On the Performance of Density Cumulant Functional Theory for Capturing Static Correlation Effects and Ab Initio Computational Studies of C_2F_4 and Ge_4H_4

by

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(Under the direction of Henry F. Schaefer III)

Abstract

The performance of density cumulant functional theory (DCT) for capturing static correlation effects is reported and discussed. In this respect, DCT is competitive with the popular coupled-cluster methods CCSD and CCSD(T), and the DCT natural orbital occupation numbers provide a convenient diagnostic for the appearance of multireference effects. In addition, ab initio computational studies of tetrafluoroethylene (C_2F_4) and tetragermacyclobutadiene (Ge_4H_4) are reported. First, a theoretical investigation of the low-lying electronic states and conical intersections of C_2F_4 provides a complementary description of nonadiabatic processes that were recently probed by femtosecond photoionization spectroscopy. Second, a coupled-cluster study of the ground-state potential energy surface of Ge_4H_4 demonstrates its preference for unusual bonding arrangements in contrast to the planar ring structure of cyclobutadiene (C_4H_4).

INDEX WORDS: ab initio quantum chemistry, computational chemistry, conical intersections, density cumulant functional theory, electronic structure theory, electronic excited states, static correlation, tetrafluoroethylene, tetragermacyclobutadiene

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

A central tenet of modern chemistry is that the properties of matter are determined by the properties of atoms and molecules.¹ Electronic structure theory provides the quantum mechanical framework for modeling the properties of atoms and molecules from first principles by *explicitly* considering the role of electrons in driving chemical phenomena.^{2–4} Ab initio electronic structure computations have been crucial for linking qualitative chemical concepts to a quantum mechanical foundation, interpreting experimental results, and quantitatively predicting molecular properties, at times for which experimental determination is impracticable.^{5,6}

In this introductory chapter, key aspects of electronic structure theory are reviewed that are relevant to the original research presented in Chapters 2–4. These topics include ab initio wave function methods, density cumulant functional theory, static correlation, excited electronic states, and conical intersections. This chapter ends with an overview of the original research presented herein.

1.1 Electronic Structure Theory

The distribution of electrons in atoms and molecules is determined by the electronic Schrödinger equation²

$$\hat{H}_{\rm el}\Psi_{\rm el}\left(\mathbf{x}_{\rm el};\mathbf{R}_{\rm nuc}\right) = E_{\rm el}\left(\mathbf{R}_{\rm nuc}\right)\Psi_{\rm el}\left(\mathbf{x}_{\rm el};\mathbf{R}_{\rm nuc}\right)$$
(1.1)

under the Born–Oppenheimer approximation.⁷ For a given nuclear configuration (\mathbf{R}_{nuc}), the electronic wave function (Ψ_{el}) is a function of the spatial and spin coordinates of the electrons (\mathbf{x}_{el}) and the electronic energy (E_{el}) is a real number. The electronic Hamiltonian (\hat{H}_{el}) is the sum of one-electron operators

$$\hat{h} = \sum_{i=1}^{N_{\rm el}} \left(-\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_{\rm nuc}} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right)$$
(1.2)

and two-electron operators

$$\hat{g} = \sum_{i$$

where $N_{\rm el}$ is the number of electrons and $N_{\rm nuc}$ is the number of nuclei. (Atomic units are assumed.)

If $\hat{H}_{\rm el} = \hat{h}$, then the electronic Hamiltonian would be a sum of $N_{\rm el}$ independent oneelectron Hamiltonians. For such a fictitious system, the electronic wave function is a product of $N_{\rm el}$ molecular orbitals (MOs), i.e., one-electron wave functions, and the electronic energy is a sum of the corresponding orbital energies.⁴ In fact for such a system, an antisymmetrized product of orthonormal MOs (i.e., a Slater determinant) satisfies the antisymmetry postulate of quantum mechanics for a system of indistinguishable fermions.⁸ However, the presence of the interelectronic repulsion operator \hat{g} complicates solution of Eq. 1.1 by introducing correlation between electrons and necessitates the application of approximate methods to make progress. In principle, Eq. 1.1 can be solved for all possible nuclear configurations \mathbf{R}_{nuc} . Collecting the sum of the electronic energy and the internuclear repulsion energy at each \mathbf{R}_{nuc} maps out a potential energy surface (PES) for nuclear motion. Computing a complete PES is impractical for most molecules, but focusing on the minimum energy and transition state structures, including a localized description of the PES around these stationary points, is often sufficient for accurate predictions of chemical interest such as reaction enthalpies, reaction rates, reaction pathways, and spectroscopic constants.⁹ The PES concept is a consequence of the Born–Oppenheimer approximation. However, the Born–Oppenheimer approximation breaks down as PESs become degenerate leading to a coupling of electronic and nuclear motions (i.e., vibronic coupling). Section 1.6 discusses intersecting PESs, which are important for nonadiabatic processes.^{10–12}

1.2 AB INITIO WAVE FUNCTION METHODS

The electronic Schrödinger equation (Eq. 1.1) is a formidable many-body problem due to the interelectronic repulsive interactions \hat{g} . A wealth of experience shows that an independent particle model (e.g., Hartree–Fock theory) with strategically added corrections from sophisticated treatments of electron correlation (i.e., accounting for the instantaneous interactions between electrons) can systematically approach the exact solution of Eq. 1.1 for many systems of chemical interest.^{3,13} This section reviews the standard wave function models that have found wide-spread use in electronic structure computations and that are applied in Chapters 2–4. The underlying assumption of these methods is that Hartree–Fock theory provides a good starting approximation to the electronic wave function. Section 1.4 will cover methods appropriate for cases where Hartree–Fock theory fails. A full exposition of the theoretical details is avoided here in favor of emphasizing the important features of each method and their key differences.

Hartree–Fock Theory

The Hartree–Fock wave function $\Phi_{\rm HF}$ is a single configuration state function (CSF), which for closed-shell and high-spin open-shell molecules can be expressed as a single Slater determinant.³ In this section, a single determinant Hartree–Fock wave function is assumed. The Hartree–Fock energy is the expectation value of the electronic Hamiltonian $E_{\rm HF} = \langle \Phi_{\rm HF} | \hat{H}_{\rm el} | \Phi_{\rm HF} \rangle$. Hartree–Fock theory employs the variational principle by minimizing $E_{\rm HF}$ with respect to the MOs in $\Phi_{\rm HF}$ under the constraint that the MOs remain orthonormal.² This procedure leads to a pseudo-eigenvalue equation for the MOs (ϕ_i)

$$\hat{f}\phi_i = \epsilon_i \phi_i \tag{1.4}$$

where \hat{f} is the one-electron Fock operator given by

$$\hat{f} = \hat{h} + \hat{J} - \hat{K}$$
 (1.5)

(A spin-orbital basis is assumed.) The action of the Coulomb operator (\hat{J}) is defined as

$$\hat{J}(\mathbf{x}_{1})\phi_{i}(\mathbf{x}_{1}) = \sum_{j=1}^{N_{\rm el}} \left\{ \int \frac{\phi_{j}(\mathbf{x}_{2})\phi_{j}(\mathbf{x}_{2})}{r_{12}} d\mathbf{x}_{2} \right\} \phi_{i}(\mathbf{x}_{1}) , \qquad (1.6)$$

and the action of the exchange operator (\hat{K}) is defined as

$$\hat{K}(\mathbf{x}_{1})\phi_{i}(\mathbf{x}_{1}) = \sum_{j=1}^{N_{\rm el}} \left\{ \int \frac{\phi_{j}(\mathbf{x}_{2})\phi_{i}(\mathbf{x}_{2})}{r_{12}} d\mathbf{x}_{2} \right\} \phi_{j}(\mathbf{x}_{1}) .$$
(1.7)

Eq. 1.4 requires an iterative solution due to the MO dependence of \hat{f} .

The MOs are typically expressed as a linear combination of atomic orbital (AO) basis functions centered on the nuclei

$$\phi_i(\mathbf{r}) = \sum_{\mu}^{N_{\rm AO}} C_{\mu i} \chi_{\mu}(\mathbf{r}) \tag{1.8}$$

so that the integro-differential equations of Hartree–Fock theory (Eq. 1.4) are converted to a matrix representation for the chosen basis functions¹⁴

$$\mathbf{FC} = \mathbf{SC}\epsilon \;, \tag{1.9}$$

where **F** is the matrix representation of \hat{f} , **S** is the overlap of the AO basis functions, **C** is the matrix of MO expansion coefficients in Eq. 1.8, and ϵ is the diagonal matrix of MO energies. The Roothaan equations (Eq. 1.9) are amenable to computer implementation for molecular systems, and two different approaches are usually applied. In restricted Hartree–Fock theory (RHF), restricted spin-orbitals are used (i.e., for each spin-orbital involving an alpha spin-function, there is a corresponding spin-orbital with the same spatial orbital multiplied by a beta spin-function).^{14,15} In contrast, the above spin-restriction is removed for unrestricted Hartree–Fock theory (UHF).¹⁶

The Hartree–Fock equations have an important physical interpretation. The Fock operator \hat{f} can be viewed as an effective one-electron Hamiltonian where the interelectronic repulsive interactions \hat{g} are replaced by an effective one-electron potential or a mean field

$$\hat{v}(\mathbf{x}) = \sum_{i=1}^{N_{\rm el}} \left\{ \hat{J}_i(\mathbf{x}) - \hat{K}_i(\mathbf{x}) \right\} .$$
(1.10)

In this picture, each electron is described by its own wave function (MO) and interacts with the mean field created by the other electrons. Conceptually, Hartree–Fock theory is important because it retains some resemblance of a system of independent particles which is useful for qualitative chemical concepts that are otherwise obscured by the complexity of the $N_{\rm el}$ -electron wave function.^{17,18} Quantitatively, Hartree–Fock theory provides adequate predictions of molecular geometries and ionization potentials, but the crude approximation to the interelectronic repulsive interactions often leads to unacceptable error when high accuracy is required.³ More sophisticated treatments of the interelectronic repulsive interactions are required to recover electron correlation effects.

Configuration Interaction

The most straightforward approach for incorporating electron correlation starting from $\Phi_{\rm HF}$ is the method of configuration interaction (CI).¹⁹ The full CI (FCI) wave function is a linear combination of all possible CSFs (Slater determinants) for a set of Hartree–Fock MOs.

$$\Psi_{\rm CI} = \sum_{i=0} a_i \phi_i = c_0 \Phi_{\rm HF} + \sum_{\rm S} c_{\rm S} \Phi_{\rm S} + \sum_{\rm D} c_{\rm D} \Phi_{\rm D} + \sum_{\rm T} c_{\rm T} \Phi_{\rm T} + \dots + \sum_{N_{\rm el}} c_{N_{\rm el}} \Phi_{N_{\rm el}} \qquad (1.11)$$

Eq. 1.11 is a convenient way of expressing the FCI wave function where $\Phi_{\rm S}$ refers to the singly excited determinants (i.e., the determinants that differ from $\Phi_{\rm HF}$ by only one MO), $\Phi_{\rm D}$ refers to the doubly excited determinants, ..., and $\Phi_{N_{\rm el}}$ refers the Slater determinants that differ from $\Phi_{\rm HF}$ in all orbitals. The CI coefficients $\{c_i\}$ of Eq. 1.11 are determined by employing the variational principle, which leads to the matrix eigenvalue equation

$$\mathbf{Hc} = E\mathbf{c} \ . \tag{1.12}$$

H is the matrix representation of the electronic Hamiltonian in the basis of the CSFs (determinants) in the FCI wave function, \mathbf{c} is an eigenvector of \mathbf{H} whose elements are the CI coefficients of Eq. 1.11, and E is the CI energy. The FCI wave function is the best wave function possible for a given choice of the AO basis functions. The FCI method is impractical

for all but the smallest systems with small basis sets. However, FCI results provide useful benchmarks for evaluating more practical electron correlation methods.

A hierarchy of truncated CI methods are well-defined by truncating the expansion for Ψ_{CI} (Eq. 1.11). The most common is the CISD method which includes the singly and doubly excited determinants. Improved CI wave functions may be obtained at greater computational cost by including higher excited determinants in the trial wave function (e.g., CISDT, CISDTQ), but this approach has largely lost favor in the computational chemistry community due to its lack of size-consistency and extensivity, a well-known problem of truncated CI methods. A common approximate remedy of this problem is the Davidson correction that accounts for the "disconnected" quadruple excitation (i.e., the correlation of two non-interacting electron pairs), which are the most important contributions to the correlation energy after the singles and doubles. The CISD method with the Davidson correction (CISD+Q) offers an improvement over CISD, but Møller–Plesset perturbation theory (MPPT) and coupled-cluster (CC) theory are rigorously size extensive alternatives even in their truncated forms.

Møller–Plessett Perturbation Theory

Møller–Plessett perturbation theory (MPPT)^{13,20,21} employs Rayleigh-Schrödinger perturbation theory based on a Hartree–Fock reference wave function and a decomposition of the electronic Hamiltonian

$$\hat{H}_{\rm el} = \hat{H}_0 + \hat{V} = \sum_i^{N_{\rm el}} \hat{f}_i + \left\{ \frac{1}{r_{12}} - \sum_{i=1}^{N_{\rm el}} \left(\hat{J}_i - \hat{K}_i \right) \right\} .$$
(1.13)

In Eq. 1.13 the fluctuation potential \hat{V} is treated as the perturbation to the zeroth-order Hamiltonian, which is a sum of one-electron Fock operators. Although the Hartree–Fock determinant is the zeroth-order wave function in MPPT, the Hartree–Fock energy is correct to first-order so that the second-order energy is required to recover part of the correlation energy.

The advantage of MPPT is that the energy and wave function can be systematically improved order-by-order. However, there are two main disadvantages: (1) MPPT is not variational and (2) there is no guarantee that the MPPT expansion of the energy and wave function will converge.²² Therefore, MPPT to fourth-order (MP4)²³⁻²⁵ is typically the highest order MPPT method employed, with most applications only employing MPPT to second-order (MP2).²⁶⁻²⁸ MP2 often provides a good balance between computational cost and recovery of electron correlation effects, particularly for large systems.

Coupled Cluster Theory

Coupled-cluster (CC) theory $^{29-32}$ employs an exponential wave function ansatz:

$$\Psi_{\rm CC} = \exp(\hat{T})\Phi_{\rm HF} , \qquad (1.14)$$

where the excitation operator \hat{T} is conveniently decomposed as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_{N_{\rm el}} .$$
(1.15)

The action of the *i*th excitation operator on $\Phi_{\rm HF}$ generates a linear combination of all *i*th excited Slater determinants weighted by the unknown amplitudes (t_i) .

$$\hat{T}_1 \Phi_{\rm HF} = \sum_{\rm S} t_{\rm S} \Phi_{\rm S} \tag{1.16}$$

$$\hat{T}_2 \Phi_{\rm HF} = \sum_{\rm D} t_{\rm D} \Phi_{\rm D} \tag{1.17}$$

$$\hat{T}_{3}\Phi_{\rm HF} = \sum_{\rm T} t_{\rm T}\Phi_{\rm T} \tag{1.18}$$

$$\cdots = \cdots \tag{1.19}$$

If the full excitation operator \hat{T} is used, then the CC wave function is equivalent to the FCI wave function, and there is no advantage of using the exponential parameterization of CC theory over the linear parameterization of FCI. A hierarchy of truncated CC methods are defined based on the truncation of the excitation operator \hat{T} , e.g., CCD (CC with doubles), CCSD (CC with singles and doubles), CCSDT (CC with singles, doubles, and triples). The exponential ansatz ensures a size-extensive method, even for a truncated CC method. In contrast to CISD, CCSD includes contribution form the disconnected quadruple excitations due to the presence of $\hat{T}_2\hat{T}_2$ in the expansion of exponential operator $\exp(\hat{T})$. In fact, CC methods that include at least the single excitation operator in the definition of \hat{T} will include contributions from all Slater determinants that appear in the FCI wave function, but only partial contributions from the disconnected excitations are included.

Conventional CC theory is not variational. The *t*-amplitudes and CC correlation energy is found by projecting the Schrödinger equation of the similarity transformed Hamiltonian $\exp(-\hat{T})\hat{H}_{\rm el}\exp(\hat{T})$ onto the manifold of Slater determinants corresponding to the unknown *t*-amplitudes. Experience shows that the nonvariational nature of conventional CC methods does not adversely affect the results. In fact, CCSD with an approximate treatment of the triples contribution based on perturbation theory [CCSD(T)], is often referred to as the "gold standard" due to its remarkable ability to produce accurate geometries, energies, and other molecular properties at reasonable computational cost for small systems. Another drawback of CC theory is that the resulting equations for the *t*-amplitudes and the electronic energy are rather complicated because they are nonlinear in the unknown amplitudes. The coupled electron pair approximation or CEPA methods may be viewed as a linear approximation to the CC equations.^{33,34}

1.3 Density Cumulant Functional Theory

The electronic Hamiltonian \hat{H}_{el} contains only one- and two-electron operators, so its expectation value only requires knowledge of the one- and two-electron reduced density matrices (1-RDM and 2-RDM)

$$E = \langle \Psi | \hat{H}_{\rm el} | \Psi \rangle = h_p^q \gamma_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \gamma_{rs}^{pq} , \qquad (1.20)$$

where the quantities of interest in the MO basis (p, q, r, s) include the conventional oneelectron integrals (h_p^q) , the antisymmetrized two-electron integrals (\bar{g}_{pq}^{rs}) , the 1-RDM (γ_q^p) , and the 2-RDM γ_{rs}^{pq} .³ (The Einstein summation convention is assumed in this section.) If higher order density matrices are not required to compute properties of interest, then finding the electronic wave function is not necessary as the 1-RDM and 2-RDM will be sufficient.

An alternative to finding approximate solutions to the electronic Schrödinger equation for a parameterized wave function (Section 1.2) is to parameterize the 1-RDM and 2-RDM and minimize the electronic energy with respect to these parameters.^{35,36} Although this is an attractive approach, there are two major obstacles. First, the elements of the 1-RDM and 2-RDM are not independent and therefore cannot be freely varied when building a method based on Eq. 1.20. Second, the 1-RDM and 2-RDM must be derivable from a valid N-electron wave function, which places conditions on the 1-RDM and the 2-RDM known as the N-representability conditions.³⁷ A number of methods have been developed based on parameterization of the 1-RDM and 2-RDM;^{38–40} however, density cumulant functional theory (DCT) is the focus of the section.^{41–43}

DCT addresses the two problems mentioned above by employing the 2-RDM cumulants (λ_{pq}^{rs}) as parameters. The λ_{pq}^{rs} are expressed in terms of the 1-RDM and 2-RDM as

$$\gamma_{pq}^{rs} = \gamma_p^r \gamma_q^s - \gamma_p^s \gamma_q^r + \lambda_{pq}^{rs} .$$
(1.21)

The λ_{pq}^{rs} vanish identically for a Hartree–Fock wave function, but are nonzero for a correlated wave function. In other words, the 2-RDM cumulants are the irreducible part of the 2-RDM that cannot be expressed through the 1-RDM, and they contain information about electron correlation absent in a mean field approach like Hartree–Fock theory. In DCT, the 1-RDM is decomposed into an idempotent component due to the mean-field solution (κ_q^p) and an electron correlation component (τ_q^p).

$$\gamma_q^p = \kappa_q^p + \tau_q^p \tag{1.22}$$

Although τ_q^p is dependent on λ_{pq}^{rs} , κ_q^p and λ_{pq}^{rs} are independent and fully parameterize the 1-RDM and 2-RDM.

The DCT electronic energy is expressed as

$$E = \frac{1}{2} \left(h_p^q + f_p^q \right) \left(\kappa_q^p + \tau_q^p \right) + \frac{1}{4} \bar{g}_{pq}^{rs} \lambda_{rs}^{pq}$$
(1.23)

where the generalized Fock matrix is defined as

$$f_p^q = h_p^q + \bar{g}_{pr}^{qs} (\kappa_r^s + \tau_r^s) .$$
 (1.24)

The energy expression in Eq. 1.23 is made stationary with respect to variations of κ_q^p and λ_{rs}^{pq} while enforcing the appropriate N-representability conditions on λ_{rs}^{pq} . The N-representability conditions for κ_q^p are trivially satisfied by construction and do not require further comment. However, the N-representability conditions for λ_{rs}^{pq} are not trivial, and approximate conditions based on perturbation theory are employed. If the electronic state of interest is welldescribed by a single Slater determinant, it is expected that the error in the approximate N-representability conditions will be small since the elements of λ_{rs}^{pq} will not be expected to be large. The relationship between τ_q^p and λ_{rs}^{pq} have been computed approximately based on perturbative analysis in the DC-06 method 41,42 and exactly in the DC-12 method. 44 Full orbital relaxation for DC-12 (ODC-12) has been shown to be a stable method competitive with CCSD and CCSD(T) for a wide variety of molecular properties. 45

1.4 STATIC CORRELATION AND MULTIREFERENCE METHODS

The single reference methods described in Section 1.2 assume that a single CSF dominates the FCI solution, and those methods are biased towards that CSF. This assumption breaks down as two or more CSFs are degenerate or nearly degenerate. *Static correlation* refers to such cases where multiple configurations are important to obtain a valid zeroth-order approximation to the wave function. Multiconfigurational SCF (MCSCF) methods provide a starting point where static correlation is important by treating these CSFs on an equal footing.³ An MCSCF wave function

$$\Psi_{\text{MCSCF}} = \sum_{i} c_i \Phi_i^{\text{CSF}} \tag{1.25}$$

is a linear combination of a small number of CSFs, and the MCSCF energy is found by minimizing the expectation value of \hat{H}_{el} with respect to the CI coefficients ($\{c_i\}$) and the MOs used in the CSFs. The simultaneous optimization of the CI coefficients and the MOs is a challenging variational problem, but popular electronic structure software packages provide efficient and robust MCSCF methods.

A major drawback of MCSCF methods is that they can hardly be considered black-box since trial and error along with chemical intuition is required to determine the CSFs that should be included in the MCSCF trial wave function. A popular MCSCF method is the complete active space SCF (CASSCF) method.^{46,47} In CASSCF, an active space is defined as a subset of the valence electrons and a subset of the MOs, and all possible CFSs obtained by varying the orbital occupations in the active space are included in the CASSCF wave function. Therefore, choosing an appropriate active space is key in a CASSCF calculation.

Post-MCSCF methods are required for achieving accurate results. Multireference configuration interaction (MRCI) applies the CI approach to a MCSCF wave function.^{48,49} The most widely used method is MRCISD which includes all single and double excitations from the configurations in the MCSCF wave function. The CASPT2 method applies perturbation theory through second-order to a CASSCF wave function.^{50,51} CASPT2 is a computationally cheaper method than MRCISD, but it is less accurate. Multireference coupled cluster theory (MRCC) applies the ideas of coupled cluster theory to a MCSCF wave function, but there are multiple formulations of MRCC theories.^{52,53} One such approach is Mukherjee's state-specific MRCC (Mk-MRCC),^{54,55} and results from Mk-MRCC computations will be reviewed in Chapter 2.

1.5 Excited Electronic States

The single reference methods (Section 1.2) and multireference methods (Section 1.4) reviewed above are sometimes used to describe excited electronic states. However, methods designed for excited states have been developed, and two such methods employed in Chapter 3 are reviewed here.

State average CASSCF (SA-CASSCF) minimizes the average energy for a select set of electronic states based on a common active space.^{56,57} Two advantages of SA-CASSCF is that it avoids the root-flipping problems during the optimization and yields a single set of MOs for all states considered. This results in a robust method and a balanced description of multiple states in a single computation. The resulting SA-CASSCF wave functions can be used as a starting point for MRCI, CASPT2, and MRCC computations for more accurate results.

Equation of motion coupled cluster (EOM-CC) theory, provides a single-reference formalism for treating excited states.^{58–60} EOM-CC with singles and doubles for excited states (EOM-EE-CCSD) starts with a CCSD solution for the ground electronic state well-described by a single determinant. The target EOM states are obtained by diagonalizing the similarity transformed Hamiltonian $\bar{H} = \exp^{-\hat{T}} \hat{H} \exp^{T}$, where \hat{T} is defined from the CCSD *t*-amplitudes for the reference state. In this sense, EOM-CC resembles configuration interaction. A drawback to EOM-EE-CCSD is that the results degrade when the reference state becomes multireference. For example, modeling a reaction path for a bond-breaking reaction will fail if the reference state becomes a multiconfigurational problem. An alternate EOM-CC approach is spin-flip EOM-CC (EOM-SF-CCSD), where the reference state is taken to be a high spin state that is well described by a single determinant, and spin-flip operators are applied in the EOM-CC formalism to reach the target spin state, which presumably is a multireference problem.

1.6 Conical Intersections

The methods described above all rely on the validity of the Born–Oppenheimer approximation. Although these methods are successful in addressing a variety of chemical problems, they fail for nonadiabatic processes where vibronic coupling between electronic states must be considered. Conical intersections occur when two or more PESs become degenerate, and their importance is widely accepted in photochemical mechanisms.^{61,62} In this section, the basics of conical intersections are reviewed.

Two intersecting PESs create a N - 2 degenerate conical intersection seam space, where N is the number of nuclear degrees of freedom $(N_{\text{atom}} - 6)$. At each point in the seam space, there exists a two-dimensional orthogonal space known as the branching plane where the degeneracy of the two PESs are lifted. Any two linearly independent vectors in this plane

can be chosen as the base vectors, but the usual choice is the energy difference gradient

$$\mathbf{g}_{IJ} = \frac{\partial E_I}{\partial \mathbf{R}} - \frac{\partial E_J}{\partial \mathbf{R}} \tag{1.26}$$

and the interstate coupling vector

$$\mathbf{h}_{IJ} \simeq (E_I - E_J) \left\langle \Psi_I | \frac{\partial}{\partial \mathbf{R}} | \Psi_J \right\rangle . \tag{1.27}$$

If the PESs are plotted in the branching plane for a given point of conical intersection, the two PESs take the form of a double cone that intersects only at that point of conical intersection.

A convenient way of characterizing a conical intersection seam is to find the minimum energy conical intersections (MECIs), which are minimum energy structures in the seam space but not necessarily a stationary point on either PES. Finding the MECI is a nontrivial problem because it requires the simultaneous computation of at least two PESs. One way to proceed is SA-CASSCF where the active space is chosen to provide an adequate description of the two electronic states of interest. However, inclusion of dynamic correlation through methods of CASPT2, MRCI, and EOM-CCSD have been studied for characterizing MECIs.

Although the MECIs may provide a simple and qualitatively useful picture of nonadiabatic processes, a complete description requires the dynamics of the nuclei to be considered. The approach to the conical intersection is dictated by the features on the excited state PES, so the MECI may be inaccessible on the upper PES. Many dynamics schemes to model the nuclear dynamics for nonadiabatic processes have been proposed.⁶³ However, these methods are still not in wide-spread use due to the computational demands and the fact that they are not black-box methods. A recently proposed compromise to the simple MECI and the full dynamics pictures is to find the minimum energy paths in the conical intersection seam using chain-of-states methods (e.g., the nudged elastic band method) often used to find minimum energy pathways on a single PES.⁶⁴

1.7 Prospectus

Chapter 2 reports the performance of DCT for capturing static correlation effects. Molecular properties computed with the ODC-12 and DC-12 variants of DCT are compared to CCSD, CCSD(T), MRCISD, and Mk-MRCCSD results for molecular systems with significant multideterminant character of the electronic wave function. These systems include the beryllium dimer, diatomic carbon, *m*-benzyne, 2,6-pyridyne, twisted ethylene, and square-planar cyclobutadiene. The DCT natural orbital occupations are evaluated as a potential diagnostic for the presence of multireference effects.

The low-lying electronic states of tetrafluoroethylene (C_2F_4) are characterized in Chapter 3. We report vertical excitation energies, equilibrium geometries, minimum energy conical intersections, and potential energy curves along relevant coordinates. Two relaxation pathways are reported from the Rydberg-3s excited state to the ground state, and the theoretical results are discussed in conjunction with recent femtosecond photoionization experiments. This work represents the first theoretical characterization of important conical intersections of C_2F_4 and their role in nonadiabatic relaxation.

In Chapter 4, the ground state potential energy surface of Ge_4H_4 is characterized with coupled-cluster theory. This study focuses on the cyclic isomers related to the all Ge cyclobutadiene analog and the lowest energy isomers, which exhibit a variety of bonding motifs. The results are discussed in the context of qualitative MO bonding models, related computational studies, and recent synthetic research. This research reports three new isomers of Ge_4H_4 and represents the highest-level theoretical study to date for this system.

Chapter 2

CAN DENSITY CUMULANT FUNCTIONAL THEORY DESCRIBE STATIC CORRELATION EFFECTS?*

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2.1 Abstract

We evaluate the performance of density cumulant functional theory (DCT) for capturing static correlation effects. In particular, we examine systems with significant multideterminant character of the electronic wave function, such as the beryllium dimer, diatomic carbon, m-benzyne, 2,6-pyridyne, twisted ethylene, as well as the barrier for double-bond migration in cyclobutadiene. We compute molecular properties of these systems using the ODC-12 and DC-12 variants of DCT and compare these results to multireference configuration interaction and multireference coupled-cluster theories, as well as single-reference coupled-cluster theory with single, double (CCSD) and perturbative triple excitations [CCSD(T)]. For all systems the DCT methods show intermediate performance between that of CCSD and CCSD(T), with significant improvement over the former method. In particular, for the beryllium dimer, *m*-benzyne, and 2,6-pyridyne, the ODC-12 method along with CCSD(T) correctly predict the global minimum structures, while CCSD predictions fail qualitatively, underestimating the multireference effects. Our results suggest that the DC-12 and ODC-12 methods are capable of describing emerging static correlation effects but should be used cautiously when highly accurate results are required. Conveniently, the appearance of multireference effects in DCT can be diagnosed by analyzing the DCT natural orbital occupations, which are readily available at the end of the energy computation.

2.2 INTRODUCTION

The electron correlation problem is central in quantum chemistry.^{65,66} Out of a variety of ab initio methods for electron correlation, the most commonly used are single-reference methods, which rely on the validity of Hartree–Fock theory as the underlying approximation. Single-reference (SR) methods efficiently capture dynamic electron correlation, which arises due to instantaneous electron repulsions, and are sufficiently accurate when the fron-

tier molecular orbitals of a system are well-separated in energy. Conventional SR theories, such as Møller–Plesset perturbation theory,^{2,3} configuration interaction,^{2,3} and coupled cluster^{13,31,32} theories, have been shown to provide highly accurate solutions to the Shrödinger equation for systems of modest size near geometric equilibrium. In particular, coupled cluster theory in combination with basis set extrapolation techniques^{67,68} or explicitly correlated approaches^{69–71} is often capable of achieving chemical accuracy, provided that a high enough excitation level is used in the expansion of the molecular wavefunction.⁷²

Conventional wave function-based SR methods for electron correlation suffer from two major drawbacks. First, their performance degrades with increasing static correlation effects, which usually require more sophisticated and costly multireference treatments.^{52,53,73,74} Second, the high computational cost of SR methods limits their applicability to rather small molecules. As a result, the development of new SR theories is still an active area of research, ranging from linear-scaling local correlation methods^{75–78} to novel approaches that are more efficient and accurate compared to conventional SR theories.^{79–86} Many of these alternative approaches are formulated by simplifying the equations of SR coupled cluster theory^{79–84} or directly obtaining the reduced density matrices and cumulants thereof,⁸⁷ circumventing the computation of the *N*-electron wavefunction. In particular, density cumulants^{88–91} have recently found a widespread use in electronic structure theory in many areas, for example, as a tool for reconstruction of the high-order density matrices in the contracted Schrödinger equation theory,^{90,92–97} canonical transformation theory,^{98–101} multireference methods based on generalized normal-ordering,⁸⁸ and as a central variable in parametric reduced density matrix methods.^{38–40}

We have recently developed and implemented density cumulant functional theory (DCT), ^{42–45,102} first proposed by Kutzelnigg in 2006.⁴¹ In its simplest formulation, ^{42,44,45} DCT resembles linearized coupled cluster theory with double excitations (LCCD, also known as CEPA-0), ^{33,34,103,104} and contains fewer terms in the equations compared to coupled cluster with singles and doubles (CCSD), while including high-order correlation effects in the description of the one-particle density matrix and orbital relaxation.^{44,45} An additional advantage over CCSD is that in DCT, the computation of molecular equilibrium properties and geometries is very efficient due to the stationarity of the energy functional with respect to all of its parameters and orbital rotations.^{43,45} Our recent benchmark study demonstrated that the DC-12 and ODC-12 variants of DCT show intermediate performance between that of CCSD and CCSD with perturbative triples [CCSD(T)] in the description of noncovalent interactions, barrier heights for hydrogen-transfer reactions, radical stabilization energies, and adiabatic ionization energies.¹⁰⁵ These DCT methods have also shown encouraging performance for the covalent bond stretching of diatomic molecules. However, the performance of DCT for recovering static correlation effects beyond bond stretching of diatomic molecules has not been explored.

An intrinsic assumption of the current formulation of DCT is that the one-particle density matrix can be well approximated by a density matrix of a single determinant, making the theory inherently single-reference. It is therefore natural to ask the question: how accurate is DCT in systems with significant multireference character? For example, it is known that SR coupled cluster theory with high-order connected excitations (triple, quadruple, etc.) can recover a substantial degree of multireference correlation.^{106–108} On the other hand, linearized theories, such as CEPA-0, which bear resemblance to DCT, have been shown to provide inadequate results for systems with even minor multireference effects.^{82,105} To answer the question above, in this paper we test the performance of the DC-12 and ODC-12 methods for a set of systems with significant static correlation effects in the electronic wave function. We begin by considering four molecules with a two-determinant character in the ground state: the beryllium dimer, diatomic carbon, *m*-benzyne, and 2,6-pyridine. We then evaluate the performance of DCT for the description of the potential energy barriers for twisting of ethylene and the double-bond migration in cyclobutadiene. We focus on equilibrium properties such as the optimized geometry, harmonic vibrational frequencies, dissociation energies, and adiabatic singlet-triplet excitation energies. The results of the DC-12 and ODC-12 methods are compared to available experimental data, as well as high-level multireference computations. To assess the relative performance, we compare the DCT results to those of the conventional SR methods such as CCSD, CCSD(T), and CEPA-0.

2.3 Density Cumulant Functional Theory Overview

In this section, we present a brief overview of DCT. A more detailed discussion of DCT can be found in our previous research.^{41-45,102} The starting point of DCT is the molecular electronic energy expression (summation over repeated indices is implied):

$$E = h_p^q \gamma_q^p + \frac{1}{2} g_{pq}^{rs} \gamma_{rs}^{pq} , \qquad (2.1)$$

where γ_q^p and γ_{rs}^{pq} are elements of the one- and two-particle reduced density matrices (1-RDM and 2-RDM), respectively, and the one- and two-electron integrals are denoted as h_p^q and g_{pq}^{rs} . In DCT, the 2-RDM is expressed using its cumulant expansion as

$$\gamma_{rs}^{pq} = \gamma_r^p \gamma_s^q - \gamma_r^q \gamma_s^p + \lambda_{rs}^{pq} , \qquad (2.2)$$

where λ_{rs}^{pq} are the elements of the two-particle density cumulant (λ_2). The 1-RDM (γ_1) is decomposed into an idempotent (mean-field) component κ and a correlation correction τ :

$$\boldsymbol{\gamma}_1 = \boldsymbol{\kappa} + \boldsymbol{\tau} \ . \tag{2.3}$$

In Eq. (2.3) only τ depends on the density cumulant. The entire energy functional (2.1) can thus be written in terms of the independent parameters κ and λ_2 :

$$E\left[\boldsymbol{\kappa},\boldsymbol{\lambda_2}\right] = \frac{1}{2} \left(h_p^q + f_p^q\right) \left(\kappa_q^p + \tau_q^p\right) + \frac{1}{4} \bar{g}_{pq}^{rs} \lambda_{rs}^{pq}$$
$$f_p^q \equiv h_p^q + \bar{g}_{pr}^{qs} \left(\kappa_s^r + \tau_s^r\right), \ \bar{g}_{rs}^{pq} \equiv g_{rs}^{pq} - g_{rs}^{qp} \ .$$
(2.4)

In DCT, the energy functional (2.4) is minimized with respect to κ and λ_2 , provided that the resulting density matrices (2.2) and (2.3) are N-representable, that is, can be derived from an N-electron wavefunction. In the DC-12 and ODC-12 methods, approximate constraints are used to maintain N-representability of the one- and two-particle density matrix in a balanced way by parametrizing the density cumulant to second order in perturbation theory. The two methods differ in the description of the orbital relaxation: DC-12 introduces partial orbital relaxation by diagonalizing an effective Fock operator, while ODC-12 fully optimizes the orbitals by satisfying the generalized Brillouin condition.

2.4 Computational Details

The DC-12, ODC-12, and CEPA-0 computations were performed using the PSI4 software package. ¹⁰⁹ For coupled cluster theory with singles and doubles (CCSD)^{31,32} and CCSD with perturbative triples [CCSD(T)]^{110,111} we used the CFOUR software package. ^{112,113} The complete active space self-consistent field (CASSCF)^{56,57} and multireference configuration interaction with singles and doubles (MRCI)^{48,49} computations were performed using the MOLPRO program. ¹¹⁴ The MRCI energies were supplied with the Davidson correction to account for size-consistency; the resulting method is denoted as MRCI+Q. ^{115,116} All electrons were correlated in all computations. For C₂H₄ and C₄H₄, the two electrons in two orbitals active space was used. The all-electron quintuple zeta (cc-pCV5Z) basis set was employed for C₂, ^{117,118} and the augmented version of this basis set (aug-cc-pCV5Z) was used for Be₂.¹¹⁹

For *m*-benzyne, 2,6-pyridine, ethylene, and cyclobutadiene, we employed the cc-pCVTZ basis set. Equilibrium geometries were computed using analytic differentiation of the energy for all methods except DC-12, where gradients were evaluated numerically with a five-point formula. To compute harmonic vibrational frequencies, numerical differentiation of analytic energy gradients was performed. For closed-shell molecules, the results were obtained using the restricted orbitals, which preserve the spin and spatial symmetry of the exact wavefunction. For triplet states, spin-unrestricted orbitals were used. To aid convergence in computing the ODC-12 potential energy curves for the twisting of ethylene and the double-bond migration in cyclobutadiene, we employed a 0.09 and 0.1 a.u. level shifts, respectively, as implemented in Psi4. New to this research is the determination of natural orbitals from the ODC-12 method, which are obtained by diagonalizing the one-particle reduced density matrix.

2.5 Results

2.5.1 Beryllium Dimer

We begin by considering the beryllium dimer (Be_2), a weakly bound molecule that presents a challenge for single-reference ab initio methods due to the near-degeneracy of the 2s and 2p orbitals of the Be atom.^{120,121} Previous computational studies using coupled cluster theory suggested that the connected triple excitations need to be included at least at the perturbative level to qualitatively describe the potential energy curve of the Be_2 molecule.^{107,122–124} For more accurate results, full iterative inclusion of triples and perturbative quadruples have been shown to be important.^{107,122–124} Recent high-level computational and experimental work has tackled this difficult molecule with remarkable success.^{125–128} In this section, we investigate the equilibrium properties of Be_2 using the DC-12 and ODC-12 methods combined with the augmented core-valence aug-cc-pCV5Z basis set.

Table 2.1: Equilibrium bond distances (r_e) , harmonic vibrational frequencies (ω_e) , and dissociation energies (D_e) of the Be₂ molecule computed using the DC-12, ODC-12, CCSD, CCSD(T), and CEPA-0 methods with the aug-cc-pCV5Z basis set.

Theory	$r_{\rm e}$ (Å)	$\omega_{\rm e}~({\rm cm}^{-1})$	$D_{\rm e}~({\rm cm}^{-1})$
CEPA-0	2.301	318	1589
CCSD	4.414	30	58
$\operatorname{CCSD}(T)$	2.467	242	671
DC-12	2.570	195	597
ODC-12	2.499	226	596
c-CCSDT(Q)/CBS ^a	^a 2.439	$227.6^{\rm e}$	955
DMRG ^b			931
Expt. ^c	2.454	222.6^{e}	930 ± 2
Expt. ^d	2.438	222.6^{e}	935

^a Reference 126. Composite method.

^b Reference 125. Density matrix renormalization group with canonical transcorrelation approach.

 $^{\rm c}$ Reference 127.

^d Reference 128.

^e Fundamental frequencies.

Table 2.1 provides the Be₂ equilibrium bond lengths (r_e), harmonic vibrational frequencies (ω_e), and dissociation energies (D_e) computed using five methods, as well as available high-level theoretical and experimental results. The CCSD method fails to qualitatively reproduce the experimental results predicting a very long bond distance ($r_e = 4.414$ Å) and a dissociation energy of only 58 cm⁻¹. In contrast, CEPA-0 overestimates the dissociation energy by ~ 600 cm⁻¹ and predicts a very short Be–Be distance ($r_e = 2.301$ Å). Out of the five single-reference methods, the best results are obtained using the CCSD(T) method, which gives absolute errors Δr_e , $\Delta \omega_e$, and ΔD_e relative to experiment of ~ 0.03 Å, ~ 20 cm⁻¹, and ~ 250 cm⁻¹, respectively. Both DC-12 and ODC-12 qualitatively reproduce the experimental results. The performance of ODC-12 is only slightly worse than that of CCSD(T), with Δr_e , $\Delta \omega_e$, and ΔD_e values of ~ 0.06 Å, ~ 3 cm⁻¹, and ~ 330 cm⁻¹, relative to experiment. These results are particularly encouraging, since both DC-12 and ODC-12 do not explicitly contain connected three-particle excitations and are, therefore, much cheaper. Figure 2.1 shows the plots of the Be₂ frontier natural orbitals $(2\sigma_u \text{ and } 3\sigma_g)$ computed using the ODC-12 method. The ODC-12 natural occupation numbers $(2\sigma_u)^{1.71} (3\sigma_g)^{0.16}$ show significant deviation from two and zero, indicating the multireference nature of Be₂.



Figure 2.1: (a) $2\sigma_u$ and (b) $3\sigma_g$ natural orbitals and occupations for the singlet ground state of beryllium dimer computed using the ODC-12 method with the aug-cc-pCV5Z basis set.

2.5.2 CARBON DIMER

The C₂ molecule is another challenging system for electronic structure methods, largely due to the multireference character of the $\tilde{X}^{-1}\Sigma_{\rm g}^{+}$ ground state.^{47,129–132} Table 2.2 shows the equilibrium bond distances $(r_{\rm e})$, harmonic frequencies $(\omega_{\rm e})$, dissociation energies $(D_{\rm e})$, and adiabatic excitation energies $(T_{\rm e})$ computed using the DCT and coupled cluster methods for the ground $(\tilde{X}^{-1}\Sigma_{\rm g}^{+})$ and lowest-lying triplet $(\tilde{a}^{-3}\Pi_{\rm u})$ states of C₂. Table 2.2 also contains reference data computed using multireference configuration interaction theory with single and double excitations (MRCI+Q). CCSD and CCSD(T) perform very well for the ground state equilibrium properties $(r_{\rm e} \text{ and } \omega_{\rm e})$ with deviations of ≤ 0.005 Å in $r_{\rm e}$ and ≤ 55 cm⁻¹ in $\omega_{\rm e}$, relative to experiment¹³³ and MRCI+Q. However, for the dissociation and adiabatic excitation energies $(D_{\rm e} \text{ and } T_{\rm e} = E(\tilde{a}^{3}\Pi_{\rm u}) - E(\tilde{X}^{1}\Sigma_{\rm g}^{+}))$, only CCSD(T) exhibits reliable performance with $\Delta D_{\rm e} = 1.3$ and $\Delta T_{\rm e} = 0.4$ kcal mol⁻¹. The CCSD method underestimates $D_{\rm e}$ by 20.5 kcal mol⁻¹, relative to experiment, and incorrectly predicts the $\tilde{a}^{-3}\Pi_{\rm u}$ state to be the ground state, with a large absolute error $\Delta T_{\rm e} = 10.4$ kcal mol⁻¹. CEPA-0 overestimates the binding in C₂, which results in much larger $D_{\rm e}$ and $T_{\rm e}$ values compared to experiment (by 5.4 and 11.7 kcal mol⁻¹, respectively) and a short C–C bond distance with $\Delta r_{\rm e} = 0.05$ Å. Of the two DCT levels of theory, the best agreement with experiment was demonstrated by ODC-12 that shows intermediate performance between CCSD and CCSD(T) with $\Delta D_{\rm e} = 9.3$ and $\Delta T_{\rm e} = 4.1$ kcal mol⁻¹. Both DCT methods, however, fail at predicting the correct ground state of C₂, favoring the \tilde{a} ${}^{3}\Pi_{\rm u}$ state to lie lower in energy than \tilde{X} ${}^{1}\Sigma_{\rm g}^{+}$. The ODC-12 natural occupations for the C₂ ground state valence orbitals are $(2\sigma_{\rm g})^{1.96} (1\pi_{\rm u})^{3.76} (2\sigma_{\rm u})^{1.54} (3\sigma_{\rm g})^{0.45} (1\pi_{\rm g})^{0.19} (3\sigma_{\rm u})^{0.01}$, indicating substantial multireference character.

Table 2.2: Equilibrium geometries $(r_{\rm e})$, harmonic vibrational frequencies $(\omega_{\rm e})$, dissociation energies $(D_{\rm e})$, and adiabatic excitation energies $[T_{\rm e} = E(\tilde{a}^3\Pi_{\rm u}) - E(\tilde{X}^1\Sigma_{\rm g}^+)]$ of the C₂ molecule computed using the ODC-12, DC-12, CCSD, CCSD(T), MRCI+Q, and CEPA-0 methods with the cc-pCV5Z basis set. For MRCI+Q, the complete active space self-consistent field reference with eight electrons in eight active orbitals was used.

	Theory	$r_{\rm e}$ (Å)	$\omega_{\rm e}~({\rm cm}^{-1})$	$D_{\rm e} \; (\rm kcal \; mol^{-1})$	$T_e \; (\text{kcal mol}^{-1})$
$\tilde{X}^1 \Sigma_{\rm g}^+$					
0	CEPA-0	1.193	2421	151.1	13.8
	CCSD	1.238	1907	125.2	-8.3
	CCSD(T)	1.241	1870	145.3	2.5
	DC-12	1.225	1973	128.7	-7.1
	ODC-12	1.225	1954	136.0	-2.0
	MRCI+Q	1.243	1862	150.0	1.7
	$Expt.^{a}$	1.243	1855		2.05
	$Expt.^{b}$			146.6	
	$Expt.^{c}$			147.8	
$\tilde{a}^3 \Pi_{\mathrm{u}}$					
	CEPA-0	1.305	1684		
	CCSD	1.302	1697		
	CCSD(T)	1.311	1653		
	DC-12	1.302	1770		
	ODC-12	1.305	1679		
	MRCI+Q	1.313	1640		
	$Expt.^{a}$	1.312	1641		

^a Reference 133.

^b Reference 134.

^d Reference 135

2.5.3 *m*-Benzyne

The *m*-benzyne molecule (C_6H_4 , Figure 2.2b) is a prototypical example of a singlet diradical with a multireference ground state.^{136–138} Its wavefunction has two major configurations: (1) the Hartree–Fock solution $|\Phi_1\rangle = |\dots (11a_1)^2 (7b_2)^0\rangle$ and (2) a doubly excited determinant $|\Phi_2\rangle = |\dots (11a_1)^0 (7b_2)^2\rangle$. The molecular orbitals $(11a_1)$ and $(7b_2)$ correspond to the bonding and antibonding combinations of the carbon p-orbitals in the meta position (Figure 2.3). As a result, the two electronic configurations $|\Phi_1\rangle$ and $|\Phi_2\rangle$ favor two chemically distinct geometries, the bicyclic and monocyclic, respectively (Figure 2.2), and the equilibrium structure is determined by the relative contributions of these configurations in the molecular wave function. Recently, equilibrium structures of *m*-benzyne computed using the state-specific multireference coupled cluster Mk-MRCCSD method have been reported.^{55,139,140} At the Mk-MRCCSD/cc-pCVTZ level of theory *m*-benzyne has a monocyclic ground state structure with significant contribution of the $|\Phi_2\rangle$ determinant in the wave function. In this section, we present the ground-state optimized geometries and the singlet–triplet adiabatic excitation energies ($\Delta E_{\rm ST}$) computed using the ODC-12 method with the cc-pCVTZ basis set and discuss its performance against the high-level Mk-MRCCSD method.

Table 2.3 reports the equilibrium properties of *m*-benzyne computed using the CCSD, CCSD(T), ODC-12 and Mk-MRCCSD methods. ODC-12 and CCSD(T) predict the monocyclic ground state structures, in a qualitative agreement with Mk-MRCCSD (Figure 2.2b). For CCSD the bicyclic structure was obtained, with a very short distance between the carbon atoms in the meta position (r_e (C₂-C₆) = 1.556 Å, Table 2.3 and Figure 2.2a). The failure of CCSD at predicting the correct ground state structure for *m*-benzyne has been demonstrated by Smith, Crawford, and Cremer.¹⁴¹ For ODC-12 and CCSD(T), the r_e (C₂-C₆) values are 2.101 and 2.043 Å, respectively, with deviations of ~ 0.09 and 0.03 Å compared to Mk-MRCCSD (r_e (C₂-C₆) = 2.014 Å).



Figure 2.2: Optimized structures of *m*-benzyne computed using the ODC-12, CCSD, CCSD(T), and Mk-MRCCSD methods with the cc-pCVTZ basis set. Only the distance between two carbon atoms in the meta position is shown ($r_e(C_2-C_6)$), in angstroms).

An important characteristic of the thermodynamic stability of singlet carbenes, such as *m*-benzyne, is the singlet-triplet adiabatic excitation energy ($\Delta E_{\rm ST}$). For *m*-benzyne, the experimental $\Delta E_{\rm ST}$ has been reported.¹⁴³ Subtracting the zero-point vibrational contribution,⁵⁵ the experimental $\Delta E_{\rm ST} = 20.3 \pm 0.3$ kcal mol⁻¹. CCSD(T) and Mk-MRCCSD predict $\Delta E_{\rm ST}$ values of 20.7 and 21.0 kcal mol⁻¹, respectively, while CCSD underestimates the singlet-triplet energy by a factor of 2 ($\Delta E_{\rm ST} = 9.7$ kcal mol⁻¹). The ODC-12 method shows better performance compared to CCSD, with $\Delta E_{\rm ST} = 16.7$ kcal mol⁻¹. The ODC-12 natural orbitals provide information about the extent of the *m*-benzyne diradical character. Figure 2.3 shows the plots of the (11*a*₁) and (7*b*₂) natural orbitals of *m*-benzyne computed at the ODC-12/cc-pCVTZ optimized geometry. The corresponding natural occupation numbers are (11*a*₁)^{1.70} (7*b*₂)^{0.28}, indicating the significant diradical character of *m*-benzyne.

Table 2.3: Equilibrium structural parameters for the singlet ground state of *m*-benzyne computed using the ODC-12, CCSD, CCSD(T), and Mk-MRCCSD methods with the cc-pCVTZ basis set. The bond lengths (r_e) are in angstroms, and the bond angles (θ_e) are in degrees. The adiabatic singlet-triplet excitation energy $\Delta E_{\rm ST}$ is reported in kcal mol⁻¹. The numbering of atoms is shown in Figure 2.2.

Coordinate	CCSD	$\operatorname{CCSD}(T)$	ODC-12	Mk-MRCCSD ^a
$r_{\rm e} ({\rm C_2 - C_6})$	1.556	2.043	2.101	2.014
$r_{\rm e} ({\rm C}_1 - {\rm C}_2)$	1.345	1.368	1.370	1.359
$r_{\rm e} ({\rm C}_2 - {\rm C}_3)$	1.379	1.375	1.373	1.370
$r_{\rm e} ({\rm C}_3 - {\rm C}_4)$	1.406	1.400	1.398	1.395
$r_{\rm e} ({\rm C_1-H})$	1.079	1.077	1.075	1.075
$r_{\rm e} ({\rm C_3-H})$	1.076	1.081	1.080	1.079
$r_{\rm e} (C_4 - H)$	1.083	1.085	1.083	1.083
$\theta_{e}(C_2 - C_1 - C_6)$	70.7	96.7	100.2	95.6
$\theta_{e}(C_{1}-C_{2}-C_{3})$	160.9	138.0	135.2	138.9
$\theta_{e}(C_2 - C_3 - C_4)$	107.8	116.9	117.4	116.5
$\theta_{e}(C_{3}-C_{4}-C_{5})$	111.8	113.7	114.7	113.6
$\theta_{\rm e}({\rm C}_2 - {\rm C}_3 - {\rm H})$	126.2	120.7	120.6	120.9
0 /				
$\Delta E_{\rm ST}$	9.7^{b}	20.7^{b}	16.7	21.0^{b}

^a Reference 139.

^b Reference 142. Geometries were optimized at the RHF-CCSD(T)/cc-pVTZ and ROHF-UCCSD(T)/cc-pVTZ levels of theory for the singlet and triplet state, respectively.



Figure 2.3: (a) $11a_1$ and (b) $7b_2$ natural orbitals and occupations for the singlet ground state of *m*-benzyne computed using the ODC-12 method with the cc-pCVTZ basis set.
2.5.4 2,6-pyridyne

In this section we consider 2,6-pyridyne (C₅H₃N), a N-substituted parent compound of *m*benzyne (Figure 2.4). Similarly to *m*-benzyne, the 2,6-pyridyne wave function is dominated by two determinants $|\Phi_1\rangle = |...(11a_1)^2(7b_2)^0\rangle$ and $|\Phi_2\rangle = |...(11a_1)^0(7b_2)^2\rangle$, which favor the bicyclic and monocyclic ground state geometries, respectively. At the Mk-MRCCSD level of theory, mono- and bicyclic minima on the 2,6-pyridyne potential energy surface have been reported.^{140,144} However, geometry optimization using CCSD(T) only results in the monocyclic structure.¹⁴⁴ It has been suggested that the Mk-MRCCSD bicyclic geometry is an artifact of theory, due to the lack of triple excitations.¹⁴⁵



Figure 2.4: Optimized structures of (a) bicyclic 2,6-pyridyne and (b) monocyclic 2,6-pyridyne computed using the ODC-12, CCSD, CCSD(T), and Mk-MRCCSD methods with the cc-pCVTZ basis set. For the CCSD(T) method, there is no bicyclic stationary point. Only the distance between two carbon atoms in the meta position is shown (r_e (C₂-C₆), in angstroms).

Table 2.4 and Figure 2.4 show the CCSD and ODC-12 optimized geometries for 2,6pyridyne, along with CCSD(T) and Mk-MRCCSD results from Ref. 144. Both CCSD and ODC-12 locate two minima on the C_5H_3N potential energy surface, corresponding to the bicyclic and monocyclic structures. For the bicyclic structure, the distance between the carbon atoms in the meta position optimized using the two levels of theory are similar (r_e (C_2-C_6) = 1.478 and 1.518 Å, respectively) and are close to that of Mk-MRCCSD (1.483 Å, Figure 2.4a). For the monocyclic structure, the CCSD method predicts a much smaller $r_{\rm e}$ (C₂-C₆) distance compared to Mk-MRCCSD (1.818 versus 2.017 Å, respectively), while the ODC-12 optimization results in a larger $r_{\rm e}$ (C₂-C₆) = 2.094 Å (Figure 2.4b). The relative energies of the two geometries ($\Delta E = E_{\rm mono} - E_{\rm bi}$) computed at four levels of theory are shown in Table 2.4. The ODC-12 and Mk-MRCCSD methods energetically favor the monocyclic structure with ΔE values of -3.6 and -7.2 kcal mol⁻¹, while CCSD favors the bicyclic structure with a positive ΔE of 1.8 kcal mol⁻¹.

Table 2.4: Equilibrium structural parameters for the monocylic and bicyclic structures of 2,6-pyridyne computed using the ODC-12, CCSD, CCSD(T), and Mk-MRCCSD methods with the cc-pCVTZ basis set. The bond lengths (r_e) are in angstroms, and the bond angles (θ_e) are in degrees. The energy difference between the two structures $\Delta E = E_{\text{mono}} - E_{\text{bi}}$ is also reported (in kcal mol⁻¹). The numbering of atoms is shown in Figure 2.4.

	Coordinate	CCSD	$CCSD(T)^{a}$	ODC-12	Mk-MRCCSD ^a
Monocyclic					
	$r_{\rm e} \; ({\rm C}_2 - {\rm C}_6)$	1.818	2.014	2.094	2.017
	$r_{\rm e} (N_1 - C_2)$	1.331	1.347	1.337	1.336
	$r_{\rm e} \; ({\rm C}_2 - {\rm C}_3)$	1.373	1.380	1.378	1.374
	$r_{\rm e} ({\rm C}_3 - {\rm C}_4)$	1.394	1.396	1.394	1.391
	$r_{\rm e} \ (C_3 - H)$	1.077	1.080	1.079	1.078
	$r_{\rm e} \ ({\rm C}_4 - {\rm H})$	1.084	1.086	1.083	1.083
	$\theta_{e}(C_2 - N_1 - C_6)$	86.2	96.8	103.2	98.0
	$\theta_{e}(N_{1}-C_{2}-C_{3})$	146.9	138.1	133.8	137.5
	$\theta_{e}(C_2-C_3-C_4)$	114.5	117.0	117.1	116.8
	$\theta_{e}(C_{3}-C_{4}-C_{5})$	110.9	112.9	115.1	113.5
	$\theta_{\rm e}({\rm C}_2 - {\rm C}_3 - {\rm H})$	120.7	119.5	120.1	119.8
Bicyclic					
	$r_{\rm e} \; ({\rm C_2 - C_6})$	1.478		1.518	1.483
	$r_{\rm e} ({\rm N}_1 - {\rm C}_2)$	1.337		1.340	1.337
	$r_{\rm e} ({\rm C}_2 - {\rm C}_3)$	1.380		1.380	1.380
	$r_{\rm e} ({\rm C}_3 - {\rm C}_4)$	1.411		1.412	1.411
	$r_{\rm e} ({\rm C_3-H})$	1.075		1.077	1.075
	$r_{\rm e} ({\rm C}_4 - {\rm H})$	1.084		1.084	1.084
	$\theta_{e}(C_2 - N_1 - C_6)$	67.1		69.0	67.4
	$\theta_{e}(N_{1}-C_{2}-C_{3})$	164.6		162.6	164.3
	$\theta_{e}(C_2 - C_3 - C_4)$	105.9		107.2	106.1
	$\theta_{e}(C_{3}-C_{4}-C_{5})$	111.9		111.3	111.8
	$\theta_{\rm e}({\rm C}_2 - {\rm C}_3 - {\rm H})$	127.2		126.2	127.0
ΔE		+1.8		-7.2	-3.6

^a Reference 144.

Figure 2.5 shows the plots of the ODC-12 natural orbitals for the mono- and bicyclic 2,6-pyridyne structures. For the bicyclic geometry, the ODC-12 natural occupations are $(11a_1)^{1.90} (7b_2)^{0.08}$, indicating nearly single-reference character of the wavefunction. The optimized monocyclic geometry exhibits a significant two-determinant character of the wavefunction with natural orbital configuration of $(11a_1)^{1.50} (7b_2)^{0.49}$. These results suggest that the monocyclic 2,6-pyridyne exhibits noticeably larger diradical character than *m*-benzyne.



Figure 2.5: $11a_1$ and $7b_2$ natural orbitals and occupations for the singlet ground state of (a,b) bicyclic 2,6-pyridyne and (c,d) monocyclic 2,6-pyridyne computed using the ODC-12 method with the cc-pCVTZ basis set.

2.5.5 Twisted Ethylene

Twisted ethylene (C_2H_4) is one of the most well-known multireference problems in quantum chemistry.^{146–148} At the D_{2d} -symmetry geometry with 90° torsional angle, the C_2H_4 singlet ground state electronic wave function has contributions from two equally important determinants originating from the degeneracy of its frontier π -molecular orbitals. As a consequence, accurate description of the C₂H₄ torsional potential energy curve (PEC) requires multireference treatment,¹⁴⁹ although it has been shown that single-reference spin-flip approaches can be similarly effective.¹⁵⁰

Figure 2.6 shows the C_2H_4 torsional PEC computed using the CCSD, CCSD(T), and ODC-12 levels of theory (cc-pCVTZ basis set). The results of these single-reference methods are compared to MRCI+Q computed using a CASSCF reference. The CASSCF active space comprised two electrons in two frontier π -orbitals. The C–H and C–C bond lengths, as well as the H–C–C bond angle, were optimized while constraining the molecular geometry to D_2 symmetry. The PEC computed using the CCSD method exhibits a sharp unphysical cusp at 90°, with a large error (~ 20 kcal mol⁻¹) in the potential energy barrier compared to MRCI+Q. At the CCSD(T) level of theory, the C_2H_4 torsional PEC still exhibits the cusp but shows much better agreement with MRCI+Q and a 6 kcal mol⁻¹ error at 90°. The performance of ODC-12 is similar to CCSD(T) for values of the dihedral angle from 0° to 85°. In the range between 85° and 90° the ODC-12 energy decreases, which results in the unphysical dip on the PEC at 90°. While the overall performance of ODC-12 in describing the C_2H_4 torsional PEC is superior to CCSD, the unphysical shape of the ODC-12 PEC demonstrates the inability of this method to produce reliable results in systems with degenerate frontier molecular orbitals.



Figure 2.6: Potential energy of ethylene (C_2H_4) as a function of the H–C–C–H torsional angle computed using the CCSD, CCSD(T), MRCI+Q, and ODC-12 methods (cc-pCVTZ basis set). The C–H and C–C bond lengths, as well as the H–C–C bond angle were optimized while constraining the molecular geometry to D_2 symmetry. For each method, energies were computed relative to the energy of the D_{2h} global minimum structure. For the MRCI+Q, the CASSCF reference wave function with two electrons in two orbitals was used. A level shift of 0.09 au was used for the ODC-12 computations.

2.5.6 DOUBLE-BOND MIGRATION IN CYCLOBUTADIENE

Finally, we analyze the performance of DCT in describing the potential energy barrier for the double-bond migration in cyclobutadiene (C_4H_4). The ground state of C_4H_4 has a rectangular structure with two single C–C bonds ($R_s = 1.56$ Å, CCSD(T)/cc-pCVTZ) and two double C–C bonds ($R_d = 1.34$ Å). Symmetric deformation of the molecule by simultaneously stretching the double bonds and shortening the single bonds results in a square-planar transition state, which has multireference character.^{151–154} To compute the PEC for the double-bond migration in C_4H_4 , we follow the procedure outlined in Ref. 153. In short, the potential energy is computed along the coordinate R, which represents one of the two unique C–C bond lengths. The other C–C bond length is set to $R' = (2R_0 - R)$, where $R_0 = 1.4668$ Å. The C–H bond length and the H–C–C bond angle were kept fixed at 1.079 Å and 135°, respectively.

Figure 2.7 shows the PEC for the C_4H_4 double-bond migration computed using the CCSD, CCSD(T), ODC-12, and MRCI+Q methods with the cc-pCVTZ basis set. The MRCI+Q PEC exhibits two minima at R = 1.36 Å and 1.59 Å, as well as a smooth barrier at R = 1.467 Å. All three single-reference methods produce a characteristic cusp at R = 1.467 Å, which corresponds to the point of the exact degeneracy of the frontier molecular orbitals, according to CASSCF with two electrons in two active orbitals. The ODC-12 and CCSD(T) show similar performance in describing the PEC, overestimating the height of the barrier by ~ 5-7 kcal mol⁻¹. The CCSD method exhibits much worse stability with respect to increasing multireference effects, giving rise to ~ 12 kcal mol⁻¹ error relative to MRCI+Q.



Figure 2.7: Potential energy of cyclobutadiene (C_4H_4) for the double-bond migration reaction coordinate computed using the CCSD, CCSD(T), MRCI+Q/CAS(2,2), and ODC-12 methods (cc-pCVTZ basis set). For each method, energies were computed relative to the energy of the D_{2h} global minimum structure. The reaction coordinate R is defined as one of the two unique C-C bond lengths. The other C-C bond length R' is set to $R' = 2R_0 - R$, where $R_0 = 1.4668$ Å. The C-H bond length and the H-C-C bond angle were fixed at 1.079 Å and 135°, respectively. A level shift of 0.1 au was used for the ODC-12 computations.

2.6 Discussion and Conclusions

Density cumulant functional theory $^{41-45,102}$ (DCT) has recently emerged as a promising method for describing dynamic correlation in molecules. Among its attractive features are (i) size-consistency and size-extensivity; (ii) direct access to relaxed density matrices and molecular properties; (iii) efficient analytic gradients; and (iv) high-order correlation effects in the description of the one-particle density matrix. While the DCT equations are non-linear, as in coupled cluster theory, the non-linearities are hidden in the efficient tensor contractions, which simplifies the computer implementation and parallelization. Our recent benchmark study 105 has demonstrated that the DC-12 and ODC-12 variants of DCT exhibit intermediate performance between that of CCSD and CCSD(T). In particular, for the thermodynamic properties of open-shell systems, the results of ODC-12 have been shown competitive with CCSD(T). 105

In this study, we investigated performance of the DC-12 and ODC-12 methods for systems with significant multireference character of the electronic wave function. An important assumption in DCT is that the one-particle density matrix can be decomposed into a meanfield contribution and a correlation component. Such mean-field contribution corresponds to a density matrix of a single Slater determinant. Thus, the DCT methods are intrinsically single-reference. Despite this, in the present study we have demonstrated that the DC-12 and ODC-12 methods can tolerate a significant two-configurational character of the wave function. In particular, we have shown that for the multireference Be₂, *m*-benzyne, and 2,6-pyridyne molecules the DCT methods make qualitatively correct predictions about the ground-state energetics and equilibrium structures, while the CCSD method fails, underestimating multireference effects. This is particularly encouraging, since the inadequate performance of CCSD in these systems has often been attributed to the lack of triple excitations,^{126,130,141} while the DC-12 and ODC-12 methods do not explicitly describe connected three-electron correlation effects and are much more efficient than CCSD(T).

Nevertheless, as with other single-reference methods, DCT has limitations. When the frontier molecular orbitals of a system become near-degenerate, the results of the ODC-12 method may become unreliable. We have demonstrated that ODC-12 is unable to provide reasonable descriptions of the potential energy barriers for twisting of ethylene and doublebond migration in cyclobutadiene. Thus, we emphasize that the ODC-12 method is not suitable for heavily multireference problems with large contributions of more than one Slater determinant, especially if highly accurate results are desired. In such cases, the appropriate multireference methods should be used. Conveniently, the appearance of multireference effects in DCT can be diagnosed by analyzing the natural orbital occupations, which are readily available at the end of the energy computation. We are planning a multireference generalization of DCT that allows for a balanced description of static and dynamic correlation.

2.7 Acknowledgments

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Chapter 3

Conical Intersections and Low-Lying Electronic States of Tetrafluoroethylene*

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3.1 Abstract

The low-lying electronic states of tetrafluoroethylene (C_2F_4) are characterized theoretically for the first time using equation-of-motion coupled cluster theory (EOM-CCSD), complete active space self-consistent field (CASSCF) theory, and second-order perturbation theory (CASPT2). Computations are performed for vertical excitation energies, equilibrium geometries, minimum-energy conical intersections, and potential energy curves along three geometric coordinates: (1) twisting of the F-C-C-F dihedral angle, (2) pyramidalization of the CF₂ group, and (3) migration of a fluorine atom resulting in an ethylidene-like (CF₃CF) structure. The results suggeset two relaxation pathways from the Rydberg-3s excited electronic state to the ground state. These relaxation pathways are discussed in conjunction with the femtosecond photoionization spectroscopy results of Trushin et al. [*ChemPhysChem* **2004**, *5*, 1389].

3.2 INTRODUCTION

Tetrafluoroethylene (C_2F_4) is used primarily in the production of fluoropolymers^{155,156} and is involved in plasma etching of silicon dioxide.^{157,158} Due to its small size, C_2F_4 is also a good model system for studying photophysical processes (e.g., photodissociation) that involve alkenes with electronegative substituents. Unlike C_2H_4 , C_2F_4 has a relatively weak C-C bond and undergoes thermal dissociation to form singlet CF_2 .^{159–162} In addition, C_2F_4 undergoes photodissociation upon exposure to ultraviolet (UV) radiation, which produces both singlet and triplet CF_2 .^{163–165} A key feature of C_2F_4 that affects its chemistry is the π -bond dissociation energy (\approx 52 kcal mol⁻¹),^{166,167} which is smaller than that of C_2H_4 (64–65 kcal mol⁻¹).¹⁶⁷ Based on ab initio computations, Wang and Borden¹⁶⁷ concluded that the weakness of the π bond is due to the preference of fluorinated organic radicals for pyramidal geometries about the C nuclei.^{168,169} In fact, the geometry optimization of the triplet state of C_2F_4 results in a pyramidal distortion of each CF_2 group.¹⁷⁰

The excited states of C_2F_4 have been much less studied than those of $C_2H_4^{64,146,147,149,171,172}$ and $C_2H_2F_2$.¹⁷³ The electronic spectrum of C_2F_4 has been investigated using UV spectroscopy^{174,175} and electron-impact spectroscopy.^{175,176} Arulmozhiraja and co-workers predicted the vertical excitation energies for several singlet and triplet excited states of C_2F_4 by using symmetry-adapted cluster configuration interaction theory (SAC-CI).¹⁷⁷ Winstead and McKoy computed the cross sections for elastic and inelastic collisions of low-energy electrons with C_2F_4 .¹⁷⁸ Although the geometry of the lowest-energy triplet state of C_2F_4 has been optimized,^{167,170} we are not aware of any computational study of the singlet excited states of C_2F_4 away from the ground-state equilibrium geometry.

Trushin and co-workers studied the excited-state dynamics of C_2F_4 by using femtosecond pump-probe photoionization spectroscopy.¹⁷⁹ They suggested that the excitation to the Rydberg-3s (R) electronic state at 197 nm is followed by relaxation to the ground state (N) in two consecutive steps. In the first step, the excitation relaxes to an intermediate valence π - π^* (V) state accompanied by significant C-C bond stretching and twisting about the C-C bond within 29 fs. This process is then followed by the slower (118 fs) relaxation from the V state to the vibrationally hot ground state together with further twisting, pyramidalization of the CF₂ group, and, possibly, migration of an F atom. Trushin et al. suggested that the C_2F_4 molecule in the hot ground state has enough excess energy to dissociate or undergo intersystem crossing to the lowest triplet state, from which dissociation is also possible.

Herein, we apply equation-of-motion coupled-cluster theory (EOM-CCSD), and complete active space self-consistent field (CASSCF) and second-order perturbation theory (CASPT2) to characterize the low-lying electronic states of C_2F_4 . We present the vertical excitation energies and explore potential energy surfaces for the key electronic states along the three important geometric coordinates: torsion, pyramidalization, and F migration. We conclude by discussing possible relaxation pathways of C_2F_4 from the excited R state to the ground state in the light of our computational results and the experimental results of Trushin and co-workers.¹⁷⁹



Figure 3.1: C_2F_4 geometric coordinates employed in the present study: (a) torsion coordinate τ defined as the $F_3-C_1-C_2-F_6$ dihedral angle; (b) pyramidalization coordinate β defined as the angle between the C_1-C_2 bond and the $F_5-C_2-F_6$ group; (c) F-migration coordinate θ defined as the $C_2-C_1-F_3$ bond angle.

3.3 Methods

To compute the ground state C_2F_4 equilibrium geometry, we employed coupled-cluster theory with single and double excitations (CCSD).^{180,181} For the geometry optimization of the Rydberg-3s (R) excited state, equation-of-motion CCSD for electronic excitations method (EOM-EE-CCSD)^{59,60,182} implemented in the CFOUR software package¹¹² was used. For the structures along the torsional coordinate, however, the EOM-EE-CCSD method predicted an unphysical shape of the potential energy curves (PECs) due to a poor description of the multideterminant nature of the wavefunction. It has been shown that the spin-flip EOM-CCSD method (EOM-SF-CCSD)¹⁸³ adequately describes the C-C π -bond breaking along the torsional coordinate in C_2H_4 .^{60,184} We therefore employed the EOM-SF-CCSD method implemented in the Q-CHEM software package^{185,186} to compute the PECs of the low-lying excited states away from the ground-state equilibrium geometry. For each PEC, the EOM-SF-CCSD energy points were computed at the optimized geometries that were obtained by fixing the coordinate of interest (e.g., torsion, pyramidalization, or F-migration) while minimizing the energy with respect to all other symmetry-adapted coordinates, by using the complete active space self-consistent field theory (CASSCF) with second-order perturbative corrections for the dynamic correlation (CASPT2).

The CASSCF and CASPT2 computations^{47,50,51,187,188} were performed using the MOL-PRO software package.¹¹⁴ For CASPT2 various active spaces were used denoted as CASPT2-CAS(n,m) in which n is the number of electrons and m is the number of orbitals in the active space. To find the minimum-energy conical intersections (MECIs), we employed the state-averaged CASSCF labeled as SA(N)-CAS(n,m), in which N is the number of states averaged in the CASSCF calculation. All SA(N)-CAS(n,m) calculations were performed in C_1 symmetry.

In all computations the 6-311(2+)G^{*} basis set¹⁸⁹ was used, which can be represented as the conventional 6-311G^{*} basis set with two additional sets of diffuse s and p functions on each C ($\zeta_1 = 0.043800$, $\zeta_2 = 0.0131927711$) and F ($\zeta_1 = 0.107600$, $\zeta_2 = 0.0324096386$) atom. The six core molecular orbitals were frozen in all correlated computations.

3.4 Results

3.4.1 VERTICAL EXCITATION ENERGIES

Table 3.1 shows the vertical excitation energies (ΔE) for 11 singlet electronic excited states computed at the EOM-EE-CCSD level of theory with the 6-311(2+)G^{*} and d-aug-cc-pVTZ basis sets using the CCSD/6-311(2+)G^{*} optimized ground-state geometry (Figure 3.2a). For the EOM-EE-CCSD/6-311(2+)G^{*} method, the excitation energies corrected by the N-state zero-point vibrational energy (ZPVE) are also presented, denoted as ΔE_v . In addition, Table 3.1 includes previously reported results from UV spectroscopy^{174,175} and SAC-CI computations.¹⁷⁷ We characterize each state with the appropriate D_{2h} term symbol and a short label describing the nature of the electronic transition (e.g., π - σ^*). We also use N and R labels to denote the ground state and the Rydberg-3s excited state, respectively, similarly to the Mulliken notation used for C₂H₄.¹⁴⁶

Table 3.1: Vertical excitation energies ΔE (eV) for 11 low-lying singlet electronic excited states of C₂F₄ computed using the EOM-EE-CCSD method with the 6-311(2+)G^{*} and d-aug-cc-pVTZ basis sets. For the EOM-EE-CCSD/6-311(2+)G^{*} method, the excitation energies corrected by the N-state zero-point vibrational energy ΔE_v (eV) are also reported, as well as the corresponding oscillator strengths $[f \times 10^3]$ in brackets. Previously reported SAC-CI/aug-cc-pVTZ^{**} and experimental results are also shown. The lowest triplet state (T, 1³B_{1u}) has $\Delta E = 5.04$ eV at the EOM-SF-CCSD/6-311(2+)G^{*} level of theory.

State	Assignment	SAC-CI/ EOM-EE-CCSD/		EOM-EE-CCSD/		Experiment
		aug-cc-pVTZ ^{**a} d-aug-cc-pVTZ ^b		$6-311(2+)G^{*b}$		
		ΔE	ΔE	ΔE	$\Delta E_{\rm v}$	
$1^{1}A_{g}(N)$						
$1 {}^{1}B_{3u}$ (R)	π -3s/ σ^*	7.09	6.90	6.91	6.31 [19.8]	$6.37^{\rm c}, \ 6.40^{\rm d}$
$1 \ {}^{1}B_{1g}$	π - σ^*	7.01	7.21	7.27	$6.67 \ [0.0]$	
$1 \ {}^{1}B_{2g}$	π -3p _{σz}	8.24	8.04	8.04	7.44 [0.0]	$8.01^{ m c,d}$
$2 \ ^{1}A_{g}$	π -3p $_{\pi}$	8.24	8.17	8.12	$7.52 \ [0.0]$	
$2 {}^{1}B_{1g}$	π -3p _{σy}	8.76	8.71	8.70	$8.10 \ [0.0]$	
$2 {}^{1}B_{3u}$	π -3d $_{\sigma}$	9.03	8.94	8.94	8.34 [21.5]	$8.64^{ m c,d}$
$1 \ {}^{1}B_{1u}$	π -3d $_{\pi}/\pi^*$	9.19	9.02	9.09	8.49 [138.9]	8.39^{d}
$1 \ ^{1}A_{u}$	π -3d $_{\sigma}$	9.30	9.21	9.19	8.59[0.0]	
$2 {}^{1}B_{1u}$	π - π^*	9.41	9.18	9.20	8.60 [365.9]	$8.89^{\circ}, 9.02^{\circ}$
$3 \ {}^{1}B_{3u}$	π -3d $_{\sigma}$	9.29	9.23	9.29	8.69 [2.8]	
$1 \ {}^{1}B_{2u}$	π -3d $_{\pi}$	9.22	9.26	9.57	8.97 [1.8]	

^a Reference 177. Excitation energies were computed using the experimental geometry. Two additional sets of diffuse s, p, and d functions (**) on each atom were added to the aug-cc-pVTZ basis set.

^b Present work. Excitation energies were computed using the CCSD/6-311(2+)G* optimized ground-state geometry (Figure 3.2a).

^c Reference 173. UV spectroscopy.

^d Reference 175. UV spectroscopy.

The best agreement with the available experiments is demonstrated by the EOM-EE-CCSD/6-311(2+)G* and EOM-EE-CCSD/d-aug-cc-pVTZ results (Table 3.1). Both levels of theory yield similar ΔE excitation energies, differing by less than 0.1 eV from each other for 10 out of 11 computed electronic transitions. Previously reported SAC-CI computations¹⁷⁷ perform significantly worse relative to UV experiment, with ΔE errors larger than



Figure 3.2: Optimized C_2F_4 geometries for the (a) ground state N (D_{2h} symmetry) computed at the CCSD level of theory, (b) lowest-energy triplet state T (C_2) computed using CCSD, and (c) Rydberg-3s singlet state R (D_{2h}) computed using EOM-EE-CCSD. The 6-311(2+)G* basis set was used. All bond lengths are in Å, angles are in degrees. The β coordinate is the out-of-plane angle between the C-C bond and the CF₂ plane. The τ_{ijkl} coordinate is the dihedral angle between the *i*-*j*-*k* and *j*-*k*-*l* planes.

those of EOM-EE-CCSD by approximately 0.2 eV. Correcting for the zero-point vibrational effects at the EOM-EE-CCSD/6-311(2+)G* level of theory reduces the errors relative to UV spectroscopy experiments for most of the electronic transitions. Particularly, the $\Delta E_{\rm v}$ excitation energies for the R (6.31 eV) and V (8.60 eV) states deviate by only about 0.1 eV and 0.3 eV relative to those obtained from UV spectroscopy (6.40 and 8.39 eV)^{174,175}. For the R state, the excitation energy from electron-impact spectroscopy¹⁷⁶ (6.62 eV) is closer to the computed ΔE value (6.91 eV) without the ZPVE correction.

To assess the performance of the spin-flip EOM-CCSD (EOM-SF-CCSD) method, we compared the EOM-EE-CCSD/6-311(2+)G* ΔE excitation energies with those obtained at the EOM-SF-CCSD level of theory for the ground state optimized geometry. Both methods agree closely for the four lowest-energy excited states with the corresponding EOM-SF-CCSD (EOM-EE-CCSD) ΔE excitation energies of 6.91 eV (6.91 eV) for the 1 ¹B_{3u} state, 7.16 eV (7.27 eV) for the 1 ¹B_{1g} state, 8.05 eV (8.04 eV) for the 1 ¹B_{2g} state, and 8.22 eV (8.12 eV) for the 2 ¹A_g state. For the lowest triplet state T (1 ³B_{1u}), the EOM-SF-CCSD/6-311(2+)G*

 ΔE value (5.04 eV) is in a good agreement with that obtained using the SAC-CI method (5.12 eV)¹⁷⁷ and electron-impact spectroscopy (4.68 and 4.79 eV).^{175,176}

Overall, our results suggest that the EOM-EE-CCSD and EOM-SF-CCSD methods in combination with the 6-311(2+)G^{*} or d-aug-cc-pVTZ basis sets are appropriate levels of theory for the description of the low-lying excited electronic states of C_2F_4 at the ground-state equilibrium geometry. As the excitation energies computed with the compact 6-311(2+)G^{*} basis set are similar to those computed using the larger d-aug-cc-pVTZ basis set, we employ the former basis set to study the low-lying excited states away from the equilibrium geometry.

3.4.2 Optimized Geometries

Figure 3.2a shows the equilibrium geometry of the C_2F_4 ground state N optimized at the CCSD level of theory. The D_{2h} symmetry structure has a C–C bond length r_e (C–C) = 1.325 Å, C–F bond lengths r_e (C–F) = 1.316 Å, and F–C–C bond angles \angle (F–C–C) = 123.3°, which are in good agreement with the recently reported semiexperimental r_e structural parameters of 1.3236 ± 0.0037 Å, 1.3111 ± 0.0023 Å, and 123.3 ± 0.3°, respectively.¹⁹⁰

The equilibrium geometry of the lowest-energy triplet state T optimized using the CCSD method is shown in Figure 3.2b. The geometry optimization results in a twisted C_2 -symmetry structure with each CF₂ group pyramidalized around a carbon atom. The C-C bond is much longer (1.495 Å) than that of the N state (1.325 Å), whereas the lengths of the C-F bonds are just slightly increased (1.328 and 1.320 Å) relative to the ground state distance (1.316 Å). The C-C bond makes an out-of-plane angle (β , Figure 3.2b) of 42.1° with each CF₂ group. There are two unique F-C-C angles of 115.5° and 114.2° with the C-F bonds. These structural parameters are in a good agreement with the MP2/6-31G* optimized triplet C₂F₄ geometry reported by Borisov.¹⁷⁰

The Rydberg-3s (R)-state equilibrium geometry computed at the EOM-EE-CCSD level of theory is presented in Figure 3.2c. The optimized structure has D_{2h} symmetry with r_{e} (C-C) = 1.395 Å, r_e (C-F) = 1.267 Å, and $\angle (F-C-C) = 120.1^{\circ}$. On comparison with the N-state geometry (Figure 3.2a), the R state has a longer C-C bond (by 0.070 Å), shorter C-F bonds (by 0.049 Å), and smaller F-C-C bond angles (by 3.2°). The equilibrium structure of the R state is in close agreement with the CCSD/6-311(2+)G* optimized D_{2h} geometry of the C₂F₄ cation, which has r_e (C-C) = 1.417 Å, r_e (C-F) = 1.260 Å, and $\angle (F-C-C) = 120.7^{\circ}$, with a noticeable difference only for the C-C bond length (0.022 Å).

3.4.3 POTENTIAL ENERGY CURVES AND MINIMUM ENERGY CONICAL INTERSECTIONS

Torsion

Figure 3.3a shows the energy as a function of the F-C-C-F dihedral angle τ (Figure 3.1a) for five low-lying electronic states of C_2F_4 computed at the EOM-SF-CCSD level of theory. For each value of τ , the rest of the C_2F_4 geometry was optimized for the R state at the CASPT2-CAS(2,2) level of theory constrained to D_2 symmetry. The active space included the C-C π -bond orbital (6b₃) and the 3s orbital of C (8a). The optimal values of the C-C and C-F bond lengths as well as the F-C-C bond angles as functions of τ are shown in Figure 3.4. At $\tau = 0^\circ$, the optimized values of r_e (C-C) = 1.403 Å, r_e (C-F) = 1.268 Å, and \angle (F-C-C) = 120.1° are in close agreement with the R-state equilibrium geometry (3.2c). In addition to the Mulliken labels (N, T, and R), each electronic state in Figure 3.3a is denoted with the appropriate D_2 symmetry term symbol. The EOM-SF-CCSD energies are relative to the EOM-SF-CCSD/6-311(2+)G* energy of the N state computed at the N-state CCSD/6-311(2+)G* optimized geometry.

Upon twisting of the dihedral angle τ from 0° to 90° (Figure 3.3a), the energy of the N state increases by approximately 3 eV and the energy of the R state increase by about 2 eV, whereas the energies of the T and 1 ¹B₁ states decrease by about 1.5 eV. Both N and R states have minima at $\tau = 0^{\circ}$ on their potential energy curves (PECs), in agreement with their equilibrium structures (Figures 3.2a and 3.2c). For the T and 1 ¹B₁ states, the PECs



Figure 3.3: Energy (in eV) of several low-lying electronic states of C_2F_4 as a function of the F-C-C-F dihedral angle τ computed at the EOM-SF-CCSD/6-311(2+)G^{*} level of theory. Potential energy curves for only five lowest-energy states are shown out of the 16 electronic states investigated here. Energies are relative to the EOM-SF-CCSD/6-311(2+)G^{*} energy of the N-state computed at the N-state CCSD/6-311(2+)G^{*} optimized geometry. (a) For each value of τ , constrained geometry optimization under the D_2 symmetry was performed for the R state at the CASPT2-CAS(2,2)/6-311(2+)G^{*} level of theory. (b) Other coordinates are fixed at those for the N-state CCSD/6-311(2+)G^{*} optimized geometry (Figure 3.2a).

exhibit minima at $\tau = 90^{\circ}$ for the constrained D_2 geometry optimization. For τ between 0 and 15°, the 1 ¹B₁ state PEC is nearly flat due to an avoided crossing of this state with the higher-lying 2 ¹B₁ state originating from the 2 ¹B_{1u} state of the planar C₂F₄ (Table 3.1). The avoided crossing changes the character of the 1 ¹B₁ state wavefunction, which becomes dominated by the π - π * excitation in the 25 \leq 90° range. We will refer to 1 ¹B₁ as the V state in the rest of our discussion due to its similarities with the V state of C₂H₄ for highly distorted geometries. The 2 ¹A state PEC exhibits a maximum at $\tau \approx 50^{\circ}$, which corresponds to an avoided crossing with the higher-energy ¹A state. In the range of 0° $\leq \tau \leq 50^{\circ}$ the 2 ¹A state has predominantly Rydberg-3p character. However, for 55° $\leq \tau \leq 90^{\circ}$ its wavefunction is dominated by the $(\pi)^2 \rightarrow (\pi^*)^2$ double excitation, similarly to the Z state of C₂H₄. We will therefore denote 2 ¹A as the Z state. Near $\tau = 90^{\circ}$, the PECs of the N and T states as well as the V and Z states become nearly degenerate (Figure 3.3a), a feature also exhibited for C_2H_4 .¹⁴⁷

Figure 3.4 demonstrates that the twisting of the dihedral angle τ does not significantly affect the R-state geometry. The major effect is observed for the C–C bond length, which increases by approximately 0.05 Å from 0° to 90°. For the constrained R-state optimized geometry (Figure 3.3a), the R and V PECs intersect at $\tau_{\rm CI} \approx 45^{\circ}$ (CI=conical intersection) with the energy of 6.9 eV, relative to the N-state equilibrium. If computed using the frozen Nstate equilibrium structural parameters (Figure 3.3b), this intersection is found at $\tau_{\rm CI} \approx 22^{\circ}$, which indicates a strong dependence of $\tau_{\rm CI}$ on the C₂F₄ structure. We computed the geometry of the R–V MECI at the SA(4)-CAS(2,4) level of theory (Figure 3.5a) without any constraints on the molecular symmetry. The MECI has D_2 symmetry with $r_{\rm e}$ (C–C) = 1.381 Å, $r_{\rm e}$ (C–F) = 1.270 Å, and \angle (F–C–C) = 124.0°. The optimized dihedral angle $\tau_{\rm CI}$ is 34.6°, which is bounded by the $\tau_{\rm CI}$ values predicted for the frozen equilibrium N and optimized R-state geometries (22° and 45°, respectively, Figures 3.3a and 3.3b). The MECI relative energy computed using the EOM-SF-CCSD method is 6.9 eV, the same as that of the R–V CI energy in Figure 3.3a.



Figure 3.4: Optimized parameters of the C_2F_4 geometry for the singlet Rydberg-3s (R) state (Figure 3.2c) as a function of the F-C-C-F dihedral angle τ computed at the CASPT2-CAS(2,2)/6-311(2+)G* level of theory. The geometry optimization was constrained to display D_2 symmetry.



Figure 3.5: Minimum-energy C_2F_4 structures on the conical intersection seam between the (a) R and V states (D_2 symmetry) computed at the SA(4)-CAS(2,4) level of theory; (b) V and N states (C_s) computed using SA(2)-CAS(2,2); and (c) V and N states (nearly C_{3v}) computed using the SA(2)-CAS(2,2) level of theory. The 6-311(2+)G* basis set was used. All bond lengths are in Å, angles are in degrees. The β coordinate is the out-of-plane angle between the C-C bond and the CF₂ plane (Figure 3.1b). The τ_{ijkl} coordinate is the dihedral angle between the *i-j-k* plane and the *j-k-l* plane.

Pyramidalization

Figure 3.6 depicts the energy as a function of the pyramidalization coordinate β for the four lowest-lying electronic states computed at the EOM-SF-CCSD level of theory. The β coordinate is defined as the out-of-plane angle between the C-C bond and a CF_2 group (Figure 3.1b). For each value of β , the constrained geometry optimization for the V state was performed under C_s symmetry using the CASPT2-CAS(2,2) method. The active space consisted of the 17a' and 8a'' orbitals. Increasing the angle β from 0° to 90° raises the energy of the Z state by approximately 3.5 eV leading to an avoided crossing at $\beta \approx 55^{\circ}$. For the V state, the pyramidalization lowers the energy by about 1 eV leading to a CI with the N state at $\beta_{\rm CI} \approx 72^{\circ}$ (3.8 eV). The geometry of the N–V MECI computed at the SA(2)-CAS(2,2) level of theory is shown in Figure 3.5b. The MECI structure has C_s symmetry with $\beta_{\rm CI}$ of 71.5°, a C–C bond length of 1.514 Å, and an EOM-SF-CCSD relative energy of 3.8 eV, in agreement with that of the N–V conical intersection in Figure 3.6. Figure 3.7 shows the optimized C_2F_4 structural parameters of the V state as a function of β . Upon pyramidalization from 0° to 90° , the C–C bond length is increased from 1.35 Å to 1.55 Å. Another noticeable change is observed for the F-C-F angle of the pyramidalized CF_2 group, which is decreased from 118° to a nearly tetrahedral value of 103° .



Figure 3.6: Energy (in eV) of the several low-lying electronic states of C_2F_4 as a function of the out-of-plane angle β formed by the C–C bond and the CF₂ group (Figure 3.1b) computed at the EOM-SF-CCSD/6-311(2+)G^{*} level of theory. Potential energy curves for only the four lowest-energy states are shown, among the six electronic states employed in the computations. For each value of β , a constrained geometry optimization under the C_s symmetry was performed for the V state at the CASPT2-CAS(2,2)/6-311(2+)G^{*} level of theory. Energies are relative to the EOM-SF-CCSD/6-311(2+)G^{*} energy of the N state computed at the N-state CCSD/6-311(2+)G^{*} optimized geometry.



Figure 3.7: Optimized parameters of the C_2F_4 geometry for the singlet V state as a function of the out-of-plane angle β formed by the C–C bond and the CF₂ group (Figure 3.1b) computed at the CASPT2-CAS(2,2)/6-311(2+)G* level of theory. The geometry optimization was constrained under the C_s symmetry.

F-Migration

To study the effect of the F-atom migration on the low-lying electronic states of C_2F_4 , we define the F-migration coordinate θ as the $C_2-C_1-F_3$ bond angle (Figure 3.1c). Figure 3.8 shows the energy as a function of θ for the N, T, V, and Z states computed at the EOM-SF-CCSD level of theory. For each value of θ , the C_2F_4 geometry was optimized for the V state constrained to C_s symmetry at the CASPT2-CAS(6,6) level of theory. The active space included the 15a'-19a' and 8a'', orbitals. In Figure 3.8, the θ value of 125° corresponds to the nearly D_{2d} -symmetric (twisted) structure. Decreasing the value of θ models the F-migration pathway under the C_s symmetry constraint.

Figure 3.8 demonstrates that the N and T states remain nearly degenerate for the range of values $75 \le \theta \le 125^{\circ}$. The near-degeneracy between these two states is lifted significantly for the C₂F₄ structures with the migrated F atom ($40 \le \theta \le 75^{\circ}$), at which the T state is lower in energy. For all of the geometries considered in this context, the Z state is noticeably higher in energy than the N, T, and V states. Interestingly, the V-state PEC is rather insensitive to the change of θ and has a barrier of approximately 0.8 eV at $\theta \approx 65^{\circ}$. The PECs of the N and V states intersect at two rather different $\theta_{\rm CI}$ values of about 79° and 39°. For $\theta_{\rm CI} \approx 39^{\circ}$, the CI point could not be reached due to convergence problems. We attempted to find the N–V MECIs starting from the geometries with $\theta_{\rm CI}$ of 79° and 40° using the SA(2)-CAS(2,2) method. For $\theta = 79^{\circ}$, the optimization results in the N–V MECI found along the pyramidalization pathway (Figure 3.5b). For $\theta = 40^{\circ}$, the computation leads to a distinct MECI structure with the migrated F atom (Figure 3.5c). Although no symmetry constraints were employed in the optimization, the N–V MECI in Figure 3.5c has nearly C_{3v} symmetry with an optimized value of $\theta_{CI} = 32.2^{\circ}$, C–C bond distance of 1.448 Å, and C–F bond lengths of 1.320 Å (CF₃ group) and 1.271 Å. The structure has an energy of 5.0 eV (at the EOM-SF-CCSD level of theory) above the ground state global minimum.



Figure 3.8: Energy (in eV) of the four low-lying electronic states of C_2F_4 as a function of the F-migration coordinate θ computed at the EOM-SF-CCSD/6-311(2+)G^{*} level of theory. The θ coordinate is defined as the $C_2-C_1-F_3$ bond angle in Figure 3.1c. Potential energy curves for only four lowest-energy states are shown among the six electronic states employed in the computation. For each value of θ , constrained geometry optimization under the C_s symmetry was performed for the V state at the CASPT2-CAS(6,6)/6-311(2+)G^{*} level of theory. Energies are relative to the EOM-SF-CCSD/6-311(2+)G^{*} energy of the N state computed at the N-state CCSD/6-311(2+)G^{*} optimized geometry.

Figure 3.9 shows the optimized C_2F_4 structural parameters as a function of θ . Decreasing the θ value from 125° to 40° results in the lengthening of a C–C bond by approximately 0.05Å, increase of the $C_2-C_1-F_4$ angle (Figure 3.1c) from 120° to about 180°, and pyramidalization around the C atom of the CF_3 group ($\beta \approx 40^\circ$).



Figure 3.9: Optimized parameters of the C_2F_4 geometry in the singlet V state as a function of the F-migration coordinate θ computed at the CASPT2-CAS(6,6)/6-311(2+)G* level of theory. The θ coordinate is defined as the $C_2-C_1-F_3$ bond angle in Figure 3.1c. The β coordinate is the out-of-plane angle formed by the C_1-C_2 bond and the $F_3-C_2-F_5$ group (Figure 3.1c). The geometry optimization was constrained under the C_s symmetry.

3.5 Discussion and Conclusions

In this work, we have characterized theoretically the low-lying electronic states of C_2F_4 using the EOM-CCSD, CASSCF, and CASPT2 methods. Our computational results demonstrate that the radiationless decay of C_2F_4 from the singlet Rydberg-3s (R) electronic state to the ground state (N) can proceed through two distinct routes summarized in Figure 3.10. Upon 6.3 eV vertical excitation to the R state (ΔE_v , Table 3.1), a C_2F_4 molecule can relax to the π - π^* valence state (V) primarily by twisting of the F-C-C-F dihedral angle (τ , Figure 3.1a) and C-C bond stretching. Although the R state has a D_{2h} equilibrium geometry, its potential surface along the torsional coordinate is rather flat for τ from 0° to 25°, for which the conical intersection (CI) between the R and V states was predicted ($\tau_{\text{CI}} \approx 22^\circ$, Figure 3.3b). The R-V MECI (Figure 3.5a) has energy of 6.3 eV at the EOM-SF-CCSD level of theory including the N-state ZPVE correction, which indicates that the R-V CI is energetically accessible.



Figure 3.10: Schematic diagram summarizing the computed C_2F_4 relaxation pathway after the excitation to the singlet Rydberg-3s (R) state. The computed EOM-SF-CCSD energies are relative to the EOM-SF-CCSD energy of the N state computed at the N-state CCSD optimized geometry corrected by the N-state zero-point vibrational energy. The 6-311(2+)G* basis set was used. The geometries of the minimum-energy conical intersections (MECIs) are shown in Figure 3.5.

Our results suggest that the C_2F_4 energy in the V state can be lowered by further motion along the torsional coordinate τ . From a twisted D_{2d} structure, CIs between the V and N states have been found along two other coordinates: pyramidalization of a CF_2 group and F-migration to a CF_3 -CF structure (β and θ , Figures 3.1b and 3.1c, respectively). Although the pyramidalization is accompanied by an additional energy lowering of about 1 eV, the migration of a F atom does not lower the V-state energy and needs to overcome an approximately 0.8 eV barrier, according to our EOM-SF-CCSD computed potential energy curve for θ (Figure 3.8). In fact, the computed relative energies for the N–V MECIs along these two coordinates are 3.2 eV and 4.4 eV, respectively, including the N-state ZPVE correction. Although both MECIs are energetically accessible from a vertical excitation to the R state, the relaxation along the pyramidalization pathway is energetically more favorable. Interestingly, at both of the N–V MECI geometries the lowest-energy triplet state (T) is lower in energy than the singlet N state, which makes the intersystem crossing to the T state favorable energetically.

The results of our theoretical research are in broad agreement with the relaxation pathway proposed by Trushin et al.¹⁷⁹ based on their femtosecond pump-probe photoionization spectroscopy study of the C_2F_4 excitation to the R state. In particular, our computations support the experimental evidence that the relaxation to the ground state proceeds via an intermediate valence π - π ^{*} state and is accompanied by twisting and pyramidalization. Our research is also consistent with earlier theoretical studies of the low-lying excited states of the related C_2H_4 and $C_2H_2F_2$ molecules,^{149,173} for which similar relaxation pathways have been predicted. For C_2H_4 , the relative energies of the V–N MECIs along pyramidalization and H-migration pathways were computed by Lischka and coworkers to be 4.7 and 4.9 eV, respectively,¹⁴⁹ which demonstrates that the V–N conical intersection along the C_2F_4 pyramidalization pathway is much more accessible energetically than that for C_2H_4 . This is consistent with the well-known preference of the fluorinated compounds for pyramidalization upon electronic excitation. To definitely judge the importance of each relaxation pathway for C_2F_4 , however, dynamics simulations need to be performed, perhaps similar to those reported recently for C_2H_4 .^{64,171,172}

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Chapter 4

Tetragermacyclobutadiene: Energetically Disfavored with Respect to Its Structural Isomers*

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4.1 Abstract

Germanium has been a central feature in the renaissance of main-group inorganic chemistry. Herein, we present the stationary-point geometries of tetragermacyclobutadiene and its related isomers on the singlet potential energy surface at the CCSD(T)/cc-pVTZ level of theory. Three of these 12 structures are reported for the first time and one of them is predicted to lie only 0.4 kcal mol⁻¹ above the previously reported global minimum. Focalpoint analyses has provided electronic energies at the CCSD(T) level of theory, which are extrapolated to the complete basis-set limit and demonstrate the convergence behavior of the electronic energies with improving levels of theory and increasing basis-set size. The lowest-energy structure is the bicyclic structure, which lies 35 kcal mol⁻¹ below the "all-Ge" cyclobutadiene structure. The reaction energies for the association of known Ge hydrides (e.g., digermene) to form Ge_4H_4 indicate that Ge_4H_4 could be observed experimentally. We investigate the bonding patterns by examining the frontier molecular orbitals. Our results demonstrate that (1) the cyclic isomers of $(GeH)_4$ distort to maximize the mixing of the p orbitals that are involved in the π system of tetragermacyclobutadiene and (2) the lowestenergy isomers exhibit unusual bonding arrangements (e.g., bridging H bonds) that maximize the nonbonding electron density at the Ge centers.

4.2 INTRODUCTION

Cyclobutadiene is an elusive molecule with a long and storied history^{191–195} that continues to inspire research today.^{196–204} Recent synthetic work has led to the preparation of cyclobutadiene derivatives that contain Si and Ge atoms.^{205–210} In particular, in 2011, Suzuki et al. reported the first Si analogue of cyclobutadiene that was not part of a transition metalcoordination compound.²¹¹



This tetrasilacyclobutadiene derivative exhibits a planar, rhombic, charge-separated structure that contrasts to the rectangular-planar structure of cyclobutadiene. Also, in 2011, Sekiguchi and co-workers reported the first two coordination compounds that contained a tetragermacyclobutadiene ligand, which showed an almost-rectangular geometry and minimal distortion from planarity.²¹²



Molecules that contain heavy-atom elements often display unusual structure, bonding, and reactivity when compared to their first-row analogues.^{213–216} Therefore, motivated by this recent synthetic activity, further computational work may provide new direction and insight into the structure and bonding of molecules that contain Ge_4 motifs.

These examples employed bulky protecting groups to stabilize the Si and Ge rings. However, recent advances in the study of Ge hydrides that contain more than two Ge centers have suggested new possibilities for the development of Ge chemistry.^{217–220} In particular, Kouvetakis and co-workers demonstrated the utility of trigermane (all-Ge analogue of propane) and tetragermane (all-Ge analogue of *n*-butane and isobutane) as precursors for semiconducting materials.²¹⁸ Ge₄H₄ not only serves as a computationally tractable model system for large molecules that contain Ge₄ motifs, but also deserves attention as a potential intermediate in synthetic procedures that employ larger Ge hydrides.

Previous computational research on model compounds E_4H_4 (E = Si, Ge, Sn, and Pb) provides insight into how heavy-atom bonding and structural patterns relate to the analogous carbon paradigms.^{221–232} A number of thorough theoretical studies exist for Si₄H₄ and its dianion, but little has been reported for Ge₄H₄. As far as more-general studies are concerned, Haunschild and Frenking explored the singlet potential energy surfaces (PES) for E_4H_4 (E = B-Tl and C-Pb) by using B3LYP with the def2-TZVPP basis set.²²³ The broad scope of the Frenking study highlights similarities and differences between Group 13 and Group 14 E_4H_4 isomers. Also, Nazari and Dorrodi examined substitution effects for E_4R_4 (E = C-Ge) by using B3LYP with the 6-311++G^{*} basis set.²²² Whereas these reports have included computations on the Ge₄H₄ system, among many others, no high-level theoretical study has been devoted entirely to tetragermacyclobutadiene and its related structural isomers.

Thus, given the immense utility of Ge compounds in electronic and optics,^{233–235} we believe that a thorough, quantitative study of Ge_4H_4 is in order. Herein, we present highlevel ab initio computations of important Ge_4H_4 structural isomers on the singlet PES. This study is not an attempt to systematically identify all of the minima and transition states of Ge_4H_4 . Rather, our focus is on providing highly accurate results for (1) the cyclic isomers that are related to the synthetic work noted above and (2) the lowest-energy structural isomers that would be most readily detected in experiments that involve Ge hydrides. In the next section, we provide the details of our computations and focal-point analyses (FPA). Then, we provide the optimized geometries, FPA, and energies for possible reactions that involve Ge_4H_4 to assess the stability of such structures. We conclude this report with a comparison of our results to recent synthetic work and related computational studies, as well as a discussion of our results in the context of the growing literature concerning multiplebonding interactions in Group 14 compounds.

4.3 Computational Methods

Hartree-Fock (HF), Møller-Plesset second-order perturbation theory (MP2), ¹⁸¹ coupled-cluster singles and doubles (CCSD),¹⁸¹ CCSD with perturbative triples [CCSD(T)],²³⁶ and complete active space self-consistent field theory $(CASSCF)^{56,57}$ with a (12,12) active space were used as implemented in the Molpro computational package.^{114,237} A restricted HF (RHF) wavefunction was used as a reference for the MP2, CCSD, and CCSD(T) methods. The correlation-consistent valence-polarized basis sets (cc-pVXZ for X=D, T, Q, 5) as developed by Dunning and co-workers were used in all of the electronic-structure computations.^{118,238} The geometries of all of the structural isomers were optimized at the CCSD(T)/cc-pVTZlevel of theory. The harmonic frequencies were computed numerically by finite differences of single-point energies. Zero-point vibrational energy (ZPVE) corrections were calculated as half the sum of all real harmonic frequencies. $FPA^{239-243}$ of the CCSD(T)/cc-pVTZ optimized geometries were performed at the HF, MP2, CCSD, and CCSD(T) levels of theory with the cc-pVXZ basis sets. The HF energy was extrapolated by using Equation (4.1),⁶⁷ where $E_{\rm HF}^{\rm CBS}$, B, and C are parameters, with $E_{\rm HF}^{\rm CBS}$ as the HF energy that is extrapolated to the complete basis set (CBS) limit, and X is the cardinal number that indicates the particular basis set (cc-pVXZ).

$$E_{\rm HF}(X) = E_{\rm HF}^{\rm CBS} + B \exp^{-CX}$$

$$\tag{4.1}$$

The MP2, CCSD, and CCSD(T) energies were extrapolated by using Equation (4.2),⁶⁸ where $E_{\text{Corr}}^{\text{CBS}}$ and G are parameters, with $E_{\text{Corr}}^{\text{CBS}}$ as the correlation energy that is extrapolated to the

CBS limit.

$$E_{\rm Corr}(X) = E_{\rm Corr}^{\rm CBS} + GX^{-3} \tag{4.2}$$

4.4 Results

4.4.1 Structures

In this section, we present the optimized geometries of 12 structural isomers of Ge_4H_4 and, for ease of presentation, group them into two categories: (1) tetragermacyclobutadiene and its related cyclic isomers; and (2) the six lowest-energy isomers. These isomers are numbered in order of decreasing energy. The six cyclic isomers shown in Figure 4.1 (1–6) form a natural group, because they exhibit related bonding patterns that include a four-membered Ge ring, in which each Ge atom is bonded to a H atom. These isomers are most closely related to the experimental structures discussed previously.²¹² The six lowest-energy isomers shown in Figure 4.2 (7–12) exhibit structural features (e.g., bridging H bonds) that are not present in the cyclic isomers. We also present the Ge–Ge and Ge–H bond lengths in digermane (13), trans-pyramidal digermene (14), and trans-bent digermyne (15) in Figure 4.3 for comparison. Structures 13, 14, and 15 are Ge analogues of the prototypical C compounds that exhibit a single bond, a double bond, and a triple bond, respectively. In addition, we include bond lengths for the C_{2v} "butterfly" isomer of Ge₂H₂ (16), the global minimum, for comparison to the structures that exhibit bridging H bonds.


Figure 4.1: The CCSD(T)/cc-pVTZ optimized geometries of the six cyclic (GeH)₄ structural isomers of Ge₄H₄. Bond lengths are reported in angstroms and angles are reported in degrees. The folding angle τ_{ijkl} is defined as the torsion angle about the shortest transannular Ge-Ge distance. The out-of-plane angle γ_{Hi} is the angle between the Ge-H and the plane that is defined by the three adjacent Ge nuclei.



7 (*C*₁)





8 (*C*₁)

Figure 4.2: The CCSD(T)/cc-pVTZ optimized geometries of the six lowest energy isomers of Ge₄H₄. Bond lengths are reported in angstroms and angles are reported in degrees. The folding angle τ_{ijkl} is defined as the torsion angle about the shortest transannular Ge-Ge distance.



Figure 4.3: The CCSD(T)/cc-pVTZ optimized geometries for the reference molecules. Bond lengths are reported in anystroms.

The Cyclic Isomers

The Ge-Ge bond lengths around the Ge ring fall into four categories: (1) bonds that are shorter than a double bond (2.273 Å); (2) bonds of length between single and double bonds (2.350-2.389 Å); (3) bonds of roughly single-bond length (2.446-2.465 Å); and (4) bonds that are longer than a conventional single bond (2.495-2.559 Å). Our assessment of these bonding categories is based on the Ge-Ge bond lengths in structures **13**, **14**, and **15**. The Ge-Ge bonding pattern in structures **1** and **2** consists of alternating long (category 4) and short Ge-Ge bonds (categories 1 and 2), similar to the C-C bonding pattern in cyclobutadiene. The short bond lengths in structures **1** and **2** are two of the shortest among these cyclic isomers. Structures **4** and **5** exhibit two consecutive long Ge-Ge bonds (category 4) and two consecutive short Ge-Ge bonds (category 2). The long bond lengths in structures **4** and **5** are two of the longest among these cyclic isomers. All four Ge-Ge bond lengths are equal in structures **3** and **6** (category 3) and are of similar length to the Ge-Ge bonds

in tetragermatetrahedrane (2.485 Å at the CCSD(T)/cc-pVTZ level of theory). In fact, Nagase and Nakano argued that the Si analogue of structure **6** could be viewed as a "twobond stretch" isomer of tetrasilatetrahedrane, with a similar C_{2v} structure to structure **3** as an intermediate.²³⁰ They argue that this isomerization occurs "almost without a barrier", owing to the relatively weak Si–Si bonds compared to C–C bonds. Following this reasoning, we suspect that the same result is true for tetragermatetrahedrane, structure **3**, and structure **6**, but further investigation of this phenomenon takes us too far afield from the main point of our study.

The transannular Ge-Ge distances are one indication of potential Ge-Ge bonding across the Ge ring. The distance is too long to be significant for structures **1**, **2**, and **6** (3.256–3.375 Å). In contrast, structures **3**, **4**, and **5** contain short transannular Ge-Ge distances of 2.556, 2.749, and 2.841 Å, respectively. The short transannular Ge-Ge distance for structure **3** falls into category 4 of the Ge-Ge bond lengths presented above, which suggests that this structure is best described as bicyclic.

One of the most intriguing features of these cyclic isomers is the variation in the deviation from planarity among the structures. We measured this deviation by considering a folding angle that was defined as the torsion angle about the shortest transannular Ge-Ge distance. The folding angle is 180.0° for structure 1, 142.0° for structure 2, 104.6° for structure 3, 142.7° for structure 4, 159.3° for structure 5, and 122.1° for structure 6. Clearly, there is no correlation between the degree of distortion from planarity and the energy, but the fact that all of the minima in this region of the PES show significant distortion from planarity indicates a primary difference between the bonding in the unsaturated C rings and that in the Ge analogues.

Another interesting feature of these cyclic isomers is the correlation between the Ge-H bond length and the out-of-plane bending angle of the Ge-H bond. The in-plane Ge-H bonds in structure **1** are the shortest Ge-H bonds (1.534 Å). In contrast, the axial Ge-H

bonds in structures **3–6** are the longest Ge–H bonds (1.568–1.611 Å). The remaining Ge–H bond lengths (1.542–1.562 Å) in the equatorial positions are intermediate between these two extremes and are comparable to the Ge–H bond lengths in structures **13–15**.

The Lowest-Energy Isomers

The six lowest-energy isomers (7-12) involve two types of Ge₄ frameworks: (1) a tetrahedranelike framework for structures 7, 9, and 10 and (2) a cyclic framework for structures 8, 11, and 12. Aside from the previously noted transannular bonding, the Ge atoms in structures 1-6 participate in two Ge-Ge bonds and one Ge-H bond. In contrast, many of the Ge atoms in structures 7-12 participate in different bonding patterns.

Structures 7, 9, and 10 are most different from structures 1–6 and we consider those structures first. The Ge–Ge bonds that are connected to the bridging H bonds in these isomers are considerably longer than the Ge–Ge bonds in structures 1–6. However, these bond lengths are comparable to the short transannular Ge–Ge distances in structures 4 and 5. The remaining Ge–Ge bond lengths are comparable to the longer bond lengths (category 4) in structures 1–6. The Ge–H bond in structure 9 is the shortest reported in this study at 1.526 Å. The other Ge–H bond lengths in these three isomers range from 1.655–1.793 Å, comparable to the Ge–H bond length in structure 16. These Ge–H bond lengths are considerably longer than those in structures 1–6.

The Ge-Ge bond lengths in structures 8, 11, and 12 are comparable to the Ge-Ge bond lengths in structures 1–6. The Ge-Ge transannular distance is only significant for structure 12 (2.783 Å), which is comparable to those in structures 4 and 5. Interestingly, the folding angle (137.1° for 8, 148.8° for 11, and 157.7° for 12) increases as the energy decreases for these three isomers. Also, the Ge-Ge bond length that is connected to the bridging H bond in structure 11 is only 2.512 Å, which is short compared to the analogous bonds in structures 7, 9, and 10. However, the associated Ge–H bond lengths in these isomers are comparable to that in structure 16.

4.4.2 Energetics

Table 4.1 summarizes the energetics data for all 12 isomers and includes the FPA energies, the vertical singlet-triplet gaps, and the HOMO-LUMO energy gaps. Tables 4.2 and 4.3 present the FPA. We use structure **12** as a reference for calculating the relative energies. The focal-point table does not explicitly show that we have converged the results within chemical accuracy (1 kcal mol⁻¹). Based on previous experience, the CCSDT(Q) correction is typically one order of magnitude less than the CCSD(T) correction. Therefore, we conclude that the FPA energies reported herein are within chemical accuracy.

Structure	FPA	Vertical singlet-triplet	HOMO-LUMO
	(kcal mol^{-1})	gap (kcal mol ⁻¹)	gap (kcal mol ⁻¹)
1	41.5	7.2	129
2	34.6	2.4	125
3	29.0	45.5	170
4	19.4	39.9	175
5	19.1	36.6	170
6	8.0	41.3	166
7	4.6	74.4	205
8	3.5	39.2	172
9	2.0	75.7	211
10	0.6	77.8	210
11	0.4	n.a. ^b	185
12	0.0	45.3	179

Table 4.1: Energetics data for structures 1–12.

^a The FPA results are the CCSD(T) relative energies at the complete basis-set limit with structure **12** as a reference. The FPA results include ZPVE corrections. The vertical singlet-triplet gap and the HOMO-LUMO gap are reported at the CCSD(T)/ccpVTZ//CCSD(T)/cc-pVTZ level of theory.

^b The triplet state did not converge (n.a.=not available).

Table 4.2: Focal-point analysis (kcal mol⁻¹) for the isomerization of structure **12** into structures **1**–**6**; δ denotes the change in isomerization energy ($\Delta E_{\rm e}$) with respect to the preceding level of theory (HF \rightarrow MP2 \rightarrow CCSD \rightarrow CCSD(T)).

Basis	$\Delta E_{\rm o}$				ΔE_{c}
set	$\frac{-}{HF}$	$+\delta MP2$	$+\delta CCSD$	$+\delta CCSD(T)$	NET
$12 \rightarrow 1^{a}$ cc-pVDZ cc-pVTZ cc-pVQZ cc-pV5Z CBS limit	+51.42 +50.23 +49.81 +49.82 [+49.82]	-2.35 -2.63 -2.84 -3.11 [-3.40]	$\begin{array}{c} -2.59 \\ -2.29 \\ -2.21 \\ -2.10 \\ [-1.99] \end{array}$	$ \begin{array}{c} -1.23 \\ -1.29 \\ -1.26 \\ -1.27 \\ [-1.27] \end{array} $	$\begin{array}{c} [+45.25] \\ [+44.02] \\ [+43.50] \\ [+43.33] \\ [+43.17] \end{array}$
$12 \rightarrow 2^{b}$ cc-pVDZ cc-pVTZ cc-pVQZ cc-pV5Z CBS limit	+45.32 +45.19 +45.02 +45.00 [+44.99]	-2.59 -2.86 -2.81 -2.80 [-2.79]	-5.14 -4.64 -4.42 -4.32 [-4.22]	-2.25 -2.14 -2.14 -2.14 [-2.14]	$\begin{matrix} [+35.33] \\ [+35.55] \\ [+35.65] \\ [+35.73] \\ [+35.83] \end{matrix}$
$12 \rightarrow 3^{c}$ cc-pVDZ cc-pVTZ cc-pVQZ cc-pV5Z CBS limit	+44.31 +43.68 +43.70 +43.72 [+43.73]	-12.70 -14.31 -14.77 -15.04 [-15.32]	$^{+4.10}_{+4.70}_{+4.81}_{+4.86}_{[+4.91]}$	$\begin{array}{c} -2.44 \\ -2.73 \\ -2.87 \\ -2.93 \\ [-2.99] \end{array}$	$\begin{array}{c} [+33.27] \\ [+31.33] \\ [+30.88] \\ [+30.62] \\ [+30.33] \end{array}$
$12 \rightarrow 4^{d}$ cc-pVDZ cc-pVTZ cc-pVQZ cc-pV5Z CBS limit	+23.12 +22.99 +22.98 +22.95 [+22.95]	-0.07 -0.91 -1.03 -1.12 [-1.21]	-0.94 -0.78 -0.75 -0.74 [-0.74]	-0.30 -0.39 -0.44 -0.45 [-0.47]	
$12 \rightarrow 5^{e}$ cc-pVDZ cc-pVTZ cc-pVQZ cc-pV5Z CBS limit	+24.79 +24.89 +24.88 +24.86 [+24.85]	-2.82 -3.24 -3.27 -3.30 [-3.32]	-0.37 -0.15 -0.06 -0.04 [-0.01]	-1.09 -1.17 -1.20 -1.22 [-1.24]	$[+20.52] \\ +20.33] \\ +20.34] \\ +20.30] \\ +20.28]$
$12 \rightarrow 6^{f}$ cc-pVDZ cc-pVTZ cc-pVQZ cc-pV5Z CBS limit	+26.27 +26.62 +26.64 +26.65 [+26.66]	$\begin{array}{c} -22.00 \\ -22.55 \\ -22.62 \\ -22.61 \\ [-22.61] \end{array}$	+7.37 +8.52 +8.88 +8.94 [+9.00]	-3.74 -4.08 -4.28 -4.37 [-4.47]	$[+7.90] \\ [+8.50] \\ [+8.62] \\ [+8.60] \\ [+8.58]$

^a $\Delta E_{\rm e}({\rm final}) = \Delta E_{\rm e}({\rm CBS \ CCSD}({\rm T})) + \Delta {\rm ZPVE} = 41.50 \ {\rm kcal \ mol^{-1}}.$

^b $\Delta E_{\rm e}({\rm final}) = 34.58$ kcal mol⁻¹.

 $^{\rm c}\Delta E_{\rm e}({\rm final}) = 28.97 \text{ kcal mol}^{-1}.$

^d $\Delta E_{\rm e}({\rm final}) = 19.36 \text{ kcal mol}^{-1}$.

 $e \Delta E_{\rm e}({\rm final}) = 19.14 \text{ kcal mol}^{-1}$.

^f $\Delta E_{\rm e}({\rm final}) = 7.96 \text{ kcal mol}^{-1}$.

Table 4.3: Focal-point analysis (kcal mol^{-1}) for the isomerization of structure **12** into structures 7–11; δ denotes the change in isomerization energy ($\Delta E_{\rm e}$) with respect to the preceding level of theory (HF \rightarrow MP2 \rightarrow CCSD \rightarrow CCSD(T)).

Basis	ΔE_e HF	$+\delta MP2$	$+\delta CCSD$	$+\delta CCSD(T)$	ΔE_e NET
$12 \rightarrow 7^{a}$	+28.66	-22.14	+4.12	-2.72	[+7 92]
cc-pVTZ	+28.28	-24.48	+6.34	-3.69	[+6.46]
cc-pVQZ	+28.34	-24.48	+6.83	-3.98	[+6.72]
cc-pV5Z	+28.24	-24.42	+6.83	-4.09	[+6.57]
CBS limit	[+28.21]	[-24.30]	[+0.83]	[-4.20]	[+0.49]
$12 { ightarrow} 8^{ m b}$					
cc- $pVDZ$	+6.95	-3.40	+0.56	-1.01	[+3.12]
cc- $pVTZ$	+7.05	-3.42	+0.74	-1.01	[+3.35]
cc-pVQZ	+7.00	-3.42	+0.82	-1.02	[+3.39]
CBS limit	+7.00	-3.41	+0.85	-1.02	[+3.42]
ODS mint	$[\pm 1.01]$	[-0.41]	[+0.00]	[-1.05]	$[\pm 0.40]$
$12 { ightarrow} 9^{ m c}$					
cc-pVDZ	+15.19	-10.80	+0.57	-0.98	[+3.99]
cc-pVTZ	+15.17	-12.53	+1.83	-1.65	[+2.83]
cc-pVQZ	$^{+15.30}_{-15.24}$	-12.49 -12.46	$^{+2.00}_{-2.03}$	-1.83 -1.89	[+3.04] [+2.02]
CBS limit	[+15.22]	[-12.43]	[+2.00]	[-1.96]	[+2.92] [+2.84]
0 - 10	[,]	[[_!]	[]	['=:o=]
$12 \rightarrow 10^{ m d}$		10 40			[2 2 2]
cc-pVDZ	+20.07	-16.58	+1.45	-1.98	[+2.96]
cc - p V T Z	+19.95 ±10.00	-18.04 -18.54	+3.30 ± 3.75	-2.84 -3.08	[+1.78] $[\pm 2.11]$
cc-pVQZ	$^{+19.99}_{+19.87}$	-18.04 -18.40	$^{+3.73}_{+3.73}$	-3.08 -3.17	[+2.11] [+2.03]
CBS limit	[+19.83]	[-18.24]	[+3.71]	[-3.26]	[+2.04]
10 110	r]	с J	r. 1	L J	r. 1
$12 \rightarrow 11^{e}$	+ 2.01	2.25	0.15	0.15	[+0.97]
cc-pVDZ	+3.91 ±4.05	-3.35 -4.13	-0.15 ± 0.62	-0.15 -0.36	[+0.27] $[\pm 0.10]$
cc-pV1Z	+4.03	-4.13 -4.03	+0.02 +0.79	-0.30 -0.42	$[\pm 0.19]$ $[\pm 0.42]$
cc-pV5Z	+4.06	-3.98	+0.79	-0.44	+0.43
CBS limit	[+4.05]	[-3.92]	[+0.79]	[-0.47]	[+0.45]
$A = (C = 1)$ $A = (CDC = COCD = (T)) + A = (T = 1 = 1 = 1)^{-1}$					

 $\Delta E_{\rm e}({\rm final}) = \Delta E_{\rm e}({\rm CBS~CCSD(T)}) + \Delta {\rm ZPVE} = 4.55 \text{ kcal mol}^{-1}.$

 $\Delta E_{\rm e}({\rm Infal}) = \Delta E_{\rm e}({\rm CD5~CCSD})$ ^b $\Delta E_{\rm e}({\rm final}) = 3.49 \text{ kcal mol}^{-1}.$ ^c $\Delta E_{\rm e}({\rm final}) = 1.97 \text{ kcal mol}^{-1}.$ ^d $\Delta E_{\rm e}({\rm final}) = 0.62 \text{ kcal mol}^{-1}.$ ^e $\Delta E_{\rm e}({\rm final}) = 0.35 \text{ kcal mol}^{-1}.$

The FPA table demonstrates how the level of theory and basis-set size affect the convergence behavior of the energy. In all cases, the MP2 correction is negative. The MP2 correction is the largest for the most-non-planar isomers (3, 6, 7, 9, and 10), ranging from -10.8 kcal mol⁻¹ to -22.1 kcal mol⁻¹. In contrast, the MP2 corrections for the other isomers range from -0.1 kcal mol⁻¹ to -3.4 kcal mol⁻¹.

The magnitude of the energy difference between the cc-pVDZ and cc-pV5Z results approaches 2 kcal mol⁻¹ at certain levels of theory, but the energy differences between the results with the cc-pVTZ and cc-pV5Z sets are generally less than 0.5 kcal mol⁻¹, thus suggesting that the cc-pVTZ basis set is adequate for providing quantitative results. In particular, the cc-pVTZ to cc-pV5Z correction at the CCSD(T) level of theory is largest for the most-non-planar isomers (**3**, **6**, **7**, **9**, and **10**), ranging from 0.2–0.4 kcal mol⁻¹. The same correction for the other isomers is less than 0.1 kcal mol⁻¹. This result is not surprising, given that the non-planar structures exhibit bonding patterns (e.g., bridging H bonds) that intuitively suggest the need for a large basis set to obtain an adequate description of the electronic distribution.

We include the vertical singlet-triplet energy gap (ΔE_v) at the CCSD(T)/cc-pVTZ level of theory to gauge the possible diradical character of these isomers. Structures **1** and **2** have the smallest ΔE_v values, of less than 10 kcal mol⁻¹. Structures **7**, **9**, and **10** have the largest ΔE_v values, ranging from 74–78 kcal mol⁻¹. The other isomers have ΔE_v values that range from 37–46 kcal mol⁻¹. The magnitude of the HOMO-LUMO energy gaps correlates well with the singlet-triplet separation, which is another indicator of diradical character.

We employed CASSCF (12,12) computations to determine the quality of the single reference treatment in the correlation methods that were used in this study. All of the leading configuration interaction (CI) coefficients are at least 0.91, except for structures $\mathbf{1}$ (0.885) and $\mathbf{2}$ (0.845). Therefore, a multireference treatment of compounds $\mathbf{1}$ and $\mathbf{2}$ may be appropriate for further study, but we are convinced that our single-reference treatment is suitable for the conclusions reached herein.

Table 4.4 presents the experimentally known reaction energies for the formation of Ge_4H_4 from common Ge hydrides. We only report the reaction energy for structure **12**, the lowestenergy isomer, herein, but we comment on the energies of all of the isomers. These results include the ZPVE correction. The formation of Ge_4H_4 through the association of germane or digermane molecules is not energetically favorable. However, for structures **3–12**, the association of two digermene moieties to form Ge_4H_4 is energetically favorable. Finally, the formation of Ge_4H_4 from the association of two molecules of structure **16** for structures **1–12** is energetically favorable. We include these results to gauge the possibility of observing these isomers experimentally. However, we expect these isomers to be highly reactive, by analogy to cyclobutadiene.

Table 4.4: Focal-point reaction energies for the formation of structure **12** from common Ge hydrides; ZPVE corrections are included.

Reaction	Reaction energy
	(kcal mol^{-1})
$4\mathrm{GeH}_4 \longrightarrow \mathrm{Ge}_4\mathrm{H}_4 + 6\mathrm{H}_2$	29.3
$2 \operatorname{Ge}_2 \operatorname{H}_6 \longrightarrow \operatorname{Ge}_4 \operatorname{H}_4 + 4 \operatorname{H}_2$	38.4
$2\operatorname{Ge}_2\operatorname{H}_4 \longrightarrow \operatorname{Ge}_4\operatorname{H}_4 + 2\operatorname{H}_2$	-33.3
$2\operatorname{Ge}_2\operatorname{H}_2 \longrightarrow \operatorname{Ge}_4\operatorname{H}_4$	-59.1

4.4.3 MOLECULAR ORBITALS

Figures 4.4 and 4.5 show pictorial representations of the frontier molecular orbitals (MOs) of structures 1-12. These MOs include the HOMO, the LUMO, the HOMO-1, and the LUMO+1. The HOMO and LUMO of cyclobutadiene and of the Si and Ge (1) analogues are qualitatively similar. The HOMO exhibits π -bonding character along the short E-E (E=C, Si, and Ge) bond and the LUMO exhibits π -bonding character along the long E-E

bond. At the CCSD(T)/cc-pVTZ level of theory, the ratio of the long E-E bond to the short E-E bond is 1.167, 1.101, and 1.098 for C_4H_4 , Si_4H_4 , and Ge_4H_4 , respectively. These ratios suggest that the π -bonding character in the short bond becomes less important in the heavy-atom analogues. The distortion from planarity on going from structure 1 to structure 2 further corroborates the observed weak π bond in structure 1. The MOs for structure 2 exhibit the "slipped π bond" that has been reported for Ge_2H_2 .^{244,245} The preference for non-planar structure 2 over structure 1 is also found in the Si analogues.²²⁸ The HOMOs for structures 4 and 5 exhibit a bonding π system for the Ge_3H_3 cyclic subsystem that involves the short Ge–Ge bonds. The HOMO of structure 6 is analogous to the LUMO+1 of structure 1, but, because of the distortion from planarity, the 4p orbitals exhibit σ bonding in the center of the ring. This behavior was also previously found in the Si analogue of structure $6.^{228}$ Many of the valence MOs for the lower-energy isomers indicate nonbonding electron density about the Ge centers. The characteristics of these MOs for the lower-energy isomers are found in the Si analogues, but are absent in the known isomers of C_4H_4 . We explore these differences in the Discussion section.



Figure 4.4: Pictorial representations of selected canonical molecular orbitals using the ccpVTZ basis set for **1-6**. Energies are reported in atomic units. The MOs labeled LUMO and LUMO+1 for **6** are the doubly degenerate LUMO.



Figure 4.5: Pictorial representations of selected canonical molecular orbitals using the ccpVTZ basis set for 7-12. Energies are reported in atomic units. For 9, the MOs labeled HOMO-1 and HOMO are the doubly degenerate HOMO, and the MOs labeled LUMO and LUMO+1 are the double degenerate LUMO. The LUMO+1 for 10 is one of a doubly degenerate pair.

4.4.4 Mulliken Population Analyses

In light of the charge-separated arguments proposed for explaining the structure of the planar, rhombic tetrasilacyclobutadiene derivative,²¹¹ we performed Mulliken population analysis to gauge the significance of charge separation in the structure isomers of Ge_4H_4 . Partial charges are reported for structures 1-6 in Figure 4.6 and for structures 7-12 in Figure 4.7. The atomic partial charges are, in general, small (less than 0.25 in magnitude). The Ge atoms usually exhibit a partial positive charge and the H atoms always exhibit a partial negative charge. For structures 1, 2, and 6, the magnitude of the partial atomic charges increases as the angle between the Ge-H bond and the Ge ring increases (0.029, 0.065, 0.084 for 1, 2, and 6, respectively). For structures 3, 4, and 5, we add the partial charges on each Ge–H pair to determine whether the corners of the rings in the rhombic-like structures exhibit the charge-separated pattern that is found in the tetrasilacyclobutadiene derivative.²¹¹ In doing so, we find that the Ge-H pairs exhibit a positive partial charge for the corners along the short transannular diagonal and a negative charge along the long transannular diagonal. The magnitudes of these Ge-H partial charges range from 0.042-0.085. The axial H atoms in structures 3, 4, and 5 have the largest negative charge (-0.097, -0.14, and -0.12, respectively).



Figure 4.6: Partial atomic charges from Mulliken population analysis for 1-6 using the ccpVTZ basis set.

5 (*C*_s)

6 (D_{2d})

-0.051

4 (*C_s*)







9 (C_{3v})



8 (*C*₁)

Figure 4.7: Partial atomic charges from Mulliken population analysis for **7-12** using the cc-pVTZ basis set.

4.4.5 VIBRATIONAL ANALYSES

We computed the harmonic vibrational frequencies for each optimized geometry to determine the nature of each stationary point. Structure **1** is not a minimum on the singlet PES at any level of theory, in contrast to cyclobutadiene. At the CCSD(T)/cc-pVTZ level of theory, there are three normal modes with imaginary frequencies, one of which involves distortion to structure **2**. Structure **2** is a minimum on the PES at the MP2/cc-pVDZ and CCSD/cc-pVTZ levels of theory, but is a transition state at the HF/cc-pVDZ and CCSD(T)/cc-pVTZ levels of theory. Structure **2** collapses into structure **4** along the normal mode that corresponds to the imaginary frequency. We include this structure in this report because (1) the Si analogue has been reported to be a stationary point at the HF/DZP level of theory;²²⁸ (2) is has a close relationship to tetragermacyclobutadiene (**1**); and (3) it was not reported in the previous studies on Ge₄H₄. We note that, in unpublished results, the Si analogue of structure **2** has also been found to be a saddle point at the CCSD(T)/cc-pVTZ level of theory. Structures **3–12** are minima on the singlet PES at the CCSD(T)/cc-pVTZ level of theory.

4.5 DISCUSSION

Exploratory synthetic work to produce compounds with heavy-atom multiple bonds has led to stark contrasts between the bonding and reactivity of first-row and heavier atoms.^{213,214} Computational chemistry has been at the forefront in predicting and describing new structural isomers of heavy-atom analogues of well-known molecules in organic chemistry that exhibit unconventional bonding patterns. In particular, the synthetic and computational work performed on E_2R_2 systems (E = C–P) has utilized "non-classical" bonding concepts (e.g., "slipped π bonds") that have provided insight into the structures and energetics of Group 14 heavy-atom compounds. Theoretical prediction,^{246,247} followed by experimental validation,^{248,249} of the C_{2v} "butterfly" isomer of Si₂H₂ and Ge₂H₂ (**16**) have demonstrated the value of high-quality ab initio computational studies in this field of main-group chemistry. Herein, we have tackled a slightly more-complex model system, Ge_4H_4 . In this section, we discuss the results of our study in the context of qualitative MO bonding models that have been used for similar heavy-atom main-group molecules, related computational studies, recent synthetic research, and possible future work on this and related systems.

The structural differences between molecules that contain first-row elements and their heavy-atom analogues are often rationalized by using molecular-orbital arguments. Synthetic and computational work has shown that C compounds prefer multiple bonds, in contrast to their Si and Ge analogues. These structural differences can be understood by considering the radial extent of the valence atomic orbitals of C, Si, and Ge. The s and p orbitals of a C atom are similar in size and form hybridized orbitals that participate in bonding interactions. In contrast, the valence s and p orbitals of Si and Ge atoms differ in size, with the s orbital more compact, lower in energy, and more nonbonding in character.²⁵⁰ As a result, the electrons that are associated with the valence s orbitals in Si and Ge atoms are better described as nonbonding electrons and increase the electron density about the heavy-atom centers. The low-energy isomers in this study indeed exhibit decreased double-bonding character and increased electron density about the Ge centers, as suggested by their structure and their MOs.

Molecular-orbital arguments have been successful in explaining the observation that synthesized E_2R_2 compounds range from linear triply bonded C_2R_2 structures to singly bonded Pb_2R_2 structures, with perpendicular bonds and a lone pair of electrons on the Pb centers.²¹⁴ The Si, Ge, and Sn analogues fall within these two extremes. Of relevance to this work, the common picture of Ge_2R_2 is a *trans*-bent structure, with a double bond and diradical character on the Ge centers. The common argument supporting this observation emphasizes the importance of "symmetry allowed, intramolecular mixing of an unoccupied nonbonding or antibonding orbital with a bonding orbital (generally the HOMO in multiplebonded species)".²¹⁴ With this picture in mind, it is not surprising that the lower-energy structural isomers of the Si and Ge analogues of cyclobutadiene exhibit a substantial degree of distortion from planarity and nonbonding electron density about the heavy-atom centers, as reported in this and related research. Thus, we see that the lowest-energy cyclic isomer that can be described by $(GeH)_4$ (6) shows substantial out-of-plane distortion and a geometry that is suggestive of accumulation of nonbonding electron density about the Ge centers. In addition, the well-known global minimum C_{2v} "butterfly" structure of Si₂H₂ and Ge₂H₂, which exhibits bridging H bonds, is a predictor of the structural features of the lowest-energy isomers that are found in this work. Grev at al. noted that a common trend in E_2H_2 systems is that isomers with more lone-pair electron character on heavier Group 14 atoms have lower energy, with the "butterfly" isomer being the extreme.²⁴⁷ This trend is certainly found in our results: The lowest energy isomers of Ge₄H₄ include bridging H bonds and Ge centers that are only involved in two bonds.

Early computational research on Si_4H_4 necessarily employed modest levels of theory (e.g., SCF/DZP and CISD/DZP) compared to today's standards. However, these works predicted Si analogues of most of the cyclic structures presented in this work and were tremendously insightful in interpreting the results of our study. Computational work on Ge_4H_4 in the literature is scarce, but two recent works deserve notice here. First, Nazari and Doroodi studied substituent effects on the cyclic isomers of C_4R_4 , Si_4R_4 , and Ge_4R_4 , with R including H, F, Cl, OH, MgH, BH₂, NH₂, and Li.²²² Whilst this work is important in considering possible new synthetic strategies, we do not consider it further herein because it is outside the scope of this study. Second, Haunschild and Frenking performed a search on the singlet PES of E_4H_4 , where E corresponded to Group 13 and Group 14 elements. They identified over 40 structures, which included 11 minima for Ge_4H_4 . Whilst their study identified new structures and far-reaching trends among Group 13 and Group 14 compounds, our results demonstrate that this study was not definitive in identifying all of the stationary points on

the singlet PES. In this study, we identified three isomers (2, 3, 11) that were stationary points at the CCSD(T)/cc-pVTZ level of theory that were not identified in the previous study. Furthermore, we suggest that a more systematic search on the PES with structures that involve many of the bonding features present in structures 7–12 may find additional low-energy isomers on the PES. We did not pursue such a systematic search because our primary focus in this study was to investigate the cyclic isomers of Ge_4H_4 and their relation to current synthetic work.

The recent study by Sekiguchi and co-workers²¹² reported four new four-membered cyclic Ge compounds: a 2π -electron tetragermetene, a 6π -electron tetragermacyclobutadiene dianion, and two 18-electron tetragermacyclobutadiene transition-metal complexes. The tetragermacyclobutadiene ligand in the transition-metal complexes exhibited minimal distortion from planarity, with Ge–Ge bond lengths ranging from 2.354–2.371 Å (by X-ray crystallography). These bond lengths lay between those in structures **13** and **14** and are intermediate between the single (2.440–2.563 Å) and double bonds (2.239–2.298 Å) that have been found experimentally for cyclic compounds that involved Ge–Ge bonds.²¹²

In contrast to our study, the tetragermacyclobutadiene ligand in these transition-metal complexes is best considered as a 6π -electron system that would favor a square-planar structure with a stong π system. In fact, Sekiguchi and co-workers report that the (tetragermacyclobutadiene)tricarbonyliron complex exhibits "a remarkable π -donating ability of the tetragermacyclobutadiene ligand toward the transition metal, surpassing that of tetrasilacy-clobutadiene and cyclobutadiene ligands." ²¹² Structures **1** and **2**, as the structures that are most similar to the tetragermacyclobutadiene ligand, demonstrate π -MOs that are similar to that of cyclobutadiene. The LUMOs in structures **1** and **2** have a negative orbital energy and, in the absence of any interactions with a transition metal, the natural tendency of the Ge ring is to distort so that the p orbitals mix better among themselves. Thus, the LUMO+1 of structure **1**, the anti-bonding π orbital, decreases in energy to become the

HOMO for structure **6**, which exhibits bonding in the center of the ring and nonbonding lobs about the Ge nuclei. In addition, the LUMO of structure **6** is a doubly degenerate MO, in which the p orbitals exhibit σ -bonding interactions, which corresponds to the doubly degenerate HOMO of the D_{4h} isomer (not reported here). The LUMO of structure **6** not only reinforces the σ -bonding interactions, but also exhibits non-bonding lobes about the Ge nuclei. These interactions, which are not involved in the RHF reference wavefunction, become important when electron correlation is incorporated. This result is demonstrated by structure **6** becoming the lowest-energy cyclic isomer among structures **1**–**6** when adding electron correlation, as demonstrated in the focal-point table. This trend is also observed for Si₄H₄.²²⁸

The recent report by Suzuki et al. demonstrated the first Si analogue of cyclobutadiene that was not part of a transition-metal complex.²¹¹ The unusual planar, rhombic structure of the Si ring was rationalized based on a polar Jahn-Teller distortion from a square-planar Si ring. The charge-separated structure exhibited partial positive charge around the Si centers along the short transannular diagonal and partial negative charge around the Si centers along the long transannular diagonal. We observed a similar electrostatic picture, based on Mulliken population analysis, for structures **3**, **4**, and **5**, which have rhombic-like Ge rings. These observations sharply contrast with the "covalent" Jahn-Teller distortion from the square-planar D_{4h} isomer of cyclobutadiene to the rectangular-planar D_{2h} isomer.

Recent work by Kouvetakis and co-workers has demonstrated the utility of higher-order Ge hydrides (e.g., tetragermane) in important practical applications for the electronics and optics industires.^{218–220} In addition, research into the mass spectroscopy of Ge compounds has led to the ability to identify higher-order Ge hydrides.²¹⁷ Highly accurate computational work on Ge hydrides will be of further aid in the identification of these molecules and in the development of bonding models to describe new Ge chemistry. We expect that many of the isomers discussed herein will be highly reactive, based on the known dimerization of cyclobutadiene. However, it is conceivable that some of these isomers may be important intermediates in the chemistry of Ge hydrides (e.g., the dehydrogenation of tetragermane).

This work has presented three new isomers of Ge_4H_4 , including structure **11**, which is only 0.4 kcal mol⁻¹ higher in energy than the previously reported global minimum.²²³ The six lowest-energy isomers reported in this study are the most likely to be observed from an energetics standpoint and the reaction energies reported in Table 4.4 indicate that such observation is certainly possible. Furture work related to this study should 1) provide accurate vibrational frequencies and intensitites for the lowest-energy isomers; 2) systematically search for other low-energy isomers, focusing on the observed structure features in structures **7–12**; 3) involve computational work on the Ge_4R_4 dianion, similar to the recent work on the Si_4R_4 dianion by Kim et al.;²²¹ and 4) study how different substituents affect the stabilization of the planar, rhombic, charge-separated structure for Ge_4R_4 , in an analogous manner to the recently reported tetrasilacyclobutadiene derivative.²¹¹ Further work on molecules that contain unsaturated Ge–Ge bonds should continue to identify new structures and reactivities, with the goal of providing a deeper understanding of Group 14 chemistry.

4.6 Conclusions

Herein, we have reported the CCSD(T)/cc-pVTZ optimized geometries of Ge_4H_4 for 12 structural isomers and we have provided focal-point-extrapolated energies of CCSD(T) quality at the complete basis-set limit. In particular, we focused on the cyclic isomers that were related to tetragermacyclobutadiene and the six lowest-energy isomers, which were separated by less than 5 kcal mol⁻¹. The three lowest-energy isomers, that is isomers **10**, **11** (previously unreported), and **12**, are separated by less than 1.0 kcal mol⁻¹. Partial atomic charges from Mulliken population analysis for the cyclic isomers demonstrate the same electrostatic picture as that found in the recently synthesized planar, rhombic, charge-separated tetrasilacyclobutadiene derivative.²¹¹ Increased mixing of the p orbitals that are involved in the π system of tetragermacyclobutadiene appear to be a driving force for the distortion of planarity with maximal mixing observed in structure **6**. The six lowest-energy isomers favor structures that maximize the nonbonding electornic character around the Ge nuclei. These structures demonstrate that Ge₄ compounds prefer rings and tetrahedrane-like clusters to open-chain arrangements. We conclude that these isomers could be identified experimentally, based on the energies of reactions that involve known Ge hydrides.

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CHAPTER 5

CONCLUSIONS

In this dissertation, three computational studies are presented that highlight different aspects of electronic structure theory. These include examining the limits of density cumulant functional theory (DCT) for recovering static correlation effects, characterizing the excited states and conical intersections of C_2F_4 , and exploring the ground-state potential energy surface for Ge_4H_4 . In these concluding remarks, the significance of these three studies are discussed.

The development of new electronic structure methods requires extensive benchmarks to demonstrate a method's capabilities and its shortcomings. In Chapter 2, the performance of DCT is examined for recovering static correlation effects that are best described by multireference methods. By design, the original formulation of DCT is biased toward systems that are well-described by a Hartree–Fock reference wave function. However, many molecular systems (e.g., diradicals) that exhibit static correlation effects (e.g., small HOMO-LUMO gap) may be effectively treated with single-reference methods if high-rank correlation effects are included (e.g. CCSDT(Q)). The computational study in Chapter 2 demonstrates that for the molecular systems studied, the ODC-12 variant of DCT performs intermediate of CCSD and CCSD(T). The DCT natural orbital occupation numbers provide a convenient diagnostic for the onset of static correlation effects. The results of this study are an encouraging step toward understanding the strengths and weaknesses of DCT. A multireference extension of DCT would be a welcome addition to the development of this new way of treating the electron correlation problem.

The growing application of ultrafast spectroscopy to investigate chemical processes at short timescales (fs) is greatly supported by complimentary theoretical studies. The computational study reported in Chapter 3 demonstrates the utility of electronic structure methods for describing adiabatic processes. In particular, we characterized two possible relaxation pathways for C_2F_4 from the excited Rydberg state back to the ground state. The results are consistent with the known experimental facts. Computational studies investigating photophysical processes will be improved in the future with faster implementations of excited state methods like EOM-CC, improved algorithms for finding conical intersections using highly accurate methods such as MRCI and EOM-CC, and efficient software for dynamics simulations for nonadiabatic processes.

In Chapter 4, the computational study of Ge_4H_4 demonstrates the application of coupled cluster theory for characterizing the variety of bonding and structure found in germanium hydride molecules. Ab initio computational methods have been instrumental in determining the unexpected structures and bonding of heavy atom main group compounds and driving synthetic efforts in exploratory chemistry research. In this study, three isomers of Ge_4H_4 are reported for the first time, and high-level coupled cluster computations are reported to strengthen our predictions. Further, these results are discussed in context of the broader field of main group chemistry of the heavier elements.

In closing, the computational studies presented in this dissertation demonstrate the power of ab initio methods for investigating molecular properties and chemical processes.

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