Chapter 2
Multi-reference Møller-Plesset perturbation theory
Implementation to third order and applications

Abstract

The generalised Møller-Plesset perturbation theory for open-shell and multi-configurational reference functions as formulated by Wolinski, Sellers and Pulay is implemented in a multi-reference CI program that allows general reference functions. Extension to third order is straightforward at the cost of one CI iteration. The method is applied to several small model problems, i.e. the singlet-triplet splitting in methylene, the dispersion energy of helium dimer, and the dissociation energy of N₂ and O₂. Also the method was applied to a larger system, i.e. the transition energy 1A_g → 1B_u in 1,1’-bicyclohexylidene was calculated. The results depend little on the projection operators chosen in the definition of the zeroth-order Hamiltonian. The dissociation energies obtained are fairly good. In most calculations, MRMP3 is closer to higher order methods [Multi-Reference CI (MRCI), MRCI with Davidsons correction, and MRCEPA(0)] than MRMP2. However, in the calculation of the dissociation energy of dioxygen the MRMP2 results are closer to the higher order methods than those of the MRMP3 results. The method is not free of problems, however, as we have found divergences on the potential energy surface of N₂ at the MRMP3 level. For the calculation of dispersion energies, which depend on the reordering among the reference states, the MRMP2/3 method brings no improvement over the single-reference approach, although this may be cured at higher orders in perturbation theory. The method was also applied to a larger system, i.e. the 1A_g → 1B_u transition energy in 1,1’-bicyclohexylidene was calculated. Size consistency corrected MRCI, MRCEPA(0) and MRMP3 all agree closely on the transition energy, which is, however, still too high compared to the experimental value.
2.1 Introduction

The calculation of potential energy surfaces is perhaps the most important application of quantum chemistry. Since during a reaction bonds are broken and reformed, a single-determinant description is not of consistent quality. The commonly used Restricted Hartree Fock (RHF) method breaks down for radical bond breaking while the Unrestricted Hartree Fock (UHF) method leads to spin contamination. The Multi-Configurational SCF (MCSCF) approach remedies these shortcomings by including all configurations that are important in various regions of the potential energy, creating a qualitatively correct zeroth-order wavefunction. Though the use of a multi-reference function is a useful prerequisite for obtaining a consistent description and it ensures a proper description of the non-dynamic correlation energy, it is not sufficient since in general the dynamic correlation energy, which is essentially impossible to include to a significant extent in MCSCF, changes with the molecular geometry [1-3].

The principal ways to describe the dynamic correlation energy are the variational Configuration Interaction (CI) technique, the Coupled Cluster (CC) approach, and the use of Perturbation Theory (PT). Whereas the former methods offer a more complete description of the correlation, low orders of PT are much more efficient. The Møller-Plesset form of PT shares with the more expensive CC techniques the desirable property of size consistency [4,5].

Perturbation theory may be generalized to the multi-reference case in different ways, for example using effective Hamiltonians, using different types of $H_0$ using, different expansions for the wavefunction, etc. [5-22]. In this paper we explore the performance of the generalisation of Møller-Plesset Perturbation Theory (MPPT) [23] as formulated by Wolinski et al. [24,25]. Different approaches to multi-reference MPPT are the CASPT approach implemented in MOLCAS [26-28] and the multi-configurational MPPT approach in MOLPRO [29]. We discuss some aspects of the implementation of the theory. In addition we consider the implications of various choices possible in the zeroth order Hamiltonian. We study a set of problems ranging from the breaking of double and triple bonds for closed and open shell systems to the dispersion energy in Van der Waals systems, and to the calculation of transition energies in large organic molecules. A number of these cases have been studied by Werner [29].
also. However for the diatomic molecules we concentrated on calculating the potential energy surface instead of the spectroscopic constants.

2.2 Theory

The theory corresponds closely to the closed shell Møller-Plesset theory and will indeed reduce to this approach in the single-reference closed shell case. We will therefore recapitulate the single-reference closed shell approach first. As usual in perturbation theory, the total Hamiltonian is split into a zeroth order part and a perturbation:

\[ H = H_0 + V \]  \hspace{1cm} (1)

\( H_0 \) in Møller-Plesset Perturbation Theory is the closed-shell Fock operator

\[ H_0 = F = \sum_i f_i \]  \hspace{1cm} (2)

where \( f \) is the usual one-electron closed-shell Fock operator, the elements of which are obtained from the one-electron density matrix \( P \) and the one- and two-electron integrals as

\[ f_{\mu\nu} = \hbar_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left( \mu\nu|\lambda\sigma \right) - \frac{1}{2} \left( \mu\lambda|\sigma\nu \right) \]  \hspace{1cm} (3)

The zeroth order energy is the sum of orbital energies

\[ E_0 = E^{(0)} = \langle \Psi_0 | H_0 | \Psi_0 \rangle = \sum_i e_i \]  \hspace{1cm} (4)

and the first, second and third order energies are given by

\[ E_1 = E^{(0)} + E^{(1)} = \langle \Psi_0 | H | \Psi_0 \rangle = E_{ref} \]  \hspace{1cm} (5)

were \( E_{ref} \) is the energy of the Hartree-Fock determinant and

\[ E_2 = E_1 + \langle \Psi_0 | V | \Psi_1 \rangle = E_1 + \langle \Psi_0 | H | \Psi_1 \rangle \]  \hspace{1cm} (6)
\[ E_3 = \langle \Psi_0 + \Psi_1 | H - E_1 | \Psi_0 + \Psi_1 \rangle + E_1 \]
\[ = \langle \Psi_0 + \Psi_1 | H - E_{\text{ref}} | \Psi_0 + \Psi_1 \rangle \] (7)

The first order wavefunction is formally obtained by
\[ \Psi_1 = - (H_0 - E_0)^{-1} Q \Psi_0 \] (8)

where \( Q = 1 - |\Psi_0 \rangle \langle \Psi_0| \) to guarantee that \( \Psi_1 \) will have no component in \( \Psi_0 \). \( \Psi_1 \) is computed by expanding it formally in the space of all determinants obtained from the reference determinant by substituting virtual orbitals for occupied ones. If canonical molecular orbitals are used, the zeroth order Hamiltonian (the Fock operator) is diagonal in the configuration basis. Only doubly substituted determinants can contribute to \( \Psi_1 \) and the matrix inversion implied in Eq. (8) becomes trivial. Equation (7) shows that calculating the MP3 energy requires a matrix vector product with the Hamilton matrix, which costs as much as a single iteration in a CI calculation.

In the general case of a multi-configurational or spin restricted open shell RHF wavefunction, one may still define a Fock operator through the first order density matrix as in Eq. (2) [30]. By comparing this (spin-averaged) zeroth-order Hamiltonian with the unrestricted Fock matrix, it is evident that \( H_0 \) defined by Eqs. (2,3) has some deficiency for high-spin open-shell systems, and there has been a number of attempts to improve it for these cases [9,12,18,31]. We will not comment on perturbation theories aimed at restricted Hartree-Fock reference only [32-34], as in our opinion an open-shell PT should be the limiting case of a multi-reference theory. The most promising of the modifications suggested for \( H_0 \) appears to be the one by Andersson [31], because it allows to remove the often low lying singly and doubly excited states in the orthogonal complement space to the reference function from the MP2 and MP3 equations.

A difficulty in all open-shell and multi-reference perturbation theories is that the zeroth-order wavefunction \( \Psi_0 \) is not necessarily an eigenfunction of \( H_0 \) defined by Fock operators. To restore the eigenfunction property we can define a projector on \( \Psi_0 \) as
\[ P_0 = |\Psi_0 \rangle \langle \Psi_0| \] (9)

Using this projector, a plausible choice for \( H_0 \) is
\[ H_0 = P_0 F P_0 + (1 - P_0) F (1 - P_0) \]  

Unfortunately, this zeroth-order Hamiltonian does not lead to a practically useful general PT since it is not block-diagonal in the excitation levels, and thus the first-order wavefunction with this \( H_0 \) contains not only doubly but also triply, quadruply, etc. substituted configurations. To escape this problem \( H_0 \) may be defined as [25]

\[ H_0 = P_0 F P_0 + P_1 F P_1 + P_2 F P_2 + \cdots \]  

where \( P_1 \) is a projector on the singly substituted states, \( P_2 \) on the doubly substituted ones, etc. We denote this as model 1. It is not trivial to define substitution levels for a multi-configurational reference state. Wolinski and Pulay [24] defined them by applying repeatedly the single substitution operator manifold \( (E_{ij} - E_{ji}) \) to \( \Psi_0 \), and orthogonalising the resulting set to any lower order substituted subspace. This method allows the consistent definition of arbitrary high orders of PT, although the practical usefulness of high orders is doubtful. This formulation leads naturally to the internally contracted [35] form of CI theory, with the advantage that the configuration list is dramatically shortened, although at the expense of a more complicated structure of the matrix elements.

In most early CI programs, single and double substitutions were treated together. In this vein Anderson et al. [26] have defined their zeroth-order Hamiltonian as

\[ H_0 = P_0 F P_0 + P_{1+2} F P_{1+2} \]  

where the part of the Hamiltonian that is needed only in fourth and higher orders (i.e. the orthogonal complement of the reference function, and three-fold and higher excitations) is left out. For historical reasons we call this model 3; its projection operators are defined as model 1, i.e. using a contracted formalism. Although MRMP is not strictly size consistent in various implementations, test calculations on Be-dimer (\( R_{\text{Be-Be}} = 200 \) bohr, basis 6-311g*, CAS reference in \( 3\sigma, 4\sigma^*, 5\sigma, 6\sigma^*, 1\pi_x, 2\pi_x^*, 1\pi_y, 2\pi_y^* \) orbitals) yielded a size consistency error of less than 0.1 \( \mu \text{H} \) for model 1, whereas model 3 was found to be not strictly size consistent. A number of applications have been reported by this method at the second order level by Roos and co-workers [36-45].
An alternative definition of the projectors to the space of substituted configurations is to consider the substitution operators applied to each reference configuration separately, not to the full reference wavefunction. This uncontracted approach leads to much larger substituted subspaces, the ratio to the contracted approach being roughly the number of configurations in the reference space. This is the principal disadvantage of this method, since it is not applicable to long reference expansions, say $10^5$ or $10^6$ configurations. Using an $H_0$ that is formally identical with Eq. (12), except that the projector $P_{1+2}$ projects to the space spanned by applying the substitution operators to each reference configuration, Murphy and Messmer [46] implemented this form of multi-configurational PT first. We call this model 0. As model 1 and model 3 differ only in some small coupling terms between singles and doubles and are numerically almost equivalent, we will concentrate on models 0 and 1.

Finally, Werner [29] defined a compromise method that uses uncontracted functions for the internal and singly external configuration spaces, and internally contracted states for the rest of the space. We have not studied this possibility.

Unlike in the closed-shell case, it is not possible in general to define canonical orbitals that are eigenfunctions of the Fock operator, Eq. (3), particularly if a limited CI expansion is used (not a Complete Active Space [47-49]). This means that, unless the Fock operator is truncated to a diagonal form, the first-order wavefunction must be determined using the full formula Eq. (8). Although this looks formidable at first, the first order wavefunction can be determined by an efficient iterative procedure, since the matrix $H_0$ is very sparse, just as in the case of closed-shell Møller-Plesset theory with non-canonical (localised) orbitals [50]. The use of a non-diagonal $H_0$ is essential for the formulation of the theory in an orbital-invariant manner, and it usually also leads to better results than a zeroth-order Hamiltonian truncated to diagonal form [51].

### 2.3 Implementation

We implemented the multi-reference Møller-Plesset formalism as an option in the Direct CI program of Saunders and van Lenthe [52]. This program uses a basis of spin-adapted Configuration State Functions (CSF). Both the projected formalism using the CSFs as a basis, and the contracted formalism using the
contracted reference state and the contracted excited states as a basis were implemented.

The singly and doubly excited states needed in both approaches are obtained by applying the substitution operators to the MCSCF reference function [24], and subsequent orthonormalisation of the resulting states. This is a deviation from the internally contracted CI methods [53], where possible non-orthogonalities can be handled by diagonalisation. The orthogonalisations are only required within very restricted subspaces, i.e. configuration spaces having the same number of holes in the doubly occupied and the same number of particles in the virtual spaces of the multi-configurational reference function. In the case of model 0 no orthogonalisation is required except for excitations completely within the active orbitals of the MCSCF wavefunction [46]. The orthogonalisation may be performed through diagonalising the overlap matrix as is done by Andersson [26] or through a Löwdin orthogonalisation [54] as done by Werner [29], but we choose the Modified Gramm-Schmidt (MGS) method. A slight problem with MGS is that it is numerically less accurate [55]. Therefore, if a vector has been orthogonalised to a set of orthogonal vectors using MGS the orthogonality should be checked. If needed, a second iteration on the vector may be performed to achieve orthogonality within the desired accuracy.

In both the projected and contracted form Eq. (8) is solved using the Jacobi method [56,57] which involves evaluating

\[ C_{1}^{n+1} = C_{1}^{n} - D^{-1} \left[ (H - E_{\text{ref}}) C_{0} + (H_{0} - E_{0}) C_{1}^{n} \right] \]  

(13)

each iteration. Here $D$ is the diagonal of the Fock operator $H_{0}$ possibly adjusted with a level shifter. The part between square brackets is the residue, the norm of which may be used to monitor the convergence of the iteration process. The $HC_{0}$ term in Eq. (13) is obtained from the first iteration of the Direct CI program using the MCSCF vector $C_{0}$ as CI vector. Convergence is accelerated using a standard DIIS procedure [58,59]. In this method only a matrix-vector multiplication with the zeroth order Hamiltonian is required in each iteration. The efficiency of this multiplication is important to the overall efficiency and depends on the formalism (projected or contracted) used. Therefore the details involved in the multiplication which are important to the efficiency will be
discussed in the next two paragraphs for the projected and contracted formalism respectively.

In the projected form the matrix-vector multiplication uses the CSF basis of the direct CI program [52] (for notation we refer to [52] also). The standard symbolic matrix elements of this program are used to evaluate the matrix elements of \( H_0 \). Many of the routines originally written for handling the CI Hamiltonian may be reused as such or in a slightly modified form. Basically, these routines use internal matrix elements that are precomputed, the external part is generated on the fly. Only the original precomputed elements for \( H \) need to be replaced by the elements for \( H_0 \). To generate these elements the projection operators have to be incorporated in the Fock matrix elements. In CSF basis the projector on the reference function may be written as

\[
|\Psi_0\rangle|\Psi_0\rangle = \sum_{ST\sigma\tau} |\Psi^{S\sigma}\rangle C^{S\sigma} C^{T\tau} |\Psi^{T\tau}\rangle
\]  

where \( S \) and \( T \) label the internal occupation patterns, and \( \sigma \) and \( \tau \) label the spin patterns in the internal MOs. A projector on an excited state (here two electrons are excited from the internal space to the external space) becomes

\[
|E_{ij}^{ab}\Psi_0\rangle|E_{ij}^{ab}\Psi_0\rangle = \sum_{ST\sigma\tau} |E_{ij}^{ab}\Psi^{S\sigma}\rangle C^{S\sigma} C^{T\tau} |E_{ij}^{ab}\Psi^{T\tau}\rangle
\]  

(14)

Taking into account that the Fock operator is a one-electron operator the internal occupation pattern may differ in one place to allow a CSF \( E^{ab}_{ij}\Psi^{VU} \) to contribute to a CSF \( E^{ab}_{ij}\Psi^{S\sigma} \). This leads to

\[
|E_{ij}^{ab}\Psi_0\rangle|E_{ij}^{ab}\Psi_0\rangle |F|E_{ij}^{ab}\Psi_0\rangle|E_{ij}^{ab}\Psi_0\rangle =
\sum_{ST\sigma\tau U,V\rho\nu} |E_{ij}^{ab}\Psi^{S\sigma}\rangle C^{S\sigma} C^{T\tau} |E_{ij}^{ab}\Psi^{T\tau}\rangle |F|E_{ij}^{ab}\Psi^{U\rho}\rangle C^{U\rho} C^{V\nu} |E_{ij}^{ab}\Psi^{V\nu}\rangle
\]

(15)

which results in a contribution to the matrix-vector product with \( H_0 \) of the form

\[
Z_{ab}^{S\sigma} = \sum_{\nu} B_{ab}^{S\sigma\nu} F C^{V\nu}_{ab} + \sum_{\nu} B_{ab}^{S\sigma\nu} F C^{\overline{V}\nu}_{ab}
\]  

(16)
where $B$ represents coupling coefficients (the bar over $V$ and $v$ indicates triplet coupling of the electrons in the external MOs).

On the other hand the excitation operator may differ for one-electron to allow a CSF $E_{ij}^{ac} \Psi^{U \rho}$ to contribute to a CSF $E_{ij}^{ab} \Psi^{S \sigma}$. This leads to

$$
\left| E_{ij}^{ab} \Psi_0 \right| \left| E_{ij}^{ab} \Psi_0 \right| F \left| E_{ij}^{ac} \Psi_0 \right| \left| E_{ij}^{ac} \Psi_0 \right| =
\sum_{STU} \left| E_{ij}^{ab} \Psi^{S \sigma} \right| C^{S \sigma} C^{T \tau} \left| E_{ij}^{ab} \Psi^{T \tau} \right| F \left| E_{ij}^{ac} \Psi^{T \tau} \right| C^{T \tau} C^{U \rho} \left| E_{ij}^{ac} \Psi^{U \rho} \right|
$$

which results in a contribution to the matrix-vector product with $H_0$ of the form

$$
Z_{ab}^{S \sigma} = \sum_{\rho} B_{ac}^{S \sigma U \rho} F_{bc} C_{ac}^{U \rho} + \sum_{\rho} B_{ac}^{S \sigma U \rho} F_{bc} C_{ac}^{U \rho}
$$

This means that the Fock matrix transformed to CSF basis behaves as a one-electron operator among the external orbitals in the sense that it only couples CSFs differing one orbital in the external space. However, it couples all internal occupation patterns and in that sense it behaves similar to a multiple electron operator. In practice this means that the integrals needed in the matrix-vector multiplication may be classified as shown in table I

<table>
<thead>
<tr>
<th>CSF interactions</th>
<th>Integral type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum-vacuum</td>
<td></td>
</tr>
<tr>
<td>Doublet-Doublet</td>
<td>[ij][k] and [ij]</td>
</tr>
<tr>
<td>Singlet-Singlet</td>
<td></td>
</tr>
<tr>
<td>Triplet-Triplet</td>
<td></td>
</tr>
<tr>
<td>Doublet-Vacuum</td>
<td></td>
</tr>
<tr>
<td>Singlet-Doublet</td>
<td>[ia]</td>
</tr>
<tr>
<td>Triplet-Triplet</td>
<td></td>
</tr>
<tr>
<td>Doublet-Doublet</td>
<td></td>
</tr>
<tr>
<td>Singlet-Singlet</td>
<td>[ij][ab], [ial][jb] and [ab]</td>
</tr>
<tr>
<td>Triplet-Triplet</td>
<td></td>
</tr>
</tbody>
</table>
Comparing this integral classification with the one for the total Hamiltonian [52] it is clear that $H_0$ does not behave as a true one-electron operator in this basis. The appearance of two-electron integrals leads to a rather expensive matrix-vector multiplication. In less detail this was pointed out by Roos et al. [30] also.

In the contracted formalism the Fock operator behaves as a true one-electron operator, but the contracted states differ from the configurations used by the original CI code in such a way that special multiplicators have to be written. However, these multiplicators may be derived from the CSF-based multiplicators. Following the MP2, MP3 merely constitutes a single iteration of the Direct CI process, using $\Psi_1$ as the CI vector. Because the CI part of the program still works in CSF space, $\Psi_1$ must be transformed back to the CSF basis. Therefore the transformations from contracted state basis to CSF basis and vice versa are implemented. These transformations together with the CI matrix multiplication effectively offer a single CI iteration in the contracted space. As a spin-off, this allows one to implement a contracted CI approach also.

Our contracted formalism differs slightly from the formalisms implemented by Werner and Andersson. Andersson [26] implemented an $H_0$ such that no internally excited states will contribute to $\Psi_1$, whereas our $H_0$ may result in contributions in the entire first order interacting space. Werner [29] has for efficiency reasons implemented an approach in which the internal and semi-internal states are left uncontracted. Only the external states are internally contracted. In our approach all states are contracted.

The projected and the contracted implementation differ in various ways. First, the projected approach is less work to implement than the contracted one because many of the CSF based routines available may be reused. Although this may seem attractive there is a runtime penalty in using the projected approach. This is shown in table II were we compare the timings of the projected and contracted approach for one of our test examples, the dissociation of N$_2$ in a 6-311G+g(d,p) basis set, using a 6 orbital - 6 electron CASSCF wavefunction as reference (a comparison of the efficiency of MRCI and MRMP is given in the 1,1'-bicyclohexylidene example). This produces a total of 219042 symmetry allowed CSFs and 6964 excited states for model 1. All these calculations are performed on an Apollo DN10000 workstation, a rather modest machine by today’s standards.
### Table II. Timing comparison for MRMP models and MRCI

<table>
<thead>
<tr>
<th></th>
<th>Symbolic* (seconds)</th>
<th>Time/Iteration (seconds)</th>
<th># Iterations</th>
<th>Total (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRSDCI</td>
<td>210</td>
<td>270</td>
<td>12</td>
<td>3500</td>
</tr>
<tr>
<td>Proj. MP2-model 1</td>
<td>320</td>
<td>110</td>
<td>31</td>
<td>3700</td>
</tr>
<tr>
<td>Proj. MP2-model 0</td>
<td>270</td>
<td>73</td>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td>Contr. MP2-model 1</td>
<td>220</td>
<td>1.5</td>
<td>10</td>
<td>235</td>
</tr>
</tbody>
</table>

* The symbolic includes the calculation of the MRCI and MRMP coupling constants, and the generation and orthogonalisation of excited states.

The projected MP2 is more efficient than the CI because $H_0$ contains fewer interactions than $H$. Specifically, integral types having three or four external orbital indices (e.g. \([ab|cd]\)) are absent in $H_0$. Furthermore, projected MP2 model 0 is more efficient than model 1. This is partly because there are no projectors between the doubles and the singlets and triplets in model 0 so there are fewer interactions among those CSFs. Also, the model 0 $H_0$ is more diagonal dominant thus facilitating the convergence of the linear system solver. However, the contracted MP2 is much more efficient than the projected MP2. Because in the contracted formalism only the true first order interacting space of the reference function is taken into account the contracted space is much smaller than the CSF space. For example, the CSF reference space in this case even holds six fold excited states whereas in the contracted formalism these states were removed while transforming to the contracted basis.

In an MP3 calculation however the contracted formalism has the disadvantage that the contracted $\Psi_1$ must be transformed to CSF base which is not needed in the projected approach. In practice, this transformation costs a small fraction of the total CPU time needed to calculate the MP3 energy.

Concluding, the comparison between projected MP and contracted MP shows that the contracted approach is the method of choice. Thus all results in the following sections are calculated using the contracted formalism.
2.4 Applications

We show the application of the contracted MRMP method to various problems. We concentrate on comparing the various models. We compare the Møller-Plesset results to MRCI [52], with and without a multi-reference Davidson size consistency correction and MRCEPA(0) [60]. The Davidson correction [61] was calculated using the overlap of the reference function and the CI wavefunction as $c_0$ and the difference of the energies of the two wavefunctions as correlation energy [62].

As a first application we studied the singlet-triplet splitting of methylene to assess the amount of correlation energy recovered in the multi-reference perturbation approach. The other applications, except for the last one, are concerned with various aspects of potential energy surfaces. The dispersion coefficient of helium dimer is discussed as an application to pure dynamic correlation interactions. The potential energy curves of N$_2$ and O$_2$ are discussed as well as the dissociation energies of N$_2$, O$_2$ and ethene. Finally, the transition energy in 1,1’-bicyclohexylidene between the A$_g$ and B$_u$ state is calculated to demonstrate the performance in large molecules.

2.4.1 Singlet-triplet splitting of methylene

The energy separation between the $^3$B$_1$ ground state and the $^1$A$_1$ first excited state of CH$_2$ was calculated by Bauschlicher and Taylor [63] as a calibration of other correlation approaches. We therefore use their DZP basis and their geometry. The results for both models 1 and 3 are given in table III.

For the reference functions a 2-configuration MCSCF function for the singlet and the associated single-configuration function for a triplet, and a CASSCF function where all electrons are distributed over the 5 active orbitals were chosen.
Table III  Singlet-triplet splitting for methylene

<table>
<thead>
<tr>
<th></th>
<th>Singlet (hartree)</th>
<th>Triplet (hartree)</th>
<th>Delta E (kcal/mole)</th>
<th>Error (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-MCSCF</td>
<td>-38.907659</td>
<td>-38.927947</td>
<td>12.73</td>
<td>0.76</td>
</tr>
<tr>
<td>2-MP2-1</td>
<td>-39.005802</td>
<td>-39.031047</td>
<td>15.84</td>
<td>3.87</td>
</tr>
<tr>
<td>2-MP3-1</td>
<td>-39.021856</td>
<td>-39.042263</td>
<td>12.81</td>
<td>0.83</td>
</tr>
<tr>
<td>2-MP2-3</td>
<td>-39.005858</td>
<td>-39.031192</td>
<td>15.90</td>
<td>3.93</td>
</tr>
<tr>
<td>2-MP3-3</td>
<td>-39.021953</td>
<td>-39.042350</td>
<td>12.80</td>
<td>0.83</td>
</tr>
<tr>
<td>2-CI</td>
<td>-39.022155</td>
<td>-39.041602</td>
<td>12.20</td>
<td>0.23</td>
</tr>
<tr>
<td>2-CI+Dav</td>
<td>-39.027748</td>
<td>-39.046911</td>
<td>12.03</td>
<td>0.05</td>
</tr>
<tr>
<td>2-MRCEPA(0)</td>
<td>-39.028373</td>
<td>-39.047386</td>
<td>11.93</td>
<td>-0.04</td>
</tr>
<tr>
<td>CASSCF</td>
<td>-38.945528</td>
<td>-38.965954</td>
<td>12.82</td>
<td>0.85</td>
</tr>
<tr>
<td>CASMP3-1</td>
<td>-39.023437</td>
<td>-39.043826</td>
<td>12.79</td>
<td>0.82</td>
</tr>
<tr>
<td>CASMP2-3</td>
<td>-39.013245</td>
<td>-39.037852</td>
<td>15.44</td>
<td>3.47</td>
</tr>
<tr>
<td>CASMP3-3</td>
<td>-39.023633</td>
<td>-39.043901</td>
<td>12.72</td>
<td>0.75</td>
</tr>
<tr>
<td>CASCI</td>
<td>-39.025803</td>
<td>-39.044929</td>
<td>12.00</td>
<td>0.03</td>
</tr>
<tr>
<td>CASCEPA(0)</td>
<td>-39.028030</td>
<td>-39.046816</td>
<td>11.79</td>
<td>-0.18</td>
</tr>
<tr>
<td>Full CI</td>
<td>-39.027181</td>
<td>-39.046260</td>
<td>11.97</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Firstly, one notices that the single-reference approach (SCF/SDCI) is inadequate and therefore multi-reference techniques are essential. From the perturbation approaches model 1 and model 3 yield essentially the same results. Second order perturbation theory is slightly worse than the two-configuration MCSCF/ROHF level, due to the inadequacy of the spin-averaged Fock matrix as $H_0$ for the triplet state. This agrees with the results of other groups [27]. The modified $H_0$ recommended by Andersson [31] performs significantly better in this case. Third order perturbation theory is an improvement over the second order but the resulting singlet-triplet splitting is no more accurate than that
obtained from the MCSCF/ROHF calculations. The MRCI calculation with the Davidson correction and the MRCEPA(0) calculation, both starting with the 2-configuration MCSCF/ROHF wavefunctions, agree with the full CI results for the splitting, although their energy goes slightly below the full CI result.

In [29] Werner gives a comprehensive comparison of CAS reference approaches to this case. Our CASMP results are in agreement with Werner's overview.

2.4.2 The C\textsubscript{6} dispersion coefficient of the He-dimer

The attractive component of the weak interaction energy of the He-dimer is caused solely by the correlation energy. Whereas the single-configuration SCF wavefunction for the system, does describe a proper dissociation to separate He atoms, no attractive minimum is found in the Hartree-Fock approximation. The C\textsubscript{6} van der Waals coefficient, which corresponds to the dominant induced-dipole-induced-dipole term in the multipole expansion, is calculated by fitting the C\textsubscript{6} and the C\textsubscript{8} coefficients to energies calculated at 10, 20 and 2000 Bohr inter-nuclear distance. We used the [6s3p2d] C1D2 basis set [64,65]. The full CI calculations were performed using the program of Harrison [66].

For this property the normal MP2 method fails badly. All approaches using a single-configuration as reference function severely underestimate the dispersion energy. To obtain the dispersion energy between correlated He atoms triple excitations have to be included [67]. In the multi-reference calculations this is achieved using the direct product of a 5-configuration double excitation wavefunction for each He atom as the reference space.

The results in table IV show that the multi-reference CI calculations indeed reach almost the basis set limit for C\textsubscript{6}. Furthermore, the MRCI and the Contracted MRCI (MRCCI) yield the same results. This shows that all essential contributions to the dispersion energy are contained in the contracted multi-reference singles-doubles space. However, the multi-reference Møller-Plesset theory performs no better than the single-reference approach regardless of the model used, so the multi-configuration character of the reference function does not yield improved results. Therefore, higher order perturbation theory is required to obtain a proper C\textsubscript{6} coefficient.
Table IV $C_6$ Dispersion coefficient for He$_2$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$C_6$ (au)</th>
<th>Method</th>
<th>$C_6$ (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>1.11</td>
<td>MRMP2</td>
<td>1.05</td>
</tr>
<tr>
<td>MP3</td>
<td>1.32</td>
<td>MRMP3</td>
<td>1.32</td>
</tr>
<tr>
<td>SDCI</td>
<td>1.32</td>
<td>MRCI</td>
<td>1.44</td>
</tr>
<tr>
<td>SDCI+Dav.</td>
<td>1.39</td>
<td>MRCI+Dav.</td>
<td>1.44</td>
</tr>
<tr>
<td>CEPA-0</td>
<td>1.39</td>
<td>MRCEPA(0)</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MRCCI</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Full CI 1.45 Full CI 1.45

2.4.3 Dissociation of O$_2$ and N$_2$

Any performance study of a generalised perturbation method should at least consider an open shell system. The dissociation of the triplet ground state O$_2$ molecule into two triplet ground state O atoms is a typical example of such systems. Therefore, we calculated the potential energy surface of the molecule using MRMP2 and MRMP3 and compare the results to MRCI, MRCI+Davidson, and MRCEPA(0) results. The calculations were performed within D$_{2h}$ symmetry B$_{1u}$ using a DZP-basis with spherical harmonic d-functions (exponent 1.2) (see [68] for the DZ part of the basis). A CAS in the 5$\sigma$, 6$\sigma^*$, 1$\pi_x$, 2$\pi_x^*$, 1$\pi_y$, and 2$\pi_y^*$ orbitals is used for the reference, and the 1S orbitals are frozen at the MCSCF level.

The results are shown in figure I. The MCSCF curve has a maximum at 4.0 bohr. This causes the strong curvature around that point. This maximum has been found in other studies [69-73] also, and there has been much discussion about its nature. Because perturbation theory has been plagued by convergence problems we feared for divergences at this maximum. However, the MRMP2 and MRMP3 behave nicely at that point. Further, the plot shows that correlating methods improve the bonding energy considerably. All correlating methods seem to give comparable results.
Figure I: Bonding energy of $O_2$ in DZP-basis plotted against the internuclear distance

The bonding energy is plotted vertically in hartree. The internuclear distance $R$ is plotted horizontally in bohr on a logarithmic scale. The horizontal scale starts at 1.5 bohr. The distance at infinity $R_{\text{inf}}$ is 200 bohr.

As a reference molecule to compare the $O_2$ calculations to we chose $N_2$. This singlet molecule dissociates into two quartet atoms, breaking a triple bond without further complications. The calculations on $N_2$ were performed using the 6-311g* [74] basis, and a CAS in the $5\sigma$, $6\sigma^*$, $1\pi_x$, $2\pi_x^*$, $1\pi_y$, and $2\pi_y^*$ orbitals as reference space. The 1S orbitals are frozen at the MCSCF level and not correlated. The bonding energies of $N_2$ are plotted in figure II.
**Figure II**: Bonding energy of N\(_2\) in 6-311g\(^*\) basis plotted against the internuclear distance

The bonding energy is plotted vertically in hartree. The internuclear distance \(R\) is plotted horizontally in bohr on a logarithmic scale. The horizontal scale starts at 1.5 bohr. The distance at infinity \(R_{\text{inf}}\) is 200 bohr.

In contrast to the O\(_2\) plot the N\(_2\) curves show that correlating methods do not seem to be so important for the bonding energy. Again all correlating methods seem to give comparable results, except for the MRMP3 at 5.0 Bohr which shows a “peak”. The “peak” in this curve suggests that the perturbation series is divergent at that geometry. In a forthcoming article we will consider a test for the convergence behaviour of perturbation series at dubious geometries [75] and study this case in more detail.

The dissociation energies of O\(_2\) and N\(_2\) obtained from the calculations are presented in tables V and VI respectively.
### Table V Dissociation energy of O₂

<table>
<thead>
<tr>
<th>Method</th>
<th>E($R_{eq}$) (hartree)</th>
<th>E($R_{inf}$) (hartree)</th>
<th>Delta E (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF</td>
<td>-149.732663</td>
<td>-149.598813</td>
<td>83.99</td>
</tr>
<tr>
<td>MRCEPA(0)</td>
<td>-150.004409</td>
<td>-149.839666</td>
<td>103.38</td>
</tr>
<tr>
<td>MRMP2</td>
<td>-149.991294</td>
<td>-149.824555</td>
<td>104.63</td>
</tr>
<tr>
<td>MRMP3</td>
<td>-149.992384</td>
<td>-149.835002</td>
<td>98.76</td>
</tr>
<tr>
<td>MRCI</td>
<td>-149.990020</td>
<td>-149.825954</td>
<td>102.95</td>
</tr>
<tr>
<td>MRCI+Dav.</td>
<td>-150.007358</td>
<td>-149.839323</td>
<td>105.45</td>
</tr>
<tr>
<td>Experiment</td>
<td>n.a.</td>
<td>n.a.</td>
<td>114.13</td>
</tr>
</tbody>
</table>

The equilibrium distance $R_{eq}$ is 2.3081604 bohr, and the infinite distance $R_{inf}$ is 200 bohr. The experimental values were calculated from thermodynamic data [85] and MCSCF zero point vibration energies in the DZP basis set calculated with GAMESS-UK [82].

### Table VI Dissociation energy of N₂

<table>
<thead>
<tr>
<th>Method</th>
<th>E($R_{eq}$) (hartree)</th>
<th>E($R_{inf}$) (hartree)</th>
<th>Delta E (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF</td>
<td>-109.107223</td>
<td>-108.789473</td>
<td>199.39</td>
</tr>
<tr>
<td>MRCEPA(0)</td>
<td>-109.314009</td>
<td>-108.984356</td>
<td>206.86</td>
</tr>
<tr>
<td>MRMP2</td>
<td>-109.288746</td>
<td>-108.968016</td>
<td>201.26</td>
</tr>
<tr>
<td>MRMP3</td>
<td>-109.305037</td>
<td>-108.981735</td>
<td>202.88</td>
</tr>
<tr>
<td>MRCI</td>
<td>-109.304247</td>
<td>-108.975167</td>
<td>206.50</td>
</tr>
<tr>
<td>MRCI+Dav.</td>
<td>-109.315312</td>
<td>-108.985580</td>
<td>206.91</td>
</tr>
<tr>
<td>Experiment</td>
<td>n.a.</td>
<td>n.a.</td>
<td>220.26</td>
</tr>
</tbody>
</table>

The equilibrium distance $R_{eq}$ is 2.0929693 bohr, and the infinite distance $R_{inf}$ is 200 bohr. The experimental values were calculated from thermodynamic data [85] and MCSCF zero point vibration energies in the DZP basis set calculated with GAMESS-UK [82].
In O\textsubscript{2} the dissociation energies calculated with MRCEPA(0), MRCI and MRMP2 are all quite close to each other. However the MRMP3 results in a dissociation energy that is too low. It underestimates the correlation energy in the molecule. In N\textsubscript{2} the MRCEPA(0) and MRCI calculation agree even more closely upon the dissociation energy than in O\textsubscript{2}. But the perturbation theory finds dissociation energies too low both at second order and third order. Again it seems that the perturbation theory underestimates the correlation energy at the equilibrium geometry. This is in accordance with the conclusions by Werner [29] although his results are much more accurate due to the use of much larger basis sets.

<table>
<thead>
<tr>
<th></th>
<th>E CH\textsubscript{2}</th>
<th>E C\textsubscript{2}H\textsubscript{4}</th>
<th>Delta-E</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(hartree)</td>
<td>(hartree)</td>
<td>(kcal/mol)</td>
</tr>
<tr>
<td>SCF</td>
<td>-38.927946</td>
<td>-78.050543</td>
<td>-122.15</td>
</tr>
<tr>
<td>MCSCF</td>
<td>-38.927946</td>
<td>-78.103024</td>
<td>-155.08</td>
</tr>
<tr>
<td>MRMP2</td>
<td>-39.031047</td>
<td>-78.327354</td>
<td>-166.46</td>
</tr>
<tr>
<td>MRMP3</td>
<td>-39.042263</td>
<td>-78.351993</td>
<td>-167.84</td>
</tr>
<tr>
<td>MRCI</td>
<td>-39.041700</td>
<td>-78.342357</td>
<td>-162.50</td>
</tr>
<tr>
<td>MRCI+Dav.</td>
<td>-39.047028</td>
<td>-78.361232</td>
<td>-167.66</td>
</tr>
<tr>
<td>MRCEPA(0)</td>
<td>-39.047507</td>
<td>-78.364167</td>
<td>-168.90</td>
</tr>
<tr>
<td>Experiment</td>
<td>n.a.</td>
<td>n.a.</td>
<td>-182.17</td>
</tr>
</tbody>
</table>

The experimental values were calculated from thermodynamic data [85] and MCSCF zero point vibration energies in the DZP basis set calculated with GAMESS-UK [82]

2.4.4 Dissociation of ethene

The dissociation of ethene into two \(^3\text{B}_1\) fragments requires a 4 orbital 4 electron CASSCF reference function. We used the triplet basis set from the methylene calculations. The methylene geometries were also taken to be the \(^3\text{B}_1\) geometries. The ethene geometry was optimised at the Hartree-Fock level using...
this basis set \((R_{CC} 1.325 \text{ Å}, R_{CH} 1.077\text{Å}, \sigma_{HCC} 121.56^\circ)\). The results are given in table VII.

The CASSCF is quite an improvement with respect to the SCF. The MRMP2 reduces the difference with CI an order of magnitude further, at much less cost, and the MP3 is virtually indistinguishable from the Davidson corrected CI.

2.4.5 The \(A_g\) and \(B_u\) ground states of 1,1’-bicyclohexylidene

1,1’-bicyclohexylidene is the smallest member of the family of oligo(cyclohexylidenes), shown in figure III.

![Figure III: Structure of oligo(cyclohexylidenes)](image)

In oligo(cyclohexylidenes) the X and Y groups are CH\(_2\) by default.

These molecules may be used as molecular building blocks for functional materials, in particular materials showing non-linear optical activity [76]. As a consequence there is quite some interest in the interpretation of the UV-spectrum. Recently, Hoogesteeger et al. [77] have studied this spectrum using results obtained with the MRD-CI [78-81] program of Buenker et al. included in GAMESS-UK [82]. However, due to the program limitations the size of the configuration space was severely restricted. The program presented in this article allows for much larger configuration spaces and therefore offers a way to validate the results by Hoogesteeger et al. In this context the energy of the \(1A_g\) and the \(1B_u\) states were recalculated at the MRMP2, MRMP3, MRCI, and MRCEPA(0) level with the MRCI program of Saunders et al. [52] using the geometry from Hoogesteeger and the same basis set, i.e. 6-31G [83]. Only the 5 most important configurations were selected as reference configurations as shown in table 4 in [77]. The results are shown in table VIII.
**Tabel VIII:** Comparison of MRD-CI energies for the 1A<sub>g</sub> and 1B<sub>u</sub> states of 1,1'-bicyclohexylidene to the MRMP2/3, MRCI and MRCEPA(0) energies.

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy 1A&lt;sub&gt;g&lt;/sub&gt; (hartree)</th>
<th>Energy 1B&lt;sub&gt;u&lt;/sub&gt; (hartree)</th>
<th>Transition energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRD-CI</td>
<td>-465.938378</td>
<td>-465.597163</td>
<td>9.28</td>
</tr>
<tr>
<td>MRMP2</td>
<td>-466.960643</td>
<td>-466.698324</td>
<td>7.14</td>
</tr>
<tr>
<td>MRMP3</td>
<td>-467.046972</td>
<td>-466.752633</td>
<td>8.01</td>
</tr>
<tr>
<td>MRCEPA(0)</td>
<td>-467.105770</td>
<td>-466.812577</td>
<td>7.98</td>
</tr>
<tr>
<td>MRCI</td>
<td>-466.762505</td>
<td>-466.446343</td>
<td>8.60</td>
</tr>
<tr>
<td>MRCI+Davidson</td>
<td>-466.951134</td>
<td>-466.644702</td>
<td>8.34</td>
</tr>
<tr>
<td>MRCI+Pople</td>
<td>-467.075290</td>
<td>-466.781485</td>
<td>8.00</td>
</tr>
<tr>
<td>Experiment</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5.95</td>
</tr>
</tbody>
</table>

The Davidson corrections were calculated according to [61], and the Pople corrections were calculated according to [84].

Because Hoogesteeger *et al.* performed CI calculations using only 5431 CSFs for the 1A<sub>g</sub> state and 3413 CSFs for the 1B<sub>u</sub> state the energies were relatively high. MRCI, size consistency corrected MRCI, and MRCEPA(0) calculations involving 11446335 CSFs and 17997035 CSFs for the 1A<sub>g</sub> and the 1B<sub>u</sub> state gave improved estimates of the transition energy. However MRCI performed relatively poor compared to MRMP3, MRCEPA(0) and MRCI+Pople [84] suggesting that its lack of size consistency introduces a significant error. The MRMP2/3 calculations employed 1786521 and 1834052 contracted excited states for the 1A<sub>g</sub> state and 1B<sub>u</sub> state respectively, i.e. 6-10 fewer coefficients than in MRCI or MRCEPA(0). In spite of this, results agree closely with those of higher level calculations. We consider this encouraging. The MRMP2 transition energy is a bit low relative to MRCEPA(0) and size-consistency corrected MRCI but the MRMP3 agrees nicely with MRCEPA(0) and MRCI+Pople correction. Note that the MRMP2 and MRMP3 calculations on the 1A<sub>g</sub> state took only 734 and 3440 seconds of CPU-time respectively compared to 42200 seconds for the MRCI and MRCEPA(0) calculations on a 90 MHz R8000 SGI PowerChallenge. Thus stressing the efficiency of the perturbation approaches. The basis set in this calculation was rather small valence double zeta, i.e. no polarization or diffuse functions were included. This helps to avoid
complications from Rydberg states mixing in. However, it is also probably responsible for the 2 eV discrepancy in the transition energy, compared to experiment.

### 2.5 Conclusions

We have implemented a generalised MRMP method using both a contracted and an uncontracted formalism. The contracted formalism is much more efficient than the uncontracted formalism and is therefore the method of choice. Different zeroth order hamiltonians may be chosen through selecting different projections. Comparing model 1 and model 3 it should be noted that the results obtained are essentially the same. This indicates that model 1 is preferable because it is the computationally more efficient one and has smaller size consistency errors.

The applications show that the MRMP performs reasonably well on calculating the singlet-triplet splitting of methylene and the dissociation energies of O\(\textsubscript{2}\), N\(\textsubscript{2}\) and ethene. However, the MRMP3 dissociation energy for O\(\textsubscript{2}\) was less accurate than the MRMP2 result. Also, potential energy surfaces could be calculated quite well although a problem was found in the N\(\textsubscript{2}\) surface. However, MRMP2/3 fails in calculating the dispersion energy of the Helium dimer. Higher order perturbation theory is required for this property. In the calculation of the transition energy of 1,1’-bicyclohexyldiene the size consistency corrected MRCI, the MRCEPA(0) and the MRMP3 agreed very closely on the transition energy. This means that the MRMP3 calculations led to significant improvements over the MRD-CI calculations by Hoogesteeger et al. at a much lesser cost than the MRCEPA(0) and the MRCI calculations.

### Acknowledgements

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