\right\rangle\sigma^{ac}_{lm}\sigma^{be}_{jk}\sigma^{de*}_{lm}$$
$$+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\left\langle kl||jm\right\rangle\sigma^{ab}_{ln}\sigma^{cd}_{ik}\sigma^{cd*}_{mn}+\mathcal{P}^{-}_{(ijab)}\left\langle ae||cd\right\rangle\sigma^{bd}_{il}\sigma^{cf}_{jk}\sigma^{ef*}_{kl}+\mathcal{P}^{-}_{(ijab)}\left\langle ak||cl\right\rangle\sigma^{be}_{jk}\sigma^{cd}_{im}\sigma^{de*}_{lm}$$
$$+\mathcal{P}^{-}_{(ijab)}\left\langle dk||jc\right\rangle\sigma^{ac}_{il}\sigma^{be}_{km}\sigma^{de*}_{lm}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\left\langle ak||cl\right\rangle\sigma^{bc}_{ij}\sigma^{de}_{km}\sigma^{de*}_{lm}+\mathcal{P}^{-}_{(ij)}\left\langle dk||ic\right\rangle\sigma^{ab}_{km}\sigma^{ce}_{jl}\sigma^{de*}_{lm}$$
$$+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\left\langle ef||cd\right\rangle\sigma^{ac}_{ik}\sigma^{bd}_{jl}\sigma^{ef*}_{kl}+\frac{2}{3}\mathcal{P}^{-}_{(ab)}\left\langle dk||cl\right\rangle\sigma^{ac}_{ij}\sigma^{be}_{km}\sigma^{de*}_{lm}+\frac{1}{12}\mathcal{P}^{-}_{(ab)}\left\langle be||cd\right\rangle\sigma^{af}_{ij}\sigma^{cd}_{kl}\sigma^{ef*}_{kl}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ab)}\langle be||cd\rangle\,\sigma^{af}_{kl}\sigma^{cd}_{ij}\sigma^{ef*}_{kl}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\langle kl||im\rangle\,\sigma^{ac}_{jn}\sigma^{bd}_{kl}\sigma^{cd*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle ak||ic\rangle\,\sigma^{be}_{jk}\sigma^{cd}_{lm}\sigma^{de*}_{lm}$$

$$+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle ak||cl\rangle\,\sigma^{be}_{ij}\sigma^{cd}_{km}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle ak||cl\rangle\,\sigma^{be}_{im}\sigma^{cd}_{jk}\sigma^{de*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}\langle ak||cl\rangle\,\sigma^{bc}_{km}\sigma^{de}_{ij}\sigma^{de*}_{lm}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(ij)}\langle dk||jc\rangle\,\sigma^{ab}_{lm}\sigma^{ce}_{ik}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle kl||mn\rangle\,\sigma^{ac}_{ik}\sigma^{bd}_{jl}\sigma^{cd*}_{mn}+\frac{2}{3}\langle ab||cd\rangle\,\sigma^{ce}_{ik}\sigma^{df}_{jl}\sigma^{ef*}_{kl}$$

$$+\frac{2}{3}\langle kl||ij\rangle\,\sigma^{ac}_{km}\sigma^{bd}_{ln}\sigma^{cd*}_{mn}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle ae||cd\rangle\,\sigma^{bd}_{ij}\sigma^{cf}_{kl}\sigma^{ef*}_{kl}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle dk||jc\rangle\,\sigma^{ab}_{ik}\sigma^{ce}_{lm}\sigma^{de*}_{lm}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle kl||im\rangle\,\sigma^{ab}_{jl}\sigma^{cd}_{kn}\sigma^{cd*}_{mn}-\frac{1}{6}\mathcal{P}^{-}_{(ab)}\langle ef||cd\rangle\,\sigma^{ac}_{ij}\sigma^{bd}_{kl}\sigma^{ef*}_{kl}-\frac{1}{3}\langle kl||ij\rangle\,\sigma^{ab}_{ln}\sigma^{cd}_{km}\sigma^{cd*}_{mn}$$

$$-\frac{2}{3}\langle dk||cl\rangle\,\sigma^{ab}_{km}\sigma^{ce}_{ij}\sigma^{de*}_{lm}-\frac{1}{3}\langle ab||cd\rangle\,\sigma^{ce}_{kl}\sigma^{df}_{ij}\sigma^{ef*}_{kl}$$

$$\frac{1}{4}\mathcal{P}^{-}_{(ab)}\langle be||cd\rangle\,\sigma^{acd}_{ijk}\sigma^{e*}_{k}+\frac{1}{4}\mathcal{P}^{-}_{(ij)}\langle kl||jm\rangle\,\sigma^{abc}_{ikl}\sigma^{c*}_{m}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle ak||cl\rangle\,\sigma^{bcd}_{ijk}\sigma^{d*}_{l}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle dk||jc\rangle\,\sigma^{abc}_{ikl}\sigma^{d*}_{l}$$

$$+\langle ab||cd\rangle\,\sigma^{c}_{i}\sigma^{d}_{j}+\mathcal{P}^{-}_{(ijab)}\langle ak||jc\rangle\,\sigma^{b}_{k}\sigma^{c}_{i}+\langle kl||ij\rangle\,\sigma^{a}_{k}\sigma^{b}_{l}$$

$$+\frac{1}{36}\mathcal{P}^{-}_{(ab)}\langle bc||ij\rangle\,\sigma^{ade}_{klm}\sigma^{cde*}_{klm}+\frac{1}{36}\langle cd||ij\rangle\,\sigma^{abe}_{klm}\sigma^{cde*}_{klm}+\frac{1}{12}\mathcal{P}^{-}_{(ijab)}\langle ac||ik\rangle\,\sigma^{bde}_{jlm}\sigma^{cde*}_{klm}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ab)}\langle bc||kl\rangle\,\sigma^{ade}_{ijm}\sigma^{cde*}_{klm}+\frac{1}{36}\langle ab||kl\rangle\,\sigma^{cde}_{ijm}\sigma^{cde*}_{klm}+\frac{1}{36}\mathcal{P}^{-}_{(ij)}\langle ab||jk\rangle\,\sigma^{cde}_{ilm}\sigma^{cde*}_{klm}$$

$$+\frac{1}{48}\langle cd||kl\rangle\,\sigma^{abe}_{ijm}\sigma^{cde*}_{klm}+\frac{1}{12}\mathcal{P}^{-}_{(ij)}\langle cd||jk\rangle\,\sigma^{abe}_{ilm}\sigma^{cde*}_{klm}$$

$$+\frac{5}{12}\langle kl||cd\rangle\,\sigma^{c}_{k}\sigma^{abd}_{ijl}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle kl||cd\rangle\,\sigma^{a}_{k}\sigma^{bcd}_{ijl}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle kl||cd\rangle\,\sigma^{c}_{i}\sigma^{abd}_{jkl}$$

$$+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle ab||jk\rangle\,\sigma^{c}_{i}\sigma^{c*}_{k}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle bc||ij\rangle\,\sigma^{a}_{k}\sigma^{c*}_{k}$$

$$=\ 0$$

UCC4+5[s,t] triples amplitudes:

$$\langle\Phi^{abc}_{ijk}|\bar{H}|\Phi_0\rangle\ =$$

$$\frac{1}{2}\langle ab||de\rangle\,\sigma^{cde}_{ijk}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle bc||de\rangle\,\sigma^{ade}_{ijk}+\frac{1}{2}\langle lm||ij\rangle\,\sigma^{abc}_{klm}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle lm||jk\rangle\,\sigma^{abc}_{ilm}+\mathcal{P}^{-}_{(ijab)}\langle al||id\rangle\,\sigma^{bcd}_{jkl}+\mathcal{P}^{-}_{(ab)}\langle al||kd\rangle\,\sigma^{bcd}_{ijl}$$

$$+\mathcal{P}^{-}_{(ij)}\langle cl||id\rangle\,\sigma^{abd}_{jkl}+\langle cl||kd\rangle\,\sigma^{abd}_{ijl}$$

$$+\mathcal{P}^{-}_{(ab)}f_{ad}\sigma^{bcd}_{ijk}+f_{cd}\sigma^{abd}_{ijk}+\mathcal{P}^{-}_{(ij)}f_{lj}\sigma^{abc}_{ikl}$$

$$
\begin{aligned}
&\quad - f_{lk}\sigma^{abc}_{ijl} \\
&+ \mathcal{P}^{-}_{(ij)} \langle ab||jd\rangle \sigma^{cd}_{ik} + \mathcal{P}^{-}_{(ijab)} \langle ac||id\rangle \sigma^{bd}_{jk} + \mathcal{P}^{-}_{(ab)} \langle ac||kd\rangle \sigma^{bd}_{ij} \\
&\quad + \mathcal{P}^{-}_{(ab)} \langle al||ij\rangle \sigma^{bc}_{kl} + \mathcal{P}^{-}_{(ijab)} \langle al||jk\rangle \sigma^{bc}_{il} + \langle cl||ij\rangle \sigma^{ab}_{kl} \\
&\quad + \mathcal{P}^{-}_{(ij)} \langle cl||jk\rangle \sigma^{ab}_{il} - \langle ab||kd\rangle \sigma^{cd}_{ij} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle al||de\rangle \sigma^{bc}_{il}\sigma^{de}_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle al||de\rangle \sigma^{bc}_{kl}\sigma^{de}_{ij} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle cl||de\rangle \sigma^{ab}_{il}\sigma^{de}_{jk} \\
&\quad + \frac{1}{2} \langle cl||de\rangle \sigma^{ab}_{kl}\sigma^{de}_{ij} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle lm||id\rangle \sigma^{ac}_{lm}\sigma^{bd}_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle lm||jd\rangle \sigma^{ab}_{lm}\sigma^{cd}_{ik} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle lm||kd\rangle \sigma^{ac}_{lm}\sigma^{bd}_{ij} + \mathcal{P}^{-}_{(abc)} \langle al||de\rangle \sigma^{bd}_{ik}\sigma^{ce}_{jl} + \mathcal{P}^{-}_{(abc)} \langle bl||de\rangle \sigma^{ad}_{ij}\sigma^{ce}_{kl} \\
&\quad + \mathcal{P}^{-}_{(abc)} \langle bl||de\rangle \sigma^{ad}_{il}\sigma^{ce}_{jk} + \mathcal{P}^{-}_{(ijk)} \langle lm||id\rangle \sigma^{ab}_{jl}\sigma^{cd}_{km} + \mathcal{P}^{-}_{(ijk)} \langle lm||id\rangle \sigma^{ac}_{kl}\sigma^{bd}_{jm} \\
&\quad + \mathcal{P}^{-}_{(ijk)} \langle lm||id\rangle \sigma^{ad}_{jl}\sigma^{bc}_{km} - \frac{1}{2} \langle lm||kd\rangle \sigma^{ab}_{lm}\sigma^{cd}_{ij} \\
&+ \mathcal{P}^{-}_{(ij)} \langle ab||de\rangle \sigma^{d}_{j}\sigma^{ce}_{ik} + \mathcal{P}^{-}_{(ijab)} \langle ac||de\rangle \sigma^{d}_{i}\sigma^{be}_{jk} + \mathcal{P}^{-}_{(ab)} \langle ac||de\rangle \sigma^{d}_{k}\sigma^{be}_{ij} \\
&\quad + \mathcal{P}^{-}_{(abc)} \langle al||id\rangle \sigma^{b}_{l}\sigma^{cd}_{jk} + \mathcal{P}^{-}_{(ijk)} \langle al||id\rangle \sigma^{d}_{j}\sigma^{bc}_{kl} + \mathcal{P}^{-}_{(abc)} \langle al||jd\rangle \sigma^{c}_{l}\sigma^{bd}_{ik} \\
&\quad + \mathcal{P}^{-}_{(abc)} \langle al||kd\rangle \sigma^{b}_{l}\sigma^{cd}_{ij} + \mathcal{P}^{-}_{(ijk)} \langle bl||id\rangle \sigma^{d}_{k}\sigma^{ac}_{jl} + \mathcal{P}^{-}_{(ijk)} \langle cl||id\rangle \sigma^{d}_{j}\sigma^{ab}_{kl} \\
&\quad + \mathcal{P}^{-}_{(ab)} \langle lm||ij\rangle \sigma^{b}_{l}\sigma^{ac}_{km} + \mathcal{P}^{-}_{(ijab)} \langle lm||ik\rangle \sigma^{a}_{l}\sigma^{bc}_{jm} + \mathcal{P}^{-}_{(ij)} \langle lm||ik\rangle \sigma^{c}_{l}\sigma^{ab}_{jm} \\
&\quad - \langle ab||de\rangle \sigma^{d}_{k}\sigma^{ce}_{ij} - \langle lm||ij\rangle \sigma^{c}_{l}\sigma^{ab}_{km} \\
&+ \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle ad||ij\rangle \sigma^{bce}_{klm}\sigma^{de*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} \langle ad||jk\rangle \sigma^{bce}_{ilm}\sigma^{de*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle ad||lm\rangle \sigma^{bce}_{ijk}\sigma^{de*}_{lm} \\
&\quad + \frac{1}{6} \langle cd||ij\rangle \sigma^{abe}_{klm}\sigma^{de*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle cd||jk\rangle \sigma^{abe}_{ilm}\sigma^{de*}_{lm} + \frac{1}{6} \langle cd||lm\rangle \sigma^{abe}_{ijk}\sigma^{de*}_{lm} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle de||il\rangle \sigma^{abc}_{jkm}\sigma^{de*}_{lm} + \frac{1}{6} \langle de||kl\rangle \sigma^{abc}_{ijm}\sigma^{de*}_{lm} + \frac{1}{12} \langle ab||lm\rangle \sigma^{cde}_{ijk}\sigma^{de*}_{lm} \\
&\quad + \frac{1}{12}\mathcal{P}^{-}_{(ab)} \langle bc||lm\rangle \sigma^{ade}_{ijk}\sigma^{de*}_{lm} + \frac{1}{12} \langle de||ij\rangle \sigma^{abc}_{klm}\sigma^{de*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} \langle de||jk\rangle \sigma^{abc}_{ilm}\sigma^{de*}_{lm} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle ab||il\rangle \sigma^{cde}_{jkm}\sigma^{de*}_{lm} + \frac{1}{6} \langle ab||kl\rangle \sigma^{cde}_{ijm}\sigma^{de*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} \langle ac||jl\rangle \sigma^{bde}_{ikm}\sigma^{de*}_{lm} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle bc||kl\rangle \sigma^{ade}_{ijm}\sigma^{de*}_{lm} + \frac{1}{3}\mathcal{P}^{-}_{(ijab)} \langle ad||il\rangle \sigma^{bce}_{jkm}\sigma^{de*}_{lm} + \frac{1}{3}\mathcal{P}^{-}_{(ab)} \langle ad||kl\rangle \sigma^{bce}_{ijm}\sigma^{de*}_{lm} \\
&\quad + \frac{1}{3}\mathcal{P}^{-}_{(ij)} \langle cd||il\rangle \sigma^{abe}_{jkm}\sigma^{de*}_{lm} + \frac{1}{3} \langle cd||kl\rangle \sigma^{abe}_{ijm}\sigma^{de*}_{lm} \\
&+ \frac{1}{6} \langle lm||de\rangle \sigma^{ab}_{lm}\sigma^{cde}_{ijk} + \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle lm||de\rangle \sigma^{bc}_{lm}\sigma^{ade}_{ijk} + \frac{1}{6} \langle lm||de\rangle \sigma^{de}_{ij}\sigma^{abc}_{klm}
\end{aligned}
$$

$$
\begin{aligned}
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle lm||de\rangle \sigma^{de}_{jk}\sigma^{abc}_{ilm} + \frac{1}{3}\mathcal{P}^{-}_{(ij)} \langle lm||de\rangle \sigma^{ab}_{il}\sigma^{cde}_{jkm} + \frac{1}{3} \langle lm||de\rangle \sigma^{ab}_{kl}\sigma^{cde}_{ijm} \\
&\quad + \frac{1}{3}\mathcal{P}^{-}_{(ijab)} \langle lm||de\rangle \sigma^{ac}_{jl}\sigma^{bde}_{ikm} + \frac{1}{3}\mathcal{P}^{-}_{(ab)} \langle lm||de\rangle \sigma^{ad}_{ij}\sigma^{bce}_{klm} + \frac{1}{3}\mathcal{P}^{-}_{(ijab)} \langle lm||de\rangle \sigma^{ad}_{jk}\sigma^{bce}_{ilm} \\
&\quad + \frac{1}{3}\mathcal{P}^{-}_{(ab)} \langle lm||de\rangle \sigma^{ad}_{lm}\sigma^{bce}_{ijk} + \frac{1}{3}\mathcal{P}^{-}_{(ab)} \langle lm||de\rangle \sigma^{bc}_{kl}\sigma^{ade}_{ijm} + \frac{1}{3} \langle lm||de\rangle \sigma^{cd}_{ij}\sigma^{abe}_{klm} \\
&\quad + \frac{1}{3}\mathcal{P}^{-}_{(ij)} \langle lm||de\rangle \sigma^{cd}_{jk}\sigma^{abe}_{ilm} + \frac{1}{3} \langle lm||de\rangle \sigma^{cd}_{lm}\sigma^{abe}_{ijk} + \frac{1}{3}\mathcal{P}^{-}_{(ij)} \langle lm||de\rangle \sigma^{de}_{il}\sigma^{abc}_{jkm} \\
&\quad + \frac{1}{3} \langle lm||de\rangle \sigma^{de}_{kl}\sigma^{abc}_{ijm} + \frac{2}{3}\mathcal{P}^{-}_{(ijab)} \langle lm||de\rangle \sigma^{ad}_{il}\sigma^{bce}_{jkm} + \frac{2}{3}\mathcal{P}^{-}_{(ab)} \langle lm||de\rangle \sigma^{ad}_{kl}\sigma^{bce}_{ijm} \\
&\quad + \frac{2}{3}\mathcal{P}^{-}_{(ij)} \langle lm||de\rangle \sigma^{cd}_{il}\sigma^{abe}_{jkm} + \frac{2}{3} \langle lm||de\rangle \sigma^{cd}_{kl}\sigma^{abe}_{ijm} \\
&+ \frac{1}{3}\mathcal{P}^{-}_{(ij)} \langle ab||il\rangle \sigma^{cd}_{jk}\sigma^{d*}_{l} + \frac{1}{3} \langle ab||kl\rangle \sigma^{cd}_{ij}\sigma^{d*}_{l} + \frac{1}{3}\mathcal{P}^{-}_{(ijab)} \langle ac||jl\rangle \sigma^{bd}_{ik}\sigma^{d*}_{l} \\
&\quad + \frac{1}{3}\mathcal{P}^{-}_{(ab)} \langle ad||ij\rangle \sigma^{bc}_{kl}\sigma^{d*}_{l} + \frac{1}{3}\mathcal{P}^{-}_{(ijab)} \langle ad||jk\rangle \sigma^{bc}_{il}\sigma^{d*}_{l} + \frac{1}{3}\mathcal{P}^{-}_{(ab)} \langle bc||kl\rangle \sigma^{ad}_{ij}\sigma^{d*}_{l} \\
&\quad + \frac{1}{3} \langle cd||ij\rangle \sigma^{ab}_{kl}\sigma^{d*}_{l} + \frac{1}{3}\mathcal{P}^{-}_{(ij)} \langle cd||jk\rangle \sigma^{ab}_{il}\sigma^{d*}_{l} \\
&+ \frac{1}{6}\mathcal{P}^{-}_{(abc)} \langle ae||id\rangle \sigma^{bf}_{jk}\sigma^{cd}_{lm}\sigma^{ef*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(abc)} \langle ae||id\rangle \sigma^{bf}_{lm}\sigma^{cd}_{jk}\sigma^{ef*}_{lm} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(abc)} \langle ae||jd\rangle \sigma^{bd}_{ik}\sigma^{cf}_{lm}\sigma^{ef*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(abc)} \langle ae||jd\rangle \sigma^{bd}_{lm}\sigma^{cf}_{ik}\sigma^{ef*}_{lm} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(abc)} \langle ae||kd\rangle \sigma^{bf}_{ij}\sigma^{cd}_{lm}\sigma^{ef*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(abc)} \langle ae||kd\rangle \sigma^{bf}_{lm}\sigma^{cd}_{ij}\sigma^{ef*}_{lm} \\
&\quad + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} \langle al||mn\rangle \sigma^{bc}_{il}\sigma^{de}_{jk}\sigma^{de*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} \langle al||mn\rangle \sigma^{bc}_{kl}\sigma^{de}_{ij}\sigma^{de*}_{mn} \\
&\quad + \frac{1}{12}\mathcal{P}^{-}_{(ij)} \langle cl||mn\rangle \sigma^{ab}_{il}\sigma^{de}_{jk}\sigma^{de*}_{mn} + \frac{1}{12} \langle cl||mn\rangle \sigma^{ab}_{kl}\sigma^{de}_{ij}\sigma^{de*}_{mn} \\
&\quad + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} \langle ef||id\rangle \sigma^{ac}_{lm}\sigma^{bd}_{jk}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} \langle ef||jd\rangle \sigma^{ab}_{lm}\sigma^{cd}_{ik}\sigma^{ef*}_{lm} \\
&\quad + \frac{1}{12}\mathcal{P}^{-}_{(ab)} \langle ef||kd\rangle \sigma^{ac}_{lm}\sigma^{bd}_{ij}\sigma^{ef*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} \langle ae||id\rangle \sigma^{bc}_{lm}\sigma^{df}_{jk}\sigma^{ef*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle ae||kd\rangle \sigma^{bc}_{lm}\sigma^{df}_{ij}\sigma^{ef*}_{lm} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} \langle al||im\rangle \sigma^{bc}_{jl}\sigma^{de}_{kn}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} \langle al||im\rangle \sigma^{bc}_{kn}\sigma^{de}_{jl}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} \langle al||jm\rangle \sigma^{bc}_{ln}\sigma^{de}_{ik}\sigma^{de*}_{mn} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} \langle bl||im\rangle \sigma^{ac}_{jn}\sigma^{de}_{kl}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} \langle bl||im\rangle \sigma^{ac}_{kl}\sigma^{de}_{jn}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle bl||km\rangle \sigma^{ac}_{ln}\sigma^{de}_{ij}\sigma^{de*}_{mn} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle ce||id\rangle \sigma^{ab}_{lm}\sigma^{df}_{jk}\sigma^{ef*}_{lm} + \frac{1}{6} \langle ce||kd\rangle \sigma^{ab}_{lm}\sigma^{df}_{ij}\sigma^{ef*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} \langle cl||im\rangle \sigma^{ab}_{jl}\sigma^{de}_{kn}\sigma^{de*}_{mn} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} \langle cl||im\rangle \sigma^{ab}_{kn}\sigma^{de}_{jl}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle cl||jm\rangle \sigma^{ab}_{ln}\sigma^{de}_{ik}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle dl||ij\rangle \sigma^{ac}_{kl}\sigma^{be}_{mn}\sigma^{de*}_{mn} \\
&\quad + \frac{1}{6}\mathcal{P}^{-}_{(ab)} \langle dl||ij\rangle \sigma^{ac}_{mn}\sigma^{be}_{kl}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle dl||ik\rangle \sigma^{ab}_{jl}\sigma^{ce}_{mn}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ij)} \langle dl||ik\rangle \sigma^{ab}_{mn}\sigma^{ce}_{jl}\sigma^{de*}_{mn}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\langle dl||ik\rangle\,\sigma^{ae}_{jl}\sigma^{bc}_{mn}\sigma^{de*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\langle dl||ik\rangle\,\sigma^{ae}_{mn}\sigma^{bc}_{jl}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle ab||dl\rangle\,\sigma^{cf}_{ik}\sigma^{de}_{jm}\sigma^{ef*}_{lm}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle ab||dl\rangle\,\sigma^{cf}_{jm}\sigma^{de}_{ik}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle ac||dl\rangle\,\sigma^{bf}_{ij}\sigma^{de}_{km}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle ac||dl\rangle\,\sigma^{bf}_{im}\sigma^{de}_{jk}\sigma^{ef*}_{lm}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle ac||dl\rangle\,\sigma^{bf}_{jk}\sigma^{de}_{im}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle ac||dl\rangle\,\sigma^{bf}_{km}\sigma^{de}_{ij}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ij)}\langle ab||dl\rangle\,\sigma^{cd}_{ik}\sigma^{ef}_{jm}\sigma^{ef*}_{lm}\\
&+\frac{1}{6}\mathcal{P}^{-}_{(ij)}\langle ab||dl\rangle\,\sigma^{cd}_{jm}\sigma^{ef}_{ik}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}\langle ac||dl\rangle\,\sigma^{bd}_{ij}\sigma^{ef}_{km}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\langle ac||dl\rangle\,\sigma^{bd}_{im}\sigma^{ef}_{jk}\sigma^{ef*}_{lm}\\
&+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}\langle ac||dl\rangle\,\sigma^{bd}_{jk}\sigma^{ef}_{im}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}\langle ac||dl\rangle\,\sigma^{bd}_{km}\sigma^{ef}_{ij}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}\langle al||mn\rangle\,\sigma^{bd}_{ik}\sigma^{ce}_{jl}\sigma^{de*}_{mn}\\
&+\frac{1}{6}\mathcal{P}^{-}_{(abc)}\langle bl||mn\rangle\,\sigma^{ad}_{ij}\sigma^{ce}_{kl}\sigma^{de*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}\langle bl||mn\rangle\,\sigma^{ad}_{il}\sigma^{ce}_{jk}\sigma^{de*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}\langle ef||id\rangle\,\sigma^{ab}_{jl}\sigma^{cd}_{km}\sigma^{ef*}_{lm}\\
&+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}\langle ef||id\rangle\,\sigma^{ac}_{kl}\sigma^{bd}_{jm}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}\langle ef||id\rangle\,\sigma^{ad}_{jl}\sigma^{bc}_{km}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle ae||id\rangle\,\sigma^{bc}_{jm}\sigma^{df}_{kl}\sigma^{ef*}_{lm}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle ae||dl\rangle\,\sigma^{bc}_{im}\sigma^{df}_{jk}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle ae||dl\rangle\,\sigma^{bc}_{km}\sigma^{df}_{ij}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle ae||dl\rangle\,\sigma^{bd}_{ik}\sigma^{cf}_{jm}\sigma^{ef*}_{lm}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle ae||dl\rangle\,\sigma^{bd}_{jm}\sigma^{cf}_{ik}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle ae||dl\rangle\,\sigma^{bf}_{ij}\sigma^{cd}_{km}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle ae||dl\rangle\,\sigma^{bf}_{im}\sigma^{cd}_{jk}\sigma^{ef*}_{lm}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle ae||dl\rangle\,\sigma^{bf}_{jk}\sigma^{cd}_{im}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle ae||dl\rangle\,\sigma^{bf}_{km}\sigma^{cd}_{ij}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle al||im\rangle\,\sigma^{bd}_{jk}\sigma^{ce}_{ln}\sigma^{de*}_{mn}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ijkabc)}\langle al||im\rangle\,\sigma^{bd}_{jn}\sigma^{ce}_{kl}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle al||km\rangle\,\sigma^{bd}_{ij}\sigma^{ce}_{ln}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle be||id\rangle\,\sigma^{ac}_{km}\sigma^{df}_{jl}\sigma^{ef*}_{lm}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(abc)}\langle bl||jm\rangle\,\sigma^{ad}_{ik}\sigma^{ce}_{ln}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle ce||id\rangle\,\sigma^{ab}_{jm}\sigma^{df}_{kl}\sigma^{ef*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle ce||dl\rangle\,\sigma^{ab}_{im}\sigma^{df}_{jk}\sigma^{ef*}_{lm}\\
&+\frac{1}{3}\langle ce||dl\rangle\,\sigma^{ab}_{km}\sigma^{df}_{ij}\sigma^{ef*}_{lm}+\frac{1}{3}\langle dl||ij\rangle\,\sigma^{ab}_{km}\sigma^{ce}_{ln}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle dl||ij\rangle\,\sigma^{ac}_{lm}\sigma^{be}_{kn}\sigma^{de*}_{mn}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle dl||ik\rangle\,\sigma^{ab}_{lm}\sigma^{ce}_{jn}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle dl||ik\rangle\,\sigma^{ac}_{jm}\sigma^{be}_{ln}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle dl||im\rangle\,\sigma^{ab}_{jn}\sigma^{ce}_{kl}\sigma^{de*}_{mn}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle dl||im\rangle\,\sigma^{ab}_{kl}\sigma^{ce}_{jn}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle dl||im\rangle\,\sigma^{ab}_{ln}\sigma^{ce}_{jk}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle dl||im\rangle\,\sigma^{ac}_{jl}\sigma^{be}_{kn}\sigma^{de*}_{mn}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle dl||im\rangle\,\sigma^{ac}_{kn}\sigma^{be}_{jl}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle dl||im\rangle\,\sigma^{ae}_{jk}\sigma^{bc}_{ln}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle dl||im\rangle\,\sigma^{ae}_{jn}\sigma^{bc}_{kl}\sigma^{de*}_{mn}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}\langle dl||im\rangle\,\sigma^{ae}_{kl}\sigma^{bc}_{jn}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}\langle dl||jk\rangle\,\sigma^{ab}_{im}\sigma^{ce}_{ln}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}\langle dl||jk\rangle\,\sigma^{ac}_{lm}\sigma^{be}_{in}\sigma^{de*}_{mn}\\
&+\frac{1}{3}\langle dl||km\rangle\,\sigma^{ab}_{ln}\sigma^{ce}_{ij}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle dl||km\rangle\,\sigma^{ae}_{ij}\sigma^{bc}_{ln}\sigma^{de*}_{mn}+\frac{1}{3}\mathcal{P}^{-}_{(ijkabc)}\langle ae||id\rangle\,\sigma^{bd}_{jl}\sigma^{cf}_{km}\sigma^{ef*}_{lm}\\
&-\frac{1}{12}\langle ef||kd\rangle\,\sigma^{ab}_{lm}\sigma^{cd}_{ij}\sigma^{ef*}_{lm}-\frac{1}{6}\langle dl||ij\rangle\,\sigma^{ab}_{kl}\sigma^{ce}_{mn}\sigma^{de*}_{mn}-\frac{1}{6}\langle dl||ij\rangle\,\sigma^{ab}_{mn}\sigma^{ce}_{kl}\sigma^{de*}_{mn}\\
&-\frac{1}{6}\langle ab||dl\rangle\,\sigma^{cd}_{ij}\sigma^{ef}_{km}\sigma^{ef*}_{lm}-\frac{1}{6}\langle ab||dl\rangle\,\sigma^{cd}_{km}\sigma^{ef}_{ij}\sigma^{ef*}_{lm}-\frac{1}{6}\langle cl||km\rangle\,\sigma^{ab}_{ln}\sigma^{de}_{ij}\sigma^{de*}_{mn}\\
&-\frac{1}{3}\langle dl||ij\rangle\,\sigma^{ab}_{lm}\sigma^{ce}_{kn}\sigma^{de*}_{mn}-\frac{1}{3}\mathcal{P}^{-}_{(ab)}\langle dl||ij\rangle\,\sigma^{ac}_{km}\sigma^{be}_{ln}\sigma^{de*}_{mn}-\frac{1}{3}\langle ab||dl\rangle\,\sigma^{cf}_{ij}\sigma^{de}_{km}\sigma^{ef*}_{lm}
\end{aligned}
$$

$$
\begin{aligned}
& - \frac{1}{3} \langle ab||dl\rangle \sigma_{km}^{cf} \sigma_{ij}^{de} \sigma_{lm}^{ef*} \\
& + \frac{1}{2}\mathcal{P}_{(ij)}^{-} \langle ab||jd\rangle \sigma_{ikl}^{cde} \sigma_{l}^{e*} + \frac{1}{2}\mathcal{P}_{(ijab)}^{-} \langle ac||id\rangle \sigma_{jkl}^{bde} \sigma_{l}^{e*} + \frac{1}{2}\mathcal{P}_{(ab)}^{-} \langle ac||kd\rangle \sigma_{ijl}^{bde} \sigma_{l}^{e*} \\
& + \frac{1}{2}\mathcal{P}_{(ab)}^{-} \langle al||ij\rangle \sigma_{klm}^{bcd} \sigma_{m}^{d*} + \frac{1}{2}\mathcal{P}_{(ijab)}^{-} \langle al||jk\rangle \sigma_{ilm}^{bcd} \sigma_{m}^{d*} + \frac{1}{2} \langle cl||ij\rangle \sigma_{klm}^{abd} \sigma_{m}^{d*} \\
& + \frac{1}{2}\mathcal{P}_{(ij)}^{-} \langle cl||jk\rangle \sigma_{ilm}^{abd} \sigma_{m}^{d*} + \mathcal{P}_{(ab)}^{-} \langle ac||dl\rangle \sigma_{ijk}^{bde} \sigma_{l}^{e*} + \mathcal{P}_{(ab)}^{-} \langle ae||dl\rangle \sigma_{ijk}^{bcd} \sigma_{l}^{e*} \\
& + \mathcal{P}_{(ijab)}^{-} \langle al||jm\rangle \sigma_{ikl}^{bcd} \sigma_{m}^{d*} + \mathcal{P}_{(ab)}^{-} \langle bl||km\rangle \sigma_{ijl}^{acd} \sigma_{m}^{d*} + \langle ce||dl\rangle \sigma_{ijk}^{abd} \sigma_{l}^{e*} \\
& + \mathcal{P}_{(ij)}^{-} \langle cl||jm\rangle \sigma_{ikl}^{abd} \sigma_{m}^{d*} + \mathcal{P}_{(ij)}^{-} \langle dl||ik\rangle \sigma_{jlm}^{abc} \sigma_{m}^{d*} + \mathcal{P}_{(ij)}^{-} \langle dl||im\rangle \sigma_{jkl}^{abc} \sigma_{m}^{d*} \\
& + \langle dl||km\rangle \sigma_{ijl}^{abc} \sigma_{m}^{d*} + \mathcal{P}_{(ijab)}^{-} \langle ae||id\rangle \sigma_{jkl}^{bcd} \sigma_{l}^{e*} + \mathcal{P}_{(ab)}^{-} \langle ae||kd\rangle \sigma_{ijl}^{bcd} \sigma_{l}^{e*} \\
& + \mathcal{P}_{(ij)}^{-} \langle ce||id\rangle \sigma_{jkl}^{abd} \sigma_{l}^{e*} + \langle ce||kd\rangle \sigma_{ijl}^{abd} \sigma_{l}^{e*} - \frac{1}{2} \langle ab||kd\rangle \sigma_{ijl}^{cde} \sigma_{l}^{e*} \\
& - \langle ab||dl\rangle \sigma_{ijk}^{cde} \sigma_{l}^{e*} - \langle cl||km\rangle \sigma_{ijl}^{abd} \sigma_{m}^{d*} - \langle dl||ij\rangle \sigma_{klm}^{abc} \sigma_{m}^{d*} \\
& + \frac{1}{2}\mathcal{P}_{(abc)}^{-} \langle al||de\rangle \sigma_{l}^{c} \sigma_{ijk}^{bde} + \frac{1}{2}\mathcal{P}_{(ijk)}^{-} \langle lm||id\rangle \sigma_{j}^{d} \sigma_{klm}^{abc} + \mathcal{P}_{(ijab)}^{-} \langle al||de\rangle \sigma_{i}^{d} \sigma_{jkl}^{bce} \\
& + \mathcal{P}_{(ab)}^{-} \langle al||de\rangle \sigma_{k}^{d} \sigma_{ijl}^{bce} + \mathcal{P}_{(ij)}^{-} \langle cl||de\rangle \sigma_{i}^{d} \sigma_{jkl}^{abe} + \langle cl||de\rangle \sigma_{k}^{d} \sigma_{ijl}^{abe} \\
& + \mathcal{P}_{(ijab)}^{-} \langle lm||id\rangle \sigma_{l}^{b} \sigma_{jkm}^{acd} + \mathcal{P}_{(ij)}^{-} \langle lm||id\rangle \sigma_{l}^{d} \sigma_{jkm}^{abc} + \mathcal{P}_{(ij)}^{-} \langle lm||jd\rangle \sigma_{l}^{c} \sigma_{ikm}^{abd} \\
& + \mathcal{P}_{(ab)}^{-} \langle lm||kd\rangle \sigma_{l}^{b} \sigma_{ijm}^{acd} + \langle lm||kd\rangle \sigma_{l}^{d} \sigma_{ijm}^{abc} + \mathcal{P}_{(ab)}^{-} \langle bl||de\rangle \sigma_{l}^{d} \sigma_{ijk}^{ace} \\
& - \langle cl||de\rangle \sigma_{l}^{d} \sigma_{ijk}^{abe} - \langle lm||kd\rangle \sigma_{l}^{c} \sigma_{ijm}^{abd} \\
= {} & 0
\end{aligned}
$$

C.2.2. PP-UCC4 Secular matrix

PP-UCC4 secular matrix singles/singles block:

$$
\begin{aligned}
&\langle \Phi_i^a | \bar{H} - E_0 | \Phi_j^b \rangle \ = \\
&\quad - \langle aj||bi \rangle \\
&\quad + \frac{1}{2} \langle ac||ik \rangle \, \sigma_{jk}^{bc*} \\
&\quad + \frac{1}{2} \langle jk||bc \rangle \, \sigma_{ik}^{ac} \\
&\quad + f_{ab}\delta_{ij} - f_{ji}\delta_{ab} \\
&\quad - \langle aj||bc \rangle \, \sigma_i^c - \langle jk||bi \rangle \, \sigma_k^a \\
&\quad - \langle aj||ik \rangle \, \sigma_k^{b*} - \langle ac||bi \rangle \, \sigma_j^{c*} \\
&\quad + \langle ac||bk \rangle \, \sigma_k^{c*}\delta_{ij} - \langle jc||ik \rangle \, \sigma_k^{c*}\delta_{ab} \\
&\quad + \langle ak||bc \rangle \, \sigma_k^{c}\delta_{ij} - \langle jk||ic \rangle \, \sigma_k^{c}\delta_{ab} \\
&\quad - \frac{1}{4} \langle ac||kl \rangle \, \sigma_{kl}^{bc*}\delta_{ij} - \frac{1}{4} \langle cd||ik \rangle \, \sigma_{jk}^{cd*}\delta_{ab} \\
&\quad - \frac{1}{4} \langle jk||cd \rangle \, \sigma_{ik}^{cd}\delta_{ab} - \frac{1}{4} \langle kl||bc \rangle \, \sigma_{kl}^{ac}\delta_{ij} \\
&\quad - f_{ak}\sigma_k^{b*}\delta_{ij} - f_{ci}\sigma_j^{c*}\delta_{ab} \\
&\quad - f_{jc}\sigma_i^{c}\delta_{ab} - f_{kb}\sigma_k^{a}\delta_{ij} \\
&\quad + \frac{1}{4} \langle aj||bk \rangle \, \sigma_{il}^{cd}\sigma_{kl}^{cd*} + \frac{1}{4} \langle ae||cd \rangle \, \sigma_{ik}^{cd}\sigma_{jk}^{be*} + \frac{1}{4} \langle ak||bi \rangle \, \sigma_{kl}^{cd}\sigma_{jl}^{cd*} \\
&\qquad + \frac{1}{4} \langle jk||lm \rangle \, \sigma_{ik}^{ac}\sigma_{lm}^{bc*} + \frac{1}{4} \langle de||bc \rangle \, \sigma_{ik}^{ac}\sigma_{jk}^{de*} + \frac{1}{4} \langle kl||im \rangle \, \sigma_{kl}^{ac}\sigma_{jm}^{bc*} \\
&\qquad + \frac{1}{2} \langle ak||bl \rangle \, \sigma_{ik}^{cd}\sigma_{jl}^{cd*} + \frac{1}{2} \langle jd||ic \rangle \, \sigma_{kl}^{ac}\sigma_{kl}^{bd*} + \frac{1}{2} \langle jd||ck \rangle \, \sigma_{il}^{ac}\sigma_{kl}^{bd*} \\
&\qquad + \frac{1}{2} \langle dk||ic \rangle \, \sigma_{kl}^{ac}\sigma_{jl}^{bd*} - \frac{1}{4} \langle aj||ic \rangle \, \sigma_{kl}^{cd}\sigma_{kl}^{bd*} - \frac{1}{4} \langle jc||bi \rangle \, \sigma_{kl}^{ad}\sigma_{kl}^{cd*} \\
&\qquad - \frac{1}{2} \langle ak||cl \rangle \, \sigma_{ik}^{cd}\sigma_{jl}^{bd*} - \frac{1}{2} \langle ck||bl \rangle \, \sigma_{ik}^{ad}\sigma_{jl}^{cd*} - \langle aj||ck \rangle \, \sigma_{il}^{cd}\sigma_{kl}^{bd*} \\
&\qquad - \langle ad||bc \rangle \, \sigma_{ik}^{ce}\sigma_{jk}^{de*} - \langle jk||il \rangle \, \sigma_{km}^{ac}\sigma_{lm}^{bc*} - \langle ck||bi \rangle \, \sigma_{kl}^{ad}\sigma_{jl}^{cd*} \\
&\quad + \frac{1}{2} \langle ac||bk \rangle \, \sigma_i^{d}\sigma_{jk}^{cd*} + \frac{1}{2} \langle ad||ic \rangle \, \sigma_k^{c}\sigma_{jk}^{bd*} + \frac{1}{2} \langle ad||ck \rangle \, \sigma_i^{c}\sigma_{jk}^{bd*}
\end{aligned}
$$

$$
\begin{aligned}
&\quad + \frac{1}{2} \langle ck||il\rangle \, \sigma_{k}^{a}\sigma_{jl}^{bc*} - \frac{1}{4} \langle aj||kl\rangle \, \sigma_{i}^{c}\sigma_{kl}^{bc*} - \frac{1}{4} \langle cd||bi\rangle \, \sigma_{k}^{a}\sigma_{jk}^{cd*} \\
&\quad - \frac{1}{2} \langle aj||ik\rangle \, \sigma_{l}^{c}\sigma_{kl}^{bc*} - \frac{1}{2} \langle ac||bi\rangle \, \sigma_{k}^{d}\sigma_{jk}^{cd*} - \frac{1}{2} \langle ak||il\rangle \, \sigma_{k}^{c}\sigma_{jl}^{bc*} \\
&\quad - \frac{1}{2} \langle jc||ik\rangle \, \sigma_{l}^{a}\sigma_{kl}^{bc*} \\
&+ \frac{1}{2} \langle ak||bc\rangle \, \sigma_{ik}^{cd}\sigma_{j}^{d*} + \frac{1}{2} \langle jd||bc\rangle \, \sigma_{ik}^{ac}\sigma_{k}^{d*} + \frac{1}{2} \langle jk||cl\rangle \, \sigma_{ik}^{ac}\sigma_{l}^{b*} \\
&\quad + \frac{1}{2} \langle dk||bc\rangle \, \sigma_{ik}^{ac}\sigma_{j}^{d*} - \frac{1}{4} \langle aj||cd\rangle \, \sigma_{ik}^{cd}\sigma_{k}^{b*} - \frac{1}{4} \langle kl||bi\rangle \, \sigma_{kl}^{ac}\sigma_{j}^{c*} \\
&\quad - \frac{1}{2} \langle aj||bc\rangle \, \sigma_{ik}^{cd}\sigma_{k}^{d*} - \frac{1}{2} \langle jk||bi\rangle \, \sigma_{kl}^{ac}\sigma_{l}^{c*} - \frac{1}{2} \langle jk||bl\rangle \, \sigma_{ik}^{ac}\sigma_{l}^{c*} \\
&\quad - \frac{1}{2} \langle jk||ic\rangle \, \sigma_{kl}^{ac}\sigma_{l}^{b*} \\
&+ \frac{1}{4} \langle jd||bc\rangle \, \sigma_{ikl}^{ace}\sigma_{kl}^{de*} + \frac{1}{8} \langle kl||bm\rangle \, \sigma_{ikl}^{acd}\sigma_{jm}^{cd*} + \frac{1}{2} \langle jk||cl\rangle \, \sigma_{ikm}^{acd}\sigma_{lm}^{bd*} \\
&\quad + \frac{1}{2} \langle dk||bc\rangle \, \sigma_{ikl}^{ace}\sigma_{jl}^{de*} + \frac{1}{4} \langle ak||bc\rangle \, \sigma_{ikl}^{cde}\sigma_{jl}^{de*} - \frac{1}{8} \langle aj||cd\rangle \, \sigma_{ikl}^{cde}\sigma_{kl}^{be*} \\
&\quad - \frac{1}{8} \langle jk||bi\rangle \, \sigma_{klm}^{acd}\sigma_{lm}^{cd*} - \frac{1}{4} \langle jk||ic\rangle \, \sigma_{klm}^{acd}\sigma_{lm}^{bd*} - \frac{1}{4} \langle jk||bl\rangle \, \sigma_{ikm}^{acd}\sigma_{lm}^{cd*} \\
&\quad - \frac{1}{8} \langle aj||bc\rangle \, \sigma_{ikl}^{cde}\sigma_{kl}^{de*} - \frac{1}{8} \langle je||cd\rangle \, \sigma_{ikl}^{acd}\sigma_{kl}^{be*} - \frac{1}{8} \langle kl||bi\rangle \, \sigma_{klm}^{acd}\sigma_{jm}^{cd*} \\
&+ \frac{1}{2} \langle ck||il\rangle \, \sigma_{km}^{ad}\sigma_{jlm}^{bcd*} + \frac{1}{4} \langle ac||bk\rangle \, \sigma_{il}^{de}\sigma_{jkl}^{cde*} + \frac{1}{8} \langle ak||lm\rangle \, \sigma_{ik}^{cd}\sigma_{jlm}^{bcd*} \\
&\quad + \frac{1}{4} \langle ad||ic\rangle \, \sigma_{kl}^{ce}\sigma_{jkl}^{bde*} + \frac{1}{2} \langle ad||ck\rangle \, \sigma_{il}^{ce}\sigma_{jkl}^{bde*} - \frac{1}{8} \langle aj||ik\rangle \, \sigma_{lm}^{cd}\sigma_{klm}^{bcd*} \\
&\quad - \frac{1}{8} \langle aj||kl\rangle \, \sigma_{im}^{cd}\sigma_{klm}^{bcd*} - \frac{1}{4} \langle jc||ik\rangle \, \sigma_{lm}^{ad}\sigma_{klm}^{bcd*} - \frac{1}{8} \langle cd||bi\rangle \, \sigma_{kl}^{ae}\sigma_{jkl}^{cde*} \\
&\quad - \frac{1}{8} \langle de||ic\rangle \, \sigma_{kl}^{ac}\sigma_{jkl}^{bde*} - \frac{1}{4} \langle ak||il\rangle \, \sigma_{km}^{cd}\sigma_{jlm}^{bcd*} - \frac{1}{8} \langle ac||bi\rangle \, \sigma_{kl}^{de}\sigma_{jkl}^{cde*} \\
&+ \frac{1}{4} \langle ak||lm\rangle \, \sigma_{k}^{c}\sigma_{lm}^{bc*}\delta_{ij} + \frac{1}{2} \langle ac||bk\rangle \, \sigma_{l}^{d}\sigma_{kl}^{cd*}\delta_{ij} + \frac{1}{2} \langle ad||ck\rangle \, \sigma_{l}^{c}\sigma_{kl}^{bd*}\delta_{ij} \\
&\quad + \frac{1}{2} \langle ck||il\rangle \, \sigma_{k}^{d}\sigma_{jl}^{cd*}\delta_{ab} - \frac{1}{4} \langle de||ic\rangle \, \sigma_{k}^{c}\sigma_{jk}^{de*}\delta_{ab} - \frac{1}{2} \langle jc||ik\rangle \, \sigma_{l}^{d}\sigma_{kl}^{cd*}\delta_{ab} \\
&+ \frac{1}{4} \langle kl||bm\rangle \, \sigma_{kl}^{ac}\sigma_{m}^{c*}\delta_{ij} + \frac{1}{2} \langle ak||bc\rangle \, \sigma_{kl}^{cd}\sigma_{l}^{d*}\delta_{ij} + \frac{1}{2} \langle jk||cl\rangle \, \sigma_{ik}^{cd}\sigma_{l}^{d*}\delta_{ab} \\
&\quad + \frac{1}{2} \langle dk||bc\rangle \, \sigma_{kl}^{ac}\sigma_{l}^{d*}\delta_{ij} - \frac{1}{4} \langle je||cd\rangle \, \sigma_{ik}^{cd}\sigma_{k}^{e*}\delta_{ab} - \frac{1}{2} \langle jk||ic\rangle \, \sigma_{kl}^{cd}\sigma_{l}^{d*}\delta_{ab} \\
&+ \frac{1}{2} \langle ad||bc\rangle \, \sigma_{kl}^{ce}\sigma_{kl}^{de*}\delta_{ij} + \frac{1}{2} \langle ak||cl\rangle \, \sigma_{km}^{cd}\sigma_{lm}^{bd*}\delta_{ij} + \frac{1}{2} \langle jk||il\rangle \, \sigma_{km}^{cd}\sigma_{lm}^{cd*}\delta_{ab} \\
&\quad + \frac{1}{2} \langle ck||bl\rangle \, \sigma_{km}^{ad}\sigma_{lm}^{cd*}\delta_{ij} - \frac{1}{8} \langle ae||cd\rangle \, \sigma_{kl}^{cd}\sigma_{kl}^{be*}\delta_{ij} - \frac{1}{8} \langle jk||lm\rangle \, \sigma_{ik}^{cd}\sigma_{lm}^{cd*}\delta_{ab}
\end{aligned}
$$

$$- \frac{1}{8} \langle de||bc \rangle \sigma_{kl}^{ac} \sigma_{kl}^{de*} \delta_{ij} - \frac{1}{8} \langle kl||im \rangle \sigma_{kl}^{cd} \sigma_{jm}^{cd*} \delta_{ab} - \frac{1}{2} \langle ak||bl \rangle \sigma_{km}^{cd} \sigma_{lm}^{cd*} \delta_{ij}$$

$$- \frac{1}{2} \langle jd||ic \rangle \sigma_{kl}^{ce} \sigma_{kl}^{de*} \delta_{ab} - \frac{1}{2} \langle jd||ck \rangle \sigma_{il}^{ce} \sigma_{kl}^{de*} \delta_{ab} - \frac{1}{2} \langle dk||ic \rangle \sigma_{kl}^{ce} \sigma_{jl}^{de*} \delta_{ab}$$

$$+ \frac{1}{4} \langle dk||bc \rangle \sigma_{klm}^{ace} \sigma_{lm}^{de*} \delta_{ij} + \frac{1}{4} \langle jk||cl \rangle \sigma_{ikm}^{cde} \sigma_{lm}^{de*} \delta_{ab} + \frac{1}{8} \langle ak||bc \rangle \sigma_{klm}^{cde} \sigma_{lm}^{de*} \delta_{ij}$$

$$+ \frac{1}{8} \langle kl||bm \rangle \sigma_{kln}^{acd} \sigma_{mn}^{cd*} \delta_{ij} - \frac{1}{8} \langle je||cd \rangle \sigma_{ikl}^{cdf} \sigma_{kl}^{ef*} \delta_{ab} - \frac{1}{8} \langle jk||ic \rangle \sigma_{klm}^{cde} \sigma_{lm}^{de*} \delta_{ab}$$

$$+ \frac{1}{8} \langle ac||bk \rangle \sigma_{lm}^{de} \sigma_{klm}^{cde*} \delta_{ij} + \frac{1}{4} \langle ck||il \rangle \sigma_{km}^{de} \sigma_{jlm}^{cde*} \delta_{ab} + \frac{1}{8} \langle ak||lm \rangle \sigma_{kn}^{cd} \sigma_{lmn}^{bcd*} \delta_{ij}$$

$$+ \frac{1}{4} \langle ad||ck \rangle \sigma_{lm}^{ce} \sigma_{klm}^{bde*} \delta_{ij} - \frac{1}{8} \langle jc||ik \rangle \sigma_{lm}^{de} \sigma_{klm}^{cde*} \delta_{ab} - \frac{1}{8} \langle de||ic \rangle \sigma_{kl}^{cf} \sigma_{jkl}^{def*} \delta_{ab}$$

$$\frac{1}{2} \langle jk||cd \rangle \sigma_{km}^{ad} \sigma_{il}^{ce} \sigma_{lm}^{be*} + \frac{1}{8} \langle jk||bc \rangle \sigma_{lm}^{ac} \sigma_{ik}^{de} \sigma_{lm}^{de*} + \frac{1}{16} \langle jk||bc \rangle \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{lm}^{de*}$$

$$+ \frac{1}{4} \langle kl||bc \rangle \sigma_{lm}^{ac} \sigma_{ik}^{de} \sigma_{jm}^{de*} + \frac{1}{4} \langle kl||bc \rangle \sigma_{kl}^{ae} \sigma_{im}^{cd} \sigma_{jm}^{de*} + \frac{1}{12} \langle jk||cd \rangle \sigma_{ik}^{ae} \sigma_{lm}^{cd} \sigma_{lm}^{be*}$$

$$+ \frac{1}{12} \langle kl||bc \rangle \sigma_{im}^{ac} \sigma_{kl}^{de} \sigma_{jm}^{de*} + \frac{1}{48} \langle kl||cd \rangle \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{jm}^{be*} + \frac{1}{6} \langle jk||bc \rangle \sigma_{ik}^{ae} \sigma_{lm}^{cd} \sigma_{lm}^{de*}$$

$$+ \frac{1}{2} \langle kl||bc \rangle \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{jm}^{de*} + \frac{1}{6} \langle jk||bc \rangle \sigma_{im}^{ac} \sigma_{kl}^{de} \sigma_{lm}^{de*} + \frac{1}{24} \langle kl||cd \rangle \sigma_{kl}^{ae} \sigma_{im}^{cd} \sigma_{jm}^{be*}$$

$$- \frac{1}{16} \langle jk||bc \rangle \sigma_{km}^{ac} \sigma_{il}^{de} \sigma_{lm}^{de*} - \frac{1}{4} \langle jk||cd \rangle \sigma_{lm}^{ad} \sigma_{ik}^{ce} \sigma_{lm}^{be*} + \langle kl||cd \rangle \sigma_{im}^{ad} \sigma_{kl}^{ce} \sigma_{jm}^{be*}$$

$$+ \langle kl||cd \rangle \sigma_{il}^{ae} \sigma_{km}^{cd} \sigma_{jm}^{be*} - \frac{1}{8} \langle kl||cd \rangle \sigma_{il}^{ad} \sigma_{km}^{ce} \sigma_{jm}^{be*} - \frac{1}{3} \langle kl||bc \rangle \sigma_{il}^{ae} \sigma_{km}^{cd} \sigma_{jm}^{de*}$$

$$- \frac{1}{48} \langle jk||cd \rangle \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{lm}^{be*} - \frac{1}{4} \langle jk||cd \rangle \sigma_{km}^{ae} \sigma_{il}^{cd} \sigma_{lm}^{be*} - \frac{1}{2} \langle jk||bc \rangle \sigma_{km}^{ae} \sigma_{il}^{cd} \sigma_{lm}^{de*}$$

$$- \frac{1}{3} \langle jk||cd \rangle \sigma_{im}^{ad} \sigma_{kl}^{ce} \sigma_{lm}^{be*} - \frac{1}{6} \langle kl||cd \rangle \sigma_{lm}^{ad} \sigma_{ik}^{ce} \sigma_{jm}^{be*} - \frac{5}{48} \langle jk||cd \rangle \sigma_{ik}^{ad} \sigma_{lm}^{ce} \sigma_{lm}^{be*}$$

$$- \frac{5}{48} \langle kl||bc \rangle \sigma_{il}^{ac} \sigma_{km}^{de} \sigma_{jm}^{de*} - \frac{1}{48} \langle kl||bc \rangle \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{jm}^{de*} - \frac{1}{24} \langle jk||bc \rangle \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{lm}^{de*}$$

$$- \frac{1}{48} \langle kl||cd \rangle \sigma_{kl}^{ad} \sigma_{im}^{ce} \sigma_{jm}^{be*}$$

$$+ \frac{1}{2} \langle cd||ik \rangle \sigma_{lm}^{ae} \sigma_{km}^{bd*} \sigma_{jl}^{ce*} + \frac{1}{8} \langle ac||ik \rangle \sigma_{lm}^{de} \sigma_{lm}^{bc*} \sigma_{jk}^{de*} + \frac{1}{16} \langle ac||ik \rangle \sigma_{lm}^{de} \sigma_{lm}^{be*} \sigma_{jk}^{cd*}$$

$$+ \frac{1}{4} \langle ac||kl \rangle \sigma_{im}^{de} \sigma_{lm}^{bc*} \sigma_{jk}^{de*} + \frac{1}{4} \langle ac||kl \rangle \sigma_{im}^{de} \sigma_{kl}^{be*} \sigma_{jm}^{cd*} + \frac{1}{12} \langle ac||kl \rangle \sigma_{im}^{de} \sigma_{jm}^{bc*} \sigma_{kl}^{de*}$$

$$+ \frac{1}{12} \langle cd||ik \rangle \sigma_{lm}^{ae} \sigma_{jk}^{be*} \sigma_{lm}^{cd*} + \frac{1}{6} \langle ac||ik \rangle \sigma_{lm}^{de} \sigma_{jk}^{be*} \sigma_{lm}^{cd*} + \frac{1}{48} \langle cd||kl \rangle \sigma_{im}^{ae} \sigma_{lm}^{be*} \sigma_{jk}^{cd*}$$

$$+ \frac{1}{2} \langle ac||kl \rangle \sigma_{im}^{de} \sigma_{lm}^{be*} \sigma_{jk}^{cd*} + \frac{1}{6} \langle ac||ik \rangle \sigma_{lm}^{de} \sigma_{jm}^{bc*} \sigma_{kl}^{de*} + \frac{1}{24} \langle cd||kl \rangle \sigma_{im}^{ae} \sigma_{kl}^{be*} \sigma_{jm}^{cd*}$$

$$- \frac{1}{16} \langle ac||ik \rangle \sigma_{lm}^{de} \sigma_{km}^{bc*} \sigma_{jl}^{de*} + \langle cd||kl \rangle \sigma_{im}^{ae} \sigma_{jm}^{bd*} \sigma_{kl}^{ce*} + \langle cd||kl \rangle \sigma_{im}^{ae} \sigma_{jl}^{be*} \sigma_{km}^{cd*}$$

$$
\begin{aligned}
&-\frac{1}{48}\langle cd||ik\rangle\,\sigma^{ae}_{lm}\sigma^{be*}_{jm}\sigma^{cd*}_{kl}-\frac{1}{24}\langle ac||ik\rangle\,\sigma^{de}_{lm}\sigma^{be*}_{jm}\sigma^{cd*}_{kl}-\frac{1}{8}\langle cd||kl\rangle\,\sigma^{ae}_{im}\sigma^{bd*}_{jl}\sigma^{ce*}_{km}\\
&-\frac{1}{48}\langle ac||kl\rangle\,\sigma^{de}_{im}\sigma^{be*}_{jm}\sigma^{cd*}_{kl}-\frac{1}{3}\langle cd||ik\rangle\,\sigma^{ae}_{lm}\sigma^{bd*}_{jm}\sigma^{ce*}_{kl}-\frac{5}{48}\langle ac||kl\rangle\,\sigma^{de}_{im}\sigma^{bc*}_{jl}\sigma^{de*}_{km}\\
&-\frac{1}{4}\langle cd||ik\rangle\,\sigma^{ae}_{lm}\sigma^{be*}_{km}\sigma^{cd*}_{jl}-\frac{1}{4}\langle cd||ik\rangle\,\sigma^{ae}_{lm}\sigma^{bd*}_{lm}\sigma^{ce*}_{jk}-\frac{1}{2}\langle ac||ik\rangle\,\sigma^{de}_{lm}\sigma^{be*}_{km}\sigma^{cd*}_{jl}\\
&-\frac{1}{3}\langle ac||kl\rangle\,\sigma^{de}_{im}\sigma^{be*}_{jl}\sigma^{cd*}_{km}-\frac{1}{6}\langle cd||kl\rangle\,\sigma^{ae}_{im}\sigma^{bd*}_{lm}\sigma^{ce*}_{jk}-\frac{1}{48}\langle cd||kl\rangle\,\sigma^{ae}_{im}\sigma^{bd*}_{kl}\sigma^{ce*}_{jm}\\
&-\frac{5}{48}\langle cd||ik\rangle\,\sigma^{ae}_{lm}\sigma^{bd*}_{jk}\sigma^{ce*}_{lm}
\end{aligned}
$$

$$
\begin{aligned}
&+\langle cd||kl\rangle\,\sigma^{ae}_{mn}\sigma^{bd*}_{mn}\sigma^{ce*}_{kl}\delta_{ij}+\langle cd||kl\rangle\,\sigma^{ef}_{im}\sigma^{cd*}_{km}\sigma^{ef*}_{jl}\delta_{ab}+\frac{1}{3}\langle ac||kl\rangle\,\sigma^{de}_{mn}\sigma^{be*}_{ln}\sigma^{cd*}_{km}\delta_{ij}\\
&+\frac{1}{6}\langle ac||kl\rangle\,\sigma^{de}_{mn}\sigma^{bc*}_{ln}\sigma^{de*}_{km}\delta_{ij}+\frac{1}{96}\langle ac||kl\rangle\,\sigma^{de}_{mn}\sigma^{be*}_{mn}\sigma^{cd*}_{kl}\delta_{ij}+\frac{1}{96}\langle cd||ik\rangle\,\sigma^{ef}_{lm}\sigma^{cd*}_{kl}\sigma^{ef*}_{jm}\delta_{ab}\\
&+\frac{1}{6}\langle cd||ik\rangle\,\sigma^{ef}_{lm}\sigma^{ce*}_{lm}\sigma^{df*}_{jk}\delta_{ab}+\frac{1}{3}\langle cd||ik\rangle\,\sigma^{ef}_{lm}\sigma^{ce*}_{kl}\sigma^{df*}_{jm}\delta_{ab}+\langle cd||kl\rangle\,\sigma^{ae}_{mn}\sigma^{be*}_{kl}\sigma^{cd*}_{mn}\delta_{ij}\\
&+\langle cd||kl\rangle\,\sigma^{ef}_{im}\sigma^{cd*}_{jm}\sigma^{ef*}_{kl}\delta_{ab}+\langle cd||kl\rangle\,\sigma^{ef}_{im}\sigma^{ce*}_{kl}\sigma^{df*}_{jm}\delta_{ab}+\langle cd||kl\rangle\,\sigma^{ae}_{mn}\sigma^{be*}_{ln}\sigma^{cd*}_{km}\delta_{ij}\\
&+\langle cd||kl\rangle\,\sigma^{ae}_{mn}\sigma^{bd*}_{ln}\sigma^{ce*}_{km}\delta_{ij}+\langle cd||kl\rangle\,\sigma^{ef}_{im}\sigma^{ce*}_{km}\sigma^{df*}_{jl}\delta_{ab}-\frac{1}{24}\langle ac||kl\rangle\,\sigma^{de}_{mn}\sigma^{bc*}_{mn}\sigma^{de*}_{kl}\delta_{ij}\\
&-\frac{1}{24}\langle cd||ik\rangle\,\sigma^{ef}_{lm}\sigma^{cd*}_{lm}\sigma^{ef*}_{jk}\delta_{ab}-\frac{1}{12}\langle ac||kl\rangle\,\sigma^{de}_{mn}\sigma^{be*}_{kl}\sigma^{cd*}_{mn}\delta_{ij}-\frac{1}{32}\langle cd||kl\rangle\,\sigma^{ae}_{mn}\sigma^{bd*}_{kl}\sigma^{ce*}_{mn}\delta_{ij}\\
&-\frac{1}{12}\langle cd||ik\rangle\,\sigma^{ef}_{lm}\sigma^{cd*}_{jm}\sigma^{ef*}_{kl}\delta_{ab}-\frac{1}{32}\langle cd||kl\rangle\,\sigma^{ef}_{im}\sigma^{cd*}_{jl}\sigma^{ef*}_{km}\delta_{ab}
\end{aligned}
$$

$$
\begin{aligned}
&+\langle kl||cd\rangle\,\sigma^{cd}_{km}\sigma^{ef}_{il}\sigma^{ef*}_{jm}\delta_{ab}+\langle kl||cd\rangle\,\sigma^{ad}_{ln}\sigma^{ce}_{km}\sigma^{be*}_{mn}\delta_{ij}+\frac{1}{3}\langle jk||cd\rangle\,\sigma^{ce}_{kl}\sigma^{df}_{im}\sigma^{ef*}_{lm}\delta_{ab}\\
&+\frac{1}{96}\langle kl||bc\rangle\,\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{de*}_{mn}\delta_{ij}+\frac{1}{3}\langle kl||bc\rangle\,\sigma^{ae}_{ln}\sigma^{cd}_{km}\sigma^{de*}_{mn}\delta_{ij}+\frac{1}{6}\langle jk||cd\rangle\,\sigma^{ce}_{lm}\sigma^{df}_{ik}\sigma^{ef*}_{lm}\delta_{ab}\\
&+\frac{1}{96}\langle jk||cd\rangle\,\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{ef*}_{lm}\delta_{ab}+\frac{1}{6}\langle kl||bc\rangle\,\sigma^{ac}_{ln}\sigma^{de}_{km}\sigma^{de*}_{mn}\delta_{ij}+\langle kl||cd\rangle\,\sigma^{ae}_{kl}\sigma^{cd}_{mn}\sigma^{be*}_{mn}\delta_{ij}\\
&+\langle kl||cd\rangle\,\sigma^{cd}_{im}\sigma^{ef}_{kl}\sigma^{ef*}_{jm}\delta_{ab}-\frac{1}{32}\langle kl||cd\rangle\,\sigma^{ad}_{kl}\sigma^{ce}_{mn}\sigma^{be*}_{mn}\delta_{ij}+\langle kl||cd\rangle\,\sigma^{ad}_{mn}\sigma^{ce}_{kl}\sigma^{be*}_{mn}\delta_{ij}\\
&+\langle kl||cd\rangle\,\sigma^{ce}_{km}\sigma^{df}_{il}\sigma^{ef*}_{jm}\delta_{ab}+\langle kl||cd\rangle\,\sigma^{ce}_{kl}\sigma^{df}_{im}\sigma^{ef*}_{jm}\delta_{ab}+\langle kl||cd\rangle\,\sigma^{ae}_{ln}\sigma^{cd}_{km}\sigma^{be*}_{mn}\delta_{ij}\\
&-\frac{1}{24}\langle jk||cd\rangle\,\sigma^{cd}_{lm}\sigma^{ef}_{ik}\sigma^{ef*}_{lm}\delta_{ab}-\frac{1}{24}\langle kl||bc\rangle\,\sigma^{ac}_{mn}\sigma^{de}_{kl}\sigma^{de*}_{mn}\delta_{ij}-\frac{1}{12}\langle kl||bc\rangle\,\sigma^{ae}_{kl}\sigma^{cd}_{mn}\sigma^{de*}_{mn}\delta_{ij}\\
&-\frac{1}{12}\langle jk||cd\rangle\,\sigma^{cd}_{im}\sigma^{ef}_{kl}\sigma^{ef*}_{lm}\delta_{ab}-\frac{1}{32}\langle kl||cd\rangle\,\sigma^{cd}_{il}\sigma^{ef}_{km}\sigma^{ef*}_{jm}\delta_{ab}
\end{aligned}
$$

PP-UCC4 secular matrix singles/doubles block:

$$\begin{aligned}
&\langle \Phi_i^a | \bar{H} | \Phi_{jk}^{bc} \rangle \ = \\
&\mathcal{P}^-_{(jk)} \langle aj||il \rangle \, \sigma_{kl}^{bc*} + \mathcal{P}^-_{(bc)} \langle ad||bi \rangle \, \sigma_{jk}^{cd*} \\
&+ \mathcal{P}^-_{(jk)} \langle ak||bc \rangle \, \delta_{ij} + \mathcal{P}^-_{(bc)} \langle jk||ci \rangle \, \delta_{ab} \\
&+ \frac{1}{2} \langle ad||il \rangle \, \sigma_{jkl}^{bcd*} \\
&+ \frac{1}{2} \mathcal{P}^-_{(jk)} \langle ak||lm \rangle \, \sigma_{lm}^{bc*} \delta_{ij} + \frac{1}{2} \mathcal{P}^-_{(bc)} \langle de||ci \rangle \, \sigma_{jk}^{de*} \delta_{ab} + \mathcal{P}^-_{(jkbc)} \langle ad||bl \rangle \, \sigma_{kl}^{cd*} \delta_{ij} \\
&\quad + \mathcal{P}^-_{(jkbc)} \langle jd||il \rangle \, \sigma_{kl}^{bd*} \delta_{ac} \\
&+ \frac{1}{2} \mathcal{P}^-_{(bc)} \langle jk||cd \rangle \, \sigma_i^d \delta_{ab} + \frac{1}{2} \mathcal{P}^-_{(jk)} \langle kl||bc \rangle \, \sigma_l^a \delta_{ij} \\
&+ \mathcal{P}^-_{(jk)} f_{al} \sigma_{kl}^{bc*} \delta_{ij} + \mathcal{P}^-_{(bc)} f_{di} \sigma_{jk}^{cd*} \delta_{ab} \\
&+ \mathcal{P}^-_{(jkbc)} f_{jb} \delta_{ac} \delta_{ik} \\
&+ \mathcal{P}^-_{(jkbc)} \langle aj||bl \rangle \, \sigma_l^{c*} \delta_{ik} + \mathcal{P}^-_{(jk)} \langle ad||bc \rangle \, \sigma_k^{d*} \delta_{ij} + \mathcal{P}^-_{(bc)} \langle jk||il \rangle \, \sigma_l^{c*} \delta_{ab} \\
&\quad + \mathcal{P}^-_{(jkbc)} \langle jd||ci \rangle \, \sigma_k^{d*} \delta_{ab} \\
&+ \frac{1}{4} \mathcal{P}^-_{(jk)} \langle ad||lm \rangle \, \sigma_{klm}^{bcd*} \delta_{ij} + \frac{1}{4} \mathcal{P}^-_{(bc)} \langle de||il \rangle \, \sigma_{jkl}^{cde*} \delta_{ab} \\
&+ \frac{1}{2} \mathcal{P}^-_{(jkbc)} \langle jd||lm \rangle \, \sigma_{lm}^{cd*} \delta_{ab} \delta_{ik} + \frac{1}{2} \mathcal{P}^-_{(jkbc)} \langle de||bl \rangle \, \sigma_{jl}^{de*} \delta_{ac} \delta_{ik} \\
&+ \frac{1}{2} \mathcal{P}^-_{(jkbc)} \langle jl||bd \rangle \, \sigma_l^d \delta_{ac} \delta_{ik} \\
&+ \mathcal{P}^-_{(jkbc)} f_{jl} \sigma_l^{c*} \delta_{ab} \delta_{ik} + \mathcal{P}^-_{(jkbc)} f_{db} \sigma_j^{d*} \delta_{ac} \delta_{ik} \\
&+ \mathcal{P}^-_{(jkbc)} f_{dl} \sigma_{jl}^{bd*} \delta_{ac} \delta_{ik} \\
&+ \mathcal{P}^-_{(jkbc)} \langle jd||bl \rangle \, \sigma_l^{d*} \delta_{ac} \delta_{ik} \\
&+ \frac{1}{8} \mathcal{P}^-_{(jkbc)} \langle de||lm \rangle \, \sigma_{jlm}^{bde*} \delta_{ac} \delta_{ik} \\
&+ \frac{1}{4} \mathcal{P}^-_{(jk)} \langle aj||de \rangle \, \sigma_{il}^{de} \sigma_{kl}^{bc*} + \frac{1}{4} \langle al||bc \rangle \, \sigma_{il}^{de} \sigma_{jk}^{de*} + \frac{1}{4} \mathcal{P}^-_{(bc)} \langle lm||bi \rangle \, \sigma_{lm}^{ad} \sigma_{jk}^{cd*} \\
&\quad + \frac{1}{2} \mathcal{P}^-_{(jkbc)} \langle aj||cd \rangle \, \sigma_{il}^{de} \sigma_{kl}^{be*} + \frac{1}{2} \mathcal{P}^-_{(bc)} \langle al||cd \rangle \, \sigma_{il}^{de} \sigma_{jk}^{be*} + \frac{1}{2} \mathcal{P}^-_{(jkbc)} \langle je||bd \rangle \, \sigma_{il}^{ad} \sigma_{kl}^{ce*} \\
&\quad + \frac{1}{2} \mathcal{P}^-_{(jkbc)} \langle jl||ci \rangle \, \sigma_{lm}^{ad} \sigma_{km}^{bd*} + \frac{1}{2} \mathcal{P}^-_{(jkbc)} \langle jl||cm \rangle \, \sigma_{il}^{ad} \sigma_{km}^{bd*} + \frac{1}{2} \mathcal{P}^-_{(jk)} \langle jl||id \rangle \, \sigma_{lm}^{ad} \sigma_{km}^{bc*}
\end{aligned}$$

$$
\begin{aligned}
&+ \frac{1}{2}\mathcal{P}^{-}_{(jk)} \langle kl||dm\rangle \, \sigma^{ad}_{il}\sigma^{bc*}_{jm} + \frac{1}{2}\mathcal{P}^{-}_{(bc)} \langle el||cd\rangle \, \sigma^{ad}_{il}\sigma^{be*}_{jk} - \frac{1}{4} \langle jk||id\rangle \, \sigma^{ad}_{lm}\sigma^{bc*}_{lm} \\
&- \frac{1}{2} \langle jk||dl\rangle \, \sigma^{ad}_{im}\sigma^{bc*}_{lm} - \frac{1}{2} \langle dl||bc\rangle \, \sigma^{ae}_{il}\sigma^{de*}_{jk} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(jk)} \langle ak||de\rangle \, \sigma^{de}_{lm}\sigma^{bc*}_{lm}\delta_{ij} + \frac{1}{8}\mathcal{P}^{-}_{(bc)} \langle lm||ci\rangle \, \sigma^{de}_{lm}\sigma^{de*}_{jk}\delta_{ab} + \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle aj||bd\rangle \, \sigma^{de}_{lm}\sigma^{ce*}_{lm}\delta_{ik} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(jk)} \langle al||bc\rangle \, \sigma^{de}_{lm}\sigma^{de*}_{jm}\delta_{ik} + \frac{1}{4}\mathcal{P}^{-}_{(bc)} \langle jk||id\rangle \, \sigma^{de}_{lm}\sigma^{ce*}_{lm}\delta_{ab} + \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle je||cd\rangle \, \sigma^{ad}_{lm}\sigma^{be*}_{lm}\delta_{ik} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle jf||de\rangle \, \sigma^{de}_{il}\sigma^{bf*}_{kl}\delta_{ac} + \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle jl||bi\rangle \, \sigma^{de}_{lm}\sigma^{de*}_{km}\delta_{ac} + \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle jl||bm\rangle \, \sigma^{de}_{il}\sigma^{de*}_{km}\delta_{ac} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle lm||bn\rangle \, \sigma^{ad}_{lm}\sigma^{cd*}_{kn}\delta_{ij} + \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle al||bd\rangle \, \sigma^{de}_{lm}\sigma^{ce*}_{km}\delta_{ij} + \frac{1}{2}\mathcal{P}^{-}_{(bc)} \langle jk||dl\rangle \, \sigma^{de}_{im}\sigma^{ce*}_{lm}\delta_{ab} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle je||cd\rangle \, \sigma^{df}_{il}\sigma^{ef*}_{kl}\delta_{ab} + \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle jl||bm\rangle \, \sigma^{ad}_{ln}\sigma^{cd*}_{mn}\delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle jl||id\rangle \, \sigma^{de}_{lm}\sigma^{be*}_{km}\delta_{ac} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(jk)} \langle jl||dm\rangle \, \sigma^{ad}_{ln}\sigma^{bc*}_{mn}\delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle jl||dm\rangle \, \sigma^{de}_{il}\sigma^{ce*}_{km}\delta_{ab} + \frac{1}{2}\mathcal{P}^{-}_{(jk)} \langle dl||bc\rangle \, \sigma^{ae}_{lm}\sigma^{de*}_{km}\delta_{ij} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle el||bd\rangle \, \sigma^{ad}_{lm}\sigma^{ce*}_{km}\delta_{ij} + \frac{1}{2}\mathcal{P}^{-}_{(bc)} \langle el||bd\rangle \, \sigma^{df}_{il}\sigma^{ef*}_{jk}\delta_{ac} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(jkbc)} \langle jf||de\rangle \, \sigma^{de}_{lm}\sigma^{cf*}_{lm}\delta_{ab}\delta_{ik} + \frac{1}{8}\mathcal{P}^{-}_{(jkbc)} \langle lm||bn\rangle \, \sigma^{de}_{lm}\sigma^{de*}_{jn}\delta_{ac}\delta_{ik} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle je||bd\rangle \, \sigma^{df}_{lm}\sigma^{ef*}_{lm}\delta_{ac}\delta_{ik} + \frac{1}{4}\mathcal{P}^{-}_{(jkbc)} \langle jl||cm\rangle \, \sigma^{de}_{ln}\sigma^{de*}_{mn}\delta_{ab}\delta_{ik} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle jl||dm\rangle \, \sigma^{de}_{ln}\sigma^{be*}_{mn}\delta_{ac}\delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle el||bd\rangle \, \sigma^{df}_{lm}\sigma^{ef*}_{jm}\delta_{ac}\delta_{ik}
\end{aligned}
$$

PP-UCC4 secular matrix singles/triples block:

$$
\begin{aligned}
&\langle \Phi^{a}_{i}|\bar{H}|\Phi^{bcd}_{jkl}\rangle \; = \\
&\mathcal{P}^{-}_{(jk)}f_{am}\sigma^{bcd*}_{jlm}\delta_{ik} + \mathcal{P}^{-}_{(bc)}f_{ei}\sigma^{bde*}_{jkl}\delta_{ac} - f_{am}\sigma^{bcd*}_{jkm}\delta_{il} \\
&\quad - f_{ei}\sigma^{bce*}_{jkl}\delta_{ad} \\
&\quad + \mathcal{P}^{-}_{(jkl)} \langle aj||bm\rangle \, \sigma^{cd*}_{km}\delta_{il} + \mathcal{P}^{-}_{(jkl)} \langle aj||cm\rangle \, \sigma^{bd*}_{lm}\delta_{ik} + \mathcal{P}^{-}_{(jkl)} \langle aj||dm\rangle \, \sigma^{bc*}_{km}\delta_{il} \\
&\quad + \mathcal{P}^{-}_{(jk)} \langle ae||bc\rangle \, \sigma^{de*}_{jl}\delta_{ik} + \mathcal{P}^{-}_{(bc)} \langle ae||bd\rangle \, \sigma^{ce*}_{jk}\delta_{il} + \mathcal{P}^{-}_{(jkbc)} \langle ae||bd\rangle \, \sigma^{ce*}_{kl}\delta_{ij} \\
&\quad + \mathcal{P}^{-}_{(bc)} \langle jk||im\rangle \, \sigma^{bd*}_{lm}\delta_{ac} + \mathcal{P}^{-}_{(jk)} \langle jl||im\rangle \, \sigma^{bc*}_{km}\delta_{ad} + \mathcal{P}^{-}_{(jkbc)} \langle jl||im\rangle \, \sigma^{cd*}_{km}\delta_{ab} \\
&\quad + \mathcal{P}^{-}_{(bcd)} \langle je||bi\rangle \, \sigma^{de*}_{kl}\delta_{ac} + \mathcal{P}^{-}_{(bcd)} \langle ke||bi\rangle \, \sigma^{ce*}_{jl}\delta_{ad} + \mathcal{P}^{-}_{(bcd)} \langle le||bi\rangle \, \sigma^{de*}_{jk}\delta_{ac}
\end{aligned}
$$

$$- \langle ae||bc\rangle \sigma^{de*}_{jk}\delta_{il} - \langle jk||im\rangle \sigma^{bc*}_{lm}\delta_{ad}$$

$$+ \langle jk||bc\rangle \delta_{ad}\delta_{il} + \mathcal{P}^{-}_{(bc)} \langle jk||cd\rangle \delta_{ab}\delta_{il} + \mathcal{P}^{-}_{(jkbc)} \langle jl||bd\rangle \delta_{ac}\delta_{ik}$$

$$+ \mathcal{P}^{-}_{(jk)} \langle kl||bc\rangle \delta_{ad}\delta_{ij}$$

$$+ \frac{1}{2} \langle jk||mn\rangle \sigma^{bc*}_{mn}\delta_{ad}\delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(bc)} \langle jk||mn\rangle \sigma^{cd*}_{mn}\delta_{ab}\delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle jl||mn\rangle \sigma^{bd*}_{mn}\delta_{ac}\delta_{ik}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(jk)} \langle kl||mn\rangle \sigma^{bc*}_{mn}\delta_{ad}\delta_{ij} + \frac{1}{2} \langle ef||bc\rangle \sigma^{ef*}_{jk}\delta_{ad}\delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(jk)} \langle ef||bc\rangle \sigma^{ef*}_{kl}\delta_{ad}\delta_{ij}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(jkbc)} \langle ef||bd\rangle \sigma^{ef*}_{jl}\delta_{ac}\delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(bc)} \langle ef||cd\rangle \sigma^{ef*}_{jk}\delta_{ab}\delta_{il} + \mathcal{P}^{-}_{(jklbcd)} \langle je||bm\rangle \sigma^{ce*}_{km}\delta_{ad}\delta_{il}$$

$$+ \mathcal{P}^{-}_{(jkl)} f_{jm}\sigma^{bc*}_{km}\delta_{ad}\delta_{il} + \mathcal{P}^{-}_{(jkl)} f_{jm}\sigma^{bd*}_{lm}\delta_{ac}\delta_{ik} + \mathcal{P}^{-}_{(jkl)} f_{jm}\sigma^{cd*}_{km}\delta_{ab}\delta_{il}$$

$$+ \mathcal{P}^{-}_{(bcd)} f_{eb}\sigma^{ce*}_{jl}\delta_{ad}\delta_{ik} + \mathcal{P}^{-}_{(bcd)} f_{eb}\sigma^{de*}_{jk}\delta_{ac}\delta_{il} + \mathcal{P}^{-}_{(bcd)} f_{eb}\sigma^{de*}_{kl}\delta_{ac}\delta_{ij}$$

$$+ f_{em}\sigma^{bce*}_{jkm}\delta_{ad}\delta_{il} + \mathcal{P}^{-}_{(jk)} f_{em}\sigma^{bce*}_{klm}\delta_{ad}\delta_{ij} + \mathcal{P}^{-}_{(jkbc)} f_{em}\sigma^{bde*}_{jlm}\delta_{ac}\delta_{ik}$$

$$+ \mathcal{P}^{-}_{(bc)} f_{em}\sigma^{cde*}_{jkm}\delta_{ab}\delta_{il}$$

PP-UCC4 secular matrix doubles/singles block:

$$\langle \Phi^{ab}_{ij}|\bar{H}|\Phi^{c}_{k}\rangle \; =$$

$$\mathcal{P}^{-}_{(ij)} \langle ab||cj\rangle \delta_{ik} + \mathcal{P}^{-}_{(ab)} \langle bk||ij\rangle \delta_{ac}$$

$$+ \mathcal{P}^{-}_{(ab)} \langle ak||cd\rangle \sigma^{bd}_{ij} + \mathcal{P}^{-}_{(ij)} \langle kl||ci\rangle \sigma^{ab}_{jl}$$

$$+ \frac{1}{2} \langle kl||cd\rangle \sigma^{abd}_{ijl}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle ab||jl\rangle \sigma^{c*}_{l}\delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle bd||ij\rangle \sigma^{d*}_{k}\delta_{ac}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle bk||de\rangle \sigma^{de}_{ij}\delta_{ac} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle lm||cj\rangle \sigma^{ab}_{lm}\delta_{ik} + \mathcal{P}^{-}_{(ijab)} \langle al||cd\rangle \sigma^{bd}_{jl}\delta_{ik}$$

$$+ \mathcal{P}^{-}_{(ijab)} \langle kl||id\rangle \sigma^{ad}_{jl}\delta_{bc}$$

$$+ \mathcal{P}^{-}_{(ijab)} f_{ai}\delta_{bc}\delta_{jk}$$

$$+ \mathcal{P}^{-}_{(ab)} f_{kd}\sigma^{bd}_{ij}\delta_{ac} + \mathcal{P}^{-}_{(ij)} f_{lc}\sigma^{ab}_{jl}\delta_{ik}$$

$$+ \mathcal{P}^{-}_{(ij)} \langle ab||cd\rangle \sigma^{d}_{j}\delta_{ik} + \mathcal{P}^{-}_{(ijab)} \langle ak||jd\rangle \sigma^{d}_{i}\delta_{bc} + \mathcal{P}^{-}_{(ijab)} \langle al||ci\rangle \sigma^{b}_{l}\delta_{jk}$$

$$
\begin{aligned}
&\quad + \mathcal{P}^{-}_{(ab)} \langle kl||ij \rangle \sigma^{b}_{l} \delta_{ac} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(ab)} \langle kl||de \rangle \sigma^{bde}_{ijl} \delta_{ac} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} \langle lm||cd \rangle \sigma^{abd}_{jlm} \delta_{ik} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ad||il \rangle \sigma^{d*}_{l} \delta_{bc} \delta_{jk} \\
&+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle al||de \rangle \sigma^{de}_{il} \delta_{bc} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle lm||id \rangle \sigma^{bd}_{lm} \delta_{ac} \delta_{jk} \\
&+ \mathcal{P}^{-}_{(ijab)} f_{ad} \sigma^{d}_{i} \delta_{bc} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} f_{li} \sigma^{b}_{l} \delta_{ac} \delta_{jk} \\
&+ \mathcal{P}^{-}_{(ijab)} f_{ld} \sigma^{ad}_{il} \delta_{bc} \delta_{jk} \\
&+ \mathcal{P}^{-}_{(ijab)} \langle al||id \rangle \sigma^{d}_{l} \delta_{bc} \delta_{jk} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(ijab)} \langle lm||de \rangle \sigma^{ade}_{ilm} \delta_{bc} \delta_{jk} \\
&\frac{1}{4} \langle ab||cl \rangle \sigma^{de}_{ij} \sigma^{de*}_{kl} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} \langle ak||lm \rangle \sigma^{bd}_{ij} \sigma^{cd*}_{lm} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} \langle de||ci \rangle \sigma^{ab}_{jl} \sigma^{de*}_{kl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ak||jl \rangle \sigma^{bd}_{im} \sigma^{cd*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ad||cj \rangle \sigma^{be}_{il} \sigma^{de*}_{kl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ae||id \rangle \sigma^{bd}_{jl} \sigma^{ce*}_{kl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle al||jm \rangle \sigma^{bd}_{il} \sigma^{cd*}_{km} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle bd||cl \rangle \sigma^{ae}_{ij} \sigma^{de*}_{kl} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle be||dl \rangle \sigma^{ad}_{ij} \sigma^{ce*}_{kl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle kd||il \rangle \sigma^{ab}_{jm} \sigma^{cd*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle dl||jm \rangle \sigma^{ab}_{il} \sigma^{cd*}_{km} - \frac{1}{4} \langle kd||ij \rangle \sigma^{ab}_{lm} \sigma^{cd*}_{lm} \\
&\quad - \frac{1}{2} \langle ab||dl \rangle \sigma^{de}_{ij} \sigma^{ce*}_{kl} - \frac{1}{2} \langle dl||ij \rangle \sigma^{ab}_{lm} \sigma^{cd*}_{km} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(ab)} \langle bk||lm \rangle \sigma^{de}_{ij} \sigma^{de*}_{lm} \delta_{ac} + \frac{1}{8}\mathcal{P}^{-}_{(ij)} \langle de||cj \rangle \sigma^{ab}_{lm} \sigma^{de*}_{lm} \delta_{ik} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} \langle ab||cl \rangle \sigma^{de}_{im} \sigma^{de*}_{lm} \delta_{jk} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ak||il \rangle \sigma^{de}_{jm} \sigma^{de*}_{lm} \delta_{bc} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ad||ci \rangle \sigma^{be}_{lm} \sigma^{de*}_{lm} \delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ae||jd \rangle \sigma^{bd}_{lm} \sigma^{ce*}_{lm} \delta_{ik} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle al||im \rangle \sigma^{de}_{jl} \sigma^{de*}_{km} \delta_{bc} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle al||mn \rangle \sigma^{bd}_{jl} \sigma^{cd*}_{mn} \delta_{ik} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} \langle kd||ij \rangle \sigma^{be}_{lm} \sigma^{de*}_{lm} \delta_{ac} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ef||id \rangle \sigma^{ad}_{jl} \sigma^{ef*}_{kl} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle ab||dl \rangle \sigma^{de}_{jm} \sigma^{ce*}_{lm} \delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ad||cl \rangle \sigma^{be}_{jm} \sigma^{de*}_{lm} \delta_{ik} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ae||jd \rangle \sigma^{df}_{il} \sigma^{ef*}_{kl} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ae||dl \rangle \sigma^{bd}_{jm} \sigma^{ce*}_{lm} \delta_{ik} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle ae||dl \rangle \sigma^{df}_{ij} \sigma^{ef*}_{kl} \delta_{bc} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle al||im \rangle \sigma^{bd}_{ln} \sigma^{cd*}_{mn} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle kd||il \rangle \sigma^{ae}_{jm} \sigma^{de*}_{lm} \delta_{bc} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle dl||ij \rangle \sigma^{be}_{lm} \sigma^{de*}_{km} \delta_{ac} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle dl||im \rangle \sigma^{ab}_{ln} \sigma^{cd*}_{mn} \delta_{jk} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle dl||im \rangle \sigma^{be}_{jl} \sigma^{de*}_{km} \delta_{ac} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(ijab)} \langle al||mn \rangle \sigma^{de}_{il} \sigma^{de*}_{mn} \delta_{bc} \delta_{jk} + \frac{1}{8}\mathcal{P}^{-}_{(ijab)} \langle ef||id \rangle \sigma^{bd}_{lm} \sigma^{ef*}_{lm} \delta_{ac} \delta_{jk} \\
&\quad + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle ae||id \rangle \sigma^{df}_{lm} \sigma^{ef*}_{lm} \delta_{bc} \delta_{jk} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} \langle al||jm \rangle \sigma^{de}_{ln} \sigma^{de*}_{mn} \delta_{bc} \delta_{ik}
\end{aligned}
$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle ae||dl\rangle\,\sigma^{df}_{im}\sigma^{ef*}_{lm}\delta_{bc}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle dl||im\rangle\,\sigma^{ae}_{ln}\sigma^{de*}_{mn}\delta_{bc}\delta_{jk}$$

PP-UCC4 secular matrix doubles/doubles block:

$$\begin{aligned}
&\langle\Phi^{ab}_{ij}|\bar{H}-E_0|\Phi^{cd}_{kl}\rangle\ =\\
&\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle ab||im\rangle\,\sigma^{cd*}_{lm}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle ab||jm\rangle\,\sigma^{cd*}_{km}\delta_{il}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle ae||ij\rangle\,\sigma^{de*}_{kl}\delta_{bc}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle be||ij\rangle\,\sigma^{ce*}_{kl}\delta_{ad}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle kl||ce\rangle\,\sigma^{be}_{ij}\delta_{ad}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}\langle kl||de\rangle\,\sigma^{ae}_{ij}\delta_{bc}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle km||cd\rangle\,\sigma^{ab}_{jm}\delta_{il}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(ij)}\langle lm||cd\rangle\,\sigma^{ab}_{im}\delta_{jk}\\
&+\mathcal{P}^{-}_{(ij)}\langle ab||cd\rangle\,\delta_{ik}\delta_{jl}+\mathcal{P}^{-}_{(ijab)}\langle ak||cj\rangle\,\delta_{bd}\delta_{il}+\mathcal{P}^{-}_{(ijab)}\langle ak||di\rangle\,\delta_{bc}\delta_{jl}\\
&\quad+\mathcal{P}^{-}_{(ijab)}\langle al||ci\rangle\,\delta_{bd}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}\langle al||dj\rangle\,\delta_{bc}\delta_{ik}+\mathcal{P}^{-}_{(ab)}\langle kl||ij\rangle\,\delta_{ac}\delta_{bd}\\
&+\frac{1}{4}\mathcal{P}^{-}_{(ij)}\langle ab||mn\rangle\,\sigma^{cd*}_{mn}\delta_{ik}\delta_{jl}+\frac{1}{4}\mathcal{P}^{-}_{(ab)}\langle ef||ij\rangle\,\sigma^{ef*}_{kl}\delta_{ac}\delta_{bd}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle ae||im\rangle\,\sigma^{ce*}_{km}\delta_{bd}\delta_{jl}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle ae||im\rangle\,\sigma^{de*}_{lm}\delta_{bc}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle ae||jm\rangle\,\sigma^{ce*}_{lm}\delta_{bd}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle ae||jm\rangle\,\sigma^{de*}_{km}\delta_{bc}\delta_{il}\\
&+\frac{1}{4}\mathcal{P}^{-}_{(ab)}\langle kl||ef\rangle\,\sigma^{ef}_{ij}\delta_{ac}\delta_{bd}+\frac{1}{4}\mathcal{P}^{-}_{(ij)}\langle mn||cd\rangle\,\sigma^{ab}_{mn}\delta_{ik}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle km||ce\rangle\,\sigma^{ae}_{im}\delta_{bd}\delta_{jl}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle km||de\rangle\,\sigma^{ae}_{jm}\delta_{bc}\delta_{il}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle lm||ce\rangle\,\sigma^{ae}_{jm}\delta_{bd}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}\langle lm||de\rangle\,\sigma^{ae}_{im}\delta_{bc}\delta_{jk}\\
&+\mathcal{P}^{-}_{(ijab)}f_{ac}\delta_{bd}\delta_{ik}\delta_{jl}+\mathcal{P}^{-}_{(ijab)}f_{ad}\delta_{bc}\delta_{il}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}f_{ki}\delta_{ad}\delta_{bc}\delta_{jl}\\
&\quad+\mathcal{P}^{-}_{(ijab)}f_{li}\delta_{ac}\delta_{bd}\delta_{jk}\\
&+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle ae||mn\rangle\,\sigma^{ce*}_{mn}\delta_{bd}\delta_{il}\delta_{jk}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle ae||mn\rangle\,\sigma^{de*}_{mn}\delta_{bc}\delta_{ik}\delta_{jl}\\
&\quad+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle ef||im\rangle\,\sigma^{ef*}_{km}\delta_{ad}\delta_{bc}\delta_{jl}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle ef||im\rangle\,\sigma^{ef*}_{lm}\delta_{ac}\delta_{bd}\delta_{jk}\\
&+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle km||ef\rangle\,\sigma^{ef}_{im}\delta_{ad}\delta_{bc}\delta_{jl}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle lm||ef\rangle\,\sigma^{ef}_{im}\delta_{ac}\delta_{bd}\delta_{jk}\\
&\quad+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle mn||ce\rangle\,\sigma^{ae}_{mn}\delta_{bd}\delta_{il}\delta_{jk}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}\langle mn||de\rangle\,\sigma^{ae}_{mn}\delta_{bc}\delta_{ik}\delta_{jl}\\
&+\mathcal{P}^{-}_{(ijab)}f_{am}\sigma^{c*}_{m}\delta_{bd}\delta_{il}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}f_{am}\sigma^{d*}_{m}\delta_{bc}\delta_{ik}\delta_{jl}+\mathcal{P}^{-}_{(ijab)}f_{ei}\sigma^{e*}_{k}\delta_{ad}\delta_{bc}\delta_{jl}
\end{aligned}$$

$$
\begin{aligned}
&+\mathcal{P}^{-}_{(ijab)} f_{ei}\sigma_{l}^{e*}\delta_{ac}\delta_{bd}\delta_{jk}\\
&+\mathcal{P}^{-}_{(ijab)} f_{ke}\sigma_{i}^{e}\delta_{ad}\delta_{bc}\delta_{jl}+\mathcal{P}^{-}_{(ijab)} f_{le}\sigma_{i}^{e}\delta_{ac}\delta_{bd}\delta_{jk}+\mathcal{P}^{-}_{(ijab)} f_{mc}\sigma_{m}^{a}\delta_{bd}\delta_{il}\delta_{jk}\\
&+\mathcal{P}^{-}_{(ijab)} f_{md}\sigma_{m}^{a}\delta_{bc}\delta_{ik}\delta_{jl}
\end{aligned}
$$

PP-UCC4 secular matrix doubles/triples block:

$$
\begin{aligned}
&\langle\Phi_{ij}^{ab}|\bar{H}|\Phi_{klm}^{cde}\rangle \;=\\
&\mathcal{P}^{-}_{(klm)}\langle ak||cd\rangle\,\delta_{be}\delta_{im}\delta_{jl}+\mathcal{P}^{-}_{(klm)}\langle ak||ce\rangle\,\delta_{bd}\delta_{il}\delta_{jm}+\mathcal{P}^{-}_{(klm)}\langle ak||de\rangle\,\delta_{bc}\delta_{im}\delta_{jl}\\
&\quad+\mathcal{P}^{-}_{(klm)}\langle bk||cd\rangle\,\delta_{ae}\delta_{il}\delta_{jm}+\mathcal{P}^{-}_{(klm)}\langle bk||ce\rangle\,\delta_{ad}\delta_{im}\delta_{jl}+\mathcal{P}^{-}_{(klm)}\langle bk||de\rangle\,\delta_{ac}\delta_{il}\delta_{jm}\\
&\quad+\mathcal{P}^{-}_{(cde)}\langle kl||ci\rangle\,\delta_{ae}\delta_{bd}\delta_{jm}+\mathcal{P}^{-}_{(cde)}\langle kl||cj\rangle\,\delta_{ad}\delta_{be}\delta_{im}+\mathcal{P}^{-}_{(cde)}\langle km||ci\rangle\,\delta_{ad}\delta_{be}\delta_{jl}\\
&\quad+\mathcal{P}^{-}_{(cde)}\langle km||cj\rangle\,\delta_{ae}\delta_{bd}\delta_{il}+\mathcal{P}^{-}_{(cde)}\langle lm||ci\rangle\,\delta_{ae}\delta_{bd}\delta_{jk}+\mathcal{P}^{-}_{(cde)}\langle lm||cj\rangle\,\delta_{ad}\delta_{be}\delta_{ik}\\
&+\mathcal{P}^{-}_{(klm)} f_{an}\sigma_{kn}^{cd*}\delta_{be}\delta_{im}\delta_{jl}+\mathcal{P}^{-}_{(klm)} f_{an}\sigma_{kn}^{ce*}\delta_{bd}\delta_{il}\delta_{jm}+\mathcal{P}^{-}_{(klm)} f_{an}\sigma_{kn}^{de*}\delta_{bc}\delta_{im}\delta_{jl}\\
&\quad+\mathcal{P}^{-}_{(klm)} f_{bn}\sigma_{kn}^{cd*}\delta_{ae}\delta_{il}\delta_{jm}+\mathcal{P}^{-}_{(klm)} f_{bn}\sigma_{kn}^{ce*}\delta_{ad}\delta_{im}\delta_{jl}+\mathcal{P}^{-}_{(klm)} f_{bn}\sigma_{kn}^{de*}\delta_{ac}\delta_{il}\delta_{jm}\\
&\quad+\mathcal{P}^{-}_{(cde)} f_{fi}\sigma_{kl}^{cf*}\delta_{ae}\delta_{bd}\delta_{jm}+\mathcal{P}^{-}_{(cde)} f_{fi}\sigma_{km}^{cf*}\delta_{ad}\delta_{be}\delta_{jl}+\mathcal{P}^{-}_{(cde)} f_{fi}\sigma_{lm}^{cf*}\delta_{ae}\delta_{bd}\delta_{jk}\\
&\quad+\mathcal{P}^{-}_{(cde)} f_{fj}\sigma_{kl}^{cf*}\delta_{ad}\delta_{be}\delta_{im}+\mathcal{P}^{-}_{(cde)} f_{fj}\sigma_{km}^{cf*}\delta_{ae}\delta_{bd}\delta_{il}+\mathcal{P}^{-}_{(cde)} f_{fj}\sigma_{lm}^{cf*}\delta_{ad}\delta_{be}\delta_{ik}\\
&+\mathcal{P}^{-}_{(klmcde)} f_{kc}\delta_{ad}\delta_{be}\delta_{il}\delta_{jm}\\
&+\mathcal{P}^{-}_{(klmcde)} f_{fn}\sigma_{kn}^{cf*}\delta_{ad}\delta_{be}\delta_{il}\delta_{jm}
\end{aligned}
$$

PP-UCC4 secular matrix triples/singles block:

$$
\begin{aligned}
&\langle\Phi_{ijk}^{abc}|\bar{H}|\Phi_{l}^{d}\rangle \;=\\
&\mathcal{P}^{-}_{(ab)} f_{le}\sigma_{ijk}^{ace}\delta_{bd}+\mathcal{P}^{-}_{(ij)} f_{md}\sigma_{ikm}^{abc}\delta_{jl}-f_{le}\sigma_{ijk}^{abe}\delta_{cd}\\
&\quad-f_{md}\sigma_{ijm}^{abc}\delta_{kl}
\end{aligned}
$$

$$
\begin{aligned}
&+ \mathcal{P}^{-}_{(ij)} \langle ab||de\rangle \sigma^{ce}_{ik}\delta_{jl} + \mathcal{P}^{-}_{(ab)} \langle ac||de\rangle \sigma^{be}_{ij}\delta_{kl} + \mathcal{P}^{-}_{(ijab)} \langle ac||de\rangle \sigma^{be}_{jk}\delta_{il} \\
&\quad + \mathcal{P}^{-}_{(abc)} \langle al||ie\rangle \sigma^{ce}_{jk}\delta_{bd} + \mathcal{P}^{-}_{(abc)} \langle al||je\rangle \sigma^{be}_{ik}\delta_{cd} + \mathcal{P}^{-}_{(abc)} \langle al||ke\rangle \sigma^{ce}_{ij}\delta_{bd} \\
&\quad + \mathcal{P}^{-}_{(ijk)} \langle am||di\rangle \sigma^{bc}_{jm}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} \langle bm||di\rangle \sigma^{ac}_{km}\delta_{jl} + \mathcal{P}^{-}_{(ijk)} \langle cm||di\rangle \sigma^{ab}_{jm}\delta_{kl} \\
&\quad + \mathcal{P}^{-}_{(ab)} \langle lm||ij\rangle \sigma^{ac}_{km}\delta_{bd} + \mathcal{P}^{-}_{(ij)} \langle lm||ik\rangle \sigma^{ab}_{jm}\delta_{cd} + \mathcal{P}^{-}_{(ijab)} \langle lm||ik\rangle \sigma^{bc}_{jm}\delta_{ad} \\
&\quad - \langle ab||de\rangle \sigma^{ce}_{ij}\delta_{kl} - \langle lm||ij\rangle \sigma^{ab}_{km}\delta_{cd} \\
&+ \langle ab||ij\rangle \delta_{cd}\delta_{kl} + \mathcal{P}^{-}_{(ij)} \langle ab||jk\rangle \delta_{cd}\delta_{il} + \mathcal{P}^{-}_{(ijab)} \langle ac||ik\rangle \delta_{bd}\delta_{jl} \\
&\quad + \mathcal{P}^{-}_{(ab)} \langle bc||ij\rangle \delta_{ad}\delta_{kl} \\
&+ \frac{1}{2} \langle ab||ef\rangle \sigma^{ef}_{ij}\delta_{cd}\delta_{kl} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle ab||ef\rangle \sigma^{ef}_{jk}\delta_{cd}\delta_{il} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle ac||ef\rangle \sigma^{ef}_{ik}\delta_{bd}\delta_{jl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle bc||ef\rangle \sigma^{ef}_{ij}\delta_{ad}\delta_{kl} + \frac{1}{2} \langle mn||ij\rangle \sigma^{ab}_{mn}\delta_{cd}\delta_{kl} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} \langle mn||ij\rangle \sigma^{bc}_{mn}\delta_{ad}\delta_{kl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} \langle mn||ik\rangle \sigma^{ac}_{mn}\delta_{bd}\delta_{jl} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} \langle mn||jk\rangle \sigma^{ab}_{mn}\delta_{cd}\delta_{il} + \mathcal{P}^{-}_{(ijkabc)} \langle am||ie\rangle \sigma^{be}_{jm}\delta_{cd}\delta_{kl} \\
&+ \mathcal{P}^{-}_{(abc)} f_{ae}\sigma^{be}_{ik}\delta_{cd}\delta_{jl} + \mathcal{P}^{-}_{(abc)} f_{ae}\sigma^{ce}_{ij}\delta_{bd}\delta_{kl} + \mathcal{P}^{-}_{(abc)} f_{ae}\sigma^{ce}_{jk}\delta_{bd}\delta_{il} \\
&\quad + \mathcal{P}^{-}_{(ijk)} f_{mi}\sigma^{ab}_{jm}\delta_{cd}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} f_{mi}\sigma^{ac}_{km}\delta_{bd}\delta_{jl} + \mathcal{P}^{-}_{(ijk)} f_{mi}\sigma^{bc}_{jm}\delta_{ad}\delta_{kl} \\
&+ f_{me}\sigma^{abe}_{ijm}\delta_{cd}\delta_{kl} + \mathcal{P}^{-}_{(ij)} f_{me}\sigma^{abe}_{jkm}\delta_{cd}\delta_{il} + \mathcal{P}^{-}_{(ijab)} f_{me}\sigma^{ace}_{ikm}\delta_{bd}\delta_{jl} \\
&\quad + \mathcal{P}^{-}_{(ab)} f_{me}\sigma^{bce}_{ijm}\delta_{ad}\delta_{kl}
\end{aligned}
$$

PP-UCC4 secular matrix triples/doubles block:

$$
\begin{aligned}
&\langle \Phi^{abc}_{ijk} | \bar{H} | \Phi^{de}_{lm} \rangle \; = \\
&\mathcal{P}^{-}_{(ijk)} \langle ab||di\rangle \delta_{ce}\delta_{jm}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} \langle ab||ei\rangle \delta_{cd}\delta_{jl}\delta_{km} + \mathcal{P}^{-}_{(ijk)} \langle ac||di\rangle \delta_{be}\delta_{jl}\delta_{km} \\
&\quad + \mathcal{P}^{-}_{(ijk)} \langle ac||ei\rangle \delta_{bd}\delta_{jm}\delta_{kl} + \mathcal{P}^{-}_{(abc)} \langle al||ij\rangle \delta_{be}\delta_{cd}\delta_{km} + \mathcal{P}^{-}_{(abc)} \langle al||ik\rangle \delta_{bd}\delta_{ce}\delta_{jm} \\
&\quad + \mathcal{P}^{-}_{(abc)} \langle al||jk\rangle \delta_{be}\delta_{cd}\delta_{im} + \mathcal{P}^{-}_{(abc)} \langle am||ij\rangle \delta_{bd}\delta_{ce}\delta_{kl} + \mathcal{P}^{-}_{(abc)} \langle am||ik\rangle \delta_{be}\delta_{cd}\delta_{jl} \\
&\quad + \mathcal{P}^{-}_{(abc)} \langle am||jk\rangle \delta_{bd}\delta_{ce}\delta_{il} + \mathcal{P}^{-}_{(ijk)} \langle bc||di\rangle \delta_{ae}\delta_{jm}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} \langle bc||ei\rangle \delta_{ad}\delta_{jl}\delta_{km} \\
&+ \mathcal{P}^{-}_{(ijkabc)} f_{ai}\delta_{bd}\delta_{ce}\delta_{jl}\delta_{km}
\end{aligned}
$$

$$
\begin{aligned}
&+ \mathcal{P}^{-}_{(abc)} f_{lf} \sigma^{af}_{ij} \delta_{be}\delta_{cd}\delta_{km} + \mathcal{P}^{-}_{(abc)} f_{lf} \sigma^{af}_{ik} \delta_{bd}\delta_{ce}\delta_{jm} + \mathcal{P}^{-}_{(abc)} f_{lf} \sigma^{af}_{jk} \delta_{be}\delta_{cd}\delta_{im} \\
&\quad + \mathcal{P}^{-}_{(abc)} f_{mf} \sigma^{af}_{ij} \delta_{bd}\delta_{ce}\delta_{kl} + \mathcal{P}^{-}_{(abc)} f_{mf} \sigma^{af}_{ik} \delta_{be}\delta_{cd}\delta_{jl} + \mathcal{P}^{-}_{(abc)} f_{mf} \sigma^{af}_{jk} \delta_{bd}\delta_{ce}\delta_{il} \\
&\quad + \mathcal{P}^{-}_{(ijk)} f_{nd} \sigma^{ab}_{in} \delta_{ce}\delta_{jm}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} f_{nd} \sigma^{ac}_{in} \delta_{be}\delta_{jl}\delta_{km} + \mathcal{P}^{-}_{(ijk)} f_{nd} \sigma^{bc}_{in} \delta_{ae}\delta_{jm}\delta_{kl} \\
&\quad + \mathcal{P}^{-}_{(ijk)} f_{ne} \sigma^{ab}_{in} \delta_{cd}\delta_{jl}\delta_{km} + \mathcal{P}^{-}_{(ijk)} f_{ne} \sigma^{ac}_{in} \delta_{bd}\delta_{jm}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} f_{ne} \sigma^{bc}_{in} \delta_{ad}\delta_{jl}\delta_{km} \\
&+ \mathcal{P}^{-}_{(ijkabc)} f_{nf} \sigma^{af}_{in} \delta_{bd}\delta_{ce}\delta_{jl}\delta_{km}
\end{aligned}
$$

PP-UCC4 secular matrix triples/triples block:

$$
\begin{aligned}
&\langle \Phi^{abc}_{ijk} | \bar{H} - E_0 | \Phi^{def}_{lmn} \rangle \ = \\
&\mathcal{P}^{-}_{(ijkabc)} f_{ad} \delta_{be}\delta_{cf}\delta_{il}\delta_{jm}\delta_{kn} + \mathcal{P}^{-}_{(ijkabc)} f_{ae} \delta_{bd}\delta_{cf}\delta_{il}\delta_{jn}\delta_{km} + \mathcal{P}^{-}_{(ijkabc)} f_{af} \delta_{bd}\delta_{ce}\delta_{il}\delta_{jm}\delta_{kn} \\
&\quad + \mathcal{P}^{-}_{(ijkabc)} f_{li} \delta_{ad}\delta_{be}\delta_{cf}\delta_{jn}\delta_{km} + \mathcal{P}^{-}_{(ijkabc)} f_{mi} \delta_{ad}\delta_{be}\delta_{cf}\delta_{jl}\delta_{kn} + \mathcal{P}^{-}_{(ijkabc)} f_{ni} \delta_{ad}\delta_{be}\delta_{cf}\delta_{jm}\delta_{kl}
\end{aligned}
$$

C.2.3. PP-UCC4 ground state and ground- to excited state densities

PP-UCC4 ground state density:

$$
\begin{aligned}
&\langle\Phi_0|\bar{D}|\Phi_0\rangle \;= \\
&d_{ai}\sigma_{i}^{a*} \\
&\;+ d_{ia}\sigma_{i}^{a} \\
&\;+ \frac{1}{2}d_{ai}\sigma_{j}^{b}\sigma_{ij}^{ab*} \\
&\;+ \frac{1}{2}d_{ba}\sigma_{ij}^{ac}\sigma_{ij}^{bc*} - \frac{1}{2}d_{ij}\sigma_{ik}^{ab}\sigma_{jk}^{ab*} \\
&\;+ \frac{1}{2}d_{ia}\sigma_{ij}^{ab}\sigma_{j}^{b*} \\
&\;+ d_{ba}\sigma_{i}^{a}\sigma_{i}^{b*} - d_{ij}\sigma_{i}^{a}\sigma_{j}^{a*} \\
&\;+ \frac{1}{12}d_{ba}\sigma_{ijk}^{acd}\sigma_{ijk}^{bcd*} - \frac{1}{12}d_{ij}\sigma_{ikl}^{abc}\sigma_{jkl}^{abc*} \\
&\;+ \frac{1}{8}d_{ai}\sigma_{jk}^{bc}\sigma_{ijk}^{abc*} \\
&\;+ \frac{1}{8}d_{ia}\sigma_{ijk}^{abc}\sigma_{jk}^{bc*} \\
&\;+ \frac{1}{24}d_{ai}\sigma_{jkl}^{bcd}\sigma_{il}^{ad*}\sigma_{jk}^{bc*} + \frac{1}{6}d_{ai}\sigma_{jkl}^{bcd}\sigma_{kl}^{ad*}\sigma_{ij}^{bc*} \\
&\;+ \frac{1}{24}d_{ia}\sigma_{il}^{ad}\sigma_{jk}^{bc}\sigma_{jkl}^{bcd*} + \frac{1}{6}d_{ia}\sigma_{kl}^{ad}\sigma_{ij}^{bc}\sigma_{jkl}^{bcd*} \\
&\;+ \frac{1}{6}d_{ai}\sigma_{jk}^{bc}\sigma_{j}^{b*}\sigma_{ik}^{ac*} - \frac{1}{3}d_{ai}\sigma_{jk}^{bc}\sigma_{j}^{a*}\sigma_{ik}^{bc*} - \frac{1}{3}d_{ai}\sigma_{jk}^{bc}\sigma_{i}^{b*}\sigma_{jk}^{ac*} \\
&\;+ \frac{1}{6}d_{ia}\sigma_{j}^{b}\sigma_{ik}^{ac}\sigma_{jk}^{bc*} - \frac{1}{3}d_{ia}\sigma_{j}^{a}\sigma_{ik}^{bc}\sigma_{jk}^{bc*} - \frac{1}{3}d_{ia}\sigma_{i}^{b}\sigma_{jk}^{ac}\sigma_{jk}^{bc*} \\
&\;+ \frac{1}{12}d_{ij}\sigma_{kl}^{ab}\sigma_{im}^{cd}\sigma_{jl}^{ab*}\sigma_{km}^{cd*} + \frac{1}{3}d_{ba}\sigma_{kl}^{ae}\sigma_{ij}^{cd}\sigma_{jl}^{bd*}\sigma_{ik}^{ce*} + \frac{1}{24}d_{ba}\sigma_{kl}^{ae}\sigma_{ij}^{cd}\sigma_{ij}^{be*}\sigma_{kl}^{cd*} \\
&\quad + \frac{1}{12}d_{ij}\sigma_{kl}^{ab}\sigma_{im}^{cd}\sigma_{km}^{ab*}\sigma_{jl}^{cd*} + \frac{1}{6}d_{ij}\sigma_{kl}^{ab}\sigma_{im}^{cd}\sigma_{kl}^{ac*}\sigma_{jm}^{bd*} - \frac{1}{6}d_{ba}\sigma_{kl}^{ae}\sigma_{ij}^{cd}\sigma_{jl}^{be*}\sigma_{ik}^{cd*} \\
&\quad - \frac{1}{3}d_{ij}\sigma_{kl}^{ab}\sigma_{im}^{cd}\sigma_{km}^{ac*}\sigma_{jl}^{bd*} - \frac{1}{12}d_{ba}\sigma_{kl}^{ae}\sigma_{ij}^{cd}\sigma_{ij}^{bd*}\sigma_{kl}^{ce*} - \frac{1}{12}d_{ba}\sigma_{kl}^{ae}\sigma_{ij}^{cd}\sigma_{kl}^{bd*}\sigma_{ij}^{ce*} \\
&\quad - \frac{1}{24}d_{ij}\sigma_{kl}^{ab}\sigma_{im}^{cd}\sigma_{jm}^{ab*}\sigma_{kl}^{cd*}
\end{aligned}
$$

PP-UCC4 ground- to excited-state density, singles:

$$
\begin{aligned}
&\langle \Phi_i^a | \bar{D} | \Phi_0 \rangle \; = \\
&d_{ai} \\
&+ d_{ab}\sigma_i^b - d_{ji}\sigma_j^a \\
&+ d_{jb}\sigma_{ij}^{ab} \\
&+ \frac{1}{2}d_{ab}\sigma_{ij}^{bc}\sigma_j^{c*} + d_{cb}\sigma_{ij}^{ab}\sigma_j^{c*} - \frac{1}{2}d_{ji}\sigma_{jk}^{ab}\sigma_k^{b*} \\
&\quad - d_{jk}\sigma_{ij}^{ab}\sigma_k^{b*} \\
&+ \frac{1}{2}d_{bj}\sigma_{ik}^{ac}\sigma_{jk}^{bc*} - \frac{1}{4}d_{aj}\sigma_{ik}^{bc}\sigma_{jk}^{bc*} - \frac{1}{4}d_{bi}\sigma_{jk}^{ac}\sigma_{jk}^{bc*} \\
&+ \frac{1}{8}d_{bj}\sigma_{ikl}^{acd}\sigma_{jkl}^{bcd*} - \frac{1}{24}d_{bi}\sigma_{jkl}^{acd}\sigma_{jkl}^{bcd*} - \frac{1}{24}d_{aj}\sigma_{ikl}^{bcd}\sigma_{jkl}^{bcd*} \\
&+ \frac{1}{8}d_{ab}\sigma_{ijk}^{bcd}\sigma_{jk}^{cd*} + \frac{1}{2}d_{cb}\sigma_{ijk}^{abd}\sigma_{jk}^{cd*} - \frac{1}{8}d_{ji}\sigma_{jkl}^{abc}\sigma_{kl}^{bc*} \\
&\quad - \frac{1}{2}d_{jk}\sigma_{ijl}^{abc}\sigma_{kl}^{bc*} \\
&+ \frac{1}{2}d_{jb}\sigma_{ijk}^{abc}\sigma_k^{c*} \\
&- \frac{1}{2}d_{aj}\sigma_i^b\sigma_j^{b*} - \frac{1}{2}d_{bi}\sigma_j^a\sigma_j^{b*} \\
&- d_{jb}\sigma_j^a\sigma_i^b \\
&+ \frac{1}{4}d_{cb}\sigma_i^d\sigma_{jk}^{ab}\sigma_{jk}^{cd*} + \frac{1}{4}d_{jk}\sigma_j^a\sigma_{il}^{bc}\sigma_{kl}^{bc*} + \frac{1}{2}d_{cb}\sigma_j^b\sigma_{ik}^{ad}\sigma_{jk}^{cd*} \\
&\quad + \frac{1}{6}d_{ab}\sigma_j^c\sigma_{ik}^{bd}\sigma_{jk}^{cd*} + \frac{1}{2}d_{jk}\sigma_i^b\sigma_{jl}^{ac}\sigma_{kl}^{bc*} + \frac{1}{2}d_{jk}\sigma_l^b\sigma_{ij}^{ac}\sigma_{kl}^{bc*} \\
&\quad + \frac{1}{12}d_{ji}\sigma_k^a\sigma_{jl}^{bc}\sigma_{kl}^{bc*} + \frac{1}{12}d_{ji}\sigma_j^b\sigma_{kl}^{ac}\sigma_{kl}^{bc*} - \frac{1}{4}d_{cb}\sigma_i^b\sigma_{jk}^{ad}\sigma_{jk}^{cd*} \\
&\quad - \frac{1}{4}d_{jk}\sigma_l^a\sigma_{ij}^{bc}\sigma_{kl}^{bc*} - \frac{1}{2}d_{cb}\sigma_j^d\sigma_{ik}^{ab}\sigma_{jk}^{cd*} - \frac{1}{2}d_{jk}\sigma_j^b\sigma_{il}^{ac}\sigma_{kl}^{bc*} \\
&\quad - \frac{1}{6}d_{ji}\sigma_k^b\sigma_{jl}^{ac}\sigma_{kl}^{bc*} - \frac{1}{12}d_{ab}\sigma_j^b\sigma_{ik}^{cd}\sigma_{jk}^{cd*} - \frac{1}{2}d_{cb}\sigma_j^a\sigma_{ik}^{bd}\sigma_{jk}^{cd*} \\
&\quad - \frac{1}{12}d_{ab}\sigma_i^c\sigma_{jk}^{bd}\sigma_{jk}^{cd*}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{1}{24} d_{ab} \sigma_{jk}^{bc} \sigma_{il}^{de} \sigma_{jkl}^{cde*} + \frac{1}{4} d_{jk} \sigma_{jm}^{ad} \sigma_{il}^{bc} \sigma_{klm}^{bcd*} + \frac{1}{4} d_{cb} \sigma_{il}^{ae} \sigma_{jk}^{bd} \sigma_{jkl}^{cde*} \\
&\quad + \frac{1}{8} d_{cb} \sigma_{il}^{ab} \sigma_{jk}^{de} \sigma_{jkl}^{cde*} + \frac{1}{4} d_{cb} \sigma_{kl}^{ae} \sigma_{ij}^{bd} \sigma_{jkl}^{cde*} + \frac{1}{24} d_{ab} \sigma_{il}^{be} \sigma_{jk}^{cd} \sigma_{jkl}^{cde*} \\
&\quad + \frac{1}{8} d_{cb} \sigma_{kl}^{ab} \sigma_{ij}^{de} \sigma_{jkl}^{cde*} - \frac{1}{4} d_{jk} \sigma_{im}^{ad} \sigma_{jl}^{bc} \sigma_{klm}^{bcd*} - \frac{1}{24} d_{ji} \sigma_{jm}^{ad} \sigma_{kl}^{bc} \sigma_{klm}^{bcd*} \\
&\quad - \frac{1}{24} d_{ji} \sigma_{lm}^{ad} \sigma_{jk}^{bc} \sigma_{klm}^{bcd*} - \frac{1}{8} d_{jk} \sigma_{ij}^{ad} \sigma_{lm}^{bc} \sigma_{klm}^{bcd*} - \frac{1}{8} d_{jk} \sigma_{lm}^{ad} \sigma_{ij}^{bc} \sigma_{klm}^{bcd*} \\
&+ \frac{1}{12} d_{jb} \sigma_{kl}^{ad} \sigma_{ij}^{bc} \sigma_{kl}^{cd*} + \frac{1}{6} d_{jb} \sigma_{kl}^{ab} \sigma_{ij}^{cd} \sigma_{kl}^{cd*} + \frac{1}{3} d_{jb} \sigma_{il}^{ab} \sigma_{jk}^{cd} \sigma_{kl}^{cd*} \\
&\quad + \frac{1}{6} d_{jb} \sigma_{il}^{ad} \sigma_{jk}^{bc} \sigma_{kl}^{cd*} + \frac{1}{3} d_{jb} \sigma_{ij}^{ad} \sigma_{kl}^{bc} \sigma_{kl}^{cd*} - \frac{1}{12} d_{jb} \sigma_{jl}^{ab} \sigma_{ik}^{cd} \sigma_{kl}^{cd*} \\
&\quad - \frac{2}{3} d_{jb} \sigma_{jl}^{ad} \sigma_{ik}^{bc} \sigma_{kl}^{cd*} \\
&+ \frac{1}{16} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{lm}^{be*} \sigma_{jk}^{cd*} + \frac{1}{24} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{jk}^{be*} \sigma_{lm}^{cd*} + \frac{1}{48} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{jk}^{bc*} \sigma_{lm}^{de*} \\
&\quad + \frac{1}{48} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{jm}^{be*} \sigma_{kl}^{cd*} + \frac{1}{2} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{kl}^{bc*} \sigma_{jm}^{de*} + \frac{1}{12} d_{aj} \sigma_{kl}^{bc} \sigma_{im}^{de} \sigma_{kl}^{bd*} \sigma_{jm}^{ce*} \\
&\quad + \frac{1}{6} d_{aj} \sigma_{kl}^{bc} \sigma_{im}^{de} \sigma_{jk}^{bd*} \sigma_{lm}^{ce*} + \frac{3}{16} d_{bj} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{lm}^{be*} \sigma_{jk}^{cd*} + \frac{1}{8} d_{bj} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{kl}^{be*} \sigma_{jm}^{cd*} \\
&\quad + \frac{1}{12} d_{bj} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{jm}^{bc*} \sigma_{kl}^{de*} + \frac{1}{12} d_{bi} \sigma_{lm}^{ae} \sigma_{jk}^{cd} \sigma_{km}^{be*} \sigma_{jl}^{cd*} + \frac{1}{24} d_{bj} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{jk}^{bc*} \sigma_{lm}^{de*} \\
&\quad + \frac{1}{6} d_{bi} \sigma_{lm}^{ae} \sigma_{jk}^{cd} \sigma_{jl}^{bc*} \sigma_{km}^{de*} + \frac{3}{16} d_{bj} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{kl}^{bc*} \sigma_{jm}^{de*} + \frac{1}{4} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{lm}^{bc*} \sigma_{jk}^{de*} \\
&\quad - \frac{1}{6} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{jl}^{bc*} \sigma_{km}^{de*} - \frac{1}{12} d_{bj} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{jl}^{be*} \sigma_{km}^{cd*} - \frac{1}{48} d_{aj} \sigma_{kl}^{bc} \sigma_{im}^{de} \sigma_{jm}^{bc*} \sigma_{kl}^{de*} \\
&\quad - \frac{1}{96} d_{aj} \sigma_{kl}^{bc} \sigma_{im}^{de} \sigma_{jk}^{bc*} \sigma_{lm}^{de*} - \frac{1}{96} d_{bi} \sigma_{lm}^{ae} \sigma_{jk}^{cd} \sigma_{jk}^{bc*} \sigma_{lm}^{de*} - \frac{1}{24} d_{bi} \sigma_{lm}^{ae} \sigma_{jk}^{cd} \sigma_{lm}^{bc*} \sigma_{jk}^{de*} \\
&\quad - \frac{1}{4} d_{bj} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{km}^{be*} \sigma_{jl}^{cd*} - \frac{1}{48} d_{bi} \sigma_{lm}^{ae} \sigma_{jk}^{cd} \sigma_{jk}^{be*} \sigma_{lm}^{cd*} - \frac{1}{24} d_{aj} \sigma_{kl}^{bc} \sigma_{im}^{de} \sigma_{lm}^{bc*} \sigma_{jk}^{de*} \\
&\quad - \frac{1}{2} d_{bj} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{km}^{bc*} \sigma_{jl}^{de*}
\end{aligned}
$$

PP-UCC4 ground- to excited-state density, doubles:

$$
\begin{aligned}
&\langle \Phi_{ij}^{ab} | \bar{D} | \Phi_0 \rangle \; = \\
&\mathcal{P}_{(ab)}^{-} d_{bc} \sigma_{ij}^{ac} + \mathcal{P}_{(ij)}^{-} d_{ki} \sigma_{jk}^{ab} \\
&\quad + d_{kc} \sigma_{ijk}^{abc}
\end{aligned}
$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{ak}\sigma^{bcd}_{ijl}\sigma^{cd*}_{kl} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ci}\sigma^{abd}_{jkl}\sigma^{cd*}_{kl} + \frac{1}{2} d_{ck}\sigma^{abd}_{ijl}\sigma^{cd*}_{kl}$$
$$+ \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ak}\sigma^{bc}_{ij}\sigma^{c*}_{k} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ci}\sigma^{ab}_{jk}\sigma^{c*}_{k}$$
$$+ d_{dc}\sigma^{abc}_{ijk}\sigma^{d*}_{k} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{bc}\sigma^{acd}_{ijk}\sigma^{d*}_{k} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ki}\sigma^{abc}_{jkl}\sigma^{c*}_{l}$$

$$- d_{kl}\sigma^{abc}_{ijk}\sigma^{c*}_{l}$$

$$+ \mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{a}_{k}\sigma^{bc}_{ij} + \mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{c}_{i}\sigma^{ab}_{jk}$$
$$+ \frac{1}{4} d_{dc}\sigma^{ab}_{kl}\sigma^{ce}_{ij}\sigma^{de*}_{kl} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{dc}\sigma^{ae}_{ij}\sigma^{bc}_{kl}\sigma^{de*}_{kl} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{dc}\sigma^{ae}_{kl}\sigma^{bc}_{ij}\sigma^{de*}_{kl}$$
$$+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{kl}\sigma^{ac}_{jk}\sigma^{bd}_{im}\sigma^{cd*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{kl}\sigma^{ac}_{km}\sigma^{bd}_{ij}\sigma^{cd*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{kj}\sigma^{ab}_{km}\sigma^{cd}_{il}\sigma^{cd*}_{lm}$$
$$+ \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{kj}\sigma^{ac}_{ik}\sigma^{bd}_{lm}\sigma^{cd*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{dc}\sigma^{ab}_{il}\sigma^{ce}_{jk}\sigma^{de*}_{kl} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{dc}\sigma^{ac}_{ik}\sigma^{be}_{jl}\sigma^{de*}_{kl}$$
$$+ \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ac}\sigma^{bc}_{jl}\sigma^{de}_{ik}\sigma^{de*}_{kl} + \frac{1}{24}\mathcal{P}^{-}_{(ab)} d_{bc}\sigma^{ac}_{kl}\sigma^{de}_{ij}\sigma^{de*}_{kl} + \frac{1}{24}\mathcal{P}^{-}_{(ij)} d_{ki}\sigma^{ab}_{lm}\sigma^{cd}_{jk}\sigma^{cd*}_{lm}$$
$$+ \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{bc}\sigma^{ae}_{ij}\sigma^{cd}_{kl}\sigma^{de*}_{kl} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{bc}\sigma^{ae}_{kl}\sigma^{cd}_{ij}\sigma^{de*}_{kl} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{ki}\sigma^{ab}_{jm}\sigma^{cd}_{kl}\sigma^{cd*}_{lm}$$
$$+ \frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ac}\sigma^{be}_{jl}\sigma^{cd}_{ik}\sigma^{de*}_{kl} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ki}\sigma^{ac}_{jl}\sigma^{bd}_{km}\sigma^{cd*}_{lm} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{kl}\sigma^{ab}_{ik}\sigma^{cd}_{jm}\sigma^{cd*}_{lm}$$
$$+ \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{kl}\sigma^{ab}_{jm}\sigma^{cd}_{ik}\sigma^{cd*}_{lm} - \frac{1}{4} d_{kl}\sigma^{ab}_{km}\sigma^{cd}_{ij}\sigma^{cd*}_{lm}$$
$$+ \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{ab}_{jk}\sigma^{cd}_{il}\sigma^{d*}_{l} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{ad}_{kl}\sigma^{bc}_{ij}\sigma^{d*}_{l} + \frac{1}{6}\mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{ab}_{il}\sigma^{cd}_{jk}\sigma^{d*}_{l}$$
$$+ \frac{1}{6}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{ad}_{ij}\sigma^{bc}_{kl}\sigma^{d*}_{l} + \frac{2}{3} d_{kc}\sigma^{ab}_{kl}\sigma^{cd}_{ij}\sigma^{d*}_{l} + \frac{2}{3}\mathcal{P}^{-}_{(ijab)} d_{kc}\sigma^{ac}_{jl}\sigma^{bd}_{ik}\sigma^{d*}_{l}$$
$$+ \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{ab}_{il}\sigma^{cde}_{jkm}\sigma^{de*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{ad}_{ij}\sigma^{bce}_{klm}\sigma^{de*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{de}_{il}\sigma^{abc}_{jkm}\sigma^{de*}_{lm}$$
$$+ \frac{1}{3} d_{kc}\sigma^{ab}_{kl}\sigma^{cde}_{ijm}\sigma^{de*}_{lm} + \frac{1}{8}\mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{ab}_{jk}\sigma^{cde}_{ilm}\sigma^{de*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{cd}_{jk}\sigma^{abe}_{ilm}\sigma^{de*}_{lm}$$
$$+ \frac{1}{6}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{bc}_{lm}\sigma^{ade}_{ijk}\sigma^{de*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ij)} d_{kc}\sigma^{de}_{jk}\sigma^{abc}_{ilm}\sigma^{de*}_{lm} + \frac{1}{3} d_{kc}\sigma^{cd}_{lm}\sigma^{abe}_{ijk}\sigma^{de*}_{lm}$$
$$+ \frac{2}{3}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{ad}_{kl}\sigma^{bce}_{ijm}\sigma^{de*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{ad}_{lm}\sigma^{bce}_{ijk}\sigma^{de*}_{lm} + \frac{1}{3} d_{kc}\sigma^{cd}_{ij}\sigma^{abe}_{klm}\sigma^{de*}_{lm}$$
$$+ \frac{1}{3} d_{kc}\sigma^{de}_{kl}\sigma^{abc}_{ijm}\sigma^{de*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{bc}_{kl}\sigma^{ade}_{ijm}\sigma^{de*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{kc}\sigma^{ad}_{il}\sigma^{bce}_{jkm}\sigma^{de*}_{lm}$$
$$+ \frac{1}{8}\mathcal{P}^{-}_{(ab)} d_{kc}\sigma^{bc}_{ij}\sigma^{ade}_{klm}\sigma^{de*}_{lm} + \frac{1}{24} d_{kc}\sigma^{ab}_{lm}\sigma^{cde}_{ijk}\sigma^{de*}_{lm} + \frac{1}{24} d_{kc}\sigma^{de}_{ij}\sigma^{abc}_{klm}\sigma^{de*}_{lm}$$
$$+ \frac{1}{6} d_{kc}\sigma^{cd}_{kl}\sigma^{abe}_{ijm}\sigma^{de*}_{lm} + \frac{1}{3}\mathcal{P}^{-}_{(ijab)} d_{kc}\sigma^{ac}_{jl}\sigma^{bde}_{ikm}\sigma^{de*}_{lm} + \frac{1}{3}\mathcal{P}^{-}_{(ijab)} d_{kc}\sigma^{ad}_{jk}\sigma^{bce}_{ilm}\sigma^{de*}_{lm}$$

$$+\frac{2}{3}\mathcal{P}^{-}_{(ij)}d_{kc}\sigma^{cd}_{il}\sigma^{abe}_{jkm}\sigma^{de*}_{lm}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}d_{ak}\sigma^{be}_{im}\sigma^{cd}_{jl}\sigma^{cde*}_{klm}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}d_{ck}\sigma^{ad}_{il}\sigma^{be}_{jm}\sigma^{cde*}_{klm}+\frac{1}{12}\mathcal{P}^{-}_{(ab)}d_{ak}\sigma^{be}_{ij}\sigma^{cd}_{lm}\sigma^{cde*}_{klm}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ab)}d_{ak}\sigma^{be}_{lm}\sigma^{cd}_{ij}\sigma^{cde*}_{klm}+\frac{1}{12}d_{ck}\sigma^{ab}_{lm}\sigma^{de}_{ij}\sigma^{cde*}_{klm}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}d_{cj}\sigma^{ad}_{ik}\sigma^{be}_{lm}\sigma^{cde*}_{klm}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ij)}d_{ci}\sigma^{ab}_{lm}\sigma^{de}_{jk}\sigma^{cde*}_{klm}+\frac{1}{12}\mathcal{P}^{-}_{(ij)}d_{ci}\sigma^{ab}_{jm}\sigma^{de}_{kl}\sigma^{cde*}_{klm}+\frac{1}{6}\mathcal{P}^{-}_{(ij)}d_{ck}\sigma^{ab}_{im}\sigma^{de}_{jl}\sigma^{cde*}_{klm}$$

$$-\frac{1}{6}\mathcal{P}^{-}_{(ab)}d_{ck}\sigma^{ad}_{ij}\sigma^{be}_{lm}\sigma^{cde*}_{klm}$$

$$+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}d_{ak}\sigma^{c}_{j}\sigma^{bd}_{il}\sigma^{cd*}_{kl}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}d_{ci}\sigma^{b}_{k}\sigma^{ad}_{jl}\sigma^{cd*}_{kl}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}d_{ak}\sigma^{b}_{l}\sigma^{cd}_{ij}\sigma^{cd*}_{kl}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(ij)}d_{ci}\sigma^{d}_{j}\sigma^{ab}_{kl}\sigma^{cd*}_{kl}+\frac{1}{3}\mathcal{P}^{-}_{(ab)}d_{bk}\sigma^{c}_{l}\sigma^{ad}_{ij}\sigma^{cd*}_{kl}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}d_{cj}\sigma^{d}_{k}\sigma^{ab}_{il}\sigma^{cd*}_{kl}$$

$$+\frac{1}{3}\mathcal{P}^{-}_{(ab)}d_{ck}\sigma^{a}_{l}\sigma^{bd}_{ij}\sigma^{cd*}_{kl}+\frac{1}{3}\mathcal{P}^{-}_{(ij)}d_{ck}\sigma^{d}_{i}\sigma^{ab}_{jl}\sigma^{cd*}_{kl}$$

PP-UCC4 ground- to excited-state density, triples:

$$\langle\Phi^{abc}_{ijk}|\bar{D}|\Phi_0\rangle \;=$$

$$\mathcal{P}^{-}_{(ab)}d_{ad}\sigma^{bcd}_{ijk}+d_{cd}\sigma^{abd}_{ijk}+\mathcal{P}^{-}_{(ij)}d_{lj}\sigma^{abc}_{ikl}$$

$$-d_{lk}\sigma^{abc}_{ijl}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ab)}d_{bl}\sigma^{acd}_{ijk}\sigma^{d*}_{l}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}d_{dj}\sigma^{abc}_{ikl}\sigma^{d*}_{l}-\frac{1}{2}d_{cl}\sigma^{abd}_{ijk}\sigma^{d*}_{l}$$

$$-\frac{1}{2}d_{dk}\sigma^{abc}_{ijl}\sigma^{d*}_{l}$$

$$+\mathcal{P}^{-}_{(ab)}d_{ld}\sigma^{b}_{l}\sigma^{acd}_{ijk}+\mathcal{P}^{-}_{(ij)}d_{ld}\sigma^{d}_{j}\sigma^{abc}_{ikl}-d_{ld}\sigma^{c}_{l}\sigma^{abd}_{ijk}$$

$$-d_{ld}\sigma^{d}_{k}\sigma^{abc}_{ijl}$$

$$+\mathcal{P}^{-}_{(ij)}d_{ld}\sigma^{ab}_{il}\sigma^{cd}_{jk}+d_{ld}\sigma^{ab}_{kl}\sigma^{cd}_{ij}+\mathcal{P}^{-}_{(ijab)}d_{ld}\sigma^{ac}_{jl}\sigma^{bd}_{ik}$$

$$+\mathcal{P}^{-}_{(ab)}d_{ld}\sigma^{ad}_{ij}\sigma^{bc}_{kl}$$

$$+\frac{1}{4}d_{ed}\sigma^{ab}_{lm}\sigma^{cdf}_{ijk}\sigma^{ef*}_{lm}+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{ed}\sigma^{ad}_{ij}\sigma^{bcf}_{klm}\sigma^{ef*}_{lm}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ed}\sigma^{ad}_{jk}\sigma^{bcf}_{ilm}\sigma^{ef*}_{lm}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{ed}\sigma^{bc}_{lm}\sigma^{adf}_{ijk}\sigma^{ef*}_{lm}+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{ed}\sigma^{bf}_{lm}\sigma^{acd}_{ijk}\sigma^{ef*}_{lm}+\frac{1}{4}d_{ed}\sigma^{cd}_{ij}\sigma^{abf}_{klm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ed}\sigma^{cd}_{jk}\sigma^{abf}_{ilm}\sigma^{ef*}_{lm} + \frac{1}{4} d_{ed}\sigma^{df}_{ij}\sigma^{abc}_{klm}\sigma^{ef*}_{lm} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ed}\sigma^{df}_{jk}\sigma^{abc}_{ilm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{lm}\sigma^{ab}_{jl}\sigma^{cde}_{ikn}\sigma^{de*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{lm}\sigma^{ac}_{il}\sigma^{bde}_{jkn}\sigma^{de*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{ac}_{kl}\sigma^{bde}_{ijn}\sigma^{de*}_{mn}$$

$$+ \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{ac}_{ln}\sigma^{bde}_{ijk}\sigma^{de*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{lm}\sigma^{de}_{ik}\sigma^{abc}_{jln}\sigma^{de*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{lm}\sigma^{de}_{in}\sigma^{abc}_{jkl}\sigma^{de*}_{mn}$$

$$+ \frac{1}{4} d_{lm}\sigma^{de}_{kn}\sigma^{abc}_{ijl}\sigma^{de*}_{mn} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ed}\sigma^{ad}_{il}\sigma^{bcf}_{jkm}\sigma^{ef*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ed}\sigma^{ad}_{kl}\sigma^{bcf}_{ijm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ed}\sigma^{af}_{jl}\sigma^{bcd}_{ikm}\sigma^{ef*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ed}\sigma^{bf}_{kl}\sigma^{acd}_{ijm}\sigma^{ef*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ed}\sigma^{cd}_{il}\sigma^{abf}_{jkm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{2} d_{ed}\sigma^{cd}_{kl}\sigma^{abf}_{ijm}\sigma^{ef*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ed}\sigma^{cf}_{jl}\sigma^{abd}_{ikm}\sigma^{ef*}_{lm} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{lm}\sigma^{ad}_{ik}\sigma^{bce}_{jln}\sigma^{de*}_{mn}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{lm}\sigma^{ad}_{in}\sigma^{bce}_{jkl}\sigma^{de*}_{mn} + \frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{lm}\sigma^{ad}_{jl}\sigma^{bce}_{ikn}\sigma^{de*}_{mn} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{ad}_{kn}\sigma^{bce}_{ijl}\sigma^{de*}_{mn}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{bd}_{ij}\sigma^{ace}_{kln}\sigma^{de*}_{mn} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{bd}_{kl}\sigma^{ace}_{ijn}\sigma^{de*}_{mn} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{bd}_{ln}\sigma^{ace}_{ijk}\sigma^{de*}_{mn}$$

$$+ \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{lm}\sigma^{cd}_{ik}\sigma^{abe}_{jln}\sigma^{de*}_{mn} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{lm}\sigma^{cd}_{in}\sigma^{abe}_{jkl}\sigma^{de*}_{mn} + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{lm}\sigma^{cd}_{jl}\sigma^{abe}_{ikn}\sigma^{de*}_{mn}$$

$$+ \frac{1}{2} d_{lm}\sigma^{cd}_{kn}\sigma^{abe}_{ijl}\sigma^{de*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ad}\sigma^{de}_{il}\sigma^{bcf}_{jkm}\sigma^{ef*}_{lm} + \frac{1}{6}\mathcal{P}^{-}_{(ab)} d_{ad}\sigma^{de}_{kl}\sigma^{bcf}_{ijm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{6}\mathcal{P}^{-}_{(ij)} d_{cd}\sigma^{de}_{il}\sigma^{abf}_{jkm}\sigma^{ef*}_{lm} + \frac{1}{6} d_{cd}\sigma^{de}_{kl}\sigma^{abf}_{ijm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{li}\sigma^{ab}_{km}\sigma^{cde}_{jln}\sigma^{de*}_{mn}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{li}\sigma^{ac}_{jm}\sigma^{bde}_{kln}\sigma^{de*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{li}\sigma^{bc}_{km}\sigma^{ade}_{jln}\sigma^{de*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ad}\sigma^{bc}_{il}\sigma^{def}_{jkm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ad}\sigma^{bc}_{kl}\sigma^{def}_{ijm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ad}\sigma^{be}_{ij}\sigma^{cdf}_{klm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ad}\sigma^{be}_{jk}\sigma^{cdf}_{ilm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ad}\sigma^{ce}_{ik}\sigma^{bdf}_{jlm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ad}\sigma^{ef}_{il}\sigma^{bcd}_{jkm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ad}\sigma^{ef}_{kl}\sigma^{bcd}_{ijm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{cd}\sigma^{ab}_{il}\sigma^{def}_{jkm}\sigma^{ef*}_{lm} + \frac{1}{12} d_{cd}\sigma^{ab}_{kl}\sigma^{def}_{ijm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{cd}\sigma^{ef}_{il}\sigma^{abd}_{jkm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{12} d_{cd}\sigma^{ef}_{kl}\sigma^{abd}_{ijm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{li}\sigma^{bd}_{jk}\sigma^{ace}_{lmn}\sigma^{de*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{li}\sigma^{bd}_{mn}\sigma^{ace}_{jkl}\sigma^{de*}_{mn}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{lj}\sigma^{cd}_{ik}\sigma^{abe}_{lmn}\sigma^{de*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{lj}\sigma^{cd}_{mn}\sigma^{abe}_{ikl}\sigma^{de*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{lk}\sigma^{bd}_{ij}\sigma^{ace}_{lmn}\sigma^{de*}_{mn}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{lk}\sigma^{bd}_{mn}\sigma^{ace}_{ijl}\sigma^{de*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ab)} d_{ad}\sigma^{bc}_{lm}\sigma^{def}_{ijk}\sigma^{ef*}_{lm} + \frac{1}{24}\mathcal{P}^{-}_{(abc)} d_{ad}\sigma^{cd}_{lm}\sigma^{bef}_{ijk}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{24} d_{cd}\sigma^{ab}_{lm}\sigma^{def}_{ijk}\sigma^{ef*}_{lm} + \frac{1}{24}\mathcal{P}^{-}_{(ijk)} d_{li}\sigma^{de}_{jl}\sigma^{abc}_{kmn}\sigma^{de*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ij)} d_{lj}\sigma^{de}_{ik}\sigma^{abc}_{lmn}\sigma^{de*}_{mn}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ad}\sigma^{bd}_{jl}\sigma^{cef}_{ikm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ad}\sigma^{cd}_{il}\sigma^{bef}_{jkm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ad}\sigma^{cd}_{kl}\sigma^{bef}_{ijm}\sigma^{ef*}_{lm}$$

$$+ \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ad}\sigma^{de}_{ij}\sigma^{bcf}_{klm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ad}\sigma^{de}_{jk}\sigma^{bcf}_{ilm}\sigma^{ef*}_{lm} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ad}\sigma^{de}_{lm}\sigma^{bcf}_{ijk}\sigma^{ef*}_{lm}$$

$$+\frac{1}{12}d_{cd}\sigma^{de}_{ij}\sigma^{abf}_{klm}\sigma^{ef*}_{lm}+\frac{1}{12}\mathcal{P}^{-}_{(ij)}d_{cd}\sigma^{de}_{jk}\sigma^{abf}_{ilm}\sigma^{ef*}_{lm}+\frac{1}{12}d_{cd}\sigma^{de}_{lm}\sigma^{abf}_{ijk}\sigma^{ef*}_{lm}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ijab)}d_{li}\sigma^{ac}_{lm}\sigma^{bde}_{jkn}\sigma^{de*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{ad}_{jl}\sigma^{bce}_{kmn}\sigma^{de*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{bd}_{kl}\sigma^{ace}_{jmn}\sigma^{de*}_{mn}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{cd}_{jl}\sigma^{abe}_{kmn}\sigma^{de*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(ij)}d_{lj}\sigma^{ab}_{lm}\sigma^{cde}_{ikn}\sigma^{de*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(ij)}d_{lj}\sigma^{de}_{lm}\sigma^{abc}_{ikn}\sigma^{de*}_{mn}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ab)}d_{lk}\sigma^{ac}_{lm}\sigma^{bde}_{ijn}\sigma^{de*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}d_{li}\sigma^{bd}_{lm}\sigma^{ace}_{jkn}\sigma^{de*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(ij)}d_{lj}\sigma^{cd}_{lm}\sigma^{abe}_{ikn}\sigma^{de*}_{mn}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(ab)}d_{lk}\sigma^{bd}_{lm}\sigma^{ace}_{ijn}\sigma^{de*}_{mn}+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{ed}\sigma^{ad}_{lm}\sigma^{bcf}_{ijk}\sigma^{ef*}_{lm}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ed}\sigma^{af}_{ik}\sigma^{bcd}_{jlm}\sigma^{ef*}_{lm}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{ed}\sigma^{bf}_{ij}\sigma^{acd}_{klm}\sigma^{ef*}_{lm}+\frac{1}{4}d_{ed}\sigma^{cd}_{lm}\sigma^{abf}_{ijk}\sigma^{ef*}_{lm}+\frac{1}{4}\mathcal{P}^{-}_{(ij)}d_{ed}\sigma^{cf}_{ik}\sigma^{abd}_{jlm}\sigma^{ef*}_{lm}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ij)}d_{lm}\sigma^{ab}_{in}\sigma^{cde}_{jkl}\sigma^{de*}_{mn}+\frac{1}{4}d_{lm}\sigma^{ab}_{kn}\sigma^{cde}_{ijl}\sigma^{de*}_{mn}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{lm}\sigma^{ac}_{jn}\sigma^{bde}_{ikl}\sigma^{de*}_{mn}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{lm}\sigma^{bc}_{kn}\sigma^{ade}_{ijl}\sigma^{de*}_{mn}+\frac{1}{4}\mathcal{P}^{-}_{(ij)}d_{lm}\sigma^{de}_{jl}\sigma^{abc}_{ikn}\sigma^{de*}_{mn}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}d_{ed}\sigma^{df}_{il}\sigma^{abc}_{jkm}\sigma^{ef*}_{lm}$$

$$+\frac{1}{2}d_{ed}\sigma^{df}_{kl}\sigma^{abc}_{ijm}\sigma^{ef*}_{lm}+\frac{1}{24}\mathcal{P}^{-}_{(ab)}d_{ad}\sigma^{ef}_{ij}\sigma^{bcd}_{klm}\sigma^{ef*}_{lm}+\frac{1}{24}\mathcal{P}^{-}_{(ijab)}d_{ad}\sigma^{ef}_{jk}\sigma^{bcd}_{ilm}\sigma^{ef*}_{lm}$$

$$+\frac{1}{24}d_{cd}\sigma^{ef}_{ij}\sigma^{abd}_{klm}\sigma^{ef*}_{lm}+\frac{1}{24}\mathcal{P}^{-}_{(ij)}d_{cd}\sigma^{ef}_{jk}\sigma^{abd}_{ilm}\sigma^{ef*}_{lm}+\frac{1}{24}\mathcal{P}^{-}_{(ijab)}d_{li}\sigma^{ac}_{mn}\sigma^{bde}_{jkl}\sigma^{de*}_{mn}$$

$$+\frac{1}{24}\mathcal{P}^{-}_{(ij)}d_{lj}\sigma^{ab}_{mn}\sigma^{cde}_{ikl}\sigma^{de*}_{mn}+\frac{1}{24}\mathcal{P}^{-}_{(ab)}d_{lk}\sigma^{ac}_{mn}\sigma^{bde}_{ijl}\sigma^{de*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(abc)}d_{ad}\sigma^{be}_{lm}\sigma^{cdf}_{ijk}\sigma^{ef*}_{lm}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{de}_{km}\sigma^{abc}_{jln}\sigma^{de*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ad}\sigma^{be}_{il}\sigma^{cdf}_{jkm}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ad}\sigma^{be}_{kl}\sigma^{cdf}_{ijm}\sigma^{ef*}_{lm}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ad}\sigma^{ce}_{jl}\sigma^{bdf}_{ikm}\sigma^{ef*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{ad}_{km}\sigma^{bce}_{jln}\sigma^{de*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{bd}_{jm}\sigma^{ace}_{kln}\sigma^{de*}_{mn}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{cd}_{km}\sigma^{abe}_{jln}\sigma^{de*}_{mn}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}d_{ed}\sigma^{ab}_{il}\sigma^{cdf}_{jkm}\sigma^{ef*}_{lm}+\frac{1}{2}d_{ed}\sigma^{ab}_{kl}\sigma^{cdf}_{ijm}\sigma^{ef*}_{lm}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ed}\sigma^{ac}_{jl}\sigma^{bdf}_{ikm}\sigma^{ef*}_{lm}+\frac{1}{2}\mathcal{P}^{-}_{(ab)}d_{ed}\sigma^{bc}_{kl}\sigma^{adf}_{ijm}\sigma^{ef*}_{lm}-\frac{1}{4}d_{ed}\sigma^{cf}_{ij}\sigma^{abd}_{klm}\sigma^{ef*}_{lm}$$

$$-\frac{1}{4}d_{ed}\sigma^{cf}_{lm}\sigma^{abd}_{ijk}\sigma^{ef*}_{lm}-\frac{1}{4}d_{lm}\sigma^{ab}_{kl}\sigma^{cde}_{ijn}\sigma^{de*}_{mn}-\frac{1}{4}d_{lm}\sigma^{ab}_{ln}\sigma^{cde}_{ijk}\sigma^{de*}_{mn}$$

$$-\frac{1}{4}d_{lm}\sigma^{de}_{ij}\sigma^{abc}_{kln}\sigma^{de*}_{mn}-\frac{1}{4}d_{lm}\sigma^{de}_{kl}\sigma^{abc}_{ijn}\sigma^{de*}_{mn}-\frac{1}{2}d_{lm}\sigma^{cd}_{ln}\sigma^{abe}_{ijk}\sigma^{de*}_{mn}$$

$$-\frac{1}{12}d_{lk}\sigma^{cd}_{ij}\sigma^{abe}_{lmn}\sigma^{de*}_{mn}-\frac{1}{12}d_{lk}\sigma^{cd}_{mn}\sigma^{abe}_{ijl}\sigma^{de*}_{mn}-\frac{1}{24}d_{lk}\sigma^{de}_{ij}\sigma^{abc}_{lmn}\sigma^{de*}_{mn}$$

$$-\frac{1}{2}d_{ed}\sigma^{cf}_{kl}\sigma^{abd}_{ijm}\sigma^{ef*}_{lm}-\frac{1}{2}d_{lm}\sigma^{cd}_{ij}\sigma^{abe}_{kln}\sigma^{de*}_{mn}-\frac{1}{24}d_{lk}\sigma^{ab}_{mn}\sigma^{cde}_{ijl}\sigma^{de*}_{mn}$$

$$-\frac{1}{12}d_{lk}\sigma^{ab}_{lm}\sigma^{cde}_{ijn}\sigma^{de*}_{mn}-\frac{1}{12}d_{lk}\sigma^{de}_{lm}\sigma^{abc}_{ijn}\sigma^{de*}_{mn}-\frac{1}{6}d_{lk}\sigma^{cd}_{lm}\sigma^{abe}_{ijn}\sigma^{de*}_{mn}$$

$$-\frac{1}{2}d_{lm}\sigma^{cd}_{kl}\sigma^{abe}_{ijn}\sigma^{de*}_{mn}$$

$$
\begin{aligned}
&+\frac{1}{2}\mathcal{P}^{-}_{(ij)}d_{ed}\sigma^{ab}_{il}\sigma^{cd}_{jk}\sigma^{e*}_{l}+\frac{1}{2}d_{ed}\sigma^{ab}_{kl}\sigma^{cd}_{ij}\sigma^{e*}_{l}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ed}\sigma^{ac}_{jl}\sigma^{bd}_{ik}\sigma^{e*}_{l}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(ab)}d_{ed}\sigma^{ad}_{ij}\sigma^{bc}_{kl}\sigma^{e*}_{l}+\frac{1}{2}\mathcal{P}^{-}_{(ij)}d_{lm}\sigma^{ab}_{jl}\sigma^{cd}_{ik}\sigma^{d*}_{m}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{lm}\sigma^{ac}_{il}\sigma^{bd}_{jk}\sigma^{d*}_{m}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(ab)}d_{lm}\sigma^{ac}_{kl}\sigma^{bd}_{ij}\sigma^{d*}_{m}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}d_{ad}\sigma^{bc}_{il}\sigma^{de}_{jk}\sigma^{e*}_{l}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}d_{ad}\sigma^{bc}_{kl}\sigma^{de}_{ij}\sigma^{e*}_{l}\\
&\quad+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ad}\sigma^{bd}_{jl}\sigma^{ce}_{ik}\sigma^{e*}_{l}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ad}\sigma^{be}_{ij}\sigma^{cd}_{kl}\sigma^{e*}_{l}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ad}\sigma^{be}_{jk}\sigma^{cd}_{il}\sigma^{e*}_{l}\\
&\quad+\frac{1}{6}\mathcal{P}^{-}_{(ij)}d_{cd}\sigma^{ab}_{il}\sigma^{de}_{jk}\sigma^{e*}_{l}+\frac{1}{6}d_{cd}\sigma^{ab}_{kl}\sigma^{de}_{ij}\sigma^{e*}_{l}+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{ab}_{km}\sigma^{cd}_{jl}\sigma^{d*}_{m}\\
&\quad+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{ac}_{jm}\sigma^{bd}_{kl}\sigma^{d*}_{m}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}d_{li}\sigma^{ac}_{lm}\sigma^{bd}_{jk}\sigma^{d*}_{m}+\frac{1}{6}\mathcal{P}^{-}_{(ijk)}d_{li}\sigma^{ad}_{jl}\sigma^{bc}_{km}\sigma^{d*}_{m}\\
&\quad+\frac{1}{6}\mathcal{P}^{-}_{(ij)}d_{lj}\sigma^{ab}_{lm}\sigma^{cd}_{ik}\sigma^{d*}_{m}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}d_{lk}\sigma^{ac}_{lm}\sigma^{bd}_{ij}\sigma^{d*}_{m}-\frac{1}{2}d_{lm}\sigma^{ab}_{kl}\sigma^{cd}_{ij}\sigma^{d*}_{m}\\
&\quad-\frac{1}{6}d_{lk}\sigma^{ab}_{lm}\sigma^{cd}_{ij}\sigma^{d*}_{m}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}d_{al}\sigma^{bc}_{jm}\sigma^{de}_{ik}\sigma^{de*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}d_{bl}\sigma^{ac}_{km}\sigma^{de}_{ij}\sigma^{de*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ij)}d_{cl}\sigma^{ab}_{jm}\sigma^{de}_{ik}\sigma^{de*}_{lm}\\
&\quad+\frac{1}{3}\mathcal{P}^{-}_{(abc)}d_{al}\sigma^{bd}_{ij}\sigma^{ce}_{km}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}d_{al}\sigma^{bd}_{im}\sigma^{ce}_{jk}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(abc)}d_{bl}\sigma^{ad}_{ik}\sigma^{ce}_{jm}\sigma^{de*}_{lm}\\
&\quad+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}d_{di}\sigma^{ab}_{jl}\sigma^{ce}_{km}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}d_{di}\sigma^{ac}_{kl}\sigma^{be}_{jm}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ijk)}d_{di}\sigma^{ae}_{jl}\sigma^{bc}_{km}\sigma^{de*}_{lm}\\
&\quad+\frac{1}{6}\mathcal{P}^{-}_{(ijab)}d_{di}\sigma^{ac}_{lm}\sigma^{be}_{jk}\sigma^{de*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ij)}d_{dj}\sigma^{ab}_{lm}\sigma^{ce}_{ik}\sigma^{de*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(ab)}d_{dk}\sigma^{ac}_{lm}\sigma^{be}_{ij}\sigma^{de*}_{lm}\\
&\quad+\frac{1}{3}\mathcal{P}^{-}_{(ij)}d_{dl}\sigma^{ab}_{im}\sigma^{ce}_{jk}\sigma^{de*}_{lm}+\frac{1}{3}d_{dl}\sigma^{ab}_{km}\sigma^{ce}_{ij}\sigma^{de*}_{lm}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)}d_{dl}\sigma^{ac}_{jm}\sigma^{be}_{ik}\sigma^{de*}_{lm}\\
&\quad+\frac{1}{3}\mathcal{P}^{-}_{(ab)}d_{dl}\sigma^{ae}_{ij}\sigma^{bc}_{km}\sigma^{de*}_{lm}-\frac{1}{6}d_{cl}\sigma^{ab}_{km}\sigma^{de}_{ij}\sigma^{de*}_{lm}-\frac{1}{6}d_{dk}\sigma^{ab}_{lm}\sigma^{ce}_{ij}\sigma^{de*}_{lm}
\end{aligned}
$$

$$
\begin{aligned}
&\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ad}_{ij}\sigma^{be}_{km}\sigma^{cf}_{ln}\sigma^{ef*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ad}_{ik}\sigma^{be}_{lm}\sigma^{cf}_{jn}\sigma^{ef*}_{mn}+\frac{1}{6}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ad}_{jk}\sigma^{be}_{im}\sigma^{cf}_{ln}\sigma^{ef*}_{mn}\\
&\quad+\frac{1}{4}\mathcal{P}^{-}_{(ij)}d_{ld}\sigma^{ab}_{lm}\sigma^{cf}_{in}\sigma^{de}_{jk}\sigma^{ef*}_{mn}+\frac{1}{4}d_{ld}\sigma^{ab}_{lm}\sigma^{cf}_{kn}\sigma^{de}_{ij}\sigma^{ef*}_{mn}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ld}\sigma^{ac}_{lm}\sigma^{bf}_{jn}\sigma^{de}_{ik}\sigma^{ef*}_{mn}\\
&\quad+\frac{1}{12}\mathcal{P}^{-}_{(ij)}d_{ld}\sigma^{ab}_{in}\sigma^{cd}_{jk}\sigma^{ef}_{lm}\sigma^{ef*}_{mn}+\frac{1}{12}d_{ld}\sigma^{ab}_{kn}\sigma^{cd}_{ij}\sigma^{ef}_{lm}\sigma^{ef*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(ijab)}d_{ld}\sigma^{ac}_{jn}\sigma^{bd}_{ik}\sigma^{ef}_{lm}\sigma^{ef*}_{mn}\\
&\quad+\frac{1}{12}\mathcal{P}^{-}_{(ab)}d_{ld}\sigma^{ad}_{ij}\sigma^{bc}_{kn}\sigma^{ef}_{lm}\sigma^{ef*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ad}_{ik}\sigma^{be}_{jl}\sigma^{cf}_{mn}\sigma^{ef*}_{mn}+\frac{1}{12}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ae}_{il}\sigma^{bd}_{jk}\sigma^{cf}_{mn}\sigma^{ef*}_{mn}\\
&\quad+\frac{1}{12}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ae}_{kl}\sigma^{bd}_{ij}\sigma^{cf}_{mn}\sigma^{ef*}_{mn}+\frac{1}{8}\mathcal{P}^{-}_{(ijab)}d_{ld}\sigma^{ad}_{jm}\sigma^{bc}_{ln}\sigma^{ef}_{ik}\sigma^{ef*}_{mn}+\frac{1}{8}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ad}_{mn}\sigma^{be}_{ik}\sigma^{cf}_{jl}\sigma^{ef*}_{mn}\\
&\quad+\frac{1}{8}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ae}_{ij}\sigma^{bd}_{mn}\sigma^{cf}_{kl}\sigma^{ef*}_{mn}+\frac{1}{8}\mathcal{P}^{-}_{(abc)}d_{ld}\sigma^{ae}_{jk}\sigma^{bd}_{mn}\sigma^{cf}_{il}\sigma^{ef*}_{mn}+\frac{1}{24}\mathcal{P}^{-}_{(ij)}d_{ld}\sigma^{ab}_{il}\sigma^{cd}_{mn}\sigma^{ef}_{jk}\sigma^{ef*}_{mn}\\
&\quad+\frac{1}{24}\mathcal{P}^{-}_{(ij)}d_{ld}\sigma^{ab}_{jm}\sigma^{cd}_{ln}\sigma^{ef}_{ik}\sigma^{ef*}_{mn}+\frac{1}{24}d_{ld}\sigma^{ab}_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ij}\sigma^{ef*}_{mn}+\frac{1}{24}d_{ld}\sigma^{ab}_{mn}\sigma^{cd}_{ij}\sigma^{ef}_{kl}\sigma^{ef*}_{mn}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{1}{24}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{mn}\sigma^{cd}_{jk}\sigma^{ef}_{il}\sigma^{ef*}_{mn} + \frac{1}{24} d_{ld}\sigma^{ab}_{mn}\sigma^{cf}_{ij}\sigma^{de}_{kl}\sigma^{ef*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{mn}\sigma^{cf}_{jk}\sigma^{de}_{il}\sigma^{ef*}_{mn} \\
&+ \frac{1}{24}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{im}\sigma^{bd}_{ln}\sigma^{ef}_{jk}\sigma^{ef*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{jl}\sigma^{bd}_{mn}\sigma^{ef}_{ik}\sigma^{ef*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{ac}_{km}\sigma^{bd}_{ln}\sigma^{ef}_{ij}\sigma^{ef*}_{mn} \\
&+ \frac{1}{24}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{mn}\sigma^{bd}_{ik}\sigma^{ef}_{jl}\sigma^{ef*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{mn}\sigma^{bf}_{ik}\sigma^{de}_{jl}\sigma^{ef*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{ad}_{ij}\sigma^{bc}_{mn}\sigma^{ef}_{kl}\sigma^{ef*}_{mn} \\
&+ \frac{1}{24}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{ad}_{mn}\sigma^{bc}_{kl}\sigma^{ef}_{ij}\sigma^{ef*}_{mn} + \frac{1}{24}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{ij}\sigma^{bc}_{mn}\sigma^{de}_{kl}\sigma^{ef*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ab}_{il}\sigma^{cf}_{jn}\sigma^{de}_{km}\sigma^{ef*}_{mn} \\
&+ \frac{1}{6}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ac}_{il}\sigma^{bf}_{kn}\sigma^{de}_{jm}\sigma^{ef*}_{mn} + \frac{1}{6}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{af}_{in}\sigma^{bc}_{kl}\sigma^{de}_{jm}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ab}_{in}\sigma^{cf}_{kl}\sigma^{de}_{jm}\sigma^{ef*}_{mn} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ac}_{in}\sigma^{bf}_{jl}\sigma^{de}_{km}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{af}_{il}\sigma^{bc}_{jn}\sigma^{de}_{km}\sigma^{ef*}_{mn} + \frac{1}{8}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{lm}\sigma^{cd}_{in}\sigma^{ef}_{jk}\sigma^{ef*}_{mn} \\
&+ \frac{1}{8} d_{ld}\sigma^{ab}_{lm}\sigma^{cd}_{kn}\sigma^{ef}_{ij}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{af}_{lm}\sigma^{bc}_{in}\sigma^{de}_{jk}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{lm}\sigma^{bc}_{kn}\sigma^{de}_{ij}\sigma^{ef*}_{mn} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ab}_{im}\sigma^{cd}_{kn}\sigma^{ef}_{jl}\sigma^{ef*}_{mn} + \frac{1}{8}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ac}_{im}\sigma^{bd}_{jn}\sigma^{ef}_{kl}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{ln}\sigma^{cf}_{ik}\sigma^{de}_{jm}\sigma^{ef*}_{mn} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{ac}_{ln}\sigma^{bf}_{ij}\sigma^{de}_{km}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{ln}\sigma^{bf}_{jk}\sigma^{de}_{im}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ab}_{im}\sigma^{cf}_{kn}\sigma^{de}_{jl}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{ln}\sigma^{cd}_{ik}\sigma^{ef}_{jm}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ac}_{im}\sigma^{bf}_{jn}\sigma^{de}_{kl}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{ac}_{ln}\sigma^{bd}_{ij}\sigma^{ef}_{km}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{ln}\sigma^{bd}_{jk}\sigma^{ef}_{im}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ld}\sigma^{ad}_{lm}\sigma^{be}_{ik}\sigma^{cf}_{jn}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ld}\sigma^{ae}_{ij}\sigma^{bd}_{lm}\sigma^{cf}_{kn}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12}\mathcal{P}^{-}_{(abc)} d_{ld}\sigma^{ae}_{im}\sigma^{bf}_{jk}\sigma^{cd}_{ln}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{af}_{im}\sigma^{bc}_{kn}\sigma^{de}_{jl}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{in}\sigma^{cf}_{jk}\sigma^{de}_{lm}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12} d_{ld}\sigma^{ab}_{kn}\sigma^{cf}_{ij}\sigma^{de}_{lm}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{jn}\sigma^{bf}_{ik}\sigma^{de}_{lm}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{ij}\sigma^{bc}_{kn}\sigma^{de}_{lm}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{il}\sigma^{cf}_{jk}\sigma^{de}_{mn}\sigma^{ef*}_{mn} + \frac{1}{12} d_{ld}\sigma^{ab}_{kl}\sigma^{cf}_{ij}\sigma^{de}_{mn}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{jl}\sigma^{bf}_{ik}\sigma^{de}_{mn}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{ij}\sigma^{bc}_{kl}\sigma^{de}_{mn}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{il}\sigma^{cf}_{mn}\sigma^{de}_{jk}\sigma^{ef*}_{mn} + \frac{1}{12} d_{ld}\sigma^{ab}_{kl}\sigma^{cf}_{mn}\sigma^{de}_{ij}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{jl}\sigma^{bf}_{mn}\sigma^{de}_{ik}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{mn}\sigma^{bc}_{kl}\sigma^{de}_{ij}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ab}_{il}\sigma^{cd}_{jn}\sigma^{ef}_{km}\sigma^{ef*}_{mn} \\
&+ \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ac}_{il}\sigma^{bd}_{kn}\sigma^{ef}_{jm}\sigma^{ef*}_{mn} + \frac{1}{12}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ad}_{in}\sigma^{bc}_{kl}\sigma^{ef}_{jm}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ijkabc)} d_{ld}\sigma^{ad}_{im}\sigma^{be}_{kl}\sigma^{cf}_{jn}\sigma^{ef*}_{mn} \\
&+ \frac{1}{4}\mathcal{P}^{-}_{(abc)} d_{ld}\sigma^{ad}_{im}\sigma^{be}_{ln}\sigma^{cf}_{jk}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(abc)} d_{ld}\sigma^{ad}_{km}\sigma^{be}_{ln}\sigma^{cf}_{ij}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(abc)} d_{ld}\sigma^{ae}_{ik}\sigma^{bf}_{lm}\sigma^{cd}_{jn}\sigma^{ef*}_{mn} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(ijk)} d_{ld}\sigma^{ad}_{im}\sigma^{bc}_{kn}\sigma^{ef}_{jl}\sigma^{ef*}_{mn} + \frac{1}{8}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{mn}\sigma^{cf}_{il}\sigma^{de}_{jk}\sigma^{ef*}_{mn} + \frac{1}{8} d_{ld}\sigma^{ab}_{mn}\sigma^{cf}_{kl}\sigma^{de}_{ij}\sigma^{ef*}_{mn} \\
&+ \frac{1}{8}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ac}_{mn}\sigma^{bf}_{jl}\sigma^{de}_{ik}\sigma^{ef*}_{mn} + \frac{1}{8}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{kl}\sigma^{bc}_{mn}\sigma^{de}_{ij}\sigma^{ef*}_{mn} + \frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{jm}\sigma^{cf}_{ln}\sigma^{de}_{ik}\sigma^{ef*}_{mn} \\
&- \frac{1}{12} d_{ld}\sigma^{ab}_{ln}\sigma^{cd}_{ij}\sigma^{ef}_{km}\sigma^{ef*}_{mn} - \frac{1}{4}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{km}\sigma^{bc}_{ln}\sigma^{de}_{ij}\sigma^{ef*}_{mn} - \frac{1}{8}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{ac}_{lm}\sigma^{bd}_{kn}\sigma^{ef}_{ij}\sigma^{ef*}_{mn}
\end{aligned}
$$

$$- \frac{1}{4}d_{ld}\sigma^{ab}_{ln}\sigma^{cf}_{ij}\sigma^{de}_{km}\sigma^{ef*}_{mn} - \frac{1}{4}d_{ld}\sigma^{ab}_{km}\sigma^{cf}_{ln}\sigma^{de}_{ij}\sigma^{ef*}_{mn} - \frac{1}{24}d_{ld}\sigma^{ab}_{km}\sigma^{cd}_{ln}\sigma^{ef}_{ij}\sigma^{ef*}_{mn}$$

C.2.4. PP-UCC4 state-to-state densities

PP-UCC4 state-to-state density, singles/singles:

$$\langle\Phi^a_i|\bar{D}|\Phi^b_j\rangle \; =$$

$$d_{ab}\delta_{ij} - d_{ji}\delta_{ab}$$

$$+ \frac{1}{2}d_{ac}\sigma^{cd}_{ik}\sigma^{bd*}_{jk} + \frac{1}{2}d_{cb}\sigma^{ad}_{ik}\sigma^{cd*}_{jk} + d_{dc}\sigma^{ac}_{ik}\sigma^{bd*}_{jk}$$

$$- \frac{1}{2}d_{jk}\sigma^{ac}_{il}\sigma^{bc*}_{kl} - \frac{1}{2}d_{ki}\sigma^{ac}_{kl}\sigma^{bc*}_{jl} - d_{kl}\sigma^{ac}_{ik}\sigma^{bc*}_{jl}$$

$$+ \frac{1}{2}d_{ck}\sigma^{ad}_{il}\sigma^{bcd*}_{jkl} - \frac{1}{4}d_{ak}\sigma^{cd}_{il}\sigma^{bcd*}_{jkl} - \frac{1}{4}d_{ci}\sigma^{ad}_{kl}\sigma^{bcd*}_{jkl}$$

$$+ \frac{1}{8}d_{cb}\sigma^{ade}_{ikl}\sigma^{cde*}_{jkl} + \frac{1}{8}d_{ac}\sigma^{cde}_{ikl}\sigma^{bde*}_{jkl} + \frac{1}{2}d_{dc}\sigma^{ace}_{ikl}\sigma^{bde*}_{jkl}$$

$$- \frac{1}{8}d_{jk}\sigma^{acd}_{ilm}\sigma^{bcd*}_{klm} - \frac{1}{8}d_{ki}\sigma^{acd}_{klm}\sigma^{bcd*}_{jlm} - \frac{1}{2}d_{kl}\sigma^{acd}_{ikm}\sigma^{bcd*}_{jlm}$$

$$+ \frac{1}{2}d_{kc}\sigma^{acd}_{ikl}\sigma^{bd*}_{jl} - \frac{1}{4}d_{kb}\sigma^{acd}_{ikl}\sigma^{cd*}_{jl} - \frac{1}{4}d_{jc}\sigma^{acd}_{ikl}\sigma^{bd*}_{kl}$$

$$- \frac{1}{2}d_{ak}\sigma^{c}_{i}\sigma^{bc*}_{jk} - \frac{1}{2}d_{ci}\sigma^{a}_{k}\sigma^{bc*}_{jk}$$

$$- \frac{1}{2}d_{jc}\sigma^{ac}_{ik}\sigma^{b*}_{k} - \frac{1}{2}d_{kb}\sigma^{ac}_{ik}\sigma^{c*}_{j}$$

$$- d_{ak}\sigma^{b*}_{k}\delta_{ij} - d_{ci}\sigma^{c*}_{j}\delta_{ab}$$

$$- d_{jc}\sigma^{c}_{i}\delta_{ab} - d_{kb}\sigma^{a}_{k}\delta_{ij}$$

$$+ \frac{1}{4}d_{jk}\sigma^{cd}_{il}\sigma^{cd*}_{kl}\delta_{ab} + \frac{1}{4}d_{ki}\sigma^{cd}_{kl}\sigma^{cd*}_{jl}\delta_{ab} + \frac{1}{2}d_{kl}\sigma^{cd}_{ik}\sigma^{cd*}_{jl}\delta_{ab}$$

$$+ d_{kl}\sigma^{ac}_{km}\sigma^{bc*}_{lm}\delta_{ij} - \frac{1}{4}d_{ac}\sigma^{cd}_{kl}\sigma^{bd*}_{kl}\delta_{ij} - \frac{1}{4}d_{cb}\sigma^{ad}_{kl}\sigma^{cd*}_{kl}\delta_{ij}$$

$$- \frac{1}{2}d_{dc}\sigma^{ac}_{kl}\sigma^{bd*}_{kl}\delta_{ij} - d_{dc}\sigma^{ce}_{ik}\sigma^{de*}_{jk}\delta_{ab}$$

$$+ \frac{1}{4}d_{kc}\sigma^{acd}_{klm}\sigma^{bd*}_{lm}\delta_{ij} + \frac{1}{4}d_{kc}\sigma^{cde}_{ikl}\sigma^{de*}_{jl}\delta_{ab} - \frac{1}{8}d_{jc}\sigma^{cde}_{ikl}\sigma^{de*}_{kl}\delta_{ab}$$

$$
\begin{aligned}
&- \frac{1}{8} d_{kb} \sigma^{acd}_{klm} \sigma^{cd*}_{lm} \delta_{ij} \\
&+ \frac{1}{2} d_{jk} \sigma^{c}_{i} \sigma^{c*}_{k} \delta_{ab} + \frac{1}{2} d_{ki} \sigma^{c}_{k} \sigma^{c*}_{j} \delta_{ab} + d_{kl} \sigma^{a}_{k} \sigma^{b*}_{l} \delta_{ij} \\
&- \frac{1}{2} d_{ac} \sigma^{c}_{k} \sigma^{b*}_{k} \delta_{ij} - \frac{1}{2} d_{cb} \sigma^{a}_{k} \sigma^{c*}_{k} \delta_{ij} - d_{dc} \sigma^{c}_{i} \sigma^{d*}_{j} \delta_{ab} \\
&+ \frac{1}{2} d_{ck} \sigma^{a}_{l} \sigma^{bc*}_{kl} \delta_{ij} + \frac{1}{2} d_{ck} \sigma^{d}_{i} \sigma^{cd*}_{jk} \delta_{ab} - \frac{1}{2} d_{ak} \sigma^{c}_{l} \sigma^{bc*}_{kl} \delta_{ij} \\
&- \frac{1}{2} d_{ci} \sigma^{d}_{k} \sigma^{cd*}_{jk} \delta_{ab} \\
&+ \frac{1}{2} d_{kc} \sigma^{ac}_{kl} \sigma^{b*}_{l} \delta_{ij} + \frac{1}{2} d_{kc} \sigma^{cd}_{ik} \sigma^{d*}_{j} \delta_{ab} - \frac{1}{2} d_{jc} \sigma^{cd}_{ik} \sigma^{d*}_{k} \delta_{ab} \\
&- \frac{1}{2} d_{kb} \sigma^{ac}_{kl} \sigma^{c*}_{l} \delta_{ij} \\
&+ d_{ck} \sigma^{c*}_{k} \delta_{ab} \delta_{ij} \\
&+ d_{kc} \sigma^{c}_{k} \delta_{ab} \delta_{ij} \\
&+ \frac{1}{3} d_{ck} \sigma^{ade}_{ilm} \sigma^{be*}_{jk} \sigma^{cd*}_{lm} + \frac{1}{6} d_{ck} \sigma^{ade}_{ilm} \sigma^{be*}_{jm} \sigma^{cd*}_{kl} + \frac{1}{12} d_{ck} \sigma^{ade}_{ilm} \sigma^{be*}_{lm} \sigma^{cd*}_{jk} \\
&\quad + \frac{1}{6} d_{ck} \sigma^{ade}_{ilm} \sigma^{bc*}_{lm} \sigma^{de*}_{jk} + \frac{1}{3} d_{ck} \sigma^{ade}_{ilm} \sigma^{bc*}_{jm} \sigma^{de*}_{kl} + \frac{1}{12} d_{ak} \sigma^{cde}_{ilm} \sigma^{be*}_{km} \sigma^{cd*}_{jl} \\
&\quad - \frac{1}{24} d_{ci} \sigma^{ade}_{klm} \sigma^{bc*}_{lm} \sigma^{de*}_{jk} - \frac{1}{24} d_{ci} \sigma^{ade}_{klm} \sigma^{bc*}_{jm} \sigma^{de*}_{kl} - \frac{1}{12} d_{ci} \sigma^{ade}_{klm} \sigma^{be*}_{jm} \sigma^{cd*}_{kl} \\
&\quad - \frac{2}{3} d_{ck} \sigma^{ade}_{ilm} \sigma^{be*}_{km} \sigma^{cd*}_{jl} - \frac{1}{24} d_{ak} \sigma^{cde}_{ilm} \sigma^{be*}_{lm} \sigma^{cd*}_{jk} - \frac{1}{24} d_{ak} \sigma^{cde}_{ilm} \sigma^{be*}_{jk} \sigma^{cd*}_{lm} \\
&\quad - \frac{1}{12} d_{ck} \sigma^{ade}_{ilm} \sigma^{bc*}_{km} \sigma^{de*}_{jl} - \frac{1}{12} d_{ci} \sigma^{ade}_{klm} \sigma^{be*}_{lm} \sigma^{cd*}_{jk} - \frac{1}{12} d_{ak} \sigma^{cde}_{ilm} \sigma^{be*}_{jm} \sigma^{cd*}_{kl} \\
&+ \frac{1}{4} d_{kl} \sigma^{acd}_{kmn} \sigma^{bcd*}_{lmn} \delta_{ij} + \frac{1}{6} d_{kl} \sigma^{cde}_{ikm} \sigma^{cde*}_{jlm} \delta_{ab} + \frac{1}{24} d_{jk} \sigma^{cde}_{ilm} \sigma^{cde*}_{klm} \delta_{ab} \\
&\quad + \frac{1}{24} d_{ki} \sigma^{cde}_{klm} \sigma^{cde*}_{jlm} \delta_{ab} - \frac{1}{6} d_{dc} \sigma^{ace}_{klm} \sigma^{bde*}_{klm} \delta_{ij} - \frac{1}{4} d_{dc} \sigma^{cef}_{ikl} \sigma^{def*}_{jkl} \delta_{ab} \\
&\quad - \frac{1}{24} d_{cb} \sigma^{ade}_{klm} \sigma^{cde*}_{klm} \delta_{ij} - \frac{1}{24} d_{ac} \sigma^{cde}_{klm} \sigma^{bde*}_{klm} \delta_{ij} \\
&+ \frac{1}{3} d_{kc} \sigma^{ae}_{ik} \sigma^{cd}_{lm} \sigma^{bde*}_{jlm} + \frac{1}{6} d_{kc} \sigma^{ac}_{lm} \sigma^{de}_{ik} \sigma^{bde*}_{jlm} + \frac{1}{12} d_{kb} \sigma^{ae}_{km} \sigma^{cd}_{il} \sigma^{cde*}_{jlm} \\
&\quad + \frac{1}{6} d_{kc} \sigma^{ae}_{im} \sigma^{cd}_{kl} \sigma^{bde*}_{jlm} + \frac{1}{3} d_{kc} \sigma^{ac}_{im} \sigma^{de}_{kl} \sigma^{bde*}_{jlm} + \frac{1}{12} d_{kc} \sigma^{ae}_{lm} \sigma^{cd}_{ik} \sigma^{bde*}_{jlm} \\
&\quad - \frac{1}{24} d_{jc} \sigma^{ac}_{lm} \sigma^{de}_{ik} \sigma^{bde*}_{klm} - \frac{1}{24} d_{jc} \sigma^{ac}_{im} \sigma^{de}_{kl} \sigma^{bde*}_{klm} - \frac{1}{12} d_{jc} \sigma^{ae}_{im} \sigma^{cd}_{kl} \sigma^{bde*}_{klm} \\
&\quad - \frac{1}{24} d_{kb} \sigma^{ae}_{lm} \sigma^{cd}_{ik} \sigma^{cde*}_{jlm} - \frac{1}{24} d_{kb} \sigma^{ae}_{ik} \sigma^{cd}_{lm} \sigma^{cde*}_{jlm} - \frac{1}{12} d_{kc} \sigma^{ac}_{km} \sigma^{de}_{il} \sigma^{bde*}_{jlm}
\end{aligned}
$$

$$
\begin{aligned}
&- \frac{1}{12} d_{kb} \sigma_{im}^{ae} \sigma_{kl}^{cd} \sigma_{jlm}^{cde*} - \frac{2}{3} d_{kc} \sigma_{km}^{ae} \sigma_{il}^{cd} \sigma_{jlm}^{bde*} - \frac{1}{12} d_{jc} \sigma_{lm}^{ae} \sigma_{ik}^{cd} \sigma_{klm}^{bde*} \\
&+ \frac{1}{6} d_{ak} \sigma_{il}^{cd} \sigma_{l}^{c*} \sigma_{jk}^{bd*} + \frac{1}{6} d_{ci} \sigma_{kl}^{ad} \sigma_{k}^{d*} \sigma_{jl}^{bc*} + \frac{1}{6} d_{ci} \sigma_{kl}^{ad} \sigma_{k}^{b*} \sigma_{jl}^{cd*} \\
&\quad + \frac{1}{6} d_{ak} \sigma_{il}^{cd} \sigma_{j}^{c*} \sigma_{kl}^{bd*} + \frac{1}{6} d_{ck} \sigma_{il}^{ad} \sigma_{l}^{b*} \sigma_{jk}^{cd*} + \frac{1}{6} d_{ck} \sigma_{il}^{ad} \sigma_{j}^{d*} \sigma_{kl}^{bc*} \\
&\quad - \frac{1}{2} d_{ck} \sigma_{il}^{ad} \sigma_{k}^{b*} \sigma_{jl}^{cd*} - \frac{1}{2} d_{ck} \sigma_{il}^{ad} \sigma_{j}^{c*} \sigma_{kl}^{bd*} - \frac{1}{12} d_{ak} \sigma_{il}^{cd} \sigma_{l}^{b*} \sigma_{jk}^{cd*} \\
&\quad - \frac{1}{12} d_{ci} \sigma_{kl}^{ad} \sigma_{j}^{d*} \sigma_{kl}^{bc*} - \frac{1}{6} d_{ak} \sigma_{il}^{cd} \sigma_{k}^{c*} \sigma_{jl}^{bd*} - \frac{1}{6} d_{ci} \sigma_{kl}^{ad} \sigma_{k}^{c*} \sigma_{jl}^{bd*} \\
&\quad - \frac{2}{3} d_{ck} \sigma_{il}^{ad} \sigma_{l}^{c*} \sigma_{jk}^{bd*} - \frac{2}{3} d_{ck} \sigma_{il}^{ad} \sigma_{k}^{d*} \sigma_{jl}^{bc*} \\
&+ \frac{1}{6} d_{jc} \sigma_{k}^{d} \sigma_{il}^{ac} \sigma_{kl}^{bd*} + \frac{1}{6} d_{kb} \sigma_{l}^{c} \sigma_{ik}^{ad} \sigma_{jl}^{cd*} + \frac{1}{6} d_{jc} \sigma_{k}^{a} \sigma_{il}^{cd} \sigma_{kl}^{bd*} \\
&\quad + \frac{1}{6} d_{kb} \sigma_{i}^{c} \sigma_{kl}^{ad} \sigma_{jl}^{cd*} + \frac{1}{6} d_{kc} \sigma_{l}^{a} \sigma_{ik}^{cd} \sigma_{jl}^{bd*} + \frac{1}{6} d_{kc} \sigma_{i}^{d} \sigma_{kl}^{ac} \sigma_{jl}^{bd*} \\
&\quad - \frac{1}{2} d_{kc} \sigma_{k}^{a} \sigma_{il}^{cd} \sigma_{jl}^{bd*} - \frac{1}{2} d_{kc} \sigma_{i}^{c} \sigma_{kl}^{ad} \sigma_{jl}^{bd*} - \frac{1}{12} d_{jc} \sigma_{i}^{d} \sigma_{kl}^{ac} \sigma_{kl}^{bd*} \\
&\quad - \frac{1}{12} d_{kb} \sigma_{l}^{a} \sigma_{ik}^{cd} \sigma_{jl}^{cd*} - \frac{1}{6} d_{jc} \sigma_{k}^{c} \sigma_{il}^{ad} \sigma_{kl}^{bd*} - \frac{1}{6} d_{kb} \sigma_{k}^{c} \sigma_{il}^{ad} \sigma_{jl}^{cd*} \\
&\quad - \frac{2}{3} d_{kc} \sigma_{l}^{c} \sigma_{ik}^{ad} \sigma_{jl}^{bd*} - \frac{2}{3} d_{kc} \sigma_{k}^{d} \sigma_{il}^{ac} \sigma_{jl}^{bd*} \\
&+ \frac{1}{4} d_{ck} \sigma_{lm}^{ad} \sigma_{klm}^{bcd*} \delta_{ij} + \frac{1}{4} d_{ck} \sigma_{il}^{de} \sigma_{jkl}^{cde*} \delta_{ab} - \frac{1}{8} d_{ak} \sigma_{lm}^{cd} \sigma_{klm}^{bcd*} \delta_{ij} \\
&\quad - \frac{1}{8} d_{ci} \sigma_{kl}^{de} \sigma_{jkl}^{cde*} \delta_{ab} \\
&+ \frac{1}{4} d_{ck} \sigma_{lm}^{ad} \sigma_{k}^{b*} \sigma_{lm}^{cd*} \delta_{ij} + \frac{1}{4} d_{ck} \sigma_{il}^{de} \sigma_{j}^{c*} \sigma_{kl}^{de*} \delta_{ab} + \frac{1}{12} d_{ak} \sigma_{lm}^{cd} \sigma_{l}^{b*} \sigma_{km}^{cd*} \delta_{ij} \\
&\quad + \frac{1}{12} d_{ak} \sigma_{lm}^{cd} \sigma_{k}^{c*} \sigma_{lm}^{bd*} \delta_{ij} + \frac{1}{12} d_{ci} \sigma_{kl}^{de} \sigma_{k}^{c*} \sigma_{jl}^{de*} \delta_{ab} + \frac{1}{12} d_{ci} \sigma_{kl}^{de} \sigma_{j}^{d*} \sigma_{kl}^{ce*} \delta_{ab} \\
&\quad + \frac{1}{3} d_{ck} \sigma_{lm}^{ad} \sigma_{k}^{d*} \sigma_{lm}^{bc*} \delta_{ij} + \frac{1}{3} d_{ck} \sigma_{il}^{de} \sigma_{l}^{c*} \sigma_{jk}^{de*} \delta_{ab} + \frac{2}{3} d_{ck} \sigma_{lm}^{ad} \sigma_{l}^{c*} \sigma_{km}^{bd*} \delta_{ij} \\
&\quad + \frac{2}{3} d_{ck} \sigma_{il}^{de} \sigma_{k}^{d*} \sigma_{jl}^{ce*} \delta_{ab} - \frac{1}{6} d_{ak} \sigma_{lm}^{cd} \sigma_{l}^{c*} \sigma_{km}^{bd*} \delta_{ij} - \frac{1}{6} d_{ci} \sigma_{kl}^{de} \sigma_{k}^{d*} \sigma_{jl}^{ce*} \delta_{ab} \\
&\quad - \frac{1}{6} d_{ck} \sigma_{lm}^{ad} \sigma_{l}^{b*} \sigma_{km}^{cd*} \delta_{ij} - \frac{1}{6} d_{ck} \sigma_{lm}^{ad} \sigma_{l}^{d*} \sigma_{km}^{bc*} \delta_{ij} - \frac{1}{6} d_{ck} \sigma_{il}^{de} \sigma_{l}^{d*} \sigma_{jk}^{ce*} \delta_{ab} \\
&\quad - \frac{1}{6} d_{ck} \sigma_{il}^{de} \sigma_{j}^{d*} \sigma_{kl}^{ce*} \delta_{ab} \\
&+ \frac{1}{4} d_{kc} \sigma_{k}^{a} \sigma_{lm}^{cd} \sigma_{lm}^{bd*} \delta_{ij} + \frac{1}{4} d_{kc} \sigma_{i}^{c} \sigma_{kl}^{de} \sigma_{jl}^{de*} \delta_{ab} + \frac{2}{3} d_{kc} \sigma_{l}^{c} \sigma_{km}^{ad} \sigma_{lm}^{bd*} \delta_{ij} \\
&\quad + \frac{1}{12} d_{jc} \sigma_{k}^{c} \sigma_{il}^{de} \sigma_{kl}^{de*} \delta_{ab} + \frac{1}{12} d_{jc} \sigma_{i}^{d} \sigma_{kl}^{ce} \sigma_{kl}^{de*} \delta_{ab} + \frac{1}{12} d_{kb} \sigma_{l}^{a} \sigma_{km}^{cd} \sigma_{lm}^{cd*} \delta_{ij}
\end{aligned}
$$

$$+\frac{1}{12}d_{kb}\sigma_{k}^{c}\sigma_{lm}^{ad}\sigma_{lm}^{cd*}\delta_{ij}+\frac{1}{3}d_{kc}\sigma_{l}^{c}\sigma_{ik}^{de}\sigma_{jl}^{de*}\delta_{ab}+\frac{1}{3}d_{kc}\sigma_{k}^{d}\sigma_{lm}^{ac}\sigma_{lm}^{bd*}\delta_{ij}$$
$$+\frac{2}{3}d_{kc}\sigma_{k}^{d}\sigma_{il}^{ce}\sigma_{jl}^{de*}\delta_{ab}-\frac{1}{6}d_{jc}\sigma_{k}^{d}\sigma_{il}^{ce}\sigma_{kl}^{de*}\delta_{ab}-\frac{1}{6}d_{kb}\sigma_{l}^{c}\sigma_{km}^{ad}\sigma_{lm}^{cd*}\delta_{ij}$$
$$-\frac{1}{6}d_{kc}\sigma_{l}^{d}\sigma_{km}^{ac}\sigma_{lm}^{bd*}\delta_{ij}-\frac{1}{6}d_{kc}\sigma_{l}^{d}\sigma_{ik}^{ce}\sigma_{jl}^{de*}\delta_{ab}-\frac{1}{6}d_{kc}\sigma_{l}^{a}\sigma_{km}^{cd}\sigma_{lm}^{bd*}\delta_{ij}$$
$$-\frac{1}{6}d_{kc}\sigma_{i}^{d}\sigma_{kl}^{ce}\sigma_{jl}^{de*}\delta_{ab}$$
$$+\frac{1}{2}d_{ck}\sigma_{l}^{d}\sigma_{kl}^{cd*}\delta_{ab}\delta_{ij}$$
$$+\frac{1}{2}d_{dc}\sigma_{kl}^{ce}\sigma_{kl}^{de*}\delta_{ab}\delta_{ij}-\frac{1}{2}d_{kl}\sigma_{km}^{cd}\sigma_{lm}^{cd*}\delta_{ab}\delta_{ij}$$
$$+\frac{1}{2}d_{kc}\sigma_{kl}^{cd}\sigma_{l}^{d*}\delta_{ab}\delta_{ij}$$
$$+d_{dc}\sigma_{k}^{c}\sigma_{k}^{d*}\delta_{ab}\delta_{ij}-d_{kl}\sigma_{k}^{c}\sigma_{l}^{c*}\delta_{ab}\delta_{ij}$$
$$+\frac{1}{12}d_{kc}\sigma_{mn}^{ae}\sigma_{kl}^{cd}\sigma_{lmn}^{bde*}\delta_{ij}+\frac{1}{3}d_{kc}\sigma_{kn}^{ae}\sigma_{lm}^{cd}\sigma_{lmn}^{bde*}\delta_{ij}+\frac{1}{3}d_{kc}\sigma_{im}^{cf}\sigma_{kl}^{de}\sigma_{jlm}^{def*}\delta_{ab}$$
$$+\frac{1}{24}d_{kc}\sigma_{ik}^{cf}\sigma_{lm}^{de}\sigma_{jlm}^{def*}\delta_{ab}+\frac{1}{24}d_{kc}\sigma_{kn}^{ac}\sigma_{lm}^{de}\sigma_{lmn}^{bde*}\delta_{ij}+\frac{1}{6}d_{kc}\sigma_{mn}^{ac}\sigma_{kl}^{de}\sigma_{lmn}^{bde*}\delta_{ij}$$
$$+\frac{1}{6}d_{kc}\sigma_{lm}^{cd}\sigma_{ik}^{ef}\sigma_{jlm}^{def*}\delta_{ab}+\frac{1}{12}d_{kc}\sigma_{kl}^{cd}\sigma_{im}^{ef}\sigma_{jlm}^{def*}\delta_{ab}-\frac{1}{24}d_{jc}\sigma_{im}^{cf}\sigma_{kl}^{de}\sigma_{klm}^{def*}\delta_{ab}$$
$$-\frac{1}{24}d_{kb}\sigma_{mn}^{ae}\sigma_{kl}^{cd}\sigma_{lmn}^{cde*}\delta_{ij}-\frac{1}{24}d_{jc}\sigma_{kl}^{cd}\sigma_{im}^{ef}\sigma_{klm}^{def*}\delta_{ab}-\frac{1}{24}d_{kb}\sigma_{kn}^{ae}\sigma_{lm}^{cd}\sigma_{lmn}^{cde*}\delta_{ij}$$
$$+\frac{1}{3}d_{ck}\sigma_{lmn}^{ade}\sigma_{kn}^{be*}\sigma_{lm}^{cd*}\delta_{ij}+\frac{1}{3}d_{ck}\sigma_{ilm}^{def}\sigma_{jm}^{cf*}\sigma_{kl}^{de*}\delta_{ab}+\frac{1}{24}d_{ck}\sigma_{lmn}^{ade}\sigma_{kn}^{bc*}\sigma_{lm}^{de*}\delta_{ij}$$
$$+\frac{1}{6}d_{ck}\sigma_{ilm}^{def}\sigma_{lm}^{cd*}\sigma_{jk}^{ef*}\delta_{ab}+\frac{1}{6}d_{ck}\sigma_{lmn}^{ade}\sigma_{mn}^{bc*}\sigma_{kl}^{de*}\delta_{ij}+\frac{1}{12}d_{ck}\sigma_{ilm}^{def}\sigma_{kl}^{cd*}\sigma_{jm}^{ef*}\delta_{ab}$$
$$+\frac{1}{12}d_{ck}\sigma_{lmn}^{ade}\sigma_{mn}^{be*}\sigma_{kl}^{cd*}\delta_{ij}+\frac{1}{24}d_{ck}\sigma_{ilm}^{def}\sigma_{jk}^{cf*}\sigma_{lm}^{de*}\delta_{ab}-\frac{1}{24}d_{ci}\sigma_{klm}^{def}\sigma_{kl}^{cd*}\sigma_{jm}^{ef*}\delta_{ab}$$
$$-\frac{1}{24}d_{ak}\sigma_{lmn}^{cde}\sigma_{mn}^{be*}\sigma_{kl}^{cd*}\delta_{ij}-\frac{1}{24}d_{ci}\sigma_{klm}^{def}\sigma_{jm}^{cf*}\sigma_{kl}^{de*}\delta_{ab}-\frac{1}{24}d_{ak}\sigma_{lmn}^{cde}\sigma_{kn}^{be*}\sigma_{lm}^{cd*}\delta_{ij}$$
$$+\frac{1}{8}d_{ck}\sigma_{lm}^{de}\sigma_{klm}^{cde*}\delta_{ab}\delta_{ij}$$
$$+\frac{1}{8}d_{kc}\sigma_{klm}^{cde}\sigma_{lm}^{de*}\delta_{ab}\delta_{ij}$$
$$+\frac{1}{12}d_{dc}\sigma_{klm}^{cef}\sigma_{klm}^{def*}\delta_{ab}\delta_{ij}-\frac{1}{12}d_{kl}\sigma_{kmn}^{cde}\sigma_{lmn}^{cde*}\delta_{ab}\delta_{ij}$$
$$+\frac{1}{6}d_{ck}\sigma_{lm}^{de}\sigma_{l}^{d*}\sigma_{km}^{ce*}\delta_{ab}\delta_{ij}-\frac{1}{3}d_{ck}\sigma_{lm}^{de}\sigma_{l}^{c*}\sigma_{km}^{de*}\delta_{ab}\delta_{ij}-\frac{1}{3}d_{ck}\sigma_{lm}^{de}\sigma_{k}^{d*}\sigma_{lm}^{ce*}\delta_{ab}\delta_{ij}$$
$$+\frac{1}{6}d_{kc}\sigma_{l}^{d}\sigma_{km}^{ce}\sigma_{lm}^{de*}\delta_{ab}\delta_{ij}-\frac{1}{3}d_{kc}\sigma_{l}^{c}\sigma_{km}^{de}\sigma_{lm}^{de*}\delta_{ab}\delta_{ij}-\frac{1}{3}d_{kc}\sigma_{k}^{d}\sigma_{lm}^{ce}\sigma_{lm}^{de*}\delta_{ab}\delta_{ij}$$

$$+\frac{1}{24}d_{kc}\sigma^{cf}_{kn}\sigma^{de}_{lm}\sigma^{def*}_{lmn}\delta_{ab}\delta_{ij}+\frac{1}{6}d_{kc}\sigma^{cf}_{mn}\sigma^{de}_{kl}\sigma^{def*}_{lmn}\delta_{ab}\delta_{ij}$$

$$+\frac{1}{6}d_{ck}\sigma^{def}_{lmn}\sigma^{cf*}_{mn}\sigma^{de*}_{kl}\delta_{ab}\delta_{ij}+\frac{1}{24}d_{ck}\sigma^{def}_{lmn}\sigma^{cf*}_{kn}\sigma^{de*}_{lm}\delta_{ab}\delta_{ij}$$

$$\frac{1}{12}d_{jk}\sigma^{ae}_{in}\sigma^{cd}_{lm}\sigma^{be*}_{km}\sigma^{cd*}_{ln}+\frac{1}{12}d_{jk}\sigma^{ae}_{mn}\sigma^{cd}_{il}\sigma^{be*}_{ln}\sigma^{cd*}_{km}+\frac{1}{12}d_{ki}\sigma^{ae}_{kn}\sigma^{cd}_{lm}\sigma^{be*}_{jm}\sigma^{cd*}_{ln}$$

$$+\frac{1}{12}d_{ki}\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{be*}_{ln}\sigma^{cd*}_{jm}+\frac{1}{3}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{bd*}_{jn}\sigma^{ce*}_{lm}+\frac{1}{12}d_{dc}\sigma^{ac}_{im}\sigma^{ef}_{kl}\sigma^{bf*}_{kl}\sigma^{de*}_{jm}$$

$$+\frac{1}{12}d_{dc}\sigma^{ac}_{im}\sigma^{ef}_{kl}\sigma^{bd*}_{lm}\sigma^{ef*}_{jk}+\frac{1}{12}d_{dc}\sigma^{ac}_{lm}\sigma^{ef}_{ik}\sigma^{bd*}_{jm}\sigma^{ef*}_{kl}+\frac{1}{12}d_{kl}\sigma^{ae}_{ik}\sigma^{cd}_{mn}\sigma^{bd*}_{mn}\sigma^{ce*}_{jl}$$

$$+\frac{1}{12}d_{kl}\sigma^{ae}_{mn}\sigma^{cd}_{ik}\sigma^{bd*}_{jl}\sigma^{ce*}_{mn}+\frac{1}{6}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{bd*}_{jm}\sigma^{ef*}_{kl}+\frac{1}{6}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{bd*}_{lm}\sigma^{ef*}_{jk}$$

$$+\frac{1}{3}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{bd*}_{mn}\sigma^{ce*}_{jl}+\frac{1}{3}d_{dc}\sigma^{ac}_{lm}\sigma^{ef}_{ik}\sigma^{bf*}_{jm}\sigma^{de*}_{kl}+\frac{1}{3}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{bd*}_{lm}\sigma^{ef*}_{jk}$$

$$+\frac{1}{16}d_{jk}\sigma^{ae}_{in}\sigma^{cd}_{lm}\sigma^{bd*}_{lm}\sigma^{ce*}_{kn}+\frac{1}{16}d_{ki}\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{bd*}_{jl}\sigma^{ce*}_{mn}+\frac{1}{3}d_{dc}\sigma^{ac}_{im}\sigma^{ef}_{kl}\sigma^{bf*}_{lm}\sigma^{de*}_{jk}$$

$$+\frac{1}{6}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{bf*}_{lm}\sigma^{de*}_{jk}+\frac{1}{6}d_{dc}\sigma^{ac}_{lm}\sigma^{ef}_{ik}\sigma^{bf*}_{lm}\sigma^{de*}_{jk}+\frac{1}{48}d_{cb}\sigma^{af}_{im}\sigma^{de}_{kl}\sigma^{cd*}_{kl}\sigma^{ef*}_{jm}$$

$$+\frac{1}{12}d_{dc}\sigma^{ac}_{lm}\sigma^{ef}_{ik}\sigma^{bf*}_{jk}\sigma^{de*}_{lm}+\frac{1}{6}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{bd*}_{lm}\sigma^{ce*}_{jn}+\frac{1}{12}d_{jk}\sigma^{ae}_{mn}\sigma^{cd}_{il}\sigma^{bd*}_{mn}\sigma^{ce*}_{kl}$$

$$+\frac{1}{12}d_{ki}\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{bd*}_{mn}\sigma^{ce*}_{jl}+\frac{1}{12}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{bf*}_{kl}\sigma^{de*}_{jm}+\frac{1}{12}d_{cb}\sigma^{af}_{lm}\sigma^{de}_{ik}\sigma^{cf*}_{kl}\sigma^{de*}_{jm}$$

$$+\frac{1}{24}d_{ac}\sigma^{cf}_{im}\sigma^{de}_{kl}\sigma^{be*}_{jl}\sigma^{df*}_{km}+\frac{1}{24}d_{cb}\sigma^{af}_{im}\sigma^{de}_{kl}\sigma^{ce*}_{jl}\sigma^{df*}_{km}+\frac{1}{6}d_{jk}\sigma^{ae}_{in}\sigma^{cd}_{lm}\sigma^{bd*}_{mn}\sigma^{ce*}_{kl}$$

$$+\frac{1}{6}d_{ki}\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{bd*}_{jn}\sigma^{ce*}_{lm}+\frac{1}{6}d_{kl}\sigma^{ae}_{mn}\sigma^{cd}_{ik}\sigma^{be*}_{ln}\sigma^{cd*}_{jm}+\frac{1}{3}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{bd*}_{ln}\sigma^{ce*}_{jm}$$

$$+\frac{1}{6}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{bd*}_{jm}\sigma^{ce*}_{ln}+\frac{1}{3}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{bd*}_{jm}\sigma^{ef*}_{kl}+\frac{1}{12}d_{cb}\sigma^{af}_{lm}\sigma^{de}_{ik}\sigma^{cd*}_{lm}\sigma^{ef*}_{jk}$$

$$+\frac{1}{12}d_{dc}\sigma^{ac}_{im}\sigma^{ef}_{kl}\sigma^{bd*}_{kl}\sigma^{ef*}_{jm}+\frac{1}{12}d_{dc}\sigma^{ac}_{lm}\sigma^{ef}_{ik}\sigma^{bd*}_{jk}\sigma^{ef*}_{lm}+\frac{1}{6}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{bf*}_{lm}\sigma^{de*}_{jk}$$

$$+\frac{1}{6}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{be*}_{lm}\sigma^{cd*}_{jn}+\frac{1}{6}d_{dc}\sigma^{ac}_{im}\sigma^{ef}_{kl}\sigma^{bf*}_{jm}\sigma^{de*}_{kl}+\frac{1}{6}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{bf*}_{jm}\sigma^{de*}_{kl}$$

$$+\frac{1}{6}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{be*}_{jm}\sigma^{cd*}_{ln}+\frac{1}{24}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{bd*}_{jm}\sigma^{ef*}_{kl}+\frac{1}{24}d_{ac}\sigma^{cf}_{im}\sigma^{de}_{kl}\sigma^{bf*}_{kl}\sigma^{de*}_{jm}$$

$$+\frac{1}{12}d_{jk}\sigma^{ae}_{in}\sigma^{cd}_{lm}\sigma^{bd*}_{kn}\sigma^{ce*}_{lm}+\frac{1}{12}d_{ki}\sigma^{ae}_{kn}\sigma^{cd}_{lm}\sigma^{bd*}_{jn}\sigma^{ce*}_{lm}+\frac{1}{6}d_{kl}\sigma^{ae}_{mn}\sigma^{cd}_{ik}\sigma^{bd*}_{mn}\sigma^{ce*}_{jl}$$

$$+\frac{1}{48}d_{ac}\sigma^{cf}_{im}\sigma^{de}_{kl}\sigma^{bf*}_{lm}\sigma^{de*}_{jk}+\frac{1}{48}d_{jk}\sigma^{ae}_{mn}\sigma^{cd}_{il}\sigma^{bd*}_{kl}\sigma^{ce*}_{mn}+\frac{1}{48}d_{cb}\sigma^{af}_{lm}\sigma^{de}_{ik}\sigma^{cf*}_{jm}\sigma^{de*}_{kl}$$

$$+\frac{1}{48}d_{ki}\sigma^{ae}_{kn}\sigma^{cd}_{lm}\sigma^{bd*}_{lm}\sigma^{ce*}_{jn}+\frac{1}{12}d_{kl}\sigma^{ae}_{ik}\sigma^{cd}_{mn}\sigma^{be*}_{ln}\sigma^{cd*}_{jm}+\frac{1}{24}d_{cb}\sigma^{af}_{im}\sigma^{de}_{kl}\sigma^{cf*}_{kl}\sigma^{de*}_{jm}$$

$$+\frac{1}{24}d_{cb}\sigma^{af}_{lm}\sigma^{de}_{ik}\sigma^{cf*}_{jk}\sigma^{de*}_{lm}+\frac{1}{48}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{bf*}_{jm}\sigma^{de*}_{kl}+\frac{1}{12}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{be*}_{jl}\sigma^{cd*}_{mn}$$

$$+\frac{1}{12}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{bd*}_{lm}\sigma^{ef*}_{jk}+\frac{1}{6}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{bf*}_{kl}\sigma^{de*}_{jm}+\frac{1}{6}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{bf*}_{jk}\sigma^{de*}_{lm}$$

$$+\frac{1}{6}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{bd*}_{jl}\sigma^{ce*}_{mn}+\frac{1}{3}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{be*}_{km}\sigma^{df*}_{jl}+\frac{1}{12}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{bd*}_{kl}\sigma^{ef*}_{jm}$$

$$+\frac{1}{12}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{bd*}_{jk}\sigma^{ef*}_{lm}+\frac{1}{6}d_{kl}\sigma^{ae}_{ik}\sigma^{cd}_{mn}\sigma^{bd*}_{jn}\sigma^{ce*}_{lm}+\frac{1}{6}d_{cb}\sigma^{af}_{lm}\sigma^{de}_{ik}\sigma^{cd*}_{kl}\sigma^{ef*}_{jm}$$

$$+\frac{1}{6}d_{kl}\sigma^{ae}_{ik}\sigma^{cd}_{mn}\sigma^{bd*}_{jl}\sigma^{ce*}_{mn}+\frac{1}{3}d_{kl}\sigma^{ae}_{mn}\sigma^{cd}_{ik}\sigma^{bd*}_{jn}\sigma^{ce*}_{lm}+\frac{1}{6}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{be*}_{mn}\sigma^{cd*}_{jl}$$

$$+\frac{1}{6}d_{jk}\sigma^{ae}_{mn}\sigma^{cd}_{il}\sigma^{bd*}_{kn}\sigma^{ce*}_{lm}+\frac{1}{6}d_{ki}\sigma^{ae}_{kn}\sigma^{cd}_{lm}\sigma^{bd*}_{mn}\sigma^{ce*}_{jl}+\frac{1}{8}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{be*}_{ln}\sigma^{cd*}_{jm}$$

$$+\frac{1}{8}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{be*}_{jn}\sigma^{cd*}_{lm}+\frac{1}{4}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{be*}_{jl}\sigma^{df*}_{km}-\frac{1}{6}d_{dc}\sigma^{ac}_{lm}\sigma^{ef}_{ik}\sigma^{bd*}_{km}\sigma^{ef*}_{jl}$$

$$-\frac{1}{24}d_{jk}\sigma^{ae}_{in}\sigma^{cd}_{lm}\sigma^{be*}_{lm}\sigma^{cd*}_{kn}-\frac{1}{24}d_{jk}\sigma^{ae}_{mn}\sigma^{cd}_{il}\sigma^{be*}_{kl}\sigma^{cd*}_{mn}-\frac{1}{24}d_{ki}\sigma^{ae}_{kn}\sigma^{cd}_{lm}\sigma^{be*}_{lm}\sigma^{cd*}_{jn}$$

$$-\frac{1}{24}d_{ki}\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{be*}_{jl}\sigma^{cd*}_{mn}-\frac{1}{12}d_{kl}\sigma^{ae}_{mn}\sigma^{cd}_{ik}\sigma^{be*}_{jn}\sigma^{cd*}_{lm}-\frac{1}{3}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{be*}_{jm}\sigma^{df*}_{kl}$$

$$-\frac{1}{3}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{bf*}_{km}\sigma^{de*}_{jl}-\frac{1}{6}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{be*}_{lm}\sigma^{cd*}_{jn}-\frac{1}{4}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{bd*}_{jm}\sigma^{ce*}_{ln}$$

$$-\frac{1}{6}d_{dc}\sigma^{ac}_{im}\sigma^{ef}_{kl}\sigma^{bd*}_{jl}\sigma^{ef*}_{km}-\frac{1}{3}d_{dc}\sigma^{ac}_{lm}\sigma^{ef}_{ik}\sigma^{bf*}_{km}\sigma^{de*}_{jl}-\frac{1}{6}d_{dc}\sigma^{ac}_{im}\sigma^{ef}_{kl}\sigma^{bf*}_{jl}\sigma^{de*}_{km}$$

$$-\frac{1}{6}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{bd*}_{jl}\sigma^{ef*}_{km}-\frac{1}{6}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{be*}_{jl}\sigma^{cd*}_{mn}-\frac{1}{3}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{bd*}_{lm}\sigma^{ce*}_{jn}$$

$$-\frac{1}{8}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{be*}_{kl}\sigma^{df*}_{jm}-\frac{1}{8}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{be*}_{jk}\sigma^{df*}_{lm}-\frac{1}{3}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{bd*}_{jl}\sigma^{ce*}_{mn}$$

$$-\frac{1}{48}d_{cb}\sigma^{af}_{lm}\sigma^{de}_{ik}\sigma^{ce*}_{jk}\sigma^{df*}_{lm}-\frac{1}{48}d_{jk}\sigma^{ae}_{in}\sigma^{cd}_{lm}\sigma^{be*}_{mn}\sigma^{cd*}_{kl}-\frac{1}{48}d_{jk}\sigma^{ae}_{mn}\sigma^{cd}_{il}\sigma^{be*}_{kn}\sigma^{cd*}_{lm}$$

$$-\frac{1}{48}d_{ki}\sigma^{ae}_{kn}\sigma^{cd}_{lm}\sigma^{be*}_{mn}\sigma^{cd*}_{jl}-\frac{1}{48}d_{ki}\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{be*}_{jn}\sigma^{cd*}_{lm}-\frac{1}{12}d_{ac}\sigma^{cf}_{im}\sigma^{de}_{kl}\sigma^{be*}_{jm}\sigma^{df*}_{kl}$$

$$-\frac{1}{6}d_{jk}\sigma^{ae}_{mn}\sigma^{cd}_{il}\sigma^{bd*}_{ln}\sigma^{ce*}_{km}-\frac{1}{6}d_{ki}\sigma^{ae}_{mn}\sigma^{cd}_{kl}\sigma^{bd*}_{ln}\sigma^{ce*}_{jm}-\frac{1}{24}d_{jk}\sigma^{ae}_{in}\sigma^{cd}_{lm}\sigma^{bd*}_{km}\sigma^{ce*}_{ln}$$

$$-\frac{1}{24}d_{ki}\sigma^{ae}_{kn}\sigma^{cd}_{lm}\sigma^{bd*}_{jm}\sigma^{ce*}_{ln}-\frac{1}{3}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{be*}_{lm}\sigma^{df*}_{jk}-\frac{1}{3}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{bd*}_{ln}\sigma^{ce*}_{jm}$$

$$-\frac{1}{6}d_{cb}\sigma^{af}_{lm}\sigma^{de}_{ik}\sigma^{ce*}_{jm}\sigma^{df*}_{kl}-\frac{1}{3}d_{kl}\sigma^{ae}_{mn}\sigma^{cd}_{ik}\sigma^{bd*}_{ln}\sigma^{ce*}_{jm}-\frac{1}{3}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{bd*}_{mn}\sigma^{ce*}_{jl}$$

$$-\frac{1}{16}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{bd*}_{jl}\sigma^{ef*}_{km}-\frac{1}{16}d_{cb}\sigma^{af}_{im}\sigma^{de}_{kl}\sigma^{cf*}_{km}\sigma^{de*}_{jl}-\frac{1}{12}d_{cb}\sigma^{af}_{im}\sigma^{de}_{kl}\sigma^{ce*}_{jm}\sigma^{df*}_{kl}$$

$$-\frac{1}{12}d_{ac}\sigma^{cf}_{im}\sigma^{de}_{kl}\sigma^{bf*}_{jl}\sigma^{de*}_{km}-\frac{1}{6}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{be*}_{jm}\sigma^{df*}_{kl}-\frac{1}{6}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{be*}_{lm}\sigma^{df*}_{jk}$$

$$-\frac{1}{12}d_{cb}\sigma^{af}_{im}\sigma^{de}_{kl}\sigma^{cf*}_{jl}\sigma^{de*}_{km}-\frac{1}{12}d_{kl}\sigma^{ae}_{ik}\sigma^{cd}_{mn}\sigma^{be*}_{mn}\sigma^{cd*}_{jl}-\frac{1}{12}d_{kl}\sigma^{ae}_{mn}\sigma^{cd}_{ik}\sigma^{be*}_{jl}\sigma^{cd*}_{mn}$$

$$-\frac{1}{3}d_{kl}\sigma^{ae}_{ik}\sigma^{cd}_{mn}\sigma^{bd*}_{ln}\sigma^{ce*}_{jm}-\frac{1}{6}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{im}\sigma^{bf*}_{jl}\sigma^{de*}_{km}-\frac{1}{12}d_{kl}\sigma^{ae}_{in}\sigma^{cd}_{km}\sigma^{be*}_{mn}\sigma^{cd*}_{jl}$$

$$
\begin{aligned}
&-\frac{1}{48}d_{ac}\sigma^{cf}_{im}\sigma^{de}_{kl}\sigma^{be*}_{kl}\sigma^{df*}_{jm}-\frac{1}{6}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{be*}_{jm}\sigma^{cd*}_{ln}-\frac{1}{3}d_{dc}\sigma^{af}_{lm}\sigma^{ce}_{ik}\sigma^{bd*}_{km}\sigma^{ef*}_{jl}\\
&-\frac{1}{3}d_{dc}\sigma^{af}_{im}\sigma^{ce}_{kl}\sigma^{bf*}_{jl}\sigma^{de*}_{km}-\frac{1}{6}d_{kl}\sigma^{ae}_{ik}\sigma^{cd}_{mn}\sigma^{be*}_{jn}\sigma^{cd*}_{lm}-\frac{1}{6}d_{cb}\sigma^{af}_{im}\sigma^{de}_{kl}\sigma^{cd*}_{km}\sigma^{ef*}_{jl}\\
&-\frac{1}{3}d_{kl}\sigma^{ae}_{kn}\sigma^{cd}_{im}\sigma^{bd*}_{jn}\sigma^{ce*}_{lm}-\frac{1}{6}d_{ac}\sigma^{cf}_{im}\sigma^{de}_{kl}\sigma^{be*}_{lm}\sigma^{df*}_{jk}\\
&+\frac{1}{6}d_{kl}\sigma^{ae}_{ko}\sigma^{cd}_{mn}\sigma^{be*}_{no}\sigma^{cd*}_{lm}\delta_{ij}+\frac{1}{6}d_{kl}\sigma^{ae}_{no}\sigma^{cd}_{km}\sigma^{be*}_{lo}\sigma^{cd*}_{mn}\delta_{ij}+\frac{1}{3}d_{dc}\sigma^{cg}_{im}\sigma^{ef}_{kl}\sigma^{de*}_{km}\sigma^{fg*}_{jl}\delta_{ab}\\
&+\frac{1}{12}d_{ac}\sigma^{cf}_{ln}\sigma^{de}_{km}\sigma^{bf*}_{mn}\sigma^{de*}_{kl}\delta_{ij}+\frac{1}{96}d_{jk}\sigma^{cd}_{lm}\sigma^{ef}_{in}\sigma^{cd*}_{kl}\sigma^{ef*}_{mn}\delta_{ab}+\frac{1}{96}d_{ki}\sigma^{cd}_{kl}\sigma^{ef}_{mn}\sigma^{cd*}_{lm}\sigma^{ef*}_{jn}\delta_{ab}\\
&+\frac{1}{12}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ik}\sigma^{cd*}_{lm}\sigma^{ef*}_{jn}\delta_{ab}+\frac{1}{6}d_{dc}\sigma^{ac}_{mn}\sigma^{ef}_{kl}\sigma^{bd*}_{ln}\sigma^{ef*}_{km}\delta_{ij}+\frac{1}{3}d_{dc}\sigma^{ac}_{mn}\sigma^{ef}_{kl}\sigma^{bf*}_{ln}\sigma^{de*}_{km}\delta_{ij}\\
&+\frac{1}{12}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{cd*}_{jn}\sigma^{ef*}_{lm}\delta_{ab}+\frac{1}{24}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{cd*}_{jl}\sigma^{ef*}_{mn}\delta_{ab}+\frac{1}{24}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ik}\sigma^{cd*}_{jl}\sigma^{ef*}_{mn}\delta_{ab}\\
&+\frac{1}{24}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ik}\sigma^{cd*}_{jn}\sigma^{ef*}_{lm}\delta_{ab}+\frac{1}{12}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{cd*}_{mn}\sigma^{ef*}_{jl}\delta_{ab}+\frac{1}{12}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{be*}_{mn}\sigma^{df*}_{kl}\delta_{ij}\\
&+\frac{1}{12}d_{dc}\sigma^{ce}_{kl}\sigma^{fg}_{im}\sigma^{de*}_{jl}\sigma^{fg*}_{km}\delta_{ab}+\frac{1}{6}d_{cb}\sigma^{af}_{mn}\sigma^{de}_{kl}\sigma^{cd*}_{km}\sigma^{ef*}_{ln}\delta_{ij}+\frac{1}{16}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{be*}_{kl}\sigma^{df*}_{mn}\delta_{ij}\\
&+\frac{1}{3}d_{dc}\sigma^{ce}_{kl}\sigma^{fg}_{im}\sigma^{dg*}_{jl}\sigma^{ef*}_{km}\delta_{ab}+\frac{1}{3}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{bd*}_{ln}\sigma^{ef*}_{km}\delta_{ij}+\frac{1}{3}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{ce*}_{ln}\sigma^{df*}_{jm}\delta_{ab}\\
&+\frac{1}{3}d_{kl}\sigma^{ae}_{no}\sigma^{cd}_{km}\sigma^{bd*}_{mo}\sigma^{ce*}_{ln}\delta_{ij}+\frac{1}{3}d_{kl}\sigma^{ae}_{ko}\sigma^{cd}_{mn}\sigma^{bd*}_{ln}\sigma^{ce*}_{mo}\delta_{ij}+\frac{1}{12}d_{cb}\sigma^{af}_{mn}\sigma^{de}_{kl}\sigma^{cf*}_{ln}\sigma^{de*}_{km}\delta_{ij}\\
&+\frac{1}{6}d_{dc}\sigma^{ce}_{kl}\sigma^{fg}_{im}\sigma^{de*}_{km}\sigma^{fg*}_{jl}\delta_{ab}+\frac{1}{3}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{bf*}_{ln}\sigma^{de*}_{km}\delta_{ij}+\frac{1}{12}d_{kl}\sigma^{ae}_{ko}\sigma^{cd}_{mn}\sigma^{be*}_{mn}\sigma^{cd*}_{lo}\delta_{ij}\\
&+\frac{1}{12}d_{kl}\sigma^{ae}_{no}\sigma^{cd}_{km}\sigma^{be*}_{lm}\sigma^{cd*}_{no}\delta_{ij}+\frac{1}{12}d_{dc}\sigma^{cg}_{im}\sigma^{ef}_{kl}\sigma^{dg*}_{km}\sigma^{ef*}_{jl}\delta_{ab}+\frac{1}{6}d_{ac}\sigma^{cd}_{km}\sigma^{ef}_{ln}\sigma^{bf*}_{mn}\sigma^{de*}_{kl}\delta_{ij}\\
&+\frac{1}{48}d_{jk}\sigma^{cd}_{lm}\sigma^{ef}_{in}\sigma^{cd*}_{kn}\sigma^{ef*}_{lm}\delta_{ab}+\frac{1}{48}d_{ki}\sigma^{cd}_{kn}\sigma^{ef}_{lm}\sigma^{cd*}_{lm}\sigma^{ef*}_{jn}\delta_{ab}+\frac{1}{24}d_{jk}\sigma^{cd}_{lm}\sigma^{ef}_{in}\sigma^{cd*}_{mn}\sigma^{ef*}_{kl}\delta_{ab}\\
&+\frac{1}{24}d_{ki}\sigma^{cd}_{mn}\sigma^{ef}_{kl}\sigma^{cd*}_{lm}\sigma^{ef*}_{jn}\delta_{ab}+\frac{1}{6}d_{dc}\sigma^{cg}_{im}\sigma^{ef}_{kl}\sigma^{dg*}_{jl}\sigma^{ef*}_{km}\delta_{ab}+\frac{1}{6}d_{dc}\sigma^{ce}_{kl}\sigma^{fg}_{im}\sigma^{df*}_{kl}\sigma^{eg*}_{jm}\delta_{ab}\\
&+\frac{1}{6}d_{dc}\sigma^{cg}_{im}\sigma^{ef}_{kl}\sigma^{df*}_{jm}\sigma^{eg*}_{kl}\delta_{ab}-\frac{1}{24}d_{ac}\sigma^{cd}_{mn}\sigma^{ef}_{kl}\sigma^{bf*}_{mn}\sigma^{de*}_{kl}\delta_{ij}-\frac{1}{6}d_{kl}\sigma^{ae}_{no}\sigma^{cd}_{km}\sigma^{be*}_{mo}\sigma^{cd*}_{ln}\delta_{ij}\\
&-\frac{1}{3}d_{kl}\sigma^{ae}_{ko}\sigma^{cd}_{mn}\sigma^{bd*}_{no}\sigma^{ce*}_{lm}\delta_{ij}-\frac{1}{12}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{bf*}_{kl}\sigma^{de*}_{mn}\delta_{ij}-\frac{1}{6}d_{kl}\sigma^{ae}_{no}\sigma^{cd}_{km}\sigma^{bd*}_{no}\sigma^{ce*}_{lm}\delta_{ij}\\
&-\frac{1}{12}d_{dc}\sigma^{ac}_{mn}\sigma^{ef}_{kl}\sigma^{bf*}_{mn}\sigma^{de*}_{kl}\delta_{ij}-\frac{1}{12}d_{kl}\sigma^{ae}_{no}\sigma^{cd}_{km}\sigma^{bd*}_{lm}\sigma^{ce*}_{no}\delta_{ij}-\frac{1}{3}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ik}\sigma^{ce*}_{lm}\sigma^{df*}_{jn}\delta_{ab}\\
&-\frac{1}{24}d_{dc}\sigma^{ac}_{mn}\sigma^{ef}_{kl}\sigma^{bd*}_{kl}\sigma^{ef*}_{mn}\delta_{ij}-\frac{1}{48}d_{ac}\sigma^{cf}_{kl}\sigma^{de}_{mn}\sigma^{bf*}_{mn}\sigma^{de*}_{kl}\delta_{ij}-\frac{1}{48}d_{cb}\sigma^{af}_{mn}\sigma^{de}_{kl}\sigma^{cf*}_{kl}\sigma^{de*}_{mn}\delta_{ij}\\
&-\frac{1}{16}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{cd*}_{jm}\sigma^{ef*}_{ln}\delta_{ab}-\frac{1}{3}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{ce*}_{mn}\sigma^{df*}_{jl}\delta_{ab}-\frac{1}{3}d_{kl}\sigma^{ae}_{no}\sigma^{cd}_{km}\sigma^{bd*}_{lo}\sigma^{ce*}_{mn}\delta_{ij}\\
&-\frac{1}{3}d_{dc}\sigma^{cg}_{im}\sigma^{ef}_{kl}\sigma^{df*}_{jl}\sigma^{eg*}_{km}\delta_{ab}-\frac{1}{6}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ik}\sigma^{ce*}_{mn}\sigma^{df*}_{jl}\delta_{ab}-\frac{1}{3}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{be*}_{ln}\sigma^{df*}_{km}\delta_{ij}
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{12}d_{dc}\sigma^{ce}_{kl}\sigma^{fg}_{im}\sigma^{de*}_{jm}\sigma^{fg*}_{kl}\delta_{ab}-\frac{1}{12}d_{dc}\sigma^{cg}_{im}\sigma^{ef}_{kl}\sigma^{dg*}_{kl}\sigma^{ef*}_{jm}\delta_{ab}-\frac{1}{12}d_{jk}\sigma^{cd}_{lm}\sigma^{ef}_{in}\sigma^{ce*}_{lm}\sigma^{df*}_{kn}\delta_{ab}\\
&-\frac{1}{12}d_{ki}\sigma^{ce}_{lm}\sigma^{df}_{kn}\sigma^{cd*}_{lm}\sigma^{ef*}_{jn}\delta_{ab}-\frac{1}{12}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{bd*}_{mn}\sigma^{ef*}_{kl}\delta_{ij}-\frac{1}{3}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{ce*}_{lm}\sigma^{df*}_{jn}\delta_{ab}\\
&-\frac{1}{24}d_{dc}\sigma^{af}_{mn}\sigma^{ce}_{kl}\sigma^{bd*}_{kl}\sigma^{ef*}_{mn}\delta_{ij}-\frac{1}{12}d_{kl}\sigma^{ae}_{ko}\sigma^{cd}_{mn}\sigma^{bd*}_{mn}\sigma^{ce*}_{lo}\delta_{ij}-\frac{1}{96}d_{cb}\sigma^{af}_{mn}\sigma^{de}_{kl}\sigma^{cd*}_{kl}\sigma^{ef*}_{mn}\delta_{ij}\\
&-\frac{1}{24}d_{cb}\sigma^{af}_{mn}\sigma^{de}_{kl}\sigma^{cd*}_{mn}\sigma^{ef*}_{kl}\delta_{ij}-\frac{1}{3}d_{dc}\sigma^{ce}_{kl}\sigma^{fg}_{im}\sigma^{df*}_{km}\sigma^{eg*}_{jl}\delta_{ab}-\frac{1}{96}d_{ac}\sigma^{cd}_{kl}\sigma^{ef}_{mn}\sigma^{bf*}_{mn}\sigma^{de*}_{kl}\delta_{ij}\\
&-\frac{1}{12}d_{kl}\sigma^{cd}_{km}\sigma^{ef}_{in}\sigma^{cd*}_{ln}\sigma^{ef*}_{jm}\delta_{ab}-\frac{1}{24}d_{dc}\sigma^{ac}_{mn}\sigma^{ef}_{kl}\sigma^{bf*}_{kl}\sigma^{de*}_{mn}\delta_{ij}-\frac{1}{6}d_{jk}\sigma^{cd}_{lm}\sigma^{ef}_{in}\sigma^{ce*}_{kl}\sigma^{df*}_{mn}\delta_{ab}\\
&-\frac{1}{6}d_{ki}\sigma^{ce}_{kl}\sigma^{df}_{mn}\sigma^{cd*}_{lm}\sigma^{ef*}_{jn}\delta_{ab}-\frac{1}{6}d_{kl}\sigma^{ae}_{ko}\sigma^{cd}_{mn}\sigma^{be*}_{ln}\sigma^{cd*}_{mo}\delta_{ij}-\frac{1}{6}d_{dc}\sigma^{ce}_{kl}\sigma^{fg}_{im}\sigma^{dg*}_{jm}\sigma^{ef*}_{kl}\delta_{ab}\\
&-\frac{1}{6}d_{dc}\sigma^{cg}_{im}\sigma^{ef}_{kl}\sigma^{de*}_{kl}\sigma^{fg*}_{jm}\delta_{ab}-\frac{1}{6}d_{kl}\sigma^{ae}_{ko}\sigma^{cd}_{mn}\sigma^{bd*}_{lo}\sigma^{ce*}_{mn}\delta_{ij}\\
&+\frac{1}{24}d_{dc}\sigma^{cg}_{mn}\sigma^{ef}_{kl}\sigma^{dg*}_{kl}\sigma^{ef*}_{mn}\delta_{ab}\delta_{ij}+\frac{1}{12}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ko}\sigma^{cd*}_{mo}\sigma^{ef*}_{ln}\delta_{ab}\delta_{ij}+\frac{1}{12}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ko}\sigma^{cd*}_{ln}\sigma^{ef*}_{mo}\delta_{ab}\delta_{ij}\\
&+\frac{1}{6}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ko}\sigma^{ce*}_{mn}\sigma^{df*}_{lo}\delta_{ab}\delta_{ij}+\frac{1}{3}d_{dc}\sigma^{cg}_{mn}\sigma^{ef}_{kl}\sigma^{df*}_{ln}\sigma^{eg*}_{km}\delta_{ab}\delta_{ij}-\frac{1}{3}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ko}\sigma^{ce*}_{mo}\sigma^{df*}_{ln}\delta_{ab}\delta_{ij}\\
&-\frac{1}{12}d_{dc}\sigma^{cg}_{mn}\sigma^{ef}_{kl}\sigma^{df*}_{mn}\sigma^{eg*}_{kl}\delta_{ab}\delta_{ij}-\frac{1}{12}d_{dc}\sigma^{cg}_{mn}\sigma^{ef}_{kl}\sigma^{df*}_{kl}\sigma^{eg*}_{mn}\delta_{ab}\delta_{ij}-\frac{1}{24}d_{kl}\sigma^{cd}_{mn}\sigma^{ef}_{ko}\sigma^{cd*}_{lo}\sigma^{ef*}_{mn}\delta_{ab}\delta_{ij}\\
&-\frac{1}{6}d_{dc}\sigma^{cg}_{mn}\sigma^{ef}_{kl}\sigma^{dg*}_{ln}\sigma^{ef*}_{km}\delta_{ab}\delta_{ij}
\end{aligned}
$$

PP-UCC4 state-to-state density, singles/doubles:

$$
\begin{aligned}
&\langle\Phi^{a}_{i}|\bar{D}|\Phi^{bc}_{jk}\rangle \;=\\
&\frac{1}{2}d_{ad}\sigma^{de}_{il}\sigma^{bce*}_{jkl}+d_{ed}\sigma^{ad}_{il}\sigma^{bce*}_{jkl}+\frac{1}{2}\mathcal{P}^{-}_{(jk)}d_{jl}\sigma^{ad}_{im}\sigma^{bcd*}_{klm}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(bc)}d_{dc}\sigma^{ae}_{il}\sigma^{bde*}_{jkl}-d_{lm}\sigma^{ad}_{il}\sigma^{bcd*}_{jkm}-\frac{1}{2}d_{li}\sigma^{ad}_{lm}\sigma^{bcd*}_{jkm}\\
&\;+\mathcal{P}^{-}_{(jk)}d_{al}\sigma^{bc*}_{kl}\delta_{ij}+\mathcal{P}^{-}_{(bc)}d_{di}\sigma^{cd*}_{jk}\delta_{ab}\\
&\;+\mathcal{P}^{-}_{(jkbc)}d_{jb}\delta_{ac}\delta_{ik}\\
&\;+\frac{1}{4}\mathcal{P}^{-}_{(jk)}d_{ad}\sigma^{de}_{lm}\sigma^{bce*}_{klm}\delta_{ij}+\frac{1}{4}\mathcal{P}^{-}_{(bc)}d_{li}\sigma^{de}_{lm}\sigma^{bde*}_{jkm}\delta_{ac}+\frac{1}{2}\mathcal{P}^{-}_{(jk)}d_{ed}\sigma^{ad}_{lm}\sigma^{bce*}_{klm}\delta_{ij}\\
&\quad+\frac{1}{2}\mathcal{P}^{-}_{(bc)}d_{lm}\sigma^{de}_{il}\sigma^{bde*}_{jkm}\delta_{ac}+\mathcal{P}^{-}_{(bc)}d_{ed}\sigma^{df}_{il}\sigma^{cef*}_{jkl}\delta_{ab}+\mathcal{P}^{-}_{(jk)}d_{lm}\sigma^{ad}_{ln}\sigma^{bcd*}_{jmn}\delta_{ik}\\
&\quad+\frac{1}{4}\mathcal{P}^{-}_{(jk)}d_{jl}\sigma^{ad}_{mn}\sigma^{bcd*}_{lmn}\delta_{ik}+\frac{1}{4}\mathcal{P}^{-}_{(jkbc)}d_{jl}\sigma^{de}_{im}\sigma^{cde*}_{klm}\delta_{ab}+\frac{1}{4}\mathcal{P}^{-}_{(jkbc)}d_{db}\sigma^{ae}_{lm}\sigma^{cde*}_{jlm}\delta_{ik}
\end{aligned}
$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(bc)}d_{dc}\sigma^{ef}_{il}\sigma^{def*}_{jkl}\delta_{ab}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(jk)}d_{ad}\sigma^{d}_{l}\sigma^{bc*}_{kl}\delta_{ij}+\frac{1}{2}\mathcal{P}^{-}_{(jk)}d_{jl}\sigma^{a}_{m}\sigma^{bc*}_{lm}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(jkbc)}d_{jl}\sigma^{d}_{i}\sigma^{cd*}_{kl}\delta_{ab}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(jkbc)}d_{db}\sigma^{a}_{l}\sigma^{cd*}_{jl}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(bc)}d_{dc}\sigma^{e}_{i}\sigma^{de*}_{jk}\delta_{ab}+\frac{1}{2}\mathcal{P}^{-}_{(bc)}d_{li}\sigma^{d}_{l}\sigma^{bd*}_{jk}\delta_{ac}$$

$$+\mathcal{P}^{-}_{(bc)}d_{ed}\sigma^{d}_{i}\sigma^{ce*}_{jk}\delta_{ab}+\mathcal{P}^{-}_{(jk)}d_{lm}\sigma^{a}_{l}\sigma^{bc*}_{jm}\delta_{ik}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(jk)}d_{dl}\sigma^{ae}_{im}\sigma^{bc*}_{kl}\sigma^{de*}_{jm}+\frac{2}{3}\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{ae}_{im}\sigma^{bd*}_{km}\sigma^{ce*}_{jl}+\frac{1}{6}\mathcal{P}^{-}_{(jk)}d_{dl}\sigma^{ae}_{im}\sigma^{bc*}_{jm}\sigma^{de*}_{kl}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(bc)}d_{dl}\sigma^{ae}_{im}\sigma^{be*}_{jk}\sigma^{cd*}_{lm}+\frac{2}{3}d_{dl}\sigma^{ae}_{im}\sigma^{bc*}_{lm}\sigma^{de*}_{jk}+\frac{1}{12}\mathcal{P}^{-}_{(jk)}d_{al}\sigma^{de}_{im}\sigma^{bc*}_{km}\sigma^{de*}_{jl}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(bc)}d_{di}\sigma^{ae}_{lm}\sigma^{bd*}_{lm}\sigma^{ce*}_{jk}+\frac{1}{6}\mathcal{P}^{-}_{(bc)}d_{al}\sigma^{de}_{im}\sigma^{bd*}_{jk}\sigma^{ce*}_{lm}+\frac{1}{6}\mathcal{P}^{-}_{(jk)}d_{di}\sigma^{ae}_{lm}\sigma^{bc*}_{km}\sigma^{de*}_{jl}$$

$$+\frac{1}{6}\mathcal{P}^{-}_{(jkbc)}d_{al}\sigma^{de}_{im}\sigma^{bd*}_{jm}\sigma^{ce*}_{kl}+\frac{1}{6}\mathcal{P}^{-}_{(jkbc)}d_{di}\sigma^{ae}_{lm}\sigma^{bd*}_{kl}\sigma^{ce*}_{jm}+\frac{1}{2}\mathcal{P}^{-}_{(bc)}d_{dl}\sigma^{ae}_{im}\sigma^{be*}_{lm}\sigma^{cd*}_{jk}$$

$$-\frac{1}{12}d_{al}\sigma^{de}_{im}\sigma^{bc*}_{lm}\sigma^{de*}_{jk}-\frac{1}{12}d_{di}\sigma^{ae}_{lm}\sigma^{bc*}_{lm}\sigma^{de*}_{jk}$$

$$+\mathcal{P}^{-}_{(jkbc)}d_{jl}\sigma^{c*}_{l}\delta_{ab}\delta_{ik}+\mathcal{P}^{-}_{(jkbc)}d_{db}\sigma^{d*}_{j}\delta_{ac}\delta_{ik}$$

$$+\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{bd*}_{jl}\delta_{ac}\delta_{ik}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(jkbc)}d_{jl}\sigma^{d}_{m}\sigma^{cd*}_{lm}\delta_{ab}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(jkbc)}d_{db}\sigma^{e}_{l}\sigma^{de*}_{jl}\delta_{ac}\delta_{ik}+\mathcal{P}^{-}_{(jkbc)}d_{ed}\sigma^{d}_{l}\sigma^{be*}_{jl}\delta_{ac}\delta_{ik}$$

$$+\mathcal{P}^{-}_{(jkbc)}d_{lm}\sigma^{d}_{l}\sigma^{bd*}_{km}\delta_{ac}\delta_{ij}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(jkbc)}d_{ed}\sigma^{df}_{lm}\sigma^{bef*}_{jlm}\delta_{ac}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(jkbc)}d_{lm}\sigma^{de}_{ln}\sigma^{bde*}_{kmn}\delta_{ac}\delta_{ij}+\frac{1}{8}\mathcal{P}^{-}_{(jkbc)}d_{jl}\sigma^{de}_{mn}\sigma^{cde*}_{lmn}\delta_{ab}\delta_{ik}$$

$$+\frac{1}{8}\mathcal{P}^{-}_{(jkbc)}d_{db}\sigma^{ef}_{lm}\sigma^{def*}_{jlm}\delta_{ac}\delta_{ik}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(jk)}d_{al}\sigma^{de}_{mn}\sigma^{bc*}_{ln}\sigma^{de*}_{jm}\delta_{ik}+\frac{1}{6}\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{ae}_{mn}\sigma^{be*}_{km}\sigma^{cd*}_{ln}\delta_{ij}+\frac{1}{6}\mathcal{P}^{-}_{(bc)}d_{dl}\sigma^{ef}_{im}\sigma^{bf*}_{jk}\sigma^{de*}_{lm}\delta_{ac}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(jkbc)}d_{di}\sigma^{ef}_{lm}\sigma^{bd*}_{km}\sigma^{ef*}_{jl}\delta_{ac}+\frac{1}{6}\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{ef}_{im}\sigma^{bf*}_{jm}\sigma^{de*}_{kl}\delta_{ac}+\frac{2}{3}\mathcal{P}^{-}_{(jk)}d_{dl}\sigma^{ae}_{mn}\sigma^{bc*}_{ln}\sigma^{de*}_{km}\delta_{ij}$$

$$+\frac{2}{3}\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{ef}_{im}\sigma^{bf*}_{kl}\sigma^{de*}_{jm}\delta_{ac}+\frac{2}{3}\mathcal{P}^{-}_{(bc)}d_{dl}\sigma^{ef}_{im}\sigma^{bf*}_{lm}\sigma^{de*}_{jk}\delta_{ac}+\frac{1}{4}\mathcal{P}^{-}_{(jk)}d_{dl}\sigma^{ae}_{mn}\sigma^{bc*}_{jl}\sigma^{de*}_{mn}\delta_{ik}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(bc)}d_{dl}\sigma^{ef}_{im}\sigma^{bd*}_{jk}\sigma^{ef*}_{lm}\delta_{ac}+\frac{1}{12}\mathcal{P}^{-}_{(jkbc)}d_{al}\sigma^{de}_{mn}\sigma^{bd*}_{jl}\sigma^{ce*}_{mn}\delta_{ik}+\frac{1}{6}\mathcal{P}^{-}_{(jk)}d_{dl}\sigma^{ae}_{mn}\sigma^{bc*}_{jn}\sigma^{de*}_{lm}\delta_{ik}$$

$$+\frac{1}{3}\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{ae}_{mn}\sigma^{bd*}_{mn}\sigma^{ce*}_{kl}\delta_{ij}+\frac{1}{3}\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{ef}_{im}\sigma^{bd*}_{jm}\sigma^{ef*}_{kl}\delta_{ac}+\frac{2}{3}\mathcal{P}^{-}_{(jkbc)}d_{dl}\sigma^{ae}_{mn}\sigma^{be*}_{lm}\sigma^{cd*}_{jn}\delta_{ik}$$

$$+\frac{1}{24}\mathcal{P}^{-}_{(jk)}d_{al}\sigma^{de}_{mn}\sigma^{bc*}_{mn}\sigma^{de*}_{kl}\delta_{ij}+\frac{1}{24}\mathcal{P}^{-}_{(bc)}d_{di}\sigma^{ef}_{lm}\sigma^{cd*}_{lm}\sigma^{ef*}_{jk}\delta_{ab}+\frac{1}{12}\mathcal{P}^{-}_{(jk)}d_{al}\sigma^{de}_{mn}\sigma^{bc*}_{kn}\sigma^{de*}_{lm}\delta_{ij}$$

$$+\frac{1}{12}\mathcal{P}^{-}_{(bc)}d_{di}\sigma^{ef}_{lm}\sigma^{cf*}_{jk}\sigma^{de*}_{lm}\delta_{ab}+\frac{1}{12}\mathcal{P}^{-}_{(bc)}d_{di}\sigma^{ef}_{lm}\sigma^{cf*}_{lm}\sigma^{de*}_{jk}\delta_{ab}+\frac{1}{12}\mathcal{P}^{-}_{(jk)}d_{dl}\sigma^{ae}_{mn}\sigma^{bc*}_{mn}\sigma^{de*}_{jl}\delta_{ik}$$

$$
\begin{aligned}
&+ \frac{1}{12}\mathcal{P}^{-}_{(bc)} d_{dl} \sigma^{ef}_{im} \sigma^{bd*}_{lm} \sigma^{ef*}_{jk} \delta_{ac} + \frac{1}{6}\mathcal{P}^{-}_{(jkbc)} d_{al} \sigma^{de}_{mn} \sigma^{bd*}_{km} \sigma^{ce*}_{ln} \delta_{ij} + \frac{1}{6}\mathcal{P}^{-}_{(jkbc)} d_{di} \sigma^{ef}_{lm} \sigma^{bf*}_{km} \sigma^{de*}_{jl} \delta_{ac} \\
&+ \frac{1}{3}\mathcal{P}^{-}_{(jkbc)} d_{dl} \sigma^{ef}_{mn} \sigma^{bd*}_{jn} \sigma^{ef*}_{lm} \delta_{ac} \delta_{ik} + \frac{1}{12}\mathcal{P}^{-}_{(jkbc)} d_{dl} \sigma^{ef}_{mn} \sigma^{bf*}_{mn} \sigma^{de*}_{jl} \delta_{ac} \delta_{ik} \\
&+ \frac{1}{6}\mathcal{P}^{-}_{(jkbc)} d_{dl} \sigma^{ef}_{mn} \sigma^{bd*}_{mn} \sigma^{ef*}_{jl} \delta_{ac} \delta_{ik} + \frac{1}{12}\mathcal{P}^{-}_{(jkbc)} d_{dl} \sigma^{ef}_{mn} \sigma^{bd*}_{ln} \sigma^{ef*}_{km} \delta_{ac} \delta_{ij} \\
&+ \frac{1}{6}\mathcal{P}^{-}_{(jkbc)} d_{dl} \sigma^{ef}_{mn} \sigma^{bf*}_{jn} \sigma^{de*}_{lm} \delta_{ac} \delta_{ik} + \frac{1}{3}\mathcal{P}^{-}_{(jkbc)} d_{dl} \sigma^{ef}_{mn} \sigma^{bf*}_{jl} \sigma^{de*}_{mn} \delta_{ac} \delta_{ik} \\
&+ \frac{2}{3}\mathcal{P}^{-}_{(jkbc)} d_{dl} \sigma^{ef}_{mn} \sigma^{bf*}_{ln} \sigma^{de*}_{km} \delta_{ac} \delta_{ij}
\end{aligned}
$$

PP-UCC4 state-to-state density, singles/triples:

$$
\begin{aligned}
&\langle \Phi^{a}_{i} | \bar{D} | \Phi^{bcd}_{jkl} \rangle \ = \\
&\mathcal{P}^{-}_{(jk)} d_{am} \sigma^{bcd*}_{jlm} \delta_{ik} + \mathcal{P}^{-}_{(bc)} d_{ei} \sigma^{bde*}_{jkl} \delta_{ac} - d_{am} \sigma^{bcd*}_{jkm} \delta_{il} \\
&\quad - d_{ei} \sigma^{bce*}_{jkl} \delta_{ad} \\
&\;+ \mathcal{P}^{-}_{(jkl)} d_{jm} \sigma^{bc*}_{km} \delta_{ad} \delta_{il} + \mathcal{P}^{-}_{(jkl)} d_{jm} \sigma^{bd*}_{lm} \delta_{ac} \delta_{ik} + \mathcal{P}^{-}_{(jkl)} d_{jm} \sigma^{cd*}_{km} \delta_{ab} \delta_{il} \\
&\quad + \mathcal{P}^{-}_{(bcd)} d_{eb} \sigma^{ce*}_{jl} \delta_{ad} \delta_{ik} + \mathcal{P}^{-}_{(bcd)} d_{eb} \sigma^{de*}_{jk} \delta_{ac} \delta_{il} + \mathcal{P}^{-}_{(bcd)} d_{eb} \sigma^{de*}_{kl} \delta_{ac} \delta_{ij} \\
&\;+ d_{em} \sigma^{bce*}_{jkm} \delta_{ad} \delta_{il} + \mathcal{P}^{-}_{(jk)} d_{em} \sigma^{bce*}_{klm} \delta_{ad} \delta_{ij} + \mathcal{P}^{-}_{(jkbc)} d_{em} \sigma^{bde*}_{jlm} \delta_{ac} \delta_{ik} \\
&\quad + \mathcal{P}^{-}_{(bc)} d_{em} \sigma^{cde*}_{jkm} \delta_{ab} \delta_{il}
\end{aligned}
$$

PP-UCC4 state-to-state density, doubles/singles:

$$
\begin{aligned}
&\langle \Phi^{ab}_{ij} | \bar{D} | \Phi^{c}_{k} \rangle \ = \\
&\frac{1}{2} d_{dc} \sigma^{abe}_{ijl} \sigma^{de*}_{kl} + d_{ed} \sigma^{abd}_{ijl} \sigma^{ce*}_{kl} + \frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{bd} \sigma^{ade}_{ijl} \sigma^{ce*}_{kl} \\
&\quad + \frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{li} \sigma^{abd}_{jlm} \sigma^{cd*}_{km} - d_{lm} \sigma^{abd}_{ijl} \sigma^{cd*}_{km} - \frac{1}{2} d_{kl} \sigma^{abd}_{ijm} \sigma^{cd*}_{lm} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{ai} \delta_{bc} \delta_{jk}
\end{aligned}
$$

$$
\begin{aligned}
& + \mathcal{P}^{-}_{(ab)} d_{kd} \sigma^{bd}_{ij} \delta_{ac} + \mathcal{P}^{-}_{(ij)} d_{lc} \sigma^{ab}_{jl} \delta_{ik} \\
& + \frac{1}{4} \mathcal{P}^{-}_{(ab)} d_{kl} \sigma^{ade}_{ijm} \sigma^{de*}_{lm} \delta_{bc} + \frac{1}{4} \mathcal{P}^{-}_{(ij)} d_{dc} \sigma^{abe}_{jlm} \sigma^{de*}_{lm} \delta_{ik} + \frac{1}{2} \mathcal{P}^{-}_{(ij)} d_{ed} \sigma^{abd}_{jlm} \sigma^{ce*}_{lm} \delta_{ik} \\
& \quad + \frac{1}{2} \mathcal{P}^{-}_{(ab)} d_{lm} \sigma^{ade}_{ijl} \sigma^{de*}_{km} \delta_{bc} + \mathcal{P}^{-}_{(ab)} d_{ed} \sigma^{bdf}_{ijl} \sigma^{ef*}_{kl} \delta_{ac} + \mathcal{P}^{-}_{(ij)} d_{lm} \sigma^{abd}_{iln} \sigma^{cd*}_{mn} \delta_{jk} \\
& \quad + \frac{1}{4} \mathcal{P}^{-}_{(ijab)} d_{ad} \sigma^{bde}_{ilm} \sigma^{ce*}_{lm} \delta_{jk} + \frac{1}{4} \mathcal{P}^{-}_{(ab)} d_{bd} \sigma^{def}_{ijl} \sigma^{ef*}_{kl} \delta_{ac} + \frac{1}{4} \mathcal{P}^{-}_{(ij)} d_{li} \sigma^{abd}_{lmn} \sigma^{cd*}_{mn} \delta_{jk} \\
& \quad + \frac{1}{4} \mathcal{P}^{-}_{(ijab)} d_{li} \sigma^{bde}_{jlm} \sigma^{de*}_{km} \delta_{ac} \\
& + \frac{1}{2} \mathcal{P}^{-}_{(ijab)} d_{ad} \sigma^{bd}_{il} \sigma^{c*}_{l} \delta_{jk} + \frac{1}{2} \mathcal{P}^{-}_{(ab)} d_{bd} \sigma^{de}_{ij} \sigma^{e*}_{k} \delta_{ac} + \frac{1}{2} \mathcal{P}^{-}_{(ab)} d_{kl} \sigma^{ad}_{ij} \sigma^{d*}_{l} \delta_{bc} \\
& \quad + \frac{1}{2} \mathcal{P}^{-}_{(ij)} d_{dc} \sigma^{ab}_{jl} \sigma^{d*}_{l} \delta_{ik} + \frac{1}{2} \mathcal{P}^{-}_{(ij)} d_{li} \sigma^{ab}_{lm} \sigma^{c*}_{m} \delta_{jk} + \frac{1}{2} \mathcal{P}^{-}_{(ijab)} d_{li} \sigma^{bd}_{jl} \sigma^{d*}_{k} \delta_{ac} \\
& \quad + \mathcal{P}^{-}_{(ab)} d_{ed} \sigma^{bd}_{ij} \sigma^{e*}_{k} \delta_{ac} + \mathcal{P}^{-}_{(ij)} d_{lm} \sigma^{ab}_{il} \sigma^{c*}_{m} \delta_{jk} \\
& + \mathcal{P}^{-}_{(ijab)} d_{ad} \sigma^{d}_{i} \delta_{bc} \delta_{jk} + \mathcal{P}^{-}_{(ijab)} d_{li} \sigma^{b}_{l} \delta_{ac} \delta_{jk} \\
& + \mathcal{P}^{-}_{(ijab)} d_{ld} \sigma^{ad}_{il} \delta_{bc} \delta_{jk} \\
& + \frac{1}{6} \mathcal{P}^{-}_{(ijab)} d_{lc} \sigma^{ad}_{im} \sigma^{be}_{jl} \sigma^{de*}_{km} + \frac{1}{6} \mathcal{P}^{-}_{(ij)} d_{kd} \sigma^{ab}_{jm} \sigma^{de}_{il} \sigma^{ce*}_{lm} + \frac{1}{6} \mathcal{P}^{-}_{(ab)} d_{lc} \sigma^{ad}_{ij} \sigma^{be}_{lm} \sigma^{de*}_{km} \\
& \quad + \frac{2}{3} \mathcal{P}^{-}_{(ijab)} d_{ld} \sigma^{ad}_{jm} \sigma^{be}_{il} \sigma^{ce*}_{km} + \frac{1}{6} \mathcal{P}^{-}_{(ab)} d_{ld} \sigma^{ae}_{ij} \sigma^{bd}_{lm} \sigma^{ce*}_{km} + \frac{1}{2} \mathcal{P}^{-}_{(ij)} d_{ld} \sigma^{ab}_{jl} \sigma^{de}_{im} \sigma^{ce*}_{km} \\
& \quad + \frac{1}{12} \mathcal{P}^{-}_{(ab)} d_{kd} \sigma^{ad}_{lm} \sigma^{be}_{ij} \sigma^{ce*}_{lm} + \frac{1}{12} \mathcal{P}^{-}_{(ij)} d_{lc} \sigma^{ab}_{jm} \sigma^{de}_{il} \sigma^{de*}_{km} + \frac{1}{6} \mathcal{P}^{-}_{(ij)} d_{ld} \sigma^{ab}_{im} \sigma^{de}_{jl} \sigma^{ce*}_{km} \\
& \quad + \frac{2}{3} d_{ld} \sigma^{ab}_{lm} \sigma^{de}_{ij} \sigma^{ce*}_{km} + \frac{1}{6} \mathcal{P}^{-}_{(ijab)} d_{kd} \sigma^{ad}_{jl} \sigma^{be}_{im} \sigma^{ce*}_{lm} + \frac{1}{2} \mathcal{P}^{-}_{(ab)} d_{ld} \sigma^{ae}_{lm} \sigma^{bd}_{ij} \sigma^{ce*}_{km} \\
& \quad - \frac{1}{12} d_{kd} \sigma^{ab}_{lm} \sigma^{de}_{ij} \sigma^{ce*}_{lm} - \frac{1}{12} d_{lc} \sigma^{ab}_{lm} \sigma^{de}_{ij} \sigma^{de*}_{km} \\
& + \frac{1}{4} \mathcal{P}^{-}_{(ab)} d_{ld} \sigma^{ad}_{ij} \sigma^{ef}_{lm} \sigma^{ef*}_{km} \delta_{bc} + \frac{1}{12} \mathcal{P}^{-}_{(ijab)} d_{lc} \sigma^{ad}_{il} \sigma^{be}_{mn} \sigma^{de*}_{mn} \delta_{jk} + \frac{1}{12} \mathcal{P}^{-}_{(ij)} d_{ld} \sigma^{ab}_{mn} \sigma^{de}_{il} \sigma^{ce*}_{mn} \delta_{jk} \\
& \quad + \frac{1}{6} \mathcal{P}^{-}_{(ij)} d_{ld} \sigma^{ab}_{in} \sigma^{de}_{lm} \sigma^{ce*}_{mn} \delta_{jk} + \frac{2}{3} \mathcal{P}^{-}_{(ijab)} d_{ld} \sigma^{ad}_{im} \sigma^{be}_{ln} \sigma^{ce*}_{mn} \delta_{jk} + \frac{1}{12} \mathcal{P}^{-}_{(ijab)} d_{kd} \sigma^{ad}_{jm} \sigma^{ef}_{il} \sigma^{ef*}_{lm} \delta_{bc} \\
& \quad + \frac{1}{6} \mathcal{P}^{-}_{(ijab)} d_{ld} \sigma^{af}_{im} \sigma^{de}_{jl} \sigma^{ef*}_{km} \delta_{bc} + \frac{2}{3} \mathcal{P}^{-}_{(ijab)} d_{ld} \sigma^{af}_{jl} \sigma^{de}_{im} \sigma^{ef*}_{km} \delta_{bc} + \frac{1}{12} \mathcal{P}^{-}_{(ij)} d_{lc} \sigma^{ab}_{jn} \sigma^{de}_{lm} \sigma^{de*}_{mn} \delta_{ik} \\
& \quad + \frac{1}{3} \mathcal{P}^{-}_{(ijab)} d_{ld} \sigma^{ad}_{im} \sigma^{ef}_{jl} \sigma^{ef*}_{km} \delta_{bc} + \frac{1}{3} \mathcal{P}^{-}_{(ijab)} d_{ld} \sigma^{ad}_{mn} \sigma^{be}_{jl} \sigma^{ce*}_{mn} \delta_{ik} + \frac{2}{3} \mathcal{P}^{-}_{(ij)} d_{ld} \sigma^{ab}_{ln} \sigma^{de}_{jm} \sigma^{ce*}_{mn} \delta_{ik} \\
& \quad + \frac{2}{3} \mathcal{P}^{-}_{(ab)} d_{ld} \sigma^{af}_{lm} \sigma^{de}_{ij} \sigma^{ef*}_{km} \delta_{bc} + \frac{1}{24} \mathcal{P}^{-}_{(ab)} d_{kd} \sigma^{bd}_{lm} \sigma^{ef}_{ij} \sigma^{ef*}_{lm} \delta_{ac} + \frac{1}{24} \mathcal{P}^{-}_{(ij)} d_{lc} \sigma^{ab}_{mn} \sigma^{de}_{jl} \sigma^{de*}_{mn} \delta_{ik} \\
& \quad + \frac{1}{12} \mathcal{P}^{-}_{(ab)} d_{kd} \sigma^{bf}_{ij} \sigma^{de}_{lm} \sigma^{ef*}_{lm} \delta_{ac} + \frac{1}{12} \mathcal{P}^{-}_{(ab)} d_{kd} \sigma^{bf}_{lm} \sigma^{de}_{ij} \sigma^{ef*}_{lm} \delta_{ac} + \frac{1}{12} \mathcal{P}^{-}_{(ab)} d_{ld} \sigma^{ad}_{lm} \sigma^{ef}_{ij} \sigma^{ef*}_{km} \delta_{bc} \\
& \quad + \frac{1}{12} \mathcal{P}^{-}_{(ij)} d_{lc} \sigma^{ab}_{ln} \sigma^{de}_{im} \sigma^{de*}_{mn} \delta_{jk} + \frac{1}{6} \mathcal{P}^{-}_{(ijab)} d_{kd} \sigma^{af}_{jm} \sigma^{de}_{il} \sigma^{ef*}_{lm} \delta_{bc} + \frac{1}{6} \mathcal{P}^{-}_{(ijab)} d_{lc} \sigma^{ad}_{jm} \sigma^{be}_{ln} \sigma^{de*}_{mn} \delta_{ik}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ad}_{lm}\sigma^{be}_{jn}\sigma^{ce*}_{mn}\delta_{ik}+\frac{1}{6}\mathcal{P}^{-}_{(ab)} d_{ld}\sigma^{af}_{ij}\sigma^{de}_{lm}\sigma^{ef*}_{km}\delta_{bc}+\frac{1}{4}\mathcal{P}^{-}_{(ij)} d_{ld}\sigma^{ab}_{il}\sigma^{de}_{mn}\sigma^{ce*}_{mn}\delta_{jk}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ad}\sigma^{de}_{il}\sigma^{e*}_{l}\delta_{bc}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{li}\sigma^{bd}_{lm}\sigma^{d*}_{m}\delta_{ac}\delta_{jk}+\mathcal{P}^{-}_{(ijab)} d_{ed}\sigma^{ad}_{il}\sigma^{e*}_{l}\delta_{bc}\delta_{jk}\\
&+\mathcal{P}^{-}_{(ijab)} d_{lm}\sigma^{ad}_{jl}\sigma^{d*}_{m}\delta_{bc}\delta_{ik}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ed}\sigma^{adf}_{ilm}\sigma^{ef*}_{lm}\delta_{bc}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{lm}\sigma^{ade}_{jln}\sigma^{de*}_{mn}\delta_{bc}\delta_{ik}+\frac{1}{8}\mathcal{P}^{-}_{(ijab)} d_{ad}\sigma^{def}_{ilm}\sigma^{ef*}_{lm}\delta_{bc}\delta_{jk}\\
&+\frac{1}{8}\mathcal{P}^{-}_{(ijab)} d_{li}\sigma^{bde}_{lmn}\sigma^{de*}_{mn}\delta_{ac}\delta_{jk}\\
&+\frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{af}_{mn}\sigma^{de}_{il}\sigma^{ef*}_{mn}\delta_{bc}\delta_{jk}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ad}_{mn}\sigma^{ef}_{il}\sigma^{ef*}_{mn}\delta_{bc}\delta_{jk}\\
&+\frac{1}{3}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ad}_{in}\sigma^{ef}_{lm}\sigma^{ef*}_{mn}\delta_{bc}\delta_{jk}+\frac{1}{3}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{af}_{il}\sigma^{de}_{mn}\sigma^{ef*}_{mn}\delta_{bc}\delta_{jk}\\
&+\frac{1}{12}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{ad}_{ln}\sigma^{ef}_{jm}\sigma^{ef*}_{mn}\delta_{bc}\delta_{ik}+\frac{1}{6}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{af}_{in}\sigma^{de}_{lm}\sigma^{ef*}_{mn}\delta_{bc}\delta_{jk}\\
&+\frac{2}{3}\mathcal{P}^{-}_{(ijab)} d_{ld}\sigma^{af}_{ln}\sigma^{de}_{jm}\sigma^{ef*}_{mn}\delta_{bc}\delta_{ik}
\end{aligned}
$$

PP-UCC4 state-to-state density, doubles/doubles:

$$
\begin{aligned}
&\langle\Phi^{ab}_{ij}|\bar{D}|\Phi^{cd}_{kl}\rangle \;=\\
&\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae}\sigma^{be}_{im}\sigma^{cd*}_{km}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{ae}\sigma^{be}_{jm}\sigma^{cd*}_{lm}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ae}\sigma^{ef}_{ij}\sigma^{df*}_{kl}\delta_{bc}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{be}\sigma^{ef}_{ij}\sigma^{cf*}_{kl}\delta_{ad}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{km}\sigma^{ab}_{in}\sigma^{cd*}_{mn}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{km}\sigma^{ae}_{ij}\sigma^{de*}_{lm}\delta_{bc}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{km}\sigma^{be}_{ij}\sigma^{ce*}_{lm}\delta_{ad}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{lm}\sigma^{ab}_{jn}\sigma^{cd*}_{mn}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{ae}_{ij}\sigma^{ce*}_{km}\delta_{bd}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{lm}\sigma^{be}_{ij}\sigma^{de*}_{km}\delta_{ac}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ec}\sigma^{ab}_{im}\sigma^{de*}_{km}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ec}\sigma^{ab}_{jm}\sigma^{de*}_{lm}\delta_{ik}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ec}\sigma^{bf}_{ij}\sigma^{ef*}_{kl}\delta_{ad}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ed}\sigma^{ab}_{im}\sigma^{ce*}_{lm}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{ed}\sigma^{ab}_{jm}\sigma^{ce*}_{km}\delta_{il}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ab)} d_{ed}\sigma^{af}_{ij}\sigma^{ef*}_{kl}\delta_{bc}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{mi}\sigma^{ab}_{mn}\sigma^{cd*}_{kn}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi}\sigma^{ae}_{jm}\sigma^{de*}_{kl}\delta_{bc}\\
&+\frac{1}{2}\mathcal{P}^{-}_{(ijab)} d_{mi}\sigma^{be}_{jm}\sigma^{ce*}_{kl}\delta_{ad}+\frac{1}{2}\mathcal{P}^{-}_{(ij)} d_{mj}\sigma^{ab}_{mn}\sigma^{cd*}_{ln}\delta_{ik}+\mathcal{P}^{-}_{(ab)} d_{fe}\sigma^{ae}_{ij}\sigma^{df*}_{kl}\delta_{bc}\\
&+\mathcal{P}^{-}_{(ab)} d_{fe}\sigma^{be}_{ij}\sigma^{cf*}_{kl}\delta_{ad}+\mathcal{P}^{-}_{(ij)} d_{mn}\sigma^{ab}_{im}\sigma^{cd*}_{kn}\delta_{jl}+\mathcal{P}^{-}_{(ij)} d_{mn}\sigma^{ab}_{jm}\sigma^{cd*}_{ln}\delta_{ik}\\
&+\mathcal{P}^{-}_{(ijab)} d_{ac}\delta_{bd}\delta_{ik}\delta_{jl}+\mathcal{P}^{-}_{(ijab)} d_{ad}\delta_{bc}\delta_{il}\delta_{jk}+\mathcal{P}^{-}_{(ijab)} d_{ki}\delta_{ad}\delta_{bc}\delta_{jl}
\end{aligned}
$$

$$+\mathcal{P}^{-}_{(ijab)}d_{li}\delta_{ac}\delta_{bd}\delta_{jk}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ae}\sigma^{be}_{mn}\sigma^{cd*}_{mn}\delta_{il}\delta_{jk}+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{km}\sigma^{ef}_{ij}\sigma^{ef*}_{lm}\delta_{ac}\delta_{bd}+\frac{1}{4}\mathcal{P}^{-}_{(ab)}d_{lm}\sigma^{ef}_{ij}\sigma^{ef*}_{km}\delta_{ad}\delta_{bc}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ij)}d_{ec}\sigma^{ab}_{mn}\sigma^{de*}_{mn}\delta_{il}\delta_{jk}+\frac{1}{4}\mathcal{P}^{-}_{(ij)}d_{ed}\sigma^{ab}_{mn}\sigma^{ce*}_{mn}\delta_{ik}\delta_{jl}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{mi}\sigma^{ef}_{jm}\sigma^{ef*}_{kl}\delta_{ac}\delta_{bd}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ae}\sigma^{ef}_{im}\sigma^{cf*}_{km}\delta_{bd}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ae}\sigma^{ef}_{im}\sigma^{df*}_{lm}\delta_{bc}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ae}\sigma^{ef}_{jm}\sigma^{cf*}_{lm}\delta_{bd}\delta_{ik}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ae}\sigma^{ef}_{jm}\sigma^{df*}_{km}\delta_{bc}\delta_{il}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{km}\sigma^{ae}_{in}\sigma^{de*}_{mn}\delta_{bc}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{km}\sigma^{ae}_{jn}\sigma^{ce*}_{mn}\delta_{bd}\delta_{il}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{lm}\sigma^{ae}_{in}\sigma^{ce*}_{mn}\delta_{bd}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{lm}\sigma^{ae}_{jn}\sigma^{de*}_{mn}\delta_{bc}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ec}\sigma^{af}_{im}\sigma^{ef*}_{km}\delta_{bd}\delta_{jl}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ec}\sigma^{af}_{jm}\sigma^{ef*}_{lm}\delta_{bd}\delta_{ik}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ed}\sigma^{af}_{im}\sigma^{ef*}_{lm}\delta_{bc}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{ed}\sigma^{af}_{jm}\sigma^{ef*}_{km}\delta_{bc}\delta_{il}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{mi}\sigma^{ae}_{mn}\sigma^{ce*}_{ln}\delta_{bd}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{mi}\sigma^{ae}_{mn}\sigma^{de*}_{kn}\delta_{bc}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{mi}\sigma^{be}_{mn}\sigma^{ce*}_{kn}\delta_{ad}\delta_{jl}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{mi}\sigma^{be}_{mn}\sigma^{de*}_{ln}\delta_{ac}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}d_{fe}\sigma^{ae}_{im}\sigma^{cf*}_{km}\delta_{bd}\delta_{jl}+\mathcal{P}^{-}_{(ijab)}d_{fe}\sigma^{ae}_{im}\sigma^{df*}_{lm}\delta_{bc}\delta_{jk}$$

$$+\mathcal{P}^{-}_{(ijab)}d_{fe}\sigma^{ae}_{jm}\sigma^{cf*}_{lm}\delta_{bd}\delta_{ik}+\mathcal{P}^{-}_{(ijab)}d_{fe}\sigma^{ae}_{jm}\sigma^{df*}_{km}\delta_{bc}\delta_{il}+\mathcal{P}^{-}_{(ab)}d_{fe}\sigma^{eg}_{ij}\sigma^{fg*}_{kl}\delta_{ac}\delta_{bd}$$

$$+\mathcal{P}^{-}_{(ij)}d_{mn}\sigma^{ab}_{mo}\sigma^{cd*}_{no}\delta_{il}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}d_{mn}\sigma^{ae}_{im}\sigma^{ce*}_{ln}\delta_{bd}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}d_{mn}\sigma^{ae}_{im}\sigma^{de*}_{kn}\delta_{bc}\delta_{jl}$$

$$+\mathcal{P}^{-}_{(ijab)}d_{mn}\sigma^{ae}_{jm}\sigma^{ce*}_{kn}\delta_{bd}\delta_{il}+\mathcal{P}^{-}_{(ijab)}d_{mn}\sigma^{ae}_{jm}\sigma^{de*}_{ln}\delta_{bc}\delta_{ik}$$

$$+\mathcal{P}^{-}_{(ijab)}d_{am}\sigma^{c*}_{m}\delta_{bd}\delta_{il}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}d_{am}\sigma^{d*}_{m}\delta_{bc}\delta_{ik}\delta_{jl}+\mathcal{P}^{-}_{(ijab)}d_{ei}\sigma^{e*}_{k}\delta_{ad}\delta_{bc}\delta_{jl}$$

$$+\mathcal{P}^{-}_{(ijab)}d_{ei}\sigma^{e*}_{l}\delta_{ac}\delta_{bd}\delta_{jk}$$

$$+\mathcal{P}^{-}_{(ijab)}d_{ke}\sigma^{e}_{i}\delta_{ad}\delta_{bc}\delta_{jl}+\mathcal{P}^{-}_{(ijab)}d_{le}\sigma^{e}_{i}\delta_{ac}\delta_{bd}\delta_{jk}+\mathcal{P}^{-}_{(ijab)}d_{mc}\sigma^{a}_{m}\delta_{bd}\delta_{il}\delta_{jk}$$

$$+\mathcal{P}^{-}_{(ijab)}d_{md}\sigma^{a}_{m}\delta_{bc}\delta_{ik}\delta_{jl}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ae}\sigma^{ef}_{mn}\sigma^{cf*}_{mn}\delta_{bd}\delta_{il}\delta_{jk}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ae}\sigma^{ef}_{mn}\sigma^{df*}_{mn}\delta_{bc}\delta_{ik}\delta_{jl}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{km}\sigma^{ef}_{in}\sigma^{ef*}_{mn}\delta_{ac}\delta_{bd}\delta_{jl}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{lm}\sigma^{ef}_{in}\sigma^{ef*}_{mn}\delta_{ad}\delta_{bc}\delta_{jk}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ec}\sigma^{af}_{mn}\sigma^{ef*}_{mn}\delta_{bd}\delta_{il}\delta_{jk}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{ed}\sigma^{af}_{mn}\sigma^{ef*}_{mn}\delta_{bc}\delta_{ik}\delta_{jl}$$

$$+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{mi}\sigma^{ef}_{mn}\sigma^{ef*}_{kn}\delta_{ac}\delta_{bd}\delta_{jl}+\frac{1}{4}\mathcal{P}^{-}_{(ijab)}d_{mi}\sigma^{ef}_{mn}\sigma^{ef*}_{ln}\delta_{ad}\delta_{bc}\delta_{jk}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{fe}\sigma^{ae}_{mn}\sigma^{cf*}_{mn}\delta_{bd}\delta_{il}\delta_{jk}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{fe}\sigma^{ae}_{mn}\sigma^{df*}_{mn}\delta_{bc}\delta_{ik}\delta_{jl}$$

$$+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{mn}\sigma^{ef}_{im}\sigma^{ef*}_{kn}\delta_{ac}\delta_{bd}\delta_{jl}+\frac{1}{2}\mathcal{P}^{-}_{(ijab)}d_{mn}\sigma^{ef}_{im}\sigma^{ef*}_{ln}\delta_{ad}\delta_{bc}\delta_{jk}$$

$$
\begin{aligned}
&+ \mathcal{P}^{-}_{(ijab)} d_{fe} \sigma^{eg}_{im} \sigma^{fg*}_{km} \delta_{ad} \delta_{bc} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{fe} \sigma^{eg}_{im} \sigma^{fg*}_{lm} \delta_{ac} \delta_{bd} \delta_{jk} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{mn} \sigma^{ae}_{mo} \sigma^{ce*}_{no} \delta_{bd} \delta_{ik} \delta_{jl} + \mathcal{P}^{-}_{(ijab)} d_{mn} \sigma^{ae}_{mo} \sigma^{de*}_{no} \delta_{bc} \delta_{il} \delta_{jk} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{em} \sigma^{e*}_{m} \delta_{ac} \delta_{bd} \delta_{ik} \delta_{jl} \\
&+ \mathcal{P}^{-}_{(ijab)} d_{me} \sigma^{e}_{m} \delta_{ac} \delta_{bd} \delta_{ik} \delta_{jl} \\
&+ \frac{1}{2} \mathcal{P}^{-}_{(ijab)} d_{fe} \sigma^{eg}_{mn} \sigma^{fg*}_{mn} \delta_{ac} \delta_{bd} \delta_{ik} \delta_{jl} + \frac{1}{2} \mathcal{P}^{-}_{(ijab)} d_{mn} \sigma^{ef}_{mo} \sigma^{ef*}_{no} \delta_{ac} \delta_{bd} \delta_{il} \delta_{jk}
\end{aligned}
$$

PP-UCC4 state-to-state density, doubles/triples:

$$
\begin{aligned}
&\langle \Phi^{ab}_{ij} | \bar{D} | \Phi^{cde}_{klm} \rangle \ = \\
&\mathcal{P}^{-}_{(klm)} d_{an} \sigma^{cd*}_{kn} \delta_{be} \delta_{im} \delta_{jl} + \mathcal{P}^{-}_{(klm)} d_{an} \sigma^{ce*}_{kn} \delta_{bd} \delta_{il} \delta_{jm} + \mathcal{P}^{-}_{(klm)} d_{an} \sigma^{de*}_{kn} \delta_{bc} \delta_{im} \delta_{jl} \\
&\quad + \mathcal{P}^{-}_{(klm)} d_{bn} \sigma^{cd*}_{kn} \delta_{ae} \delta_{il} \delta_{jm} + \mathcal{P}^{-}_{(klm)} d_{bn} \sigma^{ce*}_{kn} \delta_{ad} \delta_{im} \delta_{jl} + \mathcal{P}^{-}_{(klm)} d_{bn} \sigma^{de*}_{kn} \delta_{ac} \delta_{il} \delta_{jm} \\
&\quad + \mathcal{P}^{-}_{(cde)} d_{fi} \sigma^{cf*}_{kl} \delta_{ae} \delta_{bd} \delta_{jm} + \mathcal{P}^{-}_{(cde)} d_{fi} \sigma^{cf*}_{km} \delta_{ad} \delta_{be} \delta_{jl} + \mathcal{P}^{-}_{(cde)} d_{fi} \sigma^{cf*}_{lm} \delta_{ae} \delta_{bd} \delta_{jk} \\
&\quad + \mathcal{P}^{-}_{(cde)} d_{fj} \sigma^{cf*}_{kl} \delta_{ad} \delta_{be} \delta_{im} + \mathcal{P}^{-}_{(cde)} d_{fj} \sigma^{cf*}_{km} \delta_{ae} \delta_{bd} \delta_{il} + \mathcal{P}^{-}_{(cde)} d_{fj} \sigma^{cf*}_{lm} \delta_{ad} \delta_{be} \delta_{ik} \\
&+ \mathcal{P}^{-}_{(klmcde)} d_{kc} \delta_{ad} \delta_{be} \delta_{il} \delta_{jm} \\
&+ \mathcal{P}^{-}_{(klmcde)} d_{fn} \sigma^{cf*}_{kn} \delta_{ad} \delta_{be} \delta_{il} \delta_{jm}
\end{aligned}
$$

PP-UCC4 state-to-state density, triples/singles:

$$
\begin{aligned}
&\langle \Phi^{abc}_{ijk} | \bar{D} | \Phi^{d}_{l} \rangle \ = \\
&\mathcal{P}^{-}_{(ab)} d_{le} \sigma^{ace}_{ijk} \delta_{bd} + \mathcal{P}^{-}_{(ij)} d_{md} \sigma^{abc}_{ikm} \delta_{jl} - d_{le} \sigma^{abe}_{ijk} \delta_{cd} \\
&\quad - d_{md} \sigma^{abc}_{ijm} \delta_{kl} \\
&\quad + \mathcal{P}^{-}_{(abc)} d_{ae} \sigma^{be}_{ik} \delta_{cd} \delta_{jl} + \mathcal{P}^{-}_{(abc)} d_{ae} \sigma^{ce}_{ij} \delta_{bd} \delta_{kl} + \mathcal{P}^{-}_{(abc)} d_{ae} \sigma^{ce}_{jk} \delta_{bd} \delta_{il} \\
&\quad + \mathcal{P}^{-}_{(ijk)} d_{mi} \sigma^{ab}_{jm} \delta_{cd} \delta_{kl} + \mathcal{P}^{-}_{(ijk)} d_{mi} \sigma^{ac}_{km} \delta_{bd} \delta_{jl} + \mathcal{P}^{-}_{(ijk)} d_{mi} \sigma^{bc}_{jm} \delta_{ad} \delta_{kl}
\end{aligned}
$$

$$
\begin{aligned}
&+ d_{me}\sigma^{abe}_{ijm}\delta_{cd}\delta_{kl} + \mathcal{P}^{-}_{(ij)} d_{me}\sigma^{abe}_{jkm}\delta_{cd}\delta_{il} + \mathcal{P}^{-}_{(ijab)} d_{me}\sigma^{ace}_{ikm}\delta_{bd}\delta_{jl} \\
&\quad + \mathcal{P}^{-}_{(ab)} d_{me}\sigma^{bce}_{ijm}\delta_{ad}\delta_{kl}
\end{aligned}
$$

PP-UCC4 state-to-state density, triples/doubles:

$$
\begin{aligned}
&\langle \Phi^{abc}_{ijk} | \bar{D} | \Phi^{de}_{lm} \rangle \ = \\
&\mathcal{P}^{-}_{(ijkabc)} d_{ai}\delta_{bd}\delta_{ce}\delta_{jl}\delta_{km} \\
&\ + \mathcal{P}^{-}_{(abc)} d_{lf}\sigma^{af}_{ij}\delta_{be}\delta_{cd}\delta_{km} + \mathcal{P}^{-}_{(abc)} d_{lf}\sigma^{af}_{ik}\delta_{bd}\delta_{ce}\delta_{jm} + \mathcal{P}^{-}_{(abc)} d_{lf}\sigma^{af}_{jk}\delta_{be}\delta_{cd}\delta_{im} \\
&\quad + \mathcal{P}^{-}_{(abc)} d_{mf}\sigma^{af}_{ij}\delta_{bd}\delta_{ce}\delta_{kl} + \mathcal{P}^{-}_{(abc)} d_{mf}\sigma^{af}_{ik}\delta_{be}\delta_{cd}\delta_{jl} + \mathcal{P}^{-}_{(abc)} d_{mf}\sigma^{af}_{jk}\delta_{bd}\delta_{ce}\delta_{il} \\
&\quad + \mathcal{P}^{-}_{(ijk)} d_{nd}\sigma^{ab}_{in}\delta_{ce}\delta_{jm}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} d_{nd}\sigma^{ac}_{in}\delta_{be}\delta_{jl}\delta_{km} + \mathcal{P}^{-}_{(ijk)} d_{nd}\sigma^{bc}_{in}\delta_{ae}\delta_{jm}\delta_{kl} \\
&\quad + \mathcal{P}^{-}_{(ijk)} d_{ne}\sigma^{ab}_{in}\delta_{cd}\delta_{jl}\delta_{km} + \mathcal{P}^{-}_{(ijk)} d_{ne}\sigma^{ac}_{in}\delta_{bd}\delta_{jm}\delta_{kl} + \mathcal{P}^{-}_{(ijk)} d_{ne}\sigma^{bc}_{in}\delta_{ad}\delta_{jl}\delta_{km} \\
&\ + \mathcal{P}^{-}_{(ijkabc)} d_{nf}\sigma^{af}_{in}\delta_{bd}\delta_{ce}\delta_{jl}\delta_{km}
\end{aligned}
$$

PP-UCC4 state-to-state density, triples/triples:

$$
\begin{aligned}
&\langle \Phi^{abc}_{ijk} | \bar{D} | \Phi^{def}_{lmn} \rangle \ = \\
&\mathcal{P}^{-}_{(ijkabc)} d_{ad}\delta_{be}\delta_{cf}\delta_{il}\delta_{jm}\delta_{kn} + \mathcal{P}^{-}_{(ijkabc)} d_{ae}\delta_{bd}\delta_{cf}\delta_{il}\delta_{jn}\delta_{km} + \mathcal{P}^{-}_{(ijkabc)} d_{af}\delta_{bd}\delta_{ce}\delta_{il}\delta_{jm}\delta_{kn} \\
&\quad + \mathcal{P}^{-}_{(ijkabc)} d_{li}\delta_{ad}\delta_{be}\delta_{cf}\delta_{jn}\delta_{km} + \mathcal{P}^{-}_{(ijkabc)} d_{mi}\delta_{ad}\delta_{be}\delta_{cf}\delta_{jl}\delta_{kn} + \mathcal{P}^{-}_{(ijkabc)} d_{ni}\delta_{ad}\delta_{be}\delta_{cf}\delta_{jm}\delta_{kl}
\end{aligned}
$$

Bibliography

[1] `https://github.com/sympy/sympy/blob/master/examples/intermediate/coupled_cluster.py`. Accessed: 2023-10-10.

[2] M. Alagia, E. Bodo, P. Decleva, S. Falcinelli, A. Ponzi, R. Richter, and S. Stranges. The soft x-ray absorption spectrum of the allyl free radical. *Phys. Chem. Chem. Phys.*, 15:1310–1318, 2013.

[3] M. Alagia, M. Lavollée, R. Richter, U. Ekström, V. Carravetta, D. Stranges, B. Brunetti, and S. Stranges. Probing the potential energy surface by high-resolution x-ray absorption spectroscopy: The umbrella motion of the core-excited CH_3 free radical. *Phys. Rev. A*, 76:022509, Aug 2007.

[4] P. Auger. Sur les rayons β secondaires produits dans un gaz par des rayons X. *C.R.A.S.*, 177:169–171, 1923.

[5] Rodney J. Bartlett. Coupled-cluster theory and its equation-of-motion extensions. *WIREs Comput. Mol. Sci.*, 2(1):126–138, Jul 2012.

[6] Rodney J. Bartlett, Stanislaw A. Kucharski, and Jozef Noga. Alternative coupled-cluster ansätze II. The unitary coupled-cluster method. *Chem. Phys. Lett.*, 155(1):133–140, 1989.

[7] Rodney J. Bartlett and Monika Musiał. Coupled-cluster theory in quantum chemistry. *Rev. Mod. Phys.*, 79:291–352, Feb 2007.

[8] Niels Bohr. On the Constitution of Atoms and Molecules, Part I, 1913.

[9] M. Born and R. Oppenheimer. Zur Quantentheorie der Molekeln. *Annalen der Physik*, 389(20):457–484, 1927.

[10] L. S. Cederbaum, W. Domcke, and J. Schirmer. Many-body theory of core holes. *Phys. Rev. A*, 22:206–222, Jul 1980.

[11] Timothy Clark, Jayaraman Chandrasekhar, Günther W. Spitznagel, and Paul Von Ragué Schleyer. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li–F. *J. Comput. Chem.*, 4(3):294–301, 1983.

[12] C. Cohen-Tannoudji, B. Diu, and F. Laloë. *Quantum Mechanics, Volume One*. WILEY-VCH Verlag GmbH & Co. KGaA, 2005.

[13] C. Cohen-Tannoudji, B. Diu, and F. Laloë. *Quantum Mechanics, Volume Two*. WILEY-VCH Verlag GmbH & Co. KGaA, 2005.

[14] Christopher J. Cramer. *Essentials of Computational Chemistry*. John Wiley & Sons, Ltd, 2nd edition, 2004.

[15] T. D. Crawford and H. F. Schaefer III. An Introduction to Coupled Cluster Theory for Computational Chemists. *Rev. Comput. Chem.*, 14:33–136, 2000.

[16] Ernest R. Davidson. The iterative calculation of a few of the lowest eigenvalues and corresponding eigenvectors of large real-symmetric matrices. *J. Comput. Phys.*, 17(1):87–94, 1975.

[17] A. L. Dempwolff. *Development and Implementation of High-Level Propagator Methods for the Description of Electronically Stable and Unstable States*. PhD thesis, Universitï Heidelberg, 2020.

[18] Adrian L. Dempwolff, Alexandra M. Belogolova, Alexander B. Trofimov, and Andreas Dreuw. Intermediate state representation approach to physical properties of molecular electron-attached states: Theory, implementation, and benchmarking. *The Journal of Chemical Physics*, 154(10):104117, 03 2021.

[19] Adrian L. Dempwolff, Manuel Hodecker, and Andreas Dreuw. Vertical ionization potential benchmark for unitary coupled-cluster and algebraic-diagrammatic construction methods. *The Journal of Chemical Physics*, 156(5):054114, 02 2022.

[20] Adrian L. Dempwolff, Alexander C. Paul, Alexandra M. Belogolova, Alexander B. Trofimov, and Andreas Dreuw. Intermediate state representation approach to physical properties of molecular electron-detached states. I. Theory and implementation. *J. Chem. Phys.*, 152(2):024113, 2020.

[21] Adrian L. Dempwolff, Alexander C. Paul, Alexandra M. Belogolova, Alexander B. Trofimov, and Andreas Dreuw. Intermediate state representation approach to physical properties of molecular electron-detached states. II. Benchmarking. *The Journal of Chemical Physics*, 152(2):024125, 01 2020.

[22] Adrian L. Dempwolff, Matthias Schneider, Manuel Hodecker, and Andreas Dreuw. Efficient implementation of the non-Dyson third-order algebraic diagrammatic construction approximation for the electron propagator for closed- and open-shell molecules. *The Journal of Chemical Physics*, 150(6):064108, 02 2019.

[23] Paul Adrien Maurice Dirac and Ralph Howard Fowler. On the theory of quantum mechanics. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 112(762):661–677, 1926.

[24] R. Ditchfield, W. J. Hehre, and J. A. Pople. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *The Journal of Chemical Physics*, 54(2):724–728, 09 2003.

[25] A. Dreuw and M. Wormit. The algebraic diagrammatic construction scheme for the polarization propagator for the calculation of excited states. *WIREs Comput. Mol. Sci.*, 5:82–95, 2015.

[26] Andreas Dreuw. *The Algebraic-Diagrammatic Construction Scheme for the Polarization Propagator*, chapter 5, pages 109–131. John Wiley & Sons, Ltd, 2020.

[27] Andreas Dreuw, Antonia Papapostolou, and Adrian L. Dempwolff. Algebraic Diagrammatic Construction Schemes Employing the Intermediate State Formalism: Theory, Capabilities, and Interpretation. *The Journal of Physical Chemistry A*, 127(32):6635–6646, Aug 2023.

[28] Thom H. Dunning. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.*, 90(2):1007–1023, 1989.

[29] R. Eisberg and R. Resnick. *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles*, volume 2nd. John Wiley & Sons, Inc., 1985.

[30] Evgeny Epifanovsky, Andrew T. B. Gilbert, Xintian Feng, Joonho Lee, Yuezhi Mao, Narbe Mardirossian, Pavel Pokhilko, Alec F. White, Marc P. Coons, Adrian L. Dempwolff, Zhengting Gan, Diptarka Hait, Paul R. Horn, Leif D. Jacobson, Ilya Kaliman, Jörg Kussmann, Adrian W. Lange, Ka Un Lao, Daniel S. Levine, Jie Liu, Simon C. McKenzie, Adrian F. Morrison, Kaushik D. Nanda, Felix Plasser, Dirk R. Rehn, Marta L. Vidal, Zhi-Qiang You, Ying Zhu, Bushra Alam, Benjamin J. Albrecht, Abdulrahman Aldossary, Ethan Alguire, Josefine H. Andersen, Vishikh Athavale, Dennis Barton, Khadiza Begam, Andrew Behn, Nicole Bellonzi, Yves A. Bernard, Eric J. Berquist, Hugh G. A. Burton, Abel Carreras, Kevin Carter-Fenk, Romit Chakraborty, Alan D. Chien, Kristina D. Closser, Vale Cofer-Shabica, Saswata Dasgupta, Marc de Wergifosse, Jia Deng, Michael Diedenhofen, Hainam Do, Sebastian Ehlert, Po-Tung Fang, Shervin Fatehi, Qingguo Feng, Triet Friedhoff, James Gayvert, Qinghui Ge, Gergely Gidofalvi, Matthew Goldey, Joe Gomes, Cristina E. González-Espinoza, Sahil Gulania, Anastasia O. Gunina, Magnus W. D. Hanson-Heine, Phillip H. P. Harbach, Andreas Hauser, Michael F. Herbst, Mario Hernández Vera, Manuel Hodecker, Zachary C. Holden, Shannon Houck, Xunkun Huang, Kerwin Hui, Bang C. Huynh, Maxim Ivanov, Ádám Jász, Hyunjun Ji, Hanjie Jiang, Benjamin Kaduk, Sven Kähler, Kirill Khistyaev, Jaehoon Kim, Gergely Kis, Phil Klunzinger, Zsuzsanna Koczor-Benda, Joong Hoon Koh, Dimitri Kosenkov, Laura Koulias, Tim Kowalczyk, Caroline M. Krauter, Karl Kue, Alexander Kunitsa, Thomas Kus, István Ladjánszki, Arie Landau, Keith V. Lawler, Daniel Lefrancois, Susi Lehtola, Run R. Li, Yi-Pei Li, Jiashu Liang, Marcus Liebenthal, Hung-Hsuan Lin, You-Sheng Lin, Fenglai Liu, Kuan-Yu Liu, Matthias Loipersberger, Arne Luenser, Aaditya Manjanath, Prashant Manohar, Erum Mansoor, Sam F. Manzer, Shan-Ping Mao, Aleksandr V. Marenich, Thomas Markovich, Stephen Mason, Simon A. Maurer, Peter F. McLaughlin, Maximilian F.

S. J. Menger, Jan-Michael Mewes, Stefanie A. Mewes, Pierpaolo Morgante, J. Wayne Mullinax, Katherine J. Oosterbaan, Garrette Paran, Alexander C. Paul, Suranjan K. Paul, Fabijan Pavošević, Zheng Pei, Stefan Prager, Emil I. Proynov, Ádám Rák, Eloy Ramos-Cordoba, Bhaskar Rana, Alan E. Rask, Adam Rettig, Ryan M. Richard, Fazle Rob, Elliot Rossomme, Tarek Scheele, Maximilian Scheurer, Matthias Schneider, Nickolai Sergueev, Shaama M. Sharada, Wojciech Skomorowski, David W. Small, Christopher J. Stein, Yu-Chuan Su, Eric J. Sundstrom, Zhen Tao, Jonathan Thirman, Gábor J. Tornai, Takashi Tsuchimochi, Norm M. Tubman, Srimukh Prasad Veccham, Oleg Vydrov, Jan Wenzel, Jon Witte, Atsushi Yamada, Kun Yao, Sina Yeganeh, Shane R. Yost, Alexander Zech, Igor Ying Zhang, Xing Zhang, Yu Zhang, Dmitry Zuev, Alán Aspuru-Guzik, Alexis T. Bell, Nicholas A. Besley, Ksenia B. Bravaya, Bernard R. Brooks, David Casanova, Jeng-Da Chai, Sonia Coriani, Christopher J. Cramer, György Cserey, III DePrince, A. Eugene, Jr. DiStasio, Robert A., Andreas Dreuw, Barry D. Dunietz, Thomas R. Furlani, III Goddard, William A., Sharon Hammes-Schiffer, Teresa Head-Gordon, Warren J. Hehre, Chao-Ping Hsu, Thomas-C. Jagau, Yousung Jung, Andreas Klamt, Jing Kong, Daniel S. Lambrecht, WanZhen Liang, Nicholas J. Mayhall, C. William McCurdy, Jeffrey B. Neaton, Christian Ochsenfeld, John A. Parkhill, Roberto Peverati, Vitaly A. Rassolov, Yihan Shao, Lyudmila V. Slipchenko, Tim Stauch, Ryan P. Steele, Joseph E. Subotnik, Alex J. W. Thom, Alexandre Tkatchenko, Donald G. Truhlar, Troy Van Voorhis, Tomasz A. Wesolowski, K. Birgitta Whaley, III Woodcock, H. Lee, Paul M. Zimmerman, Shirin Faraji, Peter M. W. Gill, Martin Head-Gordon, John M. Herbert, and Anna I. Krylov. Software for the frontiers of quantum chemistry: An overview of developments in the Q-Chem 5 package. *The Journal of Chemical Physics*, 155(8):084801, 08 2021.

[31] Evgeny Epifanovsky, Michael Wormit, Tomasz Kuś, Arie Landau, Dmitry Zuev, Kirill Khistyaev, Prashant Manohar, Ilya Kaliman, Andreas Dreuw, and Anna I. Krylov. New implementation of high-level correlated methods using a general block tensor library for high-performance electronic structure calculations. *J. Comput. Chem.*, 34(26):2293–2309, Jul 2013.

[32] E. Fermi. Zur Quantelung des idealen einatomigen Gases. *Zeitschrift für Physik*,

36(11):902–912, Nov 1926.

[33] A. L. Fetter and J. D. Walecka. *Quantum Theory of Many-Particle Systems*. Dover Books on Physics, 2003.

[34] V. Fock. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Zeitschrift für Physik*, 61(1):126–148, Jan 1930.

[35] Walther Gerlach and Otto Stern. Der experimentelle Nachweis der Richtungsquantelung im Magnetfeld. *Zeitschrift für Physik*, 9(1):349–352, Dec 1922.

[36] Peter M.W. Gill. Molecular integrals Over Gaussian Basis Functions. volume 25 of *Advances in Quantum Chemistry*, pages 141–205. Academic Press, 1994.

[37] P. Glans, K. Gunnelin, P. Skytt, J.-H. Guo, N. Wassdahl, J. Nordgren, H. Ågren, F. Kh. Gel'mukhanov, T. Warwick, and Eli Rotenberg. Resonant X-Ray Emission Spectroscopy of Molecular Oxygen. *Phys. Rev. Lett.*, 76:2448–2451, Apr 1996.

[38] Michelle L. Gordon, David Tulumello, Glyn Cooper, Adam P. Hitchcock, Pieter Glatzel, Oliver C. Mullins, Stephen P. Cramer, and Uwe Bergmann. Inner-Shell Excitation Spectroscopy of Fused-Ring Aromatic Molecules by Electron Energy Loss and X-ray Raman Techniques. *J. Phys. Chem. A*, 107(41):8512–8520, 2003.

[39] H. Haken and H. C. Wolf. *Atom- und Quantenphysik, Einführung in die experimentellen und theoretischen Grundlagen*. Springer-Verlag, Berlin Heidelberg New York, 1987.

[40] G. G. Hall and John Edward Lennard-Jones. The molecular orbital theory of chemical valency VIII. A method of calculating ionization potentials. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 205(1083):541–552, 1951.

[41] Philipp H. P. Harbach, Michael Wormit, and Andreas Dreuw. The third-order algebraic diagrammatic construction method (adc(3)) for the polarization propagator for closed-shell molecules: Efficient implementation and benchmarking. *J. Chem. Phys.*, 141(6):064113, Aug 2014.

[42] P. C. Hariharan and J. A. Pople. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta*, 28(3):213–222, Sep 1973.

[43] D. R. Hartree. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion. *Mathematical Proceedings of the Cambridge Philosophical Society*, 24(1):111–132, 1928.

[44] Douglas Rayner Hartree and W. Hartree. Self-consistent field, with exchange, for beryllium. *Proceedings of the Royal Society of London. Series A - Mathematical and Physical Sciences*, 150(869):9–33, 1935.

[45] W. J. Hehre, R. Ditchfield, and J. A. Pople. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.*, 56(5):2257–2261, 1972.

[46] T. Helgaker, P. Jørgensen, and J. Olsen. *Molecular Electronic-Structure Theory*. John Wiley & Sons, Ltd., 2000.

[47] Arnim Hellweg and Dmitrij Rappoport. Development of new auxiliary basis functions of the Karlsruhe segmented contracted basis sets including diffuse basis functions (def2-SVPD, def2-TZVPPD, and def2-QVPPD) for RI-MP2 and RI-CC calculations. *Phys. Chem. Chem. Phys.*, 17:1010–1017, 2015.

[48] Manuel Hodecker. *Development and Application of Hermitian Methods for Molecular Properties and Excited Electronic States*. PhD thesis, Universität Heidelberg, March 2020.

[49] Manuel Hodecker, Adrian L. Dempwolff, Jochen Schirmer, and Andreas Dreuw. Theoretical analysis and comparison of unitary coupled-cluster and algebraic-diagrammatic construction methods for ionization. *The Journal of Chemical Physics*, 156(7):074104, 02 2022.

[50] Manuel Hodecker, Dirk R. Rehn, and Andreas Dreuw. Hermitian Second-Order Methods for Excited Electronic States: Unitary Coupled Cluster in Comparison with Algebraic-Diagrammatic Construction Methods. *J. Chem. Phys.*, 152(9):094106, 2020.

[51] Manuel Hodecker, Sebastian M. Thielen, Junzi Liu, Dirk R. Rehn, and Andreas Dreuw. Third-Order Unitary Coupled Cluster (UCC3) for Excited Electronic States: Efficient Implementation and Benchmarking. *J. Chem. Theory Comput.*, 16(6):3654–3663, 2020.

[52] Florian Holch, Dominique Hübner, Rainer Fink, Achim Schöll, and Eberhard Umbach. New set-up for high-quality soft-X-ray absorption spectroscopy of large organic molecules in the gas phase. *J. Electron. Spectrosc. Relat. Phenom.*, 184(8):452 – 456, 2011.

[53] Hiromi Ikeura-Sekiguchi and Tetsuhiro Sekiguchi. Unoccupied electronic states in polythiophene as probed by XAS and RAS. *Surf. Interface Anal.*, 40(3-4):673–675, 2008.

[54] F. Jensen. *Introduction to Computational Chemistry*. John Wiley & Sons, Ltd., 2nd edition, 2007.

[55] Rick A. Kendall, Thom H. Dunning, and Robert J. Harrison. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.*, 96(9):6796–6806, 1992.

[56] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.*, 72(1):650–654, 1980.

[57] W. Kutzelnigg. *Einführung in die Theoretsche Chemie*. WILEY-VCH Verlag GmbH, Weinheim, 2002.

[58] Tomasz Kuś and Anna I. Krylov. Using the charge-stabilization technique in the double ionization potential equation-of-motion calculations with dianion references. *The Journal of Chemical Physics*, 135(8):084109, 08 2011.

[59] Tomasz Kuś and Anna I. Krylov. De-perturbative corrections for charge-stabilized double ionization potential equation-of-motion coupled-cluster method. *The Journal of Chemical Physics*, 136(24):244109, 06 2012.

[60] J. Leitner, A. L. Dempwolff, and A. Dreuw. The fourth-order algebraic diagrammatic construction scheme for the polarization propagator. *The Journal of Chemical Physics*, 157(18):184101, 11 2022.

[61] Junzi Liu, Ayush Asthana, Lan Cheng, and Debashis Mukherjee. Unitary coupled-cluster based self-consistent polarization propagator theory: A third-order formulation and pilot applications. *J. Chem. Phys.*, 148(24):244110, 2018.

[62] Junzi Liu and Lan Cheng. Unitary coupled-cluster based self-consistent polarization propagator theory: A quadratic unitary coupled-cluster singles and doubles scheme. *The Journal of Chemical Physics*, 155(17):174102, 11 2021.

[63] Junzi Liu, Devin A. Matthews, and Lan Cheng. Quadratic Unitary Coupled-Cluster Singles and Doubles Scheme: Efficient Implementation, Benchmark Study, and Formulation of an Extended Version. *Journal of Chemical Theory and Computation*, 18(4):2281–2291, 2022. PMID: 35312299.

[64] Pierre-François Loos, Anthony Scemama, Aymeric Blondel, Yann Garniron, Michel Caffarel, and Denis Jacquemin. A Mountaineering Strategy to Excited States: Highly Accurate Reference Energies and Benchmarks. *J. Chem. Theory Comput.*, 14(8):4360–4379, 2018.

[65] Rouven Maier, Marco Bauer, and Andreas Dreuw. Consistent third-order one-particle transition and excited-state properties within the algebraic-diagrammatic construction scheme for the polarization propagator. *The Journal of Chemical Physics*, 159(1):014104, 07 2023.

[66] Richard D. Mattuck. *A Guide to Feynman Diagrams in the Many-Body Problem*. Dover Publications, Inc., 2nd edition, 1992.

[67] A. D. McLean and G. S. Chandler. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–18. *J. Chem. Phys.*, 72(10):5639–5648, 1980.

[68] Aaron Meurer, Christopher P. Smith, Mateusz Paprocki, Ondřej Čertík, Sergey B. Kirpichev, Matthew Rocklin, AMiT Kumar, Sergiu Ivanov, Jason K. Moore, Sar-

taj Singh, Thilina Rathnayake, Sean Vig, Brian E. Granger, Richard P. Muller, Francesco Bonazzi, Harsh Gupta, Shivam Vats, Fredrik Johansson, Fabian Pedregosa, Matthew J. Curry, Andy R. Terrel, Štěpán Roučka, Ashutosh Saboo, Isuru Fernando, Sumith Kulal, Robert Cimrman, and Anthony Scopatz. SymPy: symbolic computing in Python. *PeerJ Computer Science*, 3:e103, January 2017.

[69] Chr. Møller and M. S. Plesset. Note on an Approximation Treatment for Many-Electron Systems. *Physical Review*, 46(7):618–622, October 1934.

[70] Gordon E. Moore. Cramming more components onto integrated circuits. *Electronics*, 38(8), April 1965.

[71] H. W. L. Naus. Four electron spin qubits with exchange interaction. 2019.

[72] Patrick Norman and Andreas Dreuw. Simulating X-ray Spectroscopies and Calculating Core-Excited States of Molecules. *Chem. Rev.*, 118(15):7208–7248, 2018.

[73] O. Plekan, V. Feyer, R. Richter, M. Coreno, M. de Simone, K.C. Prince, A.B. Trofimov, E.V. Gromov, I.L. Zaytseva, and J. Schirmer. A theoretical and experimental study of the near edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectra (XPS) of nucleobases: Thymine and adenine. *Chem. Phys.*, 347(1):360 – 375, 2008.

[74] G. Polzonetti, V. Carravetta, G. Iucci, A. Ferri, G. Paolucci, A. Goldoni, P. Parent, C. Laffon, and M.V. Russo. Electronic structure of platinum complex/Zn-porphyrinato assembled macrosystems, related precursors and model molecules, as probed by X-ray absorption spectroscopy (NEXAFS): theory and experiment. *Chem. Phys.*, 296(1):87 – 100, 2004.

[75] Benjamin P. Pritchard, Doaa Altarawy, Brett Didier, Tara D. Gibson, and Theresa L. Windus. New Basis Set Exchange: An Open, Up-to-Date Resource for the Molecular Sciences Community. *Journal of Chemical Information and Modeling*, 59(11):4814–4820, 2019. PMID: 31600445.

[76] D. R. Rehn. *Development of Quantum-Chemical Methods for Excited-State and Response Properties.* PhD thesis, Universitẗ Heidelberg, 2015.

[77] C. C. J. Roothaan. New Developments in Molecular Orbital Theory. *Rev. Mod. Phys.*, 23:69–89, Apr 1951.

[78] J. Schirmer and A. Barth. Higher-order approximations for the particle-particle propagator. *Zeitschrift für Physik A Atoms and Nuclei*, 317(3):267–279, Oct 1984.

[79] J. Schirmer, L. S. Cederbaum, and O. Walter. New approach to the one-particle Green's function for finite Fermi systems. *Phys. Rev. A*, 28:1237–1259, Sep 1983.

[80] J. Schirmer and A. B. Trofimov. Intermediate state representation approach to physical properties of electronically excited molecules. *J. Chem. Phys.*, 120(24):11449–11464, 2004.

[81] J. Schirmer, A. B. Trofimov, K. J. Randall, J. Feldhaus, A. M. Bradshaw, Y. Ma, C. T. Chen, and F. Sette. K-shell excitation of the water, ammonia, and methane molecules using high-resolution photoabsorption spectroscopy. *Phys. Rev. A*, 47:1136–1147, Feb 1993.

[82] Jochen Schirmer. Beyond the random-phase approximation: A new approximation scheme for the polarization propagator. *Phys. Rev. A*, 26(5):2395–2416, 1982.

[83] Jochen Schirmer. Closed-form intermediate representations of many-body propagators and resolvent matrices. *Phys. Rev. A*, 43(9):4647–4659, 1991.

[84] Jochen Schirmer. *Many-Body Methods for Atoms, Molecules and Clusters*. Springer International Publishing, 2018.

[85] Schmidt,Norman and Clark,Tim and Urquhart,Stephen G. and Fink,Rainer H. Electron-vibron coupling in halogenated acenaphthenequinone upon o k-edge soft x-ray absorption. *J. Chem. Phys.*, 135(14):144301, 2011.

[86] E. Schrödinger. An Undulatory Theory of the Mechanics of Atoms and Molecules. *Phys. Rev.*, 28:1049–1070, Dec 1926.

[87] E. Schrödinger. Quantisierung als Eigenwertproblem. *Annalen der Physik*, 385(13):437–490, 1926.

[88] F. Schwabl. *Quantenmechanik für Fortgeschrittene*. Springer-Verlag, 3rd edition, 2004.

[89] F. Schwabl. *Quantenmechanik*. Springer-Verlag, 7th edition, 2007.

[90] J. C. Slater. The Theory of Complex Spectra. *Phys. Rev.*, 34:1293–1322, Nov 1929.

[91] J. C. Slater. Atomic Shielding Constants. *Phys. Rev.*, 36:57–64, Jul 1930.

[92] Joachim Stöhr. *NEXAFS Spectroscopy*. Springer, Berlin, 1992.

[93] Stefano Stranges, Robert Richter, and Michele Alagia. High-resolution inner-shell photoabsorption of the OH and OD free radicals. *J. Chem. Phys.*, 116(9):3676–3680, 2002.

[94] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications Inc., Mineola, New York, 1996.

[95] Francesco Tarantelli. The calculation of molecular double ionization spectra by Green's functions. *Chemical Physics*, 329(1):11–21, 2006. Electron Correlation and Multimode Dynamics in Molecules.

[96] Andrew G. Taube and Rodney J. Bartlett. New perspectives on unitary coupled-cluster theory. *Int. J. Quantum Chem.*, 106(15):3393–3401, 2006.

[97] S. M. Thielen. Implementation of the Algebraic-Diagrammatic Construction scheme for the two-hole propagator to study double ionization, master thesis, Hiedelberg, 2018.

[98] Sebastian M. Thielen, Manuel Hodecker, Julia Piazolo, Dirk R. Rehn, and Andreas Dreuw. Unitary coupled-cluster approach for the calculation of core-excited states and x-ray absorption spectra. *The Journal of Chemical Physics*, 154(15):154108, 04 2021.

[99] A. B. Trofimov, G. Stelter, and J. Schirmer. A consistent third-order propagator method for electronic excitation. *J. Chem. Phys.*, 111(22):9982–9999, 1999.

[100] M Tronc, G C King, and F H Read. Carbon K-shell excitation in small molecules by high-resolution electron impact. *J. Phys. B: At. Mol. Phys.*, 12(1):137–157, jan 1979.

[101] Yasen Velkov, Tsveta Miteva, Nicolas Sisourat, and Jochen Schirmer. Intermediate state representation approach to physical properties of dicationic states. *The Journal of Chemical Physics*, 135(15):154113, 10 2011.

[102] Marta L. Vidal, Xintian Feng, Evgeny Epifanovsky, Anna I. Krylov, and Sonia Coriani. New and Efficient Equation-of-Motion Coupled-Cluster Framework for Core-Excited and Core-Ionized States. *J. Chem. Theory Comput.*, 15(5):3117–3133, 2019.

[103] P. Väterlein, M. Schmelzer, J. Taborski, T. Krause, F. Viczian, M. Bäßler, R. Fink, E. Umbach, and W. Wurth. Orientation and bonding of thiophene and 2,2'-bithiophene on Ag(111): a combined near edge extended X-ray absorption fine structure and Xα scattered-wave study. *Surf. Sci.*, 452(1):20 – 32, 2000.

[104] Jan Wenzel. *Development and Implementation of Theoretical Methods for the Description of Electronically Core-Excited States*. PhD thesis, Universität Heidelberg, January 2016.

[105] Jan Wenzel and Andreas Dreuw. Physical Properties, Exciton Analysis, and Visualization of Core-Excited States: An Intermediate State Representation Approach. *J. Chem. Theory Comput.*, 12(3):1314–1330, 2016.

[106] Jan Wenzel, Andre Holzer, Michael Wormit, and Andreas Dreuw. Analysis and comparison of CVS-ADC approaches up to third order for the calculation of core-excited states. *J. Chem. Phys.*, 142(21):214104, 2015.

[107] Jan Wenzel, Michael Wormit, and Andreas Dreuw. Calculating core-level excitations and x-ray absorption spectra of medium-sized closed-shell molecules with the algebraic-diagrammatic construction scheme for the polarization propagator. *J. Comput. Chem.*, 35(26):1900–1915, 2014.

[108] Jan Wenzel, Michael Wormit, and Andreas Dreuw. Calculating X-ray Absorption Spectra of Open-Shell Molecules with the Unrestricted Algebraic-Diagrammatic

Construction Scheme for the Polarization Propagator. *J. Chem. Theory Comput.*, 10(10):4583–4598, 2014.

[109] G. C. Wick. The Evaluation of the Collision Matrix. *Phys. Rev.*, 80:268–272, Oct 1950.

[110] David E. Woon and Thom H. Dunning. Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties. *J. Chem. Phys.*, 100(4):2975–2988, 1994.

[111] M. Wormit. *Development and Application of Reliable Methods for the Calculation of Excited States: From Light-Harvesting Complexes to Medium-Sized Molecules.* PhD thesis, Universität Frankfurt am Main, 2009.

[112] Michael Wormit, Dirk R. Rehn, Philipp H. P. Harbach, Jan Wenzel, Caroline M. Krauter, Evgeny Epifanovsky, and Andreas Dreuw. Investigating excited electronic states using the algebraic diagrammatic construction (ADC) approach of the polarisation propagator. *Mol. Phys.*, 112(5-6):774–784, mar 2014.

GESAMTFAKULTÄT FÜR MATHEMATIK, INGENIEUR-
UND NATURWISSENSCHAFTEN

COMBINED FACULTY OF MATHEMATICS, ENGINEERING
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RUPRECHT-KARLS-
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HEIDELBERG

Eidesstattliche Versicherung gemäß § 8 der Promotionsordnung für die Gesamtfakultät für Mathematik, Ingenieur- und Naturwissenschaften der Universität Heidelberg / Sworn Affidavit according to § 8 of the doctoral degree regulations of the Combined Faculty of Mathematics, Engineering and Natural Sciences at Heidelberg University

1. Bei der eingereichten Dissertation zu dem Thema / The thesis I have submitted entitled

   Development and Benchmarking of Novel Electronic Structure Methods based on ……………………………………………

   the Algebraic Diagrammatic Construction and Unitary Coupled Cluster Schemes ……………………………………………

   handelt es sich um meine eigenständig erbrachte Leistung / is my own work.

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