Analytic evaluation of nonadiabatic coupling terms at the MR-CI level. II. Minima on the crossing seam: Formaldehyde and the photodimerization of ethylene

Michal Dallos and Hans Lischka a)
Institute for Theoretical Chemistry and Structural Biology, University of Vienna, A-1090 Vienna, Austria

Ron Shepard
Theoretical Chemistry Group, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

David R. Yarkony
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Péter G. Szalay
Department of Theoretical Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

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The method for the analytic calculation of the nonadiabatic coupling vector at the multireference configuration-interaction (MR-CI) level and its program implementation into the COLUMBUS program system described in the preceding paper [Lischka et al., J. Chem. Phys. 120, 7322 (2004)] has been combined with automatic searches for minima on the crossing seam (MXS). Based on a perturbative description of the vicinity of a conical intersection, a Lagrange formalism for the determination of MXS has been derived. Geometry optimization by direct inversion in the iterative subspace extrapolation is used to improve the convergence properties of the corresponding Newton-Raphson procedure. Three examples have been investigated: the crossing between the $1^1B_1/2^1A_1$ valence states in formaldehyde, the crossing between the $2^1A_1/3^1A_1$ $\pi-\pi^*$ valence and $n_-3p_\pi$ Rydberg states in formaldehyde, and three crossings in the case of the photodimerization of ethylene. The methods developed allow MXS searches of significantly larger systems at the MR-CI level than have been possible before and significantly more accurate calculations as compared to previous complete-active space self-consistent field approaches.

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I. INTRODUCTION

Conical intersections play a fundamental role in photochemical and photophysical processes. 1–3 These crossings can act as funnels allowing rapid radiationless transfer between different electronic states. The accurate determination of such intersections and the characterization of the intersection cone are of utmost importance for the understanding of photochemical reaction mechanisms and the description of the dynamics of such processes. The properties of conical intersections have been studied and characterized extensively e.g. by Mead and Truhlar, 4 Mead, 5 Berry, 6 Yarkony, 7 Atchity, Xantheas, and Ruedenberg, 8 Köppel, Domcke, and Cederbaum, 9 Bernardi, Olivucci, and Robb, 10 and Baer, 11 based on the classic work by von Neumann and Wigner, 11 Teller, 12 and Herzberg and Longuet-Higgins. 13 The intersection space (crossing seam) is of dimension $N^{\text{int}} - 2$ ($N^{\text{int}}$ is the number of internal degrees of freedom) for the intersection between two states of the same symmetry. 8,11 Extensive effort has been spent in order to develop efficient methods for the determination of the minima on the crossing seam (MXS) based on the Lagrangian multiplier method 14–17 and on projected gradient techniques. 18,19

In order to perform these optimizations the gradient of the energy difference between two electronic states with respect to a nuclear coordinates and the derivative of the coupling matrix element with respect to a nuclear coordinate 20–21 are required. For an efficient determination of the MXS it is crucial to have methods and computer programs for the analytic evaluation of these gradients and derivative coupling terms available. Lengsfield, Saxe, and Yarkony 20 and Saxe, Lengsfield, and Yarkony 21 have described such methods for the multireference configuration-interaction (MR-CI) approach based on MR-CI gradient techniques. For the complete active-space self-consistent field (CASSCF) method respective procedures have been described by Bearpark, Robb, and Schlegel. 19 In the preceding article 22 (Paper I) a new formulation for the analytic evaluation of the nonadiabatic coupling term based on efficient analytic MR-CI gradient methods 23–26 has been given. In this formalism the question of the resolution of invariant orbital spaces has been treated in a very general way considering cases of different orbital invariance properties of the multiconfiguration self-consistent field (MCSCF) method [which is used to generate the molecular orbitals (MO’s)] and the subsequent MR-CI calculation. This formalism allows a completely independent selection of MCSCF and MR-CI wave functions. A corre-

a)Electronic address: hans.lischka@univie.ac.at
sponding computer program implementation into the COLUMBUS program system\textsuperscript{27–30} has been performed as well. In Paper I,\textsuperscript{22} the formalism for the evaluation of the gradient terms in Cartesian coordinates has been given. In this article the procedures used for the MXS optimizations are described and interesting applications are presented.

II. DETERMINATION OF THE MXS

In this section algorithms for locating conical intersections are discussed. These algorithms are based on a perturbative description of the vicinity of a conical intersection. Although some of the material presented in this section has been reported previously\textsuperscript{7,31} the presentation included here is distinct and facilitates the description of the algorithms, which is the main purpose of this section. Here \( \mathbf{R} \) will denote the \( N \)\textsuperscript{int} internal nuclear coordinates, while \( \mathbf{r} \) will denote the electronic coordinates.

A. Perturbative description of a conical intersection

Let \( \mathbf{R}\ij \) denote a point of conical intersection of states \( I \) and \( J \). We use degenerate perturbation theory\textsuperscript{5,7} to obtain an expansion of the energy through first order in displacements from \( \mathbf{R}\ij \). We will be particularly interested in those displacements that lift the degeneracy at first order. These displacements define the branching\textsuperscript{9} or \( g\cdot h \) space.\textsuperscript{32}

The derivation of the requisite expressions begins with the first-order expansion of \( \mathbf{H}(\mathbf{R}) \), the electronic Hamiltonian matrix in \( \psi \), the configuration-state function basis, given by

\[
\mathbf{H}(\mathbf{R}) = \mathbf{H}(\mathbf{R}\ij) + \nabla \mathbf{H}(\mathbf{R}\ij) \cdot \delta \mathbf{R}
\]  

(1)

where \( \mathbf{R} = \mathbf{R}\ij + \delta \mathbf{R} \). It is convenient to express \( \mathbf{H}(\mathbf{R}) \) in the crude adiabatic basis

\[
\hat{\Psi}_j(\mathbf{r}; \mathbf{R}) = \sum_{\alpha=1}^{N_{\text{CSF}}} c_\alpha^j(\mathbf{R}\ij) \psi_\alpha(\mathbf{r}; \mathbf{R}),
\]

(2a)

where

\[
[H(\mathbf{R}) - E_j(\mathbf{R})]c_j(\mathbf{R}) = 0.
\]

(2b)

Using Eq. (2a), Eq. (1) becomes

\[
\tilde{H}_{ij}(\mathbf{R}) = \langle \hat{\Psi}_j(\mathbf{r}; \mathbf{R}) | \mathbf{H}(\mathbf{R}; \mathbf{R}) | \hat{\Psi}_i(\mathbf{r}; \mathbf{R}) \rangle = \delta_{ij} E_k(\mathbf{R}\ij) + \mathbf{h}^k(\mathbf{R}\ij) \cdot \delta \mathbf{R},
\]

(3a)

where

\[
\mathbf{h}^k(\mathbf{R}) = c_\alpha(\mathbf{R}\ij) \nabla \mathbf{H}(\mathbf{R}\ij) c_k(\mathbf{R}\ij).
\]

(3b)

In \( \tilde{\Psi}_j(\mathbf{r}; \mathbf{R}) \), the crude adiabatic basis, the adiabatic states, \( \psi_m(\mathbf{r}; \mathbf{R}) \), can be expanded as

\[
\psi_m(\mathbf{r}; \mathbf{R}) = \sum_{\alpha=1}^{N_{\text{CSF}}} \xi_m^\alpha(\mathbf{R}) \tilde{\psi}_\alpha(\mathbf{r}; \mathbf{R}).
\]

(4)

We partition\textsuperscript{33} the Hilbert space into the \( Q \) space comprised of the states \( I \) and \( J \) and its orthogonal complement, the \( P \) space. Then in the crude adiabatic basis \( \tilde{\mathbf{H}}(\mathbf{R}) \) is given by\textsuperscript{7}

\[
\begin{pmatrix}
\tilde{\mathbf{H}}^{QQ} - E_I & \tilde{\mathbf{H}}^{QP} \\
\tilde{\mathbf{H}}^{PQ} & \tilde{\mathbf{H}}^{PP} - E_J
\end{pmatrix}
\begin{pmatrix}
Q \\
P
\end{pmatrix}
= \begin{pmatrix}
0 \\
0
\end{pmatrix},
\]

(5a)

where, for \( A, B = Q \) or \( P \), \( \tilde{\mathbf{H}}^{AB}_{ij} = \mathbf{H}_{ij} \) for \( k \) restricted to the \( A \) subspace and \( l \) restricted to the \( B \) subspace and \( \xi^\alpha_l = \xi^\alpha_k \) for \( k \) restricted to the \( A \) subspace. Solving Eq. (5a) for \( Q \xi \) gives

\[
[\tilde{\mathbf{H}}^{QQ} - E_I - \tilde{\mathbf{H}}^{QP}(\tilde{\mathbf{H}}^{PP} - E_J)^{-1}\tilde{\mathbf{H}}^{PQ}]Q \xi = 0.
\]

(5b)

The reason for choosing the crude adiabatic basis can now be seen from Eq. (5b). At \( \mathbf{R}\ij \)

\[
\tilde{H}_{ij}(\mathbf{R}\ij) = \delta_{ij} E_k(\mathbf{R}\ij)
\]

so that \( \tilde{H}_{ij}^{Q}(\mathbf{R}\ij) = 0 \), the terms that couple the \( Q \) and \( P \) spaces begin at first order in \( \delta \mathbf{R} \) and the \( P \)-space contribution to the energy, the second term in Eq. (5b), begins at second order.

Therefore through first order in \( \delta \mathbf{R} \), \( E_j(\mathbf{R}) \) and \( E_J(\mathbf{R}) \) are obtained as the eigenvalues of the \( Q \)-space Hamiltonian:

\[
\begin{align*}
\tilde{H}^{QQ}(\mathbf{R}\ij + \delta \mathbf{R}) &= \left[ E_J(\mathbf{R}\ij) + s^J(\mathbf{R}\ij) \cdot \delta \mathbf{R} \right] \mathbf{I} \\
&+ \begin{pmatrix}
-\mathbf{g}^J(\mathbf{R}\ij) & \mathbf{h}^J(\mathbf{R}\ij) \\
\mathbf{h}^J(\mathbf{R}\ij) & \mathbf{g}^J(\mathbf{R}\ij)
\end{pmatrix} \cdot \delta \mathbf{R},
\end{align*}
\]

(7)

where

\[
2g^J(\mathbf{R}) = h^J(\mathbf{R}) - h^J(\mathbf{R})
\]

(8a)

and the trace

\[
2s^J(\mathbf{R}) = h^J(\mathbf{R}) + h^J(\mathbf{R}).
\]

(8b)

\( \tilde{H}^{QQ} \) is a \( 2 \times 2 \) matrix since the \( Q \) space is two dimensional. \( \tilde{H}^{QQ}(\mathbf{R}\ij + \delta \mathbf{R}) \) has eigenvalues \( E_\pm = \epsilon_- \) and \( E_J = \epsilon_+ \) where

\[
\begin{align*}
\epsilon_\pm(\mathbf{R}\ij + \delta \mathbf{R}) &= \left[ E_J(\mathbf{R}\ij) + s^J(\mathbf{R}\ij) \cdot \delta \mathbf{R} \right] \\
&\pm \left[ \left( \mathbf{g}^J(\mathbf{R}\ij) \cdot \delta \mathbf{R} \right)^2 + \left[ \mathbf{h}^J(\mathbf{R}\ij) \cdot \delta \mathbf{R} \right]^2 \right]^{1/2} \\
&= s^J(\mathbf{R}\ij) \cdot \delta \mathbf{R} \pm \Delta E(\mathbf{R}),
\end{align*}
\]

(9a)

and \( \Delta E(\mathbf{R}) = E_J(\mathbf{R}) - E_\pm(\mathbf{R}) = 2\Delta \epsilon \). In Eq. (9b) \( E_J(\mathbf{R}\ij) \) is taken as the zero of energy, \( \delta \mathbf{R} = \rho \delta \mathbf{R} \), and \( \delta \mathbf{R} \) is a unit vector. From Eq. (9b) it is seen that the \( g\cdot h \) space is two dimensional since there are exactly two directions, \( \mathbf{g}^J \) and \( \mathbf{h}^J \) along which the degeneracy is lifted at first order, that is, linearly. If either \( \mathbf{g}^J \) or \( \mathbf{h}^J \) vanishes, the intersection is not a conical intersection. From Eqs. (3b) and (8a) it is precisely these essential quantities, \( \mathbf{h}^J \) and \( \mathbf{g}^J \), that are efficiently evaluated as described in Paper I.\textsuperscript{22}

The gradient of the energy difference in Eq. (9b) is

\[
2 \nabla[\Delta \epsilon(\mathbf{R})] = \nabla[\epsilon_+(\mathbf{R}) - \epsilon_-(\mathbf{R})] = \mathbf{g}^J(\theta),
\]

(10)

where

\[
\cos \theta = \frac{\mathbf{g}^J \cdot \delta \mathbf{R}}{\Delta \epsilon}, \quad \sin \theta = \frac{\mathbf{h}^J \cdot \delta \mathbf{R}}{\Delta \epsilon}
\]

(11a)

and
\[ g^{IJ}(\theta) = \cos \theta \mathbf{g}^{IJ} + \sin \theta \mathbf{h}^{IJ}. \]  
(11b)

If \( \delta \mathbf{R} \) is parallel to \( \nabla [\Delta \varepsilon(\mathbf{R})] \), then by using Eq. (11a) it is “perpendicular” to

\[ h^{IJ}(\theta) = -\sin \theta \mathbf{g}^{IJ} + \cos \theta \mathbf{h}^{IJ}, \]  
(11c)

that is, \( \delta \mathbf{R} \cdot h^{IJ}(\theta) = 0 \). Provided \( \mathbf{g}^{IJ} \) and \( \mathbf{h}^{IJ} \) are (chosen) orthogonal [which is always possible at an \( \mathbf{R}^{*^IJ} \) (Ref. 34)] it defines a direction in the \( g \)-\( h \) plane.

This direction \( \theta \) is related to the choice of degenerate states in the following sense. Rotating electronic states \( I \) and \( J \) by \( \phi/2 \) changes the vectors defining the \( g \)-\( h \) plane as follows:

\[
\begin{pmatrix}
\cos \phi/2 & -\sin \phi/2 \\
\sin \phi/2 & \cos \phi/2
\end{pmatrix}
\begin{pmatrix}
-\mathbf{g}^{IJ} \\
\mathbf{h}^{IJ}
\end{pmatrix} =
\begin{pmatrix}
\cos \phi/2 & \sin \phi/2 \\
-\sin \phi/2 & \cos \phi/2
\end{pmatrix}
\begin{pmatrix}
-\mathbf{g}^{IJ}(\phi) \\
\mathbf{h}^{IJ}(\phi)
\end{pmatrix}.
\]  
(12)

where \( \mathbf{g}^{IJ}(\phi) \) and \( \mathbf{h}^{IJ}(\phi) \) are defined in Eqs. (11b) and (11c), respectively. Equations (11b) and (11c) are generally valid away from a degeneracy and Eq. (12) is valid at the degeneracy and affect the linear region. This identification makes the connection between the degenerate and nondegenerate perturbative expressions for the energy difference gradient near a point of conical intersection. Below we will use this observation to develop an algorithm for locating conical intersections.

**B. A Lagrange multiplier/Newton-Raphson algorithm**

Assume we are at a point \( \mathbf{R}^0 \), close to a point of conical intersection \( \mathbf{R}^{*^IJ} \), that is, \( \mathbf{R}^0 + \delta \mathbf{R} = \mathbf{R}^{*^IJ} \). From the comments following Eq. (12),

\[ 0 = \Delta \varepsilon(\mathbf{R}) = \Delta \varepsilon(\mathbf{R}^0) + \mathbf{g}^{IJ}(\mathbf{R}^0) \cdot \delta \mathbf{R} \]  
(13a)

can be used to locate an intersection of states \( I \) and \( J \). If \( \delta \mathbf{R} \) is chosen parallel to \( \mathbf{g}^{IJ} \), Eq. (13a) is sufficient and indeed a variant of this equation has been used to locate conical intersections in triatomic molecules.\(^{17}\) However, if \( \delta \mathbf{R} \) is not parallel to \( \mathbf{g}^{IJ} \), from Eq. (9a) this will introduce terms first order in \( \delta \mathbf{R} \) unless

\[ 0 = h^{IJ}(\mathbf{R}^{*^IJ}) \cdot \delta \mathbf{R}. \]  
(13b)

Requiring Eq. (13b) eliminates the biggest contribution to \( \Delta \varepsilon(\mathbf{R}) \) caused by not choosing \( \delta \mathbf{R} \) parallel to \( \mathbf{g}^{IJ} \). Equations (13a) and (13b) are at the heart of the algorithms discussed herein for locating conical intersections.

Equations (13a) and (13b) are underdetermined, that is, Eqs. (13a) and (13b) do not have a unique solution but can be satisfied on an \((N_{\text{int}}-2)\)-dimensional subspace referred to as the seam space. This is the content of the noncrossing rule of von Neuman and Wigner.\(^{11}\) To provide a (locally) unique solution we can require that the solution be the lowest energy point on the seam. A related alternative is to use the preceding requirement in the reduced dimensionality nuclear coordinate space in which \( N_{\text{con}} \) geometric constraints, \( K'(\mathbf{R}) = 0 \), \( i = 1 - N_{\text{con}} \), are imposed. In these cases, as we see below, \( \delta \mathbf{R} \) is not in general parallel to \( \mathbf{g}^{IJ} \).

This condition described above can be phrased as the constrained minimization of the energy of the \( i \)th state \([E_i(\mathbf{R})]\) subject to the geometric constraints \( K'(\mathbf{R}) = 0 \) for \( i = 1 - N_{\text{con}} \) and \( \Delta E_{ij}(\mathbf{R}) = 0 \). This constrained minimization is accomplished using a Lagrange multiplier\(^\text{35}\) formalism. In view of Eqs. (13a) and (13b) we define the Lagrangian

\[ L^{IJ}(\mathbf{R}, \lambda, \zeta) = E_i(\mathbf{R}) + \sum_{i=1}^{N_{\text{con}}} \lambda_i C_i(\mathbf{R}) + \sum_{i=1}^{N_{\text{con}}} \zeta_i K_i(\mathbf{R}), \]  
(14a)

where now \( \lambda \) and \( \zeta \) as well as \( \mathbf{R} \) are independent variables, since \( \mathbf{R} \) must satisfy the constraint equations \( C_i(\mathbf{R}) = \Delta E_{ij}(\mathbf{R}) = 0 \). Therefore we require

\[ \frac{\partial}{\partial \xi_k} L^{IJ}(\mathbf{R}) = 0 \quad \text{for} \quad \xi = \mathbf{R}, \lambda, \zeta, \]  
(14b)

which becomes, at second order, the usual system of Newton-Raphson equations

\[
\begin{pmatrix}
\nabla \nabla L^{IJ} \\
\mathbf{g}^{IJ} \\
\mathbf{h}^{IJ} \\
\mathbf{k}'
\end{pmatrix}
\begin{pmatrix}
\delta \mathbf{R} \\
\delta \lambda_1 \\
\delta \lambda_2 \\
\delta \zeta
\end{pmatrix} =
\begin{pmatrix}
\nabla L^{IJ} \\
0 \\
0 \\
0
\end{pmatrix},
\]  
(15a)

where

\[ \nabla L^{IJ}(\mathbf{R}) = \mathbf{h}^{IJ}(\mathbf{R}) + \lambda_i [\mathbf{h}^{IJ}(\mathbf{R}) - \mathbf{h}^{IJ}(\mathbf{R})] \]  
(15b)

and \( \mathbf{k}'(\mathbf{R}) = \nabla K'(\mathbf{R}) \). In deriving Eq. (15) we have noted that \( \nabla C^2(\mathbf{R}) = \mathbf{h}^{IJ}(\mathbf{R}) \), whereas \( \nabla (\Psi_j(\mathbf{r}; \mathbf{R})|H(\mathbf{r}; \mathbf{R})|\Psi_j(\mathbf{r}; \mathbf{R})_r = 0 \).

Note that Eqs. (15b) and (15c) are Eqs. (13a) and (13b). Further Eq. (15d) is given by

\[ K'(\mathbf{R}) = K'(\mathbf{R}) + \mathbf{k}' \cdot \delta \mathbf{R} = 0, \]  
(17)

which is just the statement that the \( i \)th constraint is satisfied through first order. The use of Eq. (17) facilitates prediction of successive points on a seam once the initial point is determined as described in Ref. 17. This approach based on Eq. (15) was originally introduced over a decade ago\(^{17}\) and has been analyzed in several numerical/formal studies.\(^{31,36,37}\)

As discussed already in the Introduction, calculation of the gradients (\( \mathbf{g}' \) and \( \mathbf{g}'' \)) and the derivative coupling (\( \mathbf{h}^{IJ} \)) is relatively straightforward and cheap at the MR-CI with singles and doubles (MR-CISD) level.\(^{22,24-26}\) On the other hand, the Hessian \( \nabla \nabla L^{IJ} \) can be evaluated most easily by the finite difference differentiation of \( \nabla L^{IJ} \). Since this is an expensive and numerically unstable procedure, several approximations to \( \nabla \nabla L^{IJ} \) have been considered, as will be discussed below, leading to a quasi-Newton-Raphson scheme.
For the determination of the MXS based on the Lagrange formalism two approaches and program packages have been developed. The first one (program POLYHES) is a direct implementation of the formalism described by Eq. (15). The second approach (program GDIIIS) does not introduce the geometric constraints given in Eq. (15) but uses—as will be described below—other ways to apply geometric constraints. More importantly, program GDIIIS makes use of the direct inversion in the iterative subspace (DIIS) method introduced by Pulay 38 and applied by Csaśzar and Pulay 39 to geometry optimizations (GDIIIS) that accelerate the optimization of the MXS considerably.

C. Program POLYHES

Program POLYHES is directly based on Eqs. (15) and its three-state analog 40 and is available in the program system COLUMBUS 5.9. Since $\nabla \nabla L^{ij}$ is costly to evaluate we find it convenient to start a search with $\nabla \nabla L^{ij} \approx I$. As a result, we find that the algorithm based on this approximation to Eq. (15) quickly satisfies the constraint equations, that is, locates a conical intersection with the geometrical parameters specified by $K = 0$. However, the norm of the right-hand side of Eq. (15) is nonzero, since the constrained energy gradient, $\nabla L^{ij}$, is nonzero. To complete the optimization (an approximation to) $\nabla \nabla L^{ij}$ is required. The use of divided differences is problematical near a conical intersection owing to discontinuities in the gradients. We have found that the simple expedient of changing a single nuclear coordinate that contributes significantly to $g^{ij}$ or $h^{ij}$ by $0.3a_0$ provides gradients that are sufficiently well-behaved to construct $\nabla \nabla L^{ij}$. This approximation to $\nabla \nabla L^{ij}$ can be used, unaltered, to obtain points on the seam of conical intersection in the general vicinity of the original point.

D. Program GDIIIS

The program GDIIIS is based on the modified form of the Lagrange function (14a) where the last term (geometric constraint) has been omitted. The resulting Newton-Raphson equations (referred to as NR below) are similar to Eq. (15) except that all entries corresponding to geometry constraints are eliminated. The DIIS method 38 has been used to speed up the convergence of several iterative procedures. Particularly interesting is the version developed for geometry optimizations (GDIIIS). 39 An important feature of GDIIIS is that it does not require an exact Hessian. In particular, using natural internal coordinates, 41 it has been shown for geometry optimizations that a diagonal matrix instead of the full Hessian can be used successfully without losing on the convergence. 41 Therefore, the GDIIIS procedure seems to be advantageous to speed up the convergence of the quasi-NR procedure.

Assume that a series of vectors of the geometry have been generated by an optimization procedure (e.g., Newton-Raphson), i.e., after the $i$th iteration of this procedure there are $k$ geometries available represented by the vectors $R^i, R^2, \ldots, R^k$.

If the procedure converges, $R^k$ is assumed to be the best geometry within this set. However, we can also consider this set as a subspace and look for the best vector within this subspace by forming the linear combination

$$R'^k = \sum_{i=1}^{k} c_i R^i,$$

where the coefficients $c_i$ can be obtained from a suitable minimization criteria, e.g., by minimizing the norm of the residuum vector $\sigma = \sum_i c_i e^i$ augmented by the normality condition

$$\sum_{i=1}^{k} \sum_{j=1}^{k} c_i c_j (e^i e^j) + \lambda \left( \sum_{i=1}^{k} c_i - 1 \right),$$

where $e^i$ is the error vector $R^i - R^0$ associated with the $i$th iteration step and $R^0$ is the sought-for solution vector. 39 $\lambda$ is a Lagrangian multiplier. Using for $e^i$ the corresponding geometry update step from the Newton-Raphson procedure, 39 i.e.,

$$e^i = \delta R^i = -Q^{-1} g^i,$$

where $Q$ is the Hessian and $g^i$ is the gradient in iteration $i$, the new, linearly independent geometry vector of the $(k+1)$th step is obtained by the following equation:

$$R^{k+1} = R'^k - Q^{-1} g'^k = \sum_{i=1}^{k} c_i R^i - Q^{-1} \sum_{i=1}^{k} c_i g^i.$$

This is the “best vector” of Eq. (18), which has been updated by a Newton-Raphson step using the approximate gradient

$$g'^k = \sum_{i=1}^{k} c_i g^i.$$

This procedure is generalized here for the conical intersection search by using the geometries from the corresponding Newton-Raphson equation. In order to obtain a simple and manageable procedure, the Hessian $\nabla \nabla L^{ij}$ is approximated as $\nabla \nabla L^{ij} = \text{diag}(\nabla \nabla E_i)$ in the spirit of the already mentioned similar approximations made for ground-state geometry optimizations. 41 This leads—as has already been specified above—to a quasi-Newton-Raphson approach as basis for the GDIIIS procedure. This procedure corresponds to three basic approximations: (a) the molecular Hessians of the two states are identical within the coordinate space of the seam; (b) $\nabla \nabla E_i$ is diagonal; (c) the second derivative corresponding to potential coupling is neglected. It is clear that these approximations are very severe. Our tests presented in this work (see below) and experience obtained in further applications show that in conjunction with using the natural internal coordinates, 41 the GDIIIS algorithm converges very rapidly with this simple choice for the Hessians. Geometry constraints can be conveniently introduced by zeroing the appropriate component of $\nabla L^{ij}$. In this way selected internal coordinates can be kept fixed at values given at the beginning of the calculation by an initial geometry.

The last comment on our algorithm concerns the updating procedure of Eq. (20). A strongly changing character of
the CI vectors during the geometry optimization process is observed because of the quasidegeneracy occurring in the approach to the intersection. Therefore, the gradient vector \( g^i \) [Eq. (21)] corresponding to the vector \( R^i \) had to be calculated exactly requiring an additional CI and gradient calculation. We hope that this technical problem can be eliminated in the future by a consistent definition of the CI wave functions applying some diabatization criterion.

III. APPLICATIONS

Three examples have been chosen. In the first two, intersections between energy surfaces of excited states of formaldehyde have been investigated. The first crossing involves the intersection between the \( 2^1A_1(\pi-\pi^*) \) and the \( 1^1B_1(\sigma-\pi^*) \) states at \( C_{2v} \) symmetry already discussed previously by means of grid optimization of selected geometry parameters.\(^{42}\) The second formaldehyde example deals with the intersection of the \( 2^1A_1 \) and \( 3^1A_1 \) \( (\pi-\pi^* \text{ and } n_y-3p_y) \) states. Hachey, Bruna, and Grein\(^{43}\) have studied potential curves as a function of the CO bond distance of formaldehyde in detail. From their Fig. 2 one finds an avoided crossing between these two \( A_1 \) states with a minimal separation of about 0.2 eV. Previous attempts to optimize the geometry of the upper state have lead to a very close approach of these two states, which gave rise to the suspicion that an intersection had actually been found. In this work this intersection has been actually determined.

In the third set of examples the conical intersections involved in the photocyclodimerization of two ethylene molecules are investigated. This reaction is a textbook example for the application of the Woodward–Hoffmann rules.\(^{44}\) The dimerization is symmetry-forbidden in the ground state, but allowed in the excited state. The course of the reaction has been discussed qualitatively by Michl\(^{45}\) and Michl and co-workers \(^{47–49}\) have shown that the “pericyclic” transition state on \( \pi \) orbitals of the ethylene dimer constructed from the \( \pi \) and \( \pi^* \) orbitals of the two separated ethylene molecules,\(^{44}\) three electronic states have been discussed: the ground state \( G \) with the configuration \( 1\pi^2_2\pi^2 \), a singly excited state \( S \) \( (1\pi^2_2\pi^1\pi^1) \) and a doubly excited state \( D \) \( (1\pi^2_2\pi^2_2) \). At rectangular configurations two crossings of the \( S \) and the \( D \) states are predicted. For more details we refer to the original Refs. 45 and 46. The \( S_1 \) (\( D \) state) is supposed to have a “pericyclic” minimum at a structure similar to the one of the “antiaromatic” transition state on \( S_0 \). However, Bernardi and co-workers\(^{47–49}\) have shown that the “pericyclic” minimum on the \( S_1 \) surface is not a minimum but a saddle point. Following the mode of the imaginary frequency led to a parallelogram structure, for which a conical intersection with the ground state was found. These conclusions were obtained from calculations based on CASSCF(4,4) calculations using the 4-31G basis set. To our knowledge no other ab initio calculations have been published. It is the purpose of this paper to perform a more extended search for the conical intersections at a considerably higher methodological level (MR-CISD) and with larger basis sets.

A. Computational details

The first step is a state-averaged MCSCF calculation including the two electronic states for which the intersection is to be computed. As already mentioned in paper I,\(^{22}\) the symmetrized two-electron transition density for states \( I \) and \( J \) is computed from the sum of the state vectors \( |I+J \rangle \). For that reason, the symmetry to be used in the calculations has to be reduced such that the two intersecting states have the same symmetry. The CI wave function is characterized by a set of reference configuration state functions (CSFs), from which all single and double excitations into all virtual orbitals are constructed. In case of the ethylene dimerization the interacting space restriction\(^{50}\) has been used and only the reference symmetry equal to the state symmetry was allowed. For the two formaldehyde examples all reference symmetries were allowed and the interacting space restriction was not applied. The \( K \)-shell orbitals were always frozen in the MR-CISD calculations. More details about basis sets and reference spaces will be given together with the individual examples. The COLUMBUS program system\(^{27–30}\) was used in all calculations. The atomic orbital (AO) integrals and AO gradient integrals have been computed with program modules taken from DALTON.\(^{51}\) Geometry optimizations were performed in natural internal coordinates as defined by Fogarasi et al.\(^{41}\). All MXS optimizations reported in this work were performed with the GDIIS program version.

B. The formaldehyde \( 2^1A_1(\pi-\pi^*)/1^1B_1(\sigma-\pi^*) \) intersection

The CAS consisted of six electrons and the \( \sigma(5a_1), \pi(1b_1), n(2b_2), \pi^*(2b_1), \) and \( \sigma^*(6a_1) \) orbitals. State averaging at the CASSCF level included the \( 1^1A_1 \) and \( 1^1B_1 \) states. The actual calculations were carried out in \( C_2 \) symmetry (plane perpendicular to the molecular plane). The correlation-consistent polarized valence double- and triple-zeta (cc-pVDZ and cc-pVTZ) basis sets were used.\(^{52}\)

First let us discuss the performance of the GDIIS MXS optimization algorithm taking this intersection case as a representative example. The convergence behavior is shown in Fig. 1 for calculations using the cc-pVDZ basis. The different panels show the change of the C–O stretching, C–H stretching, and CH\(_2\) scissoring coordinates and of the energies of the two states as the iterations proceed. Standard values for the diagonal elements of the Hessian matrix as recommended by Fogarasi et al.\(^{45}\) were chosen (4.1 aJ/Å\(^2\) for CO stretching, 5.5 aJ/Å\(^2\) for CH stretching, and 1.0 aJ/Å\(^2\) for all bending and out-of-plane coordinates for both states). For symmetry reasons only the three stretching and CH\(_2\) scissoring coordinates have to be optimized, but the remaining ones have also been included in the calculations. The GDIIS extrapolation has been switched on in the fourth iteration; the reason for this will be given below. As the convergence criterion the estimated geometry change (maximum value of the absolute change and mean value) for the new iteration was chosen. Convergence was achieved when the respective changes were less than 0.001 and 0.0002 Å, respectively.
By comparing the convergence behavior of the GDIIS and NR methods for the geometry parameters [Figs. 1(a)–1(c)], the advantage of the former method is clearly apparent. After the GDIIS extrapolation is switched on the final geometry value is rapidly reached. One can also observe from Fig. 1(d) that the NR algorithm brings the geometry very rapidly to the vicinity of the seam. This is rather surprising considering the very approximate nature of the molecular Hessian we use. Even afterwards, the NR procedure converges nicely, reaching convergence in about ten iterations. According to our experience, the best strategy is to make use of the effectiveness of the NR algorithm in finding the seam and to switch on the GDIIS procedure in the vicinity of the seam.

The final results of the optimization are presented in Table I. As expected from the previous calculations, the CO bond distance of the MSX is significantly stretched as compared to the ground state. Differences in the CO distance between CASSCF and MR-CISD results for the MSX amount to about 0.04 Å, whereas for the ground state corresponding differences lie only between 0.006 and 0.008 Å. The CH₃ angle is very sensitive to the computational method and basis set. It is reduced by the MR-CISD method by about 5°–7° as compared to CASSCF. Again, much smaller variations are found for the ground state.

![Graphs](https://example.com/graphs.png)

**FIG. 1.** Convergence behavior of the NR and GDIIS algorithm for the MXS search between the 2^1A_1/1^1B_1 states in formaldehyde. (a) C-O stretching coordinate; (b) C-H stretching coordinate; (c) CH₃ scissoring coordinate; panel (d) energy of both states. The cc-pVDZ basis has been used.

TABLE I. Geometries and energies for the ground state and the MSX for the 1^1B_1/2^1A_1 states of formaldehyde computed at the CASSCF and MR-CISD levels.ᵃᵇ

<table>
<thead>
<tr>
<th></th>
<th>R_{CO} (Å)</th>
<th>R_{CH} (Å)</th>
<th>∠CH₃ (deg)</th>
<th>-E (a.u.)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CASSCF</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ground state (1^1A₁)</td>
<td>1.224</td>
<td>1.095</td>
<td>117.7</td>
<td>113.928</td>
<td>787</td>
</tr>
<tr>
<td>MXS (1^1B₁/2^1A₁)</td>
<td>1.586</td>
<td>1.078</td>
<td>130.9</td>
<td>113.614</td>
<td>162</td>
</tr>
<tr>
<td><strong>MR-CISD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ground state (1^1A₁)</td>
<td>1.218</td>
<td>1.112</td>
<td>115.7</td>
<td>114.200</td>
<td>162</td>
</tr>
<tr>
<td>MXS (1^1B₁/2^1A₁)</td>
<td>1.549</td>
<td>1.097</td>
<td>123.5</td>
<td>113.893</td>
<td>023</td>
</tr>
<tr>
<td><strong>CASSCF</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ground state (1^1A₁)</td>
<td>1.220</td>
<td>1.086</td>
<td>110.9</td>
<td>-113.961</td>
<td>690</td>
</tr>
<tr>
<td>MXS (1^1B₁/2^1A₁)</td>
<td>1.570</td>
<td>1.067</td>
<td>132.7</td>
<td>-113.652</td>
<td>840</td>
</tr>
<tr>
<td><strong>MR-CISD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ground state (1^1A₁)</td>
<td>1.212</td>
<td>1.095</td>
<td>116.7</td>
<td>-114.305</td>
<td>460</td>
</tr>
<tr>
<td>MXS (1^1B₁/2^1A₁)</td>
<td>1.529</td>
<td>1.078</td>
<td>127.3</td>
<td>-114.004</td>
<td>987</td>
</tr>
</tbody>
</table>

ᵃBond distances in Å, angles in deg.
ᵇTotal energies in a.u., energy differences in eV.
C. The formaldehyde 2 \( ^1 \!A_i/3 \!A_1 \) (~p~p~ and \( n_y\!-\!3p_y \) intersection

The active orbital space consisted of two parts. The valence part is described by the \( \sigma(5a_1) \), \( \pi(1b_1) \), \( n(2b_2) \), \( \pi^*(2b_1) \), and \( \sigma^*(6a_1) \) orbitals. An auxiliary (AUX) orbital \( 3p_y(3b_2) \) was used to describe the Rydberg state. At the MCSCF level the CSF space consisted of a CAS(6,5) in the valence orbitals plus single excitations into the AUX orbital. The reference space in the MR-CISD calculations was the CAS(6,5) plus the individual Rydberg configuration \( (n,3p_y) \). State-averaging was performed at the MCSCF level over the three lowest \( ^1 \!A_1 \) states (ground state, \( n-3p_y \), and ~p~p~). \( C_{2v} \) symmetry was used in these calculations. The molecule is located in the \( (y,z) \) plane with the CO bond along the \( z \) axis. The basis sets were constructed from modified doubly \( (d) \) augmented correlation-consistent basis sets as follows. The basis set denominated \( d\text{-aug}^{-1}\text{-cc-pVDZ} \) consisted of the \( \text{aug-cc-pVDZ} \) basis\(^{52,53} \) enlarged by the additional, diffuse \( p \) function of the \( d\text{-aug} \) basis\(^{54,55} \) on carbon and oxygen and by the corresponding \( d\text{-aug} \) \( s \) function on hydrogen. Similarly, the \( d\text{-aug}^{-1}\text{-cc-pVTZ} \) basis consisted of the \( \text{aug-cc-pVTZ} \) basis\(^{52,53} \) enlarged by the additional, diffuse \( p \) function of the \( d\text{-aug} \) basis\(^{54,55} \) on carbon and oxygen and by the corresponding \( d\text{-aug} \) \( s \) function on hydrogen. The results collected in Table II show that the ~p~p~ and \( n_y\!-\!3p_y \) states cross at a CO bond distance of about 1.31 Å.

D. Photocyclodimerization of ethylene

Two crossings for rectangular structures (face-to-face approach of the two ethylene molecules) between the \( 2 \!^1 \!A_i(D)/1 \!^1 \!B_{1g}(S) \) states of \( D_{2h} \) symmetry and one of a parallelogram structure \( (C_{2h} \) symmetry) between \( 1 \!^1 \!A_i/1 \!^1 \!B_{1g} \) (ground and \( S \) states) of \( C_{2h} \) symmetry were determined. The actual symmetry used was always \( C_{2h} \) with the \( z \) axis as the \( C_2 \) axis. The four carbon atoms are located in the \( (x,y) \) plane. The distance of approach of the two ethylene subunits is the \( y \) axis. A \( \text{CAS}(4,4) \) in the four standard \( \text{MO’s} \) \( (D_{2h} : 4a_g, 4b_{2u}, 3b_{3u}, \) and \( 3b_{1u} ; \) \( C_{2h} : 6a_g, 7a_g, 6b_{2g}, 7b_{2u} ) \) of the Woodward–Hoffmann analysis\(^{44} \) was used in the state-averaged CASSCF (SA-CASSCF) calculations and also as reference space in the MR-CISD approach. Three states \( (G, S, \) and \( D) \) were included in the state averaging. Two basis sets, the cc-pVDZ and cc-pVTZ basis sets\(^{52} \) were

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### Table II. Geometries and energies for the ground state and the MSX for the \( 2 \!^1 \!A_i/3 \!A_1 \) states of formaldehyde computed at the MR-CISD level.

<table>
<thead>
<tr>
<th></th>
<th>( R_{\text{CO}} )</th>
<th>( R_{\text{CH}} )</th>
<th>( \angle \text{CH}_2 )</th>
<th>( -E )</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d\text{-aug}^{-1}\text{-cc-pVDZ} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^1 !A_1 )</td>
<td>1.225</td>
<td>1.108</td>
<td>117.0</td>
<td>114.222 791</td>
<td>0</td>
</tr>
<tr>
<td>( \text{MXS} ) (( ^1 !A_i/3 !A_1 ))</td>
<td>1.324</td>
<td>1.100</td>
<td>124.5</td>
<td>113.904 729</td>
<td>8.65</td>
</tr>
<tr>
<td>( d\text{-aug}^{-1}\text{-cc-pVTZ} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^1 !A_1 )</td>
<td>1.215</td>
<td>1.095</td>
<td>117.0</td>
<td>114.308 483</td>
<td>0</td>
</tr>
<tr>
<td>( \text{MXS} ) (( ^1 !A_i/3 !A_1 ))</td>
<td>1.309</td>
<td>1.095</td>
<td>123.4</td>
<td>113.985 265</td>
<td>8.80</td>
</tr>
</tbody>
</table>

*Bond distances in Å, angles in deg.

### Table III. Geometries and energies for the ground state and the two MXS for the intersection of the \( 2 \!^1 \!A_i(S)/1 \!^1 \!B_{1g}(D) \) states of the ethylene dimer in \( D_{2h} \) symmetry computed at the CASSCF and MR-CISD levels.

<table>
<thead>
<tr>
<th></th>
<th>( R_{\text{C-C}} )</th>
<th>( R_{\text{C-C}} )</th>
<th>( R_{\text{CH}} )</th>
<th>( \angle \text{CH}_2 )</th>
<th>( \text{OOP-CH}_2 )</th>
<th>( -E )</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CASSCF} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separated systems</td>
<td>1.345</td>
<td>1.083</td>
<td>117.0</td>
<td>0</td>
<td>156.126 815</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \text{MXS} ) (( S/D) )</td>
<td>1.418</td>
<td>1.084</td>
<td>114.8</td>
<td>25.1</td>
<td>155.842 263</td>
<td>7.74</td>
<td></td>
</tr>
<tr>
<td>( \text{MXS} ) (( S/D) )</td>
<td>1.307</td>
<td>1.083</td>
<td>116.3</td>
<td>9.0</td>
<td>155.828 453</td>
<td>8.12</td>
<td></td>
</tr>
<tr>
<td>( \text{MR-CISD} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separated systems</td>
<td>1.346</td>
<td>1.090</td>
<td>117.0</td>
<td>0</td>
<td>156.616 964</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \text{MXS} ) (( S/D) )</td>
<td>1.427</td>
<td>1.090</td>
<td>115.6</td>
<td>23.0</td>
<td>156.390 418</td>
<td>6.17</td>
<td></td>
</tr>
<tr>
<td>( \text{MXS} ) (( S/D) )</td>
<td>1.379</td>
<td>1.088</td>
<td>116.9</td>
<td>12.0</td>
<td>156.388 204</td>
<td>6.23</td>
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</tr>
<tr>
<td>( \text{MR-CISD} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separated systems</td>
<td>1.333</td>
<td>1.075</td>
<td>117.0</td>
<td>0</td>
<td>156.755 661</td>
<td>0</td>
<td></td>
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<tr>
<td>( \text{MXS} ) (( S/D) )</td>
<td>1.416</td>
<td>1.075</td>
<td>115.7</td>
<td>22.2</td>
<td>156.534 002</td>
<td>6.03</td>
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<tr>
<td>( \text{MXS} ) (( S/D) )</td>
<td>1.371</td>
<td>1.074</td>
<td>116.8</td>
<td>11.9</td>
<td>156.533 299</td>
<td>6.05</td>
<td></td>
</tr>
</tbody>
</table>

*Bond distances in Å, angles in deg.

Total energies in a.u., energy differences in eV.
selected. The energy of the separated system of two ethylene molecules in the ground state was computed as a supermolecule in the same state-averaged approach.

Results for the separated systems and the two MSX of $D_{2h}$ symmetry (MXS1 and MXS2) are reported in Table III. The $R_{C-C}$ distance measures the approach of the two ethylene molecules. In MXS2—the crossing with the larger separation between the two ethylene molecules—the $C\equiv C$ bonds are elongated by about 0.04 Å (MR-CISD values) in comparison to the isolated ethylene molecule in the ground state. An additional stretching of these bonds of approximately the same amount occurs in MXS1. Because of the stronger interaction of the two ethylene subunits in the MXS1 structure as compared to MXS2, the out-of-plane (OOP) angles are larger in the former case. The MXS1 and MXS2 intersections occur at about the same energy at about 6.0 eV (MR-CISD/cc-pVTZ result) above the energy of two ground-state ethylene molecules. The differences between the CASSCF and MR-CISD results are remarkable, especially for the MXS2 structure. The distance between the two ethylene molecules is significantly smaller by 0.12 Å and the $C\equiv C$ bond distance considerably stretched by 0.06 Å in the MR-CISD calculation. The relative energy of the MXS2 computed at the CASSCF level is located 1.9 eV higher than that at the MR-CISD level. The basis set dependence of the geometry is not very pronounced. Most sensitive is $R_{C-C}$ of MXS2. This is understandable since the $S$ state correlates asymptotically with a state where one ethylene molecule is excited to the $V$ state. The character of the $V$ state is valence type, but more diffuse than the ground state. This diffuseness, which is more important at larger C-C distances, is not sufficiently accounted for by the cc-pVDZ basis.

In Table IV structure and energy of the third crossing, MXS3, is presented. This structure is of $C_{2v}$ symmetry and has the shape of a parallelogram. Most notable is the fact that $\Delta E$ is reduced strongly by about 2 eV relative to MXS1 and MXS2. The C-C bond distance is significantly smaller than the one in MXS2. The (unnormalized) $g^{ij}$ and $h^{ij}$ vectors defined in Sec. II are depicted in Figs. 2–4 for the three intersections MXS1–MXS3. In the case of the MXS1 intersection (see Fig. 2), the $g^{ij}$ vector shows a strong tendency for the formation of cyclobutane. The $h^{ij}$ vector describes a distortion towards the parallelogram structure. The MXS2 intersection behaves differently concerning the $g^{ij}$ vector. Figure 3 demonstrates that it consists mainly of a symmetric $C\equiv C$ stretch. The distance of the two ethylene subunits remains almost unchanged. The $h^{ij}$ vector shows the same distortion to the parallelogram structure as that for MXS1. The MXS3 intersection has a completely different characteristic than MXS2. Both vectors show a strong tendency for the approach of the two ethylene molecules towards each other to form cyclobutane. The $g^{ij}$ vector has a significant component of a symmetric $C\equiv C$ stretching mode, whereas

<table>
<thead>
<tr>
<th>$R_{C-C}$</th>
<th>$R_{CC}$</th>
<th>$\angle CCC$</th>
<th>$R_{CF(1)}$</th>
<th>$R_{CF(2)}$</th>
<th>$\angle CH_2(1)$</th>
<th>$\angle CH_2(2)$</th>
<th>$\angle OOP-CH_2(1)$</th>
<th>$\angle OOP-CH_2(2)$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASSCF</td>
<td>1.458</td>
<td>2.188</td>
<td>111.4</td>
<td>1.081</td>
<td>1.082</td>
<td>113.8</td>
<td>117.6</td>
<td>26.2</td>
<td>21.4</td>
</tr>
<tr>
<td>MR-CISD</td>
<td>1.442</td>
<td>2.166</td>
<td>108.1</td>
<td>1.088</td>
<td>1.087</td>
<td>114.8</td>
<td>117.8</td>
<td>22.6</td>
<td>18.9</td>
</tr>
<tr>
<td>MR-CISD</td>
<td>1.430</td>
<td>2.154</td>
<td>107.5</td>
<td>1.072</td>
<td>1.072</td>
<td>115.0</td>
<td>117.7</td>
<td>22.3</td>
<td>20.0</td>
</tr>
</tbody>
</table>

$\Delta E$ in eV.

$g^{ij}$ and $h^{ij}$ vectors for MXS1 computed at the MR-CISD/cc-pVTZ level.

FIG. 2. $g^{ij}$ and $h^{ij}$ vectors for MXS1 computed at the MR-CISD/cc-pVTZ level.
The \( \mathbf{h}^{IJ} \) vector is more pronounced in terms of the formation of the C—C single bonds of cyclobutane.

The \( \mathbf{h} \) vectors of both rectangular structures MXS1 and MXS2 show that the energy will be decreased by a distortion to a parallelogram structure. This is in good agreement with the findings of Bernardi et al.\(^{47}\) that "the \( D_{2h} \) diradicaloid structure is not a minimum but rather is a transition state." Following the distortion to \( C_{2h} \) symmetry one arrives at MXS3 in agreement with the results of Bernardi and co-workers\(^{47-49}\) obtained from CASSCF(4,4)/4-31G calculations. Two significantly different results for the CC bond distance [2.28 Å (Refs. 47 and 49) and 2.19 Å (Ref. 48)] are reported by Bernardi et al. The CC bond distance of 2.188 Å (CASSCF) computed in this work (see Table IV) agrees very well with the second one reported by Bernardi et al. At the MR-CISD level the CC bond distance is reduced by 0.02 Å. A major difference between the two studies is the characterization of the interacting states: while these are the ground state and the \( S \) state in our study, Bernardi et al.\(^{47,48}\) describe an intersection between the ground state and the \( D \) state.

Already from the analysis of the three crossing points one can draw interesting conclusions about the mechanism of the photocyclodimerization of ethylene. Starting from a face-to-face approach of the two separated ethylene molecules in the \( S \) state, one finds that the role of the first crossing point at rectangular geometry, MXS2, is to lead to MXS3. From there, a rapid, radiationless transition to the ground state can occur with further reaction to cyclobutane. It is quite likely that in the course of the reaction the neighborhood point MXS2 can be avoided completely and that the ethylene dimer can reach MXS3 directly. A global survey of the energy surfaces is in progress in order to clarify this question.

**IV. CONCLUSIONS**

The formalism for the analytic calculation of the nonadiabatic coupling vector described in Paper I has been efficiently implemented. Here, that program has been combined with a Lagrange formalism improved by GDIIS extrapolation to give a flexible program system for the determination of minima on the crossing seam at the MR-CISD level. An analysis of the vicinity of the conical intersection based on
perrurbation theory has been used for a derivation of the Lagrange formalism. The crossings treated in this work cover quite different cases of excited states such as Rydberg and valence states, and much larger polyatomic systems can be treated now at the MR-CISD level than has been possible before. The results also demonstrate that a significantly enhanced accuracy can be achieved on the MR-CI level compared to the previous CASSCF optimizations. In the case of the photodimerization of ethylene we have computed three minima on the crossing seam, which together with an analysis of the g-h space describing the intersection cone, allow interesting new conclusions about possible reaction mechanisms.

ACKNOWLEDGMENTS

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