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Application of Double Ionization State-Specific Equation of Motion Coupled Cluster Method to Organic Diradicals

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The state-specific equation of motion coupled cluster method is applied to three systems of diradical character: automerization of cyclobutadiene, singlet−triplet gaps of trimethylmethylene, and Bergman reaction. The aim of the paper is to assess the performance of the method and test numerically the importance of orbital optimization, three-body terms in transformed Hamiltonian, and the choice of cluster equations.

I. Introduction

The equation of motion coupled cluster method (EOMCC)[1−5] and its cousins, coupled cluster linear response theory (CCLRT)[6−8] and symmetry adapted cluster configuration interaction (SAC CI),[9,10] were primarily designed for treatment of excited states and calculation of response properties. The cluster amplitudes and the transformed Hamiltonian are obtained for the ground state. Subsequently, the transformed Hamiltonian is diagonalized over the space of primary excitations dominant for the excited states (e.g., singles) plus the next higher excitation level (e.g., doubles). The assumptions underlying the scheme are the transferability of ground-state cluster amplitudes and single reference character of the ground state. In addition, excitations should be qualitatively well described by the primary space components.

The EOMCC method is also used to describe the ground and excited states of radicals for which the closed shell parent state has a different number of electrons than the target states of interest. This leads to the ionization[11] and electron attachment[12] version of EOMCC method, or their SAC CI and CCLRT counterparts.[13−18] Another strategy is the spin-flip approach,[19,20] where the parent state is a high spin determinant. In this way one can access systems that have a multiconfigurational ground state. The equation of motion method has also been used in the DIP-EOMCC version, in which the parent state has two more electrons than the target states of interest.[21,22] Also these methods are able to treat certain multireference systems, but they have the drawback that the final states are rather far removed from the parent state, and hence these methods loose their accuracy if orbital relaxation effects are important or the assumption of transferability of dynamical correlation breaks down. The closely related Fock space coupled cluster[23−29] and STEOM-CC[30−33] methods have also been used to describe multiconfigurational systems, and they are based on similar assumptions as EOMCC. The DIP-STEOM-CCSD approach has been applied, for example, to describe geometrical structure and vibrational frequencies of ozone,[34] while the DEA-STEOM approach has been applied to the notoriously difficult problem of the geometry, vibrational frequencies and excitation spectrum of the N_2O_2 molecule.[35]

The transferability of cluster amplitudes is based on the concept of valence universality,[23−26] which explains the success of the aforementioned approaches. However, the applicability of valence universality concept to general open shell problems has limitations, as similarity between parent and target state is vital.

In this paper, we discuss a generalization of EOMCC for systems that do not have a convenient close-lying parent state.[36−38] Unlike the traditional EOMCC approaches that focus on excited states, the generalization targets one particular state of interest, without the use of a parent state. The parametrization of the wave function is the same as in EOMCC, but all parameters are explicitly optimized for the state of interest. The method employs a spin-adapted cluster operator, $\hat{T}$, that excites from occupied and active orbitals into the virtual space. The transformed Hamiltonian $e^{-\hat{T}}\hat{H}e^{\hat{T}}$ is subsequently diagonalized over an active space plus single excitations out of the active space, and this results in spin-eigenstates. This modification of EOMCC is denoted state-selective equation of motion coupled cluster (SS-EOMCC). The SS-EOMCC approach has been applied previously to the diatomics O_2 and F_2,[36] the avoided crossing in the LiF molecule,[37] and to the challenging Cu_2O_2 molecule including NH_3 ligands.[38] The latter application clearly showed the potential of the approach, as SS-EOMCC with a simple active space suitable for biradicals provided a satisfactory treatment of this system, which has provided a severe challenge to CASPT2 with a very large reference space.[39,40] The SS-EOMCC approach can be regarded as a member of the family of SS-MRCC methods considering its realm of application, although it is not quite size-extensive. The scaling properties of the SS-EOMCC method are analogous to those of the traditional EOMCC approach for excitation energies, in particular the energies are core-extensive implying that energies scale properly if a closed shell system is added at infinity. For recent discussion of this contentious topic we refer to ref 41.

In the SS-EOMCC approach, the wave function is thus expected to be qualitatively correct, as a diagonalization is performed including the most important configurations, while the cluster operator is assumed to include primarily dynamical correlation effects. The use of CC theory is expected to be more effective for the treatment of dynamical correlation than using

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CI techniques, in analogy to single reference situations. For this reason one can expect that the active space in SS-EOMCC and MRCC approaches might be more compact than in MRCI or CASPT2. Compared to Hilbert space multireference approaches,[42−44] on the one hand the parametrization of the cluster operator in SS-EOMCC is more compact, which would be especially pronounced for calculations with a large model space. On the other hand, SS-EOMCC requires a diagonalization over a CAS plus singles space, which quickly becomes expensive with increase of the size of the active space. For this reason the SS-EOMCC is expected to be most effective for small to moderately sized model spaces, in which the CAS + singles diagonalization step is not rate limiting. Let us note that SS-EOMCC can also be viewed as a precursor to more fully contracted approaches currently under development in the Waterloo group, in which the final step only requires diagonalization over a CAS space. Such fully contracted multireference approaches would be applicable to very large active spaces containing perhaps thousands of reference configurations, which can then target complicated transition metal compounds.

The SS-EOMCC type of approach can also be compared to single reference type of approaches that efficiently include effects from higher excitations, e.g. CCSDt and CCSDtq,[45] or equivalently the earlier single reference based multireference coupled cluster method,[46,47] and the renormalized family of CC approaches,[48,49] which can also be quite effective to describe a variety of multireference situations. These single reference approaches have the clear advantage that they apply well in both single reference and (at least certain) multireference situations. This is unlikely to hold for the SS-EOMCC approach, which can be expected to be less accurate for single reference situations. On the upside the number of cluster operators in SS-EOMCC is significantly smaller than in the above single reference approaches and the cost-effectiveness of SS-EOMCC then depends on the cost of the single CAS + singles diagonalization step. For the DIP type SS-EOMCC approach considered here this step has negligible cost and the prime issue therefore is the accuracy of the approach, which we are aiming to establish.

Prior to applications to systems with larger active spaces, it is desirable to further test the performance of this method on simpler systems. In this paper we concentrate on a special class of systems, where the states of interest can be accessed using the double ionization scheme. This requires that only one virtual orbital is important for qualitative description of static correlation. Biradicals are suitable systems to be described by the SS-EOM-CCSD[+2] approach, as would be the breaking of single bonds. In this paper this scheme is referred to by the more general designation SS-EOM-CCSD[+2] acronyms, following ref 38, which indicates that the vacuum state has two more electrons than the state of interest. In general the SS-EOM-CCSD[+*n*] scheme would indicate *n* more electrons in the vacuum state than in the final state of interest.

The paper presents a study of three systems: the automerization barrier of cyclobutadiene, the singlet−triplet gap of trimethylmethylene, and the energetics of the Bergman reaction.

Cyclobutadiene is an example of an antiaromatic system, with two carbon−carbon single bonds and two double bonds. Between the two rectangular structures lies the transition state with a square geometry, see Figure 1. The rate of interconversion of the two rectangular ground states, which can be classified as second order in terms of the Jahn−Teller distortion, is thus determined by the height of the automerization barrier. Due to the two-determinantal character of the transition state, the description of static correlation is crucial. This system has been studied extensively both theoretically[50−66] and experimentally.[67−70]

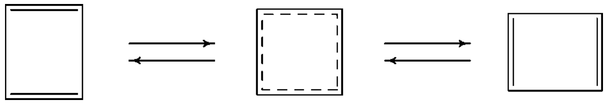

Figure 1. Automerization of cyclobutadiene.

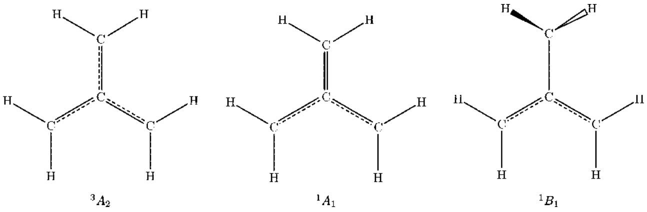

Figure 2. Ground state and low-lying excited states of trimethylmethylene.

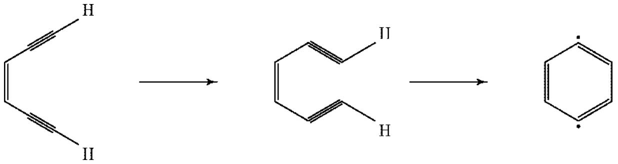

Figure 3. Bergman reaction.

Trimethylmethylene is a typical non-Kekule system, with four electrons being delocalized over three π molecular orbitals. The $^3A_2$ ground-state has D_{3h} symmetry, whereas the two low-lying singlet states $^1B_1$ and $^1A_1$ have the point group C_{2v}, cf. Figure 2. The two highest orbitals of $^3A_2$ are degenerate and both are singly occupied. For the singlet states, these orbitals are only quasi-degenerate, and multireference treatment is highly beneficial. Previous studies of the system include refs 71−79.

The Bergman reaction, i.e., the formation of 1,4-dihydrogenbenzene from hex-3-ene-1,5-diyene, cf. Figure 3, is a useful synthetic reaction, with the diradical product known to be an antitumor agent. Due to instability of the species involved, experimental studies of reaction energetics are relatively scarce.[80,81] Theoretical studies are thus a valuable source of information about this reaction.[82−93] In order to provide a balanced treatment along the reaction coordinate, a multireference treatment is preferable.

II. Theory

Let us divide the orbitals into core, active and virtual. The vacuum state used has core and active orbitals fully occupied, and thus is a single closed-shell Slater determinant. The indices *a*, *b*, *c*, ... correspond to virtual orbitals, and *i*, *j*, *k*, ... are used to denote core and active orbitals.

The wave function in the SS-EOMCC approach is parametrized as

$$|\Psi\rangle = e^{T}C|0\rangle \tag{1}$$

where $|0\rangle$ is the vacuum state, C is a CI-like operator, and T is a cluster operator. The cluster operator is truncated to singles and doubles

$$T=\sum_{i,a}\Omega_i^a+\sum_{ij,ab}t_{ab}^{ij}\Omega_{ij}^{ab} \tag{2}$$

where Ω_i^a and Ω_{ij}^{ab} are a short-hand for the spin−orbital based excitation operators

$$\Omega_i^a = a_a^\dagger a_i \quad (3)$$

$$\Omega_{ij}^{ab} = a_a^\dagger a_b^\dagger a_j a_i \quad (4)$$

The C vector is an eigenvector of transformed Hamiltonian $e^{-T}He^T$, which can be seen by premultiplying the Schrödinger equation by e^{-T}. In principle, if the full CI expansion for the operator C is used the exponential transformation e^T is completely arbirary, reflecting the fact that the spectrum of an operator is unaffected by a similarity transform. However, the aim of the approach is to use only a truncated CI expansion such that C is used primarily for description of static correlation and relaxation effects, while the operator T accounts for (short-range) dynamical correlation, and therefore the precise definition of T amplitudes, to be discussed shortly, is important in practical calculations.

The vacuum state has doubly occupied core and active orbitals, and should be regarded as an artificial construct without physical significance in general. The scope of this paper is restricted to double ionization (DIP) or equivalently the EOMCC[+2] scheme, where the vacuum state has two more electrons than the state of interest.

For the DIP case, the C operator is taken as

$$C = \sum_{ij} c_{ij} a_i a_j + \sum_{ijkb} c_{ijkb} a_i a_j a_b^\dagger a_k \quad (5)$$

and the cluster operator is defined with respect to the aforementioned vacuum state. It should be noted that the final diagonalization manifold is quite compact. The size of the vector C only scales as O^3V, which is significantly more compact than the final diagonalization space in EE-EOMCC or spin-flip EOMCC. The transformed Hamiltonian that is diagonalized in SS-EOM-CCSD[+2] is nonhermitian and includes higher body contributions. However, since the diagonalization space is restricted to single excitations, only up to three body terms are needed. In the DIP case such three-body contributions are inexpensive, but they do become rather expensive for general active spaces, and in this paper we will therefore consider the importance of including them.

The cluster equations are taken in the form of

$$\langle R|\Omega_a^i e^{-T}He^T|R\rangle = 0 \quad (6)$$

and

$$\langle R|\Omega_{ab}^{ij} e^{-T}He^T|R\rangle = 0 \quad (7)$$

where the reference state R, defined as

$$|R\rangle = \sum_{ij} R_{ij} a_i a_j |0\rangle \quad (8)$$

Equations 6 and 7 resemble standard coupled cluster equations. However, let us emphasize that these equations are not obtained by projection of the Schrödinger equation using the parametrization $|\Psi\rangle = e^T C|0\rangle$ against single and double excitations from $|R\rangle$, since that would lead to exactly redundant T_1 equations. The state R is assumed to contain the qualitatively important components of the wave function, and the equations for T amount to a projected Schrödinger equation for $e^T R|0\rangle$, but it is important to realize that this parametrization by itself would not provide an exact wave function, irrespective of the excitation level of T. Rather, the exactness of the approach is reached in the FCI limit of the operator C, upon diagonalization of the transformed Hamiltonian. The equations for T are to fair extent a matter of choice, and it is considered a numerical experiment to determine which equations for T work most satisfactorily. The above equations are relatively simple, in the sense that the detailed form of the equations can be expressed in terms of Hamiltonian integrals, t amplitudes, and the reduced density matrices of the state $|R\rangle$, which involve occupied orbitals only. In the DIP case, only the one- and two-particle reduced density matrices are needed, whereas for general active spaces in principle one would need up to 4-particle reduced density matrices. Because the equations for T depend on the state of interest, $|R\rangle$, the equations for the T amplitudes are state-specific. Moreover, the equations for T are easily spin-adapted (using spatial orbital reduced density matrices), very much like the closed-shell single reference CCSD equations. The actual implementation we use is spin-adapted, although in this paper we will write all expressions in terms of spin−orbitals for convenience.

The reference state $|R\rangle$ can be obtained from a prior CASSCF calculation, or in the case of diradicals, the triplet state can be used to generate orbitals, or even the dianion, provided that the basis set is not too large. If diffuse orbital basis sets would be used the dianion results are expected to rapidly deteriorate, and dianion orbitals should therefore not be considered a viable systematic alternative. Here they are included to investigate the sensitivity of the results to the choice of orbitals. Alternatively to using a fixed reference state (from a CI calculation over the primary space components), the reference state can be determined in a relaxed or self-consistent fashion as the singles coefficients of the full EOM-state, i.e., $R_{ij} = C_{ij}$, normalized to unity. This latter scheme can be used to define orbitals in a Brueckner fashion, which implies that the orbitals are defined in the presence of dynamical correlation. In practice this means that the t_1 amplitudes are used to define an orbital rotation, and at convergence the singles equations, eq 6, are satisfied, while $T_1 = 0$. In a recent SS-EOMCC[+2] study of the Cu_2O_2 system including NH_3 ligands,[38] it was found that the use of Brueckner orbitals can make a significant improvement. The use of Brueckner orbitals is likely to be especially relevant for transition metal systems as the orbitals from Hartree−Fock calculations or even CASSCF calculations might be relatively poor, but it is of interest to investigate the issue of orbital depence also for organic diradicals, which are the subject of this paper.

In this paper we will also investigate an approximation of cluster equations analogous to coupled electron pair approximation (CEPA),[94−97] in particular an orbital invariant version introduced by Nooijen and LeRoy.[98] As indicated in that paper various possibilities exist and the SS-EOM-CEPA version we introduce here is based on an analogy of the single reference case in which the T_2 cluster equation has the form

$$\langle 0|\Omega_{ab}^{ij}(H_{T_1} + [H_{T_1}, T])|0\rangle - \sum_{kl} \langle 0|\Omega_{ab}^{kl} T|0\rangle w_{ij}^{kl} = 0 \quad (9)$$

where |0> is the Slater determinant for ground state, H_{T_1} is a T_1-transformed Hamiltonian, and w_{ij}^{kl} intermediate is given by

$$w_{ij}^{kl} = \frac{1}{2}\sum_{c,d} v_{cd}^{kl} t_{ij}^{cd} \quad (10)$$

Here v_{cd}^{mn} is a two electron integral. Since the summations in eqs 8 and 9 are unrestricted, the cluster equations are invariant under rotations between occupied, or between virtual orbitals. Also, these equations are connected, which yields size-extensivity, and exact for a two electron system. In essence, in the orbital invariant CEPA approach the quadratic part of the T_2 equation is modified, while maintaining the most important features of the CCSD approach. Therefore, this version of CEPA does not have the drawbacks of the traditional CEPA approaches, while maintaining the linear T_2 terms in the cluster equations and a correct description of exclusion violation (EPV) terms. The reason to be interested in the orbital invariant CEPA approaches is partly because they can be considered generalizations of Coupled Cluster theory, while in addition it has been found that they can significantly improve the accuracy of the single reference CCSD approach, in particular when breaking two-electron bonds, as in HF, F_2 and O_2.[98]

In close analogy to the single reference case, the orbital-invariant CEPA equations for the doubles sector of the SS-EOM-CEPA variant are given by

$$\langle R|\Omega^{ij}_{ab}(H_{T_1} + [H_{T_1}, T_2])|R\rangle - \sum_{kl} \langle R||\Omega^{kl}_{ab}T|R\rangle w^{kl}_{ij} = 0 \quad (11)$$

$$w^{kl}_{ij} = \frac{1}{8} \sum_{c,d,m,n} v^{mn}_{cd} t^{cd}_{ij} D^{kl}_{mn} \quad (12)$$

and the single reference vacuum state has been replaced by $|R\rangle$, while D^{kl}_{mn} denotes the two-particle reduced density matrix corresponding to the reference state $|R\rangle$. The equations for single excitation coefficients are the same as in SS-EOM-CCSD[+2]. Once the cluster equations are solved, the C coefficients are subsequently obtained by the diagonalization of transformed Hamiltonian

$$\bar{H} = \mathrm{e}^{-T} H \mathrm{e}^{T} \quad (13)$$

as before. The SS-EOM-CEPA[+2] and SS-EOM-CCSD[+2] share similar properties: exact for two-electron systems if Brueckner orbitals are used, core-extensivity, and invariant under rotations of occupied and virtual orbitals. In this context the CEPA equations might simply be viewed as an alternative way to obtain the T-amplitudes, while exactness in the limit is guaranteed because of diagonalization of the transformed Hamiltonian.

In light of the above variations on the theme of SS-EOM[+2] approaches we want to address the following issues in the benchmark applications.

1. How important is the choice of orbitals in the SS-EOM-CCSD[+2] scheme? To answer this question we will use triplet, dianion, MCSCF, and self-consistent Brueckner orbitals and compare the results. The self-consistent Brueckner approach is theoretically most satisfying, but this approach is somewhat more expensive than the other variants, and this triggers the question.

2. How important are the three-body contributions in the final diagonalization step? While for the SS-EOM-CCSD[+2] scheme the inclusion of three-body contributions is not computationally expensive, this cost rapidly increases for SS-EOM-CCSD with a general active space, which is currently under development in our laboratory. Hence the question if this contribution might safely be neglected.

3. How do the coupled cluster and orbital invariant CEPA version of SS-EOM[+2] compare? It is of interest to compare the relative accuracy of the CCSD and the orbital invariant CEPA version of the theory. On the one hand one would expect relatively small changes as only the contribution from the quadratic T_2^2 contribution is modified. On the other hand we have preliminary evidence that the orbital invariant CEPA approaches[98] or the related parametrized single reference CC approaches (unpublished) might lead to significant improvements. The Brueckner version of the orbital invariant CEPA approach might be particularly effective when combined with local correlation approaches to target very large systems.[98]

TABLE 1: Automerization Barrier of Cyclobutadiene

method	orbitals	cc-pVDZ (kcal/mol)	cc-pVTZ (kcal/mol)
SS-EOM-CCSD[+2]	dianion	8.6	9.9
SS-EOM-CCSD[+2][a]	dianion	8.6	9.9
SS-EOM-CCSD[+2]	triplet	8.6	9.8
SS-EOM-CCSD[+2][a]	triplet	8.7	10.0
SS-EOM-CCSD[+2]	MCSCF	8.3	9.5
SS-EOM-CCSD[+2][a]	MCSCF	8.3	9.6
SS-EOM-CCSD[+2]	Brueckner	8.3	9.5
SS-EOM-CCSD[+2][a]	Brueckner	8.4	9.6
SS-EOM-CEPA[+2]	dianion	8.9	10.1
SS-EOM-CEPA[+2][a]	dianion	8.8	10.1
SS-EOM-CEPA[+2]	triplet	8.9	10.1
SS-EOM-CEPA[+2][a]	triplet	9.0	10.3
SS-EOM-CEPA[+2]	MCSCF	8.5	9.6
SS-EOM-CEPA[+2][a]	MCSCF	8.6	9.8
SS-EOM-CEPA[+2]	Brueckner	8.6	9.8
SS-EOM-CEPA[+2][a]	Brueckner	8.6	9.9
CCSD(T)[100]		16.4	17.3
MR BWCCSD[100]		6.5	7.6
MR MkCCSD[102]		7.6	9.1
MR AQCC[66]		7.3	8.4

[a] Three body terms in transformed Hamiltonian neglected.

4. The primary goal of the benchmark study is of course to gain insight in the general performance of the methodology, independent of the fine details.

III. Computational Details

All calculations were performed using our local version of the ACES II package.[99] Single point calculations were performed, using previously reported geometries obtained at the following levels of theory: for trimethylmethylene CASSCF(4,4),[79] for cyclobutadiene MR BWCCSD,[100] and for Bergman reaction CCSD, CCD, and MR BWCCSD geometries obtained in cc-pVDZ for reactant, transition state, and product, respectively.[88]

Standard Dunning correlation consistent basis sets cc-pVDZ and cc-pVTZ[101] were used throughout the calculations. 1s orbitals on nonhydrogen atoms were excluded from correlation treatment.

Two sets of starting orbitals were used: the orbitals of the corresponding dianion, and triplet state with the same number of electrons. Calculations were performed both with and without the Brueckner-type orbital optimization.

IV. Application Calculations

In this section, we will describe three systems which have been extensively studied in the literature and which are used to benchmark the SS-EOM-CCSD[+2] and SS-EOM-CEPA[+2] approaches.

A. Automerization of Cyclobutadiene. The results for the height of automerization barrier are listed in Table 1. Let us first concentrate on results obtained with optimized Brueckner orbitals. The SS-EOM-CCSD[+2] method gives a value of 8.3 kcal/mol in cc-pVDZ basis set and 9.5 kcal/mol in cc-pVTZ. The effect of three-body terms is very small, approximately 1 mH in absolute energies of the respective states, and only 0.1 mH in terms of energy differences. The values obtained by the CEPA version of the method are higher by 0.2 kcal/mol. Due to the Brueckner type orbital optimization these results are independent of the starting orbitals.

For the energy gaps, the results for unoptimized triplet or dianion orbital choices lie approximately 0.3−0.4 kcal/mol above

TABLE 2: Singlet Triplet Gaps in Trimethylmethylene

		$^3A_2 \rightarrow {}^1B_1$		$^3A_2 \rightarrow {}^1A_1$	
method	orbitals	cc-pVDZ (eV)	cc-pVTZ (eV)	cc-pVDZ (eV)	cc-pVTZ (eV)
SS-EOM-CCSD[+2]	dianion	0.718	0.730	0.853	0.845
SS-EOM-CCSD[+2][a]	dianion	0.721	0.732	0.866	0.858
SS-EOM-CCSD[+2]	triplet	0.715	0.681	0.870	0.851
SS-EOM-CCSD[+2][a]	triplet	0.716	0.682	0.869	0.866
SS-EOM-CCSD[+2]	MCSCF	0.711	0.724	0.859	0.857
SS-EOM-CCSD[+2][a]	MCSCF	0.714	0.727	0.863	0.860
SS-EOM-CCSD[+2]	Brueckner	0.713	0.725	0.853	0.850
SS-EOM-CCSD[+2][a]	Brueckner	0.714	0.726	0.858	0.854
SS-EOM-CEPA[+2]	dianion	0.704	0.717	0.841	0.836
SS-EOM-CEPA[+2][a]	dianion	0.704	0.718	0.860	0.850
SS-EOM-CEPA[+2]	triplet	0.698	0.674	0.841	0.836
SS-EOM-CEPA[+2][a]	triplet	0.699	0.675	0.858	0.852
SS-EOM-CEPA[+2]	MCSCF	0.695	0.705	0.844	0.834
SS-EOM-CEPA[+2][a]	MCSCF	0.697	0.707	0.858	0.838
SS-EOM-CEPA[+2]	Brueckner	0.695	0.705	0.832	0.826
SS-EOM-CEPA[+2][a]	Brueckner	0.697	0.706	0.837	0.831
SF-CIS[77]			1.017[b]		0.883[b]
SF CIS(D)[77]			1.025[b]		0.893[b]
EOM-SF-CCSD[78]			0.554		0.933
EOM-SF-CC(2,3)[78]			0.697		0.787
MR BWCCSD[79]		0.633	0.634	0.800	0.779
Experiment-ZPE				0.787	

[a] Three body terms in transformed Hamiltonian neglected. [b] cc-pVTZ basis set used for carbon, cc-pVDZ basis set for hydrogen.

the values obtained with Brueckner orbitals. The effect of three-body terms is 0.1−0.2 kcal/mol. All of these variations on the theme hence lead to essentially negligible differences. The situation is similar for the calculations with MCSCF orbitals. Again the results are nearly identical to the values with optimized Brueckner orbitals at the SS-EOM-CCSD[+2] level, while for SS-EOM-CEPA[+2] the gaps are lower by 0.1−0.2 kcal/mol.

Compared to other multireference methods, the results of SS-EOM-CCSD[+2] method are approximately 2 kcal/mol higher than MR BWCCSD, and 0.5 kcal/mol higher than MR MkCCSD. The single reference CCSD(T) method is in error by 9 kcal/mol indicating the clear benefit of using a multiconfigurational approach.

B. Singlet−Triplet Gap of Trimethylmethylene. The results of excitation energies for the $^3A_2 \rightarrow {}^1B_1$ and $^3A_2 \rightarrow {}^1A_1$ transitions of trimethylmethylene are listed in Table 2. Calculations by SS-EOM-CCSD[+2] method with optimized orbitals yield values of 0.713 and 0.725 eV in cc-pVDZ and cc-pVTZ basis sets respectively for the $^3A_2 \rightarrow {}^1B_1$ transition, and 0.853 and 0.850 for the $^3A_2 \rightarrow {}^1A_1$ transition. For the CEPA variant of the method, the results are lower by approximately 0.02 eV. The effect of three-body terms of transformed Hamiltonian is in all cases below 0.005 eV. Also, the effect of basis set is very weak.

The effect of orbital optimization is slightly more pronounced than for cyclobutadiene. In the cc-pVDZ basis set, the total energies obtained with triplet orbitals lie within 1 mH from results with optimized orbitals, while the deviation for dianion orbitals are approximately 3 mH and 1 mH for MCSCF orbitals. For energy differences, the dianion results are higher by 0.01 eV for $^3A_2 \rightarrow {}^1B_1$ and 0.02 eV for $^3A_2 \rightarrow {}^1A_1$ than their counterparts with optimized orbitals. Using triplet orbitals, the differences become 0.003 and 0.01, respectively, and using MCSCF orbitals 0.002 and 0.006 eV, respectively. The effect of three-body terms when using triplet or dianion orbitals is slightly more important than when using Brueckner orbitals. This can be understood from the general observation that the single-excitations out of the primary space in the final diagonalization are less important when Brueckner orbitals are used and relaxation effects are minimized. This effect reduces the size-extensivity error in the SS-EOM-CCSD[+2] approach, but it also reduces the effect of the three-body terms which only couple to the singly excited sector, not within the primary (or active) space.

In the cc-pVTZ basis set, the difference between total energies obtained with triplet and optimized orbitals increases by 1−2 mH, while the deviation is unchanged for dianion orbitals. For $^3A_2 \rightarrow {}^1B_1$ gap, the use of triplet orbitals leads to values lower by approximately by 0.03 eV, compared to overestimation by 0.01 eV with dianion orbitals. For $^3A_2 \rightarrow {}^1A_1$ transition, the differences between the two choices of starting orbitals are even smaller. The best agreement with the optimized orbital calculations is again obtained for the MCSCF orbitals, where the difference is almost zero for for $^3A_2 \rightarrow {}^1B_1$ and smaller than 0.01 eV for the $^3A_2 \rightarrow {}^1A_1$ transition.

Also for this system we conclude there is little significance to the variability of the computational schemes within the SS-EOMCC[+2] framework. It is interesting to note the significant improvement of the SS-EOM-CCSD[+2] approach over the spin-flip EOM-SF-CCSD results, compared to the most accurate EOM-SF-CC(2,3) benchmark. The prime differences between these approaches is the fact that for SS-EOM-CCSD[+2] the cluster amplitudes are optimized for the state of interest, while for SF-EOM they are obtained for the close-lying triplet state. The diagonalization manifold in the SS-EOM-CCSD[+2] scheme is significantly more compact as it involves only one virtual orbital, rather than two, as in the case of the SF-EOM-CC approach. The improvements of SS-EOM-CCSD[+2] over SF-EOM-CCSD testifies therefore to the effectiveness of the approach, and the relevance of the state-specific parametrization.

C. Bergman Reaction. Results of the activation and reaction energies for the Bergman reaction are listed in Table 3. SS-EOM-CCSD[+2] with Brueckner orbitals yields values of reaction energies of 6.9 kcal/mol in cc-pVDZ and 11.9 kcal/mol in cc-pVTZ basis set. The activation energies obtained are 28.9 and 31.2 kcal/mol respectively. These values are in a reasonable agreement with results from MR BWCCSD. The results at the SS-EOM-CEPA[+2] level are lower by approximately 3.5 kcal/mol for activation energy, and 4 kcal/mol for reaction energy, with cc-pVTZ results being in excellent agreement with experiment. The CEPA results also agree reasonably well with CCSD(T) calculations. The basis set dependence of these energy values is very high, and in larger basis sets the expected trent would be for the energies to increase further. This would indicate that the SS-EOM-CCSD[+2] values are clearly to high compared to experiment, while the SS-EOM-CEPA[+2] values may be more reasonable. In the comparison with experiment the geometries will also play a role, and we note that they have been obtained at somewhat different levels of accuracy, perhaps confounding a proper comparison. Regardless the comparison with experiment, however, there is a striking difference between the SS-EOM-CEPA[+2] and SS-EOM-CCSD[+2] results and this requires further discussion, which we will take up below.

Let us first consider the importance of choice of orbitals, which for the cc-PVDZ basis set is significant, especially for the reaction energy. In all cases, the results with nonoptimized orbitals yield larger differences than with optimized ones. The

TABLE 3: Study of Bergman Reaction

		$\Delta E_{\mathrm{reaction}}$		$\Delta E_{\mathrm{activation}}$	
Method	orbitals	cc-pVDZ (kcal/mol)	cc-pVTZ (kcal/mol)	cc-pVDZ (kcal/mol)	cc-pVTZ (kcal/mol)
SS-EOM-CCSD[+2]	dianion	9.4	17.4	30.7	33.3
SS-EOM-CCSD[+2][a]	dianion	8.6	16.4	30.6	33.2
SS-EOM-CCSD[+2]	triplet	9.1	15.7	33.0	33.1
SS-EOM-CCSD[+2][a]	triplet	8.9	14.8	33.4	34.0
SS-EOM-CCSD[+2]	MCSCF	7.4	12.5	29.2	31.6
SS-EOM-CCSD[+2]	MCSCF	7.5	12.6	30.0	32.4
SS-EOM-CCSD[+2]	Brueckner	6.9	11.9	28.8	31.2
SS-EOM-CCSD[+2][a]	Brueckner	7.1	12.1	29.7	32.1
SS-EOM-CEPA[+2]	dianion	8.1	12.6	26.7	29.1
SS-EOM-CEPA[+2][a]	dianion	7.2	11.7	26.6	29.0
SS-EOM-CEPA[+2]	triplet	6.1	12.4	23.7	28.6
SS-EOM-CEPA[+2][a]	triplet	5.3	10.6	24.1	28.5
SS-EOM-CEPA[+2]	MCSCF	4.1	9.1	25.6	28.0
SS-EOM-CEPA[+2][a]	MCSCF	4.1	9.2	26.7	28.9
SS-EOM-CEPA[+2]	Brueckner	3.3	8.2	25.1	27.5
SS-EOM-CEPA[+2][a]	Brueckner	3.5	8.5	26.1	28.4
CCSD[88]		25.7	27.5	35.4	38.2
MR BWCCSD[88]		8.1	12.9	30.2	32.7
CCSD(T)[88]		4.4	10.1	26.4	27.6
MR CI[88]		6.3	10.3	30.1	29.4
RB3LYP[93]		8.5[b]		29.9[b]	
Experiment[82]		8.5		28.7	

[a] Three body terms in transformed Hamiltonian neglected. [b] Calculated in 6−311+G(3df,3pd) basis. [c] Activation enthalpy calculated at 470 K, the value should be compared with experimental value 28.2 kcal/mol.

TABLE 4: Study of Bergman Reaction: Largest Cluster Amplitudes[a]

method	orbitals	largest T_2 amplitudes		largest T_1 amplitudes
		Reactant		
SS-EOM-CCSD[+2]	MCSCF	−0.044	−0.037	−0.029
SS-EOM-CEPA[+2]	MCSCF	−0.051	−0.042	−0.031
SS-EOM-CCSD[+2]	dianion	−0.043	−0.040	−0.232
SS-EOM-CCSD[+2]	triplet	−0.036	−0.035	−0.148
		Transition State		
SS-EOM-CCSD[+2]	MCSCF	−0.090	−0.047	−0.024
SS-EOM-CEPA[+2]	MCSCF	−0.140	−0.063	0.027
SS-EOM-CCSD[+2]	dianion	−0.091	−0.047	0.130
SS-EOM-CCSD[+2]	triplet	−0.079	−0.040	−0.065
		Product		
SS-EOM-CCSD[+2]	MCSCF	−0.084	−0.068	0.023
SS-EOM-CEPA[+2]	MCSCF	−0.119	−0.091	0.025
SS-EOM-CCSD[+2]	dianion	−0.085	−0.069	−0.132
SS-EOM-CCSD[+2]	triplet	−0.078	−0.056	0.023

[a] Calculations in ccpVTZ basis set, three-body terms included.

best agreement with results of Brueckner type of calculations was obtained at the MCSCF level, where the deviatons are only about 0.3 kcal/mol in cc-pVDZ basis set and 0.6 kcal/mol in cc-pVTZ basis set, with slightly larger differences (up to 0.9 kcal/mol) being obtained at the SS-EOM-CEPA level. For dianion and triplet orbitals, the deviations become quite large, ranging from 2 to 4 kcal/mol depending on the details of the computational method.

For activation energies, the effect of orbital optimization is relatively smaller. This is especially true for the cc-pVTZ basis set. Again, best agreement with calculation with optimized orbitals are obtained with MCSCF orbitals, with the deviations being approximately 0.3 kcal/mol.

The effect of three-body terms also varies with the level of calculation. For calculations with optimized and MCSCF orbitals, the effect is very small for the reaction energy, whereas for the activation energy, neglecting three-body terms leads to an increase by approximately 1 kcal/mol. Again, the effect is slightly more important at the SS-EOM-CEPA level. For dianion and triplet orbitals, the trends are less systematic, with the effect of three-body terms ranging from 0.1 to 2 kcal/mol.

Most of the above observations can be partially explained by the magnitudes of cluster amplitudes, which are shown in Table 4 for the case of cc-PVTZ calculations. The use of dianion orbitals leads to large singles amplitudes (0.13−0.23) for all cases, whereas the singles amplitudes for MCSCF orbitals are all below 0.03. The results from triplet orbitals show a large variability, with amplitudes ranging between 0.023 and 0.15 This explains that the results of calculations with MCSCF orbitals are closer to Brueckner results than the other two orbital choices. It is a bit surprising perhaps that the triplet orbitals show such a large variation.

As far as connected doubles are concerned, two large T_2 amplitudes are encountered for the transition state and product. These two amplitudes have a $\pi \rightarrow \pi^*$ character, and suggest, that the use of an larger active space might be desirable. Large T_2 amplitudes lead to a poorer description of the two respective structures, resulting in overestimation of both reaction and activation energy, and also a bigger than usual effect of three-body terms. The amplitudes obtained at SS-EOM-CEPA[+2] level are considerably larger than their SS-EOM-CCSD[+2] counterparts, which also explains a larger dependence on inclusion of three-body contributions to the transformed Hamiltonian in the CEPA variant. This effect of large T_2 amplitudes for the CEPA approach has been observed in the single reference case for bond-breaking situations, and in that case the larger T_2 amplitudes in CEPA agree well with CCSDT results. We suspect that also here the larger T_2 amplitudes might be the correct result, which would be obtained if triple excitations were included explicitly. Of course this is speculation, but it is consistent with the fact that the SS-EOM-CEPA[+2] result considerably improves over SS-EOM-CCSD[+2] compared to experiment, also when allowing for projected basis set effects. It would be of interest to obtain more computational results for the Bergman reaction as this appears to be a quite challenging system.

V. Conclusions

The state-specific equation of motion coupled cluster method was applied to study three organic systems of diradical character: automerization of cyclobutadiene (CBD), singlet−triplet gaps of trimethylmethylene (TMM), and the Bergman reaction. These benchmark studies allow us to give tentative answers to the questions raised in the theory section.

The importance of the choice of orbitals varies somewhat with the system studied. The calculations using MCSCF orbitals were found to be consistently in good agreement with results of Brueckner calculations, while the performance of dianion and triplet orbitals was fine for CBD and TMM but showed rather large variations for the Bergman case. The magnitude of the T_1 amplitudes can be used as an indication of the importance of the choice of orbitals, and overall it appears the methodology is not very sensitive to the choice of orbitals, reflecting the usual insensitivity of CC theory to orbital choice.

The effect of three-body terms in Hamiltonian is relatively minor in particular if Brueckner or MCSCF orbitals are used. The approximation is questionable when T_2 amplitudes are large, and it appears this is essentially a useful diagnostic (which can be made more robust and orbital invariant). It would appear that three-body contributions can safely be neglected if the largest T_2 amplitudes are less than 0.05 or so. This conclusion may attain relevance for SS-EOM-CCSD[+2] calculations that employ a more general active space, where multiplication of CI vector by three-body part of Hamiltonian can become computationally expensive.

For all systems considered, the SS-EOM-CEPA[+2] approach is not worse than SS-EOM-CCSD[+2] and in the case of the Bergman reaction results improve considerably. This conclusion is in agreement with other evidence (to be reported), and it appears interesting to understand this better, and to collect more evidence to support this statement. We only expect to find large deviations between the two approaches when T_2 amplitudes are large (e.g., larger than about 0.1), and if they are relatively large, the CEPA results appears to be be more reliable.

We think that this potential benefit of the CEPA variant may be quite relevant in future applications. A prime potential advantage of MRCC approaches over MRCI approaches ought to be the faster convergence of results in MRCC with the choice of active space. It would defeat the purpose of MRCC approaches if for a system like the Bergman reaction we would have to worry about the inclusion of the $\pi \rightarrow \pi^*$ excitations in the active space, while they do not play a qualitative role in the chemistry. Our results are somewhat suggestive that MRCC may not have the required insensitivity, while the orbital invariant CEPA might be more promising.

Let us finally comment on the computational cost of the SS-EOMCC[+2] approach for diradicals. The major cost of the approach is the solution of the cluster equations, which is comparable to solving CCSD equations for a closed shell system. There are significantly more contributions to the equations, but the leading order contribution scales as O^2V^4, as in closed shell CCSD. The computational cost of the final diagonalization of the transformed Hamiltonian over 2-hole and 3-hole-1-particle configurations is neglible.

The accuracy of the approach appears considerably improved over spin-flip CCSD (which is slightly more expensive), but the approach is probably not competitive regarding accuracy with renormalized triples approaches (which are considerably more expensive, however). A considerable advantage of the SS-EOMCC[+2] approach is that one obtains a qualitatively correct picture of the wave function, and it is possible to calculate multiple states at once if they require a similar active space, e.g., in a state averaged approach.

Let us conclude by reiterating that the SS-EOMCC[+2] scheme is currently being extended to be able to treat general active spaces, such that it becomes a full-fledged multireference approach. The goal is to design multireference approaches for which finding suitable active spaces is about as difficult as it is for CASSCF approaches. This is a very different (and easier) problem than finding satisfactory active spaces for MRCI or even CASPT2 type of approaches. We anticipate that the more successful multireference approaches may be eventually turn out to be of CEPA rather than of CC type, but we acknowledge it is hard to overcome the prejudice that CEPA should be considered a lower level approximation to coupled cluster theory.

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References and Notes

(1) Sekino, H.; Bartlett, R. J. *Int. J. Quant. Chem. Symp.* **1984**, *8*, 255.

(2) Geertsen, J.; Rittby, M.; Bartlett, R. J. *Chem. Phys. Lett.* **1989**, *164*, 57.

(3) Comeau, D. C.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *207*, 414.

(4) Bartlett, R. J.; Stanton, J. F. *Rev. Comp. Chem.* **1994**, *5*, 65.

(5) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029.

(6) Monkhorst, H. *Int. J. Quant. Chem. Symp.* **1977**, *11*, 421.

(7) Mukherjee, D.; Mukherjee, P. K. *Chem. Phys.* **1979**, *39*, 325.

(8) Koch, H.; Jørgensen, P. J. *J. Chem. Phys.* **1990**, *93*, 3333.

(9) Nakatsuji, H.; Hirao, K. *Chem. Phys. Lett.* **1977**, *47*, 569.

(10) Nakatsuji, H.; Hirao, K. *J. Chem. Phys.* **1978**, *68*, 2053.

(11) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1994**, *101*, 8938.

(12) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1995**, *102*, 3629.

(13) Nakatsuji, H.; Hirao, K. *Int. J. Quantum Chem.* **1981**, *20*, 1301.

(14) Nakatsuji, H.; Ohta, K.; Hirao, K. *J. Chem. Phys.* **1981**, *75*, 2952.

(15) Nakatsuji, H.; Ohta, K.; Yonezawa, T. *J. Chem. Phys.* **1983**, *87*, 3068.

(16) Nooijen, M.; Snijders, J. G. *Int. J. Quant. Chem. Symp.* **1992**, *26*, 55.

(17) Nooijen, M.; Snijders, J. G. *Int. J. Quantum Chem.* **1993**, *48*, 15.

(18) Mukherjee, D.; Mukhopadhaya, A.; Moitra, R. K. *Z. Naturforsch.* **1978**, 33.

(19) Krylov, A. I. *Chem. Phys. Lett.* **2001**, *338*, 375.

(20) Krylov, A. I. *Chem. Phys. Lett.* **2001**, *350*, 522.

(21) Wladyslawski, M.; Nooijen, M. In *ACS Symposium Series*; Hoffman, M., Dyall, K., Eds.; ACS: Washington, D.C., 2002; p 65, Vol. 828.

(22) Sattelmayer, K. W.; Schaeffer, H. F., III; Stanton, J. F. *Chem. Phys. Lett.* **2003**, *378*, 42.

(23) Lindgren, I. *Int. J. Quant. Chem. Symp.* **1978**, *12*, 33.

(24) Lindgren, I.; Mukherjee, D. *Phys. Rep.* **1987**, *151*, 93.

(25) Mukherjee, D.; Pal, S. *Adv. Quantum Chem.* **1981**, *20*, 292.

(26) Jeziorski, B.; Paldus, J. *J. Chem. Phys.* **1989**, *90*, 2714.

(27) Jankowski, K.; Paldus, J.; Grabowski, I.; Kowalski, K. *J. Chem. Phys.* **1992**, *97*, 7600.

(28) Kaldor, U. *Theor. Chim. Acta* **1991**, *80*, 427.

(29) Jankowski, K.; Malinowski, P. *J. Phys. B* **1994**, *27*, 829.

(30) Nooijen, M. *J. Chem. Phys.* **1996**, *104*, 2638.

(31) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *106*, 6441.

(32) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *107*, 6812.

(33) Nooijen, M.; Lotrich, V. *J. Chem. Phys.* **2000**, *113*, 494.

(34) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *107*, 6812.

(35) Tobita, M.; et al. *J. Chem. Phys.* **2003**, *119*, 10713.

(36) Nooijen, M. *Int. J. Mol. Sci.* **2002**, *3*, 656.

(37) Nooijen, M.; Shamasundar, K. R. *Collect. Czech. Chem. Commun.* **2005**, *70*, 1082.

(38) Kong, L.; Nooijen, M. *Int. J. Quantum Chem.* **2008**, *108*, 2097.

(39) Cramer, C. J.; Kinal, A.; Piecuch, M. W. P.; Gagliardi, L. J. *J. Phys. Chem. A* **2006**, *110*, 11557.

(40) Cramer, C. J.; Wloch, M.; Piecuch, P.; Puzzarini, C.; Gagliardi, L. J. *J. Phys. Chem. A* **2006**, *110*, 1991.

(41) Nooijen, M.; Shamasundar, K. R.; Mukherjee, D. *Mol. Phys.* **2005**, *103*, 2277.

(42) Jeziorski, B.; Monkhorst, H. J. *Phys. Rev. A* **1981**, *24*, 1668.

(43) Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 8227.

(44) Mahapatra, U. S.; Datta, B.; Mukherjee, D. *J. Chem. Phys.* **1999**, *110*, 6171.

(45) Piecuch, P.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1999**, *110*, 6103.

(46) Oliphant, N.; Adamowicz, L. *J. Chem. Phys.* **1991**, *94*, 1229.

(47) Piecuch, P.; Oliphant, N.; Adamowicz, L. *J. Chem. Phys.* **1993**, *99*, 1875.

(48) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 18.

(49) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 074107.

(50) Snyder, L. C. *J. Phys. Chem.* **1962**, *66*, 2299.

(51) Bunker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1968**, *48*, 354.

(52) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1978**, *100*, 4303.

(53) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.

(54) Dewar, M. J. S.; Merz, K. M., Jr.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 4040.

(55) Ångren, H.; Correia, N.; Flores-Riveros, A.; Jensen, H. J. Å. *Int. J. Quantum Chem.* **1986**, *19*, 237.

(56) Fratav, F.; Monev, V.; Janoschek, R. *Tetrahedron* **1982**, *38*, 2929.

(57) Čársky, P.; et al. *J. Chem. Phys.* **1988**, *89*, 3080.

(58) Čársky, P.; Downing, J. W.; Michl, J. *Int. J. Quantum Chem.* **1991**, *40*, 415.

(59) Voter, A. F.; Goddard, I. W. A. *J. Am. Chem. Soc.* **1986**, *108*, 2830.

(60) Nakamura, K.; Osamura, Y.; Iwata, S. *J. Chem. Phys.* **1989**, *36*, 67.

(61) Bonačić-Koutecký, V.; Schöffel, K.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 6140.

(62) Balková, A.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 8972.

(63) Sancho-García, J. C.; Pittner, J.; Čársky, P.; Hubač, I. *J. Chem. Phys.* **2000**, *112*, 8785.

(64) Sancho-Garcia, J. C.; Moscardo, F. *J. Chem. Phys.* **2003**, *118*, 1054.

(65) Levchenko, S. V.; Wang, T.; Krylov, A. I. *J. Chem. Phys.* **2005**, *122*, 224106.

(66) Eckert-Maksic; Vazdar; Barbatti; Lischka, *J. Chem. Phys.* **2006**, *125*, 064310.

(67) Arnold, B.; Michl, J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M., Ed.; Plenum: New York, 1989; p 1.

(68) Orendt et al., A. M. *J. Am. Chem. Soc.* **1988**, *110*, 2648.

(69) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 6473.

(70) Lefevbre, R.; Moiseyev, N. *J. Am. Chem. Soc.* **1990**, *112*, 5052.

(71) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242.

(72) Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726.

(73) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberg, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475.

(74) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053.

(75) Cramer, C. J.; Smith, B. A. *J. Chem. Phys.* **1996**, *100*, 9664.

(76) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967.

(77) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2002**, *117*, 4694.

(78) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2005**, *123*, 084107.

(79) Brabec, J.; Pittner, J. *J. Phys. Chem. A* **2006**, *110*, 11765.

(80) Roth, H.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765.

(81) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *113*, 6401.

(82) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907.

(83) Marquardt, R.; et al. *Agnew. Chem., Int. Ed. Engl.* **1998**, *37*, 955.

(84) Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1994**, *116*, 4929.

(85) Lindh, R.; Person, J. *J. Am. Chem. Soc.* **1994**, *116*, 4963.

(86) Lindh, R.; et al. *J. Am. Chem. Soc.* **1995**, *117*, 7186.

(87) Lindh, R.; Schütz, M. *J. Am. Chem. Soc.* **1996**, *258*, 409.

(88) Rey-Puiggros, O.; et al. *Collect. Czech. Chem. Commun.* **2003**, *68*, 2309.

(89) Cramer, C. J.; Nash, J. J.; Squires, R. R. *Chem. Phys. Lett.* **1997**, *277*, 311.

(90) Prall, M.; Wittkopp, A.; Fokin, A. A.; Schreiner, P. R. *J. Comput. Chem.* **2001**, *22*, 1605.

(91) Prall, M.; Wittkopp, A.; Schreiner, P. R. *J. Phys. Chem. A* **2001**, *105*, 9265.

(92) Stampfuss, P.; Wenzel, W. *Mol. Phys.* **2002**, *100*, 1807.

(93) Gráfenstein, J.; Hjerpe, A. M.; Kraka, E.; Cremer, D. *J. Phys. A* **2000**, *104*, 1748.

(94) Mayer, W. *Int. J. Quant. Chem. Symp.* **1971**, *5*, 341.

(95) Meyer, W. *J. Chem. Phys.* **1972**, *58*, 1017.

(96) Ahlrichs, R.; Lischka, H.; Staemmler, V.; Kutzelnigg, W. *J. Chem. Phys.* **1975**, *62*, 1225.

(97) Daudey, J. P.; Heully, J. L.; Malrie, J. P. *J. Chem. Phys.* **1993**, *99*, 1240.

(98) Nooijen, M.; Roy, R. J. L. *J. Molec. Struc. (Theochem)* **2006**, *768*, 25.

(99) ACES ii is a program product of Quantum Theory Project, University of Florida, J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almloef and P. R. Taylor); VPROPS (P. R. Taylor); and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Joergensen, J. Olsen, and P. R. Taylor).

(100) Demel, O.; Pittner, J. *J. Chem. Phys.* **2006**, *124*, 144112.

(101) Dunning, T. H., Jr. *Chem. Phys.* **1979**, *42*, 249.

(102) Bhaskaran Nair, K.; Demel, O.; Pittner, J. *J. Chem. Phys.*, in press.

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