

# **Novel perturbation and orthogonalization methods applied in Quantum Chemistry**

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# 1 Introduction

This report summarizes our investigations on the properties and possible applications of the unitary perturbation approach and the related orthogonalization scheme suggested by Mayer.

In general, an orthogonalization procedure provides a set of orthogonal vectors, which may be required to conform with different criteria in different applications. Although, numerous orthogonalization techniques are known, there are still situations, where the application of the well-known methods may be unsuitable.

In this thesis, we focus on special quantum chemical applications, where there is a single vector, which should be kept unchanged during orthogonalization, while all other vectors of the initial set should be treated on an equal footing. Mayer's orthogonalization scheme completely meets these requirements. Additionally, it has a closed formulation, in contrast with numerical methods of everyday use.

In Chapter 2 we study Mayer's scheme and compare it to related orthogonalization procedures, namely the Gram-Schmidt and Löwdin's symmetric orthogonalization. A theorem is formulated, stating that Mayer's scheme is identical to a method, in which  $N$  unit vectors of an  $N+1$  dimensional basis are Gram-Schmidt orthogonalized to the selected vector in the first step. In the second step, Löwdin's symmetric orthogonalization is carried out in the  $N$  dimensional subspace of Gram-Schmidt orthogonalized vectors.

Mayer's vectors are applied to derive a Hermitian formulation of the Multiconfiguration Perturbation Theory (s-MCPT). The details of this quantum chemical method, applying Perturbation Theory (PT) to multireference wavefunctions, are introduced in Chapter 3.

Mayer's orthogonalization was obtained along with a perturbational approach (Unitary Perturbation Theory, UPT). This was successfully used to improve single reference electronic wavefunctions. A multireference variant (MC UPT) of UPT is presented in Chapter 4. Here Mayer's orthogonalization scheme and UPT are combined to perturb multireference ground state wavefunctions.

Mayer's orthogonalization scheme and the concept of UPT is closely related to the Jacobi matrix diagonalization method. In Chapter 5 numerical investigation of the iterative application of Mayer's scheme as a block-diagonalization alternative is presented on both mathematical and quantum chemical examples.

## 2 Orthogonalization methods

The purpose of this chapter is to give a brief overview of orthogonalization methods commonly used in quantum chemistry. If the reader is familiar with the concept it is advised to survey the notations of Chapter 2 and start reading in Section 2.3.

Let  $\{v^i, u^i\}_{i=0}^N \in V$  be arbitrary vectors in vector space  $V$ . In this thesis we focus on the case  $V = \mathfrak{R}^{N+1}$ , the orthogonalization methods are however applicable in any inner product space. Introducing Dirac's bra-ket formalism, row vectors are denoted as bra vectors:

$$\langle v| = (v_0, v_1 \dots v_N)$$

and column vectors are denoted as ket vectors:

$$|v\rangle = \begin{pmatrix} v_0 \\ v_1 \\ \vdots \\ v_N \end{pmatrix}.$$

The inner product in  $\mathfrak{R}^{N+1}$  is defined as follows:

$$\langle v^i | v^j \rangle = \sum_{k=0}^N v_k^i v_k^j.$$

Applying the inner product, two vectors in  $V$  are orthonormal if and only if the condition  $\langle v^i | v^j \rangle = \delta_{ij}$  is satisfied. A set of linearly independent vectors is not orthonormal in the general case. This is described with the metric matrix (Gram matrix, overlap matrix):

$$\langle v^i | v^j \rangle = S_{ij}. \tag{2.1}$$

If the vector set  $\{v^i\}_{i=0}^N$  serves as a basis, it may be desired to transform into an orthonormal set to bring some simplification in practical applications. The orthonormal set is denoted by  $\{u^i\}_{i=1}^N$ , with the overlap:

$$\langle u^i | u^j \rangle = \delta_{ij}$$

There are many orthogonalization algorithms to reach this goal, which can be divided into two groups. The first group collects sequence-dependent techniques, like Gram-Schmidt (GS), Householder and Givens rotations scheme[1]. In contrary to these, the ordering of the initial

vectors is immaterial in the methods forming the second group. Löwdin's symmetric [2] (also attributed to Landshoff and Wannier[3, 4]) and Löwdin's canonical[5] (also known as Scheinler-Wigner method[6] in the physics literature) orthogonalization; and the recent developments of Chaturvedi[7] belongs to this category. Mayer's method[8] bears characteristics of both groups. Methods of both groups share the idea to find a linear transform ( $\mathbf{T}$ ) relating vectors  $v^i$  and  $u^i$ :

$$\mathbf{U} = \mathbf{T}\mathbf{V},$$

where  $\mathbf{V}$  and  $\mathbf{U}$  are matrices containing the overlapping and the orthonormal sets of vectors  $v^i$  and  $u^i$  in their columns. This formulation leads to a beneficial general characterization[9] of orthogonalization methods.

In order to compare the two groups and their properties, the next few Sections give a concise summary of the GS and Löwdin's symmetrical method. It is followed by the detailed formulation of Mayer's scheme. Section 2.4 contains our results, the proof of the relation between the GS, Löwdin's symmetrical and Mayer's method.

## 2.1 Gram-Schmidt orthogonalization

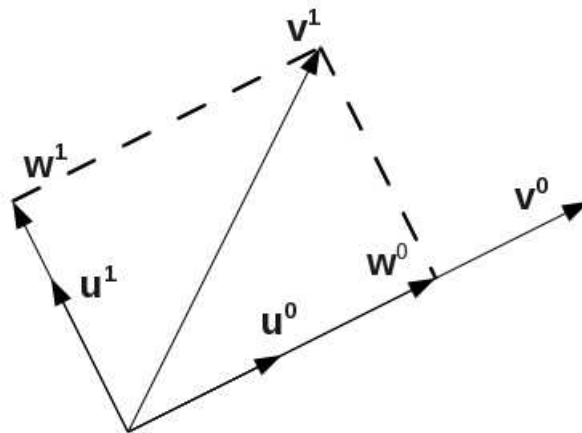
The Gram-Schmidt process is a general algorithm for orthonormalizing a set of overlapping vectors in a vector space. Besides that, by the time the process ends, one can get a linearly independent set.

Introducing the method, let us have a nonorthogonal set of vectors of  $\{v^i\}_{i=0}^N$  and define the projection operator:

$$\hat{P}_k = \frac{\langle v^k | v^k \rangle}{\langle v^k | v^k \rangle}.$$

Initially, an arbitrary vector is chosen to be the first element of the orthonormal set ( $u^0 = v^0$ ). Then, in each step  $i$  of the algorithm, the projections of vector  $v_i$  to all the previous vectors  $v^j$ , ( $j = 1, \dots, i - 1$ ) are subtracted from  $v^i$ , forming  $w^i$ :

$$|w^i\rangle = |v^i\rangle - \sum_{k=0}^{i-1} \hat{P}_k |v^i\rangle = |v^i\rangle - \sum_{k=0}^{i-1} \frac{\langle v^k | v^i \rangle}{\langle v^k | v^k \rangle} |v^k\rangle.$$

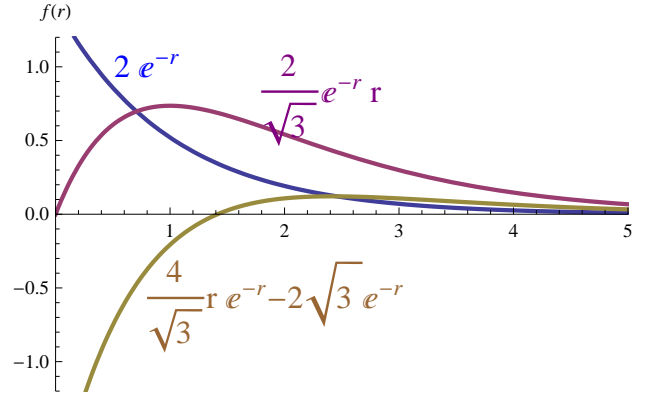


2.1 Figure: *The first step of the Gram-Schmidt orthonormalization process*

The first step of the procedure is illustrated in Fig. 2.1. After each step, one can normalize the vectors of  $w_i$  getting the orthonormal set of  $\{u_i\}_{i=0}^N$ , where  $|u_i\rangle = \frac{w^i}{\sqrt{\langle w^i | w^i \rangle}}$ . The most important properties of the GS method are the following:

- it is applicable to a linearly dependent set of input vectors,
- it has  $\mathcal{O}((N + 1)^3)$  computational cost,
- the orthonormal basis set  $\{u_i\}_{i=0}^N$  depends on ordering of the input  $\{v_i\}_{i=0}^N$  set ,
- one can select the first vector, which remains unaffected by the procedure (apart from normalization).

The order dependence of the GS procedure can be beneficial or disadvantageous too. In some applications it may be desirable to keep an original vector unchanged. Orthogonalization of Slater-type orbitals provides an example for such a situation. By a single GS step, the  $2s$  Slater-function can be orthogonalized to the unchanged  $1s$ , which forms a radial node apparent in Fig. 2.2. The GS method finds practical applications in quantum chemistry, for instance when orthogonalizing one-particle orbitals to a set kept unchanged. On the other hand, in periodic systems like a crystal or a polymer chain only an orthonormal and symmetry-equivalent orbital set can form a physically meaningful basis, i.e. basis functions on different sites should be mapped into each other by the translation operator. This requirement leads us to Löwdin's method.



2.2 Figure: Geometry dependence of the radial part of the Slater-type orbitals. The result of the Gram-Schmidt method on the  $2s$  orbital is shown in yellow.

## 2.2 Löwdin's symmetric orthogonalization

In contrast with the GS method, Löwdin's symmetric orthogonalization, in short Löwdin's orthogonalization treats the input vectors democratically. Some useful quantities are defined first, following the derivation of Mayer[10]. The overlap matrix as defined in Eq. (2.1) is Hermitian and positive definite, provided that the set  $\{v_i\}_{i=0}^N$  is linearly independent. Therefore, there exists a unitary matrix  $\mathbf{U}_S$ , which diagonalizes  $\mathbf{S}$ :

$$\mathbf{U}_S^\dagger \mathbf{S} \mathbf{U}_S = \mathbf{\Lambda}; \quad \mathbf{\Lambda} = \text{diag}(\lambda_i). \quad (2.2)$$

Introducing  $\mathbf{\Lambda}^{-1/2} = \text{diag}\left(\frac{1}{\sqrt{\lambda_i}}\right)$  the inverse of the square root of the overlap matrix is defined as follows:

$$\mathbf{S}^{-1/2} = \mathbf{U}_S \mathbf{\Lambda}^{-1/2} \mathbf{U}_S^\dagger, \quad (2.3)$$

The above  $\mathbf{S}^{-1/2}$  is indeed the inverse square root, since

$$\mathbf{S} (\mathbf{S}^{-1/2})^2 = \mathbf{U}_S \mathbf{\Lambda} \mathbf{U}_S^\dagger \mathbf{U}_S \mathbf{\Lambda}^{-1/2} \mathbf{U}_S^\dagger \mathbf{U}_S \mathbf{\Lambda}^{-1/2} \mathbf{U}_S^\dagger = \mathbf{U}_S \mathbf{\Lambda} (\mathbf{\Lambda}^{-1/2})^2 \mathbf{U}_S^\dagger = \mathbf{U}_S \mathbf{U}_S^\dagger = \mathbf{I},$$

where  $\mathbf{I}$  denotes the identity matrix.

Through this definition, the Löwdin basis is formed:

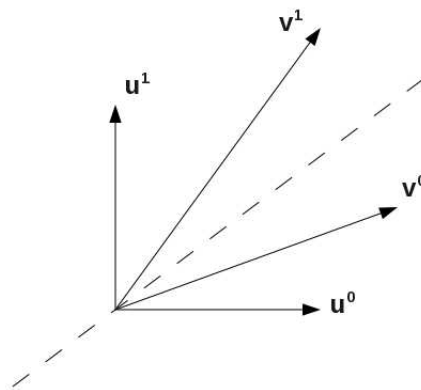
$$|u^i\rangle = \sum_{k=0}^N S_{ki}^{-1/2} |v^k\rangle, \quad (2.4)$$

where the following simplified notation is introduced:  $(S^{-1/2})_{ki} = S_{ki}^{-1/2}$ . One can easily prove

the orthonormality of the Löwdin vectors:

$$\begin{aligned} \langle u^i | u^j \rangle &= \left\langle \sum_{k=0}^N S_{ki}^{-1/2} v^k \middle| \sum_{l=0}^N S_{lj}^{-1/2} v^l \right\rangle \\ &= \sum_{k,l=0}^N (S^{-1/2})_{ki}^* \underbrace{\langle v^k | v^l \rangle}_{S_{kl}} S_{lj}^{-1/2} = \delta_{ij} \end{aligned} \quad (2.5)$$

As transparent from Eq. (2.4) treats the input vectors on an equal footing.



2.3 Figure: Löwdin's symmetric orthogonalization scheme with two vectors.

Observing Fig. 2.3., one can get a better insight into the properties of Löwdin's orthogonalization :

- here, none of the original vectors is preserved,
- Löwdin's transformation tunes the angle between the original vectors with symmetric movement until it reaches the right angle,
- the question of sequence dependence is not risen at all,
- the outcome is unique,
- Löwdin's scheme also has  $\mathcal{O}((N + 1)^3)$  computational cost,
- additionally, Löwdin's symmetric method has a beneficial extremal property, namely the deviation of the original and the resultant vectors is the smallest mean squares' sense among all the possible orthonormalizing transformations[11, 12]:

$$\langle u_{\text{Lwdn}}^i - v^i | u_{\text{Lwdn}}^i - v^i \rangle = \min.$$



Therefore, this is the method of choice when the distortion of the original vectors should be kept as small as possible.

## 2.3 Mayer's orthogonalization

The methods presented in the previous Sections have two things in common: they require numerical calculations to provide an orthonormal basis and they require a set of vectors as a start. In scientific applications, these criteria are not always met. For example orthonormal basis may be desired, that is orthogonal to a single one is provided with. It may also happen, that the  $\mathcal{O}((N+1)^3)$  scaling becomes an obstacle and one seeks a less demanding procedure.

The method introduced by Mayer[8], satisfies these above needs. Here an analytical formula is given for  $N$  orthonormal vectors that are orthogonal to the original one,  $|v\rangle$ .<sup>1</sup> Denoting the basis vectors of  $\mathfrak{R}^{N+1}$  space by  $|i\rangle$ , expansion of  $|v\rangle$  on the basis is written as

$$|v\rangle = \sum_{i=0}^N v_i |i\rangle.$$

We assume, that  $|v\rangle$  is normalized, i.e.  $\sum_{i=0}^N v_i^2 = 1$ . With this notation, the Mayer vectors are:

$$|u^k\rangle = \sum_{l=1}^N \left( \delta_{kl} - \frac{v_k v_l}{1+v_0} \right) |l\rangle - v_k |0\rangle, k \in (1, \dots, N), \quad (2.6)$$

and  $|u^0\rangle = |0\rangle$ . These vectors can be organized into a matrix, as columns:

$$U = \begin{pmatrix} v_0 & -v_1 & \dots & \dots & -v_i & \dots & -v_N \\ v_1 & 1 - \frac{v_1^2}{1+v_0} & -\frac{v_1 v_2}{1+v_0} & \dots & -\frac{v_1 v_i}{1+v_0} & \dots & -\frac{v_1 v_N}{1+v_0} \\ \vdots & -\frac{v_2 v_1}{1+v_0} & \ddots & & \vdots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots & & \vdots \\ v_j & -\frac{v_j v_1}{1+v_0} & -\frac{v_j v_2}{1+v_0} & \dots & -\frac{v_j v_i}{1+v_0} & \dots & -\frac{v_j v_N}{1+v_0} \\ \vdots & \vdots & & & \vdots & \ddots & \vdots \\ v_N & -\frac{v_N v_1}{1+v_0} & \dots & \dots & -\frac{v_N v_i}{1+v_0} & \dots & 1 - \frac{v_N^2}{1+v_0} \end{pmatrix}$$

The derivation of Mayer's vectors is presented in Section 4.1. It is straightforward to see the

<sup>1</sup>The notation consistent with the previous Sections would be  $|v^0\rangle$  for the initial vector. We however drop superscript 0 from here on, favoring the transparency of the formulae.

orthonormality of the construction:

$$\begin{aligned}
\langle u^m | u^k \rangle &= \left( v_m \langle 0 | - \sum_{n=1}^N \left( \delta_{nm} - \frac{v_n v_m}{1 + v_0} \right) \langle n | \right) \left( v_k | 0 \rangle - \sum_{l=1}^N \left( \delta_{kl} - \frac{v_k v_l}{1 + v_0} \right) | l \rangle \right) \\
&= v_m v_k + \sum_{l,n=1}^N \left( \frac{v_l v_k}{1 + v_0} - \delta_{kl} \right) \left( \frac{v_n v_m}{1 + v_0} - \delta_{nm} \right) \underbrace{\langle l | n \rangle}_{\delta_{nl}} \\
&= v_m v_k + \frac{v_k v_m}{(1 + v_0)^2} \underbrace{\sum_{l=1}^N v_l^2}_{1 - v_0^2} - \sum_{l=1}^N \delta_{kl} \frac{v_l v_m}{1 + v_0} - \sum_{l=1}^N \delta_{lm} \frac{v_l v_k}{1 + v_0} + \delta_{km} \\
&= v_m v_k \frac{(1 + v_0) + (1 - v_0) - 2}{1 + v_0} + \delta_{km} = \delta_{km}. \tag{2.7}
\end{aligned}$$

## 2.4 Properties of Mayer's orthogonalization

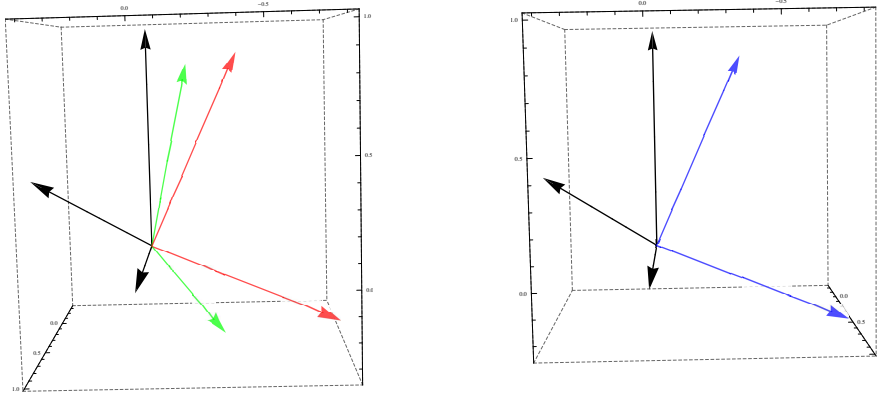
Inspecting Mayer's scheme, it is obvious, that there is a chosen vector ( $|v\rangle$ ) which is not modified by this transformation. In the two dimensional special case, the GS and Mayer's method are in fact equivalent. Turning our attention to the subspace orthogonal to the chosen vector, all the  $N$  resultant vectors are given by a sequence-independent, democratic formula. This property is reminiscent of Löwdin's symmetric method.

In this Section, these similarities are examined in more detail. If one wants to compare Mayer's orthogonalization with the GS and Löwdin's method a choice of  $N$  initial vectors in addition to  $|v\rangle$  is needed. For the sake of simplicity, let us have the initial set composed of  $|v\rangle$  and  $\{|k\rangle | k = 1, \dots, N\}$ . Note, that the case  $k = 0$  is missing. The unit vectors and  $|v\rangle$  overlap, thus one may apply the GS method to orthogonalize  $|k\rangle$ -s to  $|v\rangle$ :

$$|k'\rangle = |k\rangle - |v\rangle \langle v | k \rangle = |k\rangle - v_k |v\rangle, \tag{2.8}$$

since  $|v\rangle$  is normalized. As a result, the overlapping set  $\{|k'\rangle | k = 1, \dots, N\}$  is obtained. To preserve the properly, that  $|k'\rangle$ -s are treated on an equal footing up to this point, Löwdin's method could be a good choice to orthogonalize them in their subspace.

In Fig. 2.4 this procedure is compared with Mayer's scheme in three dimensions. Here an arbitrary initial vector (points to the left) is chosen together with two unit vectors. In the left panel the unit vectors are orthogonalized to the initial  $|v\rangle$  in GS sense. This results the green vectors in the subspace orthogonal to the initial vector. In a second step the green vectors are orthogonalized in their subspace by Löwdin's symmetric method, which leads to the red vectors. In the right panel, the same initial vector and its Mayer vectors are presented. By inspection, the result appears to be the same.



2.4 Figure: *Left panel: Original vector,  $|v\rangle$  (black, pointing to the left) and two unit vectors,  $|1\rangle$  and  $|2\rangle$  (black) overlapping with  $|v\rangle$ . Gram-Schmidt orthogonalized vectors  $|1'\rangle$  and  $|2'\rangle$  (green) are shown as well as the result of Löwdin orthogonalization on  $|1'\rangle$  and  $|2'\rangle$  (red). Right panel: Original vector (black, same as in the left panel) and its Mayer-orthogonalized vectors (blue).*

Based on the above observation, one can formulate a hypothesis, that Mayer's orthogonalization is the same as if orthogonalizing unit vectors to an initial one with the GS method, and treating the overlap of the resultant set by Löwdin's symmetric method. In what follows we present the proof of this conjecture.

As mentioned before, GS orthogonalizing the set of vectors  $\{|k\rangle|k = 1, \dots, N\}$  to  $|v\rangle$  we obtain the vectors  $|k'\rangle$  given Eq. (2.8). The overlap matrix of these vectors can be given as follows:

$$S'_{ik} = \langle i'|k'\rangle = (\langle i| - v_i\langle v|)(|k\rangle - v_k|v\rangle) = \delta_{ik} + v_i v_k \langle v|v\rangle - 2v_i v_k = \delta_{ik} - v_i v_k. \quad (2.9)$$

To subject vectors  $|k'\rangle$  to Löwdin's orthogonalization, we proceed by constructing the inverse of the square root of the overlap matrix. Since the formula of  $\mathbf{S}^{-1/2}$  does not exist in closed form in general,  $\mathbf{S}^{-1/2}$  is often calculated through numerical diagonalization of the overlap matrix, like in Eq. (2.3). In the present case the derivation of an analytical formula is possible due to the simplicity of  $\mathbf{S}'$ . To arrive at this expression, we construct the matrix Taylor-series of  $\mathbf{S}'$ . In one

dimension, for a real valued function:

$$x^{-1/2} \Big|_a = a^{-1/2} - \frac{1}{2}a^{-3/2}(x-a) + \frac{3}{8}a^{-5/2}(x-a)^2 + \dots = \sum_{i=0}^{\infty} (x-a)^i a^{-1/2-i} (-1)^i \frac{1}{i!} \prod_{j=1}^i \left(-\frac{1}{2} + j\right). \quad (2.10)$$

Let us apply this series formula for  $(\mathbf{S}')^{-1/2}$  around the  $N$  dimensional identity matrix,  $\mathbf{I}$ :

$$(\mathbf{S}')^{-1/2} \Big|_{\mathbf{I}} = \mathbf{I} + \sum_{i=1}^{\infty} (\mathbf{S}' - \mathbf{I})^i (\mathbf{I})^{-1/2-i} (-1)^i \frac{1}{i!} \prod_{j=1}^i \left(-\frac{1}{2} + j\right). \quad (2.11)$$

To evaluate this expression, we first show by complete induction, that

$$(\mathbf{S}' - \mathbf{I})_{lk}^{i+1} = -(v_0^2 - 1)^i v_l v_k$$

The first power of  $\mathbf{S}' - \mathbf{I}$  is simply:

$$(\mathbf{S}' - \mathbf{I})_{ik} = \delta_{ik} - v_i v_k - \delta_{ik} = -v_i v_k$$

The second power:

$$(\mathbf{S}' - \mathbf{I})_{lk}^2 = \sum_{a=0}^N (-v_l v_a)(-v_a v_k) = v_l v_k \sum_{a=0}^N v_a^2 = (1 - v_0^2) v_l v_k = (v_0^2 - 1)(\mathbf{S}' - \mathbf{I})_{lk} \quad (2.12)$$

Based on Eq. (2.12) we formulate the hypothesis

$$(\mathbf{S}' - \mathbf{I})^i = (v_0^2 - 1)^{i-1} (\mathbf{S}' - \mathbf{I}),$$

and the induction step:

$$\begin{aligned} (\mathbf{S}' - \mathbf{I})_{lk}^{i+1} &= (\mathbf{S}' - \mathbf{I})^i (\mathbf{S}' - \mathbf{I}) = (v_0^2 - 1)^{i-1} (\mathbf{S}' - \mathbf{I}) (\mathbf{S}' - \mathbf{I}) \\ &= (v_0^2 - 1)^{i-1} (v_0^2 - 1) (\mathbf{S}' - \mathbf{I})_{lk} = (v_0^2 - 1)^i (\mathbf{S}' - \mathbf{I})_{lk}. \end{aligned} \quad (2.13)$$

Let us now substitute the result of Eq. (2.13) into the series expansion of Eq. (2.11):

$$\begin{aligned} (\mathbf{S}')^{-1/2} \Big|_{\mathbf{I}} &= \mathbf{I} + (\mathbf{S}' - \mathbf{I}) \sum_{i=1}^{\infty} (v_0^2 - 1)^{i-1} (-1)^i \prod_{j=1}^i \frac{1}{j} \left(-\frac{1}{2} + j\right) \\ &= \mathbf{I} + (\mathbf{S}' - \mathbf{I}) \frac{1}{v_0^2 - 1} \sum_{i=1}^{\infty} \prod_{j=1}^i (v_0^2 - 1) \left(-\frac{1}{2j} - 1\right) \\ &= \mathbf{I} - \frac{1}{v_0(v_0 + 1)} (\mathbf{S}' - \mathbf{I}), \end{aligned} \quad (2.14)$$

where the summation was carried out with a symbolic algebra program. Later, in Eq. (2.17) the formula for  $\mathbf{S}^{-1/2}$  is confirmed in another way too. From Eq. (2.14) the necessary matrix elements are the following:

$$(S')_{lk}^{-1/2} = \delta_{lk} + \frac{v_l v_k}{v_0(v_0 + 1)}. \quad (2.15)$$

At this point, the final vectors can be calculated by Löwdin's method:

$$\begin{aligned} |k''\rangle &= \sum_{l=1}^N S'_{lk}^{-1/2} |l\rangle = \sum_{l=1}^N \left( \delta_{lk} + \frac{v_l v_k}{v_0(v_0 + 1)} \right) (|l\rangle - v_l |v\rangle) \\ &= |k\rangle - v_k |v\rangle + \sum_{l=1}^N \frac{v_k v_l}{v_0(1 + v_0)} |l\rangle - \frac{v_k}{v_0(1 + v_0)} \underbrace{\left( \sum_{l=1}^N v_l^2 \right)}_{1-v_0^2} \underbrace{\left( \sum_{l=0}^N v_l |l\rangle \right)}_{|v\rangle} \\ &= \sum_{l=1}^N \left( \delta_{kl} + \frac{v_k v_l}{v_0(1 + v_0)} - \frac{v_k v_l}{v_0} \right) |l\rangle - v_k |0\rangle = \sum_{l=1}^N \left( \delta_{kl} - \frac{v_k v_l}{1 + v_0} \right) |l\rangle - v_k |0\rangle. \end{aligned} \quad (2.16)$$

Looking at the result of the derivation in Eq. (2.16), one can find the definition of the Mayer vectors formulated in Eq. (2.6). Summarizing, Mayer introduced the closed formula of the orthogonalization process, where unit vectors of an  $N$  dimensional space are orthogonalized to an initial vector with GS method and the overlaps treated in the subspace of GS orthogonalized vectors by Löwdin's symmetric scheme.

It is worth to note that, due to the simplicity of Eq. (2.9), all integer and half integer matrix powers of  $\mathbf{S}'$  is available in closed form. For instance, the inverse of the overlap matrix is given by:

$$\begin{aligned} (\mathbf{S}')_{lk}^{-1} &= ((\mathbf{S}')^{-1/2} (\mathbf{S}')^{-1/2})_{lk} = \sum_{a=1}^N \left( \delta_{la} + \frac{v_l v_a}{v_0(v_0 + 1)} \right) \left( \delta_{ak} + \frac{v_a v_k}{v_0(v_0 + 1)} \right) \\ &= \delta_{lk} + \frac{v_l v_k}{v_0(v_0 + 1)} \left( 1 + 1 + \frac{1 - v_0^2}{v_0(v_0 + 1)} \right) = \delta_{lk} + \frac{v_l v_k}{v_0^2}. \end{aligned}$$

Here we can verify the formula of Eq. (2.15), by calculation the identity matrix via Eq. (2.15) and Eq. (2.9):

$$((\mathbf{S}')^{-1} \mathbf{S}')_{lk} = \sum_{a=1}^N \left( \delta_{la} + \frac{v_l v_a}{v_0^2} \right) (\delta_{ak} - v_a v_k) = \delta_{lk} + v_l v_k \left( -1 + \frac{1}{v_0^2} - \frac{1 - v_0^2}{v_0^2} \right) = \delta_{lk}. \quad (2.17)$$

In Section 3.6. the Mayer vectors are used to generate orthogonal vectors to a multiconfiguration wavefunction that serves as a reference of perturbation theory. As Mayer's orthogonalization is a general mathematical result, many more applications can be easily found to take advantage of the analytically available orthogonal vector set.

# 3 Perturbation Theory with Mayer's orthogonalization scheme

In the following Sections different quantum chemical applications of Mayer's orthogonalization are discussed. This Section concerns descriptions of the electron correlation problem by Rayleigh-Schrödinger Perturbation Theory (RS-PT).

## 3.1 Quantum Chemical introduction

It has become generally accepted in Quantum Chemistry to improve a first, relatively crude approximation step-by-step by more sophisticated methods. The Hartree-Fock (HF) method is for example a well-working first approximation, where the electron-electron interaction is treated in a mean field manner. This simplification leads to one particle equations, which is solved with self-consistent field (SCF) techniques resulting molecular orbitals and a one-determinant wavefunction. The HF method is widely applicable for low precision energy calculation and gives good approximation of some useful physical properties, such as molecular geometry or dipole moment[13].

However, there are problems where electron-electron interaction plays more important role, the so-called electron correlation problems. For instance the description of chemical bond dissociation, secondary interactions, thermodynamic and reaction kinetic or spectroscopic parameters necessitate a precision better than HF. If we define the correlation energy as the error of the HF method ( $E_{corr} = E_{exact} - E_{HF}$ ), our aim is to use a method, which possesses as many as possible of the following properties:

1. approximates acceptably the correlation energy,
2. has reasonable computational cost
3. it is size-consistent
4. provides discontinuity-free physical properties along the potential energy surface (PES)
5. there exists a way to improve the approximation in a systematic manner.

The presently available quantum chemical methods differ in the extent of fulfilling the above requirements. Of the most favored approximation strategies, we apply a two-step approximation

of the correlated energy. The first improvement describes the so-called static electron correlation (multireference methods, Section 3.2). The second step is the perturbative correction to the multireference approximation. This combination represents a reasonable approximation for the electron correlation problems, but it may violate size-consistency and point 4, and it is not variational, though systematically improvable.

## 3.2 Multireference methods in Quantum Chemistry

As it was indicated in the previous Section, there are two major strategies to describe the correlation energy. When only the so-called dynamic correlation is treated, one determinant (mainly the HF) is the starting point and is corrected by incorporating the effect of numerous with other excited ones. The results highly rely on two assumptions. The HF determinant has to be a qualitatively good approximation and the set of the excited determinants considered has to contain the most important ones. We apply Perturbation Theory for describing the dynamic correlation (Section 3.3), from the many other options (eg. Coupled Cluster, Configurational Interaction)[14].

In the present Section it is briefly outlined, what methods are available, when one determinant is not even a qualitatively good description. In this case the inclusion of the dynamic correlation does not correct this deficiency. Here one faces a situation, where a handful of determinants have similarly large importance in the total wavefunction (static electron correlation). Although, appropriately modified versions of the HF method (Unrestricted Hartree–Fock (UHF) and Restricted Open shell Hartree–Fock (ROHF) and Extended Hartree–Fock (EHF) [10]) can cope with this situation more or less, the general practical solution is the Multiconfiguration Self-Consistent Field (MCSCF) methods[14]. The MCSCF wavefunction can be defined as follows:

$$\Psi_{MCSCF} = \sum_m c_m |m\rangle, \quad (3.1)$$

where  $|m\rangle = \det|\phi_1, \dots, \phi_n|$  denotes determinants, with the orbitals  $\phi_i$  expanded in terms of atomic orbitals of  $\chi_a$  as:

$$\phi_i = \sum_a c_a(i) \chi_a.$$

The expansion of Eq. (3.1) does not extend to the full CI space, it is restricted, as will be seen below. The determinants  $|m\rangle$  considered in the expansion of  $\Psi_{MCSCF}$  form the reference space (denoted later by  $M$ ). Comparing with the HF method, MCSCF needs more user control. One has to decide before the MCSCF calculation, which  $|m\rangle$  determinants are important. This set is preferably kept as short as possible. Coefficients optimization  $c_m$  and  $c_a(i)$  are optimized

simultaneously by minimizing the energy expectation value. Note that  $c_m$  are linear, while  $c_a(i)$  are nonlinear parameters.

Among MCSCF methods, the Complete Active Space (CAS) model is widely used. Here we divide the orbitals into three groups. Orbitals of the lowest energy (core) are doubly occupied in each determinant. Similarly, the orbitals of highest energy (virtinals) are not occupied in any of  $|m\rangle$  in  $\Psi_{MCSCF}$ . In the middle, the active space orbitals are found, where electrons are distributed in all possible manner in a CAS calculation. One has to assign active electrons ( $n'$ ) and active orbitals ( $n$ ) based on problem-specific information, which construction is denoted by CAS( $n', n$ ).

The majority of our test studies are carried out with an even simpler, variational MR function, the Anti-symmetrized Product of Strongly Orthogonal Geminals (APSG)[15]. Here two electron functions (geminals) are used to form the wavefunction and due to the antisymmetrizer the Pauli-principle is fulfilled:

$$\Psi_{APSG} = \hat{A} (\psi_{N/2}(N-1, N) \dots \psi_2(3, 4)\psi_1(1, 2)) ,$$

where in geminal  $i$ :

$$\psi_i(2i-1, 2i) = \frac{1}{\sqrt{2}} \sum_{k \in i} c_k^i \phi_k^i(2i-1) \phi_k^i(2i) [\alpha(2i-1)\beta(2i) - \beta(2i-1)\alpha(2i)]$$

we sum over all molecular orbitals ( $\phi_k^i$ ) assigned to geminal  $i$ . Here one has to optimize coefficients of the molecular orbitals in a geminal ( $c_k^i$ ) and its  $d_{k\mu}^i$  expansion coefficients on atomic orbitals ( $\phi_k^i = \sum_{\mu} d_{k\mu}^i \chi_{\mu}$ ). This optimization is performed based on the variational principle.

### 3.3 Rayleigh-Schrödinger Perturbation Theory

This Section briefly summarizes perturbation theory (PT) as applied in quantum chemistry with the purpose of laying down the notations.

Our attention is focused on time-independent Rayleigh-Schrödinger Perturbation Theory, with non-degenerate ground state[16, 17]. The key concept in PT is the partitioning of the Hamiltonian ( $\hat{H}$ ) into an approximate, zero-order part  $\hat{H}^{(0)}$  and a perturbation part  $\hat{W}$ :

$$\hat{H} = \hat{H}^{(0)} + \hat{W}. \quad (3.2)$$

It is assumed that, the solution of the zero-order problem is available:

$$\hat{H}^{(0)}|\Phi_i\rangle = E_i^{(0)}|\Phi_i\rangle, \quad (3.3)$$



where  $|\Phi_i\rangle$  denotes the zero-order wavefunction and  $E_i^{(0)}$  stands for the zero-order energy of state  $i$ . The perturbational approach operates with an infinite series to approximate the solution of the exact Schrödinger-equation ( $\hat{H}|\Psi_i\rangle = E_i|\Psi_i\rangle$ ):

$$\Psi_i = \Psi_i^{(0)} + \sum_{k=1}^{\infty} \Psi_i^{(k)} \quad \text{and} \quad E_i = E_i^{(0)} + \sum_{k=1}^{\infty} E_i^{(k)}, \quad (3.4)$$

where  $\Psi_i^{(k)}$  and  $E_i^{(k)}$  are the  $k^{\text{th}}$  order wavefunction and energy correction, respectively.  $\Psi_i^{(0)}$  is the solution of the zero-order problem and its corrections are usually set to be orthogonal to the zero-order function (so-called intermediate normalization):  $\langle \Psi_i^{(0)} | \Psi_i^{(k)} \rangle = 1$ .

Referring to well-composed introductions in the literature[10], only a brief resume of perturbation formulae is given here. From now on, we introduce simplified notations, where it does not cause any confusion. The state of interest is going to be  $i = 0$ . We refer to this state, as reference state, and its index is going to be abandoned. Moreover, index notation is adopted for the solutions of the zero-order problem:

$$|\Phi_0\rangle = |0\rangle \quad \text{and} \quad |\Phi_k\rangle = |k\rangle.$$

With this notation, the first order correction is given by:

$$E^{(1)} = \langle \Phi_0 | \hat{W} | \Phi_0 \rangle = \langle 0 | W | 0 \rangle = W_{00},$$

with the following notation for the matrix elements the perturbation operator:  $W_{ik} = \langle \Phi_i | \hat{W} | \Phi_k \rangle = \langle i | \hat{W} | k \rangle$ . In our further steps, we introduce the reduced resolvent for the inverse of operator  $(E_0^{(0)} - \hat{H}^{(0)})$  expressed in the basis of the zero-order solutions in a spectral form:

$$\hat{Q} = - \sum_{k \neq 0} \frac{|k\rangle \langle k|}{E_k^{(0)} - E_0^{(0)}} = - \sum_{k \neq 0} \frac{|k\rangle \langle k|}{\Delta_k}. \quad (3.5)$$

With the use of  $\hat{Q}$ , one can get for the first order wavefunction the following expression:

$$|\Psi^{(1)}\rangle = -\hat{Q}(\hat{W} - E^{(1)})|0\rangle = - \sum_{k \neq 0} \frac{\langle k | \hat{W} | 0 \rangle}{E_k^{(0)} - E_0^{(0)}} |k\rangle = - \sum_{k \neq 0} \frac{W_{k0}}{\Delta_k} |k\rangle \quad (3.6)$$

With  $|\Psi^{(1)}\rangle$  at hand, the second order energy correction is:

$$E^{(2)} = \langle \Phi_0 | \hat{W} | \Psi^{(1)} \rangle = - \sum_{k \neq 0} \frac{\langle 0 | \hat{W} | k \rangle \langle k | \hat{W} | 0 \rangle}{E_k^{(0)} - E_0^{(0)}} = - \sum_{k \neq 0} \frac{W_{0k} W_{k0}}{\Delta_k}, \quad (3.7)$$

The above formula holds for the higher order corrections as well: the energy correction of order  $i + 1$  is obtained by  $\langle \Phi_0 | \hat{W} | \Psi^{(i)} \rangle$ . It is also true at any order, that operator  $\hat{W}$  acting on  $\Psi^{(i)}$  is

necessary to express  $\Psi^{(i+1)}$ . For the sake of comparison, corrections of the next order are also presented, because in the followings, because we are going to calculate corrections up to order three:

$$|\Psi^{(2)}\rangle = -\hat{Q}(\hat{W} - E^{(1)})|\Psi^{(1)}\rangle - \underbrace{\hat{Q}E^{(2)}|\Phi_0\rangle}_{=0}. \quad (3.8)$$

$$E^{(3)} = \langle\Phi_0|\hat{W}|\Psi^{(2)}\rangle = \sum_{k,l \neq 0} \frac{\langle 0|\hat{W}|k\rangle\langle k|\hat{W}|l\rangle\langle l|\hat{W}|0\rangle}{\Delta_k\Delta_l} - E^{(1)} \sum_{k \neq 0} \frac{\langle 0|\hat{W}|k\rangle\langle k|\hat{W}|0\rangle}{\Delta_k^2} \quad (3.9)$$

### 3.4 Partitioning in PT

From a practical point of view, the partitioning (Eq. (3.2)) has to be specified. When choosing a zero-order Hamiltonian, one has to keep in mind, that the solution of the zero-order problem should be preferably simple, and perturbation should be as small as possible in order that the two series of Eq. (3.4) converge. These guidelines do not specify a unique  $\hat{H}^{(0)}$  in general, there may be more than one promising choice based on physical and/or mathematical arguments. In single reference PT, where the Hartree-Fock problem serves as the zero-order, the Møller-Plesset (MP) partitioning[18] is the most frequent choice.

Instead of the MP philosophy, one can invoke the idea of Epstein and Nesbet (EN) [19, 20]. They considered the representation of the Hamiltonian in the basis of the determinants built with HF molecular orbitals and simply took its diagonal part as a zero-order matrix. We note here, that the EN partitioning depends on the many-electron basis used for representing the Hamiltonian, which highlights its non-physical nature.

The above mentioned partitionings have all been developed in connection with the HF wavefunction as reference. Due to the well-known drawback of the HF approximation, the need of a better starting point in PT has been long present. When working with a multireferential zero-order function, the intention for selecting the partitioning for PT has usually been to generalize one of the above choices. Among all, EN partitioning is the choice, which is the most simple to apply in the multireferential reference based PT (so-called multireference PT, MRPT). This was the partitioning used in the early works of Davidson[21]. One generalization of the MR partitioning could be to take the general Fock-matrix[22] as zero-order. An other MR partitioning idea starts from the physical interpretation of HF orbital energies. According to the Koopmans-theorem, as an approximation, the negative of the occupied orbital energies can be regarded as ionization potentials (IP) and the virtuals' as electron affinities (EA). Beyond the Koopmans-approximation, it has been also investigated, whether IP's and EA's may serve as zero-order one-particle energies[23, 24, 25].

### 3.5 Multiconfiguration Perturbation Theory (MCPT)

There have been many attempts in the literature to introduce multireference perturbation methods[26], combining the advantages of multiconfigurational SCF and perturbative description of the electron correlation problem. In our present studies, we consider the Multiconfigurational Perturbation Theory (MCPT)[27], which was established in our laboratory. The MCPT method works with the concept of the HF determinant and its excited determinants, therefore exhibits a relatively simple and general formulation. To date, this method had the limitation of working with an asymmetric zero-order operator and a biorthogonal basis set. In this Section, this asymmetric framework is introduced briefly. In the following Section a symmetric version is presented. That was possible to develop based on Mayer's vectors presented previously.

Let us suppose, that a normalized multireference function is available as a result of a calculation introduced in Section 3.2. The expression of this function on the basis of determinants is written as:

$$\Psi_0^{(0)} = c_0|0\rangle + \sum_{k \neq 0}^M c_k|k\rangle, \quad (3.10)$$

where  $M$  denotes the model space, spanned by  $|0\rangle$  and those excited determinants that are used to build  $\Psi_0^{(0)}$ . This multireference function is considered as reference function. In Eq. (3.10) one determinant is separated from the others, usually that has the largest weight, i.e.  $c_0^2 > c_k^2$ . This determinant  $|0\rangle$  is called the principal or pivotal determinant. Our intention is to use  $\Psi_0^{(0)}$  and all excited determinants that can be generated from  $|0\rangle$  as a basis. This basis will be used to formulate a zero-order operator. The fact, that  $\Psi_0^{(0)}$  and  $|k\rangle$  overlap for  $|k\rangle \in M$  represents some difficulties. Here, either an orthogonalization is needed or the overlap has to be treated in a biorthogonal manner. In this Section, we present the original MCPT formulation, which deals with the biorthogonal option. The possibility of using an orthogonalized basis is discussed in the next Section.

In the original MCPT formulation[27], elements of the biorthogonal system defined in the reciprocal space are indicated with tilde symbols:

$$\langle \tilde{\Psi}_0^{(0)} | = \frac{1}{c_0} \langle 0 | \quad (3.11)$$

$$\langle \tilde{k} | = \langle k | - \frac{c_k}{c_0} \langle 0 | \quad (3.12)$$

These vectors trivially satisfy the biorthonormality relations:

$$\begin{aligned} \langle \tilde{\Psi}_0^{(0)} | \Psi_0^{(0)} \rangle &= 1 & \text{and} & & \langle \tilde{k} | l \rangle &= \delta_{kl} \\ \langle \tilde{\Psi}_0^{(0)} | l \rangle &= 0 & \text{and} & & \langle \tilde{k} | \Psi_0^{(0)} \rangle &= 0 \end{aligned}$$

This is the unprojected MCPT (u-MCPT) variant. Alternatively, in the projected MCPT (p-MCPT) one deals with the overlap in two steps. First a GS step is taken to project the components parallel with  $\Psi_0^{(0)}$  out of the determinant  $|k\rangle$ -s. After that, a biorthogonal set is constructed to the set of the projected determinants. Elements of this reciprocal set have the form given in Eq. (3.12). Note however, that  $\Psi_0^{(0)}$  does not have a reciprocal component in this approach, since the biorthogonal treatment affects only the GS-orthogonalized  $|k\rangle$  vectors. In what follows, we focus on the u-MCPT variant and refer to the literature for the p-MCPT counterpart[27] of the expressions.

Making use of the definitions in Eq. (3.11), the zero-order Hamiltonian can be formulated in spectral form as:

$$\hat{H}^{(0)} = E_0^{(0)} |\Psi_0^{(0)}\rangle \langle \tilde{\Psi}_0^{(0)}| + \sum_{k \neq 0}^M E_k^{(0)} |k\rangle \langle \tilde{k}| + \sum_l^N E_l^{(0)} |l\rangle \langle l|, \quad (3.13)$$

where  $|k\rangle \in N$  notation refers to those determinants, which are not present in the model space. They are orthogonal to the reference. Note that,  $\hat{H}^{(0)}$  of Eq. (3.13) is non-Hermitian. Since,  $|k\rangle \in N$  determinants represent the trivial case, later set  $N$  will not be distinguished, i.e.  $|\tilde{k}\rangle = |k\rangle$  for  $|k\rangle \in N$ .

The RS-PT formulae give previously assume a Hermitian zero-order operator. With the present definition of  $\hat{H}^{(0)}$  the biorthogonal version of RS-PT is to be used, where all the functions are taken from the reciprocal space. For the sake of simplicity, the zero-order energy is set to the non-symmetrical matrix element of the Hamiltonian:

$$E_0^{(0)} = \langle \tilde{\Psi}_0^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle \quad (3.14)$$

With this choice, the first-order energy vanishes:

$$E^{(1)} = \langle \tilde{\Psi}_0^{(0)} | \hat{W} | \Psi_0^{(0)} \rangle = \langle \tilde{\Psi}_0^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle - E_0^{(0)} = 0, \quad (3.15)$$

according to Eqs. (3.14) and (3.2). Reformulating the reduced resolvent of Eq. (3.5):

$$\hat{Q} = - \sum_{k \neq 0} \frac{|k\rangle \langle \tilde{k}|}{\Delta_k},$$

one can derive the biorthogonal second- and third-order corrections[27]:

$$E^{(2)} = - \frac{1}{c_0} \sum_{k \neq 0} \frac{\langle 0 | \hat{W} | k \rangle \langle \tilde{k} | \hat{W} | \Psi_0^{(0)} \rangle}{\Delta_k} \quad (3.16)$$

$$E^{(3)} = \frac{1}{c_0} \sum_{k, l \neq 0} \frac{\langle 0 | \hat{W} | k \rangle \langle \tilde{k} | \hat{W} | l \rangle \langle \tilde{l} | \hat{W} | \Psi_0^{(0)} \rangle}{\Delta_l \Delta_k} - \underbrace{E^{(1)}}_0 \frac{1}{c_0} \sum_{k \neq 0} \frac{\langle 0 | \hat{W} | k \rangle \langle \tilde{k} | \hat{W} | \Psi_0^{(0)} \rangle}{\Delta_k^2}. \quad (3.17)$$

From the practical point of view, it is useful to express matrix elements of  $\hat{W}$  with matrix elements of  $\hat{H}$  which can be easily done to get: the matrix elements in Eqs. (3.16) and (3.17) in the following form:

$$\langle 0|\hat{W}|k\rangle = \langle 0|\hat{H}|k\rangle \quad (k \neq 0) \quad (3.18)$$

$$\langle \tilde{l}|\hat{W}|\Psi_0^{(0)}\rangle = \langle \tilde{l}|\hat{H}|\Psi_0^{(0)}\rangle - \langle \tilde{l}|\Psi_0^{(0)}\rangle E_0^{(0)} = \langle \tilde{l}|\hat{H}|\Psi_0^{(0)}\rangle \quad (3.19)$$

$$\langle \tilde{k}|\hat{W}|l\rangle = \langle \tilde{k}|\hat{H}|l\rangle - \langle \tilde{k}|\hat{H}^{(0)}|l\rangle = \langle \tilde{k}|\hat{H}|l\rangle - \delta_{kl}E_k \quad (3.20)$$

The computational cost of the MCPT formulae is proportional to the length of the summations in Eqs. (3.16) and (3.17). For this reason it is useful to investigate the matrix elements more carefully and determine the number of interacting determinants. The Hamiltonian is a two particle operator, therefore all matrix elements vanish, which are computed with two determinants differing in more than two orbitals.

In case of the second-order, the appearance of  $\langle 0|\hat{H}|k\rangle$  restricts the determinants  $|k\rangle$  to singles ( $1\times$ ) and doubles ( $2\times$ ) according to Eq. (3.18). (Since  $|0\rangle$  is not necessarily the determinant built with HF molecular orbitals, the Brillouin-theorem does not exclude its interaction with the singles.) The third-order term is more expensive:  $|k\rangle$  can be at most doubly excited, hence  $|l\rangle$  can be at most a quadruple. We get back to the practical discussion of these energy correction formulae at the end of Section 3.6.

Before stepping to the symmetric MCPT formulation, it is worthwhile to discuss the choice for energy denominators in MCPT. Different partitioning techniques were tested previously, including the introduced EN partitioning[25]. According to our experience, these partitionings may be problematic in those situations, where or more excited determinants has the similar importance in the reference function as the principal determinant. This quasi-degeneracy leads to almost zero  $\Delta_k$  values and consequently unphysical, overestimated energy corrections, especially at order three. To avoid these divergences, based on the studies of Malrieu[24], in our recent investigations we successfully used the difference of ionization potentials (IP) and electron affinities (EA) as a perturbation denominator:

$$\Delta_k^{\text{IPEA}} = \sum_b^{\text{virt.}} \epsilon_b^{\oplus} - \sum_i^{\text{occ.}} \epsilon_i^{\ominus}, \quad (3.21)$$

where  $k$  is a hyper index associated with the transition from occupied orbitals 'i' to virtuals 'b'. Here,  $\epsilon_i^{\ominus}$  is the negative of the IP, calculated by considering the effect of electron removal on  $\Psi_0^{(0)}$ , and neglecting orbital relaxation.

$$\epsilon_i^{\ominus} = \frac{\langle \Psi_0^{(0)}|\hat{H}|\Psi_0^{(0)}\rangle}{\langle \Psi_0^{(0)}|\Psi_0^{(0)}\rangle} - \frac{\langle \Psi_0^{(0)}|\hat{a}_i^+ \hat{H} \hat{a}_i|\Psi_0^{(0)}\rangle}{\langle \Psi_0^{(0)}|\hat{a}_i^+ \hat{a}_i|\Psi_0^{(0)}\rangle}$$

Similarly, the EA is computed as:

$$\epsilon_b^{\oplus} = \frac{\langle \Psi_0^{(0)} | \hat{a}_b \hat{H} \hat{a}_b^+ | \Psi_0^{(0)} \rangle}{\langle \Psi_0^{(0)} | \hat{a}_b \hat{a}_b^+ | \Psi_0^{(0)} \rangle} - \frac{\langle \Psi_0^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle}{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle}$$

Here  $\hat{a}_i$  and  $\hat{a}_i^+$  denotes the creation and annihilation operators acting on orbital  $i$ . In our examples, this partitioning will be denoted by IPEA abbreviation.

### 3.6 Symmetric MCPT with Mayer's vectors

Although the non-Hermiticity of  $\hat{H}^{(0)}$  does not produce any problem in MCPT, it is interesting to investigate the alternative option: the case of the orthogonalized basis vectors. This may be done e.g. by Löwdin-orthogonalizing the set  $\Psi_0^{(0)}$  and  $\{|k\rangle, k = 1, \dots, N\}$ . However, this approach would unfavorably transform  $\Psi_0^{(0)}$ . From this respect, the GS method would be more welcome, which would leave  $\Psi_0^{(0)}$  intact. Considering, however, a full GS orthogonalization one has no control on the resultant excited determinants. For our purpose, Mayer's orthogonalization is an ideal solution: it is cost-efficient, preserves the reference function and keeps the resulted excited ones as close to  $|k\rangle$ -s as it is possible. We refer to the method using Mayer's vectors as symmetric MCPT (s-MCPT) from now on.

Taking  $|v\rangle = |\Psi_0^{(0)}\rangle$  as an initial vector and denoting the elements of the orthogonal set produced by Mayer's method by  $u^k = |k''\rangle$  the symmetric spectral resolution of  $\hat{H}^{(0)}$  takes the form:

$$\hat{H}^{(0)} = E_0^{(0)} |v\rangle \langle v| + \sum_{k \neq 0} E_k |k''\rangle \langle k''|.$$

For keeping formulae transparent, let  $|k''\rangle = |k\rangle$  if  $k \in N$ . Due to the symmetric formulation, the reference energy can be computed as an expectation value:

$$E_0^{(0)} = \langle \Psi_0^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle$$

In order to establish the relation with the previous discussion of Mayer's vectors, we use  $|\Psi_0^{(0)}\rangle = |v\rangle$  and

$$|v\rangle = v_0 |0\rangle + \sum_{k=1}^N v_k |k\rangle.$$

According to Eq. (3.15), similarly,  $E^{(1)} = 0$  in this formulation. Substituting the reduced resolvent into Eq. (3.16) the s-MCPT second-order is found to be:

$$E^{(2)} = - \sum_{k \neq 0} \frac{\langle v | \hat{W} | k'' \rangle \langle k'' | \hat{W} | v \rangle}{\Delta_k}, \quad (3.22)$$

where

$$\begin{aligned}\langle v|\hat{W}|k''\rangle &= \langle v|\hat{H}|\left\{\sum_{l\neq 0}\left(\delta_{kl}-\frac{v_kv_l}{1+v_0}\right)|l\rangle-v_k|0\rangle\right\}\rangle+\underbrace{\langle v|\hat{H}^{(0)}|k''\rangle}_0 \\ &= \langle v|\hat{H}|k\rangle-\sum_{l\neq 0}\frac{v_kv_l}{1+v_0}\langle v|\hat{H}|l\rangle-v_k\langle v|\hat{H}|0\rangle.\end{aligned}\quad (3.23)$$

Finally, the third-order energy is the following:

$$E^{(3)}=\sum_{k,l\neq 0}\frac{\langle v|\hat{W}|k''\rangle\langle k''|\hat{W}|l''\rangle\langle l''|\hat{W}|v\rangle}{\Delta_l\Delta_k},\quad (3.24)$$

where

$$\begin{aligned}\langle k''|\hat{W}|l''\rangle &= \left\{-v_k\langle 0|+\sum_{m\neq 0}\left(\delta_{km}-\frac{v_kv_m}{1+v_0}\right)\langle m|\right\}\hat{H}\left\{-v_l|0\rangle+\sum_{n\neq 0}\left(\delta_{ln}-\frac{v_lv_n}{1+v_0}\right)|n\rangle\right\} \\ &\quad -\underbrace{\langle k''|\hat{H}^{(0)}|l''\rangle}_{\delta_{kl}E_k^{(0)}}.\end{aligned}\quad (3.25)$$

To compare the computational cost of s-MCPT energies with the cost of u-MCPT, Eqs. (3.16) and (3.17) with Eqs. (3.22) and (3.24) are to be contrasted. It turns out, s-MCPT has  $\mathcal{O}(N_M)$  times demand of u-MCPT in second-order, where  $N_M$  is the number of the determinants in the model space. The factor of  $\mathcal{O}(N_M)$  rises from the fact, that the doubles limitation for the index  $k$  is only valid, if the principal determinant is present as the bra component of the reference function. In s-MCPT  $2\times$  excitations from any determinant present in  $\Psi_0^{(0)}$  have to be taken into account. Note, that the price of computing  $\langle k|\hat{H}|\Psi_0^{(0)}\rangle$  is the same in both methods and the sum appearing in the second term of Eq. (3.22) does not introduce a cost increase, since sum over  $l$  is computable irrespective of the index  $k$ . Therefore, the number of interacting determinants expands by at most a factor of  $N_M$ . If one can efficiently describe the static correlation by a small number of determinants, the  $\mathcal{O}(N_M)$  cost increase may be affordable.

One meets a somewhat worse situation at the third-order correction. In the third-order u-MCPT formulation of Eq. (3.17) the sum over index  $k$  runs for singles and doubles ( $\mathcal{O}(N_{2\times})$  cost) and for index  $l$  runs for the First-Order Configuration Interactions (FOCI). However, matrix element Eq. (3.20). provides an other limitation,  $|l\rangle$  could be only  $2\times$  excitations from any the actual  $|k\rangle$ . Therefore, sum over index  $l$  ends up with at most  $\mathcal{O}(N_{2\times})\mathcal{O}(N_M)$  cost.

The fact, that in s-MCPT (Eq. (3.24))  $|\Psi_0^{(0)}\rangle$  figures instead of  $|0\rangle$  as the bra reference function at third-order introduces again an  $\mathcal{O}(N_M)$  cost increase as compared to u-MCPT. Additionally, the lost of the restriction was present due to matrix element Eq. (3.20) in u-MCPT for indexes  $k$  and  $l$  could result extensive cost increase in case of  $\Psi_0^{(0)}$  functions consist of a

large number of determinants. There are an additional factor, arising from the evaluation of the matrix element  $\langle k'' | \hat{W} | l'' \rangle$ , but it is not relevant here to discuss this factor, since, due to the relatively large cost, the third-order s-MCPT is not implemented in this project.

In principle, a diagrammatic implementation could be made it possible to compute the third-order in this framework in reasonable time. We however work with a less efficient, but transparent code at present.

### 3.7 Numerical results with symmetric MCPT

In this Section test calculations are presented with the s-MCPT framework, computing second-order energies. For this purpose, I have created a FORTRAN program. Three important modules were available in our group, which I could include. The first one generates the excited determinants based on their occupational number representation. The second module computes matrix elements of the Hamiltonian between determinants using the integral lists. The third module is an implementation of a one-to-one assignment between the occupation number representation of an excited determinant (occupation string) and a serial index. This assignment is necessary for a relatively efficient implementation of the s-MCPT framework. The syntactic and semantic correctness of the code was tested in small examples against u-MCPT and p-MCPT codes, which was written and verified in our group previously.

The APSG calculations were carried out with the Budapest version of the MUNGAUSS program package[28], while the CAS wavefunctions were created with the GAMESS program suite[29]. Since the investigations are still on the testing stage, only less sophisticated multireference calculations and small quantum chemical basis sets were applied.

We selected test systems having a highly multireference nature, because in order to challenge the limitations of the s-MCPT method and compare its performance against the u-MCPT and p-MCPT variations. The FCI result was used for comparison in every cases, which was computed by a program implemented the based on the algorithm of Olsen[30]. The IPEA partitioning was used in the shown examples. Another partitioning variation, the averaged IPEA partitioning introduced in our previous work[25] was also computed. Since the determination of the indexes of the creation and annihilation operators in Eq. (3.21) defined by orbitals occupied in the present principal determinant. Hence, one may want to exclude the principal choice dependence of the IPEA partitioning and form averaged denominator with the following formula:

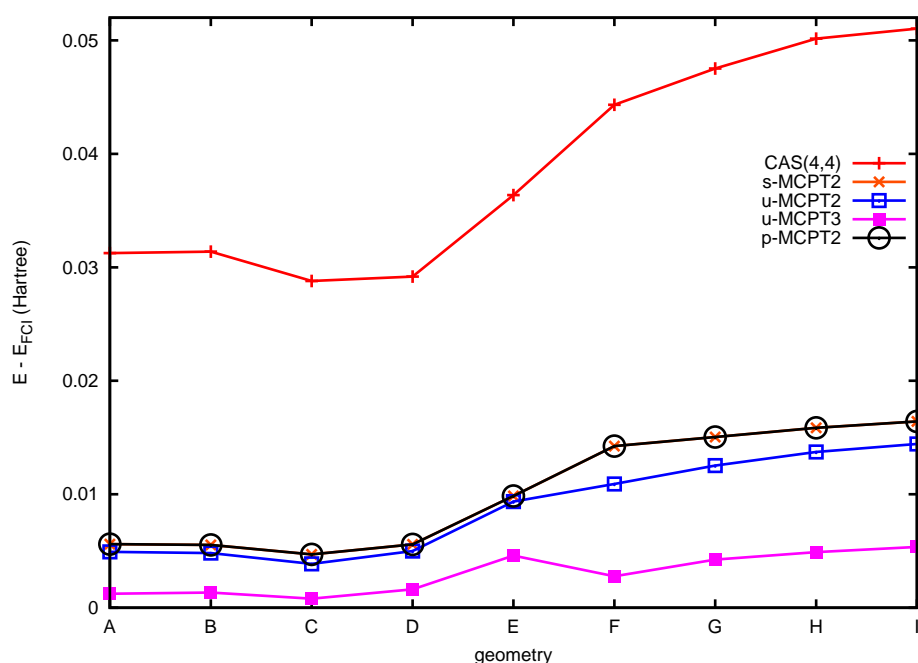
$$\Delta_k^{\text{avg-IPEA}} = \sum_{i=1}^{N_M} c_i^2 \Delta_k^{\text{IPEA}}(i),$$

where  $c_i$  are the coefficients are defined in Eq. (3.10) and index  $i$  refers to determinant  $|i\rangle$  in



$\Psi_0^{(0)}$ . Results with averaged IPEA denominators exhibit almost complete agreement with the IPEA's, therefore the averaged IPEA calculations are not shown.

The first example is the dissociation of the  $\text{BeH}_2$  molecule, where the Be nucleus is moved outwards from the equilibrium geometry perpendicular to the line of the H nuclei. At parallel with this the distance of the H nuclei is increased[31]. A CAS(4,4) reference function is applied in a Dunning-type valence double zeta (VDZ) basis set [32]. Under these conditions, there are twenty relevant determinants in the model space. Fig. 3.1. shows the error of different MCPT results as well as that of the CAS reference. Second-order results are labeled as MCPT2 and third-order results as MCPT3. Nine different geometry points are taken, where A stands for the equilibrium and I is the most distorted geometry. The Cartesian coordinates are given in the work of Purvis and Bartlett[31].

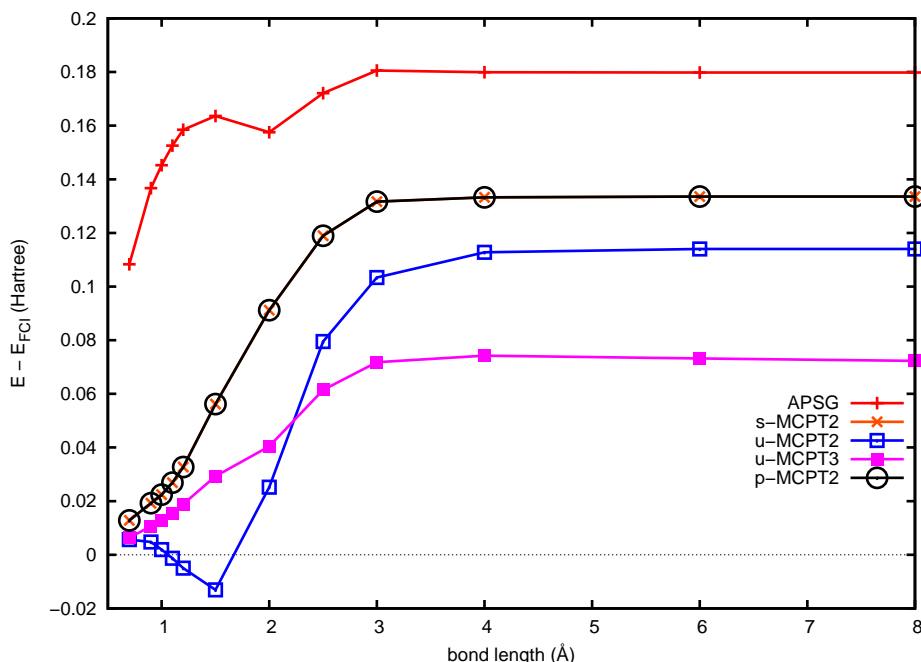


3.1 Figure: Dissociation of  $\text{BeH}_2$  at special geometries (for more details, see Ref. [31]). Error of different MCPT energies and the CAS(4,4) reference with respect to the FCI are shown. Dunning's VDZ basis was applied in all calculations. Second-order results are labeled as MCPT2 and third-order results as MCPT3.

As Fig. 3.1 reflects, the s-MCPT method gives almost equivalent result with the p-MCPT, they differ in the magnitude of microHartrees. Generally, all MCPT variants increase the parallelity and decrease the error of the reference with a satisfactory amount.

From the second example, we again infer that s-MCPT and p-MCPT methods behave similarly. Here the bond dissociation problem of the  $N_2$  molecule is presented (Fig. 3.2). A double zeta (DZ) basis set was applied and the core electrons of the N atoms were kept frozen. The reference function is an APSG with three geminals assigned to the three breaking bonds with two-two orbitals on each. This construction results eight determinants in the model space and works well along the whole PES. Fig. 3.2. shows the energy error with respect to the FCI result as a function of the bond length.

Similarly to the  $BeH_2$  case, the MCPT energies are systematically better, than the reference. This holds true around equilibrium geometries, while the results deteriorate somewhat at larger bond length. Methods p-, s-MCPT2 and u-MCPT3 compensate well the discontinuity of APSG. No difference between s-MCPT2 and p-MCPT2 is apparent in the figure.



3.2 Figure: Dissociation of  $N_2$  in DZ basis. Error of different MCPT energies and the APSG reference with respect to the FCI are shown as a function of the N-N distance.

As further examples, we also computed the  $H_2$  dimer in two arrangements. In both cases, we started from the square shaped geometry, with bond length of  $0.74 \text{ \AA}$ . The APSG reference in DZ basis was chosen with two-orbitals assigned to the geminals on each dissociating bonds. In this example, the  $H_2$  molecules were taken apart in both vertical and horizontal directions, forming a rectangle. In the second example, the  $H_2$  molecules were rotated around the axis perpendicular to the plane of the dimer and going through the center of the H-H bond. This rotation results a trapezoid shape arrangement with  $C_{2v}$  symmetry. In both cases, the conclusion

is similar to the previous observations', the new s-MCPT method gives results indistinguishable from the p-MCPT method on the scale of tens of microHartrees. (We note that, Fig. 4.1 contains the results of s-MCPT and p-MCPT in question.)

Comparison of the s-MCPT method with other multireference perturbation variants is not the subject of this work. Comprehensive studies of these types were published in Ref. [33].

# 4 Unitary Perturbation Theory (UPT)

## 4.1 Derivation of Mayer's Orthogonalization and UPT

In Section 2.3. Mayer's method of producing an orthonormal vector set orthogonal to a selected vector was presented as an orthogonalization procedure. This Section focuses on the idea which led to the introduction of Mayer's vectors and an approach based on this idea, that was named Unitary Perturbation Theory (UPT). The motive behind this study is to find a unitary transformation, which – upon acting a zero-order ground state – maps it into an improved ground state function. In the improved function, the effect of each excited state is described in an independent manner, i.e. without considering their interaction, like in first-order PT.

Adopting the original notation of Mayer[8], let us consider  $|0\rangle$  as a reference vector approximating the ground state and  $|i\rangle$  as an excited vector. In order to get a better description of the ground state one can combine these two vectors via a two-by-two rotation:

$$\begin{aligned} |0'\rangle &= |0\rangle \cos \varphi_i + |i\rangle \sin \varphi_i \\ |i'\rangle &= -|0\rangle \sin \varphi_i + |i\rangle \cos \varphi_i, \end{aligned} \quad (4.1)$$

The matrix of the Hamiltonian written in the basis of  $|0'\rangle$  and  $|i'\rangle$  is the following:

$$\begin{pmatrix} H'_{00} & H'_{0i} \\ H'_{i0} & H'_{ii} \end{pmatrix}$$

The angle  $\varphi_i$  is determined by the conditions of  $H'_{0i} = H'_{i0} = 0$  and  $H'_{00} \leq H'_{ii}$ . As a result of a simple derivation,  $\varphi_i$  is given by:

$$\varphi_i = \frac{1}{2} \arctan \left( \frac{2\langle 0|H|i\rangle}{\langle 0|\hat{H}|0\rangle - \langle i|H|i\rangle} \right). \quad (4.2)$$

The transformation between  $|0\rangle, |i\rangle$  and  $|0'\rangle, |i'\rangle$  is governed by the two dimensional rotation matrix:

$$\mathbf{U}_i^{2D} = \begin{pmatrix} \cos \varphi_i & -\sin \varphi_i \\ \sin \varphi_i & \cos \varphi_i \end{pmatrix}. \quad (4.3)$$

The above matrix, being unitary can be expressed as a matrix exponential of an antisymmetric matrix,  $\mathbf{A}_i^{2D}$ :

$$\mathbf{U}_i^{2D} = \exp(\mathbf{A}_i^{2D}), \text{ where } \mathbf{A}_i^{2D} = \begin{pmatrix} 0 & -\varphi_i \\ \varphi_i & 0 \end{pmatrix}.$$

If state  $|i\rangle$  is not the only excited state, matrix  $\mathbf{A}_i^{2D}$  has to be padded with zeros to properly describe the mixing of the ground state and the  $i^{\text{th}}$  excited state in  $N + 1$  dimension:

$$\mathbf{A}_i = \begin{pmatrix} 0 & 0 & \dots & -\varphi_i & \dots & 0 \\ 0 & 0 & \dots & 0 & \dots & 0 \\ \vdots & & & & & \vdots \\ \varphi_i & 0 & \dots & 0 & \dots & 0 \\ \vdots & & & & & \vdots \\ 0 & 0 & \dots & 0 & \dots & 0 \end{pmatrix}. \quad (4.4)$$

In traditional diagonalization approaches, transformations are performed successively with a similar unitary matrix. In the Jacobi-method the transformation matrix in the  $i^{\text{th}}$  step is given by  $\mathbf{A}_i$  of Eq. (4.4):

$$\mathbf{U}_i = \exp(\mathbf{A}_i).$$

Generally, these diagonalization procedures diminish the off-diagonal matrix elements in a systematic manner and leads to a diagonal matrix, if they are performed until convergence.

In principle, if only the lowest eigenvalue of a matrix is of interest, it is advised to take two-by-two rotations only between the ground state and the excited states. This procedure is the special case of the Jacobi method. It has to be stressed, that the two-by-two rotations in Eq. (4.3) do not commute, hence  $[U_i, U_j] \neq 0$ . Consequently, the outcome of a series of Jacobi-rotations is sequence-dependent, unless convergence is reached. Additionally, the matrix multiplication of  $\prod_{i=1}^N \mathbf{U}_i$  is complicated and time-consuming. Furthermore, while the first rotation successfully cancel the interaction between e.g.  $|0\rangle$  and  $|1\rangle$ , the second rotation between  $|0\rangle$  and  $|2\rangle$  also interferes with the interaction between  $|0\rangle$  and  $|1\rangle$  and restores its value to nonzero. For this reason, having finished with a sequence of two-by-two rotations for pairs  $|0\rangle$  and  $|1\rangle$  till  $|0\rangle$  and  $|N\rangle$  (a so-called sweep) one has to restart with  $|0\rangle$  and  $|1\rangle$  and carry on iterations. Alternatively, one has to agree with partial convergence, and a sequence-dependent improvement on the zero-order estimation.

An alternative way to look at the problem was introduced by Mayer, who exploited the exponential form of the unitary matrices to write:

$$\prod_{i=1}^N \mathbf{U}_i = \prod_{i=1}^N \exp(\mathbf{A}_i) = \exp\left(\ln\left(\prod_{i=1}^N \exp(\mathbf{A}_i)\right)\right) \approx \exp\left(\sum_{i=1}^N \mathbf{A}_i\right) = \exp(\mathbf{A}) = \mathbf{U}, \quad (4.5)$$

In the middle of Eq. (4.5) the sum of logarithm  $\sum_{i=1}^N \mathbf{U}_i$  is written instead of the logarithm of a product  $\prod_{i=1}^N \exp(\mathbf{A}_i)$ . This holds true only if matrixes  $\mathbf{U}_i$  commute. Note, however, that the goal is not to evaluate  $\prod_{i=1}^N \mathbf{U}_i$ . Starting with  $\prod_{i=1}^N \mathbf{U}_i$  merely serves as an initiative to find a simple parametrization of a unitary matrix.

Matrix  $\mathbf{U}$  on the right side properly serves this need, being parametrized by the rotation angles  $\varphi_1, \dots, \varphi_N$ . These angles constitute matrix  $\mathbf{A}$  in the following form:

$$\mathbf{A} = \begin{pmatrix} 0 & -\varphi_1 & -\varphi_2 & \dots & -\varphi_N \\ \varphi_1 & 0 & 0 & \dots & 0 \\ \varphi_2 & 0 & 0 & \dots & 0 \\ \vdots & & & & \vdots \\ \varphi_N & 0 & 0 & \dots & 0 \end{pmatrix}.$$

Moreover, this derivation treats excited vectors  $|1\rangle$  till  $|N\rangle$  an equal footing as apparent from the structure of matrix  $\mathbf{A}$ .

Most interestingly, due to the simplicity of  $\mathbf{A}$ , one can derive a closed formula for  $\mathbf{U}$ . To fulfill this aim, the matrix Taylor-series expansion of  $\mathbf{A}$  has to be exploited:

$$\exp(\mathbf{A}) = \sum_{i=1}^N \frac{1}{i!} \mathbf{A}^i = \mathbf{I} + \mathbf{A} + \frac{1}{2} \mathbf{A}^2 + \dots$$

An inspiring derivation reported in Ref. [8], results the following form for matrix  $\mathbf{U}$  of Eq. (4.5):

$$\mathbf{U} = \begin{pmatrix} \cos \varphi & -x_1 \sin \varphi & -x_2 \sin \varphi & \dots & -x_i \sin \varphi \dots \\ x_1 \sin \varphi & 1 + x_1^2(\cos \varphi - 1) & x_1 x_2(\cos \varphi - 1) & \dots & x_i x_1(\cos \varphi - 1) & \dots \\ x_2 \sin \varphi & x_1 x_2(\cos \varphi - 1) & 1 + x_2^2(\cos \varphi - 1) & \dots & x_i x_2(\cos \varphi - 1) & \dots \\ \vdots & & \vdots & & \vdots & \\ x_i \sin \varphi & x_1 x_i(\cos \varphi - 1) & x_2 x_i(\cos \varphi - 1) & \dots & 1 + x_i^2(\cos \varphi - 1) & \dots \\ \vdots & & \vdots & & \vdots & \\ x_N \sin \varphi & x_1 x_N(\cos \varphi - 1) & x_2 x_N(\cos \varphi - 1) & \dots & x_i x_N(\cos \varphi - 1) & \dots \end{pmatrix}, \quad (4.6)$$

with the notations:

$$\varphi = \left( \sum_{i=1}^N \varphi_i^2 \right)^{1/2} \quad (4.7)$$

and

$$x_i = \frac{\varphi_i}{\varphi}. \quad (4.8)$$

Since  $\mathbf{U}$  is unitary, its rows and columns form an orthonormal basis. If we substitute

$$v_0 = \cos \varphi; \quad \text{and } v_i = x_i \sin \varphi$$

into the expression for  $\mathbf{U}$ , the zeroth column with elements of  $v_i$  is the initial vector of Section 2.3. It turns out, that the other columns of  $\mathbf{U}$  are Mayer's orthogonal vectors, in the form

they are introduced in Eq. (2.6). Thinking in the opposite direction, one can always formulate Mayer's matrix  $\mathbf{U}$  based on the arbitrary  $N + 1$  dimensional vector  $|v\rangle$  by computing the value of  $\varphi$ :

$$\cos \varphi = v_0 \quad \text{and} \quad \sin \varphi = \left( \sum_{i=1}^N |v_i|^2 \right)^{1/2}$$

and setting

$$x_i = \frac{v_i}{\sin \varphi}.$$

It is transparent at this point, that Mayer's vectors are a by-product of a derivation providing an unitary matrix in closed form. We can also formulate an additional property, namely that Mayer's vectors form a rotation matrix, which approximates a transformation matrix block-diagonalizing an arbitrary real Hermitian matrix. It is also interesting to note, that the building of matrix  $\mathbf{U}$  involves just as many parameters as the number of conditions requiring that off-diagonal elements of the zeroth row and column of the Hamiltonian vanish. As a consequence, if parameters  $\varphi_i$  set from this condition, matrix  $\mathbf{U}$  gives that transformation in closed form, which block-diagonalizes the Hamiltonian.

Returning to the idea of correcting a zero-order ground state  $|0\rangle$ , Mayer also highlights, that matrix  $\mathbf{U}$  keeps its unitary nature irrespective of the value of  $\varphi$ . It is valid not only for the original expression given in Eq. (4.7). Therefore, one can consider  $\varphi$  as a parameter and determine its optimal value based on the variational principle. From an alternative point of view, this optimization represents a scaling of  $\mathbf{A}$  by one parameter. This scaling affects all angles  $\varphi_i$  (Eq. (4.8)), but keeps their mutual ratio fixed.

Now let us determine the optimal  $\varphi$  based on the variational principle. First with later purposes, we define the following  $N + 1$  dimensional auxiliary vectors:

$$|c^1\rangle = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}; \quad \text{and} \quad |c^2\rangle = \begin{pmatrix} 0 \\ x_1 \\ \vdots \\ x_N \end{pmatrix}.$$

With the use of these vectors the result of Mayer's procedure can be expressed. The zeroth column of  $\mathbf{U}$  is given by:  $|u^0\rangle = |c^1\rangle \cos \varphi + |c^2\rangle \sin \varphi$ . Introducing  $E$  for the symmetrical energy expression

$$E = \langle u^0 | \hat{H} | u^0 \rangle,$$

we seek the  $\varphi$  which satisfies:

$$\begin{aligned} \frac{\partial E}{\partial \varphi} &= 0 = \frac{\partial (\cos \varphi \langle c^1 | + \sin \varphi \langle c^2 |) \hat{H} (\cos \varphi |c^1\rangle + \sin \varphi |c^2\rangle)}{\partial \varphi (\cos \varphi \langle c^1 | + \sin \varphi \langle c^2 |) (\cos \varphi |c^1\rangle + \sin \varphi |c^2\rangle)} \\ &= 2 \left( \frac{\sin 2\varphi}{2} \left( \langle c^1 | \hat{H} |c^1\rangle - \langle c^2 | \hat{H} |c^2\rangle \right) - \cos 2\varphi \langle c^1 | \hat{H} |c^2\rangle \right) = 0. \end{aligned} \quad (4.9)$$

Without showing the details of the derivation, Eq. (4.9) yields the following explicit formula for the optimal  $\varphi$ :

$$\varphi_{\text{opt}} = \frac{1}{2} \arctan \left( \frac{2 \langle c^1 | \hat{H} |c^2\rangle}{\langle c^1 | \hat{H} |c^1\rangle - \langle c^2 | \hat{H} |c^2\rangle} \right) \quad (4.10)$$

Note that, among the two possible values for the arcus tangent function, we choose the one, which gives the lower energy.

A straightforward application of the above idea in Quantum Chemistry is to represent the electronic Hamiltonian on a basis of approximate functions, for instance on determinants build with HF molecular orbitals. Diagonalization of two-by-two submatrices provides the angles according to Eq. (4.2). (Note that, of the two possible choices for  $\varphi_i$ , one has to choose that angle, which keeps the lower eigenvalue in the top-left corner of the resultant two-by-two matrix.) After solving all two-by-two problems, one has the set of  $\varphi_i$  rotation angles to construct  $\mathbf{A}$  of Eq. (4.5) and the zeroth column of matrix  $\mathbf{U}$ . This vector may be a better approximation of the ground state, than the initial single determinant  $|0\rangle$ .

In Ref. [8] Mayer presented results with this scheme as well as the variationally optimized parameter  $\varphi$  of Eq. (4.10). Motivated by this success, we investigate the multireference application of UPT in Section 4.3.

In addition, it is interesting to note, that a related method has been presented independently by Malrieu et al.[34] and Truhlar et al.[35]. The method termed Degeneracy-Corrected Perturbation Theory (DCPT), builds the second-order energy correction by taking the contribution of each doubly excited determinant from the diagonalization of the two-by-two problems (formed by the doubly excited determinant in question and the HF determinant) discussed previously. The interaction is completely neglected in DCPT, just like in MP.

A great advantage of the second-order DCPT energy formula is that, it is divergence-free even in near-degenerate situations[35]. The UPT results, presented by Mayer[8] share the same advantageous property. The difference between UPT and DCPT methods lies in the treatment of the interaction of the excited vectors. Both methods are based on two-by-two Jacobi-rotations, but in UPT angle  $\varphi$  accumulates contribution from every excited determinant. This however is not a genuine interaction effect, since the transition matrix elements contributing to  $\varphi$  are of the type  $\langle 0 | H | i \rangle$ . Genuine interaction enters the picture, when  $\varphi$  is optimized, since transition matrix elements of the sort  $\langle i | H | j \rangle$  ( $i \neq j$ ) contribute to  $\langle c^2 | \hat{H} | c^2 \rangle$  of Eq. (4.10).



Before studying applications of UPT let us first investigate the approximation for the product of matrix exponentials in Eq. (4.5).

## 4.2 Baker-Campbell-Hausdorff correction to UPT

In the previous Section, Eq. (4.5) took advantage of the following approximation for matrix exponentials:

$$\mathbf{U}_i \mathbf{U}_j = \exp(\mathbf{A}_i) \exp(\mathbf{A}_j) \approx \exp(\mathbf{A}_i + \mathbf{A}_j).$$

Note that, the left hand side of the approximation is not symmetric in indexes  $i$  and  $j$ , while the right hand side is symmetric. In the general case, it is the Baker-Campbell-Hausdorff (BCH) formula which expresses the product of matrix exponentials by a single exponential:

$$\exp(\mathbf{A}_i) \exp(\mathbf{A}_j) = \exp(\mathbf{A}_i \circledast \mathbf{A}_j),$$

where

$$\mathbf{A}_i \circledast \mathbf{A}_j = \mathbf{A}_i + \mathbf{A}_j + \frac{1}{2}[\mathbf{A}_i, \mathbf{A}_j] + \frac{1}{12}([\mathbf{A}_i, [\mathbf{A}_i, \mathbf{A}_j]] - [\mathbf{A}_j, [\mathbf{A}_i, \mathbf{A}_j]]) + \dots \quad (4.11)$$

Since the BCH expansion is exact, the above expression is necessarily non-symmetric in indexes  $i$  and  $j$ . No closed formula is known for the BCH expansion of two arbitrary matrices, therefore the expansion is often cut after the first (few) elements in the literature. Moreover, the evaluation of higher order elements of Eq. (4.11) is still a challenging computational task[36]. As apparent from Eq. (4.11) the first two terms give just the (symmetric) sum of  $\mathbf{A}_i$  and  $\mathbf{A}_j$ , that was considered by Mayer. Our intention in the present Section is to evaluate the first non-vanishing contribution of the nested commutators to matrix  $\mathbf{U}$  of Section 4.1.

It is also clear from the expansion (4.11) that the contribution of the simple commutator  $[\mathbf{A}_i, \mathbf{A}_j]$  symmetrized in indexes  $i$  and  $j$  becomes zero. Therefore, we focus on the effect of the nested commutator involving three  $\mathbf{A}_i$  matrices.

For practical reasons, we introduce an auxiliary set of unit vectors:  $\{|a^i\rangle\}_{i=0}^N$ , where  $a_k^i = \delta_{ik}$  and we construct matrices  $\mathbf{A}_i$  in a dyadic form:

$$\mathbf{A}_i = (|a^i\rangle\langle a^0| - |a^0\rangle\langle a^i|) \varphi_i.$$

With this expression the product of matrices  $\mathbf{A}_i$  and  $\mathbf{A}_j$  is evaluated as:

$$\begin{aligned} \mathbf{A}_i \mathbf{A}_j &= \varphi_i \varphi_j (|a^i\rangle\langle a^0| - |a^0\rangle\langle a^i|) (|a^j\rangle\langle a^0| - |a^0\rangle\langle a^j|) \\ &= \varphi_i \varphi_j (|a^0\rangle\langle a^j| \underbrace{\delta_{i0}}_0 - |a^0\rangle\langle a^0| \underbrace{\delta_{ij}}_0 - |a^i\rangle\langle a^j| \underbrace{\delta_{00}}_1 + |a^i\rangle\langle a^0| \underbrace{\delta_{j0}}_0) = -\varphi_i \varphi_j |a^i\rangle\langle a^j|, \end{aligned} \quad (4.12)$$

where  $i \neq j$  and  $i, j \neq 0$  by construction. Analogously,  $\mathbf{A}_j \mathbf{A}_i = -\varphi_i \varphi_j |a^j\rangle \langle a^i|$  and therefore the commutator is given by:

$$[\mathbf{A}_i, \mathbf{A}_j] = \mathbf{A}_i \mathbf{A}_j - \mathbf{A}_j \mathbf{A}_i = \varphi_i \varphi_j (|a^j\rangle \langle a^i| - |a^i\rangle \langle a^j|) \quad (4.13)$$

Let us proceed now into the direction of the first nested commutator. Without showing the steps of the derivation we easily find for the product  $\mathbf{A}_i [\mathbf{A}_i, \mathbf{A}_j]$  the following expression:

$$\mathbf{A}_i [\mathbf{A}_i, \mathbf{A}_j] = \varphi_i^2 \varphi_j (|a^i\rangle \langle a^0| - |a^0\rangle \langle a^i|) (|a^j\rangle \langle a^i| - |a^i\rangle \langle a^j|) = \varphi_i^2 \varphi_j |a^0\rangle \langle a^j|$$

The second term of the nested commutator is of similar forms:

$$[\mathbf{A}_i, \mathbf{A}_j] \mathbf{A}_i = \varphi_i^2 \varphi_j |a^j\rangle \langle a^0|,$$

giving rise to the first nested commutator:

$$[\mathbf{A}_i, [\mathbf{A}_i, \mathbf{A}_j]] = -\varphi_i^2 \varphi_j (|a^j\rangle \langle a^0| - |a^0\rangle \langle a^j|) = -\varphi_i^2 \mathbf{A}_j, \quad (4.14)$$

and the analogous term obtained by the interchange of indexes  $i$  and  $j$  looks

$$[\mathbf{A}_j, [\mathbf{A}_i, \mathbf{A}_j]] = -\varphi_j^2 \mathbf{A}_i.$$

Let us comment here on the remarkably simple form of Eqs. (4.13) and (4.14). The important point is that the first nested commutators are proportional to matrices  $\mathbf{A}_i$  and  $\mathbf{A}_j$ . This offers a way to evaluate multiply nested commutators in a simple fashion. Due to this promising result, in our special case it may become possible to evaluate terms of the BCH formula in one of the forms, available in the present literature. An up to date and complete summary of this field is found in Ref. [36]. Below a brief overview of the basic facts and results of the BCH expansion is given.

The task is to express the matrix logarithm of

$$\exp(\mathbf{A}_i) \exp(\mathbf{A}_j) = \sum_{p,q=0}^{\infty} \frac{1}{p!q!} \mathbf{A}_i^p \mathbf{A}_j^q.$$

The Taylor-series of the logarithmic function expanded around the matrix of unity is often applied for this purpose:

$$\ln(\mathbf{Z}) \Big|_{\mathbf{I}} = \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} (\mathbf{Z} - \mathbf{I})^k.$$

With this series form, we can get the following expression:

$$\ln(\exp(\mathbf{A}_i) \exp(\mathbf{A}_j)) = \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} \sum_{\substack{p_1, \dots, p_k \\ q_1, \dots, q_k}} \frac{\mathbf{A}_i^{p_1} \mathbf{A}_j^{q_1} \dots \mathbf{A}_i^{p_k} \mathbf{A}_j^{q_k}}{p_1! q_1! \dots p_k! q_k!}. \quad (4.15)$$

It would be beneficial to express formula 4.15 in terms of nested commutators, since it is the commutators of matrices  $\mathbf{A}_i$ , which show the simple behavior in our case. Formulations satisfying this want have been already given and studied, for instance in connection with the methods of Dynkin[37] and Goldberg[38] or independently, with the intention of computational simplicity[39]. However, all of them share the drawback of meeting extreme complexity when evaluating higher terms.

The first difficulty comes from the fact, that all possible partitions of a set of size  $k$  are needed to form. The restricted sum for  $p_1, \dots, p_k$  and  $q_1, \dots, q_k$  in Eq. (4.15) e.q. runs for the partitionings. A partitioning of an arbitrary set is a set of nonempty, pairwise disjoint subsets of the original set, the union of the subsets giving the original set. This problem is related to the Bell numbers, which are only approximately available for large sets[40].

Evaluation of the nested commutators often represents a second difficulty. However, in our special case, it would be possible to evaluate those commutators, if a closed formula were available. In lack of a closed formula, a recursive variant could be also fruitful. Varadarajan has presented a recursion formula[41], which is not free from the problem of summing over all partitions of a set of size  $k$ . To date, we have not found a variant, which would allow to easily exploit our simple findings for the nested commutators and evaluate the sum over all terms of the BCH series. This is however is not our exclusive purpose here.

It is our acute interest to see at what extent the leading terms of the BCH expansion influence Mayer's matrix  $\mathbf{U}$ . For this reason, we approximate Eq. 4.11 with the first non-vanishing term, apart from the single  $\mathbf{A}_i + \mathbf{A}_j$  term. One can see from the derivation of higher terms of Eq. (4.11) that, they are proportional to  $\varphi_i^n \varphi_j^m$  with increasing integer powers of  $n$  and  $m$ . (These derivations are not relevant here.) High order terms vanish rapidly, if  $\varphi_k$ -s are small, In our examples, generally  $\varphi_k \in [-\frac{\pi}{2}, \frac{\pi}{2}]$ , but practically  $|\varphi_k| \ll 1$ , because our initial guess solution is close to the exact eigenvector. Thus, it seems appropriate to neglect high order terms.

Still, it is again stressed here, that the goal is not to evaluate  $\exp(\mathbf{A}_i) \exp(\mathbf{A}_j)$  exactly. (This would be not even symmetric in indexes  $i$  and  $j$ .) Contrary to this, our aim is to merely explore alternative forms to parametrize matrix  $\mathbf{U}$  in terms of  $\varphi_1, \dots, \varphi_N$  Jacobi-angles.

Mayer's method has the beneficial property of treating all the rotations in a sequence-independent manner. We would like to follow this philosophy, therefore, we symmetrize Eq.

(4.11) by the application of the permutation operator  $\hat{P}_{i,j}$ :

$$\begin{aligned}
& \frac{1}{2}(1 + \hat{P}_{i,j})(\mathbf{A}_i \circledast \mathbf{A}_j) = \frac{1}{2} \left( \mathbf{A}_i + \mathbf{A}_j + \frac{1}{2}[\mathbf{A}_i, \mathbf{A}_j] + \mathbf{A}_j + \mathbf{A}_i + \frac{1}{2}[\mathbf{A}_j, \mathbf{A}_i] \right) \\
& + \frac{1}{2}(1 + \hat{P}_{i,j}) \left( \frac{1}{12} ([\mathbf{A}_i, [\mathbf{A}_i, \mathbf{A}_j]] - [\mathbf{A}_j, [\mathbf{A}_i, \mathbf{A}_j]]) \right) + \dots \quad (4.16) \\
& \approx \mathbf{A}_i + \mathbf{A}_j + \frac{1}{24} ([\mathbf{A}_i, [\mathbf{A}_i, \mathbf{A}_j]] + [\mathbf{A}_j, [\mathbf{A}_j, \mathbf{A}_i]] - [\mathbf{A}_j, [\mathbf{A}_i, \mathbf{A}_j]] - [\mathbf{A}_i, [\mathbf{A}_j, \mathbf{A}_i]]) \\
& = \mathbf{A}_i + \mathbf{A}_j + \frac{1}{12} ([\mathbf{A}_i, [\mathbf{A}_i, \mathbf{A}_j]] + [\mathbf{A}_j, [\mathbf{A}_j, \mathbf{A}_i]]) = \mathbf{A}_i + \mathbf{A}_j - \frac{1}{12} (\varphi_i^2 \mathbf{A}_j + \varphi_j^2 \mathbf{A}_i),
\end{aligned}$$

where apart from Eq. (4.14) general commutator identities were exploited.

In order to get the effect of the correction term of  $-\frac{1}{12} (\varphi_i^2 \mathbf{A}_j + \varphi_j^2 \mathbf{A}_i)$  in the formula  $\mathbf{U}$  (Eq. (4.19)), let us substitute Eq. (4.16) into the derivation in Eq. (4.5). As an illustration of the general case, we first demonstrate the key steps for  $N = 3$ .

$$\ln \prod_{i=1}^3 \exp(\mathbf{A}_i) = \frac{1}{2(3-1)} \ln \left( \prod_{i=1}^3 \exp(\mathbf{A}_i) \right)^{2(3-1)} = \frac{1}{4} \ln \left( \exp(\mathbf{A}_1) \exp(\mathbf{A}_2) \exp(\mathbf{A}_3) \right)^4$$

Here we use the same approximation, as in Eq. (4.5), i.e. we suppose that every  $\mathbf{A}_k$  matrices commute with each other:

$$\begin{aligned}
\ln \prod_{i=1}^3 \exp(\mathbf{A}_i) & \approx \frac{1}{4} \left( \left( \exp(\mathbf{A}_1) \exp(\mathbf{A}_2) \right) \left( \exp(\mathbf{A}_1) \exp(\mathbf{A}_3) \right) \left( \exp(\mathbf{A}_2) \exp(\mathbf{A}_3) \right) \right. \\
& \left. \left( \exp(\mathbf{A}_2) \exp(\mathbf{A}_1) \right) \left( \exp(\mathbf{A}_3) \exp(\mathbf{A}_1) \right) \left( \exp(\mathbf{A}_3) \exp(\mathbf{A}_2) \right) \right) \quad (4.17)
\end{aligned}$$

With this assumption, we are able to reorder the expression  $\prod_{i=1}^N \exp(\mathbf{A}_i)$  forming all possible  $\mathbf{A}_i \circledast \mathbf{A}_j$  pairs. There are  $\frac{N(N-1)}{2}$  such a combination. Keeping in mind, that we would like to get a symmetrized formula, we take both  $\mathbf{A}_i \circledast \mathbf{A}_j$  and  $\mathbf{A}_j \circledast \mathbf{A}_i$  into account symmetrically. Since we have BCH correction only for non-commuting pairs, while taking the logarithm, we suppose again that every  $\mathbf{A}_k$  matrices commute with each other, except the corresponding pairs, with which we form  $\mathbf{A}_i \circledast \mathbf{A}_j$  and  $\mathbf{A}_j \circledast \mathbf{A}_i$ . Therefore, Eq. (4.17) is approximated further:

$$\begin{aligned}
\ln \prod_{i=1}^3 \exp(\mathbf{A}_i) & \approx \frac{1}{4} \left( \ln \left( \exp(\mathbf{A}_1) \exp(\mathbf{A}_2) \right) + \ln \left( \exp(\mathbf{A}_1) \exp(\mathbf{A}_3) \right) + \ln \left( \exp(\mathbf{A}_2) \exp(\mathbf{A}_3) \right) \right. \\
& \left. + \ln \left( \exp(\mathbf{A}_2) \exp(\mathbf{A}_1) \right) + \ln \left( \exp(\mathbf{A}_3) \exp(\mathbf{A}_1) \right) + \ln \left( \exp(\mathbf{A}_3) \exp(\mathbf{A}_2) \right) \right) \\
& = \frac{1}{4} \sum_{\substack{i,j=1 \\ i \neq j}}^3 \ln \left( \exp(\mathbf{A}_i) \exp(\mathbf{A}_j) \right) \quad (4.18)
\end{aligned}$$

Considering now the general case, we can exploit the result of Eq. (4.16), after the pairs are formed as follows:

$$\begin{aligned}
\ln \prod_{i=1}^N \exp(\mathbf{A}_i) &= \frac{1}{2(N-1)} \ln \left( \prod_{i=1}^N \exp(\mathbf{A}_i) \right)^{2(N-1)} \approx \frac{1}{2(N-1)} \sum_{\substack{i,j=1 \\ i \neq j}}^N \ln (\exp(\mathbf{A}_i) \exp(\mathbf{A}_j)) \\
&= \frac{1}{N-1} \sum_{i < j}^N \frac{\ln(\exp(\mathbf{A}_i) \exp(\mathbf{A}_j)) + \ln(\exp(\mathbf{A}_j) \exp(\mathbf{A}_i))}{2} \\
&= \frac{1}{N-1} \sum_{i < j}^N \frac{1}{2} (1 + \hat{P}_{i,j})(\mathbf{A}_i \otimes \mathbf{A}_j) \approx \frac{1}{N-1} \sum_{i < j}^N \left( \mathbf{A}_i + \mathbf{A}_j - \frac{1}{12} (\varphi_i^2 \mathbf{A}_j + \varphi_j^2 \mathbf{A}_i) \right) \\
&= \frac{1}{N-1} (N-1) \sum_{i=1}^N \mathbf{A}_i - \frac{1}{N-1} \sum_{j=1}^N \frac{1}{12} \mathbf{A}_j \underbrace{\sum_{\substack{i=1 \\ i \neq j}}^N \varphi_i^2}_{\varphi^2 - \varphi_j^2} \\
&= \sum_{i=1}^N \mathbf{A}_i - \frac{1}{12(N-1)} \sum_{i=1}^N (\varphi^2 - \varphi_i^2) \mathbf{A}_i = \sum_{i=1}^N \left( 1 - \frac{\varphi^2 - \varphi_i^2}{12(N-1)} \right) \mathbf{A}_i \tag{4.19}
\end{aligned}$$

It is straightforward to introduce the third-order commutator correction of Eq. (4.19) into Mayer's concept. Simply, one has to take

$$\varphi_i^{(3)} = \varphi_i - \frac{\varphi^2 - \varphi_i^2}{12(N-1)} \varphi_i \tag{4.20}$$

instead of  $\varphi_i$  to build  $\mathbf{A}$ . As it was mentioned, the different excited states are coupled in the original  $\mathbf{U}$  through  $\varphi$ . Note that, here the BCH correction brings even more coupling between them.

### 4.3 Multiconfiguration UPT

In this Section we introduce the application of Mayer's UPT to perturb multireference zero-order functions (MC UPT).

The outline of the MC UPT method is the following. Let us suppose, that we have a multireference function,  $|v\rangle = \Psi_0^{(0)}$  at hand as a result of a calculation presented in Section 3.2. Excited states are not routinely generated along with computing multireference ground state. For this reason there is no suitable orthonormal zero-order basis. This problem is frequently met in multireference methods.

In such a case Mayer's vectors may serve as zero-order excited states. Let us now suppose, that the Hamiltonian is represented on the zero-order states  $|v\rangle$  and  $|u^i\rangle$ ,  $i = 1, \dots, N$ . Using

this Hamiltonian, one can determine the set of  $\varphi_i$  rotational angles arising from two-by-two diagonalizations and construct matrix  $\mathbf{U}$  as it was described in Section 4.1. One can also determine the variationally optimal  $\varphi_{\text{opt}}^1$  and/or the commutator correction of Section 4.2, or simply work with the original  $\varphi$ . In either case, the corrected wavefunction is given by the zeroth column of matrix  $\mathbf{U}$ , denoted by  $|u^0\rangle$ . The MC UPT energy is obtained simply as an expectation value:

$$E_{\text{MCUPT}} = \langle u^0 | H | u^0 \rangle$$

. With the purpose of implementing MC UPT, we now derive the formula for  $E_{\text{MCUPT}}$ , using the notation  $H_{ab} = \langle a | \hat{H} | b \rangle$  for the matrix elements of the Hamiltonian on the basis of determinants and consider  $\mathbf{H}$  in the bracket form:

$$\mathbf{H} = \sum_{a,b=1}^N |a\rangle H_{ab} \langle b|.$$

The first step is to express matrix elements of the Hamiltonian on the basis of the zero-order vectors,  $|v\rangle$  and  $|u^i\rangle$ . This is given by:

$$\begin{aligned} H_{lk}^{(0)} &= \left( \sum_{d=1}^N \left( \delta_{ld} - \frac{v_l v_d}{1 + v_0} \right) \langle d | - v_l \langle 0 | \right) \left( \sum_{a,b=1}^N H_{ab} |a\rangle \langle b| \right) \left( \sum_{c=1}^N \left( \delta_{kc} - \frac{v_k v_c}{1 + v_0} \right) |c\rangle - v_k |0\rangle \right) \\ &= v_l v_k H_{00} - v_l H_{0k} - v_k H_{0l} + H_{lk} + \sum_{a=1}^{N_M} \frac{(2v_l v_k H_{0a} - v_k H_{la} - v_l H_{ka}) v_a}{1 + v_0} + v_l v_k \sum_{a,b=1}^{N_M} \frac{H_{ab} v_a v_b}{(1 + v_0)^2} \end{aligned} \quad (4.21)$$

Expressions for  $H_{0k}^{(0)}$  and  $H_{00}^{(0)}$  are obtained in an analogous manner. In the next step, we determine the rotation angle  $\varphi_k$ , which diagonalizes the  $k^{\text{th}}$  two-by-two submatrix:

$$\varphi_k = \frac{1}{2} \arctan \left( \frac{2H_{0k}^{(0)}}{H_{00}^{(0)} - H_{kk}^{(0)}} \right).$$

After the calculation of  $\varphi = \left( \sum_{i=1}^N \varphi_i^2 \right)^{1/2}$ ,  $u_i^0$  components of the zeroth column of matrix  $\mathbf{U}$  are given by:

$$u_0^0 = \cos \varphi; \quad \text{and} \quad u_i^0 = \sin \varphi \frac{\varphi_i}{\varphi}.$$

By the appropriate application of Eq. (2.6) the other  $|u^i\rangle$  vectors may also be obtained. We however note, that the construction of  $\{|u^i\rangle\}_{i=1}^N$  is not necessary to compute the MC UPT

<sup>1</sup>Note, that having determined  $\varphi_{\text{opt}}$  of Eq. (4.10) quantities  $x_i$  of Eq. (4.8) need not be recalculated, since  $\varphi_{\text{opt}} = \alpha\varphi = \sqrt{\sum_{i=1}^N (\alpha\varphi_i)^2} = \sqrt{\sum_{i=1}^N \varphi_{i,\text{opt}}^2}$ , hence  $x_{i,\text{opt}} = \frac{\varphi_{i,\text{opt}}}{\varphi_{\text{opt}}} = \frac{\varphi_i}{\varphi}$ .

energy, that is calculated as an expectation value with  $|u^0\rangle$  as follows:

$$E_{\text{MCUPT}} = \sum_{i,j=0}^N u_i^0 H_{ij}^{(0)} u_j^0 = \underbrace{u_0^0 H_{00}^{(0)} u_0^0}_{E_{\text{MC}}} + 2 \sum_{i=1}^N \cos \varphi H_{ij}^{(0)} \sin \varphi \frac{\varphi_i}{\varphi} + \sum_{i,j=1}^N \sin^2 \varphi \frac{\varphi_i \varphi_j}{\varphi^2} H_{ij}^{(0)}, \quad (4.22)$$

where the correction terms to the multireference energy of  $E_{\text{MC}}$  are apparent.

At this point, one has the option to use the commutator corrected  $\varphi_i^{(3)}$  of Eq. (4.20) instead of  $\varphi_i$ , use the variationally optimized  $\varphi_{\text{opt}}$  of Eq. (4.10) or both. We show numerical results with these options in Section 4.4.

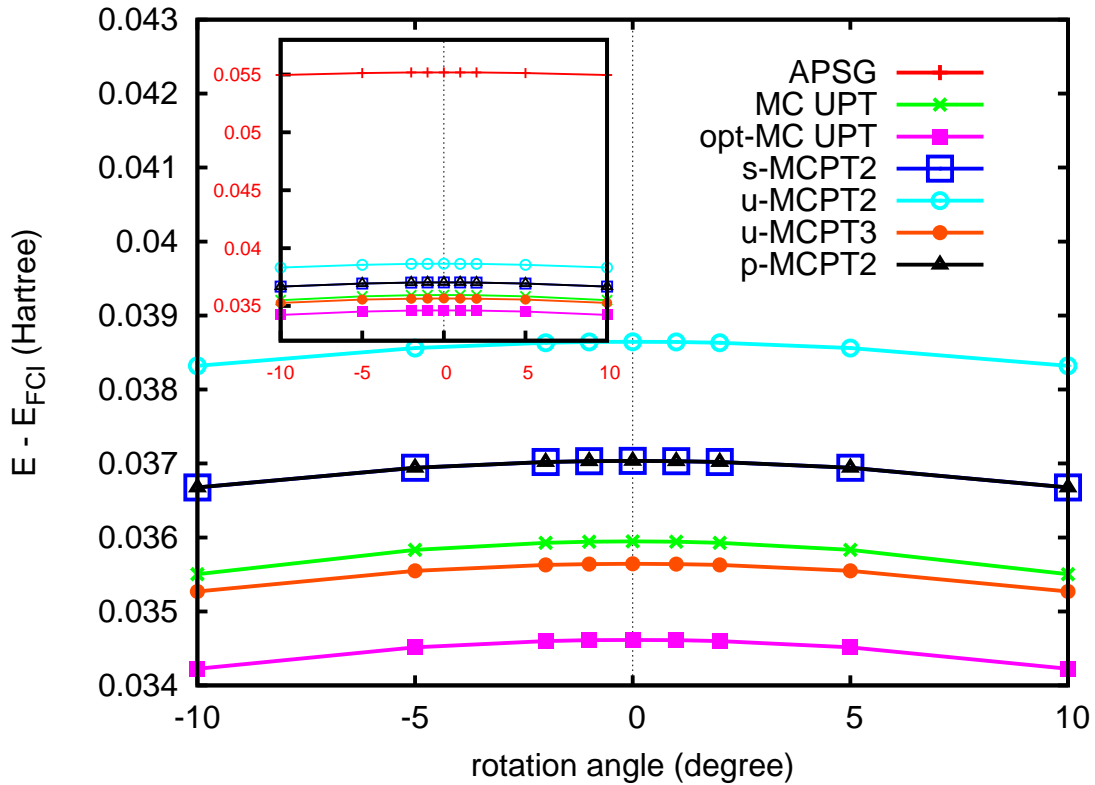
To judge computational demand one has to inspect first Eq. (4.21). When calculating a matrix element the term involving the sum over  $a$  is the rate determining term. Its time requirement is proportional to  $\mathcal{O}(N_M)$ . In order to determine the absolute cost, we have to consider, how many  $H_{lk}^{(0)}$  matrix elements are needed. Observing Eq. (4.22) it is apparent, that for the evaluation of the MC UPT energy every element belongs to the FOCI of  $|v\rangle$  is necessary. This results an overall  $\mathcal{O}(N_{\text{FOCI}}^2) \mathcal{O}(N_M)$  computational cost.

## 4.4 Numerical results with MC UPT

In this Section MC UPT results of test calculations are shown on simple examples. I have written a FORTRAN program, that evaluates MC UPT energies. The structure of the code is similar to the s-MCPT program (Section 3.7). The modules responsible for excited determinant generation, matrix element calculation and the assignation of the occupation string with its serial index are those that were introduced in Section 3.7. Additionally, a module, which builds the Hamiltonian on the basis of the reference function and its Mayer vectors has been written, as well as and an other module, which computes the MC UPT energy. For test purposes, I have written an another program, which builds  $\mathbf{U}$  from an input vector and makes a less cost-efficient  $\mathbf{U}\mathbf{H}\mathbf{U}^\dagger$  transformation. The two programs were tested against each other and the agreement of their intermediate and final results are found.

Our first example is the case of the  $\text{H}_2$  dimer. In Fig. 4.1 energy errors are shown as both  $\text{H}_2$  molecules are rotated around the axis halving the H-H bond and perpendicular to the plain of the system. Apart from MC UPT the errors obtained by MCPT variants are also shown for comparison. The MC UPT results calculated with  $\varphi_{\text{opt}}$  are denoted by opt-MC UPT.

It is apparent from the figure, that the MC UPT energies are slightly better, than the second-order MCPT energies. If optimizing parameter  $\varphi$  MC UPT outperforms even the third-order of MCPT. The same conclusion is valid for the other  $\text{H}_2$  dimer arrangement presented in Section



4.1 Figure:  $H_2$  dimer in Dunning's DZ basis. The  $H_2$  molecules are rotated around the axes perpendicular to the plane of the dimer and going through the center of the H-H bonds, resulting in a trapezoid geometry with  $C_{2v}$  symmetry. At rotation angle 0, the system is square shaped with  $0.74 \text{ \AA}$  H-H distances. Error of different MCPT and MC UPT energies with respect to the FCI are shown. The inset shows the same error curves together with the error of the APSG reference. Second-order results are labeled MCPT2 and third-order results are MCPT3. The MC UPT variant with an optimized parameter is denoted by opt-MC UPT.

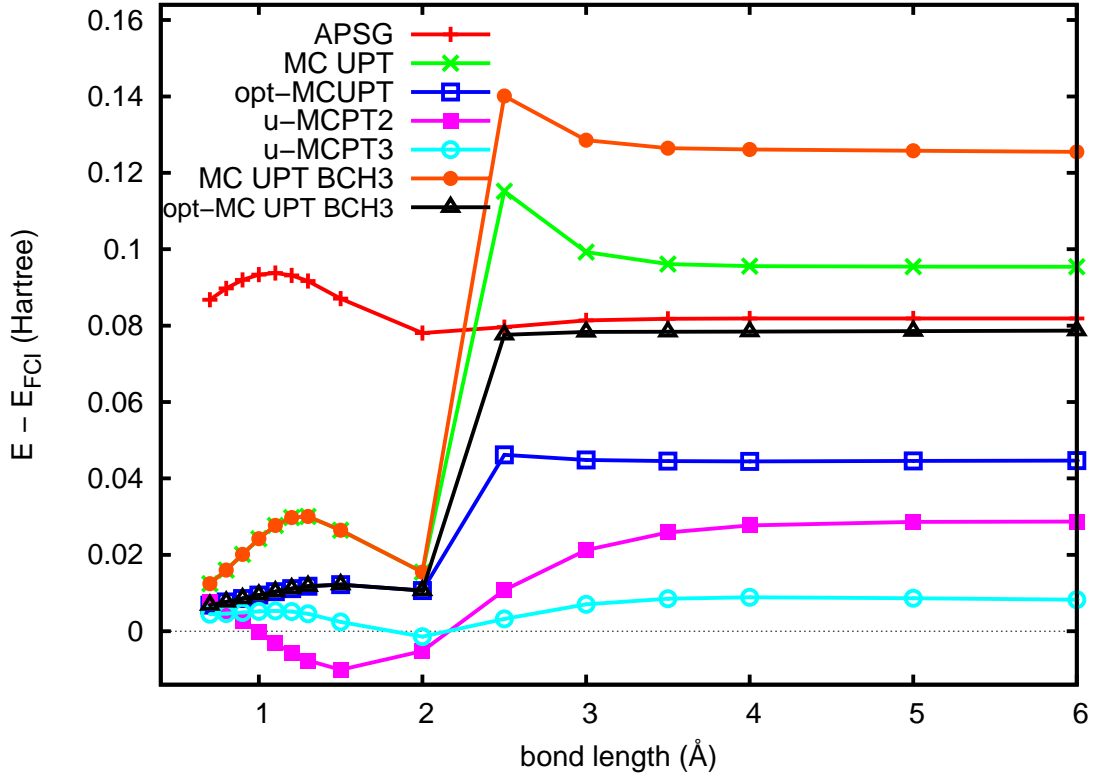
3.7 (where the  $H_2$  molecules were taken apart in two orthogonal directions). We again does not show these numbers.

The effect of the commutator correction on examples of the  $H_2$  dimer minor: the BCH corrected results differ from MC UPT and opt-MC UPT results on the order of  $0.1 \mu E_h$ .

Somewhat different conclusions may be drawn based on our second example. Here the symmetric dissociation of the  $H_2O$  molecule is presented in Dunning's type VDZ basis set. The reference function is an APSG, with two orbitals assigned to each geminals corresponding to the breaking bonds. This four determinantal reference function provides a balanced behavior along the PES as apparent in Fig. 4.2.

Looking at Fig. 4.2 one can identify two regimes, where the PT corrections behave in a





4.2 Figure: Symmetric dissociation problem of the  $H_2O$  molecule. Error of different MCPT and MC UPT energies with respect to the FCI are shown as a function of the H-O distance. Dunning's VDZ basis was applied in all calculations. Second-order results are labeled as u-MCPT2 and third-order results as u-MCPT3. The MC UPT variant with an optimized parameter is denoted by opt-MC UPT. Notation BCH3 refers to commutator corrected MC UPT results.

markedly different manner. Around equilibrium geometry both MC UPT and opt-MC UPT decrease the error of the reference in a satisfactory amount, opt-MC UPT outperforms MC UPT systematically again. The commutator corrected MC UPT BCH3 curves can not be distinguished from the MC UPT curves. At difference with the  $H_2$  dimer results, u-MCPT3 performs slightly better than the optimized MC UPT results on this example.

Above 2 Å bond length the behavior of MC UPT results change dramatically, while the APSG and MCPT results stay balanced. The source of the apparent discontinuity is still under investigation.

At this immature stage of our study, we can draw the conclusion, that it is beneficial to optimize parameter  $\varphi$ . The fact, that the commutator correction to matrix  $U$  is negligible is an accord with the fact that the number  $N$  in the denominator of Eq. (4.20) is exceedingly large, e.g.  $N = 784$  in the  $H_2$  dimer examples and  $N = 1656369$  in the  $H_2O$  dissociation. However,

the numerator of Eq. (4.20) is not proportional to  $N$ , since the sum involved in  $\varphi^2$  collects the contribution of numerous negligibly small  $\varphi_i$  angles.

# 5 Iterative Diagonalization Method (IDM) with Mayer's scheme

In this Section we present our preliminary results applying Mayer's unitary perturbative approach as an iterative matrix block-diagonalization method. Our experience in UPT and MC UPT indicates, that Mayer's method provides an improved description of reference the state. Having obtained the UPT corrected vector it is straightforward to consider it as the reference vector of a next UPT correction, and follow an iteration process. By iteration we mean a sequential repetition of the following operations: determine the  $i^{\text{th}}$  Mayer basis to the  $i^{\text{th}}$  reference function, build the Hamiltonian on this basis and take a UPT step to provide the  $(i + 1)^{\text{th}}$  reference vector along with its Mayer vectors. If the iteration converges, this approach reaches the ground state energy and wavefunction.

The above described procedure is a general way to obtain a solution of the eigenvalue problem, hence it may have relevance not only in Quantum Chemistry, but in Computational Science too. Although, the field has a vast literature, according to our present knowledge, such a diagonalization procedure, where effective Jacobi-rotations would be carried out in Mayer's sense, has not been investigated yet. Additionally, through investigating the convergence behavior of iteratively applied UPT, we may also gain a deeper insight into UPT itself.

A detailed survey of the currently available diagonalization techniques is not the intention of the present Section. We only mention the most important techniques. A detailed account of the stage in this field is found for instance in Ref. [42]. We restrict our attention to the eigenvalue problem of a real symmetric matrix of  $\mathbf{H}$ :

$$\mathbf{H}\psi_i = \lambda_i\psi_i \quad (i = 0, 1, \dots, N),$$

where  $\psi_i$  and  $\lambda_i$  are the eigenvectors and eigenvalues of  $\mathbf{H}$  respectively.

One class of diagonalization methods collects the so-called direct methods. Here a linear transformation is performed first which tridiagonalizes  $\mathbf{H}$ . In the second, so-called eigendecomposition step, all eigenvalues and eigenvectors of  $\mathbf{H}$  are obtained. For instance the QR method works in this manner. Direct methods are applied, if a robust and simple algorithm is desired and the problem is small enough, so the diagonalization is not a computational bottleneck.

Another group of methods works with iterative considerations, like Jacobi- or Givens-

rotations. The iterative diagonalization method (later shortened as IDM) with Mayer's scheme shows close relation with the Jacobi-rotations, which is briefly introduced in Section 4.1.

When only a few eigenvalues of a large matrix are necessary – as it is often the case in quantum chemical computations – those methods are preferred, which apply sequential multiplication of an approximate eigenvector with  $\mathbf{H}$ . The method of Lanczos[43] and Davidson[44] constitute examples of this sort. The unitary PT applied in an iterative manner may represent a further approach belonging to this letter category.

## 5.1 Iterative diagonalization of real symmetric matrices

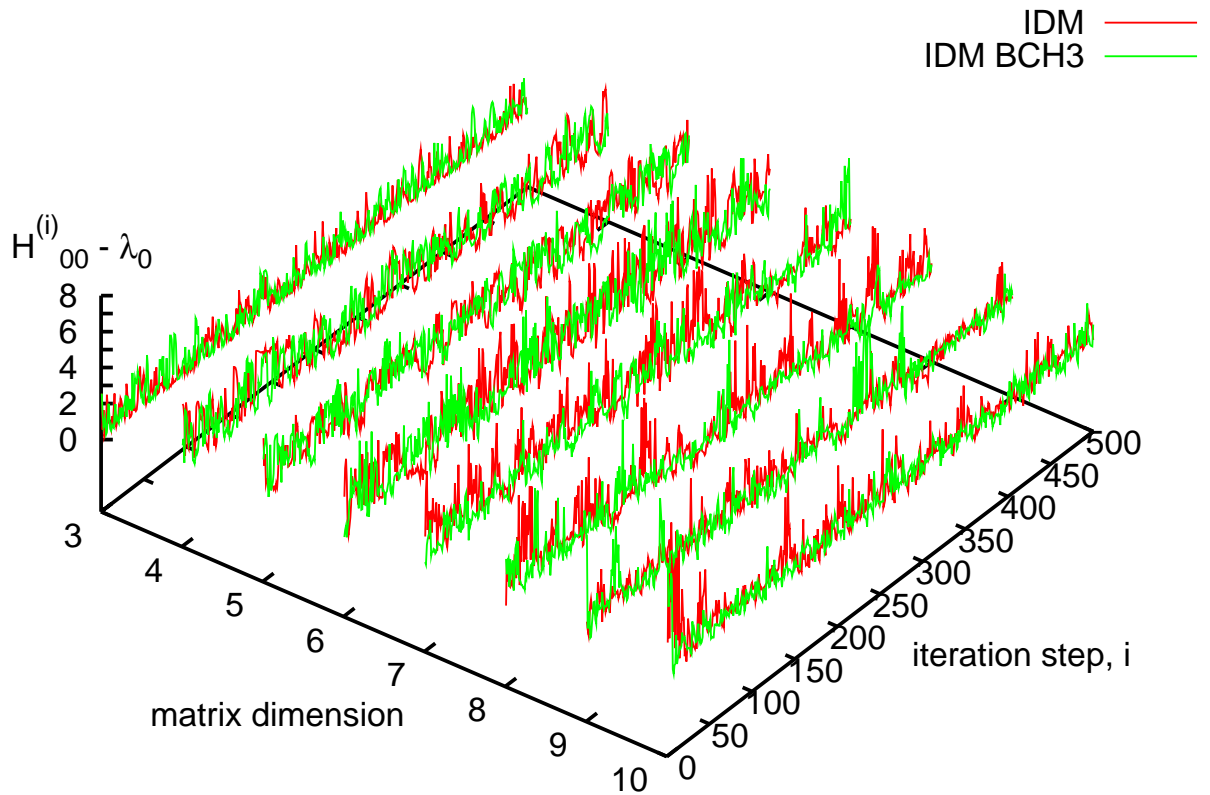
In this Section we present test calculations, which aim to investigate the convergence behavior of IDM. (Due to the relatively complex algorithm, investigation of the convergence properties with mathematical rigor has not been attempted yet.)

The results are produced by a transparent, but not cost-efficient code, that is the implementation of the presented iterative algorithm. In the  $i^{\text{th}}$  IDM step, the program constructs  $\mathbf{U}$  of Eq. (4.6) denoted here by  $\mathbf{U}^{(i)}$ . The zeroth column of  $\mathbf{U}^{(i)}$  is the MCUPT vector, computed based on the representation of the Hamiltonian in the previous step,  $\mathbf{H}^{(i-1)}$ . Other columns of  $\mathbf{U}^{(i)}$  are Mayer's vectors of the zeroth column. Now  $\mathbf{H}^{(i-1)}$  is transformed by  $\mathbf{U}^{(i)}$  to provide  $\mathbf{H}^{(i)} = \mathbf{U}^{(i)}\mathbf{H}^{(i-1)}\mathbf{U}^{(i)\dagger}$ , and the process is repeated. At step  $i$ ,  $H_{00}^{(i)}$  gives the  $i^{\text{th}}$  approximation to the lowest eigenvalue,  $\lambda_0$ , according to Eq. (4.22).

In the first test series, small random symmetric matrices (RSM) are considered of dimension from 3 to 10, where  $H_{ij} \in [0, 1[$  and  $H_{ji} = H_{ij}$  conditions are applied. The results are compared to the results of a standard Givens routine[1]. In Fig. 5.1 sequences of  $H_{00}^{(i)}$  elements (later simply trajectories) are shown as a function of the dimension of the RSM in each iteration step. The trajectory along the first 500 step illustrates the characteristics of longer trajectories as well.

From Fig. 5.1, it is apparent, that IDM does not converge in general situations. Apart from the trajectories presented in Fig. 5.1, we have computed  $5 \times 10^5$  step long trajectories of the same RSM samples, and of larger dimensional (50, 100 and 1000) matrices without finding a convergent case. As Fig. 5.1 reflects, we have also studied the IDM algorithm with commutator corrected angles of Eq. (4.20). We obtained non-identical trajectories to IDM, but again non-convergent.

Based on the trajectories of Fig. 5.1 one may raise the question, whether chaotic behavior characterizes this iteration. To examine this hypothesis, we calculated the autocorrelation



5.1 Figure: Trajectories of IDM iterations, showing the error  $H_{00}^{(i)} - \lambda_0$  at each iteration step  $i$ . Label BCH3 denotes the commutator corrected variant.

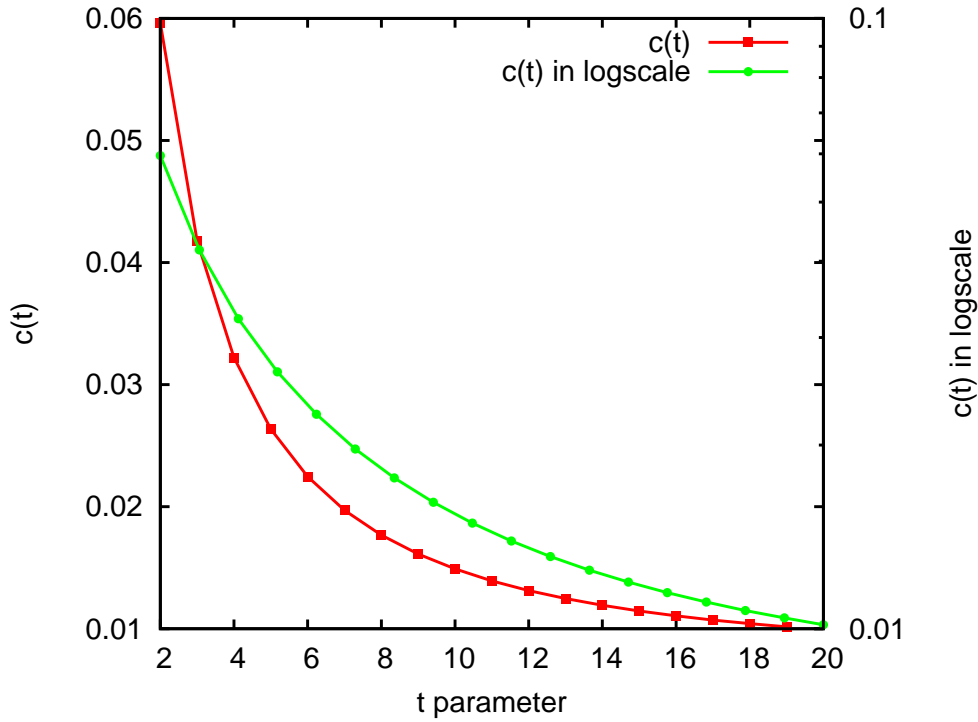
function  $c(t)$  of which has the following form:

$$c(t) = \lim_{n \rightarrow \infty} \left( \frac{1}{n} \sum_{i=1}^n (H_{00}^{(i)} - \mu)(H_{00}^{(i+t)} - \mu) \right), \quad (5.1)$$

where  $\mu$  is the average of  $H_{00}^{(i)}$  along the trajectory:

$$\mu = \frac{1}{n} \sum_{i=1}^n H_{00}^{(i)}.$$

For a converging trajectory,  $c(t) = 0$  [45]. In a chaotic system,  $c(t)$  converges to zero slowly, since elements of the trajectory – far from each other in sense of iteration steps – show high correlation. Since the  $n \rightarrow \infty$  limit is practically unachievable, we take a  $10^6$  step long trajectory sample and measure  $c(t)$  on the example of a 100 dimensional RSM. The first few points

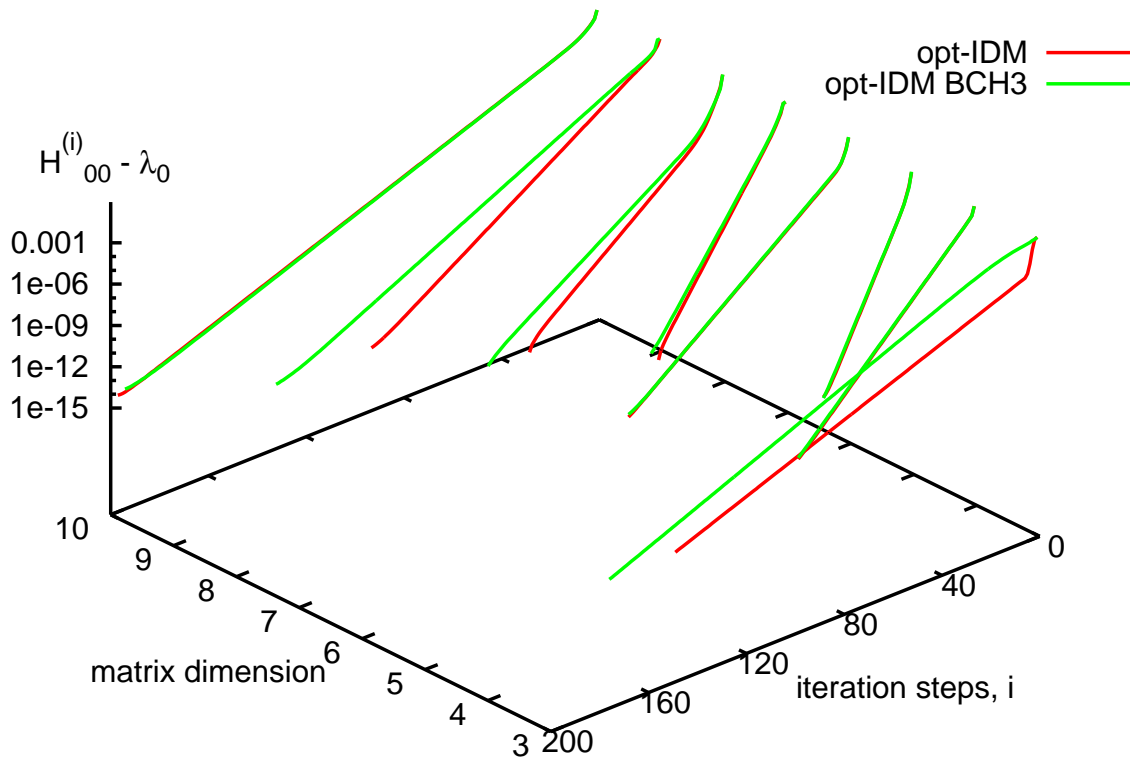


5.2 Figure: Autocorrelation function ( $c(t)$ ) of the IDM defined as in Eq. (5.1) in case of a 100 dimensional random symmetric matrix. On the right axis, the same  $c(t)$  is shown on a logarithmic scale.

of  $c(t)$  shown in Fig. 5.2 illustrates, that  $c(t)$  tends towards zero. If one depicts  $c(t)$  on a logarithmic scale (also shown in Fig. 5.2), one can conclude, that this convergence is slower, than exponential. It means, that  $c(t)$  vanishes only for large  $t$  shift parameter values. We conclude, that this IDM is not applicable for block-diagonalization of arbitrary real symmetric matrices in the present form.

It is possible however to improve the IDM algorithm, building  $U^{(i)}$  with  $\varphi_{\text{opt}}$  of Eq. (4.10) in each iteration step. This approach is denoted by opt-IDM. The trajectories obtained by opt-IDM are presented in Fig. 5.3 on the RSM examples treated before. For the sake of complete identity of the circumstances, we applied the same random seed, when generating matrices for both IDM and opt-IDM.

Apparently the opt-IDM trajectories are linear on a logarithmic scale, hence the opt-IDM method bears exponential convergence in wide range of the presented trajectories. Although, the iteration steps taken until convergence strongly vary with the dimension of the matrix. These results suggest that, opt-IDM is a reliable matrix block-diagonalization method. This still holds true in the case of larger matrices (with dimensions of 50, 100 and 1000) and in case of the variation of the initial matrix through different random seed choices. Interestingly, iteration



5.3 Figure: Trajectories of opt-IDM iterations. The difference of the approximation for the lowest eigenvalue ( $H_{00}$ ) is shown with respect to the exact eigenvalue ( $\lambda_0$ ) in logarithmic scale. The trajectories for different dimensional random symmetric matrices is shown in each iteration step. BCH3 denotes the commutator corrected variation.

with  $U^{(i)}$ -s built with commutator corrected  $\varphi_i$  and subsequently optimized  $\varphi$  (opt-IDM BCH3 curve of Fig. 5.3) produces slower convergence, than opt-IDM.

Let us look at our findings from a different angle. Determining the rotation angles in IDM from two-by-two Jacobi-rotations does not lead to a convergent iteration. The application of the variational principle resulting a  $\varphi_{\text{opt}}$ , which ensures  $H_{00}^{(0), \text{opt}} \leq H_{00}^{(0)}$ , producing convergent iterations. In view of this, one may formulate the question, whether it is the variational optimization per se, that leads to convergence, or it is a mutual effect of computing Jacobi-type  $\varphi_i$  angles together with the variational optimization of  $\varphi$ .

To answer this question, we separated the effect of the Jacobi-angles and the optimization. This means, that we carried out iterations with optimized  $\varphi$ , but with non-Jacobi-type  $\varphi_i$  calculation. Instead of the Jacobi-angles, we applied their average, modified with a uniformly

distributed noise:

$$\varphi_i^{\text{test}} = (1 + r_i)\bar{\varphi}, \quad (5.2)$$

where  $r_i \in [-0.1, 0.1]$  is a random number and  $\bar{\varphi} = \frac{1}{N} \sum_{i=1}^N \varphi_i$  with  $\varphi_i$  being the original Jacobi-angles. The  $\varphi_i^{\text{test}}$  angles of Eq. (5.2) were chosen with the aim of keeping the cumulative effect of a step in this test calculations close to the effect of an IDM step. According to our observations, iterations with this modified framework do not converge. Therefore we conclude that, the variational optimization per se is not enough, the optimization needs a good starting point of Jacobi-angles to be convergent.

## 5.2 Comparison of IDM and Jacobi-rotations

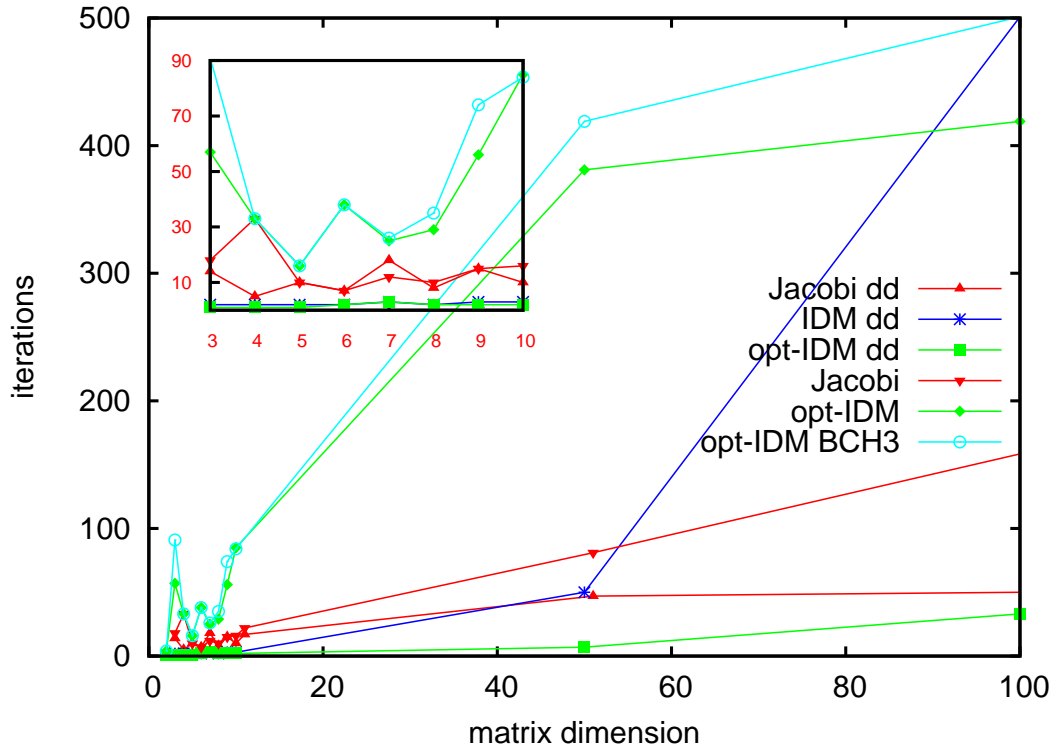
In this Section, we compare the opt-IDM and Jacobi-rotations, since they share lots of common ideas. In IDM the rotation angles are determined in the same manner as Jacobi-rotations (if none of commutator correction or  $\varphi$  optimization are applied). In case of IDM one transformation step approximates a whole Jacobi sweep. Therefore, we compare one sweep of the Jacobi-iteration with one step of IDM.

The FORTRAN edition of Numerical Recipes includes a simple implementation of the Jacobi-method[1], which we modified for our purposes. We kept only the loop necessary for the block-diagonalization of the one dimensional top-left block. Additionally, the modified version reads the matrix to be diagonalized as input and monitors the convergence of the iteration procedure.

The RSM examples presented before were chosen as first test systems. Since the Jacobi-procedure converges absolutely, observation of the trajectories is not informative. Instead of that, we compare the number of iteration steps and sweeps to reach an error below  $10^{-7}$  in  $\lambda_0$ , the lowest eigenvalue. Fig. 5.4 shows, that the Jacobi-method (curve Jacobi) has much more balanced performance, than opt-IDM. In case of the Jacobi-method the number of necessary iterations scaling roughly linearly with the dimension of the RSM. We can not conclude such a regularity in case of the opt-IDM, while the commutator corrected variant of opt-IDM (curve opt-IDM BCH3) shows even slower convergence. Generally speaking, the Jacobi-method outperforms opt-IDM in rate of convergence and shows more predictable behavior in case of RSM examples.

As a second series of examples diagonally dominant RSM-s were produced, since the Jacobi-method is to known to perform better for such matrices. Diagonally dominant matrices are produced by dividing the off-diagonal elements of RSM-s by 100. These results are also shown in Fig. 5.4, labeled 'dd'.





5.4 Figure: Number of iterations necessary to reach  $10^{-7}$  accuracy in the lowest eigenvalue of a random symmetric matrix as a function of the matrix dimension. The commutator corrected variant is denoted BCH3. opt-IDM refers to the variationally optimized approach. For Jacobi-rotations the number of sweeps is plotted on axis y. Examples with diagonally dominated random matrices are marked by dd.

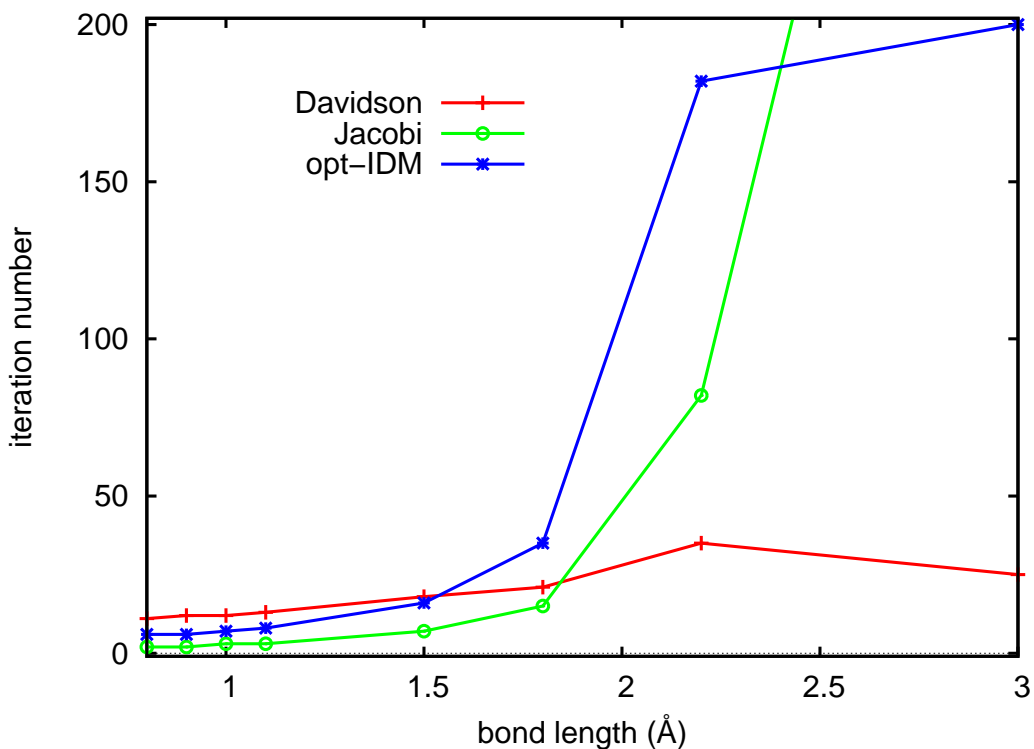
Inspecting the curves in Fig. 5.4, one can easily see, that the Jacobi-method indeed converges faster for this matrices, expected (curve Jacobi dd). Look at the opt-IDM results (curve opt-IDM dd), they also get better, systematically outperforming even the Jacobi-method. The plain IDM method (curve IDM dd), without variational optimization also converges. This is remarkable, since no convergent trajectory was found by this method on RSM examples of the previous Section.

These results suggest, that the opt-IDM method is better suited to diagonally dominated problems, and opt-IDM is able to perform better, than the Jacobi-method in this case. This is a promising result, considering that in electronic structure calculation one meets matrices with even higher diagonal over off-diagonal ratio. But we have to note, that the iteration steps needed till convergence is apparently in no direct connection with the dimension of the matrix (in contrast with the Jacobi-method). Therefore, more detailed study on the convergence behavior of the present method is needed. This is part of our plans in the near future.

As a last example, we compare the performance of the opt-IDM method with the Davidson-method[44], which is widely-applied in Quantum Chemistry. The motivation of this study comes from the observation, that the opt-IDM algorithm seems to be well-suited for diagonally dominant problems.

Our results are obtained with a determinant based direct implementation of the Davidson-method[46]. The Hamiltonian matrices necessary for the Jacobi and the IDM code produced by the matrix element computing module presented previously in Section 3.7.

The symmetric  $H_2O$  dissociation problem presented in Section 4.4 was chosen as an example. Here a smaller basis set, namely Pople's split-valence 3-21G basis was applied in order to limit the number of determinants in the FCI expansion to 225. In all cases the HF wavefunction was the starting point. In Fig. 5.5 the iteration steps necessary to reach  $10^{-7}E_h$  accuracy is plotted as a function of the O-H distance.



5.5 Figure: Symmetric dissociation problem of the  $H_2O$  molecule in Pople's split-valence 3-21G basis set. In axis  $y$  the necessary iteration steps is shown to reach  $10^{-7}E_h$  accuracy as a function of the O-H distance. Davidson- and Jacobi-type iterations are compared to the opt-IDM results.

Inspecting Fig. 5.5, the superiority of the Davidson-method is reflected at stretched geometries. Both the Jacobi and the opt-IDM method performs similarly and provides rapidly

decreasing rate of convergence as the HF approximation deteriorates.

We have performed few other pilot calculations on up to 1000 dimensional examples. These cases led to similar observation, namely the opt-IDM does not show as balanced and efficient convergence rate as the Davidson-method. Still it showed absolute convergence in every cases examined. The convergence has similar exponential characteristics as visible in Fig. 5.3. In other words, the first few correction terms are responsible for the majority of the correction. These preliminary observations motivate further studies with the UPT method.

# Summary and outlook

In this report we investigate the UPT approach and a related orthogonalization scheme suggested by Mayer. Our studies concern the properties of Mayer’s orthogonalization technique and its possible applications in Quantum Chemistry. We apply UPT to correct multireference wavefunctions and examine a novel iterative block-diagonalization procedure based on UPT.

In connection with Mayer’s orthogonalization we formulate and prove a theorem, which clarifies the relation between Mayer’s scheme and the Gram-Schmidt and Löwdin’s symmetric orthogonalization approach. The theorem states, that if  $N$  unit vectors of an  $N + 1$  dimensional basis are Gram-Schmidt orthogonalized to an arbitrary  $(N + 1)^{th}$  vector first, and the Gram-Schmidt orthogonalized vectors are Löwdin orthogonalized to each other in a second step then the Mayer vectors are recovered.

The advantages of Mayer’s orthogonalization method are, that it keeps a single vector unchanged and provides a closed formula for the other vectors, which are treated on an equal footing. These beneficial properties are exploited, when applying Mayer’s method to formulate a Hermitian MCPT alternative, termed s-MCPT. The working equations to s-MCPT are derived and coded. Based on numerical calculations we conclude, that s-MCPT provides almost identical energies to the previously introduced p-MCPT.

We also investigate the application of Mayer’s UPT to improve multireference electronic wavefunctions (MC UPT). For this purpose, we consider a multireference vector as reference function and its Mayer vectors and determine energy correction in Mayer’s UPT sense. We make use of a single variationally optimizable parameter, as it was suggested by Mayer for single reference situations. According to our preliminary numerical studies, MC UPT energies are similar to third-order MCPT results. We find discontinuities that MC UPT may produce on a PES for reasons yet not resolved.

Mayer’s orthogonalization scheme and the concept of UPT is also applied as an iterative block-diagonalization procedure. Using the variationally optimized parameter, we find that the iteration converges. The iteration rate of this procedure is similar to that of the Jacobi-rotations method both on the examples of random matrices and quantum chemical Hamiltonian matrices, while it is outperformed by the Davidson iteration.

We also introduce a correction term to UPT, taking into account terms, arising from the treatment of non-commuting quantities, which are not considered in UPT. We have found, that – in its present form – the commutator correction has minor effect in large dimensional systems.

Our further aims concern the investigation of the discontinuity in MC UPT energies, the development of size-independent formulation of the commutator correction and the analysis of the iterative diagonalization with mathematical tools.

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# Summary in Hungarian – Összefoglalás

A dolgozatban az Unitér Perturbációszámítás (Unitary Perturbation Theory, UPT) és a hozzá szorosan kapcsolódó Mayer-ortogonalizáció tulajdonságait és ezek kvantumkémiai alkalmazásait vizsgáljuk. Az UPT módszert multireferenciás elektronikus hullámfüggvény perturbatív javítására és egy iteratív blokkdiagonalizációs eljárás alapjaként is felhasználtuk.

Bemutatjuk a Mayer-ortogonalizáció tulajdonságait és ezeket összevetjük melyet a széles körben elterjedt Gram-Schmidt és a Löwdin-féle szimmetrikus ortogonalizációs módszerekkel. A három eljárás, a Mayer, a Löwdin, valamint a Gram-Schmidt közötti kapcsolatról egy tételt fogalmaztunk meg. A tétel szerint, ha egy  $N + 1$  dimenziós térben  $N$  darab bázisvektort Gram-Schmidt technikával ortogonalizálunk egy kitétetett vektorra, majd a Gram-Schmidt lépés eredményeképp kapott vektorokat az általuk kifeszített altérben Löwdin ortogonalizáljuk, akkor az eredeti, kitétetett vektor által definiált Mayer-féle vektorokat kapjuk.

A Mayer-ortogonalizáció eredményeképp egy változatlanul megőrzött kitétetett vektort és erre merőleges vektorkészletet kapunk. A merőleges készlet elemei egymással egyenrangúak és kifejtésük az eredeti bázison zárt alakban megadható. Ezen előnyös tulajdonságok felhasználásával egy szimmetrikus MCPT (s-MCPT, symmetric Multiconfiguration Perturbation Theory, szimmetrikus Multikonfigurációs Perturbációszámítás) formalizmust dolgoztunk ki. Az s-MCPT módszer munkaképleteit levezettük és beprogramoztuk. Összehasonlításuképp, numerikus számításokat végeztünk és azt találtuk, hogy az s-MCPT módszer a korábbi p-MCPT módszerrel gyakorlatilag egyező eredményeket ad.

A Mayer-féle UPT módszert multireferenciás kiinduló vektorra is alkalmaztuk. Itt a multireferenciás függvényt kitétetettnek tekintve, a nulladrendű gerjesztett vektorokat Mayer-féle ortogonalizációs elven határozzuk meg. Az MC UPT energiát az UPT módszerrel analóg módon kapjuk. Mayer egydetermináns esetben bevezetett egy variációsán optimálható paramétert is, melyet mi is alkalmaztunk multireferenciás esetben. Numerikus számításaink alapján az MC UPT eredmények pontossága harmadrendű MCPT-vel mérhető össze. Azt találtuk, hogy az MC UPT potenciális energia felületek esetenként nem folytonosok. A jelenség vizsgálata további terveink közt szerepel.

A Mayer-ortogonalizációt és az UPT módszert, mint iteratív blokkdiagonalizációs technikát is megvalósítottuk. A variációsán optimális paraméter alkalmazásával konvergens iterációkat kaptunk. A konvergencia sebessége összemérhető a Jacobi-forgatásokat alkalmazó módszerrel.

Bevezettünk egy módosítást is az UPT eljáráshoz, melyben az eredeti levezetéstől eltérő

módon vesszük figyelembe a Jacobi-forgatások nem kommutatív voltát. Azt tapasztaltuk, hogy nagy rendszerekre a módosításnak a jelenlegi formájában elhanyagolható a hatása. Későbbi célunk ezen módosítás függetlenítése a rendszermérettől.

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