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A Natural Orbital Diagnostic for Multiconfigurational Character in Correlated Wave Functions

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A Natural Orbital Diagnostic for Multiconfigurational Character in Correlated Wave Functions

Abstract

The natural orbitals and their corresponding occupation numbers are constructed for several interesting problems to demonstrate that the existence of negative natural orbital occupation numbers for single reference correlation methods provides a simple diagnostic for the need for a multiconfigurational description of the wave function.

Keywords

Wave functions, Correlation functions, Physics demonstrations

Disciplines

Chemistry

Comments

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A natural orbital diagnostic for multiconfigurational character in correlated wave functions

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The natural orbitals and their corresponding occupation numbers are constructed for several interesting problems to demonstrate that the existence of negative natural orbital occupation numbers for single reference correlation methods provides a simple diagnostic for the need for a multiconfigurational description of the wave function. © 1999 American Institute of Physics.
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I. INTRODUCTION

It is well known that not all chemical species can be well represented by a single configuration wave function. Equivalently, an adequate qualitative description of such species requires more than one simple Lewis structure.¹ Since the use of a wave function that is based on a single configuration description can lead to a poor description of the properties of the system one is studying, it is of interest to have one or more diagnostics that are general enough to apply to any level of theory as predictive tools to flag potentially suspect wave functions. Of particular import in this regard are two landmark contributions by Lowdin.² The first of these was the demonstration that for a given atomic basis, the exact wave function may be represented by a complete configuration interaction (CI) within that basis. The second important contribution was the definition of the *natural orbitals* $\{\phi_i\}$ as the eigenvectors of the first order density matrix ρ , and the demonstration that these natural orbitals provide a unique description in the limit of the exact wave function. The eigenvalues of the first-order density matrix are called the natural orbital occupation numbers λ_i (NOON). Because of the Pauli exclusion principal, no orbital may have an occupation number greater than 2 (one electron for each spin). Since the first-order density matrix is positive definite, there are no negative NOONs. In a simple closed shell, single configuration wave function, the occupied orbitals all have $\lambda_i=2.0$, while the unoccupied (virtual) orbitals have 0.0 occupation numbers.

Several diagnostics have been proposed to aid in determining when a multiconfigurational description of the wave function might be important. Pulay³ has made the very important observation that in a multiconfigurational wave function, if a putative virtual orbital has a NOON of 0.1 or greater, one should not rely on a single configuration description of the species of interest. Of course, this determination requires construction of a multiconfigurational wave function. For neutral molecule restricted Hartree–Fock (RHF) wave functions, a negative virtual orbital energy is frequently taken to be an indication that the single configuration wave function does not provide an adequate descrip-

tion of the system, while for unrestricted Hartree–Fock (UHF) wave functions, significant spin contamination may be used as a diagnostic.¹ The stability tests (e.g., RHF→UHF, real→complex) developed by Pople and co-workers also serve as diagnostics for Hartree–Fock wavefunctions.⁴

A common, although not necessarily correct, practice is to assume that correction of Hartree–Fock wave functions by adding correlation, most commonly by adding second-order perturbation corrections, ameliorates the need for a multiconfiguration description. Aside from the T_1 and S_2 diagnostics proposed by Lee and co-workers for coupled cluster and second-order perturbation theory wave functions,^{5(a)(b)} and a recently proposed alternative normalization of these called D_1 (MBPT2) and D_1 (CCSD),^{5(c)} it is less obvious how one might test single configuration-based correlated wave functions for their ability to provide a reliable description for the system of interest. In this work, we propose that the natural orbital occupation numbers provide a general, consistent diagnostic for the breakdown of single configuration-based wave functions.

For fully variational wave functions, such as Hartree–Fock (HF) self-consistent field (SCF) and multiconfigurational (MC) SCF¹ wave functions (or the exact wave function) Ψ , which satisfy the Hellmann–Feynman theorem,⁶ the first-order density is well defined as $|\Psi|^2$, and the natural orbitals are the eigenfunctions of this density matrix. The density matrix for partially variational wave functions, such as those obtained from a truncated CI, is frequently obtained in the same manner, as are the corresponding natural orbitals. For nonvariational methods, for which the Hellmann–Feynman theorem is not satisfied, several authors have noted that it is preferable to use the “relaxed” or “generalized” or “effective” density for the prediction of first-order properties, rather than simply $|\Psi|^2$, where (for example) Ψ is the sum of the zeroth-order wave function and its first-order correction in the case of second-order perturbation theory.⁷ Formally, one can write the non-Hellmann–Feynman (derivative) expression for the density as $dE(\mu)/d\mu$, where E is the energy of the system and μ is a perturbation that represents

the instantaneous electron–electron interaction (perturbative correlation).

The relaxed density may be formulated⁸ in terms of the orbital Lagrangian (which introduces orbital rotations not unlike an incomplete MCSCF procedure) and the orbital Hessian \mathbf{A} . For nonvariational methods, the relaxed density can, as demonstrated below, lead to nonphysical natural orbital occupation numbers that can be traced to the fact that the wave function has become sufficiently multiconfigurational that the method in use no longer provides an adequate description of the wave function.

In fact, the orbital Hessian \mathbf{A} is the common factor in the various tests for multireference character. Pulay's criterion³ for the size of an occupation number was obtained by exploring how TCSCF wave functions are related to previous work on UHF instability. UHF instability tests⁴ essentially amount to the testing of the orbital Hessian for the presence of negative eigenvalues, indicating the RHF wave function is not a minimum energy solution. The orbital Hessian forms the coefficient matrix in the response equations, whose solutions result in the generalized density matrix.^{7,8} Thus, the \mathbf{A} matrix characterizes the appropriateness of the underlying SCF wave function for the problem at hand. Note, however, that the inhomogeneity B^a of the response equations $AU^a = B^a$ depends on the sophistication of the correlation treatment. So, even if the SCF orbital Hessian exhibits UHF instability, the response contribution to the relaxed density matrix will not necessarily produce nonphysical NOON.

In the present paper, the natural orbital occupation numbers obtained using several correlated levels of theory are compared for a number of problems, including some that clearly require a multiconfiguration-based wave function and some for which this is less clear. The former include the dissociation curve of N_2 , the bend potential for singlet CH_2 , and several species that are known to be diradicals. The latter include the series $H_2E = EH_2$ ($E = C, Si, Ge, Sn$). Results of these analyses are presented following an outline of the methods that are included.

II. THEORETICAL METHODS

The correlation methods explored in this paper are MCSCF within the fully optimized reaction space (FORS)⁹/complete active space SCF (CASSCF)¹⁰ formalism, multireference singles and doubles CI (MR[SD]CI) from a FORS MCSCF reference space, second-order multireference perturbation theory (CASPT2¹¹), single reference second-order perturbation theory,^{12,13} and single reference singles and doubles coupled-cluster theory perturbatively corrected for triple excitations, CCSD(T).¹⁴ Several programs were used to obtain the corresponding density matrices and associated natural orbitals. The MCSCF calculations were performed using both GAMESS¹⁵ and MOLPRO.¹⁶ The MR(SD)CI and CASPT2 calculations were also done using MOLPRO. For all of these multireference methods, the densities and natural orbitals were obtained using the expectation value method; that is, by evaluating and diagonalizing $|\Psi|^2$. Most of the second-order perturbation theory (MBPT2) and all of the CCSD(T) calculations were performed using ACESII;¹⁷ some second-order perturbation theory calculations were carried

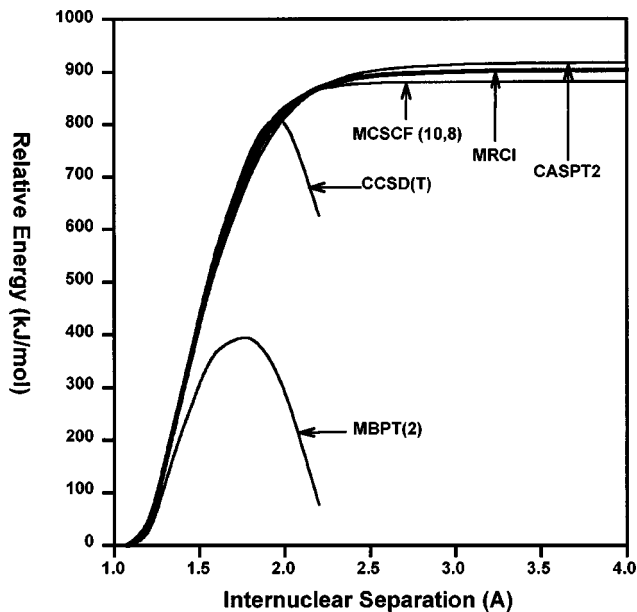


FIG. 1. Relative energy curves for N_2 dissociation at various levels of theory using the cc-PVTZ basis set. The potential energies were all set to zero at 1.078 Å to facilitate comparison of the curve shapes.

out with GAUSSIAN 94.¹⁸ The natural orbitals for these single configuration-based methods were obtained by determining and diagonalizing the relaxed density matrices.

For the dissociation curve of N_2 and the bend potential for CH_2 the polarized correlation-consistent triple zeta (cc-pVTZ) basis set developed by Dunning *et al.* was used.¹⁹ For methylene, this basis was augmented with diffuse functions. All of the other species were chosen based on previous calculations that have appeared in the literature. For these, the original basis sets were used, and they will be specified in the appropriate subsections below.

III. RESULTS AND DISCUSSION

A. Dissociation of N_2

The behavior of the N_2 natural orbital occupation numbers as a function of the internuclear distance R is summarized in Table I, and the corresponding energetics are plotted in Fig. 1. To conserve space, only a subset of the points used to construct Fig. 1 is included in the table. For the MCSCF calculations, the active space includes the six electrons (two σ and four π) associated with the $N \equiv N$ bond and the corresponding σ , σ^* , π , π^* orbitals. The MRCI and CASPT2 wave functions use this active space as their reference space.

With regard to the potential energy curves, there are only minor differences among the multireference methods, MCSCF, MRCI, and CASPT2. All three methods predict a smooth dissociation to $N+N$. In stark contrast, second-order perturbation theory deviates from the other methods almost immediately and fails to reproduce the correct curve even qualitatively. Of course, this MBPT2 curve would be improved if one used the singlet unrestricted wave function, but this would result in increasingly large spin contamination²⁰ and eventually unidentifiable spin states. The CCSD(T) energy curve is much more stable, deviating only slightly from

the multiconfigurational curves through a large portion of the dissociation process. The molecule is about 75% dissociated before the deviation similar to that observed for MBPT2 begins to appear.

The behavior of the potential energy curves is mirrored in the natural orbital occupation numbers in Table I. This table lists the occupation numbers for the σ , σ^* , π , π^* orbitals. At the equilibrium distance, the occupation numbers for the σ and σ^* orbitals are nearly 2.0 and 0.0, respectively; there are greater deviations from these values for the π and π^* orbitals. For the multiconfiguration methods, the occupation numbers change smoothly from nearly closed shell, single configuration values to six essentially singly occupied orbitals at dissociation, and the numerical values of the NOON are quite similar for these three methods. The single configuration methods are unable to treat this transformation correctly, as is already apparent from the curves in Fig. 1. Nonphysical occupation numbers (greater than 2.0 and less than 0.0) appear along the entire potential energy curve, although these deviations are small at small distances. Particularly noteworthy is the appearance of negative occupation numbers for the second-order perturbation theory natural orbitals at $R = 1.2 \text{ \AA}$, the same distance at which sharp deviations begin to appear in the potential energy curve. These negative occupation numbers increase in magnitude as R increases. For CCSD(T) there are occupation numbers that are slightly larger than 2.0 at smaller values of R , but negative values do not appear until $R = 2.0 \text{ \AA}$. As in the MBPT2 case, this is the distance at which the CCSD(T) potential energy curve begins to sharply deviate from those for the multiconfiguration methods.

The occurrence of negative natural orbital occupation numbers prompted a more detailed examination of this phenomenon, by plotting the MBPT2 total electron density as a function of the NN distance, using the 6-31G(*d*) basis set. The first negative NOON is found at $R = 1.5 \text{ \AA}$. At 2.7 \AA , the total MBPT2 density becomes negative in the bonding region between the two atoms, as illustrated in Fig. 2. At $R = 5.2 \text{ \AA}$, there is a $\text{NOON} > 14.0$ for this 14-electron system. As R increases further, the magnitude of the largest NOON continues to increase to 17 000 at 150 \AA and 100 000 at 400 \AA . The same general trends are found for both smaller (STO-3G) and larger (cc-pVTZ) basis sets, with the only differences being in the quantitative details, such as the distance at which the total density first becomes negative.

The foregoing results suggest that a negative natural orbital occupation number may be a reliable diagnostic for the need to use multiconfiguration wave functions. This is explored further in the following subsections.

B. CH₂ bend potential

The single determinant description of the lowest 1A_1 state of CH₂ has a lone pair of electrons in a doubly occupied a_1 orbital. The molecule in this state is bent with a bond angle of approximately 102 deg. As the bond angle is increased, the excited 1A_1 state, with an out-of-plane lone pair in a doubly occupied b_1 orbital, becomes lower in energy, and the a_1 and b_1 orbitals become the degenerate compo-

nents of the π_u orbital at 180 deg. Thus, the wave function for the 1A_1 state of CH₂, which is dominated by a single configuration near the equilibrium bond angle, becomes dominated by two configurations as the bond angle approaches 180 deg.

Table II shows the principal NOON for singlet CH₂ as a function of bond angle at various levels of theory. Figure 3 shows the corresponding bend potential energy curves with the relative energies set to zero at 102.1 deg (the optimum MBPT2 geometry). All methods produce potential curves with similar shapes near the minimum, but the existence of nonphysical NOON for MBPT2 already indicates problems with the single configuration description of the wave function. As the bond angle is increased, the single configuration approximation becomes progressively worse, and nonphysical NOON are observed for the CCSD(T) method beginning around 160 deg. Up to this point, the CCSD(T) occupation numbers map those of the multiconfigurational methods reasonably well. This is not the case for MBPT2, for which the NOON is essentially constant as the angle is varied.

Multireference perturbation theory eliminates the nonphysical NOON, but a new problem is revealed due to the presence of the excited 1A_1 state, which becomes an intruder state at large bond angles. The effect of intruder states on perturbation theories has been discussed extensively in the literature.²¹⁻³⁰ In the case of CH₂, the CASPT2 potential energy curve is artificially depressed as the angle approaches 180 deg. This produces an incorrect maximum in the potential energy curve around 155 deg. Going to the CASPT3 level of theory³¹ appears to correct this improper behavior, but the height of the bending barrier is still underestimated. The higher levels of perturbation theory produced no significant changes in the NOON.

The presence of an intruder state can be handled properly by two-state multiconfigurational quasidegenerate perturbation theory (MCQDPT).³² Two-state, second-order MCQDPT calculations were carried out for CH₂ using a CASSCF (6 electrons, 6 orbitals) wave function optimized for the equally weighted average of the two lowest 1A_1 states. The bend potential energy curve shown in Fig. 3 is nearly identical to the MRCI curve, indicating the correctness of this approach. No NOON was obtained for the MCQDPT2 density. Alternatively, handling the intruder state by applying the “*g*1 correction” to the zeroth-order Hamiltonian, as suggested by Andersson,³³ improves the CASPT2 results and also predicts a bend potential curve (not shown) very similar to the one obtained at the two-state MCQDPT level.

The results for CH₂ demonstrate the use of nonphysical NOON as an indicator of the breakdown of the single configuration approximation. However, there is no diagnostic for the existence of an intruder state except to examine the excited state energies in the CASSCF calculation.

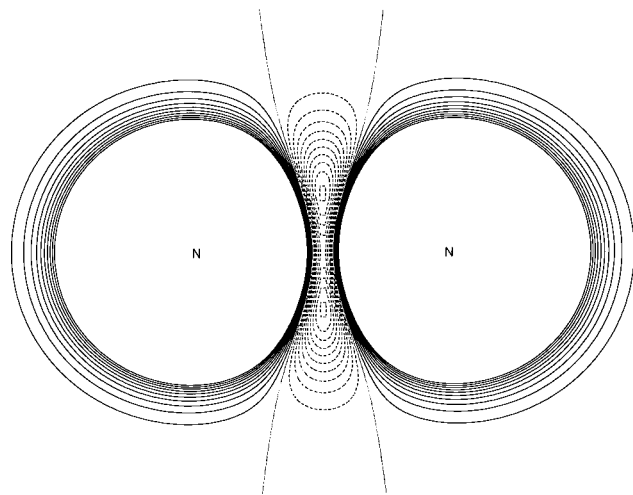
C. Silicon-containing diradicals

Our interest in silicon chemistry has led us to explore the mechanisms and associated molecular structures for many chemical reactions. Among these structures have been transition states and intermediates that are clearly “diradical” in

TABLE I. Natural orbital occupation numbers for the N₂ dissociation curve.

<i>R</i> (Å)		Natural orbital occupation numbers				Nonphysical NOON ^a			
		σ	π	π^*	σ^*				
1.078	MCSCF	1.983	1.945	0.061	0.018				
	MRCI	1.964	1.924	0.071	0.021				
	CASPT2	1.966	1.924	0.069	0.022				
	MBPT2	1.963	1.930	0.061	0.022	2.000 01			
	CCSD(T)	1.956	1.922	0.071	0.021	2.000 01(2)			
1.2	MCSCF	1.974	1.921	0.086	0.028				
	MRCI	1.955	1.899	0.096	0.031				
	CASPT2	1.956	1.900	0.094	0.032				
	MBPT2	1.952	1.907	0.085	0.034	2.000 01(2),	-0.000 01		
	CCSD(T)	1.951	1.898	0.095	0.031	2.000 01(2)			
1.4	MCSCF	1.951	1.862	0.145	0.052				
	MRCI	1.932	1.837	0.158	0.057				
	CASPT2	1.931	1.840	0.154	0.059				
	MBPT2	1.918	1.847	0.149	0.066	2.000 01(2),	-0.000 03,	-0.000 76(2)	
	CCSD(T)	1.929	1.841	0.151	0.055	2.000 02,	2.00001		
1.6	MCSCF	1.911	1.755	0.251	0.094				
	MRCI	1.892	1.730	0.264	0.098				
	CASPT2	1.887	1.732	0.260	0.103				
	MBPT2	1.857	1.749	0.254	0.123	2.000 02(2),	-0.000 18,	-0.006 61(2)	
	CCSD(T)	1.895	1.735	0.255	0.091	2.000 02,	2.00001		
1.8	MCSCF	1.825	1.558	0.446	0.179				
	MRCI	1.817	1.545	0.446	0.174				
	CASPT2	1.800	1.536	0.454	0.190				
	MBPT2	1.761	1.601	0.414	0.212	2.000 02(2),	-0.001 24,	-0.018 06(2)	
	CCSD(T)	1.826	1.486	0.500	0.162	2.000 02,	2.000 01		
2.0	MCSCF	1.663	1.325	0.677	0.341				
	MRCI	1.675	1.329	0.660	0.316				
	CASPT2	1.640	1.308	0.681	0.350				
	MBPT2	1.623	1.394	0.640	0.342	2.000 27,	2.000 02,	-0.007 56,	-0.037 66
	CCSD(T)	1.563	1.174	0.811	0.425	2.000 01(2),	-0.000 05(2),	-0.000 04(2)	
2.2	MCSCF	1.480	1.176	0.825	0.522				
	MRCI	1.502	1.182	0.807	0.487				
	CASPT2	1.463	1.165	0.824	0.527				
	MBPT2	1.442	1.128	0.939	0.519	2.023 79,	2.000 02,	-0.025 71,	-0.071 25
	CCSD(T)	1.417	2.658	0.709	0.571	3 more>2.0	19 more<0.0		
2.4	MCSCF	1.339	1.101	0.899	0.662				
	MRCI	1.359	1.104	0.885	0.631				
	CASPT2	1.326	1.094	0.896	0.665				
	CCSD(T)		Nonconvergent						
2.6	MCSCF	1.241	1.062	0.938	0.760				
	MRCI	1.255	1.062	0.927	0.734				
	CASPT2	1.230	1.056	0.935	0.760				
3.0	MCSCF	1.125	1.026	0.974	0.875				
	MRCI	1.129	1.022	0.966	0.860				
	CASPT2	1.118	1.020	0.970	0.873				
4.0	MCSCF	1.024	1.003	0.997	0.976				
	MRCI	1.019	0.998	0.992	0.972				
	CASPT2	1.019	0.998	0.992	0.972				
5.0	MCSCF	1.004	1.000	1.000	0.996				
	MRCI	0.998	0.995	0.994	0.998				
	CASPT2	0.999	0.996	0.995	0.992				

^aNumber in parentheses indicates the number of times this value occurs.

FIG. 2. Total MBPT2/6-31G(d) N_2 density at $R=2.7 \text{ \AA}$.

their nature, as indicated by their MCSCF natural orbital occupation numbers. Two such structures are considered here, as well as a related species for which the configurational mixing is somewhat smaller.

TABLE II. Natural orbital occupation numbers for the 1A_1 state of CH_2 as a function of bond angle. At each angle, the aug-cc-pVTZ/MBPT2 optimized bond length was used for all calculations. The optimum aug-cc-pVTZ/MBPT2 bond angle is 102.1 deg.

Angle	Method	Principal lone pair		Nonphysical
		NOON	NOON	NOON
90.0	MRCI	1.896	0.077	...
	CASPT2	1.891	0.088	...
	CASSCF	1.912	0.085	...
	CCSD(T)	1.901	0.071	...
	MBPT2	1.961	0.015	-0.000 03, 2.000 012
102.1	MRCI	1.887	0.086	...
	CASPT2	1.885	0.094	...
	CASSCF	1.906	0.092	...
	CCSD(T)	1.894	0.077	...
	MBPT2	1.962	0.014	-0.000 02, 2.000 011
120.0	MRCI	1.862	0.112	...
	CASPT2	1.871	0.107	...
	CASSCF	1.894	0.105	...
	CCSD(T)	1.876	0.095	...
	MBPT2	1.961	0.015	-0.000 03, 2.000 009
150.0	MRCI	1.668	0.303	...
	CASPT2	1.771	0.203	...
	CASSCF	1.797	0.201	...
	CCSD(T)	1.772	0.196	...
	MBPT2	1.961	0.016	-0.000 03, 2.000 006
170.0	MRCI	1.104	0.865	...
	CASPT2	1.133	0.833	...
	CASSCF	1.154	0.846	...
	CCSD(T)	1.612	0.354	-0.000 01
	MBPT2	1.960	0.016	-0.000 03, 2.000 004
180.0	MRCI	0.984	0.984	...
	CASPT2	0.982	0.982	...
	CASSCF	1.000	1.000	...
	CCSD(T)	1.572	0.394	-0.000 01
	MBPT2	1.960	0.016	-0.000 03, 2.000 004

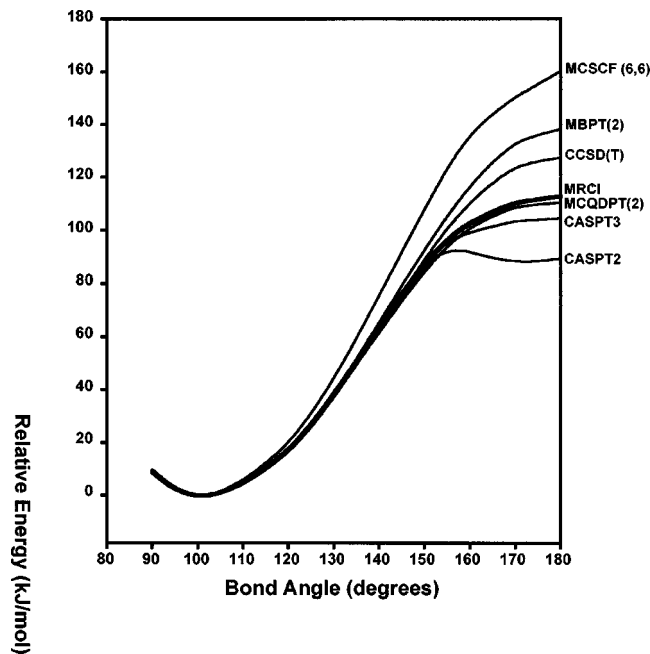


FIG. 3. Relative energy curves for CH_2 bend at various levels of theory using the aug-cc-pVTZ basis set. The potential energies were all set to zero at 102° to facilitate comparison of the curve shapes.

The ring opening of silacyclobutane to eventually yield ethylene+silene can occur via either a stepwise mechanism or a concerted one-step process.³⁴ In the stepwise mechanism, the first step proceeds via a transition state in which either a C–C or a C–Si bond is broken and is nearly diradical, whereas the concerted transition state has considerably less diradical character (configurational mixing). The MCSCF/6-31G(*d*)³⁵ active space used for the study of the ring opening mechanisms consisted of the eight electrons in the CC and CSi bonds and the corresponding eight bonding and antibonding orbitals.

Table III lists the MCSCF, MBPT2, and CCSD(T) natural orbital occupation numbers for the diradical transition state corresponding to CC bond cleavage and the concerted transition state. Only the NOON corresponding to the eight orbitals in the MCSCF active space are included in the table. For the diradical transition state, the MCSCF occupation numbers for the breaking CC bond and antibond orbitals are 1.275 and 0.726, respectively. The CCSD(T) density reproduces these values very well, while second-order perturbation theory does not. The latter method has a NOON of 1.911 and 0.094 for the bonding and antibonding orbitals, respectively. Both single reference methods have nonphysical, negative NOON, so once again the negative occupation numbers appear to function as a diagnostic for the need for a multiconfiguration wave function.

The MCSCF NOON for the concerted transition state clearly suggest significant configurational mixing; in particular, the bonding/antibonding pair 1.776/0.233. Once again, CCSD(T) reproduces these occupation numbers very well, while the MBPT2 values are essentially the same as those for the diradical transition state. Nonetheless, in this case the configurational mixing is relatively small, and no nonphysical NOON appear.

TABLE III. Natural orbital occupation numbers for silacylobutane.

A. Diradical transition state			
Orbital	MCSCF	MBPT2	CCSD(T)
1	1.981	1.970	1.959
2	1.982	1.962	1.952
3	1.972	1.959	1.950
4	1.274	1.911	1.234
5	0.726	0.427	0.735
6	0.027	0.024	0.031
7	0.019	0.022	0.030
8	0.017	0.018	0.027
Nonphysical		-0.0001	-0.007
		-0.085	
		2.042	

B. Concerted transition state			
Orbital	MCSCF	MBPT2	CCSD(T)
1	1.980	1.966	1.954
2	1.982	1.961	1.950
3	1.971	1.955	1.935
4	1.776	1.903	1.791
5	0.233	0.088	0.201
6	0.022	0.025	0.036
7	0.020	0.023	0.031
8	0.017	0.020	0.029

Silicon–oxygen compounds have a variety of practical applications. Consequently, we have previously explored several unusual Si–O compounds, including the four-membered ring $\text{Si}_2\text{O}_2\text{H}_2$.³⁶ Two configuration SCF (TCSCF) calculations on this species show that it is essentially a pure diradical. The TCSCF/6-31G(*d*) natural orbital occupation numbers are compared in Table IV with those obtained using CASPT2, second-order perturbation theory, and CCSD(T), all with the same basis set. As noted above, the TCSCF NOON are essentially 1.0 for the two orbitals in the active space. Those obtained with CASPT2 are very similar; the slight differences reflect the fact that all valence orbitals are correlated in the CASPT2 calculation. Unlike the two previous examples, in this case CCSD(T) is unable to fully capture the diradical character, as monitored by the NOON values of 1.343 and 0.643. Concomitantly, CCSD(T) has one negative occupation number. As we would by now expect, MBPT2 has even more problems. The two main active or-

TABLE IV. Natural orbital occupation numbers for $\text{Si}_2\text{O}_2\text{H}_2$.

Orbital	TCSCF	CASPT2	MBPT2	CCSD(T) ^a
σ	1.004	1.009	1.742	1.343(1.225)
σ^*	0.996	0.998	0.253	0.643(0.758)
Nonphysical			-0.0001	-0.0019 (-0.0019,
			-0.0045	-0.00001)

^aResults using the cc-pVTZ basis set are given in parentheses.

bitals have occupation numbers of 1.742 and 0.253, as well as two negative NOONs. The negative NOONs alone suggest that MBPT2 and CCSD(T) are levels of theory that should not be used for this problem; this is consistent with the diradical character indicated by the MCSCF and CASPT2 results.

D. Ethylene analogs

It was noted in a previous paper³⁷ that the diradical character of $\text{H}_2\text{E}=\text{EH}_2$ increases in the order E=C, Si, Ge, Sn, based on the results of MCSCF(4,4)/3-21G* calculations. The results of these calculations are compared with the NOON obtained from MBPT2 and CCSD(T) in Table V. Since the σ and σ^* occupation numbers are close to 2.0 and 0.0, respectively, only the π and π^* results are listed in the table. The CCSD(T) occupation numbers follow those of the MCSCF calculations, while the MBPT2 values are essentially constant. Even so, the smallest π occupation number is 1.80 for E=Sn, so while there are MBPT2 and CCSD(T) NOONs slightly greater than 2.0 for all elements except C, there are no negative values. It is therefore likely that CCSD(T) will be a reliable level of theory for each of these species.

E. Basis set effects

It is reasonable to consider the dependence of the foregoing analyses of natural orbital occupation numbers on the quality of the basis sets used for the calculations. To this end, the long distance portion of the CCSD(T) N_2 dissociation curve has been reconsidered using several of the correlation-consistent basis sets, ranging from cc-pVDZ to cc-pV5Z.¹⁹ The results of these calculations are summarized in Table VI,

TABLE V. Comparison of natural orbital occupation numbers for F_2H_4 .^a

E	Method	π	π^*	Nonphysical occupation numbers			
C	MCSCF	1.92	0.08				
	CCSD(T)	1.90	0.09				
	MBPT2	1.94	0.05				
Si	MCSCF	1.84	0.16				
	CCSD(T)	1.82	0.17	2.000 02,	2.000 01(3)		
	MBPT2	1.94	0.05	2.000 04,	2.000 03,	2.000 02(2),	2.000 01(2)
Ge	MCSCF	1.82	0.18				
	CCSD(T)	1.82	0.16	2.000 01(3)			
	MBPT2	1.94	0.05	2.000 02(2),	2.000 01(3)		
Sn	MCSCF	1.78	0.22				
	CCSD(T)	1.80	0.20	2.000 03(2)			
	MBPT2	1.94	0.05	2.000 04(2),	2.000 03,	2.000 02,	2.000 01(2)

^a3-21G basis set for Si, Ge, Sn; 3-31G* for C.

TABLE VI. CCSD(T) natural orbital occupation numbers for N₂ as a function of basis set.^a

R(Å)		Natural orbital occupation numbers				NOON<0 ^b	ΔE (kal/mol) ^c
		σ	π	π*	σ*		
1.6	aug pVDZ	1.891	1.727	0.264	0.092	0	0.0
	pVTZ	1.895	1.735	0.255	0.091	0	0.0
	aug pVTZ	1.894	1.738	0.250	0.090	2	0.0
	pVQZ	1.895	1.741	0.248	0.090	0	0.0
	pV5Z	1.895	1.743	0.246	0.090	0	0.0
1.8	aug pVDZ	1.817	1.449	0.537	0.172	2	40.8
	pVTZ	1.826	1.486	0.500	0.162	0	44.1
	aug pVTZ	1.827	1.504	0.481	0.159	2	44.4
	pVQZ	1.829	1.511	0.478	0.157	2	45.3
	pV5Z	1.830	1.518	0.467	0.156	2	45.7
2.0	aug pVDZ	1.493	1.313	0.674	0.496	2	47.0
	pVTZ	1.563	1.174	0.811	0.425	4	56.7
	aug pVTZ	1.585	1.110	0.874	0.402	7	59.0
	pVQZ	1.597	1.087	0.897	0.390	5	61.2
	pV5Z	1.606	1.061	0.922	0.382	5	62.6
2.2	aug pVDZ	1.563	-.851	2.794	0.427	19	-6.9
	pVTZ	1.417	-.709	2.659	0.571	17	-14.7
	aug pVTZ	1.348	-.643	2.583	0.642	23	-21.8
	pVQZ	1.316	-.605	2.548	0.673	20	26.1
	pV5Z	1.295	-.572	2.511	0.764	22	29.6

^aCCSD(T) does not converge with the cc-pVDZ basis set.^bIn addition to π orbitals.^cEnergy relative R=1.6.

for R (NN) ranging from 1.6–2.2 Å. One may draw several conclusions from this table: (a) The CCSD(T) does not converge for any of these distances when the smallest basis set, cc-pVDZ, is used; the longest NN distance for which convergence is obtained with this basis set is 1.4 Å; (b) While the next largest basis set, aug-cc-pVDZ, does converge for all distances in the table, there are quantitative, but not qualitative, differences between the NOON obtained with this basis set and the others; (c) As the basis set is improved further, there are only small quantitative changes in the occupation numbers as R increases, although the NOON for the “active” orbitals do *slowly* approach those obtained with the multireference wavefunctions; (d) Nonetheless, negative

NOON appear at 1.8 Å for all but one basis set (cc-pVTZ), many negative NOON occur for all basis sets at 2.0 Å, and large numbers of nonphysical NOON appear at 2.2 Å; (e) As already illustrated in Fig. 1, the CCSD(T) energy suddenly drops precipitously at 2.2 Å, another signal that the single reference method is failing here. So, while improving the basis set does result in slight quantitative modifications, at very large cost for any molecule of reasonable size, the fundamental behavior described in previous paragraphs is unaltered.

Similar conclusions can be drawn by improving the basis sets used for the other molecules considered in this work. For example, the results obtained with the cc-pVTZ basis set for

TABLE VII. Nonphysical natural orbital occupation numbers for selected molecules.

Molecule	MBPT2 NOON	CCSD(T)NOON	T_1
O ₂	2.000 03, 2.000 01, -0.000 05, -0.001 60	2.000 01	0.0390
FOOF	2.000 01(2), -0.000 01, -0.000 09, -0.000 28 -0.000 34, -0.000 35, -0.000 38, -0.000 69	2.000 01(2)	0.0298
O ₃	-0.000 04, -0.000 15, -0.000 20, -0.000 67, -0.001 52	2.000 01(3)	0.0289
OH-	-0.000 08, -0.002 02	none	0.0220
ONNO	2.000 01(2), -0.000 01(3), -0.000 02 -0.000 03, -0.000 13	2.000 01(4)	0.0198
CO	2.000 02, -0.000 01, -0.000 02(2), -0.000 13	2.000 02	0.0188
HOOF	-0.000 03, -0.000 06, -0.000 18, -0.000 22, -0.000 25, -0.000 45	2.000 01(2)	0.0183
CO ₂	-0.000 02(3), 0.000 04, -0.000 06(2)	2.000 01(2)	0.0183
P ₂	2.000 02(2), 2.000 01, -0.000 07(2)	2.000 03, 2.000 02, 2.000 01(3)	0.0179
HNO	-0.000 02, -0.000 08, -0.000 10, -0.000 39	2.000 01(2), -0.000 01	0.0164
HF	-0.000 02, -0.000 22(2)	none	0.0102
H ₂ O	-0.000 11, -0.000 38	none	0.0090

TABLE VIII. Nonphysical MBPT2 natural orbital occupation numbers for selected molecules.

Molecule	aug-cc-pVTZ	pVTZ	pVQZ
O ₂	2.000 03, 2.000 01, -0.000 05, -0.001 60	2.000 03, 2.000 01 -0.001 54	2.000 02, 2.000 01 -0.000 03(2), -0.001 68
FOOF	2.000 01(2), -0.000 01, -0.000 09, -0.000 28, -0.000 34, -0.000 35, 0.000 38, -0.000 69	2.000 01(2), -0.000 10, -0.000 20	nonconvergent
O ₃	-0.000 04, -0.000 15, -0.000 20, -0.000 67, -0.001 52	-0.000 10, -0.000 12, -0.000 20	-0.000 23, -0.000 25, -0.000 33
OH- ONNO	-0.000 08, -0.002 02 2.000 01(2), -0.000 01(3), -0.000 02, -0.000 03, -0.000 13	none 2.000 01(2) -0.000 01	none 2.000 01(2) -0.000 01, -0.000 08
CO	2.000 02, -0.000 01, -0.000 02(2), -0.000 13	2.000 02, -0.000 02(2), -0.000 03	2.000 01, -0.000 03(2), -0.000 08
HOOF	-0.000 03, -0.000 06, -0.000 18, 0.000 22, -0.000 25, -0.000 45	-0.000 01, -0.000 08	-0.000 01(2), -0.000 07, -0.000 10
CO ₂ P ₂	-0.000 02(3), -0.000 04, -0.000 06(2) 2.000 02(2), 2.000 01, -0.000 07(2)	-0.000 01, -0.000 08(2) 2.000 01, 2.000 02(2)	-0.000 03, -0.000 08(2) 2.000 01(2), 2.000 02 2.000 03, 2.000 04, -0.000 02(2)
HNO	-0.000 02, -0.000 08, -0.000 10, -0.000 39	-0.000 11	2.000 01, -0.000 05, -0.000 10
HF H ₂ O	-0.000 02, -0.000 22(2) -0.000 11, -0.000 38	none none	-0.000 01 -0.000 01

Si₂O₂H₂ are given in parentheses in Table IV. Again, while the NOONs for the active orbitals are closer to those obtained using multireference wave functions, the negative NOON is essentially the same as that for the smaller basis set, reflecting the need for a multireference description.

The T_1 diagnostic that single configuration wave functions may be suspect (for $T_1 > 0.02$) has been applied to several compounds by the developers of this technique. In Table VII a subset of these compounds, their T_1 values, and those MBPT2 and CCSD(T) natural orbital occupation numbers that are outside the physically acceptable range of 0–2, all calculated with the aug-cc-pVTZ basis set, are listed. The table is sorted in order of decreasing T_1 . For all of these molecules, the CCSD(T) NOON are within the physical range or only very slightly outside the range. On the other hand, the preponderance of negative MBPT2 NOON is striking. The overall trend is that as T_1 decreases, the occurrence of negative MBPT2 NOON and the frequency of such values decreases, but this is certainly not monotonic. To probe the basis-set dependence of these results, the MBPT2 NOON were determined for the same set using the cc-pVTZ and cc-pVQZ basis sets. The results are given in Table VIII, where the aug-cc-pVTZ values are repeated for ease of comparison. The simple molecules H₂O and HF are better behaved when the diffuse functions are removed from the basis set, but there are still small negative NOONs with the larger basis. Indeed, overall the behavior of second-order perturbation theory deteriorates as the size of the basis set is increased. Similar disturbing behavior has been noted by Olsen and co-workers.³⁸

Finally, consider the apparently simple Ne atom, for which one expects a single-configuration RHF-based wave function to be a reasonable approximation. For the cc-pVTZ basis set, the largest natural orbital occupation number obtained from an MCSCF(8,8) wave function is only 0.013. So,

this is not a system for which one expects a breakdown of second-order perturbation theory due to the need for a multiconfiguration wave function. Previously, Olsen *et al.*³⁸ have analyzed Ne to infinite order using the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets and found that the augmented basis set causes divergence of the perturbation expansion. In the current work, the MBPT2 NOON have been calculated with several of the correlation consistent basis sets. For the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, no negative NOON occurs. However, for the two largest nonaugmented basis sets, cc-pV5Z and cc-pV6Z, NOON of -0.000 01 and -0.000 03, respectively, appear. For the augmented double, triple, quadruple, and pentuple basis sets, one obtains NOONs of -0.000 08, -0.000 06, -0.000 04, and -0.000 04, respectively. While the magnitudes of these negative occupation numbers are small, their occurrence is disturbing. Since these results appear to track those of Olsen and co-workers, the appearance of negative NOONs once again appears to be a reliable and physically meaningful diagnostic for wave functions that may be unreliable.

IV. CONCLUSIONS

In this paper, we have demonstrated that a simple and apparently consistent diagnostic for the need for a multireference treatment is provided by the occurrence of nonphysical (especially negative) natural orbital occupation numbers obtained by diagonalizing the density matrix that is obtained from correlated single reference methods. Since the natural orbitals are readily obtained for most single reference methods that are provided in popular computational chemistry codes, this diagnostic is easily applied and is therefore recommended by the authors. While only the results for second-

order perturbation theory and coupled-cluster methods have been presented here, similar results are obtained for fourth-order perturbation theory.

It is also noteworthy that CCSD(T) performs extremely well for systems that have significant multiconfiguration character and for which second- and fourth-order perturbation theory breaks down. Clearly, CCSD(T) is the single reference method of choice.

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- ¹M. W. Schmidt and M. S. Gordon, *Annu. Rev. Phys. Chem.* **49**, 233 (1998).
- ²P.-O. Lowdin, *Phys. Rev.* **97**, 1474 (1955); P.-O. Lowdin and H. Shull, *ibid.* **101**, 1730 (1956)
- ³P. Pulay and T. P. Hamilton, *J. Chem. Phys.* **88**, 4926 (1988); J. M. Bofill and P. J. Pulay, *Chem. Phys.* **89**, 3637 (1989); K. Wolinski and P. Pulay, *ibid.* **90**, 3647 (1989).
- ⁴R. Seeger and J. A. Pople, *J. Chem. Phys.* **66**, 3045 (1977).
- ⁵(a) T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem., Symp.* **23**, 199 (1989); (b) T. J. Lee, M. Head-Gordon, and A. P. Rendell, *Chem. Phys. Lett.* **243**, 402 (1995); (c) C. L. Janssen and I. M. B. Nielsen, *ibid.* **290**, 423 (1998); (d) for an alternative approach based on double excitation amplitudes, see J. D. Watts, M. Urban, and R. J. Bartlett, *Theor. Chim. Acta* **90**, 341 (1995).
- ⁶H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig 1937); R. P. Feynman, *Phys. Rev.* **41**, 721 (1939).
- ⁷K. Raghavachari and J. A. Pople, *Int. J. Quantum Chem.* **XX**, 1067 (1981); G. H. F. Diercksen, B. O. Roos, and A. J. Sadlej, *Chem. Phys.* **59**, 29 (1981); J. E. Rice and R. D. Amos, *Chem. Phys. Lett.* **122**, 583 (1985); K. B. Wiberg, C. M. Hadad, T. J. LePage, C. M. Breneman, and M. J. Frisch, *J. Phys. Chem.* **96**, 671 (1992).
- ⁸A. P. L. Rendell, G. B. Backskay, N. S. Hush, and N. C. Handy, *J. Chem. Phys.* **87**, 5976 (1987).
- ⁹K. Ruedenberg and K. R. Sundberg, in *Quantum Science*, edited by J. L. Calais, O. Goscinski, J. Linderberg, and Y. Ohrn (Plenum, New York), p. 505; L. M. Cheung, K. R. Sundberg, and K. Ruedenberg, *Int. J. Quantum Chem.* **16**, 1103 (1979).
- ¹⁰P. E. Siegbahn, A. Heiberg, B. O. Roos, and B. Levy, *Phys. Scr.* **21**, 323 (1980); B. O. Roos, P. R. Taylor, and P. E. Siegbahn, *Chem. Phys.* **48**, 157 (1980); B. O. Roos, *Int. J. Quantum Chem.* **S14**, 175 (1980).
- ¹¹K. Andersson, P.-A. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **94**, 5483 (1990); K. Andersson, P.-A. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **96**, 1218 (1992).
- ¹²J. A. Pople, R. Seeger, and R. Krishnan, *Int. J. Quantum Chem.* **S11**, 149 (1979).
- ¹³R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).
- ¹⁴J. Paldus, in *Relativistic and Electron Correlation Effects in Molecules and Solids*, edited by G. Mali (Plenum, New York, 1994), p. 207; R. D. Bartlett, in *Modern Electronic Structure Theory. I*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), p. 1047.
- ¹⁵M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, K. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, Jr., *J. Comput. Chem.* **14**, 1347 (1993).
- ¹⁶MOLPRO: H.-J. Werner and P. J. Knowles, University of Sussex, 1991; H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985); P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- ¹⁷ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: 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. Balkova, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett, Integral packages: vmol (J. Almlof, P. R. Taylor); vPROPS (P. R. Taylor); ABACUS (T. Helgaker, H. J. Aa Jensen, P. Jorgensen, J. Olsen, and P. R. Taylor).
- ¹⁸M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN 92, Revision A, Gaussian, Inc., Pittsburgh, PA, 1992.
- ¹⁹T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992); D. E. Woon and T. H. Dunning, Jr., *ibid.* **98**, 1358 (1993).
- ²⁰A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1982).
- ²¹J. Finley, P.-A. Malmqvist, B. O. Roos, and L. Serrano-Andres, *Chem. Phys. Lett.* **288**, 299 (1998).
- ²²N. Forsberg and P.-A. Malmqvist, *Chem. Phys. Lett.* **274**, 196 (1997).
- ²³B. O. Roos, K. Andersson, M. P. Fulshcher, L. Serrano-Andres, K. Pierloot, M. Merchán, and V. Molina, *THEOCHEM* **388**, 257 (1996).
- ²⁴B. O. Roos, K. Andersson, M. P. Fulshcher, L. Serrano-Andres, K. Pierloot, M. Merchán, *Adv. Chem. Phys.* **93**, 219 (1996).
- ²⁵B. O. Roos and K. Andersson, *Chem. Phys. Lett.* **245**, 215 (1995).
- ²⁶K. Andersson, B. O. Roos, P.-A. Malmqvist, and P. O. Widmark, *Chem. Phys. Lett.* **230**, 391 (1994).
- ²⁷K. Andersson, P.-A. Malmqvist, B. O. Roos, A. J. Sadley, and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990).
- ²⁸K. Wolinski and P. Pulay, *J. Chem. Phys.* **90**, 3647 (1989).
- ²⁹K. Wolinski, H. L. Sellers, and P. Pulay, *Chem. Phys. Lett.* **140**, 225 (1987).
- ³⁰B. O. Roos, P. Linse, P. E. M. Siegbahn, and M. R. A. Blomberg, *Chem. Phys.* **66**, 197 (1982).
- ³¹H.-J. Werner, *Mol. Phys.* **89**, 645 (1996).
- ³²H. Nakano, *J. Chem. Phys.* **99**, 7983 (1993); *Chem. Phys. Lett.* **207**, 372 (1993).
- ³³K. Andersson, *Theor. Chim. Acta* **91**, 31 (1995).
- ³⁴M. S. Gordon, T. J. Barton, and H. Nakano, *J. Am. Chem. Soc.* **119**, 11966 (1997).
- ³⁵W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972); M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, and J. A. Pople, *ibid.* **77**, 3654 (1982).
- ³⁶M. W. Schmidt, K. A. Nguyen, M. S. Gordon, and J. A. Montgomery, Jr., *J. Am. Chem. Soc.* **113**, 5998 (1991).
- ³⁷T. L. Windus and M. S. Gordon, *J. Am. Chem. Soc.* **114**, 9559 (1992).
- ³⁸J. Olsen, O. Christiansen, H. Koch, and P. J. Jorgensen, *J. Chem. Phys.* **105**, 5082 (1996).