Conical intersections in triplet excited states of methylene from the anti-Hermitian contracted Schrödinger equation

ARTICLE in THE JOURNAL OF CHEMICAL PHYSICS - APRIL 2010

CITATIONS
11

4 AUTHORS, INCLUDING:

Jonathan J Foley
Argonne National Laboratory
17 PUBLICATIONS 75 CITATIONS
Conical intersections in triplet excited states of methylene from the anti-Hermitian contracted Schrödinger equation

James W. Snyder, Jr., Adam E. Rothman, Jonathan J. Foley IV, and David A. Mazziotti

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637, USA

(Received 21 December 2009; accepted 25 March 2010; published online 20 April 2010)

A conical intersection in triplet excited states of methylene is computed through the direct calculation of two-electron reduced density matrices (2-RDMs) from solutions of the anti-Hermitian contracted Schrödinger equation (ACSE). The study synthesizes recent extensions of the ACSE method for the treatment of excited states [G. Gidoefalvi and D. A. Mazziotti, Phys. Rev. A 80, 022507 (2009)] and arbitrary-spin states [A. E. Rothman, J. J. Foley, and D. A. Mazziotti, Phys. Rev. A 80, 052508 (2009)]. We compute absolute energies of the 1 3B1, 1 3A2, and 2 3B1 states of methylene (CH2) and the location of the conical intersection along the 1 3A2−2 3B1 potential-energy surfaces. To treat multireference correlation, we seed the ACSE with an initial 2-RDM from a multiconfiguration self-consistent field (MCSCF) calculation. The ACSE produces energies that significantly improve upon those from MCSCF and second-order multireference many-body perturbation theory, and the 2-RDMs from the ACSE nearly satisfy necessary N-representability conditions. Comparison of the results from augmented double-zeta and triple-zeta basis sets demonstrates the importance of augmented (or diffuse) functions for determining the location of the conical intersection. © 2010 American Institute of Physics. [doi:10.1063/1.3394020]

I. INTRODUCTION

A conical intersection is a point in nuclear coordinate space that occurs at the junction of two Born–Oppenheimer potential-energy curves such that the local topology near the point resembles a double cone or diabolo. As a result, conical intersections are sometimes called diabolical points.1–15 The unique topology of a conical intersection provides an efficient pathway for the radiationless decay of electronically excited states from simple molecules such as methylene CH2 to more complex, biological molecules such as luciferin.1,13–18

The triplet states of methylene, 1 3A2, and 2 3B1 that are involved in its conical intersection are both open-shell and excited. The treatment of such states is complicated because: (i) The α and β electrons in a high-spin state can no longer be treated identically and (ii) excited states must be constrained to be orthogonal to lower lying states. This latter feature in particular tends to increase the degree of multireference correlation19 that contributes to the energy and its two-electron reduced density matrix (2-RDM).

In this paper we study the conical intersection in the triplet excited states of methylene by solving the anti-Hermitian contracted Schrödinger equation (ACSE)20–28 for 2-RDMs without explicitly computing many-electron wave functions. The work harnesses recent extensions of the ACSE method for the treatment of (i) excited states24 and (ii) arbitrary-spin states.25 We determine both absolute energies of the 1 3B1, 1 3A2, and 2 3B1 states of methylene (CH2) and the location of the conical intersection along the 1 3A2−2 3B1 potential-energy surfaces. Because the location of the intersection in methylene can be determined from its point-group symmetry,1 in this paper we do not implement more advanced methods for locating conical intersections based on the derivative coupling or property matrix.

Because the 2-RDM in the ACSE can be initialized from Hartree–Fock theory or a correlated method such as multi-configuration self-consistent field (MCSCF),29 it can capture both single- and multireference correlation effects.22,25 For methylene the ACSE yields energies that significantly improve upon those from both MCSCF and multireference second-order perturbation theory (MRMP2); furthermore, the 2-RDMs within the ACSE remain nearly N-representable throughout its solution. Calculations in augmented double-zeta and triple-zeta basis sets show that the location of the conical intersection is sensitive to the use of augmented (or diffuse) functions.

The rest of this paper is organized as follows. In Sec. II, we discuss the ACSE and its recent extensions to treating arbitrary-spin and excited states. In Sec. III, we present the data from the potential-energy surface scans conducted by various correlated methods including the ACSE and compare the accuracy of our results with full configuration interaction (FCI) as the reference. In addition, we provide ACSE results from a larger polarized valance triple-zeta basis set in which the FCI cannot be computed.

II. THEORY

In Sec. II A we briefly review key features of the ACSE method including the ACSE’s definition and the three-electron RDM’s (3-RDM’s) cumulant expansion. In Sec. II B
we discuss the open-shell extension of the ACSE, recently developed by Rothman et al., in which open-shell systems are coupled to hydrogen atoms to form singlet supersystems. Finally, in Sec. II C we give the differential equations with which, as demonstrated in Ref. 24, the ACSE can be solved for excited states.

A. The ACSE

The \( p \)-RDM can be expressed in second quantization as

\[
\rho D^{ij}_{kl} = \frac{1}{p!}\bra{\Psi} \hat{a}^\dagger_i \hat{a}^\dagger_j \hat{a}_k \hat{a}_l \ket{\Psi},
\]

(1)

where \( \hat{a}^\dagger_i \) (\( \hat{a}_i \)) is a fermionic creation (annihilation) operator that creates (destroys) an electron in spin orbital \( i \). Formally, \( p \)-RDMs arise from integration (or, in a tensor product space, contraction) over electrons \( p+1 \) through \( N \) of the \( N \)-electron density matrix \( ^N \! D = \Psi \Psi^\dagger \). Using the definition of the 2-RDM in Eq. (1), we can project the \( N \)-electron Schrödinger equation onto all two-electron transitions from the wave function to obtain the CSE30–33

\[
\bra{\Psi} \{ \hat{a}^\dagger_i \hat{a}^\dagger_j \hat{a}_k \hat{a}_l \} \ket{\Psi} = 2E \, 2D^{ij}_{kl},
\]

(2)

If the CSE is separated into Hermitian and anti-Hermitian components, both parts must vanish individually for Eq. (2) to be satisfied. The anti-Hermitian portion of the CSE (ACSE) can be expressed as

\[
\bra{\Psi} [\{ \hat{a}^\dagger_i \hat{a}^\dagger_j \hat{a}_k \hat{a}_l \}, \hat{H}] \ket{\Psi} = 0,
\]

(3)

where the square brackets indicate a commutator. The CSE was derived by Cohen and Frishberg34 and Nakatsuji35 in 1976, and the ACSE was derived from the CSE by Harriman36 in 1979; later in 1979 the ACSE was obtained by Kutzelnigg37,38 who called it the generalized Brillouin condition. The ACSE enforces the set of hypervirial relations for all one- and two-body operators, which were developed by Hirshfelder.39

Because the Hamiltonian contains pairwise electronic interactions

\[
\hat{H} = \sum_{p,s} K^p_{s} \hat{a}^\dagger_p \hat{a}_s + \sum_{p,q,s,t} \! V^p_{q} \! \hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_t,
\]

(4)

where \( K^p_{s} \) represents the kinetic and nuclear attraction energies of a single electron and \( \! V^p_{q} \! \) is an electron-electron repulsion integral in physicist’s notation;\( ^N \! D \) the ACSE depends on only the 2- and 3-RDMs. To eliminate the 3-RDM from the ACSE approximately, we can reconstruct the 3-RDM from the 2-RDM according to its cumulant expansion41–46

\[
\rho D^{ij}_{kl} = D^I_{ij} \wedge D^I_{kl} \wedge D^R_{kl} + 3(\rho D^{ij}_{kl} - D^I_{ij} \wedge D^I_{kl} \wedge D^R_{kl}),
\]

(5)

where \( \wedge \) denotes the antisymmetric Grassmann (or wedge) product. The missing term in the reconstruction, known as the connected (or cumulant) part \( ^3 \Delta \) of the 3-RDM, contains information not expressible as wedge products of the one-electron and 2-RDMs.41–46 Although the connected 3-RDM can be approximated in terms of the 2-RDM, it is neglected in the multireference formulation of the ACSE in Ref. 22.

B. Solving the ACSE for open-shell systems

Because the ACSE with an initial MCSCF 2-RDM can treat strong multireference correlation effects,\( ^{22–24} \) ground-state energies and 2-RDMs of open-shell species can be obtained by the following prescription:\( ^{25} \)

1. spin-couple hydrogen atom(s) to an open-shell wave function to create a singlet;
2. contract the resulting wave function to a 2-RDM and use it to seed the ACSE;
3. solve for the ground-state 2-RDM and energy of the composite system using the ACSE; and
4. extract the open-shell system’s 2-RDM and energy from the composite 2-RDM.

Consider an \( N \)-electron, high-spin triplet wave function \( \Phi(N) \) represented in a basis of \( r \) spatial orbitals \( \{ \phi_i \} \). The spin properties of the high-spin triplet \( \Phi(N) \) are

\[
\langle \Phi(N) | \hat{S}_z^2 | \Phi(N) \rangle = S(S + 1) = 2,
\]

(6)

\[
\langle \Phi(N) | \hat{S}_z | \Phi(N) \rangle = 1,
\]

(7)

where \( \hat{S} \) is the three-component quantum-mechanical spin operator. To the basis of \( r \) orbitals, we append two hydrogen 1s orbitals \( \sigma_1 \) and \( \sigma_2 \) at “infinite separation” from each other and the \( N \)-electron molecule, meaning that the overlap of \( \sigma_1 \) and \( \sigma_2 \) is zero and that the overlap of \( \sigma_j \) with any of the other \( r \) basis functions is also identically zero, \( \langle \phi_i | \sigma_j \rangle = 0 \) for all \( i \) and \( j \). Furthermore, each hydrogen orbital is given an electron for a total of \( N+2 \) electrons in the molecule-plus-hydrogens supersystem.

Spin-coupling the hydrogen orbitals to \( \Phi(N) \) requires two steps. First, the hydrogen orbitals are coupled to obtain high- and low-spin triplet species

\[
\Sigma^{1:1} = \sigma_{1,a} \sigma_{2,a},
\]

(8)

\[
\Sigma^{1:0} = \frac{1}{\sqrt{2}}(\sigma_{1,a} \sigma_{2,b} + \sigma_{1,b} \sigma_{2,a}),
\]

(9)

\[
\Sigma^{1:-1} = \sigma_{1,b} \sigma_{2,b},
\]

(10)

where the subscripts again indicate the individual spins of the two hydrogenic orbitals. The superscripts on the left-hand side of these equations indicate the \( S \) and \( M_z \) eigenvalues, respectively, of the coupled wave functions. With Eqs. (8)–(10) in mind, a singlet supersystem can be formed as

\[
\Phi(N + 2) = \frac{1}{\sqrt{3}}(\Phi(N)^{1:1} \wedge \Sigma^{1:-1} - \Phi(N)^{1:0} \wedge \Sigma^{1:0} + \Phi(N)^{1:-1} \wedge \Sigma^{1:1}).
\]

(11)

Equation (11) requires three spin states of \( \Phi(N) \). The high-spin wave functions \( [\Phi(N)^{1:1} \text{ and } \Phi(N)^{1:-1}] \) are simply the target open-shell system and its spin inverse, obtained by interchanging \( \alpha \) and \( \beta \). The low-spin wave function may be
obtained by operating on $\Phi(N)^{1:1}$ with the lowering operator $\tilde{S}$. 

Once a singlet wave function has been constructed, contraction to the 2-RDM is trivial. The ACSE solution procedure can then be performed as described in earlier work.\textsuperscript{20–23,26} However, for the spin-coupling procedure to be meaningful, the energy of the added hydrogenic orbitals $\sigma_i$ and $\sigma_j$ must be additively separable from the open-shell target system’s energy both before and after application of the ACSE. We quantify this statement as

$$E_{N+2} = E_{\sigma_i} + E_{\sigma_j} + E_N,$$  \hspace{1cm} (12)

where the left-hand side represents the energy of the composite supersystem and the right-hand side is the energy of the open-shell species plus the energies of the hydrogenic orbitals. This energy decomposition is valid because the elements of the Hamiltonian that connect the open-shell molecule with the hydrogen atoms vanish. Furthermore, as shown in Ref. 25, the 2-RDM corresponding to the open-shell target system can be proven to be a sub-block of the composite 2-RDM.

C. Solving the ACSE for ground and excited states

Consider a sequence of infinitesimal two-body unitary transformations of an initial wave function $\Psi(\lambda)$,

$$|\Psi(\lambda + \epsilon)\rangle = e^{\epsilon \tilde{S}(\lambda)}|\Psi(\lambda)\rangle,$$  \hspace{1cm} (13)

where the transformations are ordered by a continuous time-like variable $\lambda$. For the transformation to be unitary the two-body operator $\tilde{S}$, defined by

$$\tilde{S}(\lambda) = \sum_{p,q,s,t} S_{p,q,s,t}(\lambda) 2^{\Gamma_{p,q,s,t}},$$  \hspace{1cm} (14)

with

$$2^{\Gamma_{i,j,k,l}} = a_i^* a_j^* a_k^* a_l,$$  \hspace{1cm} (15)

must be anti-Hermitian, $\tilde{S}^\dagger = -\tilde{S}$.

In the $\epsilon \rightarrow \infty$ limit, as shown in Refs. 20–22, the changes in the energy and its 2-RDM with $\lambda$ are governed by the following differential equations:

$$\frac{dE}{d\lambda} = \langle \Psi(\lambda)|[\hat{H},\tilde{S}(\lambda)]|\Psi(\lambda)\rangle,$$  \hspace{1cm} (16)

and

$$\frac{d^2D_{i,j,k,l}}{d\lambda^2} = \langle \Psi(\lambda)|[2^{\Gamma_{i,j,k,l}},\tilde{S}(\lambda)]|\Psi(\lambda)\rangle.$$  \hspace{1cm} (17)

To minimize the energy along $\lambda$, we select the following elements of the two-particle matrix $2^{\Gamma_{p,q,s,t}(\lambda)}$, which minimize $dE/d\lambda$ along its gradient with respect to these elements:\textsuperscript{21}$

$$2^{\Gamma_{p,q,s,t}(\lambda)} = \langle \Psi(\lambda)|[2^{\Gamma_{p,q,s,t}},\hat{H}]|\Psi(\lambda)\rangle.$$  \hspace{1cm} (18)

Importantly, the left side of Eq. (18) is simply the residual of the ACSE. If the residual in the ACSE vanishes, the unitary transformations become the identity operator, and the energy and 2-RDM cease to change with $\lambda$. Using the cumulant reconstruction of the 3-RDM in Eq. (5) permits us to express these equations approximately in terms of the 2-RDM. Hence, Eqs. (16)–(18) collectively provide a system of differential equations\textsuperscript{20–22} for evolving an initial 2-RDM to a final 2-RDM that solves the ACSE for stationary states. In practice, the equations are evolved in $\lambda$ until either (i) the energy or (ii) the least-squares norm of the ACSE increases.

As demonstrated in the recent extension of the ACSE to excited states,\textsuperscript{24} even though the unitary rotations are selected in Eq. (18) to minimize the energy, the system of differential equations in Eqs. (16)–(18) is capable of producing energy and 2-RDM solutions of the ACSE for both ground and excited states. Because excited states correspond to local energy minima of the ACSE and the gradient in Eq. (18) leads to a local rather than global energy minimum, an excited-state solution can be readily obtained from a good guess for the initial 2-RDM. A guess will be good when it is closer to the minimum of the desired solution of the ACSE than to any other minimum. Such 2-RDM guesses can be generated from MCSCF calculations. The initial MCSCF 2-RDM directs the optimization of the ACSE to a desired excited state because it contains important multireference correlation effects that identify the state.

III. APPLICATIONS

After discussing some additional computational details, we apply the ACSE to computing the potential-energy curves of the $1^3B_1$, $1^3A_2$, and $2^3B_1$ states of methylene.

A. Computational details

For the ground and excited triplet states of methylene, we seed the solution to the differential equations in Eqs. (16)–(18) with 2-RDMs from a specific form of the MCSCF technique known as the complete-active-space SCF (CASSCF) method.\textsuperscript{19,48} The computation of the CASSCF wave function and 2-RDM is completed using the following steps: (i) Calculation of initial molecular orbitals using the high-spin restricted-open-shell Hartree–Fock method, (ii) division of CASSCF orbitals into four classes: Frozen core orbitals that are always occupied and remain unchanged throughout the calculation, core orbitals that are completely occupied, active orbitals that are partially occupied, and virtual orbitals that are completely unoccupied, (iii) diagonalization of the many-electron Hamiltonian in the active space, (iv) rotation of all unfrozen orbitals by unitary transformations to lower the energy, and (v) repetition of steps (iii) and (iv) until the energy converges. With this prescription the CASSCF calculation produces a wave function in which the active orbitals are treated by a CI calculation, and the inactive orbitals are treated by a Hartree–Fock calculation.

Another important computational detail of the ACSE is that we filter the two-body anti-Hermitian operator $\tilde{S}(\lambda)$ governing the unitary transformations to exclude transitions that involve (i) active orbitals only or (ii) more than two virtual orbitals. As previously discussed,\textsuperscript{22} the first exclusion prevents multireference effects in the 2-RDM from adversely affecting the accuracy of the cumulant 3-RDM reconstruction in the ACSE. This is a reasonable approximation be-
cause after the active space is optimized in the CASSCF calculation, two-body rotations of the active orbitals account for a secondary correlation effect that is much smaller in magnitude than the correlation of the inactive spaces. The second exclusion eliminates terms that are computationally expensive yet essentially unimportant for the accuracy of the final energies and 2-RDMs. After this second restriction the ACSE scales in floating-point operations as \( \text{RCI} \) where \( r_c, r_a, \) and \( r_v \) are the numbers of core, active, and virtual orbitals, respectively. In contrast, both MRMP2 and multireference CI (MRCI) with single and double excitations have an exponential dependence on the size of the active space.

### B. Results

#### 1. Energies near the conical intersection in the aug-cc-pVDZ basis set

The ACSE method was applied to compute the lowest three triplet states of methylene, \( 1\B_1, 1\A_2, \) and \( 2\B_1, \) respectively. We employed the augmented correlation-consistent polarized valence double-zeta (aug-cc-pVDZ) basis set.\(^{49}\) The solution of the ACSE from seed MCSCF 2-RDMs generally required between 80 and 100 iteration steps in \( \lambda \). To converge the \( 2\B_1 \) state with MCSCF, we utilized a small amount of state-averaging with a weight of \([0.08,0.92,0.0]\), while the other two states were optimized without state-averaging. The experimental geometry was parameterized using a Jacobi coordinate scheme with the distance between the two hydrogen atoms fixed at \( R_{HH} = 2.011 \text{ Å}. \)\(^{17}\) Jacobi coordinates, shown pictorially in Fig. 1, are usually denoted by \( [R, r, \gamma] \), where \( r = R_{HH} \) while \( R \) and \( \gamma \) are the polar coordinates for the line connecting the carbon atom to the center of mass of the two hydrogen atoms.\(^{1}\) To maintain \( C_{2v} \) point-group symmetry, we moved the carbon atom orthogonally to the hydrogen-hydrogen bond \( (\gamma = 90^\circ) \) from the hydrogen-hydrogen center of mass in finite intervals of 0.1 Å. The energies from the ACSE method are compared with those from the MCSCF method,\(^{29}\) MRMP2,\(^{50}\) and FCI. The MCSCF, MRMP2, and FCI calculations were performed with the GAMESS electronic structure package.\(^{51}\)

![Fig. 1. Schematic representation of the 1A\(^\pi\) state of methylene in Jacobi coordinates.](image)

The principal electron configurations of the three methylene triplets at [0.40,2.011,90], the point closest to the conical intersection, are

\[
\text{(1) } 1\B_1 \left[ 1a_1^2 1b_1^2 3a_1 1b_1 \right], \\
\text{(2) } 1\A_2 \left[ 1a_1^2 1b_1^2 3a_1^2 1b_1 \right], \text{ and} \\
\text{(3) } 2\B_1 \left[ 1a_1^2 2a_1^2 1b_1^2 4a_1 1b_1 \right].
\]

The molecular orbitals are labeled with respect to the irreducible representations of the \( C_{2v} \) point group. Even though the geometry of the conical intersection differs from that of the equilibrium structure, these configurations agree with those provided by Yarkony for the equilibrium structure of methylene.\(^{16}\)

The differences between the potential-energy surfaces...
from MCSCF, MRMP2, and ACSE and those from FCI are displayed in Fig. 2 and Table I. The MCSCF, MRMP2, and ACSE methods have maximum energy deviations of 91.01, 12.99, and 1.74 mH for the 1 3B1 state, 118.97, 15.02, and 2.22 mH for the 1 3A2 state, and 96.51, 12.74, and 4.94 mH for the 2 3B1 state. Hence, the ACSE significantly improves upon the NPEs from MCSCF; while MRMP2 yields the lowest NPE for the 2 3B1 state, the ACSE significantly improve upon the NPEs from MCSCF; while ACSE yields the lowest NPE for the 1 3A2 state. Although the MRCI method was not applied here, it has recently been shown to yield energies that are comparable to those from the ACSE for small molecules such as hydrogen fluoride but higher than those from the ACSE for larger molecules. Because the computational cost of MRCI depends exponentially on the number of active orbitals but is generally greater than that of the ACSE.

Using the ACSE, we found the conical intersection between states 1 3A2 and 2 3B1 at approximately [0.41, 0.2, 0.011, 0.90], which is in good agreement with the other methods as well as the data from Yarkony ([0.42, 0.2, 0.011, 0.90]). For each state the accuracy in the energies from the ACSE is similar both near and far from the conical intersection. In the case of methylene the conical intersection requires the two states to be members of different irreducible representations. Therefore, if the C2v symmetry is broken by perturbing the γ parameter away from 90°, the conical intersection will become an avoided crossing. To observe the avoided crossing, we broke the C2v symmetry by changing the γ parameter from 90° to 80°. The seed 2-RDMs for all three 3A" states were obtained from an MCSCF calculation with C2v symmetry. The resulting ACSE plot in this case, displayed in Fig. 3, is indeed very similar energetically to the plot in C2v symmetry, except that the conical intersection has been supplanted by an avoided crossing. The avoided crossing shows that even when states have the same symmetry (3A" in this case), the ACSE can produce an accurate description of the energy levels both near and far from their degeneracy. The ACSE energies of states 2 and 3 exhibit maximum errors relative to FCI of 2.7 and 5.8 mH, respectively; furthermore, the NPEs of states 2 and 3 are 3.5 and 3.8 mH, respectively.

The triplet ground- and excited-state 2-RDMs produced

![Graph](image_url)
by the ACSE maintain the $N$-representability of the 2-RDM within the accuracy of the 3-RDM reconstruction. A significant set of necessary $N$-representability constraints, known as 2-positivity conditions, requires keeping the eigenvalues of three different forms of the 2-RDM, the $3D$, $3Q$, and $3G$ matrices, nonnegative. These three sets of eigenvalues correspond to probability distributions for two particles, two holes, as well as one particle and one hole, respectively. Table II provides the lowest eigenvalues of these matrices for the first three triplets of methylene at the conical intersection, normalized to $N(N−1)$, $(r−N)(r−N−1)$, and $N(r−N+1)$, respectively, where $r$ is the rank of the spin-orbital basis set. The most negative eigenvalues are 2.5–4 orders of magnitude smaller than the largest positive eigenvalues, which are of the order of unity, save for the largest eigenvalue of $3G$ that is on the order of $N$.

### 2. Energies near the conical intersection in the cc-pVTZ basis set

In this section we report the results from applying the ACSE to the triplet states of methylene in the correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis set. As a result of the larger basis-set size, we were no longer able to compute the FCI energies due to memory constraints. Therefore, the ACSE energies were compared to those from MCSCF (Ref. 29) and MRMP2, which were performed with GAMESS. The potential-energy curves from the MCSCF, MRMP2, and ACSE methods are compared in Fig. 4 and Table III. The ACSE potential-energy curves are the lowest in energy followed by the MRMP2 and MCSCF curves, which is consistent with the results from the aug-cc-pVDZ basis set. The average differences between the correlation energies of the MRMP2 and the ACSE for the $1^3B_1$, $1^3A_2$, and $2^3B_1$ states are 9.20, 9.96, and 8.27, respectively.

In the cc-pVTZ basis set the conical intersection is at approximately [0.33, 0.011, 0.90], which differs from the geometry [0.41, 0.011, 0.90] in the aug-cc-pVDZ basis set. Performing a calculation of the conical intersection with MRMP2 in the aug-cc-pVTZ (Ref. 49) yielded a geometry of [0.41, 0.011, 0.90] that is in agreement with the geometries from the aug-cc-pVDZ calculations. Therefore, even though the cc-pVTZ basis set is technically larger than the aug-cc-pVDZ basis set, the augmented functions that are present only in the aug-cc-pVDZ basis set perform a critical role in stabilizing the carbon atom at a longer distance $R$ from the center of mass of the hydrogens.

### IV. DISCUSSION AND CONCLUSIONS

The conical intersection between methylene’s excited triplet states $1^3A_2$ and $2^3B_1$ has been studied by computing 2-RDMs from the ACSE without constructing many-electron wave functions. The calculations combine recent extensions of the ACSE to excited states and arbitrary-spin states. We computed the potential-energy curves of the $1^3B_1$, $1^3A_2$, and $2^3B_1$ triplet states of methylene including the location of the $1^3A_2−2^3B_1$ conical intersection. The location of the intersection computed by the ACSE in the aug-cc-pVDZ basis set corroborates Yarkony’s results with a high degree of accuracy.

### TABLE III. The energies of the $1^3B_1$, $1^3A_2$, and $2^3B_1$ states of methylene from MRMP2 and ACSE are reported relative to the energies from MCSCF.

<table>
<thead>
<tr>
<th>State</th>
<th>$R$ (Å)</th>
<th>MCSCF energy (H)</th>
<th>MRMP2</th>
<th>ACSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^3B_1$</td>
<td>0.0</td>
<td>−38.9517</td>
<td>−114.40</td>
<td>−122.30</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>−38.9601</td>
<td>−112.43</td>
<td>−121.14</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>−38.9707</td>
<td>−108.68</td>
<td>−117.82</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>−38.9625</td>
<td>−103.41</td>
<td>−113.31</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>−38.9300</td>
<td>−98.41</td>
<td>−108.38</td>
</tr>
<tr>
<td>$1^3A_2$</td>
<td>0.0</td>
<td>−38.5873</td>
<td>−141.68</td>
<td>−155.72</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>−38.6263</td>
<td>−126.29</td>
<td>−136.19</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>−38.6829</td>
<td>−122.55</td>
<td>−132.47</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>−38.7371</td>
<td>−117.98</td>
<td>−128.06</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>−38.7707</td>
<td>−115.34</td>
<td>−123.29</td>
</tr>
<tr>
<td>$2^3B_1$</td>
<td>0.0</td>
<td>−38.8084</td>
<td>−121.22</td>
<td>−131.94</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>−38.6779</td>
<td>−118.19</td>
<td>−129.02</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>−38.6665</td>
<td>−114.71</td>
<td>−124.40</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>−38.6439</td>
<td>−112.51</td>
<td>−120.13</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>−38.6186</td>
<td>−118.43</td>
<td>−118.09</td>
</tr>
</tbody>
</table>
In accordance with previous works, the ACSE improves the accuracy of MCSCF by two orders of magnitude and MRMP2 by one order of magnitude. The average differences in the MCSCF, MRMP2, and ACSE energies from FCI are 93.89, 12.27, and 1.51 mH, respectively. Similar accuracy was obtained at the conical intersection. Furthermore, the ACSE produced 2-RDMs that are almost N-representable, which is evident from the slight deviations from the well-known 2-positivity conditions.

Both single- and multireference correlations can be accurately captured with the ACSE, which is especially important for excited, arbitrary-spin states where multiple determinants can contribute substantially to the wave function at zeroth order. In the multireference formulation of the ACSE, the ACSE is seeded with an initial MCSCF zeroth order. In the multireference formulation of the ACSE, the ACSE improves the accuracy was obtained at the conical intersection. Furthermore, 93.89, 12.27, and 1.51 mH, respectively. Similar accuracies in the MCSCF, MRMP2, and ACSE energies from FCI

ACKNOWLEDGMENTS

J.W.S. expresses his appreciation to James and Irene Snyder for their support and encouragement. D.A.M gratefully acknowledges support from the National Science Foundation, the David and Lucile Packard Foundation, the Henry-Camille Dreyfus Foundation, and Microsoft Corporation.

13 M. Desoutter-Lecomte, C. Galley, J. C. Lorquet, and M. V. Pires, J.