Energy Barriers in the Conversion of Bicyclobutane to *gauche*-1,3-Butadiene from the Anti-Hermitian Contracted Schrödinger Equation

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In 1959 Charles Coulson popularized the idea of computing a molecule's ground-state energy as a functional of the two-electron reduced density matrix (2-RDM) without the many-electron wave function. For 50 years, however, a practical, direct calculation of the 2-RDM was not achieved because the 2-RDM must be constrained by *N*-representability conditions to represent an *N*-electron system. Recently, two general approaches to the direct calculation of the 2-RDM have emerged including the solution of the anti-Hermitian contracted Schrödinger equation (ACSE) [Mazziotti, *Phys. Rev. Lett.*, **2006**, *97*, 143002]. In this article, after further extending the theoretical development of the ACSE method for multireference correlation, we apply the ACSE to studying an unresolved question regarding the opening of bicyclobutane to *gauche*-1,3-butadiene by conrotatory and disrotatory pathways. Previous theoretical values for the disrotatory energy barrier reveal a disagreement between correlation methods on the order of 10 kcal/mol. By capturing significantly more correlation energy than traditional multireference methods, the ACSE provides new insight into this discrepancy. The ACSE energy for the conrotatory energy barrier agrees with the 40.6 ± 2.5 kcal/mol experimental value.

I. Introduction

Within organic chemistry, electrocyclic reactions, which are an important class of pericyclic reactions, involve the conversion of a conjugated molecule to a cyclic (ringlike) structure.[1] A classic example of electrocyclic reactions is the formation of cyclobutene from *cis*-1,3-butadiene. Two possible pathways arise from whether the ring closing of the two end carbons of *cis*-1,3-butadiene occurs by rotation in the same direction, known as the *conrotatory* pathway, or by rotation in opposite directions, known as the *disrotatory* pathway. Qualitative rules developed by Woodward and Hoffmann[2] recognize that the energetically favorable pathway will depend on the relative quantum phases of the p_z orbitals on the end carbons. Because forming the bond with the orbital lobes in phase stabilizes the transition state, if the two p_z orbitals have the same phase, the disrotatory pathway will be favored, while if the two p_z orbitals have opposite phases, the conrotatory pathway will be favored. Woodward and Hoffmann summarized these ideas in their well-known rule for thermally activated reactions: for a conjugated chain with an even number of carbon atoms the reaction will occur by the conrotatory pathway while for a conjugated chain with an odd number of carbon atoms the reaction will occur by the disrotatory pathway.[1−3]

In this paper we study the electrocyclic conversion of bicyclo[1.1.0]butane to *gauche*-1,3-butadiene via Woodward−Hoffmann pathways by solving the anti-Hermitian contracted Schrödinger equation (ACSE).[4−11] This electrocyclic reaction has been studied both experimentally[12−16] and theoretically.[17−20] The Woodward−Hoffmann rules qualitatively predict that the conrotatory pathway is more favorable energetically than the disrotatory pathway. Computationally, solution of the ACSE in the 6-311G** basis set indicates that the conrotatory transition state is 41.2 kcal/mol higher in energy than bicyclobutane whereas the disrotatory transition state is 55.7 kcal/mol higher in energy than bicyclobutane. The conrotatory barrier from the ACSE closely agrees with the 40.6 ± 2.5 kcal/mol barrier obtained from experiment.[12] Because the disrotatory pathway involves two p_z lobes with different phases (+ and −), the disrotatory transition state is a biradical with two molecular orbitals ([+ and −] or [− and +]) that are approximately half-filled. Consequently, the underlying wave function has more than one important Slater determinant at zeroth order, and we say that the wave function is *multireferenced*. Furthermore, because the disrotatory pathway is not preferred energetically to the conrotatory pathway, the energy of the disrotatory transition state is difficult to measure experimentally. While previous studies have examined the disrotatory pathway of this reaction with the multireference self-consistent-field (MCSCF) method,[18] the complete active-space second-order perturbation theory (CASPT2) method,[18] and, more recently, renormalized coupled cluster methods,[19,20] the energy barriers predicted by these methods are in disagreement. The renormalized coupled cluster methods predict an energy barrier for the disrotatory pathway that is significantly higher than the barrier determined earlier from CASPT2. The ACSE energy of the disrotatory transition state closely agrees with the 56.4 kcal/mol barrier from the CASPT2 calculations. After formation, the *gauche*-1,3-butadiene undergoes an additional rearrangement to a lower-in-energy *trans*-1,3-butadiene, but since this second reaction is well understood and not multireferenced, it will not be examined further.

In 1959, several years before the Hohenberg−Kohn theorem[21] provided the foundation for the development of density functional theory,[22] Charles Coulson popularized the challenge of computing the ground-state energy as a functional of the two-electron reduced density matrix (2-RDM) without the many-electron wave function.[23] Unlike density functional theory, the energy functional of the 2-RDM is *known* and *linear* in the 2-RDM. However, a direct calculation of the 2-RDM cannot be performed without placing constraints on the 2-RDM, known as *N-representability conditions*,[24−26] to ensure that it corresponds to a realistic *N*-electron system. The search for *N*-

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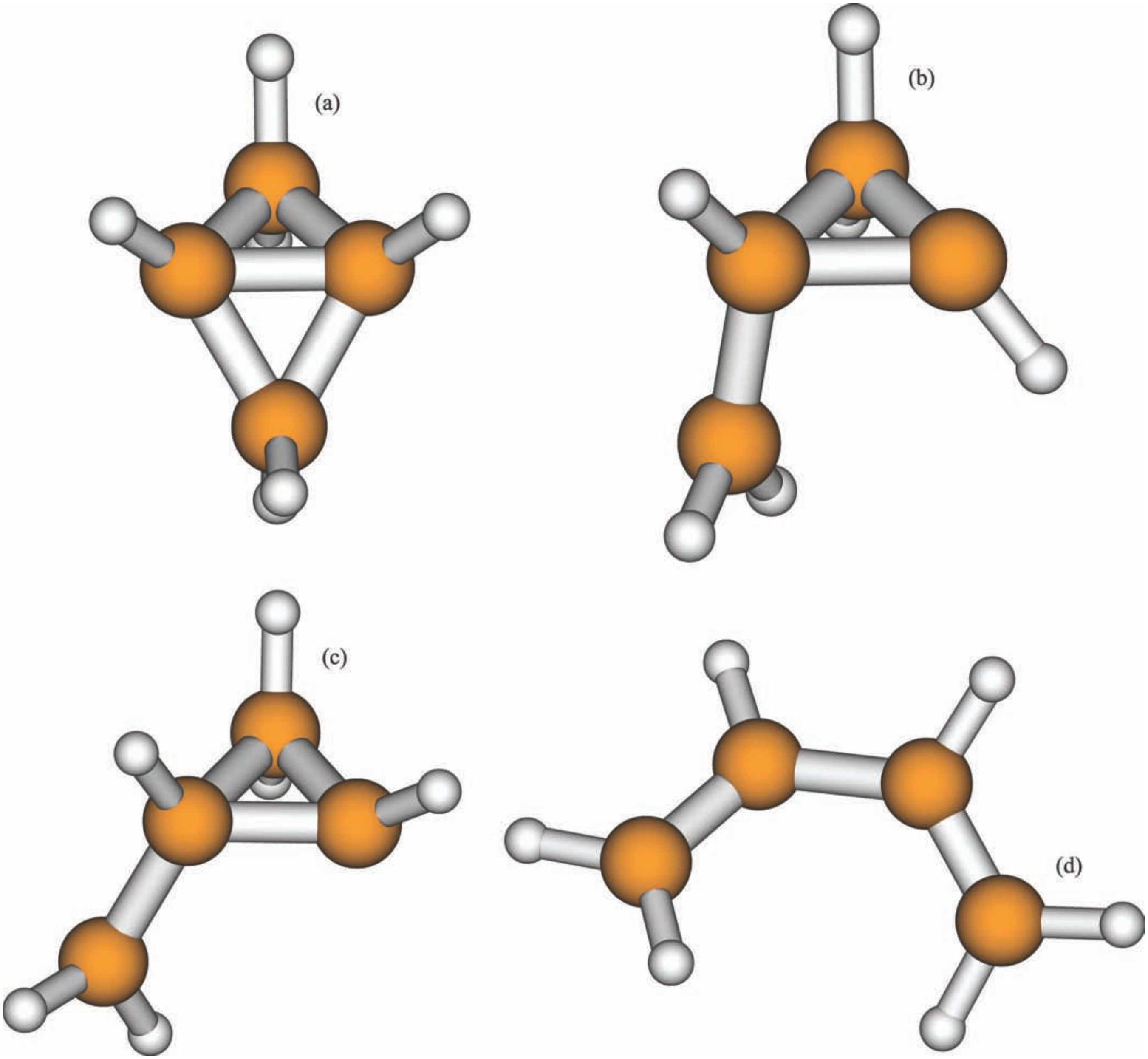

Figure 1. Ground-state molecular geometries, computed by MCSCF in the 6-311G** basis set, are given for (a) bicyclobutane (BIBUT), (b) the conrotatory transition state (TSC), (c) the disrotatory transition state (TSD), and (d) *gauche*-1,3-butadiene (GBUT). Point-group symmetries of C_{2v} and C_2 are employed for bicyclobutane and *gauche*-1,3-butadiene, respectively. Specific bond lengths and angles from an MCSCF calculation in the 6-31G basis set are reported in ref 18. The geometries do not substantially change from the 6-31G basis set to the 6-311G** basis set.

representability constraints *without* the *N*-electron wave function became known as the *N*-representability problem.[27,28] For 50 years this problem prevented the development of practical 2-RDM methods. If the wave function is known, the 2-RDM can be obtained by integrating over the coordinates for all electrons save two:

$$^2D^{1,2}_{\bar{1},\bar{2}} = \int \Psi(1, 2, \ldots, N)\Psi(\bar{1}, \bar{2}, \ldots, N)^* \, d3 \ldots dN \quad (1)$$

where each number represents three spatial and one spin coordinate for an electron.

Recently, based on theoretical and computational advances, two general types of 2-RDM methods have emerged: (i) the variational calculation of the 2-RDM subject to approximate *N*-representability conditions[29−32] and (ii) the nonvariational calculation of the 2-RDM from the solution of the contracted Schrödinger equation[33−38] or, more recently, the *anti-Hermitian contracted Schrödinger equation* (ACSE).[4−11] Integration of the Schrödinger equation over all electrons save two produces the *contracted Schrödinger equation*,[33−36,39,40] which depends on only the 2-, 3-, and 4-RDMs. The ACSE, which depends on only the 2- and 3-RDMs, was first derived by Harriman in 1979 who obtained it by selecting the anti-Hermitian part of the contracted Schrödinger equation.[41] Later that year Kutzelnigg also obtained the ACSE, which he called the two-particle Brillouin condition.[42,43] As early as 1963 Percus presented a time-dependent version of the ACSE.[44] The ACSE can also be viewed as a special subset of the hypervirial relations, which were derived for wave functions by Hirschfelder in 1960.[45] Neither the contracted Schrödinger equation nor the ACSE, however, can be solved for the 2-RDM without additional *N*-representability conditions on the 3-RDM and/or 4-RDM.[41] In 1993 Colmenero, Perez del Valle, and Valdemoro suggested reconstructing the higher-particle RDMs as functionals of the 2-RDM.[46] Using 3-RDM reconstruction,[33−35,47−50] the author recently realized the first direct solution of the ACSE for the ground-state 2-RDM and its energy.[4−11]

Because the ACSE does not depend upon a single reference wave function, it can be initialized with a mean-field 2-RDM from a Hartree−Fock calculation or a correlated 2-RDM such as a 2-RDM from an MCSCF calculation. Using initial 2-RDMs from MCSCF calculations, we have recently extended the solution of the ACSE for the treatment of multireference correlation.[10] This multireference formulation of the ACSE has some connections to the work by Yanai and Chan[51] in which an operator form of the 3-RDM reconstruction[33−35,47−50] is applied within canonical diagonalization to compute multireference correlation energies. The method of Yanai and Chan, however, also differs from the ACSE method in that (i) it is limited to using an initial MCSCF 2-RDM even in the absence of multireference correlation and (ii) it does not produce a 2-RDM, which is important for computing properties and monitoring the *N*-representability of the solution. In this paper we increase the efficiency of the multireference ACSE formulation by further reducing the computational scaling in floating-point operations. Application of the ACSE is made to computing both the energies and the 2-RDMs of bicyclobutane, the conrotatory and disrotatory transition states, and the *gauche*-1,3-butadiene. Unlike traditional second-order multireference perturbation theory whose accuracy for single-reference correlation is less than coupled cluster methods with single and double excitations (CCSD), the ACSE yields energies and properties that lie between CCSD and coupled cluster with triples. Computational examples, furthermore, show that the ACSE treats single-reference and multireference correlation with similar accuracy. As a result of its balanced treatment of single-reference and multireference correlation effects, the ACSE method provides a useful approach to reevaluating the energy barriers for disrotatory pathway that were proposed in earlier studies. From the computed 2-RDMs we also extract the occupation numbers of the natural orbitals, which are particularly useful for identifying and analyzing multireference correlation effects.

II. Theory and Methods

A. Anti-Hermitian Contracted Schrödinger Equation. Integration (or contraction) of the *N*-electron Schrödinger equation onto the space of two electrons yields the contracted Schrödinger equation,[33−36,39,40] which depends on the 2-, 3-, and 4-RDMs. Selecting the *anti-Hermitian part* of the contracted Schrödinger equation produces the ACSE,[4−11,41] which only depends on the 2- and 3-RDMs. In a finite spin−orbital basis set the ACSE can be formally written as

$$\langle\Psi|[a_i^\dagger a_j^\dagger a_l a_k, \hat{H}]|\Psi\rangle = 0 \tag{2}$$

where $\hat{H}$ is the Hamiltonian, Ψ is the *N*-electron wave function, each index denotes a spin orbital which is a product of a spatial orbital and a spin function, and $a_i^\dagger$ and a_i are second-quantized operators that create and destroy an electron in the spin orbital i, respectively. The explicit expression of the ACSE in terms of the 2- and 3-RDMs is given in refs 5−7, 33, and 43.

Solution of the ACSE for the ground-state energy and 2-RDM cannot be achieved without additional information about the 3-RDM. Fortunately, the 3-RDM can be reconstructed approximately from the 2-RDM by its *cumulant expansion*[34,46−50]

$$^3D^{i,j,k}_{q,s,t} \approx {}^1D^i_q \wedge {}^1D^j_s \wedge {}^1D^k_t + 3\,{}^2\Delta^{i,j}_{q,s} \wedge {}^1D^k_t \tag{3}$$

where

$$^2\Delta^{i,j}_{k,l} = {}^2D^{i,j}_{k,l} - {}^1D^i_k \wedge {}^1D^j_l \tag{4}$$

and the operator $\wedge$ denotes the antisymmetric tensor product known as the Grassmann wedge product.[35] Substitution of the reconstructed 3-RDM into the ACSE produces an approximate ACSE that depends only upon the 2-RDM and yet includes all second-order and many higher-order correlation terms of many-body perturbation theory. A further correction to the 3-RDM in terms of the 2-RDM, which was developed by Nakatsuji and Yasuda,[34] Mazziotti,[52] as well as Valdemoro, Tel, and Perez-Romero,[8] is essential for highly accurate results in the single-reference formulation of the ACSE.[50] This correction is not needed in the multireference formulation of the ACSE[10] because of its correlated initial 2-RDM guess.

B. System of Differential Equations. Practical solution of the ACSE for the ground-state energy and 2-RDM can be achieved by solving a system of differential equations[4−10] that, implicitly through the 2-RDM, applies a sequence of differential unitary transformations to a reference wave function $\Psi(0)$ where the unitary transformations are ordered by a continuous timelike variable λ. Although the differential equations can be interpreted as minimizing the energy through the application of differential unitary transformations upon a reference wave function $\Psi(0)$, *the final equations with cumulant 3-RDM reconstruction only depend upon the 2-RDM* where the initial 2-RDM at $\lambda = 0$ arises from the integration (contraction) of the *N*-particle density matrix $\Psi(0)\Psi(0)^*$. Since neither the ACSE nor the reconstruction of the 3-RDM depends on a mean-field reference, the reference state $\Psi(0)$ for the differential equations can be selected to be the Hartree−Fock wave function or any correlated wave function such as the multiconfiguration self-consistent field (MCSCF) wave function.

The differential equations for solving the ACSE for the ground-state energy and 2-RDM are[4−10]

$$\frac{\mathrm{d}E}{\mathrm{d}\lambda} = \langle\Psi(\lambda)|[\hat{H}, \hat{S}(\lambda)]|\Psi(\lambda)\rangle \tag{5}$$

and

$$\frac{\mathrm{d}\,{}^2D^{i,j}_{k,l}}{\mathrm{d}\lambda} = \langle\Psi(\lambda)|[a_i^\dagger a_j^\dagger a_l a_k, \hat{S}(\lambda)]|\Psi(\lambda)\rangle \tag{6}$$

where the operator $\hat{S}(\lambda)$ depends on the two-electron reduced matrix ${}^2S^{i,j}_{k,l}(\lambda)$

$$\hat{S}(\lambda) = \sum_{i,j,k,l} {}^2S^{i,j}_{k,l}(\lambda) a_i^\dagger a_j^\dagger a_l a_k \tag{7}$$

which at each λ is chosen to minimize the energy along its gradient

$$^2S^{i,j}_{k,l}(\lambda) = \langle\Psi(\lambda)|[a_i^\dagger a_j^\dagger a_l a_k, \hat{H}]|\Psi(\lambda)\rangle \tag{8}$$

The right side of eq 8 is the residual of the ACSE and the right side of eq 6 is the residual of the ACSE with $\hat{H}$ in eq 2 replaced by the anti-Hermitian $\hat{S}(\lambda)$. Because the ACSE can be expressed in terms of only the 2- and 3-RDMs, by the cumulant reconstruction of the 3-RDM, eqs 5−8 can be evaluated at each λ from only a knowledge of the 2-RDM. These equations are integrated in λ to an accuracy of 10^{-7} by an extrapolated Euler method. While the energy and 2-RDM would be evolved in λ until the residual of the ACSE in eq 8 vanishes if the 3-RDM could be reconstructed exactly from the 2-RDM, in practice the equations are evolved to a critical value of λ at which either (i) the energy or (ii) the least-squares error of the ACSE increases.

C. Multireference Solution. The solution of the ACSE has recently been generalized to treat multireference correlation by

TABLE 1: Total Energies (H) and Relative Energies (kcal/mol) Are Reported for Bicyclobutane (BIBUT), the Conrotatory Transition State (TSC), the Disrotatory Transition State (TSD), and *gauche*-1,3-Butadiene (GBUT) in the 6-31G* Basis Set[a]

	total energies (H)[b]				relative energies (kcal/mol)				
molecule	MCSCF	MRPT2	CASPT2	ACSE	MCSCF	MRPT2	CASPT2	ACSE	EXPT
BIBUT	−154.8757	−155.2935	−155.3208	−155.3634	0.0	0.0	0.0	0.0	0.0
TSC	−154.8354	−155.2330	−155.2553	−155.2969	25.3	38.0	41.5	41.8	40.6
TSD	−154.8149	−155.2074	−155.2314	−155.2735	38.2	54.0	56.3	56.4	
GBUT	−154.9600	−155.3358	−155.3579	−155.4020	−52.9	−26.6	−23.2	−24.2	

[a] Relative energies are defined with the energy of BIBUT as the reference. We compare the energies from the anti-Hermitian contracted Schrödinger equation (ACSE) with those from multiconfiguration self-consistent field (MCSCF), second-order multireference perturbation theory (MRPT2), second-order complete-active-space perturbation theory (CASPT2), and experimental measurement (EXPT). Molecular geometries are obtained from optimization in the 6-31G* basis set with the MCSCF method. The ACSE captures a significantly larger percentage of the correlation energy than either MRPT2 or CASPT2 while it yields reaction barriers (relative to BIBUT) that agree with those from CASPT2 and, where available, experiment. [b] The total energies include the vibrational zero-point energies for BIBUT, TSC, TSD, and GBUT, 0.0911, 0.0862, 0.0844, and 0.0885 H, respectively, computed from a harmonic analysis within the MCSCF method.

TABLE 2: Total Energies (H) and Relative Energies (kcal/mol) Are Reported for Bicyclobutane (BIBUT), the Conrotatory Transition State (TSC), the Disrotatory Transition State (TSD), and *gauche*-1,3-Butadiene (GBUT) in the 6-311G Basis Set[a]**

	total energies (H)[b]			relative energies (kcal/mol)			
molecule	MCSCF	MRPT2	ACSE	MCSCF	MRPT2	ACSE	EXPT
BIBUT	−154.9151	−155.3986	−155.5322	0.0	0.0	0.0	0.0
TSC	−154.8759	−155.3416	−155.4666	24.6	35.7	41.2	40.6
TSD	−154.8546	−155.3154	−155.4435	38.0	52.2	55.7	
GBUT	−155.0011	−155.4415	−155.5702	−54.0	−27.0	−23.8	

[a] Molecular geometries are obtained from optimization in the 6-311G** basis set with the MCSCF method. Increasing the basis set from 6-31G* to 6-311G** causes the total energies from the MCSCF, MRPT2, and ACSE methods to decrease by about 0.040, 0.105, and 0.170 H, respectively. In comparison to the change in the total energies, the relative energies remain essentially the same (they slightly decrease by a fraction of a kcal/mol) with the increase in basis-set size. [b] The total energies include the vibrational zero-point energies for BIBUT, TSC, TSD, and GBUT, 0.0898, 0.0850, 0.0830, and 0.0874 H, respectively, computed from a harmonic analysis within the MCSCF method.

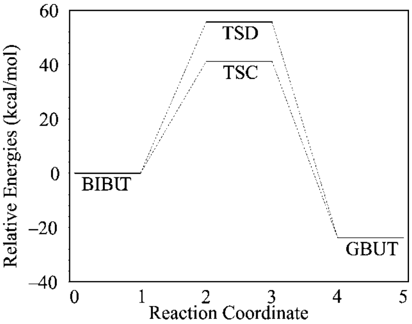

Figure 2. Ground-state energies from the solution of the ACSE in the 6-311G** basis set are shown for the conrotatory (TSC) and the disrotatory (TSD) transition states and *gauche*-1,3-butadiene (GBUT) relative to the ground-state energy of bicyclobutane (BIBUT). The ACSE predicts that the conrotatory and disrotatory transition states are 41.2 and 55.7 kcal/mol higher in energy than bicyclobutane. The energy of the conrotatory transition state agrees with the 40.6 ± 2.5 kcal/mol energy barrier from experiment.[12]

setting the initial 2-RDM in the differential equations of section 2.2 equal to the ground-state 2-RDM from a multiconfiguration self-consistent-field (MCSCF) calculation.[10] Critical correlation between the active space and the core and virtual spaces is incorporated into the MCSCF 2-RDM by the ACSE through the unitary transformations $\hat{S}(\lambda)$ in eqs 5 and 6. Selecting these unitary transformations is as critical to the multireference solution of the ACSE as choosing the initial 2-RDM from an MCSCF calculation. We set to zero the elements of ${}^2S^{i,j}_{k,l}(\lambda)$ in eq 8 with four active-orbital indices to prevent 3-RDM elements with significant reconstruction errors from appearing in the ACSE.[10] Eliminating these unitary transformations is not problematic because they arise as a secondary perturbation in response to the mixing of the active and the external (core plus virtual) spaces. In this paper, we also set to zero any element of the two-electron reduced matrix ${}^2S^{i,j}_{k,l}(\lambda)$ with more than two indices corresponding to virtual orbitals. This second exclusion, performed for computational efficiency, has a negligible effect on the accuracy of the method while reducing the computational scaling of the multireference ACSE from r^6 to $(r_c + r_a)^2 r_v^4$ floating-point operations, which can be significant since in general $r \gg r_c + r_a$. (The variables r_c, r_a, and r_v denote the number of core, active, and virtual orbitals, respectively, where their sum equals the total number (or rank) r of orbitals.)

III. Results

The electrocyclic reaction of bicyclobutane to form *gauche*-1,3-butadiene via Woodward−Hoffmann pathways is examined with the multireference solution of the ACSE. Energies of bicyclobutane, the conrotatory transition state, the disrotatory transition state, and *gauche*-1,3-butadiene are compared with those from the following methods: multireference self-consistent-field (MCSCF), second-order multireference perturbation theory (MRPT2),[53] second-order complete-active-space perturbation theory (CASPT2),[54] coupled cluster with single and double excitations (CCSD), coupled cluster with single and double excitations plus perturbative triple excitations (CCSD(T)), a completely renormalized coupled cluster method with perturbative triple excitations (CR-CC),[55] and experimental measurement (EXPT).[12] Results from two polarized basis sets, 6-31G* and 6-311G**,[56] are presented where core orbitals are fully occupied (or frozen). The ACSE calculations were performed with a code developed by the author while all other calculations, excluding the CASPT2 results that are from ref 18, were obtained from the package GAMESS (USA).[56]

In the MCSCF method orbitals are divided into three classes: (i) core orbitals that are fully occupied, (ii) active orbitals that are partially occupied (correlated), and (iii) virtual orbitals that are completely unoccupied. The division of the orbitals is performed self-consistently to lower the ground-state energy.

TABLE 3: Total Energies in Hartrees (H) and Relative Energies (kcal/mol) from Coupled-Cluster Methods Are Reported for Bicyclobutane (BIBUT), the Conrotatory Transition State (TSC), the Disrotatory Transition State (TSD), and *gauche*-1,3-Butadiene (GBUT) in the 6-311G Basis Set**[a]

	total energies (H)[b]			relative energies (kcal/mol)			
molecule	CCSD	CCSD(T)	CR-CC	CCSD	CCSD(T)	CC-CR	EXPT
BIBUT	−155.5198	−155.5461	−155.5462	0.0	0.0	0.0	0.0
TSC	−155.4461	−155.4811	−155.4803	46.3	40.8	41.3	40.6
TSD	−155.3966	−155.5167	−155.4449	77.3	18.4	63.6	
GBUT	−155.5582	−155.5853	−155.5852	−24.1	−24.6	−24.5	

[a] Molecular geometries are obtained from optimization in the 6-311G** basis set with the MCSCF method. Correlation techniques include coupled cluster with single-double excitations (CCSD), coupled cluster with single-double excitations plus perturbative triple excitations (CCSD(T)), and a completely renormalized coupled cluster method (CR-CC) with perturbative triples. For all molecules excluding TSD, the total CCSD energies are above those from the ACSE in Table 2 by about 16 mH while the total CCSD(T) and CR-CC energies are below those from the ACSE by about 16 mH. In contrast, the biradical molecule TSD is not well treated by the single-reference CCSD and CCSD(T) methods with energies too high and too low, respectively. Relative energies, except for TSD, are close to those predicted by the ACSE. [b] The total energies include the vibrational zero-point energies for BIBUT, TSC, TSD, and GBUT, 0.0898, 0.0850, 0.0830, and 0.0874 H, respectively, computed from a harmonic analysis within the MCSCF method.

TABLE 4: Lowest Eigenvalues of the ^2D, ^2Q, and ^2G Matrices from the ACSE Are Reported for Bicyclobutane (BIBUT), the Conrotatory Transition State (TSC), the Disrotatory Transition State (TSD), and *gauche*-1,3-Butadiene (GBUT) in the 6-31G* Basis Set[a]

	lowest eigenvalues		
molecule	^2D	^2Q	^2G
BIBUT	−5.2[−4]	−6.7[−5]	−5.1[−4]
TSC	−2.0[−3]	−8.2[−5]	−2.3[−3]
TSD	−2.4[−3]	−7.2[−5]	−1.3[−3]
GBUT	−5.9[−4]	−6.7[−5]	−5.5[−4]

[a] For each molecule the most negative eigenvalues are 3 to 4 orders of magnitude smaller in absolute value than the largest eigenvalues of order unity. The ^2D, ^2Q, and ^2G matrices are normalized, as in second quantization, to $N(N - 1)$, $(r - N)(r - N - 1)$, and $N(r - N + 1)$ where r is the rank of the one-electron basis set and N is the number of electrons.

All MCSCF calculations, including those used to seed the ACSE method, employed a (10,10)-active space,[18,19] which means 10 electrons in 10 active orbitals. As in previous studies of this reaction,[18−20] molecular geometries, obtained with the MCSCF method, were used with all other correlation methods. Geometries were separately optimized with MCSCF for the 6-31G* and 6-311G** basis sets. Figure 1 shows the geometries for the (a) reactant, the (b) conrotatory, and the (c) disrotatory transition states, and the (d) product in the 6-311G** basis set. All energies presented for each method include zero-point energy corrections from a normal-modes analysis at the MCSCF level of theory. Total energies are reported in hartrees (H) or millihartrees (mH) while relative energies are given in kilocalories per mole (kcal/mol) where 1 H = 627.5 kcal/mol.

Total energies (*H*) and relative energies (kcal/mol) are reported for bicyclobutane, the conrotatory transition state, the disrotatory transition state, and *gauche*-1,3-butadiene in 6-31G* (Table 1) and 6-311G** (Table 2) basis sets where relative energies are defined in reference to the energy of bicyclobutane. Like the Woodward−Hoffmann rules, the ACSE predicts that the biradical disrotatory transition state is significantly higher in energy than the conrotatory transition state. In the 6-311G** basis set the ACSE yields conrotatory and disrotatory transition states that are 41.2 and 55.7 kcal/mol higher in energy than bicyclobutane, respectively. Figure 2 displays these results schematically. The energies of the conrotatory and disrotatory transition states agree with the 41.5 and 56.4 kcal/mol barriers predicted by CASPT2 in the 6-31G* basis set and the 40.6 ± 2.5 kcal/mol conrotatory barrier determined by experiment. Because nature heavily favors the conrotatory pathway, the energy of the disrotatory transition state cannot be easily measured experimentally, which makes its theoretical prediction of even further importance. While the reaction barriers from MRPT2, CASPT2, and the ACSE are similar in Table 1 and the barriers from MRPT2 and the ACSE are similar in Table 2, in a given basis set the ACSE captures a significantly larger amount of the correlation energy than either MRPT2 or CASPT2. For example, in a 6-31G* basis set the total energies of bicyclobutane from the MRPT2, CASPT2, and ACSE methods differ from the CCSD(T) energy, which should be close to the energy from full configuration interaction in the absence of multireference correlation, by 0.079, 0.052, and 0.009 mH. Increasing the basis set from 6-31G* to 6-311G** causes the total energies from the MCSCF, MRPT2, and ACSE methods to change by about −0.040, −0.105, and −0.170 H, respectively, while relative energies change very little, decreasing by a fraction of a kcal/mol.

Recently, renormalized coupled-cluster calculations have suggested a higher barrier for the disrotatory pathway than that predicted previously by CASPT2. Table 3 gives the total and relative energies from three coupled cluster methods, CCSD, CCSD(T), and CR-CC, for bicyclobutane, the conrotatory transition state, the disrotatory transition state, and *gauche*-1,3-butadiene in the 6-311G** basis set. For all molecules excluding TSD, the total CCSD energies are above those from the ACSE in Table 2 by about 16 mH while the total CCSD(T) and CR-CC energies are below those from the ACSE by about 16 mH. Despite a computational cost like CCSD, the multireference ACSE yields energies between those from CCSD and CCSD(T) in the absence of significant multireference correlation. Relative energies, except for TSD, are close to those predicted by the ACSE. In contrast, the biradical disrotatory transition state, fraught with multireference correlation, is not well treated by the CCSD and CCSD(T) methods whose energies are too high and low, respectively. In fact, the CCSD(T) predicts a disrotatory pathway that is energetically more favorable than the conrotatory pathway by more than 20 kcal/mol. As discussed in ref 19, the completely renormalized coupled cluster method (CR-CC) improves significantly upon the energies of CCSD and CCSD(T), and in Table 3 it predicts a 63.6 kcal/mol barrier for the disrotatory pathway in the 6-311G** basis set, which is higher than that previously computed by CASPT2.[18] A similar barrier for the pathway was obtained in ref 19 even though a different polarized triple-ζ basis set was employed. Comparison of the CR-CC energies with those from the ACSE provides some

TABLE 5: Natural Occupation Numbers Are Reported for Bicyclobutane (BIBUT), the Conrotatory Transition State (TSC), the Disrotatory Transition State (TSD), and *gauche*-1,3-Butadiene (GBUT) in the 6-311G from the Multiconfiguration Self-Consistent Field (MCSCF) and the Anti-Hermitian Contracted Schrödinger Equation (ACSE) Methods**[a]

	occupation numbers of natural orbitals							
	BIBUT		TSC		TSD		GBUT	
orbital index	MCSCF	ACSE	MCSCF	ACSE	MCSCF	ACSE	MCSCF	ACSE
9	1.0000	0.9829	1.0000	0.9830	1.0000	0.9825	1.0000	0.9838
10	1.0000	0.9822	1.0000	0.9820	1.0000	0.9814	1.0000	0.9826
11	0.9966	0.9807	0.9916	0.9795	0.9915	0.9789	0.9918	0.9806
12	0.9881	0.9740	0.9893	0.9761	0.9894	0.9759	0.9905	0.9787
13	0.9874	0.9726	0.9844	0.9698	0.9844	0.9697	0.9887	0.9758
14	0.9845	0.9683	0.9834	0.9682	0.9837	0.9683	0.9662	0.9539
15	0.9836	0.9674	0.8779	0.8646	0.5533	0.5483	0.9543	0.9402
16	0.0237	0.0313	0.1239	0.1298	0.4473	0.4451	0.0480	0.0544
17	0.0124	0.0190	0.0188	0.0251	0.0191	0.0256	0.0316	0.0366
18	0.0115	0.0167	0.0113	0.0161	0.0118	0.0165	0.0113	0.0155
19	0.0096	0.0143	0.0102	0.0151	0.0105	0.0155	0.0096	0.0134
20	0.0026	0.0113	0.0094	0.0140	0.0091	0.0139	0.0079	0.0116
21	0.0000	0.0101	0.0000	0.0097	0.0000	0.0102	0.0000	0.0094
22	0.0000	0.0091	0.0000	0.0091	0.0000	0.0095	0.0000	0.0089

[a] The ACSE occupation numbers consistently manifest more correlation than those from MCSCF, which reflects that the ACSE includes electron correlation beyond the active space. While the occupation numbers for orbitals 15 and 16, which are the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals in a molecular orbital picture, are fairly close to 1 and 0 for BIBUT, TSC, and GBUT, they are nearly degenerate for the biradical TSD.

additional insight into the discrepancy between the CR-CC and the CASPT2/ACSE results. While the CR-CC total energies for bicyclobutane, the conrotatory transition state, and *gauche*-1,3-butadiene are consistently about 16 mH below the ACSE total energies, the CR-CC total energy for the disrotatory transition state is only 1 mH lower than the total energy from the ACSE. Although certainly not definitive, in the context of previous ACSE results showing consistent accuracy in the presence and absence of multireference correlation, this result suggests that the CR-CC method may be missing some multireference correlation that would lower the energy of the biradical disrotatory transition state by about 15 mH or 9.5 kcal/mol.

The multireference solution of the ACSE generates both energies and 2-RDMs. Previous work has shown that the 2-RDMs from the ACSE very nearly satisfy well-known *N*-representability conditions including an important set of conditions requiring three forms of the 2-RDM, the ^2D, ^2Q, and ^2G matrices, to be positive semidefinite. A matrix is *positive semidefinite* if and only if its eigenvalues are nonnegative. These matrices restrict the probability distributions for two particles, two holes, and one particle and one hole to be nonnegative. For each molecule in the bicyclobutane reaction the most negative eigenvalues of these three matrices, given in Table 4 for the 6-31G* basis set, are 3 to 4 orders of magnitude smaller in absolute value than the largest eigenvalues on the order of unity. The 1-RDM occupation numbers also lie between 0 and 1 in accordance with the *N*-representability conditions for the 1-RDM.[25] Furthermore, for each singlet molecule the expectation value of the total spin operator $\langle \hat{S}^2 \rangle$ yields zero within the 10^{-7} accuracy of the integrator.

Table 5 reports the occupation numbers of the natural orbitals for the four molecules in the 6-311G** basis set from the MCSCF and ACSE methods. Natural orbitals are defined as the eigenfunctions of the 1-RDM. (Since the two spin blocks of the 1-RDM are identical for a singlet system, we show the natural-orbital occupation numbers for just one of the blocks.) Because the determinant formed from the lowest *N* natural spin orbitals has the maximum overlap with the *N*-electron wave function, the natural occupation numbers provide important information for identifying and analyzing multireference correlation effects. For the molecules with a dominant single reference, bicyclobutane, the conrotatory transition state, and *gauche*-1,3-butadiene, the occupation numbers for orbitals 15 and 16, which are the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals in a molecular orbital picture, are fairly close to 1 and 0, but for the biradical disrotatory transition state they are nearly degenerate. This near degeneracy of the HOMO and LUMO occupation numbers is the signature within the 1-RDM of multireference correlation, and it implies that in the wave function there are at least two determinants (or references) with nearly degenerate contributions at zeroth order of perturbation theory. Unlike the MCSCF occupation numbers, which are unequal to 1 or 0 only for the 10 active orbitals, all of the ACSE occupation numbers are fully correlated. The ACSE occupation numbers consistently display more correlation than those from MCSCF, which reflects that the ACSE includes electron correlation beyond the active space.

IV. Discussion

The barriers in the Woodward−Hoffmann pathways for the electrocyclic conversion of bicyclobutane to *gauche*-1,3-butadiene have been studied with the multireference solution of the anti-Hermitian contracted Schrödinger equation (ACSE).[4−11] The ACSE method enables the direct calculation of multireference correlation energies and 2-RDMs without the fully correlated many-electron wave function. Qualitatively, the Woodward−Hoffmann rules indicate that the electrocyclic reaction of bicyclobutane to form *gauche*-1,3-butadiene prefers the conrotatory pathway to the disrotatory pathway. The solution of the ACSE in the 6-311G** basis set predicts 41.2 and 55.7 kcal/mol reaction barriers for the conrotatory and disrotatory pathways, respectively. These energies agree with the barriers of 41.5 and 56.3 kcal/mol determined previously by second-order complete-active-space perturbation theory (CASPT2) in the 6-31G* basis set[18] and the conrotatory barrier of 40.6 ± 2.5 kcal/mol measured by experiment.[12] On the basis of completely renormalized coupled-cluster (CR-CC) computations, however, it was recently proposed that the disrotatory barrier might be higher than the earlier CASPT2 barrier.[19] Because the

ACSE captures significantly more single-reference correlation than second-order multireference perturbation techniques, the ACSE offers a measure of the barriers, balanced between single-reference and multireference correlation effects, that corroborates the earlier CASPT2 results. While not definitive, comparison of the CR-CC and ACSE total energies for reactant, product, and transition states suggests the CR-CC method may be missing some multireference correlation of the biradical disrotatory transition state that would lower its energy by about 9.5 kcal/mol.

The multireference solution of the ACSE provides not only energies but also electron-density probabilities and molecular properties. The Woodward−Hoffmann rules energetically disfavor the disrotatory pathway because the p_z orbitals of the two end carbons interact in the transition state with opposite phases to produce an entangled (or multireferenced) wave function. Both the multiconfiguration self-consistent-field (MCSCF) and the ACSE confirm this entanglement through natural-orbital occupation numbers. While the occupation numbers of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals are close to 0 and 1, respectively, for bicyclobutane, the conrotatory transition state, and the *gauche*-1,3-butadiene, they are nearly degenerate for the disrotatory transition state. The degeneracy, which corresponds to two determinants contributing almost equally to the *N*-electron wave function, demonstrates that the disrotatory transition state is a biradical.

Application of the ACSE to studying the electrocyclic conversion of bicyclobutane to *gauche*-1,3-butadiene illustrates the ACSE's ability to capture significant multireference correlation. Because the ACSE does not depend on a specific reference wave function, it can be seeded with a mean-field 2-RDM from a Hartree−Fock calculation or a correlated 2-RDM from an MCSCF computation. The solution of the ACSE by the differential equations in section II.B introduces correlations between the active and external (core or virtual) spaces through a sequence of unitary transformations. Unitary transformations involving four active orbitals or more than two virtual orbitals are excluded. Introduced for efficiency in this paper, this latter exclusion has a negligible effect on the accuracy of the energies and 2-RDMs while decreasing the computational scaling in floating-point operations from r^6 to $(r_c + r_a)^2 r_v^4$. Future work will further enhance the efficiency of the ACSE through the inclusion of molecular point-group symmetries. The multireference ACSE offers an important tool for studying chemical and condensed-matter phenomena through the direct calculation of energies and 2-RDMs.

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