

# **Methodological Developments in the Theory of Geminals**

Tamás Zoboki

Supervisor: Prof. Dr. Péter Surján

Doctoral School of Chemistry

Theoretical, Physical and Structural Chemistry Doctoral Program

Head of the Doctoral School: Prof. Dr. György Inzelt

Head of the Doctoral Programme: Prof. Dr. Péter Surján

Laboratory of Theoretical Chemistry

Institute of Chemistry

Eötvös Loránd University

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# Introduction

This thesis summarizes the scientific work done by the author between September 2010 and December 2014. The main aim of this dissertation was providing a self-contained text with full derivations that can be used as a learning material as well for newcomers to the field of geminals. In this respect, at some points the content of the different chapters may seem over-explained. While this might be embarrassing for professional researchers, people that are not familiar with the literature of geminals may find this approach useful.

The dissertation is divided into four distinct parts. Chapter 1. provides a brief overview of the literature for both geminals and Multi-reference Coupled Cluster Theory. The second chapter summarizes and explains the theoretical background without which the new results in the field of geminals cannot be fully understood. The third chapter introduces the theoretical advances elaborated by the author. The content of sections (3.1) and (3.2) were published in the articles [1] and [2] respectively. Section 3.3 contains unpublished results elaborated during the writing process of the thesis. The fourth important chapter is the Appendix, which contains derivations too lengthy to be included in the main body of the text or mathematical concepts which are used throughout and were only included for the sake of completeness.

If despite of the general goal (providing a self-contained, well-explained work that can be read without being referred to external sources too often), some points of this dissertation still seem unexplained or hard to understand, the author would like to sincerely apologize and take all responsibility.

# Bibliographical Overview

## 1.1 Overview of the literature of geminals

A very comprehensive overview of the history of geminal theory can be found in the book chapter written by Surján for Topics in Current Chemistry [3]. We find it unnecessary to cite all of the articles that are present in that monograph. We would only like to highlight the most important articles that have direct connection to the work presented in this dissertation.

The most important impact on our work was the Interaction of Chemical Bonds article series [4, 5, 6, 7, 8] by Surján et al. Part I. [4] introduces the partitioning of the Hamiltonian based on geminal subsets, the second-quantized formulation of geminal operators, their algebra and the equation for the electronic energy corresponding to the Antisymmetrized Product of Strictly Localized Geminals (AP-SLG) wave function. Part II. [5] advances further with introducing a biorthogonal perturbation theory based on the AP-SLG wave function as the zeroth order, on the top of which the different excitations are defined by using excitation operators similar to those appearing in the Hamiltonian itself. This article is a solely theoretical paper with no calculations presented. Nevertheless, it is very important from our point of view, the second-order perturbation correction for the dispersive term of the Hamiltonian (which is a central object in our oncoming investigations) appears firstly in this paper. Later it turned out that this is the term that causes complications during simultaneous dissociation of chemical bonds of a molecule. The main aim of the Coupled Cluster-based theory introduced in section (3.2) is getting rid of the unwanted divergences. Part III. of the series [6] further improves the idea presented in part II. by expanding the geminals in localized molecular orbitals and also presents a few calculations. Part IV. [7] introduces a Linear Coupled Cluster theory based on the AP-SLG reference with the cluster operator containing one-electron excitations. Part V. [8] is

mostly about the implementation of the theory presented in part II., it also introduces the graphical notation for the different partitions of the Hamiltonian used by us in subsection (2.3.5). This is the first article in the series which talks about the energetically optimized Antisymmetrized Product of Strongly Orthogonal Geminals (APSG) wave function instead of AP-SLG.

In [9] Surján and Rosta approach the topic of [8] from a different aspect, namely by pointing out an unusual property of this geminal-based perturbation theory: it can be viewed as an application for two-body zeroth-order Hamiltonians in Multi-reference Perturbation Theory. In this article, many applications are presented and also the problem initializing our work in a geminal-based Linear Coupled Cluster theory is mentioned explicitly: describing simultaneous breaking of equivalent bonds is impossible to describe with this theory due to divergence of the dispersive correction.

The diagrammatic approach in geminal theory was initiated by Paldus et. al [10, 11]. They went as far as expressing the APSG energy equation in terms of diagrams but no further energy corrections have been introduced by them. Nevertheless, their work was the most influential one regarding the description of the diagrams appearing in the geminal-based Dispersive Coupled Cluster theory. This yet unpublished theoretical construct is outlined in section (3.3).

## **1.2 Overview of the literature of Multi-reference Coupled Cluster Theory**

Reference states in quantum chemical calculations are used as zeroth-order states obtained at a simpler level to be corrected by perturbative or more sophisticated theories. Coupled Cluster (CC) theory [12, 13, 14, 15, 16, 17] for example offers a powerful tool to describe molecular electronic structure for single reference (SR) problems, i.e. when the electronic wave function can be qualitatively described by a single Slater-determinant. Many chemical processes require the use of two or more determinants even for a qualitative description. Just like Multi-reference (MR) Perturbation Theory (PT) [18, 19, 20, 21, 22, 23, 24, 25, 26], the MR generalization of CC theory is a widely discussed problem, for which several ideas have been proposed, each having their advantages and disadvantages[27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44].

A central problem in MR-CC theory is the construction of permitted excitations and their amplitudes by ensuring the same number of amplitude equations as the number of unknowns, preserving at the same time the commutation of excitation operators. The latter condition is essential to ensure extensivity manifested in the SR case by the ansatz

$$|\Psi\rangle = e^{\hat{T}}|\text{HF}\rangle,$$

where  $|\text{HF}\rangle$  is the SR state (typically the Hartree-Fock determinant) and  $\hat{T}$  is the excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots = \sum_i^{\text{occ}} \sum_p^{\text{virt}} t_i^p p^+ i^- + \sum_{\substack{i,j \\ i < j}}^{\text{occ}} \sum_{\substack{p,q \\ p < q}}^{\text{virt}} t_{ij}^{pq} p^+ q^+ j^- i^- + \dots, \quad (1.1)$$

where  $i, j, \dots$  refer to occupied and  $p, q, \dots$  refer to virtual indices relative to the Fermi vacuum  $|\text{HF}\rangle$  and  $\hat{T}_1, \hat{T}_2, \dots$  describe single, double, ... excitations, respectively. Creation/annihilation indices categorized into disjoint subsets results in the important fact that terms in  $\hat{T}_1, \hat{T}_2, \dots$  commute, ensuring extensivity of CC corrections. The simple categorization is clearly impossible if the reference state consists of several determinants. Of possible workarounds we mention the Jeziorski-Monkhorst Ansatz[45]

$$|\Psi\rangle = \sum_{\mu} C_{\mu} e^{\hat{T}_{\mu}} |\Phi_{\mu}\rangle,$$

which deals with the MR reference state  $|\Phi\rangle = \sum_{\mu} C_{\mu} |\Phi_{\mu}\rangle$ , and cluster operators  $\hat{T}_{\mu}$  are defined similar to eq.(1.1), the occupancies referring to that of  $|\Phi_{\mu}\rangle$ . Special attention has to be paid in these theories to eliminate possible redundancies in excitations and amplitudes[46]. One may obtain a theory free of the redundancy problem by picking up a dominant component  $|\Phi_0\rangle$  in  $|\Phi\rangle$  and define occupancies with respect to this pivot determinant[47, 48, 49]. It is also possible to follow an internally contracted approach which has received much interest lately[50, 51, 52, 53].

The MR problem leads to complications also in PT. In SR-PT the formalism remains simple since  $|\text{HF}\rangle$  and excited determinants altogether form eigenvectors of a one-body operator, the Fockian ( $\hat{F}$ ). If the reference state  $|\Phi\rangle$  is of multi-reference character, no one-body operator emerges as a zero-order Hamiltonian, whose eigenvectors could be easily constructed. To resolve this problem, Dyall[54] was the first to propose the use of two-body zero-order Hamiltonian. In our Laboratory[4, 5, 6, 8, 9], we have developed a



MRPT using this philosophy applied to the APSG[55, 56, 57, 58, 59, 60, 61, 62, 63, 3, 64] reference state.

A method "between" simple PT and the more sophisticated CC theory is Linearized Coupled Cluster (LCC) formulation[65, 66, 67, 68, 69, 70, 71]. It emerges from CC by dropping all non-linear terms in the amplitude equations. It was shown that LCC equations can also be derived by optimizing the partition via level shifts in a PT framework [72, 73]. This latter statement holds both in the SR and MR cases[72, 73, 74, 75].

Section (3.2) outlines a linearized CC (LCC) theory based on the APSG reference state. The formulation ensures extensivity, provides a uniquely soluble set of amplitude equations and is free from the deficiencies of the PT presented in [9] concerning description of simultaneous single bond dissociations. Our theory is related to that of Li et al. [76, 77], with notable differences.

The present formulation relies strongly on the quasi-particle picture of geminals [4, 5, 6, 7, 8, 78, 79, 80, 81, 82, 83, 84, 85, 86] and strictly maintains the size-consistency of the approach. Another difference is the way geminal subspaces are chosen: we start from localized molecular orbitals and optimize them variationally, while Li et al. [76, 77] use the "maximum similarity rule" introduced in [76].

# Theoretical Background

In this chapter, we aim to introduce all the concepts needed to be able to fully understand theoretical advances presented in the third chapter. Along this line, the mathematical form of geminals, the wave function ansatz built up of them (the so-called APSG wave function), the notion of strong orthogonality, the optimization of geminals and a possible perturbative approach towards geminals are discussed in details.

## 2.1 Introduction

Finding a solution to the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi \tag{2.2}$$

is the central problem, if one would like to investigate quantum mechanical systems whose Hamiltonians are not a function of time. This equation does not have an analytical solution for real systems (for the H-atom, it exists only in the center-of-mass coordinate system and for  $H_2^+$  only within the Born-Oppenheimer approximation). That is the reason why for real life problems, only an approximative solution of eq. (2.2) can be found. This is usually done by assuming a wave function form having some free parameters, and later on finding the values of the parameters in a manner depending on the chosen method. The wave function also has to satisfy some physical requirements as well, the most important of which is fulfilling Pauli's principle, the fermionic wave function should be antisymmetric for an exchange of particles.

The simplest possible antisymmetric wave function ansatz consists of a single determinant

$$|\Psi_{\text{HF}}\rangle = \hat{A}[\varphi_1(1)\varphi_2(2)\dots\varphi_n(n)],$$

where  $\hat{A}$  is the antisymmetrizer and  $\{\varphi_i(i)\}_{i=1}^n$  are the occupied molecular orbitals expanded on some finite basis (usually atom-centered):

$$\varphi_i(i) = \sum_{\mu} c_{\mu}^i \chi_{\mu}(i).$$

The method described above is the well-known Hartree-Fock method which is a very good approximation for most molecules in their equilibrium structures, but fails to describe non-equilibrium chemical species, bond breaking processes and in some cases the equilibrium wave function as well.

On the other hand, the most elaborate wave function model which is not analytical, but is exact for the chosen basis set is the Full Configuration Interaction (Full CI) wave function:

$$|\Psi_{\text{FCI}}\rangle = C_0|\Psi_{\text{HF}}\rangle + \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} C_i^a |\Psi_i^a\rangle + \sum_{\substack{i,j \\ i < j}}^{\text{occ.}} \sum_{\substack{a,b \\ a < b}}^{\text{virt.}} C_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \dots$$

Besides the Hartree-Fock solution ( $\Psi_{\text{HF}}$ ), Full CI contains all the single ( $\Psi_i^a$ ), double ( $\Psi_{ij}^{ab}$ ) etc. excited determinants which can be obtained from the Hartree-Fock wave function by replacing occupied orbital  $i$  with virtual orbital  $a$ , or both occupied orbitals  $i$  and  $j$  with virtual orbitals  $a$  and  $b$  etc. ( $C_0, C_i^a, C_{ij}^{ab}$  etc. are linear coefficients determined from the variational principle,  $C_0 = 1$  if  $\langle \Psi_{\text{FCI}} | \Psi_{\text{HF}} \rangle = 1$  is assumed). Full CI can describe all processes which the Hartree-Fock is incapable of. However it is computationally very demanding, even for medium-sized molecules in reasonable basis sets, it is simply inaccessible.

Most quantum chemical methods make a compromise between the border-line cases, they usually aim at correcting the shortcomings of the Hartree-Fock in a way that is less expensive than Full CI. This led to the emerge of several methods, some of which became standards in the quantum chemical community (e.g. Møller-Plesset Perturbation Theory, Coupled Cluster Theory). Besides the obvious differences in their approach, a common feature of these theories is that most of them rely on the one-electron orbital picture. In most cases, these formalisms assume that a one-electron orbital has been determined in one way or another. Despite the enormous amount of work that has been invested in the development of these models, no universal method has been developed yet that is capable of describing all chemical phenomena with a reasonable computational cost. A possible

reason might be the fundamental flaw of the one-electron orbital picture.

## 2.2 The geminal model

There are other possibilities as well, if one tries to view the many-electron problem from a completely different aspect. As a generalization of one-electron molecular orbitals, the two electron orbitals (the so-called *geminals*) can be defined:

$$\psi_i(2i-1, 2i) = \sum_{\substack{\mu, \nu \\ \mu < \nu}} C_{\mu\nu}^i \hat{A}[\chi_\mu(2i-1)\chi_\nu(2i)] = \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i \hat{A}[\chi_\mu(2i-1)\chi_\nu(2i)] \quad (2.3)$$

In eq. (2.3)  $i$  is the geminal index,  $\hat{A}$  is the antisymmetrizer,  $\chi_\mu$  and  $\chi_\nu$  are the one-electron orbitals which will be specified later in subsection 2.6.2. Handling inequalities in derivations can be misleading sometimes, to avoid confusion one can introduce the full  $\mathbf{C}$  matrix, not just the upper triangle. In that case  $\mathbf{C}$  should be antisymmetric ( $C_{\mu\nu} = -C_{\nu\mu}$ ) and a 1/2 factor should be introduced to avoid double counting of configurations.

If only closed-shell molecules are treated, the wave function is built up from the geminals in the following way:

$$|\Psi_{\text{APSG}}\rangle = \hat{A}'[\psi_1(1, 2)\psi_2(3, 4) \dots \psi_i(2i-1, 2i) \dots \psi_N(2N-1, 2N)] \quad (2.4)$$

Subscript *APSG* is an abbreviation of Antisymmetrized Product of Strongly Orthogonal Geminals. Hereafter we will refer to the wave function form of eq. (2.4) as the *APSG wave function*. The primed antisymmetrizer operator ( $\hat{A}'$ ) permutes the electronic coordinates between the different geminals, but not within them as they are already antisymmetric (It is to be noted that applying the full antisymmetrizer instead of the primed one would only affect the norm of the wave function). The APSG wave function has a multi-reference character, thus it contains some proportion of the correlation energy (*intra-geminal correlation*). It should also be mentioned that *strong orthogonality* will only be introduced later on, it is not yet reflected in eq. (2.4). Nevertheless, we introduced the notion of APSG early on as we only worked with this special subtype of geminal wave functions.

## 2.3 Second-quantized approach in geminal theory

In the early days of geminal theory, all derivations were done in a first-quantized manner. This way of thinking was quite cumbersome in most cases, for example derivation of the pseudo-eigenvalue equation system for the optimized geminals (see subsection 2.6.1 later) resulted in a complicated coupled differential equation system (analogous to the Hartree-Fock equations). That's why it is highly recommended to introduce second-quantized formalism for geminals as well. Derivations in this way become more transparent and easier to carry through. In this section we introduce the second-quantized treatment of geminals and continue to use this formalism from now on.

### 2.3.1 Geminal algebra

As a first step, the creation and annihilation operators are assigned to the two-electron entities. The second-quantized equivalents of eq. (2.3) are

$$\psi_i^+ = \sum_{\substack{\mu, \nu \\ \mu < \nu}} C_{\mu\nu}^i \chi_\mu^+ \chi_\nu^+ = \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i \chi_\mu^+ \chi_\nu^+ \quad (2.5)$$

for the creation and

$$\psi_i^- = \sum_{\substack{\mu, \nu \\ \mu < \nu}} C_{\mu\nu}^i \chi_\nu^- \chi_\mu^- = \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i \chi_\nu^- \chi_\mu^- \quad (2.6)$$

for the annihilation operator. The creation and annihilation operators are obviously the adjoints of each other (real  $C_{\mu\nu}$  coefficients are assumed):

$$(\psi_i^+)^{\dagger} = \psi_i^-.$$

The APSG wave function (2.4) can be written using the geminal creation operators (2.5) as

$$|\Psi_{\text{APSG}}\rangle = \psi_1^+ \psi_2^+ \dots \psi_N^+ |\text{vac}\rangle,$$

where  $|\text{vac}\rangle$  is the 'real vacuum' not containing any particles.

Geminals are two-electron objects, they behave like bosons which can be easily seen from the commutation relations of the creation and annihilation operators ( $[\cdot, \cdot]_-$  refers to the true commutator in this context). Substituting eq. (2.5) into the commutator:

$$[\psi_i^+, \psi_k^+]_- = \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k [\chi_\mu^+ \chi_\nu^+, \chi_\lambda^+ \chi_\sigma^+]_- = \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k [\chi_\mu^+ \chi_\nu^+ \chi_\lambda^+ \chi_\sigma^+ - \chi_\lambda^+ \chi_\sigma^+ \chi_\mu^+ \chi_\nu^+]$$

According to eq. (6.1) in the Appendix, moving a fermion creation operator through two other creation operators does not induce a sign change, so the expression in brackets is 0:

$$[\psi_i^+, \psi_k^+]_- = 0. \quad (2.7)$$

Similarly (using eqs. (2.6) and (6.2) in this case):

$$[\psi_i^-, \psi_k^-]_- = 0. \quad (2.8)$$

The commutator of a geminal annihilation and creation operator is a completely different case. For real bosons it should be  $[\psi_i^-, \psi_k^+]_- = \delta_{ik}$ . Unfortunately, for geminals this does not hold necessarily, this causes the complexity of geminal algebra if further restrictions on geminals are not introduced. In the most general case, the above mentioned commutator can be written using eqs. (2.5) and (2.6) as

$$[\psi_i^-, \psi_k^+]_- = \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k [\chi_\nu^- \chi_\mu^-, \chi_\lambda^+ \chi_\sigma^+]_- \quad (2.9)$$

Expanding the commutator expression in eq. (2.9) and using eq. (6.3) multiple times:

$$\begin{aligned} [\chi_\nu^- \chi_\mu^-, \chi_\lambda^+ \chi_\sigma^+]_- &= \chi_\nu^- \chi_\mu^- \chi_\lambda^+ \chi_\sigma^+ - \chi_\lambda^+ \underbrace{\chi_\sigma^+ \chi_\nu^-}_{\delta_{\sigma\nu} - \chi_\nu^- \chi_\sigma^+} \chi_\mu^- = \chi_\nu^- \chi_\mu^- \chi_\lambda^+ \chi_\sigma^+ - \delta_{\sigma\nu} \chi_\lambda^+ \chi_\mu^- + \underbrace{\chi_\lambda^+ \chi_\nu^-}_{\delta_{\nu\lambda} - \chi_\nu^- \chi_\lambda^+} \underbrace{\chi_\sigma^+ \chi_\mu^-}_{\delta_{\sigma\mu} - \chi_\mu^- \chi_\sigma^+} \\ &= \delta_{\nu\lambda} \delta_{\sigma\mu} - \delta_{\sigma\nu} \chi_\lambda^+ \chi_\mu^- - \delta_{\sigma\mu} \chi_\nu^- \chi_\lambda^+ - \delta_{\nu\lambda} \chi_\mu^- \chi_\sigma^+ + \chi_\nu^- \chi_\mu^- \chi_\lambda^+ \chi_\sigma^+ + \chi_\nu^- \underbrace{\chi_\lambda^+ \chi_\mu^-}_{\delta_{\mu\lambda} - \chi_\mu^- \chi_\lambda^+} \chi_\sigma^+ = \delta_{\nu\lambda} \delta_{\sigma\mu} \\ &\quad - \delta_{\sigma\nu} \chi_\lambda^+ \chi_\mu^- - \delta_{\sigma\mu} \underbrace{\chi_\nu^- \chi_\lambda^+}_{\delta_{\lambda\nu} - \chi_\lambda^+ \chi_\nu^-} - \delta_{\nu\lambda} \underbrace{\chi_\mu^- \chi_\sigma^+}_{\delta_{\sigma\mu} - \chi_\sigma^+ \chi_\mu^-} + \delta_{\mu\lambda} \underbrace{\chi_\nu^- \chi_\sigma^+}_{\delta_{\sigma\nu} - \chi_\sigma^+ \chi_\nu^-} = (\delta_{\mu\lambda} \delta_{\sigma\nu} - \delta_{\nu\lambda} \delta_{\sigma\mu}) + \delta_{\sigma\mu} \chi_\lambda^+ \chi_\nu^- \\ &\quad + \delta_{\nu\lambda} \chi_\sigma^+ \chi_\mu^- - \delta_{\sigma\nu} \chi_\lambda^+ \chi_\mu^- - \delta_{\mu\lambda} \chi_\sigma^+ \chi_\nu^- \end{aligned}$$

Substituting this expression back to eq. (2.9) and carrying out simple manipulations (changing the notation for indices and using the antisymmetry of the geminal coefficient matrices) one obtains:

$$\begin{aligned}
[\psi_i^-, \psi_k^+]_- &= \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k [\delta_{\mu\lambda} \delta_{\sigma\nu} - \delta_{\nu\lambda} \delta_{\sigma\mu} + \delta_{\sigma\mu} \chi_\lambda^+ \chi_\nu^- + \delta_{\nu\lambda} \chi_\sigma^+ \chi_\mu^- - \delta_{\sigma\nu} \chi_\lambda^+ \chi_\mu^- - \delta_{\mu\lambda} \chi_\sigma^+ \chi_\nu^-] \\
&= \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i C_{\mu\nu}^k - \sum_{\nu} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\sigma, \lambda \\ \sigma \neq \lambda}} C_{\mu\nu}^i C_{\sigma\nu}^k \chi_\sigma^+ \chi_\mu^- = \hat{Q}_{ik}
\end{aligned} \tag{2.10}$$

Thus  $[\psi_i^-, \psi_k^+]_-$  is not  $\delta_{ik}$ , like it should be for real bosons. It's a complicated matrix of operators ( $\hat{Q}_{ik}$ ) instead, that's why geminals are considered 'quasi-bosons'. Working with an algebra like this makes derivation and programming of formulas extremely complicated. To overcome this difficulty, restrictions are usually imposed on geminals to simplify the algebra. In this way we lose from the generality of the model, but on the other hand we gain some convenience in the formulation. The details of such restrictions are given in the following subsection.

### 2.3.2 Strong orthogonality and Arai's theorem

One restriction imposed on geminal functions to make their treatment easier is that of 'strong orthogonality'. For two arbitrary geminals it can be given as

$$\int_{-\infty}^{+\infty} \psi_i(1, 2) \psi_k(1, 3) d\mathbf{r}_{\underline{1}} = 0 \quad (i \neq k) \tag{2.11}$$

Before substituting the mathematical form of geminals into this equation, we rewrite eq. (2.3) (using up the antisymmetry of the geminal coefficient matrix and the definition of the antisymmetrizer) for electrons labeled 1 and 2 as

$$\begin{aligned}
\psi_i(1, 2) &= \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i \hat{A}[\chi_\mu(1) \chi_\nu(2)] = \frac{1}{2} \cdot \frac{1}{\sqrt{2}} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} (C_{\mu\nu}^i \chi_\mu(1) \chi_\nu(2) - C_{\mu\nu}^i \chi_\nu(1) \chi_\mu(2)) \\
&= \frac{1}{2} \cdot \frac{1}{\sqrt{2}} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} (C_{\mu\nu}^i - C_{\nu\mu}^i) \chi_\mu(1) \chi_\nu(2) = \frac{1}{\sqrt{2}} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i \chi_\mu(1) \chi_\nu(2)
\end{aligned} \tag{2.12}$$

Now we can return back to eq. (2.11) and write

$$\int_{-\infty}^{+\infty} \psi_i(1, 2) \psi_k(1, 3) d\mathbf{r}_{\underline{1}} = \frac{1}{2} \int_{-\infty}^{+\infty} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k \chi_\mu(1) \chi_\nu(2) \chi_\lambda(1) \chi_\sigma(3) d\mathbf{r}_{\underline{1}}$$

$$= \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k \delta_{\mu\lambda} \chi_\nu(2) \chi_\sigma(3) = \frac{1}{2} \sum_{\mu} \sum_{\substack{\nu \\ \nu \neq \mu}} \sum_{\substack{\sigma \\ \sigma \neq \mu}} C_{\mu\nu}^i C_{\mu\sigma}^k \chi_\nu(2) \chi_\sigma(3) \stackrel{!}{=} 0.$$

The above expression can only be zero for all  $\chi_\nu(2)$  and  $\chi_\sigma(3)$  basis functions if the following holds:

$$\sum_{\mu} C_{\mu\nu}^i C_{\mu\sigma}^k = 0 \quad (i \neq k) \quad (2.13)$$

Thus eqs. (2.11) and (2.13) are equivalent. In 1960, Arai showed a theorem in connection with strong orthogonality which turned out to be very important in the theory of geminals [87]. Here we will recite the theorem and give a small proof of it for the sake of completeness (this is a shortened version of Arai's original proof).

**Theorem:** Given a set of strongly orthogonal geminals expanded on an orthogonal set of one-electron functions, it is always possible to find a unitary transformation of the one-electron orbitals, such that the geminals in the new basis set are expanded on disjoint subsets of the transformed basis (a basis function appears in the expansion of only one geminal and no others).

**Proof:** Eq. (2.13) can be considered a homogeneous system of linear equations comprising  $N$  equations ( $N$  being the number of basis functions) with  $C_{\bullet\sigma}^k$  being the independent variables of the system (in this case column vectors of  $\mathbf{C}^k$ ) and  $C_{\mu\nu}^i$  elements constituting the coefficient matrix of the equation system. Eq. (2.13) can be fulfilled in two cases: if either  $\mathbf{C}^i$  and/or  $\mathbf{C}^k$  are zero matrices or  $\det \mathbf{C}^i = 0$ . We can omit the first possibility as both geminal  $i$  and  $k$  are nonzero functions. Thus we only have to deal with the second option and investigate the determinant of  $\mathbf{C}^i$ . Eq. (2.13) in this sense implies that the column vectors of  $\mathbf{C}^k$  compose a linearly dependent set of vectors. By a suitable transformation of the independent variables, we can get rid of one of the column vectors of  $\mathbf{C}^k$  and one of the equations. We can continue this elimination process until the remaining columns of  $\mathbf{C}^k$  form a linearly independent set of vectors and  $\det \mathbf{C}^i \neq 0$ . At this point satisfying eq. (2.13) means that for each  $\mu$  index either  $C_{\mu\nu}^i$  or  $C_{\mu\sigma}^k$  should be zero, thus both geminals are expanded on mutually exclusive subsets of basis functions if the strong orthogonality condition holds. Q.E.D.

In 1961, Löwdin generalized Arai's results for group functions as well[88].



### 2.3.3 Weak orthogonality

It is quite easy to see that if two geminals are orthogonal in the strong sense, they must be orthogonal in the weak sense as well, integrating a zero function will obviously be zero:

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \underbrace{\psi_i(1, 2)\psi_k(1, 2)}_{=0} d\mathbf{r}_1 d\mathbf{r}_2 = 0$$

For normalized geminals, one can write briefly

$$\langle \psi_i | \psi_k \rangle = \delta_{ik}. \quad (2.14)$$

Expanding the left-hand side of eq. (2.14) using eqs. (2.5) and (2.6):

$$\begin{aligned} \langle \psi_i | \psi_k \rangle &= \langle \text{vac} | \psi_i^- \psi_k^+ | \text{vac} \rangle = \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k \langle \text{vac} | \overbrace{\chi_\nu^- \chi_\mu^- \chi_\lambda^+ \chi_\sigma^+} | \text{vac} \rangle = \\ &= \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\lambda, \sigma \\ \lambda \neq \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k (\delta_{\nu\sigma} \delta_{\mu\lambda} - \delta_{\nu\lambda} \delta_{\mu\sigma}) = \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i C_{\mu\nu}^k - \frac{1}{4} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i C_{\nu\mu}^k = \\ &= \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} C_{\mu\nu}^i C_{\mu\nu}^k = \delta_{ik} \end{aligned} \quad (2.15)$$

Eqs. (2.15) and (2.13) are consequences of the weak and the strong orthogonality restrictions respectively, we can substitute both expressions back to the commutator relation for a geminal annihilation and creation operator in eq. (2.10):

$$\begin{aligned} [\psi_i^-, \psi_k^+]_- &= \hat{Q}_{ik} = \delta_{ik} - \delta_{ik} \sum_{\nu} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\sigma \\ \sigma \neq \nu}} C_{\mu\nu}^i C_{\sigma\nu}^i \chi_\sigma^+ \chi_\mu^- = \\ &= \delta_{ik} \left( 1 - \sum_{\nu} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\sigma \\ \sigma \neq \nu}} C_{\mu\nu}^i C_{\sigma\nu}^i \chi_\sigma^+ \chi_\mu^- \right) = \delta_{ik} \hat{Q}_i \end{aligned} \quad (2.16)$$

In this way the matrix of operators  $\hat{Q}_{ik}$  could be diagonalised.

### 2.3.4 Simplifying matrix elements

The advantage of strong orthogonality can be understood by looking at an example matrix element:

$$\langle \text{vac} | \psi_i^- \psi_j^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_j^+ \psi_i^+ | \text{vac} \rangle$$

When strong orthogonality is introduced, it is quite easy to arrive at a simpler form. As all basis orbitals belong to the subset of one geminal only (Arai's theorem), a geminal label can be assigned to each of the basis orbital labels. If for example  $\mu$  belongs to the subset of geminal  $i$ , we write the following:  $\mu \in i$ . For the sake of simplicity let's assume that both  $\mu$  and  $\nu$  orbital indices belong to the subset of geminal  $i$  in the above example ( $\mu, \nu \in i$ ). In this case, moving the geminal annihilation operator  $\psi_j^-$  from the left to the right will look like the following:

$$\begin{aligned} & \langle \text{vac} | \psi_i^- \psi_j^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_j^+ \psi_i^+ | \text{vac} \rangle \stackrel{\text{eq.(2.8)}}{=} \langle \text{vac} | \psi_i^- \psi_k^- \psi_j^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_j^+ \psi_i^+ | \text{vac} \rangle \\ & \stackrel{\mu, \nu \notin j}{=} \langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_j^- \psi_k^+ \psi_j^+ \psi_i^+ | \text{vac} \rangle \stackrel{\text{eq.(2.7)}}{=} \langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_j^- \psi_k^+ \psi_i^+ \psi_j^+ | \text{vac} \rangle \\ & \stackrel{\text{eq.(2.16)}}{=} \langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_i^+ \psi_j^- \psi_j^+ | \text{vac} \rangle \stackrel{\text{eq.(2.16)}}{=} \langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_i^+ \hat{Q}_j | \text{vac} \rangle \\ & \quad + \underbrace{\langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_i^+ \psi_j^- \psi_j^+ | \text{vac} \rangle}_{=0} \stackrel{\text{eq.(2.16)}}{=} \langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_i^+ | \text{vac} \rangle \\ & - \sum_\nu \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \sum_{\substack{\sigma \\ \sigma \neq \nu}} C_{\mu\nu}^j C_{\sigma\nu}^j \langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_i^+ \chi_\sigma^+ \chi_\mu^- | \text{vac} \rangle \stackrel{=0}{=} \langle \text{vac} | \psi_i^- \psi_k^- \chi_\mu^+ \chi_\nu^- \psi_k^+ \psi_i^+ | \text{vac} \rangle \end{aligned}$$

We can follow the same procedure for geminal  $k$  as well, so finally:

$$\langle \text{vac} | \psi_i^- \psi_j^- \psi_k^- \underbrace{\chi_\mu^+ \chi_\nu^-}_{\mu, \nu \in i} \psi_k^+ \psi_j^+ \psi_i^+ | \text{vac} \rangle = \langle \text{vac} | \psi_i^- \chi_\mu^+ \chi_\nu^- \psi_i^+ | \text{vac} \rangle$$

We can conclude that in case of strong orthogonality, it is possible to disregard all those geminal creation and annihilation operators in the matrix element, whose subsets does not contain the one-electron functions (creation and annihilation operators) present in the core of the matrix element.

Without the introduction of strong orthogonality one should use the commutator relation of eq. (2.10) instead of eq. (2.16) and the commutator relation of  $[\psi_i^-, \chi_\mu^+]_-$  should also be determined and used extensively during the matrix element evaluation procedure.

This would overcomplicate the formalism and make it really inconvenient to apply it even for small systems.

### 2.3.5 Partitioning of the Hamiltonian

Arai's theorem implies that the one-electron basis can be divided into subsets assigned to different geminals if the strong orthogonality condition is satisfied. Accordingly, it is possible to rewrite each sum over one-electron spatial orbitals ( $m$ ) as a sum over the geminal indices ( $a$ ) and an inner sum over the spatial orbitals belonging to the chosen geminal's subset ( $m \in a$ ) [4]:

$$\sum_m \equiv \sum_a \sum_{m \in a}$$

Therefore the second-quantized Hamiltonian in spatial orbitals (eq.(6.5)) has the following form:

$$\hat{H} = \sum_{a,b} \sum_{m \in a} \sum_{n \in b} \sum_{\sigma} h_{mn} m_{\sigma}^+ n_{\sigma}^- + \frac{1}{2} \sum_{a,b,c,d} \sum_{m \in a} \sum_{n \in b} \sum_{l \in c} \sum_{s \in d} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^-, \quad (2.17)$$

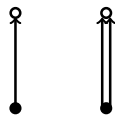
where  $a, b, c, d$  are geminal indices and  $m, n, l, s$  denote orbitals. It is possible to group the terms in eq. (2.17) based on the number of geminals from whose subsets the different orbitals come from:

$$\hat{H} = \sum_a \hat{H}_a + \sum_{\substack{a,b \\ a \neq b}} \hat{H}_{ab} + \sum_{\substack{a,b,c \\ a \neq b \neq c}} \hat{H}_{abc} + \sum_{\substack{a,b,c,d \\ a \neq b \neq c \neq d}} \hat{H}_{abcd}, \quad (2.18)$$

where  $\hat{H}_a, \hat{H}_{ab}, \hat{H}_{abc}, \hat{H}_{abcd}$  are the one-, two-, three- and four-geminal Hamiltonians respectively. The two extreme cases ( $\hat{H}_a$  and  $\hat{H}_{abcd}$ ) are the easiest to handle. In the one-geminal Hamiltonian, all orbital indices belong to the same geminal:

$$\hat{H}_a = \sum_{m,n \in a} \sum_{\sigma} h_{mn} m_{\sigma}^+ n_{\sigma}^- + \frac{1}{2} \sum_{m,n,l,s \in a} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \quad (2.19)$$

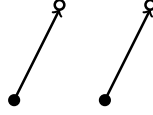
It is possible to give a graphical representation of the above Hamiltonian fragment [8]:



The filled circle (●) represents the geminal from which an electron is annihilated, while the empty circle (○) denotes the geminal to which an electron is created. The arrow represents the excitation operator. If the filled and the empty circles lie above each other, they belong to the same geminal (in this case we consider a 'local excitation'). From these rules it is now easy to figure out that the graph on the left belongs to the one-electron part of eq. (2.19). These graphical representations should not be confused with Feynman diagrams, assigning diagrammatic rules for these graphs is not possible as they represent excitations and not matrix elements. The aim of them is merely to help thinking about different types of excitations. The other easily manageable partition of eq. (2.18) is the four-geminal Hamiltonian fragment:

$$\hat{H}_{abcd} = \frac{1}{2} \sum_{m \in a} \sum_{n \in b} \sum_{l \in c} \sum_{s \in d} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}$$

The graphical representation in this case:



Non-vertical orientation of arrows reflects the non-local nature of the excitations, the electron-number changes in all four of the geminals.

The two- and three-geminal Hamiltonian components are more sophisticated and it needs some algebra to arrive at their final form. The unsimplified formula for the two-geminal Hamiltonian is

$$\begin{aligned} \hat{H}_{ab} = & \sum_{m \in a} \sum_{n \in b} \sum_{\sigma}^1 h_{mn} m_{\sigma}^{+} n_{\sigma}^{-} + \frac{1}{2} \sum_{m, n \in a} \sum_{l, s \in b} \sum_{\sigma, \sigma'}^2 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \\ & + \frac{1}{2} \sum_{m, l \in a} \sum_{n, s \in b} \sum_{\sigma, \sigma'}^3 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} + \frac{1}{2} \sum_{m, s \in a} \sum_{n, l \in b} \sum_{\sigma, \sigma'}^4 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \\ & + \frac{1}{2} \sum_{m, n, l \in a} \sum_{s \in b} \sum_{\sigma, \sigma'}^5 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} + \frac{1}{2} \sum_{m, n, s \in a} \sum_{l \in b} \sum_{\sigma, \sigma'}^6 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \\ & + \frac{1}{2} \sum_{m, l, s \in a} \sum_{n \in b} \sum_{\sigma, \sigma'}^7 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} + \frac{1}{2} \sum_{n, l, s \in a} \sum_{m \in b} \sum_{\sigma, \sigma'}^8 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \end{aligned}$$

The 1. and 2. components of the above equation are quite straightforward, it is not possible to simplify them further. However, with some algebra, the remaining terms can be transformed to simpler forms. In the 3. component, doing a  $s \leftrightarrow l$  index notation change and introducing a negative sign by changing the order of  $s_{\sigma}^{-}$  and  $l_{\sigma'}^{-}$  according to eq. (6.4), leads to the so-called 'dispersive Hamiltonian' together with the 4. term:

$$\hat{H}_{ab}^{\text{disp}} = \frac{1}{2} \sum_{m,s \in a} \sum_{n,l \in b} \sum_{\sigma, \sigma'} \left( [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} - [mn|sl] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma'}^{-} l_{\sigma}^{-} \right) \quad (2.20)$$

This operator performs two local excitations on two separate geminals, not changing the electron number within them. The effect of dispersion is often accounted for the excitation of two chemical species inducing local dipole moments responsible for their interaction. Because of this analogy, (2.20) is called 'dispersive', although we cannot state that this is the interaction operator that causes the London forces, it is just a nomenclature.

The 5. and 6. component of the two-geminal Hamiltonian can be shown to be equivalent. To prove this, one must examine the 5. term and introduce notation changes ( $s \leftrightarrow l$  and  $m \leftrightarrow n$ ), make use of integral symmetry ( $[nm|sl] = [mn|ls]$ ), reverse the order of  $l_{\sigma'}^{-}$  and  $s_{\sigma}^{-}$  and also that of  $m_{\sigma'}^{+}$  and  $n_{\sigma}^{+}$ , and finally use that the spin indices  $\sigma$  and  $\sigma'$  appear symmetrically in the formula, they are identical. One can merge the 5. and 6. term after all these operations and get rid of the  $\frac{1}{2}$  factor. Analogous transformations can be done with the 7. and the 8. components as well. Thus, the final form of the two-geminal Hamiltonian (with the graphical representation of operator fragments) reads

$$\begin{aligned} \hat{H}_{ab} = & \sum_{m \in a} \sum_{n \in b} \sum_{\sigma} h_{mn} m_{\sigma}^{+} n_{\sigma}^{-} && \begin{array}{c} \circ \\ \diagup \\ \bullet \end{array} \\ & + \frac{1}{2} \sum_{m,s \in a} \sum_{n,l \in b} \sum_{\sigma, \sigma'} \left( [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} - [mn|sl] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma'}^{-} l_{\sigma}^{-} \right) && \begin{array}{c} \circ \\ \downarrow \\ \bullet \end{array} \quad \begin{array}{c} \circ \\ \downarrow \\ \bullet \end{array} \\ & + \sum_{m,n,s \in a} \sum_{l \in b} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} && \begin{array}{c} \circ \\ \downarrow \\ \bullet \end{array} \quad \begin{array}{c} \bullet \\ \diagdown \\ \circ \end{array} \\ & + \sum_{m,l,s \in a} \sum_{n \in b} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma'}^{-} l_{\sigma}^{-} && \begin{array}{c} \circ \\ \downarrow \\ \bullet \end{array} \quad \begin{array}{c} \circ \\ \diagup \\ \bullet \end{array} \end{aligned}$$

$$+\frac{1}{2} \sum_{m,n \in a} \sum_{l,s \in b} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}$$

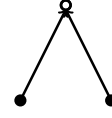


The only partition of eq. (2.18) that has not been discussed yet is the three-geminal Hamiltonian. Without any algebraic manipulations, it has the following form:

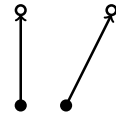
$$\begin{aligned} \hat{H}_{abc} = & \frac{1}{2} \sum_{m,n \in a} \sum_{l \in b} \sum_{s \in c} \sum_{\sigma, \sigma'}^1 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} + \frac{1}{2} \sum_{m,s \in a} \sum_{n \in b} \sum_{l \in c} \sum_{\sigma, \sigma'}^2 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \\ & + \frac{1}{2} \sum_{m,l \in a} \sum_{n \in b} \sum_{s \in c} \sum_{\sigma, \sigma'}^3 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} + \frac{1}{2} \sum_{n,s \in a} \sum_{m \in b} \sum_{l \in c} \sum_{\sigma, \sigma'}^4 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \\ & + \frac{1}{2} \sum_{n,l \in a} \sum_{m \in b} \sum_{s \in c} \sum_{\sigma, \sigma'}^5 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} + \frac{1}{2} \sum_{l,s \in a} \sum_{m \in b} \sum_{n \in c} \sum_{\sigma, \sigma'}^6 [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \end{aligned}$$

Doing exactly the same algebraic manipulations as in the case of the 5. and 6. term of the two-geminal Hamiltonian, it is easy to figure out that the 3. and the 4. and also the 2. and the 5. terms are equal, we can get rid of the  $\frac{1}{2}$  factor and keep just one of them. The final form of the three-geminal Hamiltonian is thus

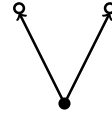
$$\hat{H}_{abc} = \frac{1}{2} \sum_{m,n \in a} \sum_{l \in b} \sum_{s \in c} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}$$



$$\sum_{m,l \in a} \sum_{n \in b} \sum_{s \in c} \sum_{\sigma, \sigma'} ([mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} - [mn|sl] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-})$$



$$+\frac{1}{2} \sum_{l,s \in a} \sum_{m \in b} \sum_{n \in c} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}$$



## 2.4 Spin states of geminals

There is another important feature of geminals which should be mentioned. The two-electron function of eq. (2.3) (which is created by the operator of eq. (2.5)) is not necessarily an eigenfunction of the two-electron  $\hat{S}^2$  and  $\hat{S}_z$  spin-operators. To satisfy this condition we have to introduce a restricted form of two-electron functions (and the notion of spatial orbitals at the same time). From two electrons, only singlet and triplet states can be acquired, the singlet or triplet  $M_S = 0$  geminal creation operator can be written in the most general form as

$$\psi_i^+ = \sum_{m,n \in i} C_{mn}^i m_\alpha^+ n_\beta^+ = \sum_{m \in i} C_{mm}^i m_\alpha^+ m_\beta^+ + \sum_{\substack{m,n \in i \\ m < n}} (C_{mn}^i m_\alpha^+ n_\beta^+ + C_{nm}^i n_\alpha^+ m_\beta^+)$$

Choosing  $C^i$  to be symmetric:

$$\psi_i^+ = \sum_{m \in i} C_{mm}^i m_\alpha^+ m_\beta^+ + \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^i (m_\alpha^+ n_\beta^+ + n_\alpha^+ m_\beta^+)$$

$$\hat{S}^2 \psi_i^+ |\text{vac}\rangle = 0, \quad (2.21)$$

which (according to the  $\hat{S}^2$  eigenvalue equation of (6.7)) means that  $S = 0$ , so  $\psi_i$  is singlet. For the antisymmetric case:

$$\psi_i^+ = \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^i (m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+)$$

$$\hat{S}^2 \psi_i^+ |\text{vac}\rangle = 2\psi_i^+ |\text{vac}\rangle, \quad (2.22)$$

here  $S = 1$  and  $\psi_i$  refers to a triplet geminal. The explicit proof of eqs. (2.21) and (2.22) can be found in section 6.3 of the Appendix.

A triplet geminal can have  $M_S = \pm 1$  quantum numbers as well. These states will be referred to as 'spin-polarized geminals' from this point. An  $M_S = +1$  geminal in spatial orbitals is

$$\psi_{i\uparrow}^+ = \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{i\uparrow} m_\alpha^+ n_\alpha^+ = \frac{1}{2} \sum_{m,n \in i} C_{mn}^{i\uparrow} m_\alpha^+ n_\alpha^+,$$

while an  $M_S = -1$  geminal can be written as

$$\psi_{i\downarrow}^+ = \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{i\downarrow} m_{\beta}^+ n_{\beta}^+ = \frac{1}{2} \sum_{m,n \in i} C_{mn}^{i\downarrow} m_{\beta}^+ n_{\beta}^+.$$

The factor  $\frac{1}{2}$  is needed to avoid double counting of configurations.  $C^i$  is antisymmetric here as well. One special feature of spin-polarized geminals is their connection to the  $M_S = 0$  triplet geminals. Normalization of the latter gives the following restriction to the  $C^i$  coefficient matrix:

$$\langle \psi_i^- | \psi_i^+ \rangle = \sum_{m,n,l,s \in i} C_{mn}^i C_{ls}^i \langle n_{\beta}^- m_{\alpha}^- l_{\alpha}^+ s_{\beta}^+ \rangle = \sum_{m,n \in i} C_{mn}^i C_{mn}^i = 1. \quad (2.23)$$

For an  $M_S = +1$  triplet geminal the normalization condition has the following form:

$$\begin{aligned} \langle \psi_{i\uparrow}^- | \psi_{i\uparrow}^+ \rangle &= \frac{1}{4} \sum_{m,n,l,s \in i} C_{mn}^{i\uparrow} C_{ls}^{i\uparrow} \langle n_{\alpha}^- m_{\alpha}^- l_{\alpha}^+ s_{\alpha}^+ \rangle = \frac{1}{4} \sum_{m,n,l,s \in i} C_{mn}^{i\uparrow} C_{ls}^{i\uparrow} (\delta_{ns} \delta_{ml} - \delta_{nl} \delta_{ms}) = \\ &= \frac{1}{2} \sum_{m,n \in i} C_{mn}^{i\uparrow} C_{mn}^{i\uparrow} = 1 \end{aligned} \quad (2.24)$$

Fulfilling eqs. (2.23) and (2.24) is only possible if the following relation holds for the coefficient matrix elements of the nonspin-polarized and spin-polarized triplet geminals:

$$C_{mn}^{i\uparrow} = C_{mn}^{i\downarrow} = \sqrt{2} C_{mn}^i$$

## 2.5 Natural geminals

For singlet states, a simpler form of geminals can be obtained. To see this, we start from the second-quantized form of a geminal creation operator and insert two Kronecker-deltas:

$$\begin{aligned} \psi_i^+ &= \sum_{m,n \in i} C_{mn}^i m_{\alpha}^+ n_{\beta}^+ = \sum_{m,n,l,s \in i} \delta_{ml} C_{ls}^i \delta_{sn} m_{\alpha}^+ n_{\beta}^+ = \sum_{m,n,l,s \in i} \left( \sum_{p \in i} V_{mp} V_{pl}^T \right) C_{ls}^i \left( \sum_{q \in i} V_{sq} V_{qn}^T \right) m_{\alpha}^+ n_{\beta}^+ = \\ &= \sum_{p,q \in i} \left( \sum_{l,s \in i} V_{pl}^T C_{ls}^i V_{sq} \right) \underbrace{\left( \sum_{m \in i} V_{mp} m_{\alpha}^+ \right)}_{\varphi_{p\alpha}^+} \underbrace{\left( \sum_{n \in i} V_{nq} n_{\beta}^+ \right)}_{\varphi_{q\beta}^+}, \end{aligned}$$



where  $\mathbf{V}$  is an orthogonal matrix,  $\mathbf{V}^T = \mathbf{V}^{-1}$ . Choosing the rows of matrix  $\mathbf{V}$  to be the eigenvectors of  $\mathbf{C}^i$ , we get a diagonal matrix composed of the eigenvalues of  $\mathbf{C}^i$ :

$$\psi_i^+ = \sum_{p,q \in i} c_p^i \delta_{pq} \varphi_{p\alpha}^+ \varphi_{q\beta}^+ = \sum_p c_p^i \varphi_{p\alpha}^+ \varphi_{p\beta}^+ \quad (2.25)$$

Eq. (2.25) is the natural form of geminals. The origin of the name lies in the fact, that this form also makes the density matrix of the corresponding geminal to be diagonal. The orbitals  $\varphi_i$  are called natural orbitals not surprisingly.

## 2.6 Variational optimization of geminals

Up until now we have only discussed the general features of geminals, like their commutation relations and spin states, but we did not mention anything about the differences between geminals in various chemical environments. The two large distinctions between the two-electron wave functions in different molecules are the chosen basis set and the coefficient matrix  $\mathbf{C}^i$  for geminal  $i$  in this case. Both of these two features of geminals will be determined variationally [3].

Like in the case of all variational methods, we commence our treatment with the variational principle:

$$\langle \delta\Psi | \hat{H} - E | \Psi \rangle = 0.$$

We are only dealing with those variations which are orthogonal to the function to be varied ( $\langle \delta\Psi | \Psi \rangle = 0$ ):

$$\langle \delta\Psi | \hat{H} | \Psi \rangle = 0. \quad (2.26)$$

The function to be varied is the APSG wave function which for a system having  $2N$ -electrons is

$$|\Psi_{\text{APSG}}\rangle = \psi_1^+ \psi_2^+ \dots \psi_N^+ |\text{vac}\rangle$$

Variation of the wave function is equivalent to variation of the geminals themselves:

$$\psi_i^+ \longrightarrow \psi_i^+ + \delta\psi_i^+$$

Thus the varied wave function will be

$$|\Psi'\rangle = (\psi_1^+ + \delta\psi_1^+)(\psi_2^+ + \delta\psi_2^+) \dots (\psi_N^+ + \delta\psi_N^+) |\text{vac}\rangle = |\Psi_{\text{APSG}}\rangle + \sum_{i=1}^N \psi_1^+ \psi_2^+ \dots \delta\psi_i^+ \dots \psi_N^+ |\text{vac}\rangle + \mathcal{O}(2).$$

The first-order variation from the above equation is

$$|\delta\Psi\rangle = \sum_{i=1}^N \psi_1^+ \psi_2^+ \dots \delta\psi_i^+ \dots \psi_N^+ |\text{vac}\rangle \quad (2.27)$$

Variation of geminals should not take them out of the function class they were originally in. In second-quantized language, it means that  $\delta\psi_i^+$  should be a two-electron operator as well:

$$\delta\psi_i^+ = \sum_{\mu,\nu} \eta_{\mu\nu} \chi_\mu^+ \chi_\nu^+, \quad (2.28)$$

with  $\eta_{\mu\nu}$  being some arbitrary coefficient matrix. The sum of two-electron operators in eq. (2.28) can be partitioned into groups based on the number and type of geminals involved:

$$\delta\psi_i^+ = \sum_{\mu,\nu \in i} \eta_{\mu\nu}^i \chi_\mu^+ \chi_\nu^+ + \sum_{\mu \in i} \sum_{k \neq i} \sum_{v \in k} \eta_{\mu\nu}^{ik} \chi_\mu^+ \chi_\nu^+ + \sum_{k \neq i} \sum_{l \neq i} \sum_{\mu \in k} \sum_{v \in l} \eta_{\mu\nu}^{kl} \chi_\mu^+ \chi_\nu^+ \quad (2.29)$$

The third term destroys geminal  $i$  completely, which is definitely not a first-order effect from an orbital rotation perspective (see section (6.4) in the Appendix for more information,  $\hat{T}^2$  is needed for this type of variation). In this respect it should be omitted from the set of allowed variations. Thus for each variation we assign the following two-electron operator:

$$\delta\psi_i^+ = \sum_{\mu,\nu \in i} \eta_{\mu\nu}^i \chi_\mu^+ \chi_\nu^+ + \sum_{\mu \in i} \sum_{k \neq i} \sum_{v \in k} \eta_{\mu\nu}^{ik} \chi_\mu^+ \chi_\nu^+ \quad (2.30)$$

### 2.6.1 Optimizing the geminal coefficient matrices

In this subsection we will only discuss the variational procedure for obtaining the optimal geminal coefficient matrices  $\mathbf{C}^i$  according to the treatment presented in [3]. As we will see, this is equivalent to considering variations according to the first term of eq. (2.30) only. This component conserves the particle number in geminal  $i$ , it does not take

the function out of the original two-electron space. In this case, it can be expanded on the basis of some two electron functions orthogonal to the  $i$ -th geminal appearing in the APSG wave function (from this point we will denote this geminal by  $\psi_{i0}$  referring to the 'ground state geminal', the different states of geminals will be explained at the end of this subsection):

$$\delta\psi_i^+ = \sum_{\mu,\nu \in i} \eta_{\mu\nu}^i \chi_\mu^+ \chi_\nu^+ = \sum_{q \neq 0} \delta t_{iq} \psi_{iq}^+, \quad (2.31)$$

where  $\psi_{iq}$  are the labeled ( $q \neq 0$ ) two-electron states orthogonal to the ground state geminal  $\psi_{i0}$ . We can substitute eq. (2.31) back to eq. (2.27) to get

$$|\delta\Psi\rangle = \sum_{i=1}^N \sum_{q \neq 0} \delta t_{iq} \psi_{i0}^+ \dots \psi_{iq}^+ \dots \psi_{N0}^+ |\text{vac}\rangle = \sum_{i=1}^N \sum_{q \neq 0} \delta t_{iq} \psi_{iq}^+ \psi_{i0}^- |\Psi_{\text{APSG}}\rangle.$$

Substituting the adjoint of the above equation back to eq. (2.26) we obtain

$$\sum_{i=1}^N \sum_{q \neq 0} \delta t_{iq} \langle \psi_{\text{APSG}} | \psi_{i0}^+ \psi_{iq}^- \hat{H} | \Psi_{\text{APSG}} \rangle = 0,$$

which for all arbitrary  $\delta t_{iq}$  coefficients can only be true if

$$\langle \psi_{\text{APSG}} | \psi_{i0}^+ \psi_{iq}^- \hat{H} | \Psi_{\text{APSG}} \rangle = 0 \quad (2.32)$$

for all  $q \neq 0$  functions. Eq. (2.32) is called the *local Brillouin condition* because of its similarity to the Brillouin theorem appearing in Hartree-Fock theory. It is 'local' because it contains local excitations not changing the particle number within the geminals.

Because of this local nature of excitations, only those terms are needed to be considered in the Hamiltonian (eq. (2.18)) which do not change the electron number within the geminals. In this way eq. (2.32) can be rewritten as

$$\langle \psi_{\text{APSG}} | \psi_{i0}^+ \psi_{iq}^- \hat{H}' | \Psi_{\text{APSG}} \rangle = 0, \quad (2.33)$$

where  $\hat{H}'$  is the Hamiltonian fragment not changing the electron numbers of geminals (see eqs. (2.19) and (2.20)):

$$\hat{H}' = \sum_a \hat{H}_a + \sum_{\substack{a,b \\ a \neq b}} \hat{H}_{ab}^{\text{disp}} = \sum_a \sum_{m,n \in a} \sum_{\sigma} h_{mn} m_{\sigma}^+ n_{\sigma}^- + \frac{1}{2} \sum_a \sum_{m,n,l,s \in a} \sum_{\sigma,\sigma'} [mn|ls] m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma'}^- l_{\sigma}^-$$

$$+\frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} \sum_{m,s \in a} \sum_{n,l \in b} \sum_{\sigma, \sigma'} ([mn|sl] m_{\sigma}^{+} s_{\sigma'}^{-} n_{\sigma}^{+} l_{\sigma'}^{-} - [mn|ls] m_{\sigma}^{+} s_{\sigma'}^{-} n_{\sigma}^{+} l_{\sigma'}^{-})$$

The one-geminal Hamiltonian can only give a non-trivial contribution to the left side of eq. (2.33), if  $a = i$ , otherwise the local Brillouin condition would be fulfilled automatically because of the weak orthogonality of  $\psi_{i0}$  (in the ket vector) and the  $\psi_{iq}$  states (in the bra vector). With the dispersive Hamiltonian we are left with two possibilities:  $i = a$  or  $i = b$  (the  $i \neq a \neq b$  geminals can be safely omitted from the calculations due to strong orthogonality). In the first case ( $i = a$ ), an expectation value that contains the  $\psi_{b0}$  geminal in the bra and ket APSG wave functions of the local Brillouin condition looks like

$$\frac{1}{2} \sum_{b \neq i} \sum_{m,s \in i} \sum_{n,l \in b} \sum_{\sigma, \sigma'} ([mn|sl] \langle \text{vac} | \psi_{b0}^{-} n_{\sigma}^{+} l_{\sigma'}^{-} \psi_{b0}^{+} | \text{vac} \rangle m_{\sigma}^{+} s_{\sigma'}^{-} - [mn|ls] \langle \text{vac} | \psi_{b0}^{-} n_{\sigma}^{+} l_{\sigma'}^{-} \psi_{b0}^{+} | \text{vac} \rangle m_{\sigma}^{+} s_{\sigma'}^{-})$$

After writing down the  $i = b$  case, interchanging  $m$  with  $s$  and  $n$  with  $l$  and using up the symmetry of the integrals ( $[mn|sl] = [nm|ls]$ ), one can arrive at the conclusion that the two cases are exactly the same. Thus one of the terms should be kept and the factor  $\frac{1}{2}$  can be omitted. The only thing left now is the evaluation of the above matrix elements:

$$\begin{aligned} \langle \text{vac} | \psi_{b0}^{-} n_{\sigma}^{+} l_{\sigma'}^{-} \psi_{b0}^{+} | \text{vac} \rangle &= \sum_{\kappa, \tau, \eta, \rho \in b} C_{\kappa\tau}^{b0} C_{\eta\rho}^{b0} \langle \text{vac} | \tau_{\beta}^{-} \kappa_{\alpha}^{-} n_{\sigma}^{+} l_{\sigma'}^{-} \eta_{\alpha}^{+} \rho_{\beta}^{+} | \text{vac} \rangle = \\ &= \sum_{\kappa, \tau, \eta, \rho \in b} C_{\kappa\tau}^{b0} C_{\eta\rho}^{b0} (\delta_{n\kappa} \delta_{l\eta} \delta_{\tau\rho} \delta_{\sigma'\alpha} + \delta_{n\tau} \delta_{l\rho} \delta_{\kappa\eta} \delta_{\sigma'\beta}) = \sum_{\tau \in b} C_{n\tau}^{b0} C_{l\tau}^{b0} \delta_{\sigma'\alpha} + \sum_{\tau \in b} C_{\tau n}^{b0} C_{\tau l}^{b0} \delta_{\sigma'\beta}, \end{aligned}$$

and analogously

$$\langle \text{vac} | \psi_{b0}^{-} n_{\sigma}^{+} l_{\sigma'}^{-} \psi_{b0}^{+} | \text{vac} \rangle = \sum_{\tau \in b} C_{n\tau}^{b0} C_{l\tau}^{b0} \delta_{\sigma'\alpha} \delta_{\sigma'\alpha} + \sum_{\tau \in b} C_{\tau n}^{b0} C_{\tau l}^{b0} \delta_{\sigma'\beta} \delta_{\sigma'\beta}.$$

So after carrying out all these algebraic manipulations and interchanging index  $s$  with  $n$ , the two-geminal Hamiltonian has the form:

$$\sum_{b \neq i} \sum_{m,n \in i} \sum_{l,s \in b} \sum_{\sigma} ([ms|nl] - \frac{1}{2} [ms|ln]) P_{ls}^{b0} m_{\sigma}^{+} n_{\sigma}^{-},$$

where we introduced the 'density matrix' of the ground state as

$$P_{ls}^{b0} = 2 \sum_{\kappa \in b} C_{l\kappa}^{b0} C_{s\kappa}^{b0}.$$

In the above equation we explicitly used up the fact that the ground state is singlet ( $C_{lk}^{b0} = C_{kl}^{b0}$ ). Returning back to the local Brillouin condition of eq. (2.33), it is possible to provide yet another form of it:

$$\langle \text{vac} | \psi_{iq}^- \hat{H}_i^{\text{eff}} \psi_{i0}^+ | \text{vac} \rangle = 0, \quad (2.34)$$

where the  $\hat{H}_i^{\text{eff}}$  'effective one-geminal Hamiltonian' is the sum of the one-geminal Hamiltonian belonging to geminal  $i$  and the averaged dispersive Hamiltonian derived above:

$$\begin{aligned} \hat{H}_i^{\text{eff}} = \sum_{m,n \in i} \sum_{\sigma} \left( h_{mn} + \underbrace{\sum_{b \neq i} ([ms|nl] - \frac{1}{2}[ms|ln]) P_{ls}^{b0}}_{h_{mn}^{\text{eff}}} \right) m_{\sigma}^+ n_{\sigma}^- \\ + \frac{1}{2} \sum_{m,n,l,s \in i} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma'}^- l_{\sigma}^-. \end{aligned} \quad (2.35)$$

In the above expression  $h_{mn}^{\text{eff}}$  is the so-called 'effective core'. As the  $\psi_{iq}$  states are orthogonal to the ground state geminal, for eq. (2.34) to hold, it is necessary that  $\psi_{i0}$  is an eigenfunction of  $\hat{H}_i^{\text{eff}}$  with some eigenvalue  $E_{i0}$ ,  $\hat{H}_i^{\text{eff}} \psi_{i0}$  cannot have any component orthogonal to the ground state geminal:

$$\langle \psi_{iq} | \hat{H}_i^{\text{eff}} \psi_{i0} \rangle = 0 \Rightarrow \hat{H}_i^{\text{eff}} \psi_{i0} = E_{i0} \psi_{i0}$$

Because of the Hermiticity of operator  $\hat{H}_i^{\text{eff}}$ , its eigenvectors form an orthonormal and total basis set in the function class of the two-electron geminals of the given subset. The eigenvalue equation can be written as:

$$\hat{H}_i^{\text{eff}} \psi_{ip} = E_{ip} \psi_{ip}. \quad (2.36)$$

From this point, we refer to the  $\psi_{ip}$ ,  $p \neq 0$  states as 'excited geminals'. The  $\psi_{iq}$  ( $q \neq 0$ ) states mentioned earlier and the  $\psi_{ip}$  ( $p \neq 0$ ) eigenstates are not necessarily equal, but they should span the same space.

## 2.6.2 Optimizing the geminal orbitals

Optimizing the APSG wave function has a large resemblance to the standard MCSCF method. In this respect, the orbitals building up the geminals are optimized as well be-

sides the  $\mathbf{C}^i$  coefficient matrices. Optimization happens during consecutive unitary transformations of orbitals. According to the results of section (6.4) in the Appendix, such a transformation can be written as

$$|\Psi'_{\text{APSG}}\rangle = e^{-\hat{T}}|\Psi_{\text{APSG}}\rangle,$$

with the following definitions of the operators appearing in the expression:

$$\begin{aligned}\hat{T} &= \sum_{\substack{i,j \\ i>j}} T_{ij} \hat{E}_{ij}^- \\ \hat{E}_{ij}^- &= \hat{E}_{ij} - \hat{E}_{ji} \\ \hat{E}_{ij} &= \chi_{i\alpha}^+ \chi_{j\alpha}^- + \chi_{i\beta}^+ \chi_{j\beta}^-\end{aligned}$$

The energy expression as a function of the  $T_{ij}$  parameters is to be minimized:

$$E(\mathbf{T}) = \langle \Psi_{\text{APSG}} | e^{\hat{T}} \hat{H} e^{-\hat{T}} | \Psi_{\text{APSG}} \rangle = E_0 + \sum_{\substack{i,j \\ i>j}} \left( \frac{\partial E}{\partial T_{ij}} \right)_0 T_{ij} + \frac{1}{2} \sum_{\substack{i,j \\ i>j}} \sum_{\substack{k,l \\ k>l}} T_{ij} \left( \frac{\partial^2 E}{\partial T_{ij} \partial T_{kl}} \right)_0 T_{kl} + \dots,$$

where we have explicitly written down the Taylor series of the energy up to the second order. The 0 subscript in  $E_0$ ,  $\left( \frac{\partial E}{\partial T_{ij}} \right)_0$  and  $\left( \frac{\partial^2 E}{\partial T_{ij} \partial T_{kl}} \right)_0$  refers to the values of the expressions at the end-point of the previous iteration. For the first iteration it is the initial guess, which will be either Boys-localized orbitals [89] or converged orbitals of a closeby geometrical point in calculations presented in the oncoming chapters. Applying the Baker-Campbell-Hausdorff expansion:

$$\begin{aligned}E(\mathbf{T}) &= \langle \Psi_{\text{APSG}} | \hat{H} + [\hat{T}, \hat{H}] + \frac{1}{2} [\hat{T}, [\hat{T}, \hat{H}]] + \dots | \Psi_{\text{APSG}} \rangle = \\ &= E_{\text{APSG}} + \sum_{\substack{i,j \\ i>j}} T_{ij} \langle \Psi_{\text{APSG}} | [\hat{E}_{ij}^-, \hat{H}] | \Psi_{\text{APSG}} \rangle + \frac{1}{2} \sum_{\substack{i,j \\ i>j}} \sum_{\substack{k,l \\ k>l}} T_{ij} T_{kl} \langle \Psi_{\text{APSG}} | [\hat{E}_{ij}^-, [\hat{E}_{kl}^-, \hat{H}]] | \Psi_{\text{APSG}} \rangle + \dots\end{aligned}$$

Now the gradient of the energy with respect to the  $T_{ij}$  parameters can be read from the above equation:

$$g_{ij} = \frac{\partial E}{\partial T_{ij}} = \langle \Psi_{\text{APSG}} | [\hat{E}_{ij}^-, \hat{H}] | \Psi_{\text{APSG}} \rangle, \quad (2.37)$$

and the Hessian reads

$$H_{ij,kl} = \frac{\partial^2 E}{\partial T_{ij} \partial T_{kl}} = \langle \Psi_{\text{APSG}} | [\hat{E}_{ij}^-, [\hat{E}_{kl}^-, \hat{H}]] | \Psi_{\text{APSG}} \rangle. \quad (2.38)$$

The analytical form of the Hessian for the APSG wave function was derived by Kuprievich and Klymenko [90]. In our APSG calculations we considered the Hessian to be diagonal and only used the diagonal elements of their formula.

For a Newton-Raphson-type optimization, one requires the energy to be stationary to all parameters ( $\frac{\partial E}{\partial T_{ij}} = 0$ ) which results in the following equations:

$$g_{ij} + \sum_{\substack{k,l \\ k>l}} H_{ij,kl} T_{kl} = 0$$

Introducing hyperindices  $a$  for  $(ij)$  and  $b$  for  $(kl)$ :

$$g_a + \sum_b H_{ab} T_b = 0 \implies T_a = - \sum_b H_{ab}^{-1} g_b$$

The criterion for the stationarity of the energy is also equivalent to the gradients  $g_{ij}$  being 0:

$$\begin{aligned} \langle \Psi_{\text{APSG}} | [\hat{E}_{ij}^-, \hat{H}] | \Psi_{\text{APSG}} \rangle &= \langle \Psi_{\text{APSG}} | \hat{E}_{ij} \hat{H} | \Psi_{\text{APSG}} \rangle - \langle \Psi_{\text{APSG}} | \hat{E}_{ji} \hat{H} | \Psi_{\text{APSG}} \rangle - \langle \Psi_{\text{APSG}} | \hat{H} \hat{E}_{ij} | \Psi_{\text{APSG}} \rangle + \\ &+ \langle \Psi_{\text{APSG}} | \hat{H} \hat{E}_{ji} | \Psi_{\text{APSG}} \rangle = 2(F_{ij} - F_{ji}) = 0, \end{aligned}$$

where  $F_{ij} = \langle \Psi_{\text{APSG}} | \hat{E}_{ij} \hat{H} | \Psi_{\text{APSG}} \rangle$  is the generalized Fockian for the APSG wave function and we only considered real orbitals. Thus stationarity according to orbital rotations is equivalent with the generalized Fockian being symmetric. The energy is invariant with respect to rotations of those orbitals which are doubly occupied or virtual in all configurations of  $|\Psi_{\text{APSG}}\rangle$ .

It is possible to tell more about the structure of the generalized Fockian by considering the variation of the wave function, namely the second term of eq. (2.30):

$$\delta\psi_{i,nl}^+ = \sum_{\mu \in i} \sum_{k \neq i} \sum_{v \in k} \eta_{\mu v}^{ik} \chi_{\mu}^+ \chi_{v}^+,$$

where the  $nl$  subscript refers to the non-local nature of this variation. This variation has an equivalent form which can be seen by algebraic manipulations:

$$\begin{aligned}
\delta\psi_{i,nl}^+|\text{vac}\rangle &= \sum_{k\neq i} \sum_{\mu\in i} \sum_{v\in k} \kappa_{\mu\nu}^{ik} \chi_v^+ \chi_\mu^- \psi_{i0}^+|\text{vac}\rangle = \sum_{k\neq i} \sum_{v\in k} \sum_{\mu\in i} \sum_{\lambda,\sigma\in i} \kappa_{\mu\nu}^{ik} C_{\lambda\sigma}^{i0} \chi_v^+ \underbrace{\chi_\mu^- \chi_\lambda^+}_{\delta_{\mu\lambda} - \chi_\lambda^+ \chi_\mu^-} \chi_\sigma^+|\text{vac}\rangle \\
&= \sum_{k\neq i} \sum_{v\in k} \sum_{\mu,\sigma\in i} \kappa_{\mu\nu}^{ik} C_{\mu\sigma}^{i0} \chi_v^+ \chi_\sigma^+|\text{vac}\rangle - \sum_{k\neq i} \sum_{v\in k} \sum_{\mu,\sigma,\lambda\in i} \kappa_{\mu\nu}^{ik} C_{\lambda\sigma}^{i0} \chi_v^+ \chi_\lambda^+ \underbrace{\chi_\mu^- \chi_\sigma^+}_{\delta_{\mu\sigma}}|\text{vac}\rangle \\
&= - \sum_{k\neq i} \sum_{v\in k} \sum_{\mu,\sigma\in i} \kappa_{\sigma\nu}^{ik} C_{\sigma\mu}^{i0} \chi_\mu^+ \chi_\nu^+|\text{vac}\rangle + \sum_{k\neq i} \sum_{v\in k} \sum_{\mu,\sigma\in i} \kappa_{\sigma\nu}^{ik} C_{\mu\sigma}^{i0} \chi_\mu^+ \chi_\nu^+|\text{vac}\rangle \\
&= \sum_{k\neq i} \sum_{v\in k} \sum_{\mu\in i} \underbrace{\left( \sum_{\sigma\in i} 2C_{\mu\sigma}^i \kappa_{\sigma\nu}^{ik} \right)}_{\eta_{\mu\nu}^{ik}} \chi_\mu^+ \chi_\nu^+|\text{vac}\rangle
\end{aligned}$$

Substituting the above equation back to the first-order variation of the APSG wave function (eq. (2.27)) and then back to the variational principle (eq. (2.26)) the following equation is acquired:

$$\sum_{\substack{i,k \\ i\neq k}} \sum_{\mu\in i} \sum_{v\in k} \kappa_{\mu\nu}^{ik} \langle \Psi_{\text{APSG}} | \chi_\mu^+ \chi_\nu^- \hat{H} | \Psi_{\text{APSG}} \rangle = 0,$$

which for arbitrary  $\kappa_{\mu\nu}^{ik}$  can only be true if the following equation holds:

$$\langle \Psi_{\text{APSG}} | \chi_\mu^+ \chi_\nu^- \hat{H} | \Psi_{\text{APSG}} \rangle = 0,$$

that is, for a converged orbital optimization procedure, the generalized Fockian should not only be symmetric, but it should have a block structure as well, containing non-zero elements for orbitals belonging to the same geminal subset.

### 2.6.3 The APSG optimization algorithm

The optimization of geminals can run along two routes. In the first case, the geminals are restricted to be natural geminals (see section 2.5). With this restriction, only singlet geminal states are calculated. In order to get the APSG iteration started, one would need initial orbital orbitals. This is preferably some previously localized orbital set, which can be obtained either by using some localization method (in our calculations we widely used the Boys scheme [89]) or by using converged orbitals from another APSG iteration (usually it is performed in a closeby geometry). When the initial orbitals are determined, the



local Schrödinger equation (eq. (2.36)) is solved until convergence is reached. Iteration of this procedure is needed because the effective Hamiltonian of each geminal  $i$  (eq. (2.35)) depends on the coefficient matrices of the other geminals through the density matrix  $P_{ls}^{b0}$ . In other words, this system of equations has to be solved in a self-consistent manner. The geminal coefficient optimization procedure stops when the absolute value of the energy change is smaller than a  $\kappa_1$  parameter.

After convergence, the optimization of one-electron orbitals begins. First, the electronic gradients and the Hessian diagonals are calculated according to eqs. (2.37) and (2.38). These are needed to perform an infinitesimal orbital rotation in a Newton-Raphson manner:

$$T_a = T_{a,0} - \frac{\eta g_a}{d(H_{aa}, g_a)},$$

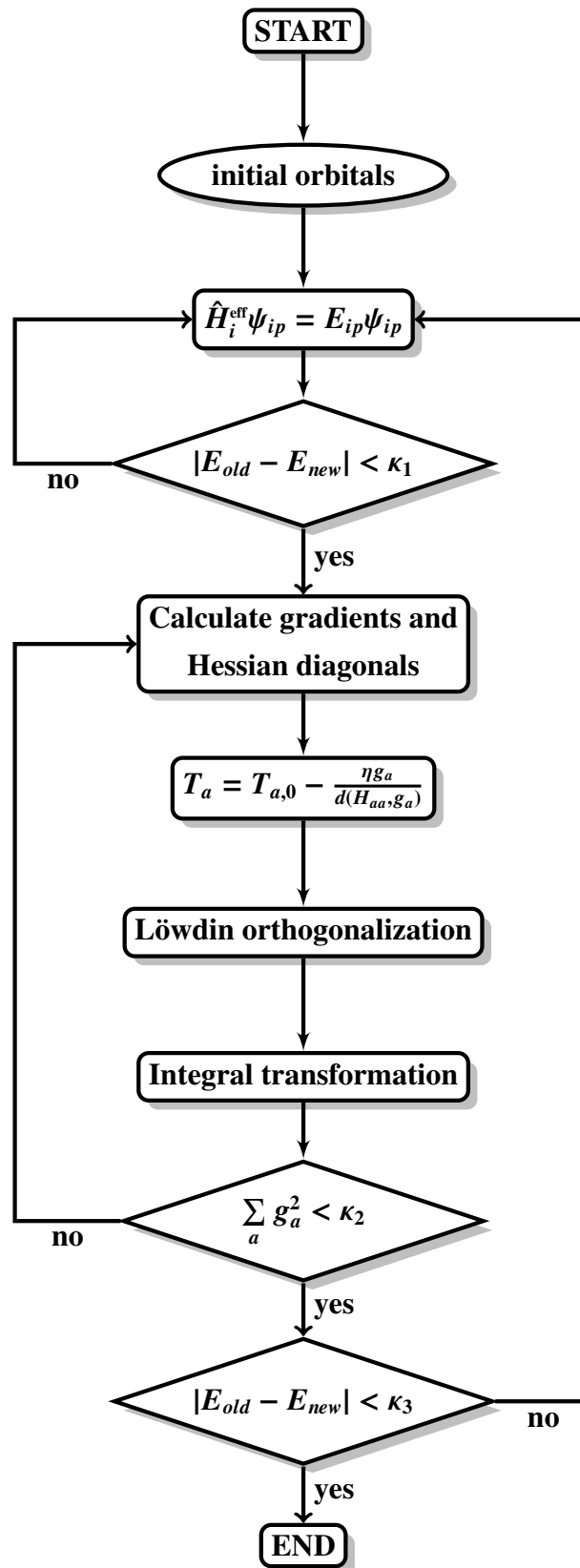
where  $T_{a,0}$  is value of the  $\mathbf{T}$  parameter matrix from the previous iteration,  $\eta$  is a numerical parameter for enhancing convergence,  $g_a$  is the gradient and  $d(H_{aa}, g_a)$  is a function of the gradient and the Hessian diagonals given by the following formula:

$$d(H_{aa}, g_a) = \sqrt{H_{aa}^2 + (\mu g_a)^2}$$

If the absolute value of the Hessian diagonals or the gradient are close to zero for a composite index  $a$ , the  $T_a$  element is not changed further. After each orbital rotation, reorthogonalization is needed due to the change of the metric. Then the one- and two-electron integrals are transformed back to the actual basis. If the sum of the squares of the gradients is greater than a critical  $\kappa_2$  value, new gradients and Hessian diagonals are calculated and the rotation of orbitals continues. When finally the sum of the squares of the gradients fall below  $\kappa_2$ , an energetic criterion is examined again. If absolute value of the energy change is less than  $\kappa_3$  then the APSG optimization ends. If not, the local Schrödinger equations are solved and the orbitals are optimized again, until there is no significant change in the energy. The block diagram of this algorithm is presented in fig. (2.1) below.

It is possible to solve the local Schrödinger equations without restricting the geminals to be natural. In this way triplet states can also be calculated. These calculations are usually preceded by a natural geminal calculation with the orbital optimization included. The geminal coefficient matrices are then calculated in this energetically optimized basis set.

Figure 2.1: The APSG optimization algorithm



## 2.7 Perturbation theory with geminals

In single reference theory, a possible development of computational results can be achieved with the introduction of perturbative corrections. An analogous treatment is possible in geminal theory as well. In this section we are going into the details of this theory and show the inappropriateness of this approach in some cases. The details of this theoretical construct are discussed in [5] and [8].

In perturbation theory the Hamiltonian, the wave function and the energy expression in the time-independent Schrödinger equation are written in the following way:

$$(\hat{H}_0 + \lambda \hat{W}) \sum_{i=0} \lambda^i |\Psi^{(i)}\rangle = \sum_{j=0} \lambda^j E^{(j)} \sum_{i=0} \lambda^i |\Psi^{(i)}\rangle,$$

where  $\lambda$  is the formal perturbation parameter,  $\hat{H}_0$  and  $\hat{W}$  are the zero-order Hamiltonian and the perturbation operator respectively,  $\Psi^{(i)}$  and  $E^{(j)}$  represent the different orders of corrections for the wave function and the energy. We will only consider ground state wave functions and energies, so state indices are not going to be labelled. After collecting the different terms on both sides corresponding to the same power of  $\lambda$ , the following equations are obtained:

$$\hat{H}_0 |\Psi^{(0)}\rangle = E^{(0)} |\Psi^{(0)}\rangle$$

$$\hat{H}_0 |\Psi^{(1)}\rangle + \hat{W} |\Psi^{(0)}\rangle = E^{(0)} |\Psi^{(1)}\rangle + E^{(1)} |\Psi^{(0)}\rangle \quad (2.39)$$

$$\hat{H}_0 |\Psi^{(2)}\rangle + \hat{W} |\Psi^{(1)}\rangle = E^{(0)} |\Psi^{(2)}\rangle + E^{(1)} |\Psi^{(1)}\rangle + E^{(2)} |\Psi^{(0)}\rangle \quad (2.40)$$

The zero-order Hamiltonian is chosen to be

$$\hat{H}_0 = \sum_i \hat{H}_i^{\text{eff}},$$

where the effective Hamiltonian for geminal  $i$  is defined in eq. (2.35). The perturbation operator according to eq. (2.18) contains the following operator fragments:

$$\hat{W} = \hat{H} - \hat{H}_0 = \sum_i (\hat{H}_i - \hat{H}_i^{\text{eff}}) + \sum_{\substack{i,j \\ i \neq j}} \hat{H}_{ij} + \sum_{\substack{i,j,k \\ i \neq j \neq k}} \hat{H}_{ijk} + \sum_{\substack{i,j,k,l \\ i \neq j \neq k \neq l}} \hat{H}_{ijkl}. \quad (2.41)$$

The first-order and the second-order energy expression can be derived in the usual way, by multiplying eqs. (2.39) and (2.40) from the left by  $\langle \Psi^{(0)} |$  (which is chosen to be

the APSG wave function in this formulation) and utilising the intermediate normalization condition which is equivalent to the different perturbational orders of the wave function being orthogonal to the zero order solution. The well-known result will be

$$\begin{aligned} E^{(1)} &= \langle \Psi^{(0)} | \hat{W} | \Psi^{(0)} \rangle \\ E^{(2)} &= \langle \Psi^{(0)} | \hat{W} | \Psi^{(1)} \rangle. \end{aligned} \quad (2.42)$$

In  $E^{(1)}$ , only those terms of  $\hat{W}$  can give any contribution which conserve the particle number within the geminals. These would be the one-geminal Hamiltonian fragments and the sum of dispersive Hamiltonians of eq. (2.20). It can be shown however, that the first-order energy correction is zero with this partition scheme:

$$\begin{aligned} E^{(1)} &= \langle \Psi^{(0)} | \left( \sum_i (\hat{H}_i - \hat{H}_i^{\text{eff}}) + \sum_{\substack{i,j \\ i \neq j}} \hat{H}_{ij}^{\text{disp}} \right) | \Psi^{(0)} \rangle \\ &= -\langle \Psi^{(0)} | \left( \sum_{\substack{i,j \\ i \neq j}} \sum_{m,n \in i} \sum_{\sigma} ([ms|nl] - \frac{1}{2}[ms|ln]) P_{ls}^{j0} m_{\sigma}^{+} n_{\sigma}^{-} \right) | \Psi^{(0)} \rangle \\ &\quad + \langle \Psi^{(0)} | \left( \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} ([mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} - [mn|sl] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}) \right) | \Psi^{(0)} \rangle = 0. \end{aligned}$$



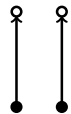

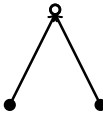
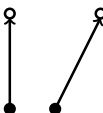
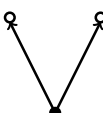
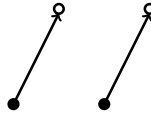
In the second term, after performing a  $s \leftrightarrow n$  notation change, changing the order of  $s_{\sigma}^{+}$  and  $n_{\sigma}^{-}$ , and also that of  $s_{\sigma'}^{+}$  and  $n_{\sigma'}^{-}$  (bringing in a sign) and evaluating the matrix element containing the  $s$  and  $l$  orbitals, it can be clearly seen that the absolute value is equal to that of the first term. This results in  $E^{(1)}$  being zero.

For the second-order energy  $E^{(2)}$  the first-order wave function has to be determined. In order to do this, the so-called *first-order interacting subspace* has to be constructed, which is composed of states orthogonal to  $|\Psi^{(0)}\rangle$  (the APSG wave function in this case). These states are obtained by excitations from the APSG reference. The different excitations can be categorized on the basis of their ability to interact with APSG, though the different fragments of the perturbation operator, see table (2.1) for details.

Denoting the excitations orthogonal to the APSG reference as  $|\Psi_i^{(0)}\rangle$ , the first-order wave function can be expanded as

$$|\Psi^{(1)}\rangle = \sum_i t_i |\Psi_i^{(0)}\rangle. \quad (2.43)$$

Table 2.1: Excitations of the first-order interacting subspace

$\hat{H}$ type	Fragment of $\hat{W}$	Excitation type
$\hat{H}_a$		$\psi_{ip}^+ \psi_{i0}^-  \Psi^{(0)}\rangle$
$\hat{H}_{ab}$		$\mu^+ \nu^+ \lambda^+ \sigma^+ \psi_{j0}^- \psi_{i0}^-  \Psi^{(0)}\rangle$ $\mu, \nu, \lambda \in i; \sigma \in j$
		$\psi_{jq}^+ \psi_{ip}^+ \psi_{j0}^- \psi_{i0}^-  \Psi^{(0)}\rangle$
		$\mu^+ \nu^+ \lambda^+ \sigma^+ \psi_{j0}^- \psi_{i0}^-  \Psi^{(0)}\rangle$ $\mu, \nu, \lambda, \sigma \in j$
$\hat{H}_{abc}$		$\mu^+ \nu^+ \lambda^+ \sigma^+ \psi_{k0}^- \psi_{i0}^-  \Psi^{(0)}\rangle$ $\mu, \nu \in j; \lambda \in i; \sigma \in k$
		$\mu^+ \nu^+ \lambda^+ \sigma^+ \psi_{ip}^+ \psi_{j0}^- \psi_{i0}^-  \Psi^{(0)}\rangle$ $\mu \in j; \nu, \lambda, \sigma \in k$
		$\mu^+ \nu^+ \psi_{j0}^-  \Psi^{(0)}\rangle$ $\mu \in i; \nu \in k$
$\hat{H}_{abcd}$		$\mu^+ \nu^+ \lambda^+ \sigma^+ \psi_{j0}^- \psi_{i0}^-  \Psi^{(0)}\rangle$ $\mu \in i; \nu \in j;$ $\lambda \in k; \sigma \in l$

Substituting this form into eq. (2.39) and projecting by  $\langle \Psi_j^{(0)} |$ , the  $t_i$  parameters can be obtained by solving a linear system of equations:

$$\sum_i \underbrace{\langle \Psi_j^{(0)} | E^{(0)} - \hat{H}_0 | \Psi_i^{(0)} \rangle}_{A_{ji}} t_i = \underbrace{\langle \Psi_j^{(0)} | \hat{W} | \Psi^{(0)} \rangle}_{d_j} \quad (2.44)$$

$$\mathbf{A} \mathbf{t} = \mathbf{d}$$

To come to terms with a serious drawback of the perturbation theory outlined above, we will consider dispersive excitations only (third row of table (2.1)) and have a look at the energy expression obtained. According to eq. (2.42)

$$E_{\text{disp}}^{(2)} = \sum_{\substack{i,j \\ i < j}} \sum_p^{(i)} \sum_q^{(j)} t_{ij}^{pq} \langle \Psi^{(0)} | \hat{H}_{ij}^{\text{disp}} | \Psi_{ij}^{pq} \rangle, \quad (2.45)$$

where we use the shorthand notation  $|\Psi_{ij}^{pq}\rangle = \psi_{jq}^+ \psi_{ip}^+ \psi_{j0}^- \psi_{i0}^- |\Psi^{(0)}\rangle$  and  $\sum_p^{(i)}$  runs over the excited states of geminal  $i$  ( $p \neq 0$ ). After multiplying eq. (2.44) with  $\mathbf{A}^{-1}$  from the left, the wave function parameters (sometimes referred to as *amplitudes*) appearing in the energy expression are

$$t_{ij}^{pq} = \sum_{\substack{k,h \\ k < h}} \sum_r^{(k)} \sum_s^{(h)} \langle \Psi_{ij}^{pq} | \hat{H}_0 - E^{(0)} | \Psi_{kh}^{rs} \rangle^{-1} \langle \Psi_{kh}^{rs} | \hat{H}_{ij}^{\text{disp}} | \Psi^{(0)} \rangle = \frac{\langle \Psi_{ij}^{pq} | \hat{H}_{ij}^{\text{disp}} | \Psi^{(0)} \rangle}{E_{ip} + E_{jq} - E_{i0} - E_{j0}}, \quad (2.46)$$

where we have used the fact that the dispersive excitations are eigenstates of the zero order Hamiltonian:

$$\begin{aligned} \langle \Psi_{ij}^{pq} | \hat{H}_0 - E^{(0)} | \Psi_{kh}^{rs} \rangle &= (E_{1,0} + \dots + E_{kr} + \dots + E_{hs} + \dots + E_{N,0} \\ &\quad - E_{1,0} - \dots - E_{k0} - \dots - E_{h0} - \dots - E_{N,0}) \delta_{ik} \delta_{jh} \delta_{pr} \delta_{qs} \\ &= (E_{ip} + E_{jq} - E_{i0} - E_{j0}) \delta_{ik} \delta_{jh} \delta_{pr} \delta_{qs} \end{aligned}$$

Substituting eq. (2.46) back to eq. (2.45) the final form of the energy expression will be:

$$E_{\text{disp}}^{(2)} = \sum_{\substack{i,j \\ i < j}} \sum_p^{(i)} \sum_q^{(j)} \frac{|\langle \Psi^{(0)} | \hat{H}_{ij}^{\text{disp}} | \Psi_{ij}^{pq} \rangle|^2}{E_{ip} + E_{jq} - E_{i0} - E_{j0}}.$$

This formula diverges if the eigenvalues belonging to the excited geminals approach that of the ground state geminals. Unfortunately, this happens in some chemical processes, like the simultaneous dissociation of two chemical bonds. In fig. (2.2) the energy profile for the symmetric dissociation of a water molecule is shown. APSG method is able to describe this process qualitatively well (this wave function model can depict static correlation effects). However, the second order perturbative correction containing only dispersive excitations (labeled as 'APSG + PT2' in fig. (2.2)) obviously fails. This is caused by the approaching of the energy levels of the ground state and the first triplet excited geminal state in the O-H bonds to each other, leading to the value of  $E_{ip} + E_{jq} - E_{i0} - E_{j0}$  approaching zero for these two geminals and these specific states.

This shortcoming of geminal perturbation theory can be overcome with a formulation having a nondiagonal  $\mathbf{A}^{-1}$ . Such a theory will be outlined in section 3.2.

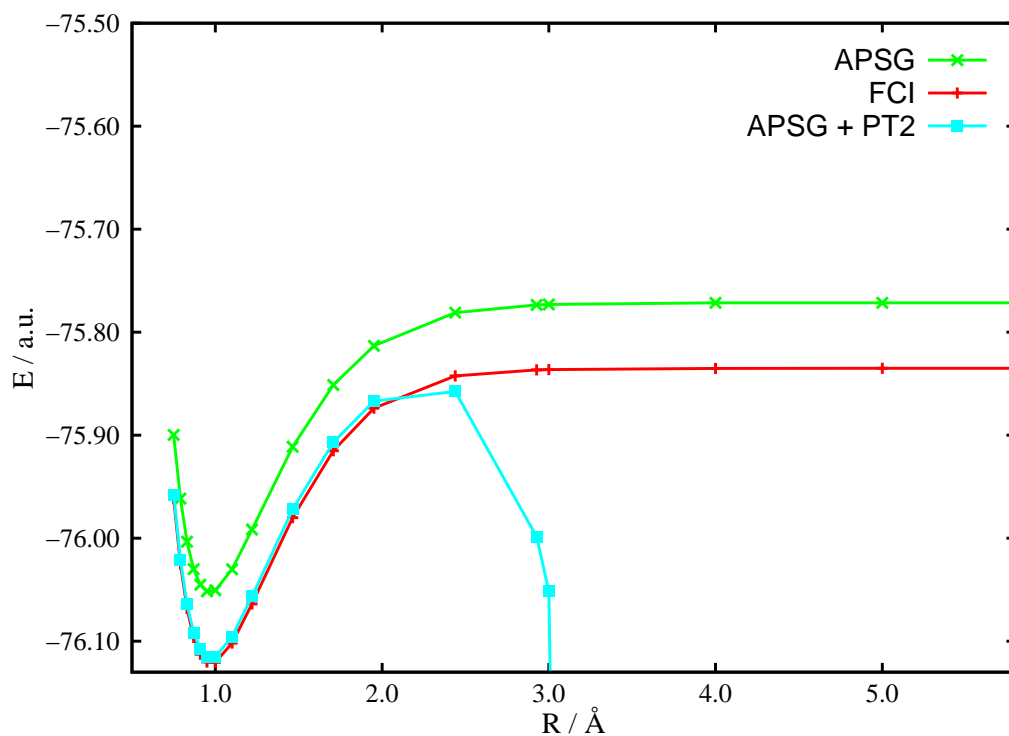


Figure 2.2: Water symmetric dissociation in 6-31G basis set with bond angle fixed at  $\angle$  (H-O-H) = 110.6°. APSG wave function is assumed as reference. Frozen core approximation is applied. The APSG reference has 4 orbitals on the bonding and 2 on the non-bonding geminals. See text for acronyms.

# Advances in Geminal Theory

This chapter is about theoretical advances made by the author concerning the geminal model. Section (3.1) deals with a previously unknown property of the APSG wave function, namely its stationarity to the unitary transformation of the geminals it is built of. Section (3.2) outlines a Coupled Cluster-type correction scheme in order to overcome the defects of the perturbative treatment of geminals presented in Section (2.7). Finally, section (3.3) introduces a diagrammatic formulation of the energy expression and the terms of the amplitude equations for the dispersive states in the geminal-based Multi-reference Coupled Cluster Theory described in section 3.2.

## 3.1 A stationary property of the APSG wave function

This section investigates a previously unknown stationary property of the APSG wave function. The material presented here is based on our publication in the Journal of Mathematical Chemistry [1].

### 3.1.1 Is the APSG wave function invariant to the unitary transformation of geminals?

The one-determinantal Hartree-Fock wave function with the use of one-electron creation operators  $\varphi_i^+$ ,  $i \in \{1, \dots, N\}$  is

$$\Psi_{\text{HF}} = \varphi_1^+ \varphi_2^+ \dots \varphi_i^+ \dots \varphi_j^+ \dots \varphi_N^+ |\text{vac}\rangle \quad (3.1)$$

It is a well-known property of this very simple wave function form, that besides a constant prefactor, it is invariant to any nonsingular transformation (the transformation matrix having a nonzero determinant) of the occupied orbitals [91]. In this subsection,



we only consider unitary transformations performed with two-by-two matrices. A subset of higher dimension unitary transformations (not all of them) can be thought of as a successive application of two-by-two rotations. In this respect, the results presented in this section are quite general and can be applied for the full APSG wave function.

For one-electron orbitals  $\varphi_i$  and  $\varphi_j$ , a two-by-two transformation looks like:

$$\begin{aligned} \boldsymbol{\varphi}' &= \mathbf{U}\boldsymbol{\varphi} \\ \begin{bmatrix} \widetilde{\varphi}_i \\ \widetilde{\varphi}_j \end{bmatrix} &= \begin{bmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{bmatrix} \begin{bmatrix} \varphi_i \\ \varphi_j \end{bmatrix} \end{aligned}$$

A two-by-two rotation can be parametrized with the above  $\mathbf{U}$  rotation matrix. Substituting the transformed orbitals  $\widetilde{\varphi}_i^+ = \cos \alpha \varphi_i^+ - \sin \alpha \varphi_j^+$  and  $\widetilde{\varphi}_j^+ = \sin \alpha \varphi_i^+ + \cos \alpha \varphi_j^+$  in place of  $\varphi_i^+$  and  $\varphi_j^+$  in eq. (3.1), one can easily prove the invariance

$$\begin{aligned} |\Psi'_{\text{HF}}\rangle &= \varphi_1^+ \varphi_2^+ \dots \widetilde{\varphi}_i^+ \dots \widetilde{\varphi}_j^+ \dots \varphi_N^+ |\text{vac}\rangle = \\ &= \left( \cos^2 \alpha \varphi_1^+ \varphi_2^+ \dots \varphi_i^+ \dots \varphi_j^+ \dots \varphi_N^+ - \sin^2 \alpha \varphi_1^+ \varphi_2^+ \dots \varphi_j^+ \dots \varphi_i^+ \dots \varphi_N^+ \right) |\text{vac}\rangle = \\ &= \left( \cos^2 \alpha + \sin^2 \alpha \right) \varphi_1^+ \varphi_2^+ \dots \varphi_i^+ \dots \varphi_j^+ \dots \varphi_N^+ |\text{vac}\rangle = \Psi_{\text{HF}} \end{aligned} \quad (3.2)$$

Here we introduced a sign change as a direct consequence of the anticommutator relation of eq. (6.1) and cancelled terms containing creation operators creating two electrons on the same orbital.

Going along the same line of thought but considering geminals instead of one-electrons orbitals, the transformation of two geminals can be written analogously as

$$\begin{bmatrix} \widetilde{\psi}_i \\ \widetilde{\psi}_j \end{bmatrix} = \begin{bmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{bmatrix} \begin{bmatrix} \psi_i \\ \psi_j \end{bmatrix} \quad (3.3)$$

A transformed wave function takes the following form:

$$|\Psi'\rangle = \psi_1^+ \psi_2^+ \dots \widetilde{\psi}_i^+ \dots \widetilde{\psi}_j^+ \dots \psi_N^+ |\text{vac}\rangle$$

However, the conditions leading to the unitary invariance of the Hartree-Fock wave function are simply not satisfied in this case (namely we cannot introduce a sign change like in eq.(3.2) because geminals are quasi-bosonic particles and also acting with two identical geminal creation operators on the vacuum is possible without getting zero, unlike in the

one-electron case). This leads to the conclusion that the APSG wave function is *not* invariant to the unitary transformation of the individual geminals. The question arises though, whether it is possible to further decrease the APSG energy by finding an appropriate  $\mathbf{U}$  matrix.

### 3.1.2 Unitary transformation of two geminals

To give a proper answer to the question raised at the end of the previous subsection, we investigate the unitary transformation of two geminals. The results obtained here can be generalized for those unitary matrices that can be generated by applying a series of two-by-two rotations subsequently. The wave function ansatz used for investigation will be:

$$|\Psi\rangle = \tilde{\psi}_2^+ \tilde{\psi}_1^+ |\text{vac}\rangle,$$

where the form of  $\tilde{\psi}_1$  and  $\tilde{\psi}_2$  is given in eq. (3.3) for the special case of  $i = 1$  and  $j = 2$ . Geminals are presented in their natural form in the wave function.

The energy of the system should be calculated with the Rayleigh-formula, because the norm of the wave function also changes during the transformation of the geminals (it is to be noted that the strong orthogonality condition is also violated during this process). The Rayleigh formula reads

$$E = \frac{\langle \Psi' | \hat{H} | \Psi' \rangle}{\langle \Psi' | \Psi' \rangle}.$$

The squared norm of the wave function is

$$\begin{aligned} \mathcal{N}^2 = \langle \Psi' | \Psi' \rangle &= \langle \text{vac} | \tilde{\psi}_2^- \tilde{\psi}_1^- \tilde{\psi}_1^+ \tilde{\psi}_2^+ | \text{vac} \rangle = \sum_{i,j,k,l=1}^2 U_{1i} U_{2j} U_{2k} U_{1l} \langle \text{vac} | \psi_i^- \psi_j^- \psi_k^+ \psi_l^+ | \text{vac} \rangle = \\ &= \sum_{i,j=1}^2 U_{1i} U_{2j} (U_{1i} U_{2j} + U_{2i} U_{1j}) - 2 \sum_{i=1}^2 U_{1i}^2 U_{2i}^2 \sum_{m \in i} (C_m^i)^4, \end{aligned}$$

while the total energy reads

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \text{vac} | \tilde{\psi}_1^- \tilde{\psi}_2^- \hat{H} \tilde{\psi}_2^+ \tilde{\psi}_1^+ | \text{vac} \rangle}{\mathcal{N}^2} = \frac{1}{\mathcal{N}^2} \left( \sum_{i,j,k,l=1}^2 U_{ijkl} \langle \text{vac} | \psi_i^- \psi_j^- \hat{H} \psi_k^+ \psi_l^+ | \text{vac} \rangle \right),$$

where  $U_{ijkl} = U_{1i}U_{2j}U_{2k}U_{1l}$ . Writing out the one- and two-electron part of the Hamiltonian, one arrives at

$$E = \frac{1}{\mathcal{N}^2} \sum_{i,j,k,l=1}^2 U_{ijkl} \left( \sum_{m,n} h_{mn} \sum_{\sigma} \langle \text{vac} | \psi_i^- \psi_j^- m_{\sigma}^+ n_{\sigma}^- \psi_k^+ \psi_l^+ | \text{vac} \rangle + \right. \\ \left. + \frac{1}{2} \sum_{m,n,l,s} \sum_{\sigma,\sigma'} [mn|ls] \langle \text{vac} | \psi_i^- \psi_j^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_k^+ \psi_l^+ | \text{vac} \rangle \right). \quad (3.4)$$

The evaluation procedure of the above equation leads to special types of matrix elements, which are unusual in standard geminal theory. These are the following::

$$\langle \text{vac} | \psi_i^- \psi_i^- m_{\sigma}^+ n_{\sigma}^- \psi_i^+ \psi_i^+ | \text{vac} \rangle \quad (m, n \in i)$$

$$\langle \text{vac} | \psi_i^- \psi_i^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_i^+ \psi_i^+ | \text{vac} \rangle \quad (m, n, l, s \in i)$$

$$\langle \text{vac} | \psi_i^- \psi_i^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_k^+ \psi_i^+ | \text{vac} \rangle \quad (l, s \in k; m, n \in i)$$

$$\langle \text{vac} | \psi_i^- \psi_k^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_i^+ \psi_i^+ | \text{vac} \rangle \quad (l, s \in i; m, n \in k)$$

The common feature of these matrix elements is that they all contain the four-electron operator  $\psi_i^+ \psi_i^+$ , whose effect on the vacuum results in a nonzero function, because of the quasi-bosonic nature of geminals.

We find it unnecessary to explicitly write out the final form of the energy expression as it does not have too much informational value. We turn our attention to applications instead.

### 3.1.3 Applications

We made a computer implementation of the energy expression in eq. (3.4) and performed calculations for two model systems.

As a sample application we performed the unitary transformation of the geminals of two hydrogen molecules in 6-311G\*\* basis set (see fig. (3.1)). The four hydrogen atoms were collinear in our numerical example, in the  $\text{H}_2$  molecules the distance between the hydrogen atoms was 0.74 Å, while the distance between the molecules was 1.26 Å. The actual arrangement of the maximum and minimum places can be understood by looking at the energy formula containing trigonometric expressions having minima at orbital rotation angles  $\alpha = \{\frac{k\pi}{2} | k \in \mathbb{Z}\}$  and maxima at angles  $\{\frac{\pi}{4} + \frac{k\pi}{2} | k \in \mathbb{Z}\}$ . In this case  $\alpha = 0$  is the identity

transformation and  $\alpha = \frac{\pi}{2}$  refers to the interchange of the two geminals. The curve has an exact minimum at the APSG wave function. This numerical experience is theoretically verified in the forthcoming subsection.

The example of two non-equivalent geminals was also studied, calculations for a helium atom and a hydrogen molecule were performed in 6-311G\*\* basis set (see fig. (3.2)). The atoms are placed collinearly, the H-H bond length is 0.74 Å and the helium atom is placed 1.26 Å far from one of the hydrogen atoms. The inset of fig. (3.2) shows the region of the energy curve close to the APSG-energy ( $\alpha = 0$ ), the horizontal line indicates the APSG-energy. The APSG energy is clearly not a minimum in this case, we obtain lower energy than the APSG-energy at  $\alpha = -0.004$ , but the actual energy difference is only at the microhartree level. The error of the ASPG optimization procedure is usually larger, so this energy gain is practically irrelevant. This result is however not surprising, in the next section it will be analytically proven that stationarity of the APSG wave function is only exact for equivalent geminals, and holds only approximately in the general case.

### 3.1.4 Analytical proof of stationarity for equivalent geminals

In fig. (3.1) the exact stationarity of the APSG wave function was obtained for two equivalent hydrogen molecules. It is possible to show this result analytically as well. For an infinitesimal transformation (small value of the  $\alpha$  parameter), matrix  $\mathbf{U}$  in eq. (3.3) can be written as

$$U = \begin{bmatrix} 1 & -\alpha \\ \alpha & 1 \end{bmatrix}$$

At this point, a simplified notation is introduced:

$$\langle \dots \rangle \equiv \langle \text{vac} | \dots | \text{vac} \rangle$$

Transforming the geminals with this matrix according to eq. (3.3) and substituting the transformed geminals into the expression for the squared norm  $\mathcal{N}^2$ , we obtain:

$$\begin{aligned} \mathcal{N}^2 &= \langle \Psi | \Psi \rangle = \langle (\psi_1^- - \alpha \psi_2^-)(\alpha \psi_1^- + \psi_2^-)(\alpha \psi_1^+ + \psi_2^+)(\psi_1^+ - \alpha \psi_2^+) \rangle = \\ &= \langle \psi_1^- \psi_2^- \psi_2^+ \psi_1^+ \rangle + 2\alpha \left( \langle \psi_1^- \psi_1^- \psi_2^+ \psi_1^+ \rangle - \langle \psi_2^- \psi_2^- \psi_2^+ \psi_1^+ \rangle \right) + \mathcal{O}(\alpha^2) = 1 + \mathcal{O}(\alpha^2). \end{aligned} \quad (3.5)$$

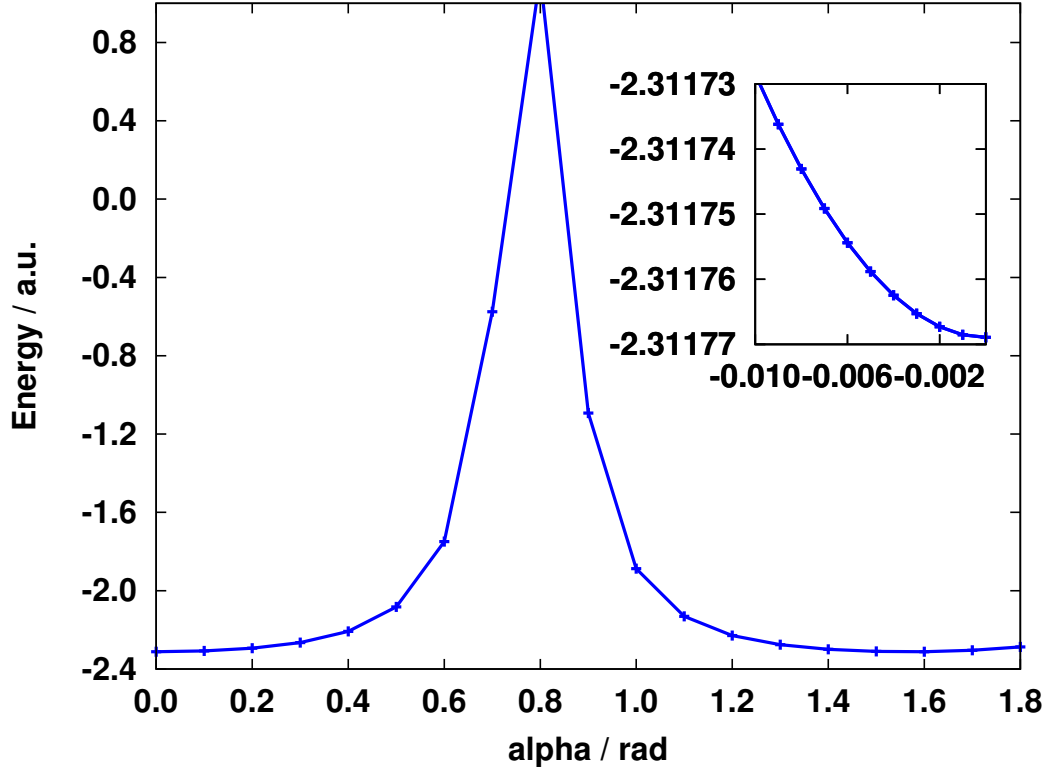


Figure 3.1: Energy of two hydrogen molecules as a function of the geminal mixing parameter  $\alpha$  (see eq. (3.3)). The inset is a zoom into the  $\alpha = 0$  region indicating that the APSG energy is a minimum indeed.

The second term of eq. (3.5) is zero because of the strong orthogonality of the two geminals,  $\psi_1$  and  $\psi_2$  are expanded in exclusive subsets of the one-electron orbitals, applying the annihilation operators the second time results in zero accordingly. In first order, the norm of the wave function is conserved, so the energy expression can be written simply as

$$\begin{aligned}
E &= \langle \Psi | \hat{H} | \Psi \rangle = \langle (\psi_1^- - \alpha \psi_2^-)(\alpha \psi_1^- + \psi_2^-) \hat{H} (\alpha \psi_1^+ + \psi_2^+) (\psi_1^+ - \alpha \psi_2^+) \rangle = \\
&= E_{\text{APSG}} + 2\alpha \left( \langle \psi_1^- \psi_1^- \hat{H} \psi_2^+ \psi_1^+ \rangle - \langle \psi_2^- \psi_2^- \hat{H} \psi_2^+ \psi_1^+ \rangle \right) + \alpha^2 \left( \langle \psi_2^- \psi_2^- \hat{H} \psi_2^+ \psi_2^+ \rangle + \langle \psi_1^- \psi_1^- \hat{H} \psi_1^+ \psi_1^+ \rangle - \right. \\
&\quad \left. - 2 \underbrace{\langle \psi_1^- \psi_1^- \hat{H} \psi_2^+ \psi_2^+ \rangle}_0 - 2E_{\text{APSG}} \right) + \mathcal{O}(\alpha^3).
\end{aligned}$$

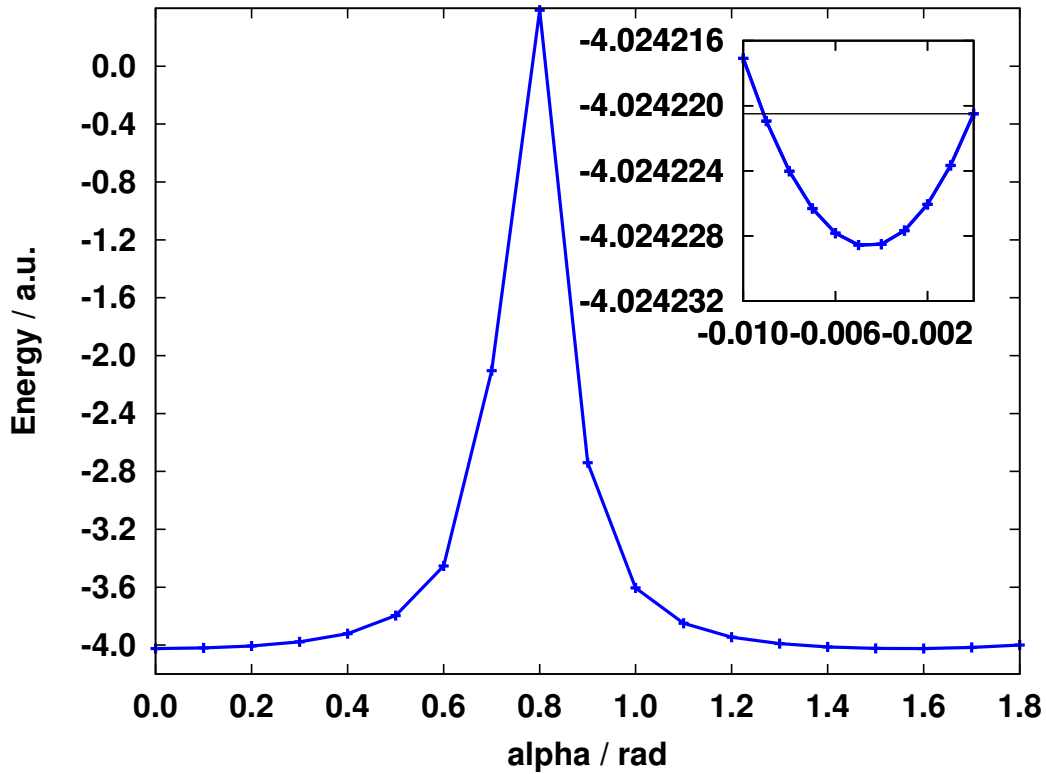


Figure 3.2: Energy of a hydrogen molecule and a helium atom as a function of the geminal mixing parameter  $\alpha$ , see eq. (3.3). The inset is a zoom into the  $\alpha = 0$  region with the horizontal line indicating the APSG-energy.

The terms of the energy expression can be listed simply by taking the terms of the squared norm ( $\mathcal{N}^2$ ) and inserting the Hamiltonian  $\hat{H}$  between the geminal annihilation and creation operators.  $\langle \psi_1^- \psi_1^- \hat{H} \psi_2^+ \psi_2^+ \rangle$  is zero because the Hamiltonian can excite only two electrons and the geminals are strongly orthogonal. The first derivative of the energy expression at  $\alpha = 0$ :

$$\left. \frac{\partial E}{\partial \alpha} \right|_{\alpha=0} = 2 \left( \langle \psi_1^- \psi_1^- \hat{H} \psi_2^+ \psi_1^+ \rangle - \langle \psi_2^- \psi_2^- \hat{H} \psi_2^+ \psi_1^+ \rangle \right),$$

which is zero for equivalent geminals ( $\psi_1 \equiv \psi_2$ ) and nonzero for non-equivalent ones (but it is usually a number with a small absolute value). This explains the difference between figs. (3.1) and (3.2). The second derivative of the energy:

$$\left. \frac{\partial^2 E}{\partial \alpha^2} \right|_{\alpha=0} = 2 \left( \langle \psi_2^- \psi_2^- \hat{H} \psi_2^+ \psi_2^+ \rangle + \langle \psi_1^- \psi_1^- \hat{H} \psi_1^+ \psi_1^+ \rangle - 2E_{\text{APSG}} \right),$$

which is positive for both equivalent and non-equivalent geminals as well. The reason behind this is that both  $\psi_1^+ \psi_1^+$  and  $\psi_2^+ \psi_2^+$  create ionized (charge-transfer) geminal states while acting on  $|\text{vac}\rangle$ . These states have higher energy than the APSG wave function (they contain less configurations), so the difference in the second derivative will have a positive absolute value.

Thus it was shown that the APSG wave function is not only stationary to the unitary transformation of orbitals (see subsection 2.6.2), but also to the transformation of the geminals themselves (for equivalent geminals it is exact stationarity, while for non-equivalent ones it is only an approximative one). This result has an important consequence from an interpretational point of view. It states that the energy-optimized geminals are unique, contrary to the one-electron orbitals of Hartree-Fock theory. In this respect they are proper mathematical representations of chemical bonds in molecules which is also confirmed by their localized nature.

## 3.2 Coupled Cluster-type corrections to the APSG wave function

In section (2.7) we have already mentioned the unsatisfactory behaviour of geminal perturbation theory in important chemical processes, in this case the simultaneous dissociation of chemical bonds. The divergence of the potential energy surface observed in fig. (2.2) is a direct consequence of a zero eigenvalue of matrix  $\mathbf{A}$  in eq. (2.44). In this section we aim at correcting this property of geminal perturbation theory by introducing a Coupled Cluster-type approach. This theory by definition belongs to the family of Multireference Coupled Cluster (MRCC) Theories, due to the multireference nature of the APSG wave function.

### 3.2.1 Linearized Coupled Cluster Theory with APSG reference

In this subsection we only consider the effect of linear Coupled Cluster corrections to the APSG wave function. The time-independent Schrödinger equation with the Coupled Cluster ansatz based on an APSG reference ( $|\text{APSG}\rangle$ ) can be written as

$$\hat{H}e^{\hat{T}}|\text{APSG}\rangle = Ee^{\hat{T}}|\text{APSG}\rangle.$$

Multiplying from the left by  $\langle\text{APSG}|e^{-\hat{T}}$ , the energy equation becomes

$$\langle\text{APSG}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\text{APSG}\rangle = E \quad (3.6)$$

The excitation operator  $\hat{T}$  is a linear combination:

$$\hat{T} = \sum_k t_k \hat{X}_k, \quad (3.7)$$

with  $t_k$  amplitudes and  $\hat{X}_k$  excitation operators (specified after elaborating the general formalism). For constructing a linear theory, the Baker-Campbell-Hausdorff has to be truncated after the second term:

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} \approx \hat{H} + [\hat{H}, \hat{T}] \quad (3.8)$$

The  $t_k$  amplitudes are obtained by multiplying the time-independent Schrödinger equation of the Coupled Cluster ansatz



$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\text{APSG}\rangle = E |\text{APSG}\rangle$$

by  $\langle \text{APSG} | \hat{X}_j^\dagger$  from the left, where  $\hat{X}_j^\dagger$  operators are constructed as the adjoints of the excitation operators in the definition of  $\hat{T}$  (eq. (3.7)):

$$\langle \text{APSG} | \hat{X}_j^\dagger e^{-\hat{T}} \hat{H} e^{\hat{T}} | \text{APSG}\rangle = E \langle \text{APSG} | \hat{X}_j^\dagger | \text{APSG}\rangle = 0 \quad (3.9)$$

We introduce the truncated Baker-Campbell-Hausdorff expression of eq. (3.8) on the left side of eq. (3.9) to obtain

$$\langle \text{APSG} | \hat{X}_j^\dagger [\hat{T}, \hat{H}] | \text{APSG}\rangle = \langle \text{APSG} | \hat{X}_j^\dagger \hat{H} | \text{APSG}\rangle,$$

where we multiplied the amplitude equations by -1, hence the sign of the inhomogeneous term disappeared and the order of the  $[\hat{H}, \hat{T}]$  commutator changed. Substituting eq. (3.7) into the above equation, we arrive at the final form of the amplitude equations which is basically a system of linear equations:

$$\sum_i \underbrace{\langle \text{APSG} | \hat{X}_j^\dagger (\hat{X}_i \hat{H} - \hat{H} \hat{X}_i) | \text{APSG}\rangle}_{A_{ji}} t_i = \underbrace{\langle \text{APSG} | \hat{X}_j^\dagger \hat{H} | \text{APSG}\rangle}_{b_j} \quad (3.10)$$

$$\mathbf{A} \mathbf{t} = \mathbf{b}.$$

The  $\hat{X}_k$  excitations used by us are defined in the third column of table (2.1). It is important to note that these excitations are only applicable in the LCC approximation as the operators corresponding to them are not commuting in general. In the LCC case this does not cause difficulties and extensivity is maintained.

As dispersive contribution causes the overall bad performance of geminal perturbation theory, it is also interesting to consider the effect of only the dispersive excitations in the cluster operator, which has the following form in this special case:

$$\hat{T} = \sum_k^{disp} t_k \hat{X}_k = \sum_{\substack{i,j \\ i < j}} \sum_p^{(i)} \sum_q^{(j)} t_{ij}^{pq} \psi_{ip}^+ \psi_{jq}^+ \psi_{j0}^- \psi_{i0}^-, \quad (3.11)$$

where  $t_{ij}^{pq}$  are the dispersive amplitudes,  $\psi_{ip}$  and  $\psi_{jq}$  refer to the excited states  $p, q$  of geminal  $i$  and  $j$  respectively, while  $\psi_{i0}$  and  $\psi_{j0}$  denote the ground state of the same geminals.

A special subset of excitations are the so-called 'spin-polarized excitations' forming the basis of the following cluster operator:

$$\hat{T} = \sum_{\substack{i,j \\ i < j}} \sum_{\substack{(i, M_S^p \neq 0) \\ p}} \sum_{\substack{(j, M_S^q \neq 0) \\ q}} t_{ij}^{pq} (\psi_{ip\uparrow}^+ \psi_{jq\downarrow}^+ + \psi_{ip\downarrow}^+ \psi_{jq\uparrow}^+) \psi_{j0}^- \psi_{i0}^-,$$

where  $p$  and  $q$  run through the triplet  $M_S \neq 0$  excited states of geminals  $i$  and  $j$  respectively and the spin-polarized geminal creation operators are expressed as

$$\psi_{ip\uparrow}^+ = \sum_{m,n \in i} C_{mn}^{ip\uparrow} m_\alpha^+ n_\alpha^+ \quad \psi_{jq\downarrow}^+ = \sum_{m,n \in j} C_{mn}^{jq\downarrow} m_\beta^+ n_\beta^+$$

The Linear Coupled Cluster energy from eqs. (3.6) and (3.8) can be expressed as

$$E = \langle \text{APSG} | \hat{H} + \hat{H} \hat{T} | \text{APSG} \rangle. \quad (3.12)$$

### 3.2.2 Numerical testing of the linearized MR-LCC theory

In this subsection we are going to present a few applications of the theory presented above, namely we are going to show energy profiles calculated by using the energy equation of eq. (3.12). In order to do this, the amplitudes are calculated by solving the system of linear equations in eq. (3.10). We are going to propose 12 different schemes based on how the  $\hat{X}_i$  and  $\hat{X}_j^\dagger$  excitations are chosen (the different sets of the states obtained after excitation are going to be called interaction spaces from this point). The different acronyms used in this subsection and their meanings:

- **APSG:** the Antisymmetric Product of Strongly Orthogonal Geminals wave function, in our calculations we did not restrict ourselves to the natural form of geminals, each geminal state can be assigned to a full coefficient matrix
- **APSG + PT2:** Second-order perturbative correction to the APSG wave function calculated with the dispersive states
- **GVB:** General Valence Bond theory (a special type of APSG wave function where each subset is two-dimensional) [92]
- **FCI:** Full Configuration Interaction wave function (in case of water, it will mean the frozen core Full CI)

- **APSG\_DISP:** Dispersive correction of the APSG wave function, the interaction space contains dispersive excitations only with  $M_S = 0$  restricted for all geminals
- **DISP\_SP:** Dispersive states (regardless of the  $M_S$  quantum number of the geminals, so the spin-polarized states (SP) are included) corresponding to the APSG or GVB reference function are taken into consideration
- **DISP\_SD:** Dispersive excitations with  $M_S = 0$  restriction for both excited geminals (DISP) + single and double excited determinants created from the determinants in the APSG or GVB reference (SD) are considered
- **DISP\_SP\_SD:** Dispersive states without any restrictions to the  $M_S$  quantum number (DISP\_SP) + single and double excited determinants created from the determinants in the APSG or GVB reference (SD) are considered
- **DISP\_SP\_1gem:** Dispersive states without any restrictions to the  $M_S$  quantum number (DISP\_SP) + one-geminal excitations to excited geminal states with respect to the APSG or GVB reference (1gem) are considered
- **DISP\_SD\_1gem:** Dispersive excitations with  $M_S = 0$  restriction for both excited geminals (DISP) + single and double excited determinants created from the determinants in the APSG or GVB reference (SD) + one-geminal excitations to excited geminal states with respect to the APSG or GVB reference (1gem) are considered
- **DISP\_SP\_SD\_1gem:** Dispersive states without any restrictions to the  $M_S$  quantum number (DISP\_SP) + single and double excited determinants created from the determinants in the APSG or GVB reference (SD) + one-geminal excitations to excited geminal states with respect to the APSG or GVB reference (1gem) are considered
- **DISP\_SP\_SPSD:** Dispersive states without any restrictions to the  $M_S$  quantum number (DISP\_SP) + single and double excited determinants created from the determinants in the spin-polarized states (SPSD, APSG or GVB reference) are considered
- **DISP\_SD\_SPSD:** Dispersive excitations with  $M_S = 0$  restriction for both excited geminals (DISP) + single and double excited determinants created from the de-

terminants in the APSG or GVB reference (SD) + single and double excited determinants created from the determinants in the spin-polarized states (SPSD) are considered

- **DISP\_SP\_SD\_SPSD:** Dispersive states without any restrictions to the  $M_S$  quantum number (DISP\_SP) + single and double excited determinants created from the determinants in the APSG or GVB reference (SD) + single and double excited determinants created from the determinants in the spin-polarized states (SPSD) are considered
- **DISP\_SP\_SPSD\_1gem:** Dispersive states without any restrictions to the  $M_S$  quantum number (DISP\_SP) + single and double excited determinants created from the determinants in the spin-polarized states (SPSD) + one-geminal excitations to excited geminal states with respect to the APSG or GVB reference (1gem) are considered
- **DISP\_SD\_SPSD\_1gem:** Dispersive excitations with  $M_S = 0$  restriction for both excited geminals (DISP) + single and double excited determinants created from the determinants in the APSG or GVB reference (SD) + single and double excited determinants created from the determinants in the spin-polarized states (SPSD) + one-geminal excitations to excited geminal states with respect to the APSG or GVB reference (1gem) are considered
- **DISP\_SP\_SD\_SPSD\_1gem:** Dispersive states without any restrictions to the  $M_S$  quantum number (DISP\_SP) + single and double excited determinants created from the determinants in the APSG or GVB reference (SD) + single and double excited determinants created from the determinants in the spin-polarized states (SPSD) + one-geminal excitations to excited geminal states with respect to the APSG or GVB reference (1gem) are considered

It is important to note that in all of the above presented calculation schemes, we took care of redundancies in the set of states. If for example the same excited determinant appeared from a single or double excitation of a determinant in the APSG or GVB reference (SD) and also from a single or double excitation from a determinant present in a spin-polarized geminal (SPSD), it was taken into account only once.

### 3.2.3 Interaction of two helium atoms

The first system on which we would like to demonstrate what the above listed models are capable of is that of two helium atoms. As it is well-known, these atoms interact by the so-called dispersive (or van der Waals) interaction. This effect cannot be described by APSG as it cannot account for inter-geminal interaction due to its construction. This limitation of the APSG model is clearly visible on fig. (3.3) (the very small minimum at around 3.3 Å is because of Basis-Set Superposition Error [93]). From fig. (3.3) it can also be seen that introduction of the different interaction subspaces leads to the formation of two subsets within the curves that are close to each other in terms of absolute energy. In order to distinguish between the different calculation methods, it is worth looking at the graph showing the energy difference between the absolute energies and the Full CI energy (figure (3.4)). From this curve the following interaction subspaces can be grouped based on the relative energies being close to each other:

- DISP\_SP, DISP\_SP\_1gem
- DISP\_SP\_SD
- DISP\_SP\_SD\_1gem
- DISP\_SP\_SD\_SPSD, DISP\_SP\_SPSD
- DISP\_SP\_SPSD\_1gem, DISP\_SP\_SD\_SPSD\_1gem

As expected, in the non-interacting case ( $R \rightarrow \infty$ ) the difference between the absolute energies and the full CI energies converges to zero. APSG itself is a full CI for non-interacting heliums, so it is no wonder that our numerical calculations also lead to the same result.

By looking at figs. (3.3) and (3.4), it can be stated that all out of the 8 different types of interaction subspaces are capable of describing the  $R \rightarrow \infty$  case and 6 of them (containing the single and double excitations from the determinants making up the reference and/or single and double excitations from the spin-polarized states) are also able to describe the equilibrium state belonging to the energy minimum. In this respect single and double excitations are definitely needed to correctly describe the potential energy curve from a quantitative point as well. Introducing these states to the interactive subspace, the energy difference relative to the FCI energy stays in the  $10^{-8}$  a.u. range for the complete energy curve.

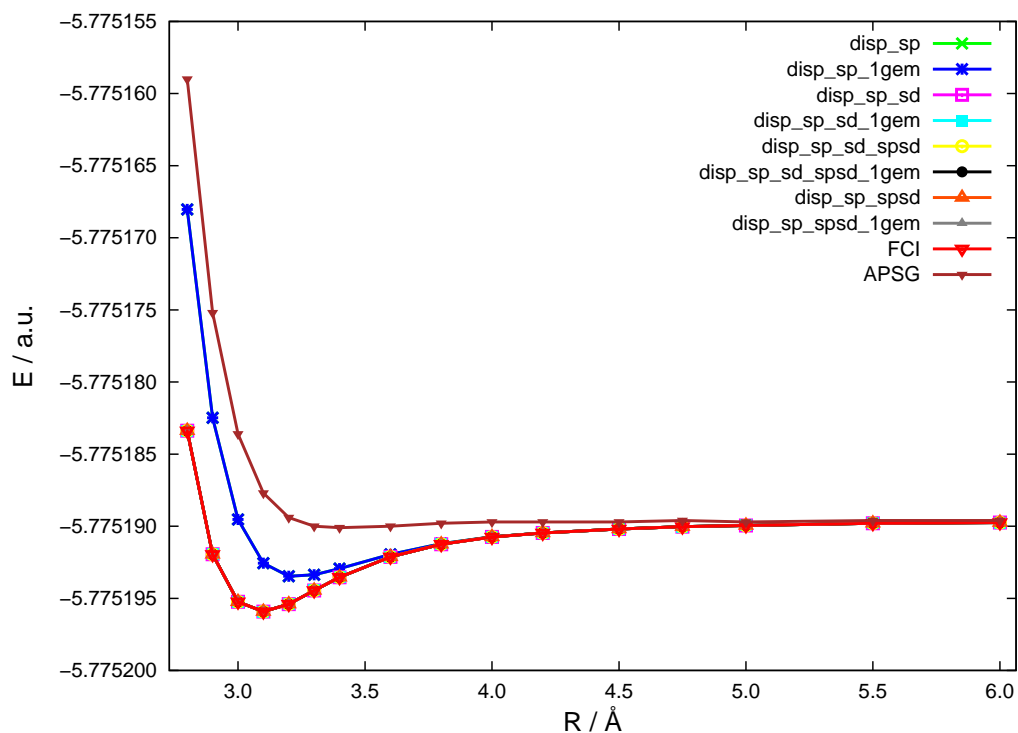


Figure 3.3: Absolute energies of the different methods for He...He interaction in cc-pVDZ basis set.

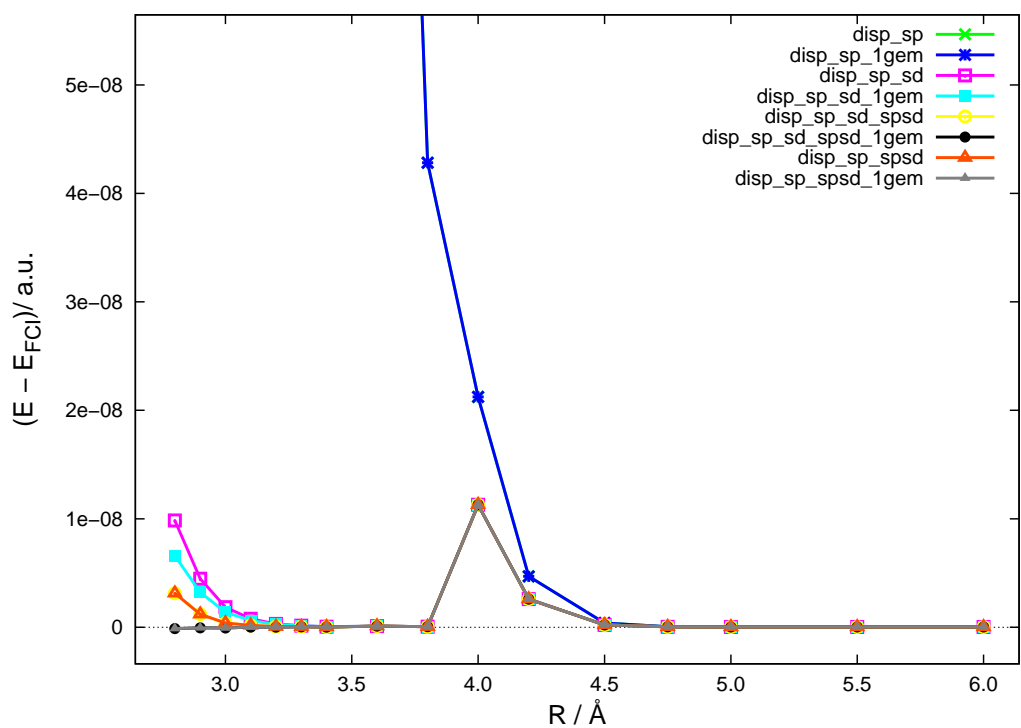


Figure 3.4: Energies of the different methods for He...He interaction relative to the Full CI energy in cc-pVDZ basis set.

### 3.2.4 Water symmetric dissociation - dispersive amplitudes

For our next example, we are going to choose the symmetric dissociation of water, which means a simultaneous stretching of both OH bonds of a water molecule. The H-O-H angle will be kept constant during this process ( $110.6^\circ$ ). In the calculations, 6-31G basis set and frozen core approximation will be applied for the water molecule, this results in 4 geminals altogether, the bonding geminals having 4 orbitals in their subsets while the non-bonding have only 2.

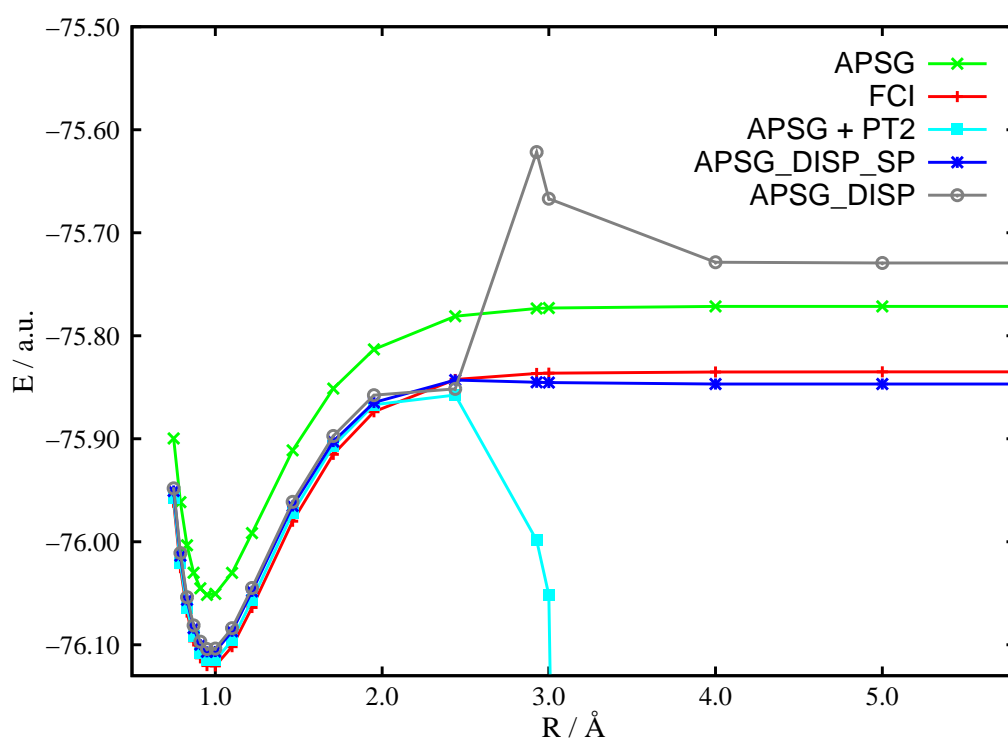


Figure 3.5: Water symmetric dissociation in 6-31G basis set with bond angle fixed at  $\angle$  (H-O-H) =  $110.6^\circ$ . APSG wave function is assumed as reference. Frozen core approximation is applied. The APSG reference has 4 orbitals on the bonding and 2 on the non-bonding geminals. See text for acronyms.

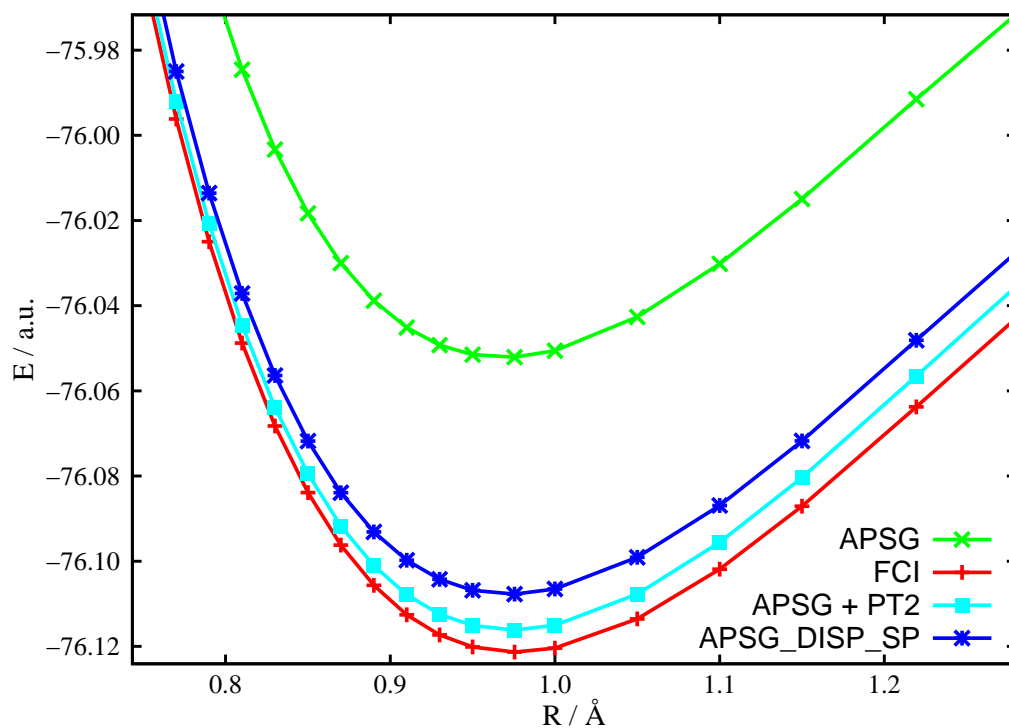


Figure 3.6: Water symmetric dissociation around equilibrium in 6-31G basis set. See text for acronyms and the legend of fig. (3.5) for other particulars.

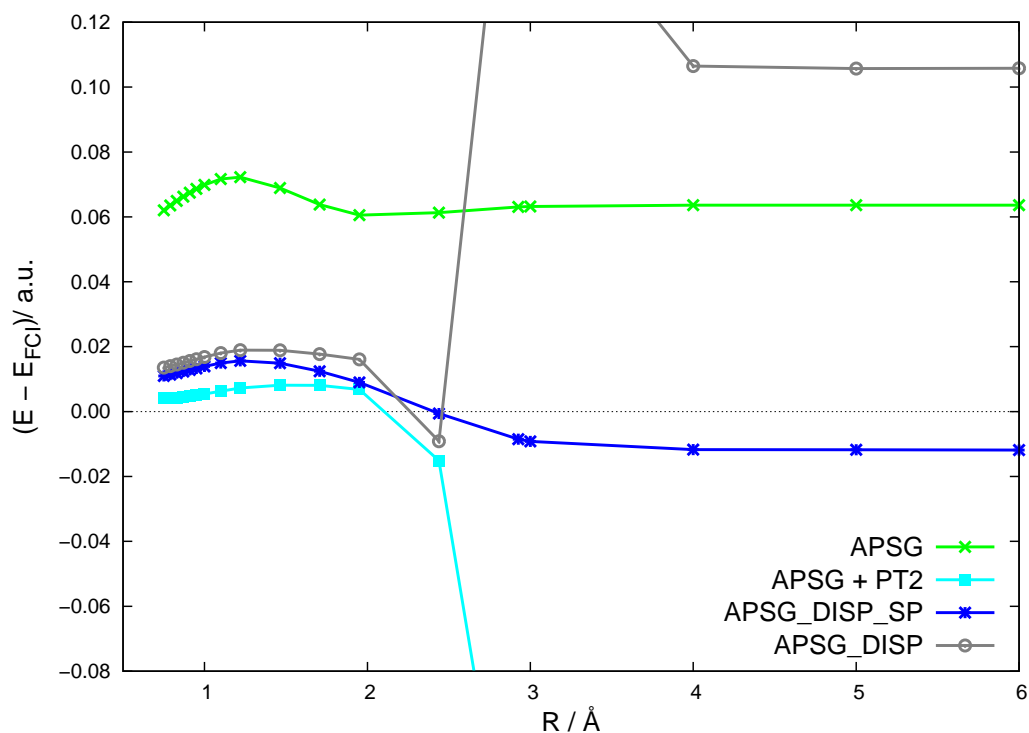


Figure 3.7: Energy differences between absolute energies of the different methods and frozen core full CI calculations for water symmetric dissociation in 6-31G basis set. See text for acronyms and the legend of fig. (3.5) for other particulars.



Fig. (3.5) shows why the introduction of the Linearized Coupled Cluster Theory with dispersive excitations can be used for describing the symmetric dissociation instead of Perturbation Theory. The disturbing divergence of the PT curve (APSG + PT2) disappears when applying LCC theory (APSG\_DISP\_SP). It has to be noted though that inclusion of spin-polarized states is inevitable, otherwise, one also arrives at a divergent energy curve (APSG\_DISP). On fig. (3.6) it is clearly displayed that at equilibrium distance both PT and LCC give a qualitatively correct description of the energy. On the other hand, a good quantitative description of the dissociation process cannot be obtained just by including the dispersive states in the interacting space, the FCI error falls in the 0.01 a.u range which is not acceptable for a good method (see fig. (3.7)). Including other states in the interaction space will be the topic of the next subsection.

### 3.2.5 Water symmetric dissociation - role of charge transfer states

In this subsection we are going to discuss the effect of charge transfer states. These are created as single and double excitations of the determinants making up the APSG (in this special case the GVB) wave function (the set of these excited determinants are denoted as SD) and also the single and double excitations of the determinants found in the spin-polarized states (short notation for the set of these states will be SPSD).

The same chemical process is investigated here as well, namely the symmetric dissociation of a water molecule. We use two basis sets for these calculations, namely the 6-31G and 6-31G\* basis sets. As the time needed to perform a successful calculation increases very sharply as we increase the basis set and the size of the geminal subsets, we chose the GVB (General Valence Bond) wave function as a reference. This corresponds to an APSG wave function where the dimension of the subsets for bonding geminals is two, while for the remaining core and non-bonding geminals it is 1. We also applied frozen core approximation.

For the 6-31G basis set, the following list of the different interaction subspaces can be written in decreasing order regarding absolute energy in the dissociated case (from fig. (3.8)):

- DISP\_SP\_SD\_SPSD; DISP\_SP\_SD\_SPSD\_1gem
- DISP\_SP; DISP\_SP\_1gem

- DISP\_SD; DISP\_SD\_1gem; DISP\_SD\_SPSD; DISP\_SD\_SPSD\_1gem
- DISP\_SP\_SPSD; DISP\_SP\_SPSD\_1gem
- DISP\_SP\_SD; DISP\_SP\_SD\_1gem

From this we can draw the conclusion that in the dissociated region, inclusion of the one-geminal excitations does not have too much effect on the absolute energies. This trend seems to be true for the 'transition region' (the set of energy values between the dissociated state and the equilibrium state) as well. Fig. (3.9) shows the energy difference between the absolute energies and the Frozen Core Full CI calculation. Unfortunately, most of the interaction subspaces result in a diverging curve in this transition region. The only exception is the calculation with the Dispersive Linear Coupled Cluster Theory (DISP\_SP) and the calculation containing the one-geminal excitations also besides the dispersive states (DISP\_SP\_1gem). In the equilibrium region, these interaction subspaces lead to no significant energy gains though. That is the reason why these calculations are not even indicated on fig. (3.10), they simply lie too far from Frozen Core Full CI in terms of energy. The other methods seem to be satisfying in this region. One important difference between the equilibrium calculations and those corresponding to the dissociated state, is that here one-geminal excitations do count, the single and double excitations from the spin-polarized states (SPSD) are those which do not have too much effect on the outcome of the calculations.

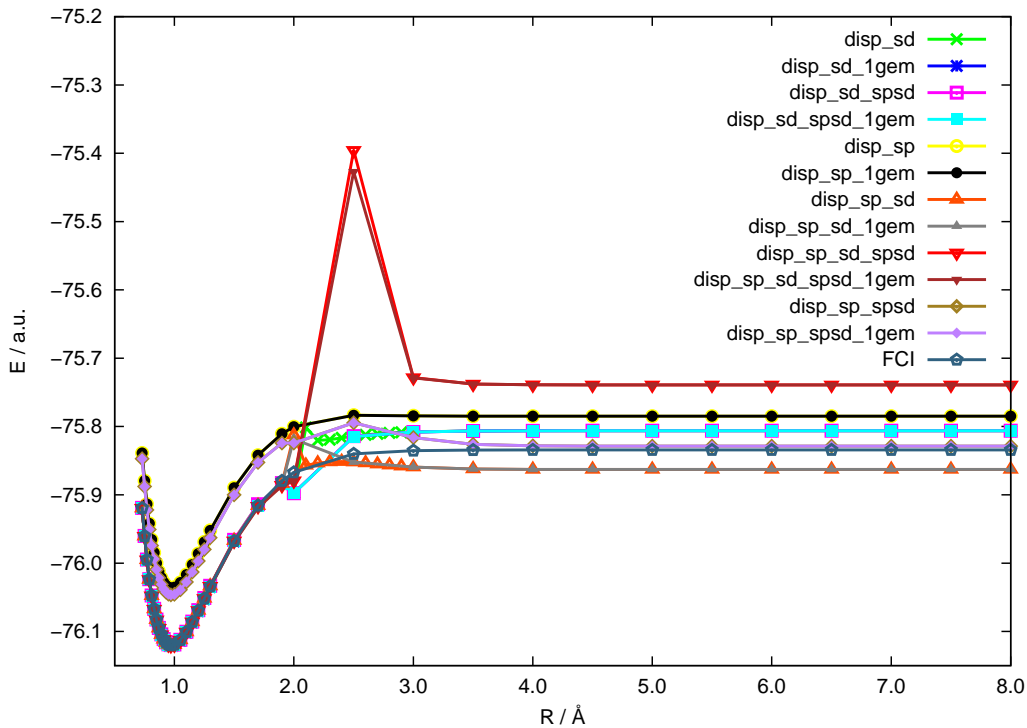


Figure 3.8: Water symmetric dissociation in 6-31G basis set calculated with different interaction spaces. H-O-H bond angle fixed at  $\angle(\text{H-O-H}) = 110.6^\circ$ . GVB wavefunction is assumed as reference and frozen core approximation is applied. The GVB reference has 2 orbitals on the bonding geminals, the unassigned orbitals consist the virtual geminal space. See text for acronyms.

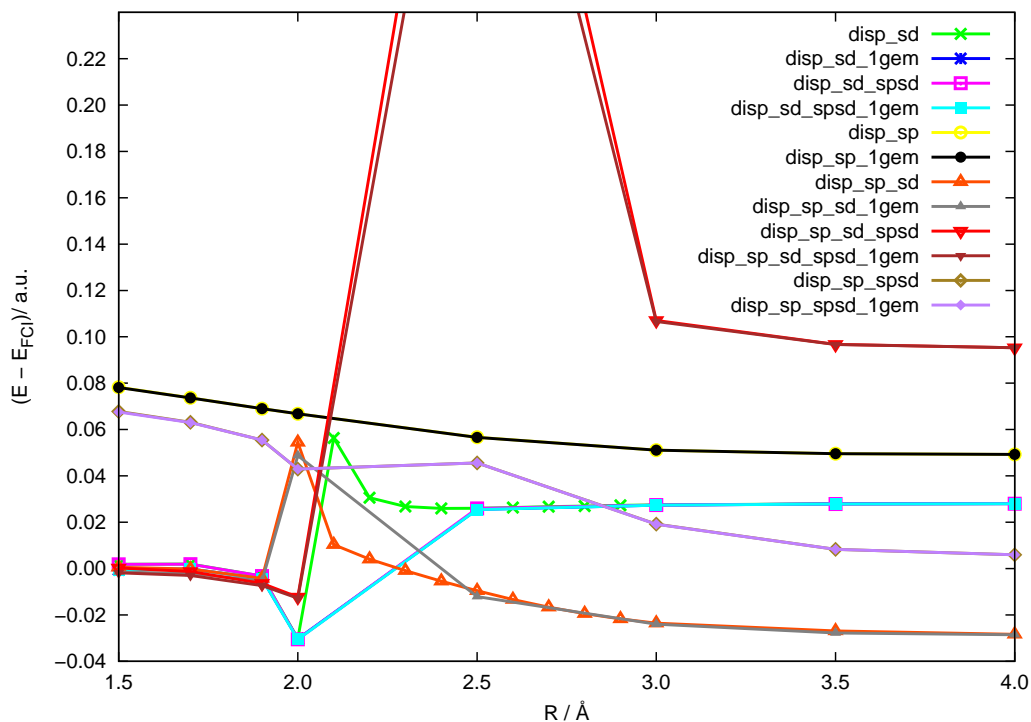


Figure 3.9: Energy difference with respect to the full CI energy calculated with different interaction spaces for water symmetric dissociation in 6-31G basis set (divergent region). See text for acronyms and legend of fig. (3.8) for other particulars.

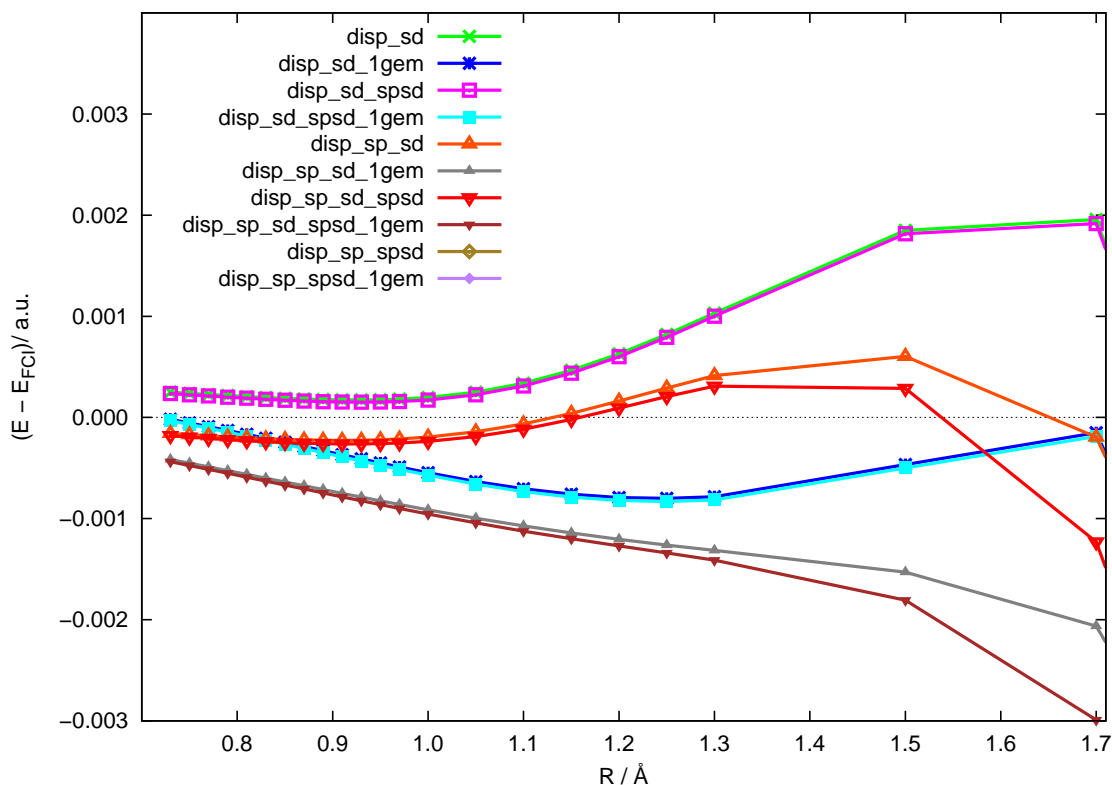


Figure 3.10: Energy difference with respect to the full CI energy calculated with different interaction spaces for water symmetric dissociation in 6-31G basis set (equilibrium region). See text for acronyms and legend of fig. (3.8) for other particulars.

The same calculations were carried out using 6-31G\* basis set. By looking at fig. (3.11) one can notice a striking difference between these curves and those present on fig. (3.8). The energy curve belonging to DISP\_SP\_SD and DISP\_SP\_SD\_1gem has a much lower value in the dissociated case than the one experienced with the non-polarised 6-31G basis set. It is also true in this case as well that DISP\_SP and DISP\_SP\_1gem are the only interaction subspaces that lead to non-divergent energy curves for the full bond length region (see fig.(3.12)). Adding extra charge transfer states however lead to better results in the equilibrium region (see fig. 3.13).

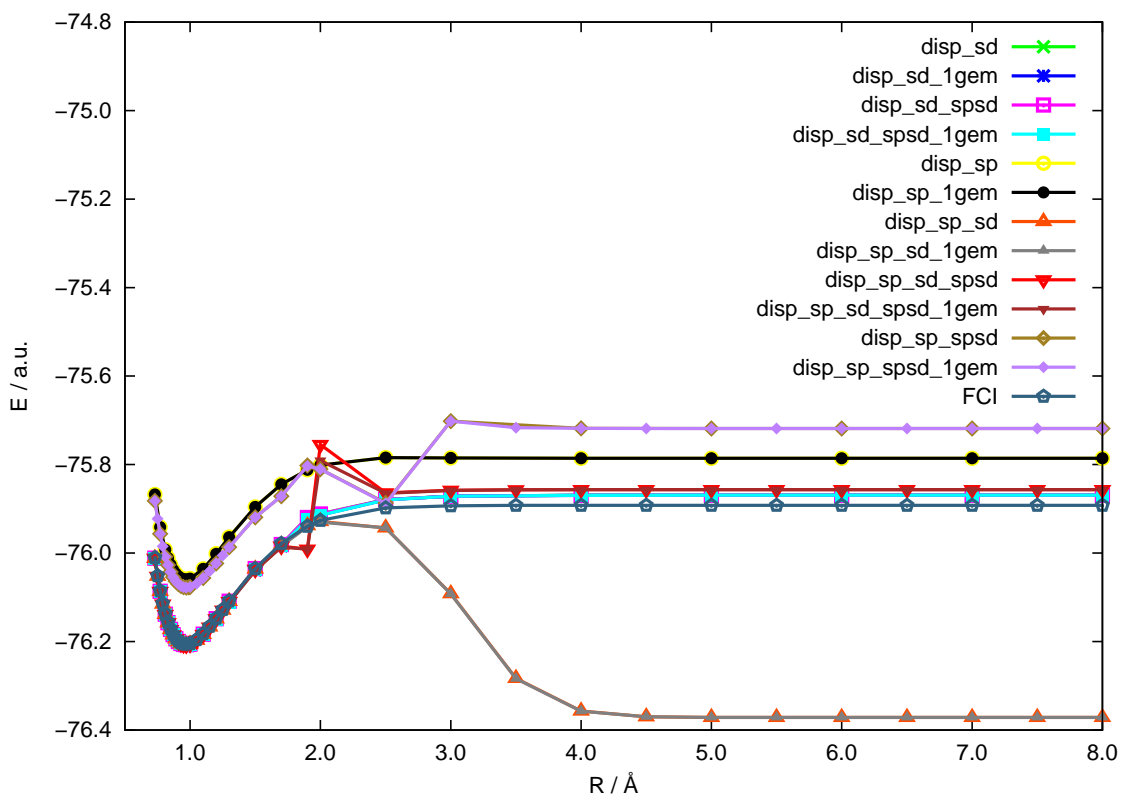


Figure 3.11: Water symmetric dissociation in 6-31G\* basis set calculated with different interaction spaces. H-O-H bond angle fixed at  $\angle(\text{H-O-H}) = 110.6^\circ$ . GVB wavefunction is assumed as reference and frozen core approximation is applied. The GVB reference has 2 orbitals on the bonding geminals, the unassigned orbitals consist the virtual geminal space. See text for acronyms.

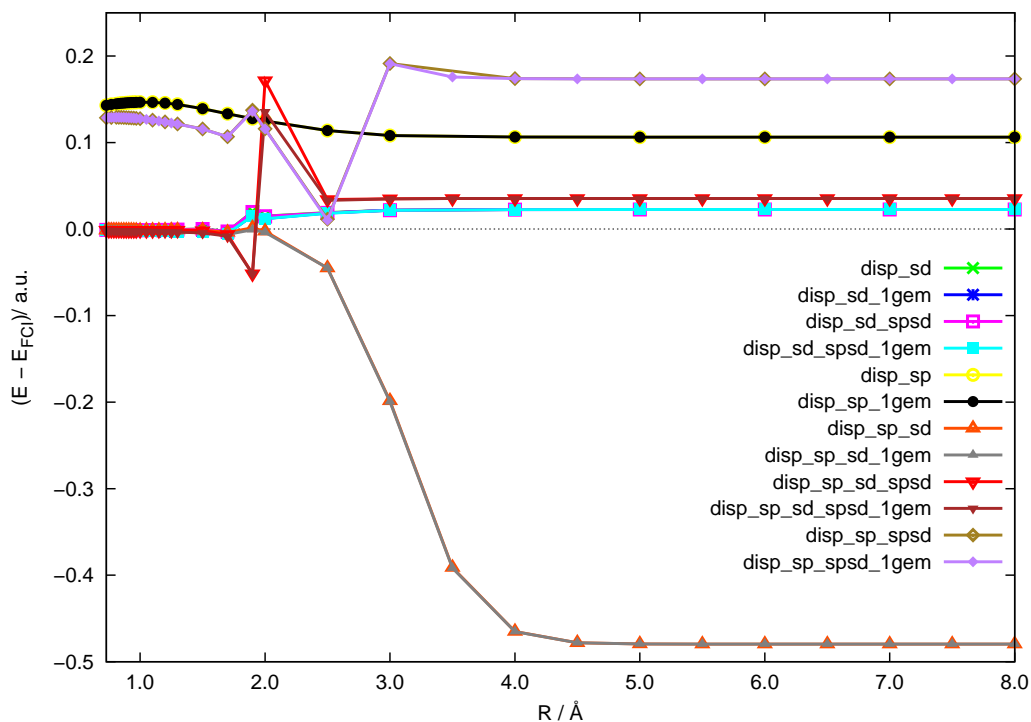


Figure 3.12: Energy difference with respect to the full CI energy calculated with different interaction spaces for water symmetric dissociation in 6-31G\* basis set. See text for acronyms and legend of fig. (3.11) for other particulars.

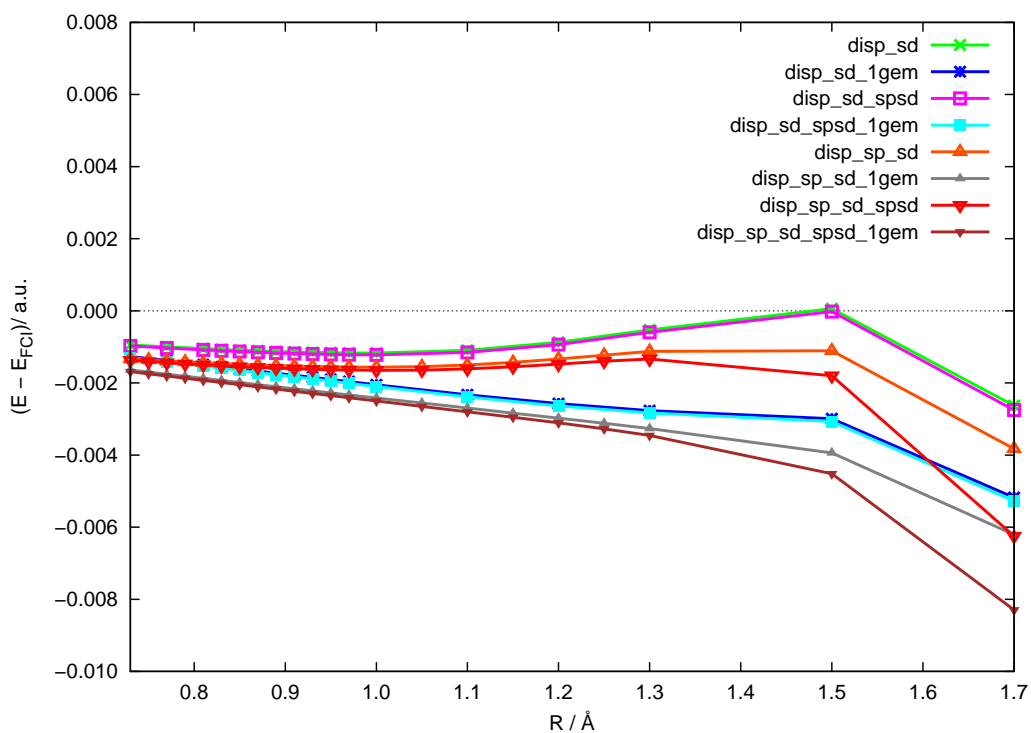


Figure 3.13: Energy difference with respect to the full CI energy calculated with different interaction spaces for water symmetric dissociation in 6-31G\* basis set (equilibrium region). See text for acronyms and legend of fig. (3.11) for other particulars.

Correct description of the transition region is a challenging task for APSG-based LCC, according to our results above. Investigation of the origin of this phenomenon became the subject of a subsequent PhD project. We refer to the thesis by P. Jeszenszki [94] for an analysis and possible solutions of the problem.

### 3.2.6 Non-linear corrections to the APSG-based Coupled Cluster Theory

In this subsection we are going to discuss the non-linear terms of the Coupled Cluster amplitude equations. Suggested by the name, we are going to arrive at non-linear equations which are to be solved in an iterative manner. In general, these equations have to be derived for each chosen interaction subspace. As the most critical part of the geminal perturbation theory was including dispersive states in the first-order interacting subspace, we only derived the forthcoming equations for these states.

Returning to the time-independent Schrödinger equation:

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\text{APSG}\rangle = E |\text{APSG}\rangle$$

$$(\hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2} [[\hat{H}, \hat{T}], \hat{T}] + \dots) |\text{APSG}\rangle = E |\text{APSG}\rangle$$

$$(\hat{H} + \hat{H}\hat{T} - \hat{T}\hat{H} + \frac{1}{2}(\hat{H}\hat{T}^2 - 2\hat{T}\hat{H}\hat{T} - \hat{T}^2\hat{H}) + \dots) |\text{APSG}\rangle = E |\text{APSG}\rangle$$

Expressing the cluster operator  $\hat{T}$  as

$$\hat{T} = \sum_{\substack{i,j \\ i < j}} \sum_r^{(i)} \sum_s^{(j)} t_{ij}^{rs} \psi_{ir}^+ \psi_{js}^+ \psi_{j0}^- \psi_{i0}^- = \sum_l t_l \hat{X}_l,$$

where  $\sum_l$  is a composite summation for  $\sum_{i,j}^{(i)} \sum_r^{(j)}$ ,  $t_l = t_{ij}^{rs}$  and  $\hat{X}_l = \psi_{ir}^+ \psi_{js}^+ \psi_{j0}^- \psi_{i0}^-$ . Projecting

by  $\langle \text{APSG} | \psi_{k0}^+ \psi_{h0}^+ \psi_{kp}^- \psi_{hq}^- = \langle \text{APSG} | \hat{X}_m^\dagger$  from the left one arrives at

$$\begin{aligned} & \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} | \text{APSG} \rangle + \sum_l t_l \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_l | \text{APSG} \rangle - \sum_l t_l \langle \text{APSG} | \underbrace{\hat{X}_m^\dagger \hat{X}_l}_{\delta_{ml}} \hat{H} | \text{APSG} \rangle \\ & + \frac{1}{2} \sum_{n,l} t_n t_l \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_n \hat{X}_l | \text{APSG} \rangle - \sum_{n,l} t_n t_l \langle \text{APSG} | \underbrace{\hat{X}_m^\dagger \hat{X}_n}_{\delta_{mn}} \hat{H} \hat{X}_l | \text{APSG} \rangle \\ & - \frac{1}{2} \sum_{n,l} t_n t_l \underbrace{\langle \text{APSG} | \underbrace{\hat{X}_m^\dagger \hat{X}_n \hat{X}_l}_{\delta_{mn}} \hat{H} | \text{APSG} \rangle}_{=0} = 0 \end{aligned}$$

Rewriting the obtained expression:

$$\begin{aligned} & \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} | \text{APSG} \rangle + \sum_l t_l \left( \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_l | \text{APSG} \rangle - \delta_{ml} E_{\text{APSG}} \right) \\ & + \frac{1}{2} \sum_{n,l} t_n t_l \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_n \hat{X}_l | \text{APSG} \rangle - \sum_l t_m t_l \langle \text{APSG} | \hat{H} \hat{X}_l | \text{APSG} \rangle = 0 \end{aligned}$$

In the third term disconnected terms can turn up if  $\hat{X}_m^\dagger$  coincides with either  $\hat{X}_n$  or  $\hat{X}_l$ . These two cases altogether are removed by the last term. So after removing the disconnected terms, we'll have:

$$\begin{aligned} & \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} | \text{APSG} \rangle + \sum_l t_l \left( \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_l | \text{APSG} \rangle - \delta_{ml} E_{\text{APSG}} \right) + \\ & + \frac{1}{2} \sum_{n,l} t_n t_l \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_n \hat{X}_l | \text{APSG} \rangle_c = 0 \end{aligned}$$

After rearranging the equation, we arrive at a system of non-linear equations that is to be solved:

$$\begin{aligned} & \sum_l t_l \left( \underbrace{\langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_l | \text{APSG} \rangle - \delta_{ml} E_{\text{APSG}}}_{A_{ml}} \right) = \\ & - \underbrace{\langle \text{APSG} | \hat{X}_m^\dagger \hat{H} | \text{APSG} \rangle}_{d_m} - \frac{1}{2} \underbrace{\sum_{n,l} t_n t_l \langle \text{APSG} | \hat{X}_m^\dagger \hat{H} \hat{X}_n \hat{X}_l | \text{APSG} \rangle_c}_{x_m(t)} \end{aligned} \quad (3.13)$$

In compact notations:

$$\mathbf{A} \mathbf{t} = -\mathbf{d} - \mathbf{x}(\mathbf{t}) \quad (3.14)$$

The expressions for the linear and non-linear terms in the above equation are fully implemented in a Fortran code. Eq. (3.14) is solved in an iterative manner, in the initial step  $\mathbf{x}(\mathbf{t}) = 0$  is assumed. Then vector  $\mathbf{t}_0$  obtained in that way is used for calculating  $\mathbf{x}(\mathbf{t})_0$  which is later subtracted from vector  $-\mathbf{d}$ . Following this pattern, vector  $\mathbf{x}(\mathbf{t}_{i-1})$  is always used for calculating  $\mathbf{t}_i$ . This iteration is performed until  $|\mathbf{t}_{i-1} - \mathbf{t}_i|$  drops below a certain threshold.



### 3.2.7 Numerical example for the non-linear correction

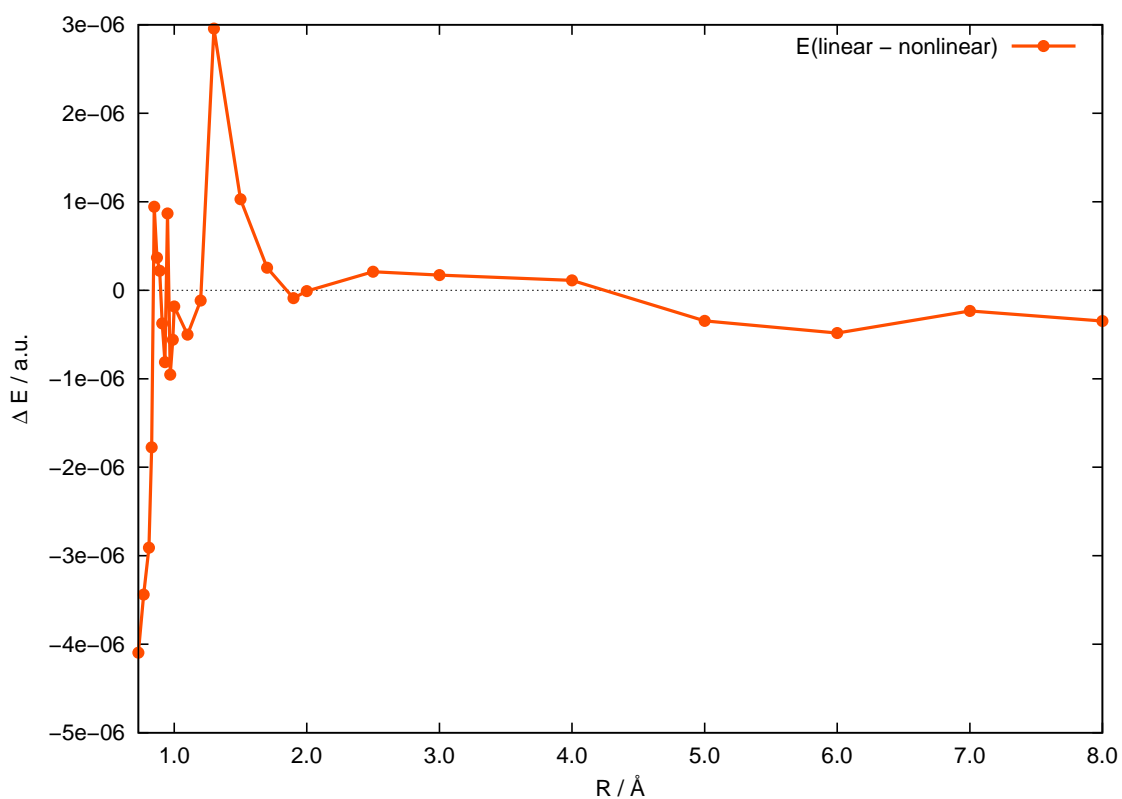


Figure 3.14: Energy difference between the linear and non-linear approximations for the Coupled Cluster amplitude equations for the dissociation of HF in 6-31G\* basis set. Frozen core approximation was used in the treatment of the fluorine atom.

Fig. (3.14) shows the difference in the absolute energies calculated with the linear approximation of the amplitude equations and also by adding the non-linear corrections and iterating the equations respectively. It can be said that non-linear corrections do not bring a significant change to the general shape of the potential curve, energy corrections lie in the  $10^{-6}$  a.u. range. In the repulsive region of the potential curve, this correction seems to be greater if we consider the absolute value, although there is no observable tendency in the sign of this correction, it is oscillating around 0. As we approach the equilibrium and dissociated region of the energy spectrum, the curve smooths out and the value of the non-linear correction becomes more predictable.

### 3.3 Diagrammatic approach in corrected geminal theories

Diagrammatics is a widely used technique in basically all areas of theoretical physics where the notion of second-quantization comes into play. In this section, we are going to show that the energy expression of (3.6) and the (3.13) amplitude equation can also be written in the form of diagrams. This formulation was inspired by the work of Paldus et al. [10, 11]. These authors laid down the general principles of diagrammatic techniques considering many different types of geminal wave functions (not just strongly orthogonal ones). However, we feel that for some reason their work remained unnoted (maybe it is because of the strictly theoretical nature of their papers). Regarding strongly orthogonal geminals, the authors went as far as writing down the APSG energy expression with diagrammatic notation but not any further. In this section, we make an attempt at creating a diagrammatic formulation of the Multi-reference Coupled Cluster Theory introduced previously. But before that, let us briefly summarize (and also simplify) the work of Paldus et al.

#### 3.3.1 Diagrammatic treatment of APSG

As mentioned in the introductory segment of the forthcoming section, the first thing we would like to do is putting down the diagrammatic formulation of the APSG energy expression and derive the corresponding diagrammatic rules. Let us remind ourselves once again to the second-quantized form of the Hamiltonian:

$$\hat{H} = \sum_{a,b} \sum_{m \in a} \sum_{n \in b} \sum_{\sigma} h_{mn} m_{\sigma}^{+} n_{\sigma}^{-} + \frac{1}{2} \sum_{a,b,c,d} \sum_{m \in a} \sum_{n \in b} \sum_{l \in c} \sum_{s \in d} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}$$

The APSG-energy is an expectation value:

$$E_{\text{APSG}} = \langle \text{APSG} | \hat{H} | \text{APSG} \rangle = \langle \text{vac} | \psi_{N}^{-} \dots \psi_{1}^{-} \hat{H} \psi_{1}^{+} \dots \psi_{N}^{+} | \text{vac} \rangle$$

The Hamiltonian in the energy-expression can be (and because of the extensive simplification this manipulation causes, should be) written in the already known form described in subsection (2.3.5). Namely, the Hamiltonian can be rewritten on the basis of the number of geminal indices each Hamiltonian-fragment contains:

$$\hat{H} = \sum_a \hat{H}_a + \sum_{\substack{a,b \\ a \neq b}} \hat{H}_{ab} + \sum_{\substack{a,b,c \\ a \neq b \neq c}} \hat{H}_{abc} + \sum_{\substack{a,b,c,d \\ a \neq b \neq c \neq d}} \hat{H}_{abcd}$$

A fragment-type can contain several different fragments which can be categorized by their electron-conserving properties regarding the different geminals. These Hamiltonian fragments can be visualized by using simple directed graphs already introduced in subsection (2.3.5) (Partitioning of the Hamiltonian). In this form of visualization, dots correspond to geminals and arrows to creation-annihilation operator-pairs. Two rows of dots are drawn, the bottom row represents those geminals from which the electrons are excited (full circles) while the top row (empty circles) is for geminals on which the creation operators act. The number of columns is also an important factor in this diagram, it determines the 'geminal-number' of the Hamiltonian-fragment. If a full circle and an empty circle are in the same column, they represent the same geminal, hence a vertical arrow is drawn for excitations conserving the electron-number within the geminal. Tilted arrows are drawn when those excitations are taken into consideration which do not conserve the electron-number of the geminals.

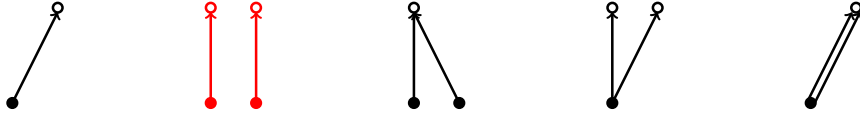
It is not difficult to see that Hamiltonian-fragments with strictly vertical arrows give actual contribution to the APSG-energy. This is a consequence of strong orthogonality. If the geminals found in the ket APSG are excited by the Hamiltonian in such a way that the number of electrons is not conserved in any of the geminals, then this excited wave function cannot be contracted with the bra APSG, simply because the number of creation operators in the different subsets will not be equal to that of the annihilation operators.

The schematic representation of the different Hamiltonian-fragments are collected here (highlighting the geminal electron-number conserving ones by red):

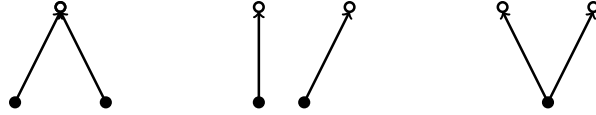
$\hat{H}_a :$



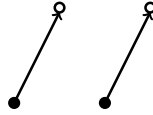
$\hat{H}_{ab} :$



$\hat{H}_{abc} :$



$\hat{H}_{abcd} :$



When deriving the APSG-energy expression, it is enough to consider the fragments having only vertical lines (highlighted by red), this gives rise to the following 'effective Hamiltonian':

$$\begin{aligned} \hat{H} \longrightarrow \hat{H}' = & \sum_a \sum_{m,n \in a} \sum_{\sigma} h_{mn} m_{\sigma}^{+} n_{\sigma}^{-} + \frac{1}{2} \sum_a \sum_{m,n,l,s \in a} \sum_{\sigma, \sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \\ & + \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} \sum_{m,s \in a} \sum_{n,l \in b} \sum_{\sigma, \sigma'} ([mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} - [mn|sl] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}) \end{aligned} \quad (3.15)$$

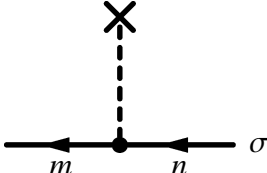
The four terms above can be assigned to easily interpretable interactions:

1. Sum of kinetic energies of electrons inside a geminal and their interaction with the nuclei.

2. Sum of repulsive Coulomb-energies between the two electrons inside the geminals.
3. Sum of repulsive Coulomb-energies between two electrons belonging to different geminals.
4. Sum of exchange energies between two electrons belonging to different geminals and having the same spin.

After this brief revision of the underlying algebra, we now turn our attention to a diagrammatic formulation of the APSG energy expression. The diagrams worked out below are more elaborated objects than those used for representing Hamiltonian-fragments. Our aim is to work out diagrams matching each term of the APSG energy, involving one-electron and two-electron integrals and also geminal coefficients.

First we deal with the Hamiltonian. The diagrammatic form of the second-quantized Hamiltonian is widely used in all subfields of many-body theory, the one-electron Hamiltonian reading

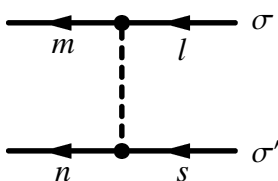
$$\sum_{m,n} \sum_{\sigma} h_{mn} m_{\sigma}^{+} n_{\sigma}^{-}$$


Here the arrow coming out of the vertex corresponds to the creation operator ( $m_{\sigma}^{+}$ ). On the other hand, the arrow going into the vertex represents the annihilation operator ( $n_{\sigma}^{-}$ ). The cross connected with a dashed line to the vertex describes the one-electron integral  $h_{mn}$ , first index of the matrix is always the outgoing arrow label, while the second index refers to the label of the incoming arrow. As we use spatial orbitals, each arrow has a definite spin ( $\sigma$ ) as well, the spin along a line is always the same. Summations through the spatial orbital indices and the spin have to be performed.

If a one-electron vertex is present in any of the diagrams, the following rule should be applied:

**The one-electron interaction vertex corresponds to a  $h_{mn}$  one-electron integral where  $m$  is the label of the line coming out of the vertex and  $n$  is the label of the line going into the vertex.**

The two-electron Hamiltonian is described as

$$\frac{1}{2} \sum_{m,n,l,s} \sum_{\sigma,\sigma'} [mn|ls] m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-}$$


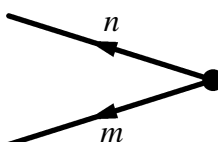
Outgoing arrows from the vertices refer to creation operators ( $m_{\sigma}^{+}, n_{\sigma'}^{+}$ ), while incoming arrows represent annihilation operators ( $s_{\sigma}^{-}, l_{\sigma'}^{-}$ ) in this case as well. Each line has a distinct spin label ( $\sigma, \sigma'$ ). The dashed line denotes  $\frac{1}{2}$  of a two-electron integral with the following label convention:

$$[top\ out\ down\ out\ | \ top\ in\ down\ in]$$

Similarly to the one-electron case, if a two-electron interaction vertex is found in any of the diagrams the following rule should be applied:

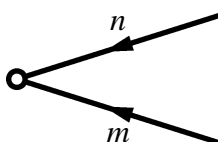
**The two-electron interaction vertex brings in a  $\frac{1}{2}[mn|ls]$  multiplication factor, where the integral fulfills the [top out down out | top in down in] label convention.**

In order to obtain the diagrammatic form of the APSG-energy, the geminals themselves should be represented as well graphically. To express our respect and gratitude towards the work of Paldus et al., we decided to keep their notation for this purpose. Accordingly, the vertices belonging to the geminal creation operators (found in the ket APSG, |APSG>) are:

$$\psi_i^{+} = \sum_{m,n \in i} C_{mn}^i m_{\alpha}^{+} n_{\beta}^{+}$$


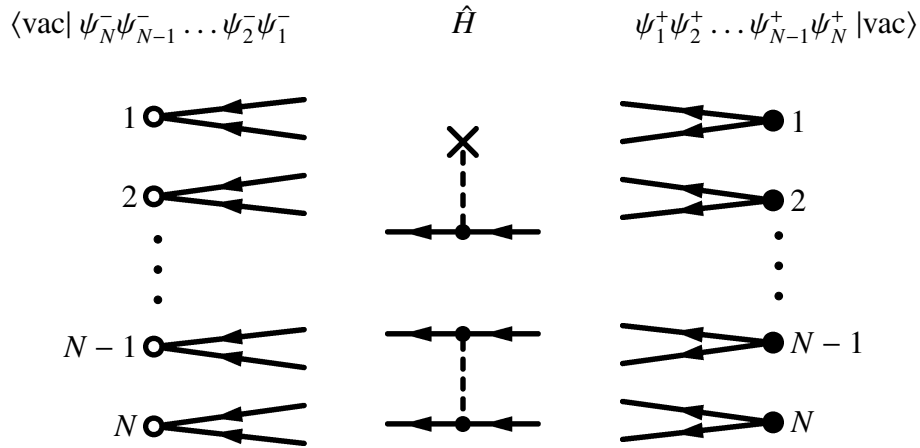
In this case, full circle represents the coefficient matrix element and the outgoing lines symbolise the creation operators, the arrow of the  $\alpha$  orbitals points downward while that of the  $\beta$  orbitals points upwards. A summation with respect to the spatial orbitals is performed.

Similarly, vertices for geminal annihilation operators in the bra wave function,  $\langle \text{APSG} |$ :

$$\psi_i^{-} = \sum_{m,n \in i} C_{mn}^{i*} n_{\beta}^{-} m_{\alpha}^{-}$$


In this case the empty circle symbolises the complex conjugate of the geminal coefficient matrix element and arrows go into the vertex as we are talking about annihilation operators. The arrow corresponding to the  $\alpha$  orbital goes into the vertex below the horizontal axis, while the  $\beta$ -arrow goes into the vertex above it. We are always working with real coefficient matrices, so forming the complex conjugate here is only a formal step.

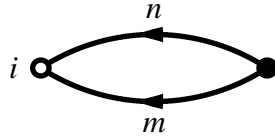
These elements should be used to find out the different components of the energy expression. Drawing up only the skeletons, the vertices and legs taking part in the interaction can be written as:



Note that both in this schematic representation of the skeletons and in the upcoming diagrams as well, a geminal is identified by a row. This means that if a full circle and an empty circle is placed in a row, the two geminals are expanded in the same subspace of orbitals. It does not imply that they are equal, as we will see examples in the future that the excitation level of geminals on the left side and right side is different.

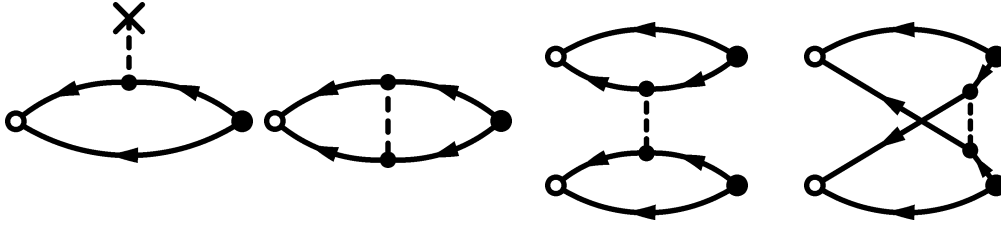
We wish to obtain a diagrammatic representation of the APSG energy, therefore it is enough to use the effective Hamiltonian  $\hat{H}'$  of eq. (3.15). This effective Hamiltonian contains only one-geminal and two-geminal Hamiltonian fragments. This means that if we choose any of the two geminals from the bra and the ket vectors, the remaining  $N-2$  will contract with itself. Each of these contractions are equivalent to the norm-squared of the geminals (which is 1 in case of normalised geminals), hence it only gives a 1x multiplication factor for each geminal-pair, which can be safely omitted from the final formula:

$$\langle \text{vac} | \psi_i^- \psi_i^+ | \text{vac} \rangle = \sum_{m,n \in i} C_{mn}^{i0} C_{mn}^{i0*} = 1$$



This is the easiest possible diagram that can be drawn by using the geminal vertices. Comparing the formula for the squared norm and the graphical representation, it is easy to figure out the diagrammatic rules for this simple case. First the skeleton of the vertices belonging to the geminal creation operators (full circle) and the geminal annihilation operator (empty circle) should be considered. Then one should label the lines connecting the circles with letters. One should assign  $C_{mn}^{i0}$  to the full circle and  $C_{mn}^{i0*}$  to the empty circle and make summations according to the existing labels.

After omitting the unnecessary terms, a simplified diagrammatics comes into play. As a consequence, another summation index emerges. For all the upcoming diagrams we will have to sum up for the geminal indices as well. As there are four components in the simplified 'effective Hamiltonian', four different skeletons can be drawn altogether:



Now that we have the skeletons, the diagrammatic rules should be established. In order to do this, some sample matrix elements are calculated and the rules are obtained by means of inductive reasoning. The mathematical form of the one-electron energy according to eq. (3.15) is

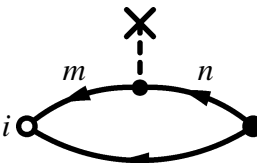
$$\begin{aligned}
E_1 &= \sum_i \sum_{m,n \in i} \sum_{\sigma} h_{mn} \langle \text{vac} | \psi_{i0}^- m_{\sigma}^+ n_{\sigma}^- \psi_{i0}^+ | \text{vac} \rangle \\
&= \sum_i \sum_{m,n \in i} \sum_{\sigma} h_{mn} \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{i0} C_{\rho\lambda}^{i0} \langle \text{vac} | \tau_{\beta}^- \kappa_{\alpha}^- m_{\sigma}^+ n_{\sigma}^- \rho_{\alpha}^+ \lambda_{\beta}^+ | \text{vac} \rangle \\
&= \sum_i \sum_{m,n \in i} \sum_{\sigma} h_{mn} \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{i0} C_{\rho\lambda}^{i0} (\delta_{\sigma\alpha} \delta_{\kappa m} \delta_{\rho n} \delta_{\tau\lambda} + \delta_{\sigma\beta} \delta_{\tau m} \delta_{\lambda n} \delta_{\kappa\rho}) \\
&= \sum_i \sum_{m,n \in i} h_{mn} \sum_{a \in i} (C_{ma}^{i0} C_{na}^{i0} + C_{am}^{i0} C_{an}^{i0}) = \sum_i \sum_{m,n \in i} h_{mn} (P_{nm}^{i0,\alpha} + P_{nm}^{i0,\beta}), \tag{3.16}
\end{aligned}$$



where the  $\mathbf{P}^{i0,\alpha}$  and  $\mathbf{P}^{i0,\beta}$  density matrices are introduced. This can be simplified further if we take into consideration that the ground state geminal is singlet, thus its coefficient matrix is symmetric ( $C_{ma}^{i0} = C_{am}^{i0} \Rightarrow \mathbf{P}^{i0,\alpha} = \mathbf{P}^{i0,\beta}$ ) and after the introduction of the full density matrix corresponding to the ground state of the  $i$ -th geminal ( $\mathbf{P}^{i0} = \mathbf{P}^{i0,\alpha} + \mathbf{P}^{i0,\beta}$ ):

$$E_1 = \sum_i \sum_{m,n \in i} h_{mn} P_{nm}^{i0}$$

However, we prefer the form of eq. (3.16) as it is more general, and takes us closer to the general application of diagrammatic rules (later on excited geminal states will appear of course in which the symmetry condition cannot be used for simplification purposes in all cases). So at this point the one-electron energy expression and its diagrammatic equivalent is

$$\sum_i \sum_{m,n \in i} h_{mn} (P_{nm}^{i0,\alpha} + P_{nm}^{i0,\beta})$$


Please note that we have left the restriction of the line with  $\alpha$  spin being always below the imaginary horizontal line connecting the two geminal vertices. If we stuck to this condition, we would always have to draw twice as much diagrams, in this case one with the Hamiltonian vertex pointing downwards. Instead we keep just one of them and take care of the other use case in the form of a diagrammatic rule. On this small example we have already managed to obtain a small set of these rules:

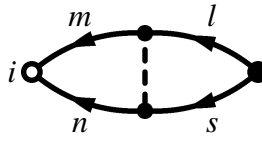
- Consider a skeleton containing the vertices belonging to the geminal creation operators (full circle), geminal annihilation operators (empty circle) and the one-electron interaction vertex.
- Label the lines connecting different vertices (except for those connecting a geminal vertex with another geminal vertex) with letters and label the different geminals as well.
- Make summations according to all labels.
- A closed loop containing a one-electron Hamiltonian corresponds to a sum of  $\mathbf{P}_{nm}^{i,\alpha}$  and  $\mathbf{P}_{nm}^{i,\beta}$  density matrix elements, where the first index corresponds to the label of the

line going into the one-electron vertex, while the second index is reserved for the line coming out of the same one-electron vertex. The density-matrix can be a transition density matrix as well if the geminal states are different in the left and right geminal vertices (we will see examples for this later on). If it is not stated otherwise (no state label is present), both geminals are in their ground states.

Next, we are going to obtain the diagrammatic rule needed to describe the electron-electron interaction energy within the geminal. The formula for the energy of the electron-electron repulsion is

$$\begin{aligned}
E_{2,1} &= \frac{1}{2} \sum_i \sum_{m,n,l,s \in i} \sum_{\sigma, \sigma'} [mn|ls] \langle \text{vac} | \psi_{i0}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^+ \psi_{i0}^+ | \text{vac} \rangle \\
&= \frac{1}{2} \sum_i \sum_{m,n,l,s \in i} \sum_{\sigma, \sigma'} [mn|ls] \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{i0} C_{\rho\lambda}^{i0} \langle \text{vac} | \tau_{\beta}^- \kappa_{\alpha}^+ m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^+ \rho_{\alpha}^+ \lambda_{\beta}^+ | \text{vac} \rangle \\
&= \frac{1}{2} \sum_i \sum_{m,n,l,s \in i} \sum_{\sigma, \sigma'} [mn|ls] \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{i0} C_{\rho\lambda}^{i0} (\delta_{\sigma\alpha} \delta_{\sigma'\beta} \delta_{m\kappa} \delta_{n\tau} \delta_{s\lambda} \delta_{l\rho} + \delta_{\sigma\beta} \delta_{\sigma'\alpha} \delta_{m\tau} \delta_{n\kappa} \delta_{s\rho} \delta_{l\lambda}) \\
&= \frac{1}{2} \sum_i \sum_{m,n,l,s \in i} [mn|ls] (C_{mn}^{i0} C_{ls}^{i0} + C_{nm}^{i0} C_{sl}^{i0}) = \frac{1}{2} \sum_i \sum_{m,n,l,s \in i} [mn|ls] (\Gamma_{ml,ns}^{\alpha,\beta,i0} + \Gamma_{ml,ns}^{\beta,\alpha,i0}),
\end{aligned}$$

where the  $\Gamma^{\alpha,\beta,i0}$  and  $\Gamma^{\beta,\alpha,i0}$  matrices are the second-order density matrices corresponding to the ground state of geminal  $i$ . In this respect the electron-electron repulsion energy within the geminal and its diagrammatic equivalent is

$$\begin{aligned}
&\frac{1}{2} \sum_i \sum_{m,n,l,s \in i} [mn|ls] (\Gamma_{ml,ns}^{\alpha,\beta,i0} + \Gamma_{ml,ns}^{\beta,\alpha,i0}) \\
&= \frac{1}{2} \sum_i \sum_{m,n,l,s \in i} [mn|ls] \Gamma_{ml,ns}^{i0}
\end{aligned}$$


Here the sum of the two second-order density matrices,  $\Gamma^{i0}$  is introduced. Our new diagrammatic rule is

A closed loop containing both interaction vertices of the two-electron operator and only one geminal label results in the appearance of a second-order density matrix element,  $\Gamma_{ml,ns}^{i0} = \Gamma_{ml,ns}^{\alpha,\beta,i0} + \Gamma_{ml,ns}^{\beta,\alpha,i0} = C_{mn}^{i0} C_{ls}^{i0} + C_{nm}^{i0} C_{sl}^{i0}$ . The  $m$  and  $n$  labels refer to

the lines coming out of the interaction vertices, while  $l$  and  $s$  denote the incoming lines. Labels  $m, l$  and  $n, s$  have the same spin (the two groups of labels correspond to opposite spins of course)

We now take a closer look at the inter-geminal interaction energy which will bring about the existence of a new diagrammatic rule (a *sign rule* to be more exact). The  $\langle \text{APSG} | m_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} | \text{APSG} \rangle$  expectation value should be analyzed where the different creation - annihilation operator pairs belong to two different geminal subsets. There are only two possibilities for this:

1.  $m_{\sigma}^{+}, l_{\sigma'}^{-} \in i$  and  $n_{\sigma}^{+}, s_{\sigma'}^{-} \in j$
2.  $m_{\sigma}^{+}, s_{\sigma'}^{-} \in i$  and  $n_{\sigma}^{+}, l_{\sigma'}^{-} \in j$

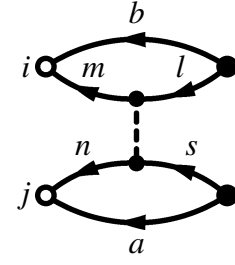
The expectation value for case 1. reads

$$\begin{aligned}
& \langle \psi_{i0}^{-} \psi_{j0}^{-} \mathbf{m}_{\sigma}^{+} n_{\sigma'}^{+} s_{\sigma}^{-} l_{\sigma'}^{-} \psi_{i0}^{+} \psi_{j0}^{+} \rangle = \langle \psi_{i0}^{-} m_{\sigma}^{+} l_{\sigma'}^{-} \psi_{i0}^{+} \rangle \langle \psi_{j0}^{-} n_{\sigma}^{+} s_{\sigma'}^{-} \psi_{j0}^{+} \rangle \\
& = \sum_{\mu, \nu, \lambda, \gamma \in i} \sum_{\kappa, \tau, \rho, \eta \in j} C_{\mu\nu}^{i0} C_{\lambda\gamma}^{i0} C_{\kappa\tau}^{j0} C_{\rho\eta}^{j0} \langle \underbrace{\psi_{\beta}^{-} \mu_{\alpha}^{-} m_{\sigma}^{+} l_{\sigma'}^{-} \lambda_{\alpha}^{+} \gamma_{\beta}^{+}}_{\text{geminal } i} \rangle \langle \underbrace{\tau_{\beta}^{-} \kappa_{\alpha}^{-} n_{\sigma}^{+} s_{\sigma'}^{-} \rho_{\alpha}^{+} \eta_{\beta}^{+}}_{\text{geminal } j} \rangle \\
& = \sum_{b \in i} (C_{mb}^{i0} C_{lb}^{i0} + C_{bm}^{i0} C_{bl}^{i0}) \sum_{a \in j} (C_{na}^{j0} C_{sa}^{j0} + C_{an}^{j0} C_{as}^{j0}) = (P_{lm}^{i0, \alpha} + P_{lm}^{i0, \beta}) (P_{sn}^{j0, \alpha} + P_{sn}^{j0, \beta})
\end{aligned}$$

The new diagrammatic rule which can be introduced at this point is very similar to the one in connection with the one-electron vertex, namely:

**A closed loop containing one vertex of a two-electron Hamiltonian corresponds to a sum of  $P_{nm}^{i, \alpha}$  and  $P_{nm}^{i, \beta}$  density matrix elements, where the first index corresponds to the label of the line going into the two-electron vertex, while the second index is reserved for the line coming out of the same two-electron vertex. The density-matrix can be a transition density matrix as well if the geminal states are different in the left and right geminal vertices (we will see examples for this later on). If it's not stated otherwise, both geminals are in their ground states. The state indices of the geminal coefficient matrices are introduced next to the geminal label in the general case.**

$$\begin{aligned} & \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,l \in i} \sum_{n,s \in j} [mn|ls] \sum_{b \in i} (C_{mb}^{i0} C_{lb}^{i0} + C_{bm}^{i0} C_{bl}^{i0}) \sum_{a \in j} (C_{na}^{j0} C_{sa}^{j0} + C_{an}^{j0} C_{as}^{j0}) \\ &= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,l \in i} \sum_{n,s \in j} [mn|ls] (P_{lm}^{i0,\alpha} + P_{lm}^{i0,\beta}) (P_{sn}^{j0,\alpha} + P_{sn}^{j0,\beta}) \end{aligned}$$



In the 2. case listed above, the expectation value of the two-electron operator with the APSG wave function can be written as

$$\begin{aligned} & \langle \psi_{i0}^- \psi_{j0}^- \mathbf{m}_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{i0}^+ \psi_{j0}^+ \rangle = - \langle \psi_{i0}^- m_{\sigma}^+ s_{\sigma'}^- \psi_{i0}^+ \rangle \langle \psi_{j0}^- n_{\sigma}^+ l_{\sigma'}^- \psi_{j0}^+ \rangle \\ &= - \sum_{\mu,\nu,\lambda,\gamma \in i} \sum_{\kappa,\tau,\rho,\eta \in j} C_{\mu\nu}^{i0} C_{\lambda\gamma}^{i0} C_{\kappa\tau}^{j0} C_{\rho\eta}^{j0} \langle \boxed{\gamma_{\beta}^- \mu_{\alpha}^- m_{\sigma}^+ s_{\sigma'}^- \lambda_{\alpha}^+ \gamma_{\beta}^+} \rangle \langle \boxed{\tau_{\beta}^- \kappa_{\alpha}^- n_{\sigma}^+ l_{\sigma'}^- \rho_{\alpha}^+ \eta_{\beta}^+} \rangle \\ &= - \sum_{a \in j} \sum_{b \in i} (C_{mb}^{i0} C_{sb}^{i0} C_{na}^{j0} C_{la}^{j0} + C_{bm}^{i0} C_{bs}^{i0} C_{an}^{j0} C_{al}^{j0}) = -(P_{sm}^{i0,\alpha} P_{ln}^{j0,\alpha} + P_{sm}^{i0,\beta} P_{ln}^{j0,\beta}) \end{aligned}$$

Note that the matrix elements belonging to different subsets are interconnected through the  $\sigma$  and  $\sigma'$  spin indices, the spin distribution in the first bracket determines that of in the second bracket. This causes the appearance of only two terms in the linear combination of geminal matrix element products. As we only have to perform just one switch in the order of second-quantized operators (namely the order of  $n_{\sigma'}^+$  and  $s_{\sigma}^-$  are reversed), a negative sign appears in the equation. Graphically this is manifested by the intersection of the  $m$  and  $n$  lines. The new rule regarding the overall sign of the diagram:

**The overall sign of a diagram will be  $(-1)^i$ , where  $i$  is the number of line intersections.**

The other rule that appears is in connection with the coefficient matrix elements (or one-electron density matrix elements from a different perspective):

**If a closed loop of lines contains both interaction vertices of the two-electron Hamiltonian and involves two geminals (it is only possible with an intersection of lines in case of strongly orthogonal geminals), the sum of density matrix element products appear, namely  $\mathbf{P}_{sm}^{i,\alpha} \mathbf{P}_{ln}^{j,\alpha} + \mathbf{P}_{sm}^{i,\beta} \mathbf{P}_{ln}^{j,\beta}$ , where  $s$  and  $m$  are the lines coming out and going into the geminal vertex  $i$  respectively, and in case of the  $l$  and  $n$  labels it is**

similar but the orbital labels belong to the subset assigned to geminal  $j$ . Depending on the geminal states in the ket and bra function, excited states of geminals may also show up resulting in the appearance of transition density matrices.

Using the new rules and the others presented before, finally we can evaluate the last term of the APSG energy expression, the exchange term:

$$\begin{aligned}
& -\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] \sum_{a \in j} \sum_{b \in i} (C_{ma}^{j0} C_{sa}^{j0} C_{nb}^{i0} C_{lb}^{i0} + C_{am}^{j0} C_{as}^{j0} C_{bn}^{i0} C_{bl}^{i0}) \\
& = -\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] (P_{sm}^{i0,\alpha} P_{ln}^{j0,\alpha} + P_{sm}^{i0,\beta} P_{ln}^{j0,\beta})
\end{aligned}$$

### 3.3.2 Diagrammatic treatment of the dispersive Coupled Cluster correction

In this subsection we would like to move forward with elaborating the diagrammatics of the geminal-based Coupled Cluster Theory elaborated in subsection (3.2). At first, we deal only with the linear correction, for which the energy expression is

$$\begin{aligned}
E = \langle \text{APSG} | \hat{H} \hat{T} | \text{APSG} \rangle &= \sum_{\substack{i,j \\ i < j}} \sum_p^{(j)} \sum_q^{(i)} t_{ij}^{pq} \langle \text{APSG} | \hat{H} \psi_{iq}^+ \psi_{jp}^+ \psi_{i0}^- \psi_{j0}^- | \text{APSG} \rangle \\
&= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_p^{(j)} \sum_q^{(i)} t_{ij}^{pq} \langle \text{APSG} | \hat{H} \psi_{iq}^+ \psi_{jp}^+ \psi_{i0}^- \psi_{j0}^- | \text{APSG} \rangle, \tag{3.17}
\end{aligned}$$

where  $t_{ij}^{pq} = t_{ji}^{qp}$  and the double appearance of the amplitudes is introduced because of simplification purposes.  $\sum_q^{(i)}$  runs along the excited states of geminal  $i$ . The Linearized Coupled Cluster correction of eq. (3.17) still contains only those terms which preserve the particle-number of the geminals (see eq. (3.15)). Moreover, only the two-geminal dispersive Hamiltonian contributes since the cluster operator is also a two-geminal operator.

The detailed energy expression is written as

$$\begin{aligned} & \frac{1}{4} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} [mn|ls] \sum_{\substack{k,h \\ k \neq h}} \sum_p \sum_q^{(k)} \sum_q^{(h)} t_{kh}^{pq} \langle \psi_{N0}^- \cdots \psi_{10}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{kp}^+ \psi_{hq}^+ \psi_{h0}^- \psi_{k0}^- \psi_{10}^+ \cdots \psi_{N0}^+ \rangle \\ & - \frac{1}{4} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} [mn|sl] \sum_{\substack{k,h \\ k \neq h}} \sum_p \sum_q^{(k)} \sum_q^{(h)} t_{kh}^{pq} \langle \psi_{N0}^- \cdots \psi_{10}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{kp}^+ \psi_{hq}^+ \psi_{h0}^- \psi_{k0}^- \psi_{10}^+ \cdots \psi_{N0}^+ \rangle \end{aligned}$$

There are two possibilities for the geminal indices to match, either  $i = h$  and  $j = k$  or  $i = k$  and  $j = h$ . If we perform a  $p \leftrightarrow q$  notation change in either of the cases and take into account that  $t_{ij}^{pq} = t_{ji}^{qp}$ , it is easily noticed that the two cases lead to the same result.

This means that the energy-expression can be simplified as

$$\begin{aligned} & \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} \sum_p \sum_q^{(i)} \sum_q^{(j)} t_{ij}^{pq} \left( [mn|ls] \langle \psi_{N0}^- \cdots \psi_{10}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{ip}^+ \psi_{jq}^+ \psi_{j0}^- \psi_{i0}^- \psi_{10}^+ \cdots \psi_{N0}^+ \rangle \right. \\ & \quad \left. - [mn|sl] \langle \psi_{N0}^- \cdots \psi_{10}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{ip}^+ \psi_{jq}^+ \psi_{j0}^- \psi_{i0}^- \psi_{10}^+ \cdots \psi_{N0}^+ \rangle \right) \end{aligned}$$

The two matrix elements in the above energy expression can be evaluated by the already known rules (note though that in this case transition density matrices appear), the first matrix element being:

$$\begin{aligned} & \sum_{\sigma, \sigma'} \langle \psi_{i0}^- \psi_{j0}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{jp}^+ \psi_{iq}^+ \rangle = - \sum_{\sigma, \sigma'} \langle \psi_{i0}^- m_{\sigma}^+ s_{\sigma}^- \psi_{iq}^+ \rangle \langle \psi_{j0}^- n_{\sigma'}^+ l_{\sigma'}^- \psi_{jp}^+ \rangle \\ & = - \sum_{a \in i} \sum_{b \in j} (C_{ma}^{i0} C_{sa}^{iq} C_{nb}^{j0} C_{lb}^{jp} + C_{am}^{i0} C_{as}^{iq} C_{bn}^{j0} C_{bl}^{jp}) = -( {}^i R_{sm}^{q0, \alpha} {}^j R_{ln}^{p0, \alpha} + {}^i R_{sm}^{q0, \beta} {}^j R_{ln}^{p0, \beta} ) \\ & = - \sum_{\sigma} {}^i R_{sm}^{q0, \sigma} {}^j R_{ln}^{p0, \sigma}, \end{aligned}$$

where  ${}^i R_{sm}^{q0, \sigma}$  denotes the transition density matrix which for spins  $\alpha$  and  $\beta$  read

$${}^i R_{sm}^{q0, \alpha} = \sum_{a \in i} C_{ma}^{i0} C_{sa}^{iq} \quad {}^i R_{sm}^{q0, \beta} = \sum_{a \in i} C_{am}^{i0} C_{as}^{iq}$$

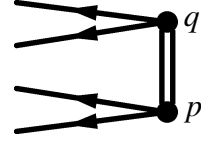
The second matrix element is

$$\sum_{\sigma, \sigma'} \langle \psi_{i0}^- \psi_{j0}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{jp}^+ \psi_{iq}^+ \rangle = - \langle \psi_{i0}^- m_{\sigma}^+ s_{\sigma}^- \psi_{iq}^+ \rangle \langle \psi_{j0}^- n_{\sigma'}^+ l_{\sigma'}^- \psi_{jp}^+ \rangle$$

$$\begin{aligned}
&= - \sum_{b \in i} \sum_{a \in j} (C_{mb}^{i0} C_{sb}^{iq} + C_{bm}^{i0} C_{bs}^{iq}) (C_{na}^{j0} C_{la}^{jp} + C_{an}^{j0} C_{al}^{jp}) = -(iR_{sm}^{q0,\alpha} + iR_{sm}^{q0,\beta})(jR_{ln}^{p0,\alpha} + jR_{ln}^{p0,\beta}) \\
&= - \sum_{\sigma} iR_{sm}^{q0,\sigma} \sum_{\sigma'} jR_{ln}^{p0,\sigma'}
\end{aligned}$$

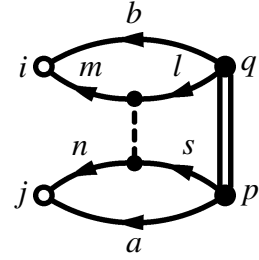
We can perform an  $s \leftrightarrow l$  notation change both in the  $[mn|ls]$  integral and in the  $(C_{mb}^{i0} C_{sb}^{iq} + C_{bm}^{i0} C_{bs}^{iq})(C_{na}^{j0} C_{la}^{jp} + C_{an}^{j0} C_{al}^{jp})$  expression. After introducing a diagrammatic notation for the cluster operator (only the excited state geminals and the amplitude should be represented somehow)

$$\hat{T} = \sum_{\substack{i,j \\ i < j}} t_{ij}^{qp} \psi_{iq}^+ \psi_{jp}^+ \psi_{j0}^- \psi_{i0}^-$$

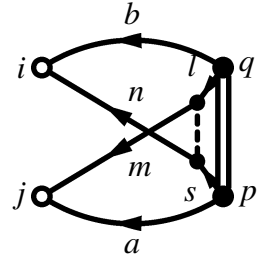


the two terms of the energy-expression can be written as

$$\begin{aligned}
&\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,l \in i} \sum_{n,s \in j} \sum_p \sum_q^{(j)} \sum_q^{(i)} t_{ij}^{qp} [mn|ls] \sum_{b \in i} \sum_{a \in j} \\
&(C_{mb}^{i0} C_{lb}^{iq} + C_{bm}^{i0} C_{bl}^{iq}) (C_{na}^{j0} C_{sa}^{jp} + C_{an}^{j0} C_{as}^{jp}) \\
&= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,l \in i} \sum_{n,s \in j} \sum_p \sum_q^{(j)} \sum_q^{(i)} t_{ij}^{qp} [mn|ls] \sum_{\sigma} iR_{lm}^{q0,\sigma} \sum_{\sigma'} jR_{sn}^{p0,\sigma'}
\end{aligned}$$



$$\begin{aligned}
&-\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{n,l \in i} \sum_{m,s \in j} \sum_p \sum_q^{(j)} \sum_q^{(i)} t_{ij}^{qp} [mn|ls] \sum_{b \in i} \sum_{a \in j} \\
&(C_{ma}^{j0} C_{sa}^{jp} C_{nb}^{i0} C_{lb}^{iq} + C_{am}^{j0} C_{as}^{jp} C_{bn}^{i0} C_{bl}^{iq}) \\
&= -\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{n,l \in i} \sum_{m,s \in j} \sum_p \sum_q^{(j)} \sum_q^{(i)} t_{ij}^{qp} [mn|ls] \sum_{\sigma} iR_{ln}^{q0,\sigma} jR_{sm}^{p0,\sigma}
\end{aligned}$$



We've just observed the appearance of yet another diagrammatic rule:

**The double plain lines in the diagram represent the cluster amplitude  $t_{ij}^{pq}$  and a summation should be carried out for the p and q excited geminal states in the two geminals.**

So far we have only dealt with energy-expressions. We've already noticed the appearance of a new type of vertex when the LCC energy has been discussed, namely the one responsible for representing the amplitude. Now we turn our attention to the amplitude equations of the geminal-based Multi-reference Coupled Cluster theory. The amplitude equations obtained by a linear truncation of the BCH-expansion:

$$\langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{H} | \text{APSG} \rangle = \langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{T} \hat{H} | \text{APSG} \rangle - \langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{H} \hat{T} | \text{APSG} \rangle, \quad (3.18)$$

where the operator used for projection is

$$\hat{E}_{kh}^{pq\dagger} = \psi_{k0}^+ \psi_{h0}^+ \psi_{kp}^- \psi_{hq}^-$$

which is the adjoint of the excitation operator appearing in the dispersive cluster operator of eq. (3.11). The different terms of the linear amplitude equation (3.18) can also be expressed in diagrammatic form. The only thing needed for that is having a diagrammatic representation of the adjoint operator  $\hat{E}_{kh}^{pq\dagger}$ . In our notation, it will be represented by the following vertex (it is enough to represent the excited states here as well, just like in the case of the cluster operator):

$$\hat{E}_{kh}^{pq\dagger} = \psi_{k0}^+ \psi_{h0}^+ \psi_{kp}^- \psi_{hq}^-$$


The inhomogeneous vector in the above amplitude equations is

$$\langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{H} | \text{APSG} \rangle$$

or in its more detailed form:

$$\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} [mn|ls] \langle \psi_{N0}^- \cdots \psi_{10}^- \psi_{h0}^+ \psi_{k0}^+ \psi_{kp}^- \psi_{hq}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{10}^+ \cdots \psi_{N0}^+ \rangle$$

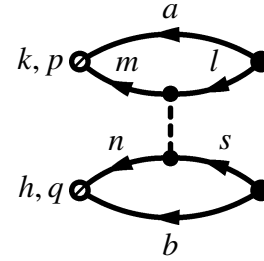
$$- \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} [mn|sl] \langle \psi_{N0}^- \cdots \psi_{10}^- \psi_{h0}^+ \psi_{k0}^+ \psi_{kp}^- \psi_{hq}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{10}^+ \cdots \psi_{N0}^+ \rangle$$



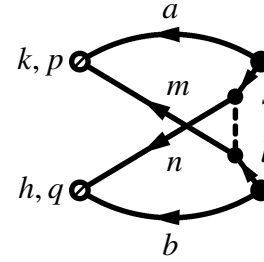
In these equations, we can only obtain nonzero values, if the geminal indices coincide ( $i, j$  with  $k, h$ ). There are two possibilities to achieve that, either  $i = k$  and  $j = h$  or  $i = h$  and  $j = k$ . After changing the labels in the second case to be similar to that of the first one and also utilising the symmetry of two-electron integrals, it can be proven that these two forms are equal.

The two terms of the inhomogeneous vector are thus

$$\begin{aligned} & \frac{1}{2} \cdot 2 \sum_{m,l \in k} \sum_{n,s \in h} [mn|ls] \sum_{a \in k} \sum_{b \in h} \\ & (C_{ma}^{kp} C_{la}^{k0} + C_{am}^{kp} C_{al}^{k0}) (C_{nb}^{hq} C_{sb}^{h0} + C_{bn}^{hq} C_{bs}^{h0}) \\ & = \sum_{m,l \in k} \sum_{n,s \in h} [mn|ls] \sum_{\sigma} {}^k R_{lm}^{0p,\sigma} \sum_{\sigma'} {}^h R_{sn}^{0q,\sigma'} \end{aligned}$$



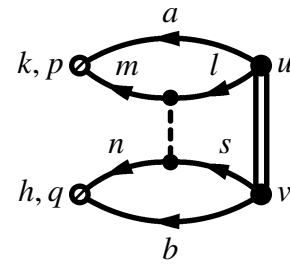
$$\begin{aligned} & -\frac{1}{2} \cdot 2 \sum_{m,s \in k} \sum_{n,l \in h} [mn|ls] \sum_{a \in k} \sum_{b \in h} \\ & (C_{ma}^{kp} C_{sa}^{k0} C_{nb}^{hq} C_{lb}^{h0} + C_{am}^{kp} C_{as}^{k0} C_{bn}^{hq} C_{bl}^{h0}) \\ & = - \sum_{m,s \in k} \sum_{n,l \in h} [mn|ls] \sum_{\sigma} {}^k R_{sm}^{0p,\sigma} {}^h R_{ln}^{0q,\sigma} \end{aligned}$$



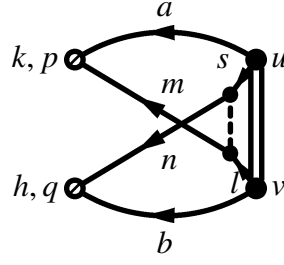
Another important term of eq. (3.18) is  $\langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{H} \hat{T} | \text{APSG} \rangle$  which has many components. These will be listed in the forthcoming pages.

The two most important terms are listed in the first place (they give the largest contribution numerically):

$$\begin{aligned} & \frac{1}{2} \cdot 2 \sum_{m,l \in k} \sum_{n,s \in h} [mn|ls] \sum_u^{(k)} \sum_v^{(h)} t_{kh}^{uv} \sum_{a \in k} \sum_{b \in h} \\ & (C_{ma}^{kp} C_{la}^{ku} + C_{am}^{kp} C_{al}^{ku}) (C_{nb}^{hq} C_{sb}^{hv} + C_{bn}^{hq} C_{bs}^{hv}) = \\ & = \sum_{m,l \in k} \sum_{n,s \in h} [mn|ls] \sum_u^{(k)} \sum_v^{(h)} t_{kh}^{uv} \sum_{\sigma} {}^k R_{lm}^{up,\sigma} \sum_{\sigma'} {}^h R_{sn}^{vq,\sigma'} \end{aligned}$$



$$\begin{aligned}
& -\frac{1}{2} \cdot 2 \sum_{m,s \in k} \sum_{n,l \in h} [mn|ls] \sum_u^{(k)} \sum_v^{(h)} t_{kh}^{uv} \sum_{a \in k} \sum_{b \in h} \\
& \left( C_{ma}^{kp} C_{sa}^{ku} C_{nb}^{hq} C_{lb}^{hv} + C_{am}^{kp} C_{as}^{ku} C_{bn}^{hq} C_{bl}^{hv} \right) = \\
& = - \sum_{m,s \in k} \sum_{n,l \in h} [mn|ls] \sum_u^{(k)} \sum_v^{(h)} t_{kh}^{uv} \sum_{\sigma} {}^k R_{sm}^{up,\sigma} {}^h R_{ln}^{vq,\sigma}
\end{aligned}$$



These terms are very similar to that of the inhomogeneous vector, notice the appearance of the 2x factor for example. The two different ways of merging the geminal indices in the Hamiltonian and the external vertices can also be performed in this case as well (the  $i, j$  geminal indices in the Hamiltonian should coincide with the  $k, h$  external geminal indices). These two possibilities lead to the same result (because of integral-symmetry) and accordingly the 2x factor arises.

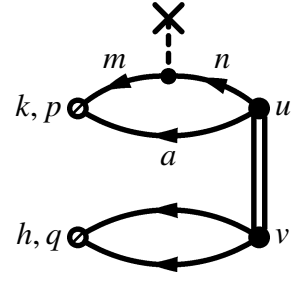
There are those terms as well in which only one external vertex (one of the excited geminals in  $\hat{E}_{kh}^{pq\dagger}$ ) interacts with the cluster operator through the Hamiltonian and the remaining excited geminal of  $\hat{T}$  simply coincides with the other excited geminal state in the  $\hat{E}_{kh}^{pq\dagger}$  operator:

$$\begin{aligned}
\sum_i \langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{H}_i \hat{T} | \text{APSG} \rangle &= \frac{1}{2} \sum_i \sum_{m,n \in i} \sum_{\sigma} \sum_{\substack{a,b \\ a \neq b}} \sum_u^{(a)} \sum_v^{(b)} t_{ab}^{uv} h_{mn} \langle \psi_{kp}^- \psi_{hq}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{au}^+ \psi_{bv}^+ \rangle \\
&+ \frac{1}{4} \sum_i \sum_{m,n,l,s \in i} \sum_{\sigma, \sigma'} \sum_{\substack{a,b \\ a \neq b}} \sum_u^{(a)} \sum_v^{(b)} t_{ab}^{uv} [mn|ls] \langle \psi_{kp}^- \psi_{hq}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{au}^+ \psi_{bv}^+ \rangle \\
&= \sum_{m,n \in k} \sum_{\sigma} \sum_u^{(k)} t_{kh}^{uq} h_{mn} \langle \psi_{kp}^- m_{\sigma}^+ n_{\sigma'}^- \psi_{ku}^+ \rangle + \sum_{m,n \in h} \sum_{\sigma} \sum_v^{(h)} t_{kh}^{pv} h_{mn} \langle \psi_{hq}^- m_{\sigma}^+ n_{\sigma'}^- \psi_{hv}^+ \rangle \\
&+ \frac{1}{2} \sum_{m,n,l,s \in k} \sum_{\sigma, \sigma'} \sum_u^{(k)} t_{kh}^{uq} [mn|ls] \langle \psi_{kp}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{ku}^+ \rangle + \frac{1}{2} \sum_{m,n,l,s \in h} \sum_{\sigma, \sigma'} \sum_v^{(h)} t_{kh}^{pv} [mn|ls] \langle \psi_{hq}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{hv}^+ \rangle
\end{aligned}$$

There will be 4 different terms altogether corresponding to four different diagrams:

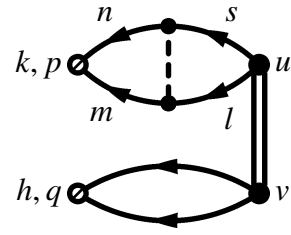
$$\sum_{m,n \in k} \sum_u^{(k)} h_{mn} t_{kh}^{uq} \sum_{a \in k} (C_{ma}^{kp} C_{na}^{ku} + C_{am}^{kp} C_{an}^{ku})$$

$$= \sum_{m,n \in k} \sum_u^{(k)} h_{mn} t_{kh}^{uq} \sum_{\sigma} {}^k R_{nm}^{up,\sigma}$$



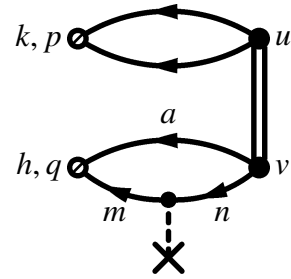
$$\frac{1}{2} \sum_{m,n,l,s \in k} \sum_u^{(k)} [mn|ls] t_{kh}^{uq} (C_{mn}^{kp} C_{ls}^{ku} + C_{nm}^{kp} C_{sl}^{ku})$$

$$= \frac{1}{2} \sum_{m,n,l,s \in k} \sum_u^{(k)} [mn|ls] t_{kh}^{uq} \sum_{\sigma} {}^k \Gamma_{ml,ns}^{\sigma,\bar{\sigma};pu}$$



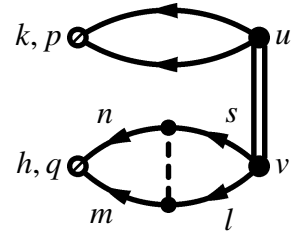
$$\sum_{m,n \in h} \sum_v^{(h)} h_{mn} t_{kh}^{pv} \sum_{a \in h} (C_{ma}^{hq} C_{na}^{hv} + C_{am}^{hq} C_{an}^{hv})$$

$$= \sum_{m,n \in h} \sum_v^{(h)} h_{mn} t_{kh}^{pv} \sum_{\sigma} {}^h R_{nm}^{vq,\sigma}$$



$$\frac{1}{2} \sum_{m,n,l,s \in h} \sum_v^{(h)} [mn|ls] t_{kh}^{pv} (C_{mn}^{hq} C_{ls}^{hv} + C_{nm}^{hq} C_{sl}^{hv})$$

$$= \frac{1}{2} \sum_{m,n,l,s \in h} \sum_v^{(h)} [mn|ls] t_{kh}^{pv} \sum_{\sigma} {}^h \Gamma_{ml,ns}^{\sigma,\bar{\sigma};qv}$$



In the above diagrams, the *second-order transition density matrix* has been introduced:

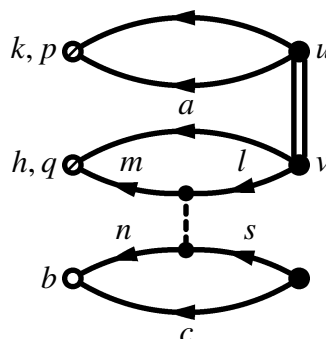
$$\sum_{\sigma} h \Gamma_{ml,ns}^{\sigma,\bar{\sigma};qv} = h \Gamma_{ml,ns}^{\alpha,\beta;qv} + h \Gamma_{ml,ns}^{\beta,\alpha;qv} = C_{mn}^{hq} C_{ls}^{hv} + C_{nm}^{hq} C_{sl}^{hv}$$

Upon analyzing the diagrams above on the basis of the different constant multipliers appearing based on the connection topology of the external vertices and the two-geminal two-electron operator, we can make up the following new diagrammatic rule:

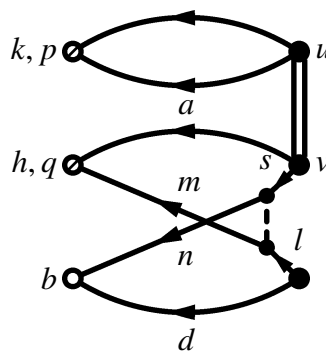
**If a two-electron Hamiltonian fragment is connected to two different geminals, a multiplication factor of two comes into play due to integral symmetry.**

Using all of the previously introduced diagrammatic rules, we can assign algebraic values to all the diagrams presented below:

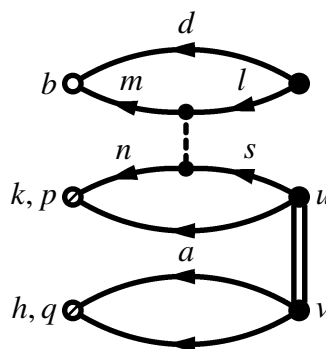
$$\begin{aligned} & \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in h} \sum_{n, s \in b} [mn|ls] \sum_v^{(h)} t_{kh}^{pv} \sum_{a \in h} \sum_{c \in b} \\ & (C_{ma}^{hq} C_{la}^{hv} + C_{am}^{hq} C_{al}^{hv}) (C_{nc}^{b0} C_{sc}^{b0} + C_{cn}^{b0} C_{cs}^{b0}) \\ = & \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in h} \sum_{n, s \in b} [mn|ls] \sum_v^{(h)} t_{kh}^{pv} \sum_{\sigma} {}^h R_{lm}^{vq, \sigma} \sum_{\sigma'} P_{sn}^{b0, \sigma'} \end{aligned}$$



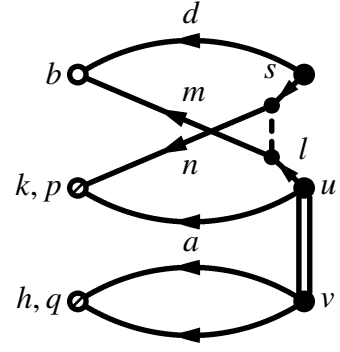
$$\begin{aligned} & - \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, s \in h} \sum_{n, l \in b} [mn|ls] \sum_v^{(h)} t_{kh}^{pv} \sum_{a \in h} \sum_{d \in b} \\ & (C_{ma}^{hq} C_{sa}^{hv} C_{nd}^{b0} C_{ld}^{b0} + C_{am}^{hq} C_{as}^{hv} C_{dn}^{b0} C_{dl}^{b0}) \\ = & - \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, s \in h} \sum_{n, l \in b} [mn|ls] \sum_v^{(h)} t_{kh}^{pv} \sum_{\sigma} {}^h R_{sm}^{vq, \sigma} P_{ln}^{b0, \sigma} \end{aligned}$$



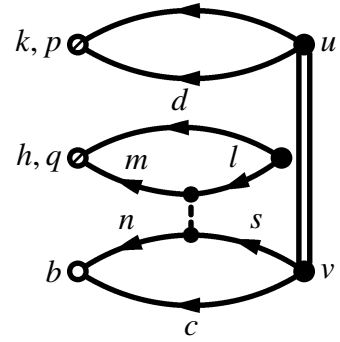
$$\begin{aligned} & \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in b} \sum_{n, s \in k} [mn|ls] \sum_u^{(k)} t_{kh}^{uq} \sum_{a \in k} \sum_{d \in b} \\ & (C_{md}^{b0} C_{ld}^{b0} + C_{dm}^{b0} C_{dl}^{b0}) (C_{na}^{kp} C_{sa}^{ku} + C_{an}^{kp} C_{as}^{ku}) = \\ = & \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in b} \sum_{n, s \in k} [mn|ls] \sum_u^{(k)} t_{kh}^{uq} \sum_{\sigma} P_{lm}^{b0, \sigma} \sum_{\sigma'} {}^k R_{sn}^{up, \sigma'} \end{aligned}$$



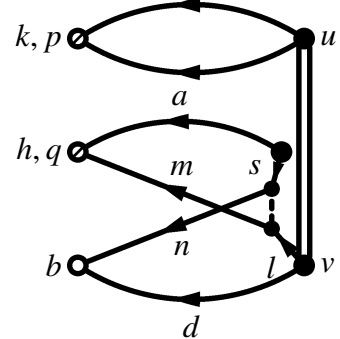
$$\begin{aligned}
& - \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, s \in b} \sum_{n, l \in k} [mn|ls] \sum_u^{(k)} t_{kh}^{uq} \sum_{a \in k} \sum_{d \in b} \\
& \quad \left( C_{md}^{b0} C_{sd}^{b0} C_{na}^{kp} C_{la}^{ku} + C_{dm}^{b0} C_{ds}^{b0} C_{an}^{kp} C_{al}^{ku} \right) \\
& = - \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, s \in b} \sum_{n, l \in k} [mn|ls] \sum_u^{(k)} t_{kh}^{uq} \sum_{\sigma} {}^k R_{ln}^{up, \sigma} P_{sm}^{b0, \sigma}
\end{aligned}$$



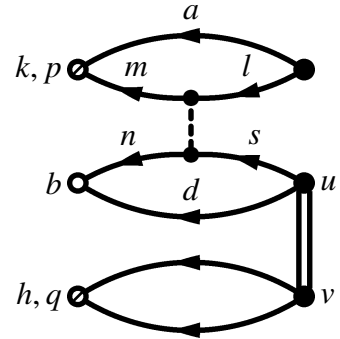
$$\begin{aligned}
& \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in h} \sum_{n, s \in b} [mn|ls] \sum_v^{(b)} t_{kb}^{pv} \sum_{d \in h} \sum_{c \in b} \\
& \quad \left( C_{md}^{hq} C_{ld}^{h0} + C_{dm}^{hq} C_{dl}^{h0} \right) \left( C_{nc}^{b0} C_{sc}^{bv} + C_{cn}^{b0} C_{cs}^{bv} \right) = \\
& = \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in h} \sum_{n, s \in b} [mn|ls] \sum_v^{(b)} t_{kb}^{pv} \sum_{\sigma} {}^h R_{lm}^{0q, \sigma} \sum_{\sigma'} {}^b R_{sn}^{v0, \sigma'}
\end{aligned}$$



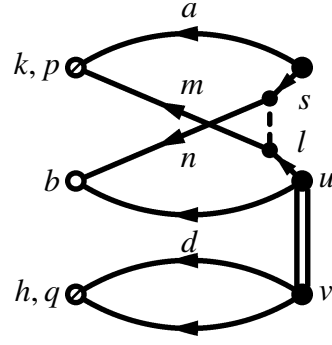
$$\begin{aligned}
& - \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, s \in h} \sum_{n, l \in b} [mn|ls] \sum_v^{(b)} t_{kb}^{pv} \sum_{a \in h} \sum_{d \in b} \\
& \quad \left( C_{ma}^{hq} C_{sa}^{h0} C_{nd}^{b0} C_{ld}^{bv} + C_{am}^{hq} C_{as}^{h0} C_{dn}^{b0} C_{dl}^{bv} \right) \\
& = - \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, s \in h} \sum_{n, l \in b} [mn|ls] \sum_v^{(b)} t_{kb}^{pv} \sum_{\sigma} {}^h R_{sm}^{0q, \sigma} {}^b R_{ln}^{v0, \sigma}
\end{aligned}$$



$$\begin{aligned}
& \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in k} \sum_{n, s \in b} [mn|ls] \sum_u^{(b)} t_{bh}^{uq} \sum_{a \in k} \sum_{d \in b} \\
& \quad \left( C_{ma}^{kp} C_{la}^{k0} + C_{am}^{kp} C_{al}^{k0} \right) \left( C_{nd}^{b0} C_{sd}^{bu} + C_{dn}^{b0} C_{ds}^{bu} \right) = \\
& = \sum_{\substack{b \\ b \neq k \neq h}} \sum_{m, l \in k} \sum_{n, s \in b} [mn|ls] \sum_u^{(b)} t_{bh}^{uq} \sum_{\sigma} {}^k R_{lm}^{0p, \sigma} \sum_{\sigma'} {}^b R_{sn}^{u0, \sigma'}
\end{aligned}$$



$$\begin{aligned}
& - \sum_b \sum_{\substack{m,s \in k \\ b \neq k \neq h}} \sum_{n,l \in b} [mn|ls] \sum_u^{(b)} t_{bh}^{uq} \sum_{a \in k} \sum_{d \in b} \\
& \quad \left( C_{ma}^{kp} C_{sa}^{k0} C_{nd}^{b0} C_{ld}^{bu} + C_{am}^{kp} C_{as}^{k0} C_{dn}^{b0} C_{dl}^{bu} \right) \\
& = - \sum_b \sum_{\substack{m,s \in k \\ b \neq k \neq h}} \sum_{n,l \in b} [mn|ls] \sum_u^{(b)} t_{bh}^{uq} \sum_{\sigma} {}^k R_{sm}^{0p,\sigma} {}^b R_{ln}^{u0,\sigma}
\end{aligned}$$



### 3.3.3 Diagonal terms

A characteristic of the diagrammatic formalism above is that the concept of normal order was not introduced. As a consequence, there appears a diagonal term including the expectation value of  $\hat{H}$  (namely the APSG energy). This is unusual with Goldstone diagrams. If one is not careful enough, it is easy to forget about it. Writing the right side of eq. (3.18) as:

$$\langle \text{APSG} | \overbrace{\hat{E}_{kh}^{pq\dagger} \hat{T} \hat{H}} | \text{APSG} \rangle - \langle \text{APSG} | \overbrace{\hat{E}_{kh}^{pq\dagger} \hat{H} \hat{T}} | \text{APSG} \rangle,$$

the term in question is exactly the first above. Note that both terms are already generated by the diagrams, the point to stress here is simply to mind the subtraction if  $\hat{H}$  is used instead of the normal ordered Hamiltonian.

### 3.3.4 Diagrams of the non-linear corrections

The non-linear correction of the amplitude equations according to eq. (3.13) is

$$\frac{1}{2} \sum_{a,b} t_a t_b \langle \text{APSG} | \hat{X}_c^\dagger \hat{H} \hat{X}_a \hat{X}_b | \text{APSG} \rangle_c$$

that is equal to the following equation after expanding all the terms:

$$\frac{1}{2} \langle \text{APSG} | \psi_{k0}^+ \psi_{h0}^+ \psi_{kp}^- \psi_{hq}^- \left( \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} \left( [mn|ls] m_\sigma^+ n_\sigma^+ s_\sigma^- l_\sigma^- - [mn|sl] m_\sigma^+ n_\sigma^+ s_\sigma^- l_{\sigma'}^- \right) \right)$$

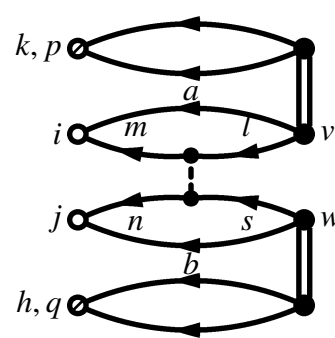
$$\begin{aligned}
& \times \left( \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} \sum_u^{(a)} \sum_v^{(b)} t_{ab}^{uv} \psi_{au}^+ \psi_{bv}^+ \psi_{a0}^- \psi_{b0}^- \right) \left( \frac{1}{2} \sum_{\substack{c,d \\ c \neq d}} \sum_w^{(c)} \sum_y^{(d)} t_{cd}^{wy} \psi_{cw}^+ \psi_{dy}^+ \psi_{c0}^- \psi_{d0}^- \right) |\text{APSG}\rangle \\
& = \frac{1}{16} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma, \sigma'} \sum_{\substack{a,b \\ a \neq b}} \sum_u^{(a)} \sum_v^{(b)} \sum_{\substack{c,d \\ c \neq d}} \sum_w^{(c)} \sum_y^{(d)} t_{ab}^{uv} t_{cd}^{wy} \\
& \times \left( [mn|ls] \langle \text{APSG} | \psi_{k0}^+ \psi_{h0}^+ \psi_{kp}^- \psi_{hq}^- m_\sigma^+ n_{\sigma'}^+ s_\sigma^- l_{\sigma'}^- \psi_{au}^+ \psi_{bv}^+ \psi_{a0}^- \psi_{b0}^- \psi_{cw}^+ \psi_{dy}^+ \psi_{c0}^- \psi_{d0}^- | \text{APSG} \rangle \right. \\
& \left. - [mn|sl] \langle \text{APSG} | \psi_{k0}^+ \psi_{h0}^+ \psi_{kp}^- \psi_{hq}^- m_\sigma^+ n_{\sigma'}^+ s_\sigma^- l_{\sigma'}^- \psi_{au}^+ \psi_{bv}^+ \psi_{a0}^- \psi_{b0}^- \psi_{cw}^+ \psi_{dy}^+ \psi_{c0}^- \psi_{d0}^- | \text{APSG} \rangle \right)
\end{aligned}$$

To further simplify the above equation, both the symmetry of the two-electron integrals (already introduced diagrammatic rule) and the symmetry of the amplitudes can be utilized ( $t_{ab}^{\mu\nu} = t_{ba}^{\nu\mu}$  and  $t_{cd}^{\omega\gamma} = t_{dc}^{\gamma\omega}$ ) which result in an overall  $2^3 = 8 \times$  multiplication factor. It is also easy to recognise that the order of the amplitudes is also irrelevant, which means that during the matching process of the  $i, j, k, h$  geminal indices with  $a, b, c, d$  the term belonging to  $t_{ki}^{\mu\nu} t_{jh}^{\omega\gamma}$  for example is exactly the same as that of  $t_{jh}^{\omega\gamma} t_{ki}^{\mu\nu}$ . This results in yet another diagrammatic rule, this time considering the appearance of multiple amplitudes.

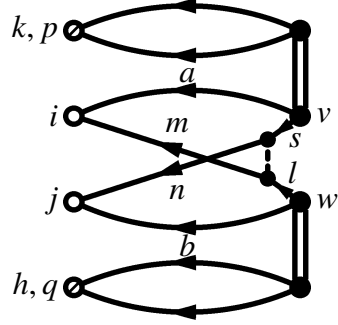
**Amplitudes appearing in the equation bring in an overall  $n_t!$  (factorial) multiplication factor, where  $n_t$  is the number of amplitudes appearing in the equations (for dispersive interaction it can have the maximum value of 2).**

After applying all of the already known diagrammatic rules and the new one as well, the two diagrams and their values corresponding to the non-linear correction are:

$$\begin{aligned}
& \sum_{\substack{i,j \\ i \neq j}} \sum_{m,l \in i} \sum_{n,s \in j} \sum_v^{(i)} \sum_w^{(j)} t_{ki}^{pv} t_{jh}^{wq} [mn|ls] \sum_{a \in i} \sum_{b \in j} \\
& \left( C_{ma}^{i0} C_{la}^{iv} + C_{am}^{i0} C_{al}^{iv} \right) \left( C_{nb}^{j0} C_{sb}^{jw} + C_{bn}^{j0} C_{bs}^{jw} \right) \\
& = \sum_{\substack{i,j \\ i \neq j}} \sum_{m,l \in i} \sum_{n,s \in j} \sum_v^{(i)} \sum_w^{(j)} t_{ki}^{pv} t_{jh}^{wq} [mn|ls] \sum_{\sigma} i R_{lm}^{v0,\sigma} \sum_{\sigma'} j R_{sn}^{w0,\sigma'}
\end{aligned}$$



$$\begin{aligned}
& - \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_v^{(i)} \sum_w^{(j)} t_{ki}^{pv} t_{jh}^{wq} [mn|ls] \sum_{a \in i} \sum_{b \in j} \\
& \left( C_{ma}^{i0} C_{sa}^{iv} C_{nb}^{j0} C_{lb}^{jw} + C_{am}^{i0} C_{as}^{iv} C_{bn}^{j0} C_{bl}^{jw} \right) = \\
& = - \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_v^{(i)} \sum_w^{(j)} t_{ki}^{pv} t_{jh}^{wq} [mn|ls] \sum_{\sigma} i R_{sm}^{v0,\sigma} j R_{ln}^{w0,\sigma}
\end{aligned}$$



### 3.3.5 Triplet $M_S \neq 0$ corrections to the energy and the amplitude equations

Up until this point we have only talked about the  $S$  spin quantum number of the geminals and came to the conclusion that it can only be either 0 or 1 because each geminal consists of only two electrons. The basis of our theory was the  $\hat{T}$  cluster operator having the following form:

$$\hat{T} = \sum_{\substack{i,j \\ i < j}} \sum_p^{(j)} \sum_q^{(i)} t_{ij}^{pq} \psi_{iq}^+ \psi_{jp}^+ \psi_{j0}^- \psi_{i0}^-$$

In this subsection we are going to discuss the possibility of the  $\langle \text{APSG} | \hat{H} \hat{T} | \text{APSG} \rangle$  dispersive Coupled Cluster correction having contributions from  $M_S \neq 0$  geminal states. More accurately, it is not just a possibility, it is actually a necessity if the spins of the bra and ket vectors are taken into account. The bra APSG vector belongs to the  $S = 0$  spin state and the Hamiltonian does not change the overall spin of the function it acts on. This means that  $\hat{T} | \text{APSG} \rangle$  must also be a singlet wave function if we aim at a nonzero energy correction. According to the theory of angular momentum in quantum mechanics, a singlet state can be formed from the triplets with the following linear combination (by using the Clebsch-Gordan coefficients):

$$\begin{aligned}
|S = 0\rangle &= \sqrt{\frac{1}{3}} |M_{S1} = +1, M_{S2} = -1\rangle - \sqrt{\frac{1}{3}} |M_{S1} = 0, M_{S2} = 0\rangle \\
&+ \sqrt{\frac{1}{3}} |M_{S1} = -1, M_{S2} = +1\rangle,
\end{aligned}$$



where  $M_{S_1}$  and  $M_{S_2}$  are the eigenvalues of the  $\hat{S}_z$  operator for the two geminals respectively. This implies that the  $M_S \neq 0$  states are necessary to be included in the  $\hat{T}$  cluster operator to form singlet states in the ket vector.

We have already seen in section (2.4) that for triplet geminals, the relationship between the  $M_S = 0$  and  $M_S \neq 0$  triplet geminal coefficient matrices is

$$C_{mn}^{iq(M_S \neq 0)} = \sqrt{2}C_{mn}^{iq(M_S = 0)},$$

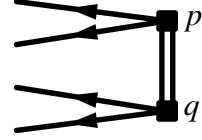
which is a consequence of the spin-polarized geminals being normalized themselves. To emphasize the difference between the triplet  $M_S = 0$  and the spin-polarized states, a different diagrammatic notation is introduced for a cluster operator containing these states. It is also worth introducing a different notation because some diagrammatic rules will be modified due to the different way these matrix elements are evaluated.

The cluster operator containing spin-polarized geminal states ( $\hat{T}_{sp}$ ) is going to have the following diagrammatic form:

$$\hat{T}_{sp} = \sum_{\substack{i,j \\ i < j}}^{(j, S_p=1)} \sum_p^{(i, S_q=1)} \sum_q t_{ij}^{qp} \psi_{iq\uparrow}^+ \psi_{jp\downarrow}^+ \psi_{j_0}^- \psi_{i_0}^-$$

or

$$\hat{T}_{sp} = \sum_{\substack{i,j \\ i < j}}^{(j, S_p=1)} \sum_p^{(i, S_q=1)} \sum_q t_{ij}^{qp} \psi_{iq\downarrow}^+ \psi_{jp\uparrow}^+ \psi_{j_0}^- \psi_{i_0}^-$$



where

$$\psi_{iq\uparrow}^+ = \frac{1}{2} \sum_{m,n \in i} C_{mn}^{iq\uparrow} m_\alpha^+ n_\alpha^+ \quad \psi_{iq\downarrow}^+ = \frac{1}{2} \sum_{m,n \in i} C_{mn}^{iq\downarrow} m_\beta^+ n_\beta^+$$

and  $(j, S_p = 1)$  and  $(i, S_q = 1)$  indicate that the sums over geminal states only run over the triplet states. The triplet energy correction due to spin-polarized geminals can be written as

$$E_{sp} = \sum_{\substack{i,j \\ i < j}}^{(j, S_p=1)} \sum_p^{(i, S_q=1)} \sum_q t_{ij}^{qp} \langle \text{APSG} | \hat{H} (\psi_{iq\uparrow}^+ \psi_{jp\downarrow}^+ \psi_{j_0}^- \psi_{i_0}^- + \psi_{iq\downarrow}^+ \psi_{jp\uparrow}^+ \psi_{j_0}^- \psi_{i_0}^-) | \text{APSG} \rangle$$

It is enough to calculate the first term only (corresponding to  $\psi_{iq\uparrow}^+ \psi_{jp\downarrow}^+$  creation operators) because the other term can be obtained by a  $iq \leftrightarrow jp$  exchange.

$$E_{\text{SP}} = \frac{1}{4} \sum_{\substack{k,h \\ k \neq h}} \sum_{\substack{m,s \in k \\ n,l \in h}} \sum_{\sigma, \sigma'} \sum_{\substack{i,j \\ i \neq j}} \sum_p^{(j, S_p=1)} \sum_q^{(i, S_q=1)} t_{ji}^{pq} \left( [mn|ls] \langle \text{APSG} | m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{iq\uparrow}^+ \psi_{jp\downarrow}^+ \psi_{j_0}^- \psi_{i_0}^- | \text{APSG} \rangle \right. \\ \left. - [mn|sl] \langle \text{APSG} | m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{iq\uparrow}^+ \psi_{jp\downarrow}^+ \psi_{j_0}^- \psi_{i_0}^- | \text{APSG} \rangle \right)$$

The two possible contractions of geminal indices ( $i = l; j = k$  and  $i = k; j = l$ ) lead to the same result due to the symmetry properties of the two-electron integrals, this is basically what we have observed in the  $M_S = 0$  case.

Two types of matrix elements should be considered according to the above equation:

$$\langle \text{APSG} | m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{iq\uparrow}^+ \psi_{jp\downarrow}^+ \psi_{j_0}^- \psi_{i_0}^- | \text{APSG} \rangle = -\langle \psi_{j_0}^- m_{\sigma}^+ s_{\sigma'}^- \psi_{jp\uparrow}^+ \rangle \langle \psi_{i_0}^- n_{\sigma}^+ l_{\sigma'}^- \psi_{iq\downarrow}^+ \rangle$$

and

$$\langle \text{APSG} | m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{iq\uparrow}^+ \psi_{jp\downarrow}^+ \psi_{j_0}^- \psi_{i_0}^- | \text{APSG} \rangle = -\langle \psi_{j_0}^- m_{\sigma}^+ s_{\sigma'}^- \psi_{jp\uparrow}^+ \rangle \langle \psi_{i_0}^- n_{\sigma}^+ l_{\sigma'}^- \psi_{iq\downarrow}^+ \rangle = 0$$

The second matrix element is obviously zero as the spin states of the bra and ket geminals are different and the operators coming from the Hamiltonian do not change the spin (think of it as evaluating a  $\langle b_{\beta}^- a_{\alpha}^- m_{\sigma}^+ s_{\sigma'}^- c_{\alpha}^+ d_{\alpha}^+ \rangle$  type matrix element for example).

Taking all the above considerations into account, the energy expression can be written as

$$-\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in j} \sum_{n,l \in i} \sum_{\sigma, \sigma'} [mn|ls] \sum_p^{(j, S_p=1)} \sum_q^{(i, S_q=1)} t_{ji}^{pq} \langle \psi_{j_0}^- m_{\sigma}^+ s_{\sigma'}^- \psi_{jp\uparrow}^+ \rangle \langle \psi_{i_0}^- n_{\sigma}^+ l_{\sigma'}^- \psi_{iq\downarrow}^+ \rangle$$

One of the matrix elements is

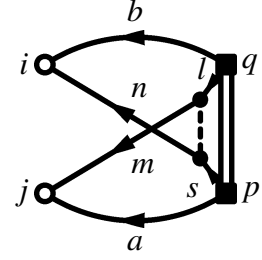
$$\langle \psi_{j_0}^- m_{\sigma}^+ s_{\sigma'}^- \psi_{jp\uparrow}^+ \rangle = \frac{1}{2} \sum_{\mu, \nu, \kappa, \tau \in j} C_{\mu\nu}^{j0} C_{\kappa\tau}^{jp\uparrow} \langle \nu_{\beta}^- \mu_{\alpha}^- m_{\sigma}^+ s_{\sigma'}^- \kappa_{\alpha}^+ \tau_{\alpha}^+ \rangle = \sum_{a \in j} C_{am}^{j0} C_{as}^{jp\uparrow} = {}^j Q_{sm}^{p\uparrow, 0}$$

and similarly

$$\langle \psi_{i0}^- n_{\sigma'}^+ l_{\sigma}^- \psi_{iq\downarrow}^+ \rangle = \sum_{b \in i} C_{nb}^{i0} C_{lb}^{iq\downarrow} = {}^i Q_{ln}^{q\downarrow,0}$$

The triplet  $M_S \neq 0$  energy correction is thus

$$\begin{aligned} & -\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] \sum_p^{(j, S_p=1)} \sum_q^{(i, S_q=1)} t_{ij}^{qp} \sum_{\sigma} {}^j Q_{sm}^{p\sigma,0} {}^i Q_{ln}^{q\bar{\sigma},0} \\ & = - \sum_{\substack{i,j \\ i < j}} \sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] \sum_p^{(j, S_p=1)} \sum_q^{(i, S_q=1)} t_{ij}^{qp} \sum_{\sigma} {}^j Q_{sm}^{p\sigma,0} {}^i Q_{ln}^{q\bar{\sigma},0} \end{aligned}$$



It should be taken into account that the relationship between the  $M_S = 0$  and  $M_S \neq 0$  amplitudes is (this can be seen from the Clebsch-Gordan coefficients):

$$t_{ij}^{qp(M_S=0)} = -t_{ij}^{qp(M_S=\pm 1)}$$

Besides the energy correction, the amplitude equations should also be evaluated. First let us consider the inhomogeneous vector ( $\langle \text{APSG} | \hat{E}_{ji}^{pq\uparrow} \hat{H} | \text{APSG} \rangle$ ). Following a similar way of thought than for the energy correction, the two terms for the inhomogeneous vector can be written as:

$$\sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] \langle \psi_{jp\uparrow}^- \psi_{iq\downarrow}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{i0}^+ \psi_{j0}^+ \rangle$$

and also

$$\sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] \langle \psi_{jp\downarrow}^- \psi_{iq\uparrow}^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma}^- l_{\sigma'}^- \psi_{i0}^+ \psi_{j0}^+ \rangle$$

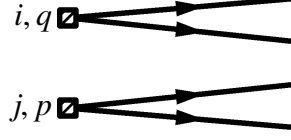
The matrix elements are the adjoints of those appearing in the energy expression, in this respect it is not surprising that we are going to arrive at similar expressions in this case as

well. After introducing the diagrammatic notation for the  $M_S \neq 0$  external vertices

$$\hat{E}_{kh}^{pq\dagger} = \psi_{k0}^+ \psi_{h0}^+ \psi_{jp\uparrow}^- \psi_{iq\downarrow}^-$$

or

$$\hat{E}_{kh}^{pq\dagger} = \psi_{k0}^+ \psi_{h0}^+ \psi_{jp\downarrow}^- \psi_{iq\uparrow}^-$$



the final diagrammatic form of the inhomogeneous vector can be written as

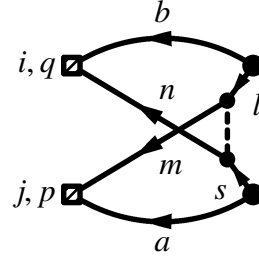
$$\sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] \sum_{a \in j} C_{am}^{jp\uparrow} C_{as}^{j0} \sum_{b \in i} C_{nb}^{iq\downarrow} C_{lb}^{i0}$$

$$= \sum_{m,s \in j} \sum_{n,l \in i} [mn|ls]^j Q_{sm}^{0,p\uparrow} Q_{ln}^{0,q\downarrow}$$

and

$$\sum_{m,s \in j} \sum_{n,l \in i} [mn|ls] \sum_{a \in j} C_{ma}^{jp\downarrow} C_{sa}^{j0} \sum_{b \in i} C_{bn}^{iq\uparrow} C_{bl}^{i0}$$

$$= \sum_{m,s \in j} \sum_{n,l \in i} [mn|ls]^j Q_{sm}^{0,p\downarrow} Q_{ln}^{0,q\uparrow}$$



In general, 5 different types of matrix elements are have to be taken into account if we want to give a full description of all the possible matrix elements that could arise in the theory of triplet  $M_S \neq 0$  geminals. These are

I.

$$\begin{aligned} \langle \psi_{ip\uparrow}^- m_{\sigma}^+ n_{\sigma'}^- \psi_{ir}^+ \rangle &= \frac{1}{2} \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{ip\uparrow} C_{\rho\lambda}^{ir} \langle \tau_{\alpha}^- \kappa_{\alpha}^- m_{\sigma}^+ n_{\sigma'}^- \rho_{\alpha}^+ \lambda_{\beta}^+ \rangle \\ &= \frac{1}{2} \sum_{\kappa \in i} (-C_{m\kappa}^{ip\uparrow} C_{\kappa n}^{ir} + C_{km}^{ip\uparrow} C_{kn}^{ir}) \delta_{\sigma\alpha} \delta_{\sigma'\beta} = \sum_{\kappa \in i} C_{km}^{ip\uparrow} C_{kn}^{ir} \delta_{\sigma\alpha} \delta_{\sigma'\beta} = {}^i Q_{nm}^{r,p\uparrow} \delta_{\sigma\alpha} \delta_{\sigma'\beta} \end{aligned}$$

II.

$$\langle \psi_{ip\downarrow}^- m_{\sigma}^+ n_{\sigma'}^- \psi_{ir}^+ \rangle = \frac{1}{2} \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{ip\downarrow} C_{\rho\lambda}^{ir} \langle \tau_{\beta}^- \kappa_{\beta}^- m_{\sigma}^+ n_{\sigma'}^- \rho_{\alpha}^+ \lambda_{\beta}^+ \rangle$$

$$= \frac{1}{2} \sum_{\kappa \in i} (-C_{\kappa m}^{ip\downarrow} C_{n\kappa}^{ir} + C_{m\kappa}^{ip\downarrow} C_{n\kappa}^{ir}) \delta_{\sigma\beta} \delta_{\sigma'\alpha} = \sum_{\kappa \in i} C_{m\kappa}^{ip\downarrow} C_{n\kappa}^{ir} \delta_{\sigma\beta} \delta_{\sigma'\alpha} = {}^i Q_{nm}^{r,p\downarrow} \delta_{\sigma\beta} \delta_{\sigma'\alpha}$$

III.

$$\begin{aligned} \langle \psi_{i\sigma}^- m_{\sigma'}^+ n_{\sigma'}^- \psi_{ip\uparrow}^+ \rangle &= \frac{1}{2} \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{ir} C_{\rho\lambda}^{ip\uparrow} \langle \tau_{\beta}^- \kappa_{\alpha}^- m_{\sigma}^+ n_{\sigma'}^- \rho_{\alpha}^+ \lambda_{\alpha}^+ \rangle \\ &= \frac{1}{2} \sum_{\kappa \in i} (-C_{\kappa m}^{ir} C_{n\kappa}^{ip\uparrow} + C_{\kappa n}^{ir} C_{m\kappa}^{ip\uparrow}) \delta_{\sigma\beta} \delta_{\sigma'\alpha} = \sum_{\kappa \in i} C_{\kappa m}^{ir} C_{n\kappa}^{ip\uparrow} \delta_{\sigma\beta} \delta_{\sigma'\alpha} = {}^i Q_{nm}^{p,\uparrow r} \delta_{\sigma\beta} \delta_{\sigma'\alpha} \end{aligned}$$

IV.

$$\begin{aligned} \langle \psi_{i\sigma}^- m_{\sigma'}^+ n_{\sigma'}^+ \psi_{ip\downarrow}^+ \rangle &= \frac{1}{2} \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{ir} C_{\rho\lambda}^{ip\downarrow} \langle \tau_{\beta}^- \kappa_{\alpha}^- m_{\sigma}^+ n_{\sigma'}^+ \rho_{\beta}^+ \lambda_{\beta}^+ \rangle \\ &= \frac{1}{2} \sum_{\kappa \in i} (C_{m\kappa}^{ir} C_{n\kappa}^{ip\downarrow} - C_{m\kappa}^{ir} C_{n\kappa}^{ip\downarrow}) \delta_{\sigma\alpha} \delta_{\sigma'\beta} = \sum_{\kappa \in i} C_{m\kappa}^{ir} C_{n\kappa}^{ip\downarrow} \delta_{\sigma\alpha} \delta_{\sigma'\beta} = {}^i Q_{nm}^{p,\downarrow r} \delta_{\sigma\alpha} \delta_{\sigma'\beta} \end{aligned}$$

V.

$$\begin{aligned} &\begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \text{---} \end{array} \\ &\langle \psi_{i\sigma}^- m_{\sigma'}^+ n_{\sigma'}^- \psi_{ip\uparrow}^+ \rangle = \frac{1}{4} \sum_{\kappa, \tau, \rho, \lambda \in i} C_{\kappa\tau}^{ir\uparrow} C_{\rho\lambda}^{ip\uparrow} \langle \tau_{\alpha}^- \kappa_{\alpha}^- m_{\sigma}^+ n_{\sigma'}^- \rho_{\alpha}^+ \lambda_{\alpha}^+ \rangle \\ &= \frac{1}{4} \sum_{\kappa \in i} (C_{\kappa m}^{ir\uparrow} C_{n\kappa}^{ip\uparrow} - C_{m\kappa}^{ir\uparrow} C_{n\kappa}^{ip\uparrow} + C_{m\kappa}^{ir\uparrow} C_{n\kappa}^{ip\uparrow} - C_{\kappa m}^{ir\uparrow} C_{n\kappa}^{ip\uparrow}) \delta_{\sigma\alpha} = \sum_{\kappa \in i} C_{m\kappa}^{ir\uparrow} C_{n\kappa}^{ip\uparrow} \delta_{\sigma\alpha} = {}^i Q_{nm}^{p\uparrow, r\uparrow} \delta_{\sigma\alpha} \end{aligned}$$

and similarly for the  $M_S = -1$  case:

$$\langle \psi_{i\sigma}^- m_{\sigma'}^+ n_{\sigma'}^- \psi_{ip\downarrow}^+ \rangle = \sum_{\kappa \in i} C_{m\kappa}^{ir\downarrow} C_{n\kappa}^{ip\downarrow} \delta_{\sigma\beta} = {}^i Q_{nm}^{p\downarrow, r\downarrow} \delta_{\sigma\beta}$$

The first important factor of  $\langle \text{APSG} | \hat{E}_{kh}^{pq\uparrow} \hat{H} \hat{T} | \text{APSG} \rangle$  is the case where the geminals appearing in the  $\hat{E}_{kh}^{pq\uparrow}$  are of the  $M_S \neq 0$ -type, while we do not have such a restriction for the operators appearing in  $\hat{T}$ .

For  $M_S(kp) = +1$  and  $M_S(hq) = -1$ , such a matrix element reads

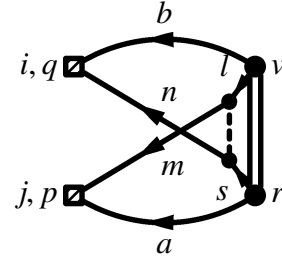
$$- \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j)} \sum_v^{(i)} t_{ji}^{rv} [mn|ls] \sum_{a \in j} C_{am}^{jp\uparrow} C_{as}^{jr} \sum_{b \in i} C_{nb}^{iq\downarrow} C_{lb}^{iv} = - \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j)} \sum_v^{(i)} t_{ji}^{rv} [mn|ls]^j Q_{sm}^{r,p\uparrow} Q_{ln}^{v,q\downarrow}$$

while for  $M_S(kp) = -1$  and  $M_S(hq) = +1$  it is

$$- \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j)} \sum_v^{(i)} t_{ji}^{rv} [mn|ls] \sum_{a \in j} C_{ma}^{jp\downarrow} C_{sa}^{jr} \sum_{b \in i} C_{bn}^{iq\uparrow} C_{bl}^{iv} = - \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j)} \sum_v^{(i)} t_{ji}^{rv} [mn|ls]^j Q_{sm}^{r,p\downarrow} Q_{ln}^{v,q\uparrow}$$

After summing these terms:

$$- \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j)} \sum_v^{(i)} t_{ji}^{rv} [mn|ls] \left( {}^j Q_{sm}^{r,p\uparrow} Q_{ln}^{v,q\downarrow} + {}^j Q_{sm}^{r,p\downarrow} Q_{ln}^{v,q\uparrow} \right)$$



Another important term of the  $\langle \text{APSG} | \hat{E}_{kh}^{pq\uparrow} \hat{H} \hat{T} | \text{APSG} \rangle$  is the opposite case of the previous one. Here, the external vertices are composed of  $M_S = 0$  geminals while the  $\hat{T}$  cluster operator consists of  $M_S \neq 0$  geminals.

For the  $M_S(\psi_{jr}^+) = +1$  and  $M_S(\psi_{iv}^+) = -1$  scenario (where  $\psi_{jr}$  and  $\psi_{iv}$  are the excited geminals appearing in  $\hat{T}$ , this matrix element reads:

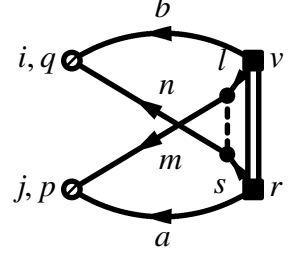
$$\begin{aligned} & - \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j, S_r=1)} \sum_v^{(i, S_v=1)} t_{ji}^{rv} [mn|ls] \sum_{a \in j} C_{am}^{jp} C_{as}^{jr\uparrow} \sum_{b \in i} C_{nb}^{iq} C_{lb}^{iv\downarrow} \\ & = - \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j, S_r=1)} \sum_v^{(i, S_v=1)} t_{ji}^{rv} [mn|ls]^j Q_{sm}^{r,\uparrow p} Q_{ln}^{v,\downarrow q} \end{aligned}$$

while for  $M_S(\psi_{jr}^+) = -1$  and  $M_S(\psi_{iv}^+) = +1$  it is

$$\begin{aligned} & - \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j, S_r=1)} \sum_v^{(i, S_v=1)} t_{ji}^{rv} [mn|ls] \sum_{a \in j} C_{ma}^{jp} C_{sa}^{jr\downarrow} \sum_{b \in i} C_{bn}^{iq} C_{bl}^{iv\uparrow} \\ & = - \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j, S_r=1)} \sum_v^{(i, S_v=1)} t_{ji}^{rv} [mn|ls]^j Q_{sm}^{r,\downarrow p} Q_{ln}^{v,\uparrow q} \end{aligned}$$

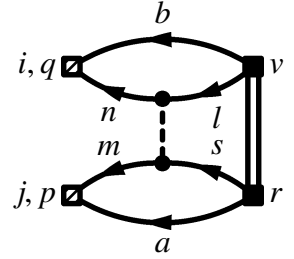
Summing these two terms up, the following equation is obtained:

$$-\sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j, S_r=1)} \sum_v^{(i, S_v=1)} t_{ji}^{rv} [mn|ls] \left( {}^j Q_{sm}^{r,\uparrow p} {}^i Q_{ln}^{v,\downarrow q} + {}^j Q_{sm}^{r,\downarrow p} {}^i Q_{ln}^{v,\uparrow q} \right)$$



The third most important of  $\langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{H} \hat{T} | \text{APSG} \rangle$  is the one in which both the  $\hat{E}$  and  $\hat{T}$  operator contains  $M_S \neq 0$  geminals. Here the matrix element and the corresponding diagram is

$$\begin{aligned} & \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j, S_r=1)} \sum_v^{(i, S_v=1)} t_{ji}^{rv} [mn|sl] \\ & \times \left( \sum_{a \in j} C_{ma}^{jp\uparrow} C_{sa}^{jr\uparrow} \sum_{b \in i} C_{nb}^{iq\downarrow} C_{lb}^{iv\downarrow} + \sum_{a \in j} C_{ma}^{jp\downarrow} C_{sa}^{jr\downarrow} \sum_{b \in i} C_{nb}^{iq\uparrow} C_{lb}^{iv\uparrow} \right) \\ & = \sum_{m,s \in j} \sum_{n,l \in i} \sum_r^{(j, S_r=1)} \sum_v^{(i, S_v=1)} t_{ji}^{rv} [mn|sl] \left( {}^j Q_{sm}^{r,\uparrow p} {}^i Q_{ln}^{v,\downarrow q} + {}^j Q_{sm}^{r,\downarrow p} {}^i Q_{ln}^{v,\uparrow q} \right) \end{aligned}$$



From the above examples the following diagrammatic rules can be derived:

**Triplet  $M_S \neq 0$  geminals are symbolized by squares. Shaded squares belong to external vertices, while full squares represent triplet geminals of the  $\hat{T}$  cluster operator. Like in the  $M_S = 0$  case, geminal vertices lying on the same horizontal line belong to the same geminal index. If a  $M_S \neq 0$  triplet geminal and a  $M_S = 0$  singlet or triplet vertex (square and circle) interact through a two-electron vertex, it results in the appearance of transition density matrix elements:**

$${}^j Q_{sm}^{r,p\uparrow} {}^i Q_{ln}^{v,q\downarrow} + {}^j Q_{sm}^{r,p\downarrow} {}^i Q_{ln}^{v,q\uparrow},$$

where the transition density matrices for the  $M_S = +1$  and  $M_S = -1$  geminals are defined as

$${}^j Q_{sm}^{r,p\uparrow} = \sum_{\kappa \in j} C_{km}^{jp\uparrow} C_{ks}^{jr} \quad {}^j Q_{sm}^{r,p\downarrow} = \sum_{\kappa \in j} C_{m\kappa}^{jp\downarrow} C_{s\kappa}^{jr}$$

When  $M_S \neq 0$  geminals are present both on the left and right side (bra and ket vector), the result is similar:

$${}^j Q_{sm}^{r\uparrow,p\uparrow} {}^i Q_{ln}^{v\downarrow,q\downarrow} + {}^j Q_{sm}^{r\downarrow,p\downarrow} {}^i Q_{ln}^{v\uparrow,q\uparrow},$$

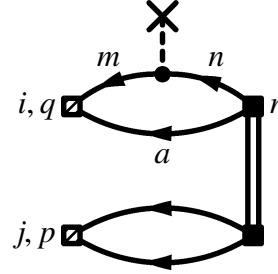
where

$${}^j Q_{sm}^{r\uparrow,p\uparrow} = \sum_{\kappa \in j} C_{m\kappa}^{jp\uparrow} C_{s\kappa}^{jr\uparrow}$$

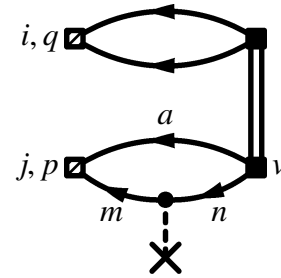
and similarly for  ${}^j Q_{sm}^{r\downarrow,p\downarrow}$ .

Like in the case of  $M_S = 0$  geminals, we also have contributions to  $\langle \text{APSG} | \hat{E}_{kh}^{pq\uparrow} \hat{H}_i \hat{T} | \text{APSG} \rangle$  in the  $M_S \neq 0$  case as well. The diagrammatic rules applicable here are very similar here to those of the latter case, the main difference is that the density matrix definitions given above should be applied instead of the ones elaborated for  $M_S = 0$  geminals. The four relevant diagrams are:

$$\begin{aligned} & \sum_{m,n \in i} \sum_r^{(i, S_r=1)} h_{mn} t_{ji}^{pr} \sum_{a \in i} (C_{ma}^{iq\uparrow} C_{na}^{ir\uparrow} + C_{ma}^{iq\downarrow} C_{na}^{ir\downarrow}) \\ &= \sum_{m,n \in i} \sum_r^{(i, S_r=1)} h_{mn} t_{ji}^{pr} ({}^i Q_{nm}^{r\uparrow,q\uparrow} + {}^i Q_{nm}^{r\downarrow,q\downarrow}) \end{aligned}$$

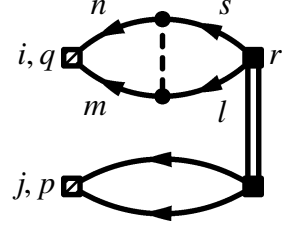


$$\begin{aligned} & \sum_{m,n \in j} \sum_v^{(j, S_v=1)} h_{mn} t_{ji}^{vq} \sum_{a \in j} (C_{ma}^{jp\uparrow} C_{na}^{jv\uparrow} + C_{ma}^{jp\downarrow} C_{na}^{jv\downarrow}) \\ &= \sum_{m,n \in j} \sum_v^{(j, S_v=1)} h_{mn} t_{ji}^{vq} \sum_{a \in j} ({}^j Q_{nm}^{v\uparrow,p\uparrow} + {}^j Q_{nm}^{v\downarrow,p\downarrow}) \end{aligned}$$

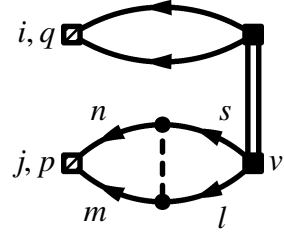




$$\begin{aligned} & \frac{1}{2} \sum_{m,n,l,s \in i} \sum_r^{(i, S_r=1)} [mn|ls] t_{ji}^{pr} (C_{mn}^{iq\uparrow} C_{ls}^{ir\uparrow} + C_{mn}^{iq\downarrow} C_{ls}^{ir\downarrow}) \\ &= \frac{1}{2} \sum_{m,n,l,s \in i} \sum_r^{(i, S_r=1)} [mn|ls] t_{ji}^{pr} (i\Gamma_{ml,ns}^{q\uparrow,r\uparrow} + i\Gamma_{ml,ns}^{q\downarrow,r\downarrow}) \end{aligned}$$

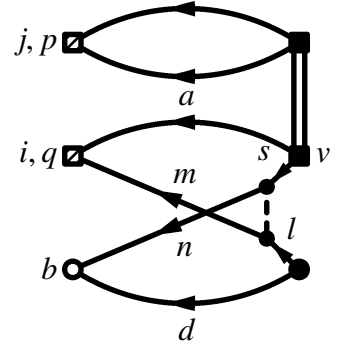


$$\begin{aligned} & \frac{1}{2} \sum_{m,n,l,s \in j} \sum_v^{(j, S_v=1)} [mn|ls] t_{ji}^{vq} (C_{mn}^{jp\uparrow} C_{ls}^{jv\uparrow} + C_{mn}^{jp\downarrow} C_{ls}^{jv\downarrow}) \\ &= \frac{1}{2} \sum_{m,n,l,s \in j} \sum_v^{(j, S_v=1)} [mn|ls] t_{ji}^{vq} (j\Gamma_{ml,ns}^{p\uparrow,v\uparrow} + i\Gamma_{ml,ns}^{p\downarrow,v\downarrow}) \end{aligned}$$

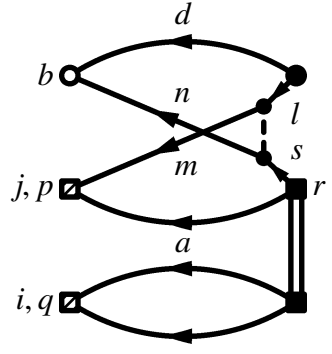


Here the *second-order transition matrix for spin-polarized geminals* is introduced. There are also some other corrections to  $\langle \text{APSG} | \hat{E}_{kh}^{pq\dagger} \hat{H}_d \hat{T} | \text{APSG} \rangle$  which are not that easy to categorize as the above terms. The diagrams corresponding to these terms are listed below, they can be evaluated by using all of the previous diagrammatic rules.

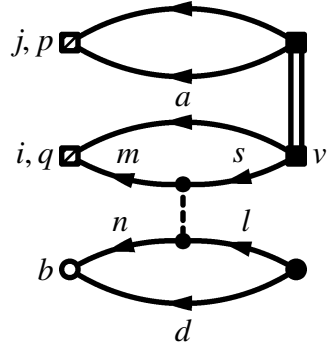
$$\begin{aligned} & - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m,s \in i} \sum_{n,l \in b} \sum_v^{(i, S_v=1)} t_{ji}^{pv} [mn|ls] \\ & \times \left( \sum_{a \in i} C_{ma}^{iq\uparrow} C_{sa}^{iv\uparrow} \sum_{d \in b} C_{nd}^{b0} C_{ld}^{b0} + \sum_{a \in i} C_{ma}^{iq\downarrow} C_{sa}^{iv\downarrow} \sum_{d \in b} C_{nd}^{b0} C_{ld}^{b0} \right) \\ &= - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m,s \in i} \sum_{n,l \in b} \sum_v^{(i, S_v=1)} t_{ji}^{pv} [mn|ls] (iQ_{sm}^{v\uparrow,q\uparrow} P_{ln}^{b0,\alpha} + iQ_{sm}^{v\downarrow,q\downarrow} P_{ld}^{b0,\beta}) \end{aligned}$$



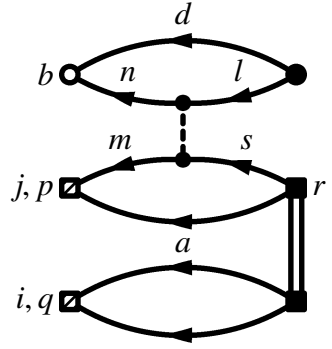
$$\begin{aligned}
& - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in j} \sum_{n, l \in b} \sum_r^{(j, S_r=1)} t_{ji}^{rq} [mn|ls] \\
& \times \left( \sum_{a \in j} C_{ma}^{jp \uparrow} C_{sa}^{jr \uparrow} \sum_{d \in b} C_{nd}^{b0} C_{ld}^{b0} + \sum_{a \in j} C_{ma}^{jp \downarrow} C_{sa}^{jr \downarrow} \sum_{d \in b} C_{dn}^{b0} C_{dl}^{b0} \right) \\
& = - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in j} \sum_{n, l \in b} \sum_r^{(j, S_r=1)} t_{ji}^{rq} [mn|ls] \left( {}^j Q_{sm}^{r \uparrow, p \uparrow} P_{ln}^{b0, \alpha} + {}^j Q_{sm}^{r \downarrow, p \downarrow} P_{ln}^{b0, \beta} \right)
\end{aligned}$$



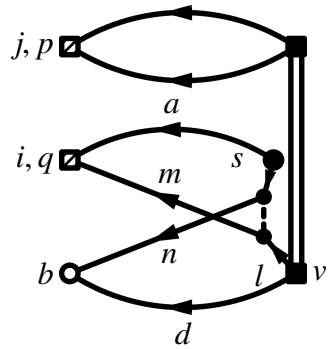
$$\begin{aligned}
& \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in i} \sum_{n, l \in b} \sum_v^{(i, S_v=1)} t_{ji}^{pv} [mn|sl] \left( \sum_{a \in i} C_{ma}^{iq \uparrow} C_{sa}^{iv \uparrow} \right. \\
& \times \sum_{d \in b} (C_{nd}^{b0} C_{ld}^{b0} + C_{dn}^{b0} C_{dl}^{b0}) + \sum_{a \in i} C_{ma}^{iq \downarrow} C_{sa}^{iv \downarrow} \sum_{d \in b} (C_{nd}^{b0} C_{ld}^{b0} + C_{dn}^{b0} C_{dl}^{b0}) \left. \right) \\
& = \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in i} \sum_{n, l \in b} \sum_v^{(i, S_v=1)} t_{ji}^{pv} [mn|sl] \left( {}^i Q_{sm}^{v \uparrow, q \uparrow} P_{ln}^{b0} + {}^i Q_{sm}^{v \downarrow, q \downarrow} P_{ln}^{b0} \right)
\end{aligned}$$

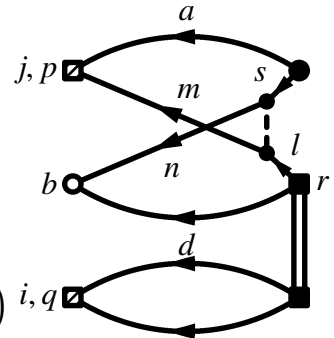


$$\begin{aligned}
& \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in j} \sum_{n, l \in b} \sum_r^{(j, S_r=1)} t_{ji}^{rq} [mn|sl] \left( \sum_{a \in j} C_{ma}^{jp \uparrow} C_{sa}^{jr \uparrow} \right. \\
& \times \sum_{d \in b} (C_{nd}^{b0} C_{ld}^{b0} + C_{dn}^{b0} C_{dl}^{b0}) + \sum_{a \in j} C_{ma}^{jp \downarrow} C_{sa}^{jr \downarrow} \sum_{d \in b} (C_{nd}^{b0} C_{ld}^{b0} + C_{dn}^{b0} C_{dl}^{b0}) \left. \right) \\
& = \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in j} \sum_{n, l \in b} \sum_r^{(j, S_r=1)} t_{ji}^{rq} [mn|sl] \left( {}^j Q_{sm}^{r \uparrow, p \uparrow} P_{ln}^{b0} + {}^j Q_{sm}^{r \downarrow, p \downarrow} P_{ln}^{b0} \right)
\end{aligned}$$

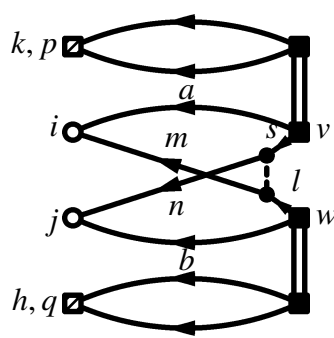


$$\begin{aligned}
& - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in i} \sum_{n, l \in b} \sum_v^{(b, S_v=1)} t_{jb}^{pv} [mn|ls] \\
& \times \left( \sum_{a \in i} C_{am}^{iq \uparrow} C_{as}^{i0} \sum_{d \in b} C_{dn}^{b0} C_{dl}^{bv \uparrow} + \sum_{a \in i} C_{ma}^{iq \downarrow} C_{sa}^{i0} \sum_{d \in b} C_{nd}^{b0} C_{dl}^{bv \downarrow} \right) \\
& = - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m, s \in i} \sum_{n, l \in b} \sum_v^{(b, S_v=1)} t_{jb}^{pv} [mn|ls] \left( {}^i Q_{sm}^{0, q \uparrow} {}^b Q_{ln}^{v \uparrow, 0} + {}^i Q_{sm}^{0, q \downarrow} {}^b Q_{ln}^{v \downarrow, 0} \right)
\end{aligned}$$



$$\begin{aligned}
& - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m,s \in j} \sum_{n,l \in b} \sum_{r \in (b, S_r=1)} t_{ib}^{qr} [mn|ls] \\
& \times \left( \sum_{a \in j} C_{am}^{jp\uparrow} C_{as}^{j0} \sum_{d \in b} C_{dn}^{b0} C_{dl}^{br\uparrow} + \sum_{a \in j} C_{ma}^{jp\downarrow} C_{sa}^{j0} \sum_{d \in b} C_{nd}^{b0} C_{ld}^{br\downarrow} \right) \\
& = - \sum_{\substack{b \\ b \neq i \neq j}} \sum_{m,s \in j} \sum_{n,l \in b} \sum_{r \in (b, S_r=1)} t_{ib}^{qr} [mn|ls] \left( {}^j Q_{sm}^{0,p\uparrow} {}^b Q_{ln}^{r\uparrow,0} + {}^j Q_{sm}^{0,p\downarrow} {}^b Q_{ln}^{r\downarrow,0} \right)
\end{aligned}$$


The last term that is needed to be taken into consideration belongs to the non-linear correction:

$$\begin{aligned}
& - \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{v \in (i, S_v=1)} \sum_{w \in (j, S_w=1)} t_{ki}^{pv} t_{jh}^{wq} [mn|ls] \\
& \times \left( \sum_{a \in i} C_{am}^{i0} C_{as}^{iv\uparrow} \sum_{b \in j} C_{nb}^{j0} C_{lb}^{jw\downarrow} + \sum_{a \in i} C_{ma}^{i0} C_{sa}^{iv\downarrow} \sum_{b \in j} C_{bn}^{j0} C_{bl}^{jw\uparrow} \right) = \\
& = - \sum_{\substack{i,j \\ i \neq j}} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{v \in (i, S_v=1)} \sum_{w \in (j, S_w=1)} t_{ki}^{pv} t_{jh}^{wq} [mn|ls] \left( {}^i Q_{sm}^{v\uparrow,0} {}^j Q_{ln}^{w\downarrow,0} \right. \\
& \quad \left. + {}^i Q_{sm}^{v\downarrow,0} {}^j Q_{ln}^{w\uparrow,0} \right)
\end{aligned}$$


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# Appendix

## 6.1 Elements of second quantization

Anticommutator relation of fermion creation operators:

$$[\chi_\mu^+, \chi_\nu^+]_+ = \chi_\mu^+ \chi_\nu^+ + \chi_\nu^+ \chi_\mu^+ = 0. \quad (6.1)$$

Similarly for annihilation operators:

$$[\chi_\mu^-, \chi_\nu^-]_+ = \chi_\mu^- \chi_\nu^- + \chi_\nu^- \chi_\mu^- = 0. \quad (6.2)$$

Anticommutator relation for a fermion creation and annihilation operator:

$$[\chi_\mu^-, \chi_\nu^+]_+ = \chi_\mu^- \chi_\nu^+ + \chi_\nu^+ \chi_\mu^- = \delta_{\mu\nu} \quad (6.3)$$

Similar relations hold for creation and annihilation operators, when spatial orbitals are introduced ( $\chi_\mu(1) = m_\sigma(1)$ , where  $m$  is the spatial, while  $\sigma$  is the spin part of the orbital):

$$[m_\sigma^+, n_{\sigma'}^+]_+ = [m_\sigma^-, n_{\sigma'}^-]_+ = 0 \quad (6.4)$$

$$[m_\sigma^-, n_{\sigma'}^+]_+ = \delta_{mn} \delta_{\sigma\sigma'}$$

The second-quantized Hamiltonian in terms of spatial orbitals:

$$\hat{H} = \sum_{m,n} h_{mn} \sum_{\sigma} m_\sigma^+ n_\sigma^- + \frac{1}{2} \sum_{m,n,l,s} [mn|ls] \sum_{\sigma,\sigma'} m_\sigma^+ n_{\sigma'}^+ s_{\sigma'}^- l_\sigma^-, \quad (6.5)$$

where  $h_{mn}$  and  $[mn|ls]$  denote the one-electron and two-electron integrals (in [12|12] convention) respectively:

$$h_{mn} = \int_{-\infty}^{+\infty} m_{\sigma}(1) \hat{h} n_{\sigma}(1) d\mathbf{r}_1 \quad \sigma = \{\alpha, \beta\}$$

$$[mn|ls] = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} m_{\sigma}(1) n_{\sigma'}(2) \frac{1}{r_{12}} l_{\sigma}(1) s_{\sigma'}(2) d\mathbf{r}_1 d\mathbf{r}_2 \quad \sigma, \sigma' = \{\alpha, \beta\}$$

## 6.2 Second quantization of spin operators

The algebraic form of the  $\hat{S}^2$  spin operator:

$$\hat{S}^2 = \hat{S}^- \hat{S}^+ + \hat{S}_z^2 + \hat{S}_z \quad (6.6)$$

$$\hat{S}^2 |\Psi\rangle = S(S+1) |\Psi\rangle, \quad (6.7)$$

where  $S$  is the spin quantum number and the different operators are defined by the following relations ( $|\alpha\rangle$  and  $|\beta\rangle$  are the basic spin functions):

$$\begin{aligned} \hat{S}^- |\alpha\rangle &= |\beta\rangle & \hat{S}^- |\beta\rangle &= 0 \\ \hat{S}^+ |\alpha\rangle &= 0 & \hat{S}^+ |\beta\rangle &= |\alpha\rangle \\ \hat{S}_z |\alpha\rangle &= \frac{1}{2} |\alpha\rangle & \hat{S}_z |\beta\rangle &= -\frac{1}{2} |\beta\rangle \end{aligned}$$

The second-quantized form of the above mentioned operators:

$$\hat{S}_z = \frac{1}{2} \sum_m (m_{\alpha}^+ m_{\alpha}^- - m_{\beta}^+ m_{\beta}^-) \quad (6.8)$$

$$\hat{S}^+ = \sum_m m_{\alpha}^+ m_{\beta}^- \quad (6.9)$$

$$\hat{S}^- = \sum_m m_{\beta}^+ m_{\alpha}^- \quad (6.10)$$

### 6.3 Proof concerning the symmetry properties of geminal coefficient matrices and their spin states

In this section we are going to prove a relationship between the symmetry properties of the  $C^{ip}$  geminal coefficient matrix and the spin states of the corresponding geminal.

#### Symmetric coefficient matrix

For the symmetric case, geminal  $\psi_{ip}$  reads

$$\psi_{ip}^+ = \sum_{m \in i}^1 C_{mm}^{ip} m_\alpha^+ m_\beta^+ + \sum_{\substack{m, n \in i \\ m < n}}^2 C_{mn}^{ip} (m_\alpha^+ n_\beta^+ + n_\alpha^+ m_\beta^+) \quad (6.11)$$

Acting with the  $\hat{S}_z$  operator on the first term of eq. (6.11):

$$\begin{aligned} \hat{S}_z \sum_{m \in i} C_{mm}^{ip} m_\alpha^+ m_\beta^+ |\text{vac}\rangle &= \frac{1}{2} \sum_{n \in i} (n_\alpha^+ n_\alpha^- - n_\beta^+ n_\beta^-) \sum_{m \in i} C_{mm}^{ip} m_\alpha^+ m_\beta^+ |\text{vac}\rangle \\ &= \frac{1}{2} \sum_{m, n \in i} C_{mm}^{ip} (n_\alpha^+ n_\alpha^- m_\alpha^+ m_\beta^+ - n_\beta^+ n_\beta^- m_\alpha^+ m_\beta^+) |\text{vac}\rangle = \frac{1}{2} \sum_{m, n \in i} C_{mm}^{ip} (n_\alpha^+ \underbrace{n_\alpha^- m_\alpha^+}_{\delta_{mn}} m_\beta^+ + n_\beta^+ m_\alpha^+ \underbrace{n_\beta^- m_\beta^+}_{\delta_{mn}}) |\text{vac}\rangle = \\ &= \frac{1}{2} \sum_{m \in i} C_{mm}^{ip} (m_\alpha^+ m_\beta^+ + m_\beta^+ m_\alpha^+) |\text{vac}\rangle = 0. \end{aligned}$$

The effect of  $\hat{S}_z^2$  is accordingly the same:

$$\hat{S}_z^2 \psi_{ip}^+ |\text{vac}\rangle = 0.$$

The only remaining operator fragment of  $\hat{S}^2$ , the effect of which we haven't investigated yet on the first term is that of  $\hat{S}^- \hat{S}^+$ :

$$\begin{aligned} \hat{S}^+ \sum_{m \in i} C_{mm}^{ip} m_\alpha^+ m_\beta^+ |\text{vac}\rangle &= \sum_{m, n \in i} C_{mm}^{ip} n_\alpha^+ n_\beta^- m_\alpha^+ m_\beta^+ |\text{vac}\rangle = - \sum_{m, n \in i} C_{mm}^{ip} n_\alpha^+ m_\alpha^+ \underbrace{n_\beta^- m_\beta^+}_{\delta_{mn}} |\text{vac}\rangle = \\ &= - \sum_{m \in i} C_{mm}^{ip} m_\alpha^+ m_\alpha^+ |\text{vac}\rangle = 0 \end{aligned}$$

$\hat{S}^+$  already nulls the first term of eq. (6.11) so we don't have to care about the effect of  $\hat{S}^-$ . Now we turn our attention to the second term of eq. (6.11). The effect of  $\hat{S}_z$ :

$$\begin{aligned}
\hat{S}_z \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ + n_\alpha^+ m_\beta^+) |\text{vac}\rangle &= \frac{1}{2} \sum_{l \in i} (l_\alpha^+ l_\alpha^- - l_\beta^+ l_\beta^-) \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ + n_\alpha^+ m_\beta^+) |\text{vac}\rangle \\
&= \frac{1}{2} \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (l_\alpha^+ l_\alpha^- m_\alpha^+ n_\beta^+ + l_\alpha^+ l_\alpha^- n_\alpha^+ m_\beta^+ - l_\beta^+ l_\beta^- m_\alpha^+ n_\beta^+ - l_\beta^+ l_\beta^- n_\alpha^+ m_\beta^+) |\text{vac}\rangle \\
&= \frac{1}{2} \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (l_\alpha^+ \underbrace{l_\alpha^- m_\alpha^+}_{\delta_{ml}} n_\beta^+ + l_\alpha^+ \underbrace{l_\alpha^- n_\alpha^+}_{\delta_{nl}} m_\beta^+ + l_\beta^+ m_\alpha^+ \underbrace{l_\beta^- n_\beta^+}_{\delta_{nl}} + l_\beta^+ n_\alpha^+ \underbrace{l_\beta^- m_\beta^+}_{\delta_{ml}}) |\text{vac}\rangle \\
&= \frac{1}{2} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ + n_\alpha^+ m_\beta^+ - m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+) |\text{vac}\rangle = 0.
\end{aligned}$$

Acting with  $\hat{S}_z^2$  on  $\psi_i$  is thus

$$\hat{S}_z^2 \psi_i^+ |\text{vac}\rangle = 0.$$

Finally, the effect of  $\hat{S}^- \hat{S}^+$ :

$$\begin{aligned}
\hat{S}^+ \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ + n_\alpha^+ m_\beta^+) |\text{vac}\rangle &= \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (l_\alpha^+ l_\beta^- m_\alpha^+ n_\beta^+ + l_\alpha^+ l_\beta^- n_\alpha^+ m_\beta^+) |\text{vac}\rangle \\
&= - \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (l_\alpha^+ m_\alpha^+ \underbrace{l_\beta^- n_\beta^+}_{\delta_{nl}} + l_\alpha^+ n_\alpha^+ \underbrace{l_\beta^- m_\beta^+}_{\delta_{ml}}) |\text{vac}\rangle = - \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (n_\alpha^+ m_\alpha^+ + m_\alpha^+ n_\alpha^+) |\text{vac}\rangle = 0.
\end{aligned}$$

Acting with  $\hat{S}^-$  on the above equation would be zero obviously. Altogether we can conclude that

$$\hat{S}^2 \left( \sum_{m \in i} C_{mm}^{ip} m_\alpha^+ m_\beta^+ + \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ + n_\alpha^+ m_\beta^+) \right) = 0,$$

thus a symmetric coefficient matrix belongs to an  $S = 0$  singlet geminal.

### Antisymmetric coefficient matrix

In the antisymmetric case, no diagonal elements of  $C^{ip}$  are present and geminal  $\psi_{ip}$  has the following creation operator:



$$\psi_{ip}^+ = \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+)$$

Transforming this geminal with operator  $\hat{S}_z$  and  $\hat{S}_z^2$ :

$$\begin{aligned} \hat{S}_z \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+) |\text{vac}\rangle &= \frac{1}{2} \sum_{l \in i} (l_\alpha^+ l_\alpha^- - l_\beta^+ l_\beta^-) \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+) |\text{vac}\rangle \\ &= \frac{1}{2} \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (l_\alpha^+ l_\alpha^- m_\alpha^+ n_\beta^+ - l_\beta^+ l_\beta^- m_\alpha^+ n_\beta^+ - l_\alpha^+ l_\alpha^- n_\alpha^+ m_\beta^+ + l_\beta^+ l_\beta^- n_\alpha^+ m_\beta^+) |\text{vac}\rangle \\ &= \frac{1}{2} \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (l_\alpha^+ \underbrace{l_\alpha^- m_\alpha^+}_{\delta_{lm}} n_\beta^+ + l_\beta^+ m_\alpha^+ \underbrace{l_\beta^- n_\beta^+}_{\delta_{ln}} - l_\alpha^+ \underbrace{l_\alpha^- n_\alpha^+}_{\delta_{ln}} m_\beta^+ - l_\beta^+ n_\alpha^+ \underbrace{l_\beta^- m_\beta^+}_{\delta_{lm}}) |\text{vac}\rangle \\ &= \frac{1}{2} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ - m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+ + n_\alpha^+ m_\beta^+) |\text{vac}\rangle = 0, \end{aligned}$$

and

$$\hat{S}_z^2 \sum_{\substack{m,n \\ m < n}} C_{mn}^i (m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+) |\text{vac}\rangle = 0.$$

Finally, the effect of  $\hat{S}^- \hat{S}^+$ :

$$\begin{aligned} \hat{S}^+ \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+) |\text{vac}\rangle &= \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^i (l_\alpha^+ l_\beta^- m_\alpha^+ n_\beta^+ - l_\alpha^+ l_\beta^- n_\alpha^+ m_\beta^+) |\text{vac}\rangle \\ &= \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (l_\alpha^+ n_\alpha^+ \underbrace{l_\beta^- m_\beta^+}_{\delta_{lm}} - l_\alpha^+ m_\alpha^+ \underbrace{l_\beta^- n_\beta^+}_{\delta_{ln}}) |\text{vac}\rangle = 2 \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} m_\alpha^+ n_\alpha^+ |\text{vac}\rangle \\ &= \hat{S}^- \left( 2 \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} m_\alpha^+ n_\alpha^+ \right) |\text{vac}\rangle = 2 \sum_{l \in i} \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} l_\beta^+ l_\alpha^- m_\alpha^+ n_\alpha^+ |\text{vac}\rangle = 2 \sum_{\substack{m,n \in i \\ m < n}} C_{mn}^{ip} (m_\alpha^+ n_\beta^+ - n_\alpha^+ m_\beta^+) |\text{vac}\rangle, \end{aligned}$$

which means that the antisymmetric coefficient matrix corresponds to an  $S = 1$  triplet geminal. ( $S(S + 1) = 2 \Rightarrow S = 1$ )

## 6.4 Mathematical description of unitary transformations

This section deals with the mathematical treatment of unitary transformations of one-electron orbitals, which is necessary to characterize the orbital optimization of geminals. For a set of one-electron orbitals  $\{\varphi_i\}_{i=1}^N$ , a unitary transformation looks as

$$\begin{aligned}\varphi'_i &= \sum_j U_{ji} \varphi_j \\ \boldsymbol{\varphi}' &= \boldsymbol{\varphi} \mathbf{U},\end{aligned}$$

where  $\boldsymbol{\varphi}'$  and  $\boldsymbol{\varphi}$  are row vectors and  $\mathbf{U}^\dagger \mathbf{U} = \mathbf{1}$ . For creation and annihilation operators in second-quantized formalism, the above relation is given as

$$\mathbf{a}'^+ = \mathbf{a}^+ \mathbf{U} \quad (6.12)$$

$$\mathbf{a}' = \mathbf{U}^\dagger \mathbf{a}, \quad (6.13)$$

where  $\mathbf{a}$ ,  $\mathbf{a}'$ ,  $\mathbf{a}^+$  and  $\mathbf{a}'^+$  are row vectors of annihilation and creation operators respectively. First we are going to show that eqs. (6.12) and (6.13) have an equivalent form:

$$\begin{aligned}a_i'^+ &= \sum_j U_{ji} a_j^+ \iff a_i'^+ = e^{-\hat{T}} a_i^+ e^{\hat{T}} \\ a_i' &= \sum_j U_{ji}^* a_j \iff a_i' = e^{-\hat{T}} a_i e^{\hat{T}},\end{aligned}$$

where  $\hat{T} = \sum_{i,j} T_{ij} a_i^+ a_j$ , matrix  $\mathbf{T}$  is anti-Hermitian ( $\mathbf{T}^\dagger = -\mathbf{T}$ ) and  $\mathbf{U} = e^{-\mathbf{T}}$ . It is enough to show this for just the creation operator, because the relation for annihilation operators can be obtained by taking the adjoint. Using up the Baker-Campbell-Hausdorff formula:

$$a_i'^+ = e^{-\hat{T}} a_i^+ e^{\hat{T}} = a_i^+ + [a_i^+, \hat{T}] + \frac{1}{2!} [[a_i^+, \hat{T}], \hat{T}] + \dots + \frac{1}{n!} [[\dots [[a_i^+, \hat{T}], \hat{T}], \dots], \hat{T}] + \dots$$

The second term can be simplified as

$$[a_i^+, \hat{T}] = a_i^+ \hat{T} - \hat{T} a_i^+ = \sum_{k,l} T_{kl} (a_i^+ a_k^+ a_l - a_k^+ a_l a_i^+) = \sum_{k,l} T_{kl} (a_i^+ a_k^+ a_l - a_k^+ \delta_{li} + a_k^+ a_i^+ a_l) = - \sum_k T_{ki} a_k^+$$

The third term is accordingly:

$$\frac{1}{2!}[[a_i^+, \hat{T}], \hat{T}] = - \sum_k T_{ki} [a_k^+, \hat{T}] = \frac{1}{2!} \sum_k T_{ki} \sum_l T_{lk} a_l^+ = \frac{1}{2!} \sum_l (T^2)_{li} a_l^+.$$

It is now easy to see that the n-th term of the above expression can be written as

$$\frac{1}{n!}[[\dots [[a_i^+, \hat{T}], \hat{T}], \dots], \hat{T}] = \frac{(-1)^n}{n!} \sum_l (\mathbf{T}^n)_{li} a_l^+$$

,

Thus we can conclude that

$$e^{-\hat{T}} a_i^+ e^{\hat{T}} = \sum_k a_k^+ (\mathbf{1} - \mathbf{T} + \frac{1}{2} \mathbf{T}^2 - \dots)_{ki} = \sum_k (e^{-\mathbf{T}})_{ki} a_k^+ = \sum_k U_{ki} a_k^+.$$

Transforming all orbitals in a  $\Psi$  one-determinant wave function can be written as

$$|\Psi'\rangle = \prod_i (e^{-\hat{T}} a_i^+ e^{\hat{T}}) |\text{vac}\rangle = e^{-\hat{T}} \left( \prod_i a_i^+ \right) e^{\hat{T}} |\text{vac}\rangle = e^{-\hat{T}} |\Psi\rangle,$$

where made use of  $e^{\hat{T}} e^{-\hat{T}} = 1$  and  $e^{\hat{T}} |\text{vac}\rangle = |\text{vac}\rangle$ . The unitary transformation of orbitals within a linear combination of determinants can be written similarly.

It is strongly recommended to restrict the excitations in  $\hat{T}$  to only those which do not mix orbitals with different spins:

$$\hat{T} = \sum_{i,j} T_{ij} (a_{i\alpha}^+ a_{j\alpha} + a_{i\beta}^+ a_{j\beta}) = \sum_{i,j} T_{ij} \hat{E}_{ij} = \sum_{\substack{i,j \\ i>j}} (T_{ij} \hat{E}_{ij} + T_{ji} \hat{E}_{ji}) = \sum_{\substack{i,j \\ i>j}} T_{ij} (\hat{E}_{ij} - \hat{E}_{ji}) = \sum_{\substack{i,j \\ i>j}} T_{ij} \hat{E}_{ij}^-$$

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