

# Can Density Cumulant Functional Theory Describe Static Correlation Effects?

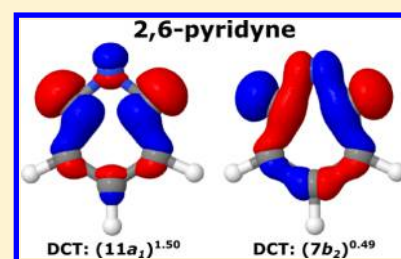
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**S** Supporting Information

**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*-benzynes, 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*-benzynes, 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.



## INTRODUCTION

The electron correlation problem is central in quantum chemistry.<sup>1,2</sup> 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 frontier molecular orbitals of a system are well-separated in energy. Conventional SR theories, such as Møller–Plesset perturbation theory,<sup>3,4</sup> configuration interaction,<sup>3,4</sup> and coupled cluster<sup>5–7</sup> theories, have been shown to provide highly accurate solutions to the Schrödinger equation for systems of modest size near geometric equilibrium. In particular, coupled cluster theory in combination with basis set extrapolation techniques<sup>8,9</sup> or explicitly correlated approaches<sup>10–12</sup> is often capable of achieving chemical accuracy, provided that a high enough excitation level is used in the expansion of the molecular wave function.<sup>13</sup>

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.<sup>14–17</sup> 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<sup>18–21</sup> to novel approaches that are more

efficient and accurate compared to conventional SR theories.<sup>22–29</sup> Many of these alternative approaches are formulated by simplifying the equations of SR coupled cluster theory<sup>22–27</sup> or directly obtaining the reduced density matrices and cumulants thereof,<sup>30</sup> circumventing the computation of the *N*-electron wave function. In particular, density cumulants<sup>31–34</sup> 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,<sup>33,35–40</sup> canonical transformation theory,<sup>41–44</sup> multireference methods based on generalized normal-ordering,<sup>31</sup> and as a central variable in parametric reduced density matrix methods.<sup>45–47</sup>

We recently developed and implemented density cumulant functional theory (DCT),<sup>48–52</sup> first proposed by Kutzelnigg in 2006.<sup>53</sup> In its simplest formulation,<sup>48,50,51</sup> DCT resembles linearized coupled cluster theory with double excitations (LCCD, also known as CEPA-0),<sup>54–57</sup> 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.<sup>50,51</sup> 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

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parameters and orbital rotations.<sup>49,51</sup> 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.<sup>58</sup> 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.<sup>59–61</sup> 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.<sup>25,58</sup> 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*-benzynes, 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.

## 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.<sup>48–53</sup> The starting point of DCT is the molecular electronic energy expression (summation over repeated indices is implied):

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

where  $\gamma_q^p$  and  $\gamma_{rs}^{pq}$  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

$$\gamma_{rs}^{pq} = \gamma_r^p \gamma_s^q - \gamma_r^q \gamma_s^p + \lambda_{rs}^{pq} \quad (2)$$

where  $\lambda_{rs}^{pq}$  are the elements of the two-particle density cumulant ( $\lambda_2$ ). The 1-RDM ( $\gamma_1$ ) is decomposed into an idempotent (mean-field) component  $\kappa$  and a correlation correction  $\tau$ :

$$\gamma_1 = \kappa + \tau \quad (3)$$

In eq 3 only  $\tau$  depends on the density cumulant. The entire energy functional 1 can thus be written in terms of the independent parameters  $\kappa$  and  $\lambda_2$ :

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

In DCT, the energy functional 4 is minimized with respect to  $\kappa$  and  $\lambda_2$ , provided that the resulting density matrices 2 and 3 are  $N$ -representable, that is, can be derived from an  $N$ -electron wave function. 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.

## COMPUTATIONAL DETAILS

The DC-12, ODC-12, and CEPA-0 computations were performed using the Psi4 software package.<sup>62</sup> For coupled cluster theory with singles and doubles (CCSD)<sup>5,6</sup> and CCSD with perturbative triples [CCSD(T)]<sup>63,64</sup> we used the Cfour software package.<sup>65,66</sup> The complete active space self-consistent field (CASSCF)<sup>67,68</sup> and multireference configuration interaction with singles and doubles (MRCI)<sup>69,70</sup> computations were performed using the Molpro program.<sup>71</sup> The MRCI energies were supplied with the Davidson correction to account for size-consistency; the resulting method is denoted as MRCI+Q.<sup>72,73</sup> All electrons were correlated in all computations. For  $C_2H_4$  and  $C_4H_4$ , the two electrons in two orbitals active space was used. The all-electron quintuple zeta (cc-pCV5Z) basis set was employed for  $C_2$ ,<sup>74,75</sup> and the augmented version of this basis set (aug-cc-pCV5Z) was used for  $Be_2$ .<sup>76</sup> For *m*-benzynes, 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 wave function. 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 au 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.

## RESULTS

**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.<sup>77,78</sup> 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<sub>2</sub> molecule.<sup>60,79–81</sup> For more accurate results, full iterative inclusion of triples and perturbative quadruples have been shown to be important.<sup>60,79–81</sup> Recent high-level computational and experimental work has tackled this difficult molecule with remarkable success.<sup>82–85</sup> In this section, we investigate the equilibrium properties of Be<sub>2</sub> using the DC-12 and ODC-12 methods combined with the augmented core–valence aug-cc-pCV5Z basis set.

Table 1 provides the Be<sub>2</sub> equilibrium bond lengths ( $r_e$ ), harmonic vibrational frequencies ( $\omega_e$ ), and dissociation

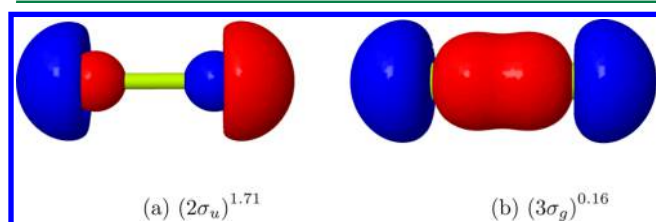
**Table 1. Equilibrium Bond Distances ( $r_e$ ), Harmonic Vibrational Frequencies ( $\omega_e$ ), and Dissociation Energies ( $D_e$ ) of the Be<sub>2</sub> Molecule Computed Using the DC-12, ODC-12, CCSD, CCSD(T), and CEPA-0 Methods with the aug-cc-pCV5Z Basis Set**

theory	$r_e$ (Å)	$\omega_e$ (cm <sup>−1</sup> )	$D_e$ (cm <sup>−1</sup> )
CEPA-0	2.301	318	1589
CCSD	4.414	30	58
CCSD(T)	2.467	242	671
DC-12	2.570	195	597
ODC-12	2.499	226	596
c-CCSDT(Q)/CBS <sup>a</sup>	2.439	227.6 <sup>c</sup>	955
DMRG <sup>b</sup>			931
expt <sup>c</sup>	2.454	222.6 <sup>c</sup>	930 ± 2
expt <sup>d</sup>	2.438	222.6 <sup>c</sup>	935

<sup>a</sup>Reference 83. Composite method. <sup>b</sup>Reference 82. Density matrix renormalization group with canonical transcorrelation approach.

<sup>c</sup>Reference 84. <sup>d</sup>Reference 85. <sup>e</sup>Fundamental frequencies.

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<sup>−1</sup>. In contrast, CEPA-0 overestimates the dissociation energy by ~600 cm<sup>−1</sup> 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  $\Delta r_e$ ,  $\Delta \omega_e$ , and  $\Delta D_e$  relative to experiment of ~0.03 Å, ~20 cm<sup>−1</sup>, and ~250 cm<sup>−1</sup>, 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  $\Delta r_e$ ,  $\Delta \omega_e$ , and  $\Delta D_e$  values of ~0.06 Å, ~3 cm<sup>−1</sup>, and ~330 cm<sup>−1</sup>, 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 1 shows the plots of the Be<sub>2</sub> frontier



**Figure 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.

natural orbitals ( $2\sigma_u$  and  $3\sigma_g$ ) computed using the ODC-12 method. The ODC-12 natural occupation numbers ( $2\sigma_u$ )<sup>1.71</sup>( $3\sigma_g$ )<sup>0.16</sup> show significant deviation from two and zero, indicating the multireference nature of Be<sub>2</sub>.

**Carbon Dimer.** The C<sub>2</sub> molecule is another challenging system for electronic structure methods, largely due to the multireference character of the  $X^1\Sigma_g^+$  ground state.<sup>86–90</sup> Table 2

**Table 2. Equilibrium Geometries ( $r_e$ ), Harmonic Vibrational Frequencies ( $\omega_e$ ), Dissociation Energies ( $D_e$ ), and Adiabatic Excitation Energies [ $T_e = E(\tilde{a}^3\Pi_u) - E(\tilde{X}^1\Sigma_g^+)$ ] of the C<sub>2</sub> 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	$r_e$ (Å)	$\omega_e$ (cm <sup>−1</sup> )	$D_e$ (kcal mol <sup>−1</sup> )	$T_e$ (kcal mol <sup>−1</sup> )
$\tilde{X}^1\Sigma_g^+$				
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 <sup>a</sup>	1.243	1855		2.05
expt <sup>b</sup>			146.6	
expt <sup>c</sup>			147.8	
$\tilde{a}^3\Pi_u$				
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 <sup>a</sup>	1.312	1641		

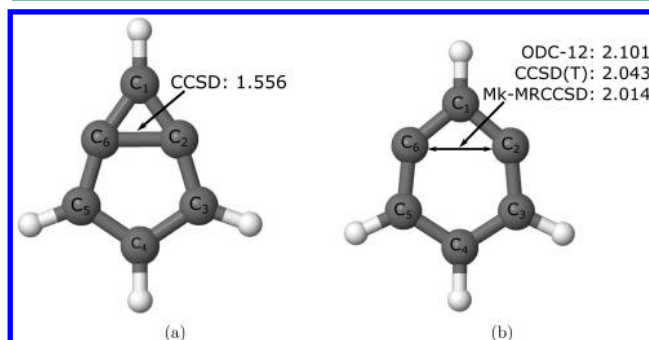
<sup>a</sup>Reference 91. <sup>b</sup>Reference 111. <sup>c</sup>Reference 112

shows the equilibrium bond distances ( $r_e$ ), harmonic frequencies ( $\omega_e$ ), dissociation energies ( $D_e$ ), and adiabatic excitation energies ( $T_e$ ) computed using the DCT and coupled cluster methods for the ground ( $\tilde{X}^1\Sigma_g^+$ ) and lowest-lying triplet ( $\tilde{a}^3\Pi_u$ ) states of C<sub>2</sub>. Table 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 ( $r_e$  and  $\omega_e$ ) with deviations of ≤0.005 Å in  $r_e$  and ≤55 cm<sup>−1</sup> in  $\omega_e$ , relative to experiment<sup>91</sup> and MRCI+Q. However, for the dissociation and adiabatic excitation energies ( $D_e$  and  $T_e = E(\tilde{a}^3\Pi_u) - E(\tilde{X}^1\Sigma_g^+)$ ), only CCSD(T) exhibits reliable performance with  $\Delta D_e = 1.3$  and  $\Delta T_e = 0.4$  kcal mol<sup>−1</sup>. The CCSD method underestimates  $D_e$  by 20.5 kcal mol<sup>−1</sup>, relative to experiment, and incorrectly predicts the  $\tilde{a}^3\Pi_u$  state to be the ground state, with a large absolute error  $\Delta T_e = 10.4$  kcal mol<sup>−1</sup>. CEPA-0 overestimates the binding in C<sub>2</sub>, which results in much larger  $D_e$  and  $T_e$  values compared to experiment (by 5.4 and 11.7 kcal mol<sup>−1</sup>, respectively) and a short C–C bond distance with  $\Delta r_e = 0.05$  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  $\Delta D_e = 9.3$  and  $\Delta T_e = 4.1$  kcal mol<sup>−1</sup>. Both DCT methods, however, fail at predicting the correct ground



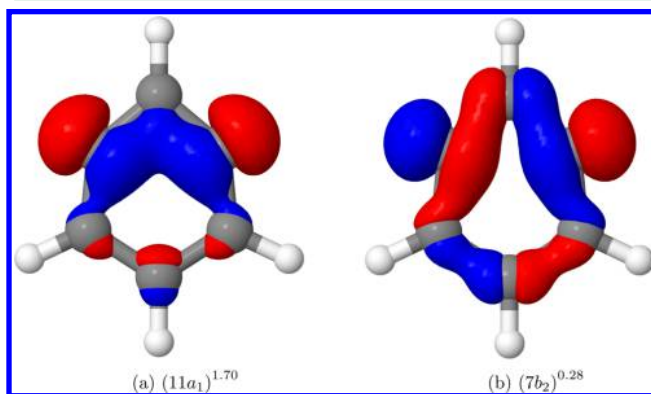
state of  $C_2$ , favoring the  $\tilde{a}^3\Pi_u$  state to lie lower in energy than  $X^1\Sigma_g^+$ . The ODC-12 natural occupations for the  $C_2$  ground state valence orbitals are  $(2\sigma_g)^{1.96} (1\pi_u)^{3.76} (2\sigma_u)^{1.54} (3\sigma_g)^{0.45} (1\pi_g)^{0.19} (3\sigma_u)^{0.01}$ , indicating substantial multireference character.

***m*-benzyne.** The *m*-benzyne molecule ( $C_6H_4$ , Figure 2b) is a prototypical example of a singlet diradical with a multi-



**Figure 2.** Optimized structures of *m*-benzyne computed using the ODC-12, CCSD, CCSD(T), and Mk-MRCCSD methods with the cc-pCVTZ basis set. The Mk-MRCCSD results were reported in ref 96. Only the distance between two carbon atoms in the meta position is shown ( $r_e(C_2-C_6)$ , in angstroms).

reference ground state.<sup>92–94</sup> Its wave function 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 3). As a



**Figure 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.

result, the two electronic configurations  $|\Phi_1\rangle$  and  $|\Phi_2\rangle$  favor two chemically distinct geometries, the bicyclic and monocyclic, respectively (Figure 2a,b), 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.<sup>95–97</sup> 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 ( $\Delta E_{ST}$ ) computed using the ODC-12 method with the cc-

pCVTZ basis set and discuss its performance against the high-level Mk-MRCCSD method.

Table 3 reports the equilibrium properties of *m*-benzyne computed using the CCSD, CCSD(T), ODC-12, and Mk-

**Table 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<sup>a</sup>

coordinate	CCSD	CCSD(T)	ODC-12	Mk-MRCCSD <sup>b</sup>
$r_e(C_2-C_6)$	1.556	2.043	2.101	2.014
$r_e(C_1-C_2)$	1.345	1.368	1.370	1.359
$r_e(C_2-C_3)$	1.379	1.375	1.373	1.370
$r_e(C_3-C_4)$	1.406	1.400	1.398	1.395
$r_e(C_1-H)$	1.079	1.077	1.075	1.075
$r_e(C_3-H)$	1.076	1.081	1.080	1.079
$r_e(C_4-H)$	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
$\theta_e(C_2-C_3-H)$	126.2	120.7	120.6	120.9
$\Delta E_{ST}$	9.7 <sup>c</sup>	20.7 <sup>b</sup>	16.7	21.0 <sup>c</sup>

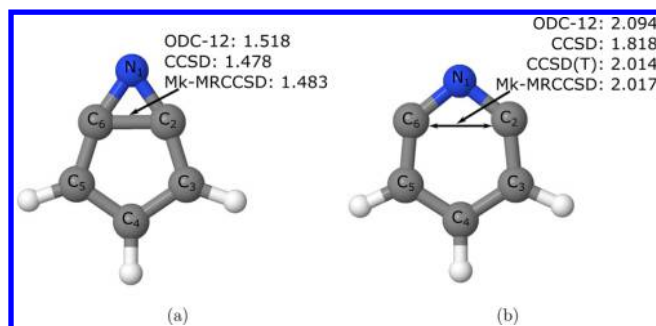
<sup>a</sup>The bond lengths ( $r_e$ ) are in angstroms, and the bond angles ( $\theta_e$ ) are in degrees. The adiabatic singlet–triplet excitation energy  $\Delta E_{ST}$  is reported in kcal mol<sup>−1</sup>. The numbering of atoms is shown in Figure 2.

<sup>b</sup>Reference 96. <sup>c</sup>Reference 113. 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.

MRCCSD methods. ODC-12 and CCSD(T) predict the monocyclic ground state structures, in a qualitative agreement with Mk-MRCCSD (Figure 2b). For CCSD the bicyclic structure was obtained, with a very short distance between the carbon atoms in the meta position ( $r_e(C_2-C_6) = 1.556$  Å, Table 3 and Figure 2a). The failure of CCSD at predicting the correct ground state structure for *m*-benzyne has been demonstrated by Smith, Crawford, and Cremer.<sup>98</sup> For ODC-12 and CCSD(T), the  $r_e(C_2-C_6)$  values are 2.101 and 2.043 Å, respectively, with deviations of ~0.09 and 0.03 Å compared to Mk-MRCCSD ( $r_e(C_2-C_6) = 2.014$  Å).

An important characteristic of the thermodynamic stability of singlet carbenes, such as *m*-benzyne, is the singlet–triplet adiabatic excitation energy ( $\Delta E_{ST}$ ). For *m*-benzyne, the experimental  $\Delta E_{ST}$  has been reported.<sup>99</sup> Subtracting the zero-point vibrational contribution,<sup>95</sup> the experimental  $\Delta E_{ST} = 20.3 \pm 0.3$  kcal mol<sup>−1</sup>. CCSD(T) and Mk-MRCCSD predict  $\Delta E_{ST}$  values of 20.7 and 21.0 kcal mol<sup>−1</sup>, respectively, while CCSD underestimates the singlet–triplet energy by a factor of 2 ( $\Delta E_{ST} = 9.7$  kcal mol<sup>−1</sup>). The ODC-12 method shows better performance compared to CCSD, with  $\Delta E_{ST} = 16.7$  kcal mol<sup>−1</sup>. The ODC-12 natural orbitals provide information about the extent of the *m*-benzyne diradical character. Figure 3 shows the plots of the  $(11a_1)$  and  $(7b_2)$  natural orbitals of *m*-benzyne computed at the ODC-12/cc-pCVTZ optimized geometry. The corresponding natural occupation numbers are  $(11a_1)^{1.70}(7b_2)^{0.28}$ , indicating the significant diradical character of *m*-benzyne.

**2,6-Pyridyne.** In this section we consider 2,6-pyridyne ( $C_5H_3N$ ), a N-substituted parent compound of *m*-benzyne (Figure 4). Similarly to *m*-benzyne, the 2,6-pyridyne wave function is dominated by two determinants  $|\Phi_1\rangle = | \dots (11a_1)^2$



**Figure 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. The Mk-MRCCSD results were reported in ref 100. Only the distance between two carbon atoms in the meta position is shown ( $r_e(\text{C}_2-\text{C}_6)$ , in Å).

$(7b_2)^0$  and  $|\Phi_2\rangle = | \dots (11a_1)^0 (7b_2)^2 \rangle$ , 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.<sup>97,100</sup> However, geometry optimization using CCSD(T) only results in the monocyclic structure.<sup>100</sup> It has been suggested that the Mk-MRCCSD bicyclic geometry is an artifact of theory, due to the lack of triple excitations.<sup>101</sup>

Table 4 and Figure 4 show the CCSD and ODC-12 optimized geometries for 2,6-pyridyne, along with CCSD(T) and Mk-MRCCSD results from ref 100. Both CCSD and ODC-12 locate two minima on the  $\text{C}_5\text{H}_3\text{N}$  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 ( $r_e(\text{C}_2-\text{C}_6) = 1.478$  and  $1.518$  Å, respectively) and are close to that of Mk-MRCCSD ( $1.483$  Å, Figure 4a). For the monocyclic structure, the CCSD method predicts a much smaller  $r_e(\text{C}_2-\text{C}_6)$  distance compared to Mk-MRCCSD ( $1.818$  vs  $2.017$  Å, respectively), while the ODC-12 optimization results in a larger  $r_e(\text{C}_2-\text{C}_6) = 2.094$  Å (Figure 4b). The relative energies of the two geometries ( $\Delta E = E_{\text{mono}} - E_{\text{bi}}$ ) computed at four levels of theory are shown in Table 4. The ODC-12 and Mk-MRCCSD methods energetically favor the monocyclic structure with  $\Delta E$  values of  $-3.6$  and  $-7.2$  kcal  $\text{mol}^{-1}$ , while CCSD favors the bicyclic structure with a positive  $\Delta E$  of  $1.8$  kcal  $\text{mol}^{-1}$ .

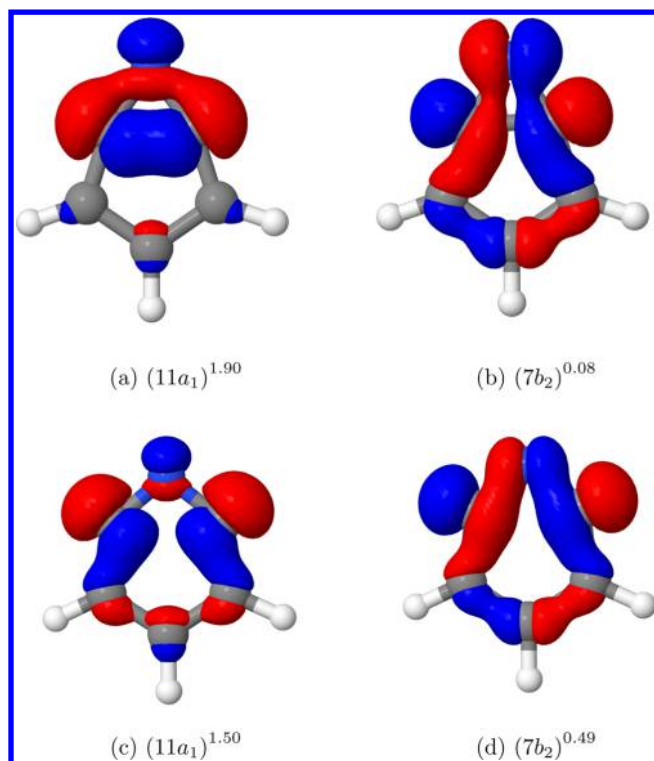
Figure 5 shows the plots of the ODC-12 natural orbitals for the mono- and bicyclic 2,6-pyridyne structures. For the bicyclic geometry, the ODC-12 natural occupations are  $(11a_1)^{1.90}(7b_2)^{0.08}$ , indicating nearly single-reference character of the wave function. The optimized monocyclic geometry exhibits a significant two-determinant character of the wave function 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*-benzynes.

**Twisted Ethylene.** Twisted ethylene ( $\text{C}_2\text{H}_4$ ) is one of the most well-known multireference problems in quantum chemistry.<sup>102–104</sup> At the  $D_{2d}$  symmetry geometry with  $90^\circ$  torsional angle, the  $\text{C}_2\text{H}_4$  singlet ground state electronic wave function has contributions from two equally important determinants originating from the degeneracy of its frontier

**Table 4.** Equilibrium Structural Parameters for the Monocyclic 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<sup>a</sup>

	coordinate	CCSD	CCSD(T) <sup>b</sup>	ODC-12	Mk-MRCCSD <sup>b</sup>
Monocyclic	$r_e(\text{C}_2-\text{C}_6)$	1.818	2.014	2.094	2.017
	$r_e(\text{N}_1-\text{C}_2)$	1.331	1.347	1.337	1.336
	$r_e(\text{C}_2-\text{C}_3)$	1.373	1.380	1.378	1.374
	$r_e(\text{C}_3-\text{C}_4)$	1.394	1.396	1.394	1.391
	$r_e(\text{C}_3-\text{H})$	1.077	1.080	1.079	1.078
	$r_e(\text{C}_4-\text{H})$	1.084	1.086	1.083	1.083
	$\theta_e(\text{C}_2-\text{N}_1-\text{C}_6)$	86.2	96.8	103.2	98.0
	$\theta_e(\text{N}_1-\text{C}_2-\text{C}_3)$	146.9	138.1	133.8	137.5
	$\theta_e(\text{C}_2-\text{C}_3-\text{C}_4)$	114.5	117.0	117.1	116.8
	$\theta_e(\text{C}_3-\text{C}_4-\text{C}_5)$	110.9	112.9	115.1	113.5
Bicyclic	$\theta_e(\text{C}_2-\text{C}_3-\text{H})$	120.7	119.5	120.1	119.8
	$r_e(\text{C}_2-\text{C}_6)$	1.478		1.518	1.483
	$r_e(\text{N}_1-\text{C}_2)$	1.337		1.340	1.337
	$r_e(\text{C}_2-\text{C}_3)$	1.380		1.380	1.380
	$r_e(\text{C}_3-\text{C}_4)$	1.411		1.412	1.411
	$r_e(\text{C}_3-\text{H})$	1.075		1.077	1.075
	$r_e(\text{C}_4-\text{H})$	1.084		1.084	1.084
	$\theta_e(\text{C}_2-\text{N}_1-\text{C}_6)$	67.1		69.0	67.4
	$\theta_e(\text{N}_1-\text{C}_2-\text{C}_3)$	164.6		162.6	164.3
	$\theta_e(\text{C}_2-\text{C}_3-\text{C}_4)$	105.9		107.2	106.1
$\Delta E$	$\theta_e(\text{C}_3-\text{C}_4-\text{C}_5)$	111.9		111.3	111.8
	$\theta_e(\text{C}_2-\text{C}_3-\text{H})$	127.2		126.2	127.0
		+1.8		-7.2	-3.6

<sup>a</sup>The bond lengths ( $r_e$ ) are in angstroms, and the bond angles ( $\theta_e$ ) are in degrees. The energy difference between the two structures  $\Delta E = E_{\text{mono}} - E_{\text{bi}}$  is also reported (in kcal  $\text{mol}^{-1}$ ). The numbering of atoms is shown in Figure 4. <sup>b</sup>Reference 100.

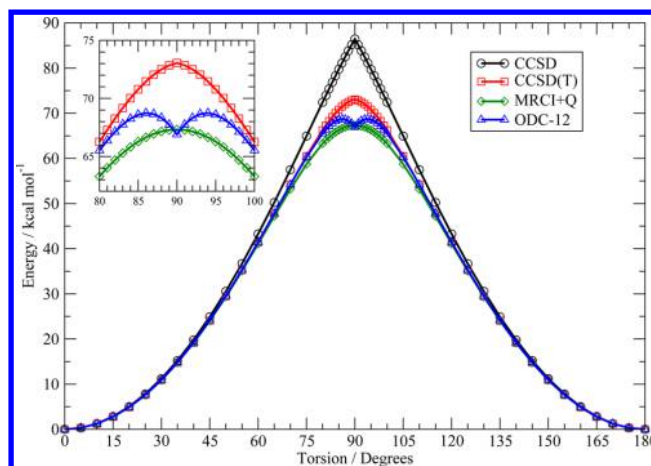


**Figure 5.**  $11a_1$  and  $7b_2$  natural orbitals and occupations for the singlet ground state of (a, b) bicyclic 2,6-pyridyne and (c, d) monocyclic 2,6-pyridyne computed using the ODC-12 method with the cc-pCVTZ basis set.

$\pi$ -molecular orbitals. As a consequence, accurate description of the  $C_2H_4$  torsional potential energy curve (PEC) requires multireference treatment,<sup>105</sup> although it has been shown that single-reference spin-flip approaches can be similarly effective.<sup>106</sup>

Figure 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  $\pi$ -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  $90^\circ$ , with a large error ( $\sim 20$  kcal mol<sup>−1</sup>) 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<sup>−1</sup> error at  $90^\circ$ . The performance of ODC-12 is similar to CCSD(T) for values of the dihedral angle from  $0^\circ$  to  $85^\circ$ . In the range between  $85^\circ$  and  $90^\circ$  the ODC-12 energy decreases, which results in the unphysical dip on the PEC at  $90^\circ$ . 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.

**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-



**Figure 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.

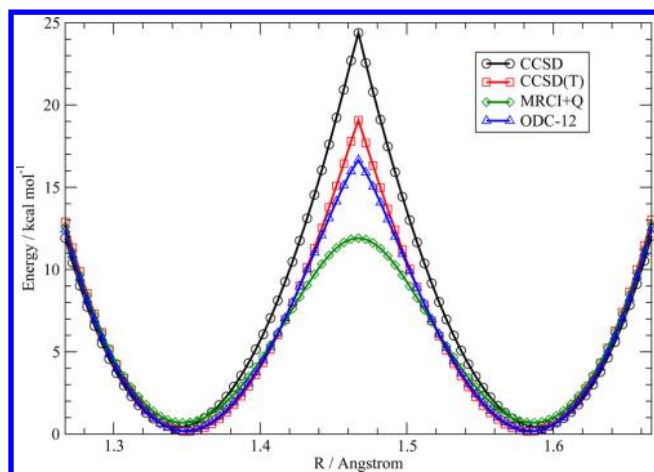
pCVTZ) and two double C–C bonds ( $R_d = 1.34$  Å). Symmetric deformation of the molecule by simultaneously stretching the double bonds and shortening the single bonds results in a square-planar transition state, which has multi-reference character.<sup>107–110</sup> To compute the PEC for the double-bond migration in  $C_4H_4$ , we follow the procedure outlined in ref 109. 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  $135^\circ$ , respectively.

Figure 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  $R = 1.36$  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  $\sim 5$ – $7$  kcal mol<sup>−1</sup>. The CCSD method exhibits much worse stability with respect to increasing multireference effects, giving rise to  $\sim 12$  kcal mol<sup>−1</sup> error relative to MRCI+Q.

## DISCUSSION AND CONCLUSIONS

DCT<sup>48–53</sup> 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 nonlinear, as in coupled cluster theory, the nonlinearities are hidden in the efficient tensor contractions, which simplifies the computer implementation and parallelization. Our recent benchmark study<sup>58</sup> has





**Figure 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  $R_0 = 1.4668 \text{ \AA}$ .<sup>109</sup> 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.

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).<sup>58</sup>

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 mean-field 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  $Be_2$ ,  $m$ -benzynes, 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,<sup>83,88,98</sup> 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 double-bond 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.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Tables with Cartesian coordinates of  $m$ -benzynes and 2,6-pyridyne optimized at the ODC-12/cc-pCVTZ level of theory. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00346.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Raghavachari, K.; Anderson, J. B. *J. Phys. Chem.* **1996**, *100*, 12960–12973.
- (2) Tew, D. P.; Klopper, W.; Helgaker, T. *J. Comput. Chem.* **2007**, *28*, 1307–1320.
- (3) Szabo, A.; Ostlund, N. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Macmillan: New York, 1982.
- (4) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; John Wiley & Sons Ltd.: New York, 2000.
- (5) Crawford, T. D.; Schaefer, H. F. *Rev. Comp. Chem.* **2000**, *14*, 33–136.
- (6) Bartlett, R. J.; Musiał, M. *Rev. Mod. Phys.* **2007**, *79*, 291–352.
- (7) Shavitt, I.; Bartlett, R. J. *Many-Body Methods in Chemistry and Physics*; Cambridge University Press: Cambridge, U.K., 2009.
- (8) Feller, D. *J. Chem. Phys.* **1993**, *98*, 7059–7071.
- (9) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639–9646.
- (10) Ten-no, S. *Chem. Phys. Lett.* **2004**, *398*, 56–61.
- (11) Klopper, W.; Manby, F. R.; Ten-no, S.; Valeev, E. F. *Int. Rev. Phys. Chem.* **2006**, *25*, 427–468.
- (12) Kong, L.; Bischoff, F. A.; Valeev, E. F. *Chem. Rev.* **2012**, *112*, 75–107.
- (13) Tajti, A.; Szalay, P. G.; Császár, A. G.; Kállay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vázquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 11599–11613.
- (14) Chan, G. K.-L.; Sharma, S. *Annu. Rev. Phys. Chem.* **2011**, *62*, 465–481.
- (15) Lyakh, D. I.; Musiał, M.; Lotrich, V. F.; Bartlett, R. J. *Chem. Rev.* **2012**, *112*, 182–243.
- (16) Szalay, P. G.; Müller, T.; Gidofalvi, G.; Lischka, H.; Shepard, R. *Chem. Rev.* **2012**, *112*, 108–181.
- (17) Köhn, A.; Hanauer, M.; Mück, L. A.; Jagau, T.-C.; Gauss, J. *WIREs Comput. Mol. Sci.* **2013**, *3*, 176–197.
- (18) Schütz, M.; Werner, H.-J. *J. Chem. Phys.* **2001**, *114*, 661–681.
- (19) Werner, H.-J.; Manby, F. R.; Knowles, P. J. *J. Chem. Phys.* **2003**, *118*, 8149–8160.
- (20) Riplinger, C.; Neese, F. *J. Chem. Phys.* **2013**, *138*, 034106.
- (21) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.* **2013**, *139*, 134101.
- (22) Wennmohs, F.; Neese, F. *Chem. Phys.* **2008**, *343*, 217–230.

- (23) Neese, F.; Wennmohs, F.; Hansen, A. *J. Chem. Phys.* **2009**, *130*, 114108.
- (24) Kollmar, C.; Neese, F. *Mol. Phys.* **2010**, *108*, 2449–2458.
- (25) Taube, A. G.; Bartlett, R. J. *J. Chem. Phys.* **2009**, *130*, 144112.
- (26) Scuseria, G. E.; Henderson, T. M.; Bulik, I. W. *J. Chem. Phys.* **2013**, *139*, 104113.
- (27) Kats, D. J. *J. Chem. Phys.* **2014**, *141*, 061101.
- (28) Robinson, J. B.; Knowles, P. J. *J. Chem. Phys.* **2011**, *135*, 044113.
- (29) Stein, T.; Henderson, T. M.; Scuseria, G. E. *J. Chem. Phys.* **2014**, *140*, 214113.
- (30) *Reduced-Density-Matrix Mechanics: With Applications to Many-Electron Atoms and Molecules, a Special Vol. of Advances in Chemical Physics*; Mazziotti, D. A., Ed.; John Wiley & Sons: Hoboken, NJ, 2007; Vol. 134.
- (31) Kutzelnigg, W.; Mukherjee, D. *J. Chem. Phys.* **1997**, *107*, 432–449.
- (32) Mazziotti, D. A. *Chem. Phys. Lett.* **1998**, *289*, 419–427.
- (33) Mazziotti, D. A. *Phys. Rev. A* **1998**, *57*, 4219–4234.
- (34) Kutzelnigg, W.; Mukherjee, D. *J. Chem. Phys.* **1999**, *110*, 2800–2809.
- (35) Colmenero, F.; Valdemoro, C. *Phys. Rev. A* **1993**, *47*, 979–985.
- (36) Nakatsuji, H.; Yasuda, K. *Phys. Rev. Lett.* **1996**, *76*, 1039–1042.
- (37) Mazziotti, D. A. *J. Chem. Phys.* **2002**, *116*, 1239–1249.
- (38) Mukherjee, D.; Kutzelnigg, W. *J. Chem. Phys.* **2001**, *114*, 2047–2061.
- (39) Mazziotti, D. A. *Phys. Rev. Lett.* **2006**, *97*, 143002.
- (40) Mazziotti, D. A. *Phys. Rev. A* **2007**, *75*, 022505.
- (41) Yanai, T.; Chan, G. K.-L. *J. Chem. Phys.* **2006**, *124*, 194106.
- (42) Yanai, T.; Chan, G. K.-L. *J. Chem. Phys.* **2007**, *127*, 104107.
- (43) Neuscamman, E.; Yanai, T.; Chan, G. K.-L. *J. Chem. Phys.* **2009**, *130*, 124102.
- (44) Yanai, T.; Kurashige, Y.; Neuscamman, E.; Chan, G. K.-L. *J. Chem. Phys.* **2010**, *132*, 024105.
- (45) Kollmar, C. *J. Chem. Phys.* **2006**, *125*, 084108.
- (46) DePrince, A. E.; Mazziotti, D. A. *Phys. Rev. A* **2007**, *76*, 042501.
- (47) Mazziotti, D. A. *Phys. Rev. Lett.* **2008**, *101*, 253002.
- (48) Simmonett, A. C.; Wilke, J. J.; Schaefer, H. F.; Kutzelnigg, W. *J. Chem. Phys.* **2010**, *133*, 174122.
- (49) Sokolov, A. Y.; Wilke, J. J.; Simmonett, A. C.; Schaefer, H. F. *J. Chem. Phys.* **2012**, *137*, 054105.
- (50) Sokolov, A. Y.; Simmonett, A. C.; Schaefer, H. F. *J. Chem. Phys.* **2013**, *138*, 024107.
- (51) Sokolov, A. Y.; Schaefer, H. F. *J. Chem. Phys.* **2013**, *139*, 204110.
- (52) Sokolov, A. Y.; Schaefer, H. F.; Kutzelnigg, W. *J. Chem. Phys.* **2014**, *141*, 074111.
- (53) Kutzelnigg, W. *J. Chem. Phys.* **2006**, *125*, 171101.
- (54) Kelly, H. P.; Sessler, A. M. *Phys. Rev.* **1963**, *132*, 2091–2095.
- (55) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017–1035.
- (56) Ahlrichs, R. *Comput. Phys. Commun.* **1979**, *17*, 31–45.
- (57) Koch, S.; Kutzelnigg, W. *Theor. Chim. Acta* **1981**, *59*, 387–411.
- (58) Copan, A. V.; Sokolov, A. Y.; Schaefer, H. F. *J. Chem. Theory Comput.* **2014**, *10*, 2389–2398.
- (59) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041–7050.
- (60) Sosa, C.; Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *88*, 5974–5976.
- (61) Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 4282–4288.
- (62) Turney, J. M.; et al. *WIREs Comput. Mol. Sci.* **2012**, *2*, 556–565.
- (63) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479–483.
- (64) Stanton, J. F. *Chem. Phys. Lett.* **1997**, *281*, 130–134.
- (65) *Cfour*, a quantum chemical program package written by Stanton, J. F., Gauss, J., Watts, J. D., Szalay, P. G., Bartlett, R. J. with contributions from, Auer, A. A., Bernholdt, D. E., Christiansen, O., Harding, M. E., Heckert, M., Heun, O., Huber, C., Jonsson, D., Jusélius, J., Lauderdale, W. J., Metzroth, T., Michauk, C., O'Neill, D. P., Price, D. R., Ruud, K., Schiffmann, F., Tajti, A., Varner, M. E., Vázquez, J. and the integral packages: Molecule (Almlöf, J., Taylor, P. R.), Props (Taylor, P. R.), Abacus (Helgaker, T., Jensen, H. J. Aa., Jørgensen, P., Olsen, J.), and ECP routines by Mitin, A. V. and van Wüllen, C. For the current version, see <http://www.cfour.de> (accessed Dec 18, 2014).
- (66) Harding, M. E.; Metzroth, T.; Gauss, J.; Auer, A. A. *J. Chem. Theory Comput.* **2008**, *4*, 64–74.
- (67) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053–5063.
- (68) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259–267.
- (69) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803–5814.
- (70) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514–522.
- (71) Werner, H.-J. et al. *Molpro*, Version 2010.1, a package of ab initio programs. 2010; see <http://www.molpro.net> (accessed Dec 18, 2014).
- (72) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61–72.
- (73) Meissner, L. *Chem. Phys. Lett.* **1988**, *146*, 204–210.
- (74) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1995**, *103*, 4572–4585.
- (75) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (76) Prascher, B. P.; Woon, D. E.; Peterson, K. A.; Dunning, T. H.; Wilson, A. K. *Theor. Chem. Acc.* **2011**, *128*, 69–82.
- (77) Evangelisti, S.; Bendazzoli, G. L.; Gagliardi, L. *Chem. Phys.* **1994**, *185*, 47–56.
- (78) Bondybey, V. E. *Chem. Phys. Lett.* **1984**, *109*, 436–441.
- (79) Shirley, W. A.; Petersson, G. A. *Chem. Phys. Lett.* **1991**, *181*, 588–590.
- (80) Lee, Y. S.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *80*, 4371–4377.
- (81) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513–522.
- (82) Sharma, S.; Yanai, T.; Booth, G. H.; Umrigar, C. J.; Chan, G. K.-L. *J. Chem. Phys.* **2014**, *140*, 104112.
- (83) Ascik, P. N.; Wilke, J. J.; Simmonett, A. C.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **2011**, *134*, 074110.
- (84) Merritt, J. M.; Bondybey, V. E.; Heaven, M. C. *Science* **2009**, *324*, 1548–1551.
- (85) Patkowski, K.; Špirko, V.; Szalewicz, K. *Science* **2009**, *326*, 1382–1384.
- (86) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399–445.
- (87) Bauschlicher, C. W.; Langhoff, S. R. *J. Chem. Phys.* **1987**, *87*, 2919–2924.
- (88) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *96*, 6073–6084.
- (89) Abrams, M. L.; Sherrill, C. D. *J. Chem. Phys.* **2004**, *121*, 9211–9219.
- (90) Sharma, S. *J. Chem. Phys.* **2015**, *142*, 024107.
- (91) Huber, K.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
- (92) Kraka, E.; Anglada, J.; Hjerpe, A.; Filatov, M.; Cremer, D. *Chem. Phys. Lett.* **2001**, *348*, 115–125.
- (93) Hess, B. A. *Eur. J. Org. Chem.* **2001**, 2185–2189.
- (94) Sander, W. *Acc. Chem. Res.* **1999**, *32*, 669–676.
- (95) Evangelista, F. A.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **2007**, *127*, 024102.
- (96) Jagau, T.-C.; Prochnow, E.; Evangelista, F. A.; Gauss, J. *J. Chem. Phys.* **2010**, *132*, 144110.
- (97) Jagau, T.-C.; Gauss, J. *Chem. Phys.* **2012**, *401*, 73–87.
- (98) Smith, C. E.; Crawford, T. D.; Cremer, D. *J. Chem. Phys.* **2005**, *122*, 174309.
- (99) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279–5290.
- (100) Prochnow, E.; Evangelista, F. A.; Schaefer, H. F.; Allen, W. D.; Gauss, J. *J. Chem. Phys.* **2009**, *131*, 064109.
- (101) Evangelista, F. A.; Prochnow, E.; Gauss, J.; Schaefer, H. F. *J. Chem. Phys.* **2010**, *132*, 074107.
- (102) Merer, A. J.; Mulliken, R. S. *Chem. Rev.* **1969**, *69*, 639–656.
- (103) Brooks, B. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 307–311.
- (104) Ben-Nun, M.; Martinez, T. J. *J. Chem. Phys.* **2000**, *259*, 237–248.



- (105) Barbatti, M.; Paier, J.; Lischka, H. *J. Chem. Phys.* **2004**, *121*, 11614–11624.
- (106) Krylov, A. I. *Chem. Phys. Lett.* **2001**, *338*, 375–384.
- (107) Čársky, P.; Bartlett, R. J.; Fitzgerald, G.; Noga, J.; Špirko, V. *J. Chem. Phys.* **1988**, *89*, 3008–3015.
- (108) Balková, A.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 8972–8987.
- (109) Li, X.; Paldus, J. *J. Chem. Phys.* **2009**, *131*, 114103.
- (110) Lyakh, D. I.; Lotrich, V. F.; Bartlett, R. J. *Chem. Phys. Lett.* **2011**, *501*, 166–171.
- (111) Ruscic, B.; Feller, D.; Peterson, K. A. *Theor. Chem. Acc.* **2014**, *133*, 1415.
- (112) Urdahl, R. S.; Bao, Y.; Jackson, W. M. *Chem. Phys. Lett.* **1991**, *178*, 425–428.
- (113) Evangelista, F. A.; Simmonett, A. C.; Schaefer, H. F.; Mukherjee, D.; Allen, W. D. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4728–4741.