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Full configuration interaction benchmark calculations for transition moments

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Full configuration-interaction (FCI) calculations have been performed for the $\tilde{a}^1A_1$–$\tilde{b}^1B_1$ and $\tilde{a}^1A_1$–$(2)^1A_1$ transitions in CH_2 and for selected dipole and quadrupole transitions in BeO. The FCI transition moments are compared to those obtained from correlation treatments that truncate the n-particle expansion. The state-averaged MCSCF/SOCI and FCI results agree well, even for BeO, where the CASSCF level nonorthogonal transition moment differs from the state-averaged CASSCF transition moment.

Key words: Transition moments — Full CI

1. Introduction

Recent advances in computational methodology that exploit the capabilities of vector processors have significantly increased the accuracy of quantum mechanical calculations. For example, electronic transition moments in diatomic molecules can be computed [1, 2] with sufficient accuracy to obtain Einstein coefficients and radiative lifetimes that rival the best experimental determinations. One advance that has made this possible is the availability of full configuration interaction (FCI) calculations; these have made it possible to evaluate errors introduced into molecular properties from truncation of the n-particle expansion [3–4]. A significant complication in the evaluation of transition state properties is that the wave functions of both states must be expanded in one set of orthogonal molecular orbitals (MO) if large CI expansions are employed. Hence FCI calculations, which are invariant to the choice of the orbital basis, again provide an excellent calibration of truncated CI methods.

The utility of FCI calculations is well illustrated by our previous study [1] of the OH $A-X$ transition moment. In this case, agreement with the FCI calculations was obtained only after the 1δ orbital was added to both the CASSCF active space and multireference CI (MRCI) reference space. This study also underscored the necessity of FCI benchmarking in a realistic one-particle basis, since this effect could not be observed in basis sets without d functions. By designing a CASSCF/MRCI treatment that reproduced the FCI in a realistic one-particle basis set, and then taking this truncated CI approach to near the one-particle basis set limit, radiative lifetimes for the $A\,^2\Sigma^+$ state of OH could be computed with sufficient accuracy to identify the most accurate experimental determinations. One simplification in the OH case is that a state-averaged CASSCF treatment provides a good orbital basis for both the $X\,^2\Pi$ and $A\,^2\Sigma^+$ states.

In this work, we study the electronic transition moments between several states of CH_2 and BeO to determine how well approximate correlation methods perform when states are not well described by a single reference configuration. Since the optimal orbitals for the lowest states of BeO are very different, these FCI benchmark calculations will help to define the limits of the state-averaged CASSCF/MRCI approach. Section 2 contains a description of the methods used. Section 3 comprises results and discussion and Sect. 4 our conclusions.

2. Methods

For the CH_2 calculations, the carbon basis set is the Dunning double-zeta contraction [5] of the Huzinaga (9s5p) primitive set [6], while the hydrogen basis set is the Dunning $(4s)/[2s]$ contraction [5], with the exponents scaled. These basis sets are augmented with H $2p(1.0)$ and C $3d(0.51)$ [7] polarization functions, and all six components of the $3d$ function are included. All calculations are performed at the optimized theoretical $\tilde{a}\,^1A_1$ geometry [7] used in our previous [8] FCI calculation of the $\tilde{a}\,^1A_1$–$\tilde{X}\,^3B_1$ separation ($r(\mathrm{CH}) = 2.11\ a_0$ and $\angle\mathrm{HCH} = 102.4°$). Both the geometry and basis set are given explicitly in [8].

For the BeO calculations, we use the oxygen basis set tabulated in our earlier studies of the OH $X^2\Pi$ dipole moment [9] and OH A–X transition moment. This oxygen basis set is the Dunning [5] $[4s\ 2p]$ contraction of the Huzinaga [6] $(9s\ 5p)$ primitive set, augmented with a diffuse $2p$ function [10] to describe the O^- character in BeO. This basis is further augmented by either a $1d$ (0.8) or $2d$ (1.5 and 0.5) set - denoted $1d$ or $2d$ basis, respectively. The Be s basis set is a $[4s]$ contraction of the van Duijneveldt [11] $9s$ primitive set. To account for the $2s$–$2p$ near-degeneracy, the four $2p$ functions optimized by Yarkony and Schaefer [12] for the $^3P(2s^12p^1)$ state are added and contracted to two functions. Since these calculations can serve as benchmarks for other methods, the Be basis set is tabulated in Table 1; the other basis sets have been tabulated in previous work [8, 9]. The $3s$ components of the $3d$ functions have been deleted in the BeO calculations, all of which have been performed at an internuclear distance of $2.515a_0$.

Table 1. The Be $(9s4p)/[4s2p]$ Gaussian basis set

Function	s		Function	p	
	Exp	Coef		Exp	Coef
1	2732.32810	0.000745	1	3.20200	0.052912
1	410.319810	0.005724	1	0.69230	0.267659
1	93.672648	0.028888	1	0.20160	0.792085
1	26.587957	0.107092	2	0.06331	1.000000
1	8.629560	0.280109			
1	3.056264	0.446089			
2	1.132424	1.000000			
3	0.181732	1.000000			
4	0.059170	1.000000			

Excluding FCI wave functions, the choice of the molecular orbital basis is always a concern in the calculation of transition moments. Since a common set of orbitals reduces the complexity of evaluating the transition moment, we use common orbitals except for one nonorthogonal calculation at the CASSCF level.

Zeroth-order descriptions of the states of CH_2 are obtained in several ways. The best single reference descriptions of the $\tilde{b}^1B_1$, $\tilde{a}^1A_1$ and $(2)^1A_1$ states are

$$\tilde{b}^1B_1 \quad 1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1 \tag{1}$$

$$\tilde{a}^1A_1 \quad 1a_1^2 2a_1^2 1b_2^2 3a_1^2 \tag{2}$$

and

$$(2)^1A_1 \quad 1a_1^2 2a_1^2 1b_2^2 1b_1^2. \tag{3}$$

Since the $\tilde{b}^1B_1$ state reference has both the $1b_1$ and $3a_1$ orbitals singly occupied, it is used to define orbitals for several of our treatments. The next level of approximation is a state-averaged calculation for the single configuration descriptions of the $\tilde{b}^1B_1$ and $\tilde{a}^1A_1$ states, i.e. average of Eqs. (1) and (2). The final reference wave functions are state-averaged CASSCF treatments. In all configurations, the $1a_1$ orbital (the C $1s$ orbital) is constrained to be doubly occupied, and the remaining six electrons are distributed in all ways among the C $2s$ and $2p$ orbitals and H $1s$ orbitals. Three different state-averaged CASSCF calculations were performed; the first averages the $\tilde{a}^1A_1$ and $\tilde{b}^1B_1$ states, the second averages the $\tilde{a}^1A_1$ and $(2)^1A_1$ states, while the third averages all three states.

More extensive correlation is added among the six valence electrons using several different approximations. For the single reference-based approaches such as single and double excitation CI (SDCI), we use either the $\tilde{b}^1B_1$ SCF orbitals or those from the state-averaged single configuration descriptions. To account for the differential effect of higher excitations on the moments we use coupled pair functional (CPF) methods [13, 14]. In this work, we use the Chong-Langhoff modified form [14] of CPF (MCPF) as implemented by Blomberg and Siegbahn [15]. In the Blomberg and Siegbahn direct MCPF program, the excitation levels are classified by spin orbital substitutions as in the original CPF implementation [13]. The moments between MCPF wave functions are computed as for SDCI wave functions after normalizing.

The CASSCF wave functions are used as the zeroth-order references for the multireference CI (MRCI) calculations. Since we include all single and double excitations from all CSFs in the CASSCF reference wave function and all orbitals in the MRCI references are active in the CASSCF, all MRCI calculations performed in this work are second-order CI (denoted SOCI). The multireference analog of the Davidson correction [16], namely $\Delta E_{SD}\ (1-\sum_R C_R^2)$, where ΔE_{SD} is the difference between the energy of the reference CSF's and the SOCI, and the C_R are the coefficients of the reference configurations in the SOCI wave function, is used to estimate the effect of higher excitations on the state separations. The equivalent CI treatment is also carried out with the externally contracted CI (CCI) approach [17], to estimate the effect of reducing the flexibility in the description of the dynamical correlation. The $\tilde{b}^1B_1$ SCF orbitals are used as the molecular orbital basis in the FCI calculations. However, the FCI results are expected to be insensitive to the MO basis, since the $1a_1$ orbital is nearly invariant to this choice based on current MRCI results and previous FCI studies of CH_2 [8].

The BeO molecule represents more of a challenge for state-averaged CASSCF methods, since many of its electronic states are not well described by a single-reference configuration. The best single configuration description of the $X\ ^1\Sigma^+$ state is

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4, \tag{4}$$

whereas the $B^1\Sigma^+$ and $(1)^1\Delta$ states are best described as

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 5\sigma^1 1\pi^4 \tag{5}$$

and

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^3 2\pi^1, \tag{6}$$

respectively. Occupation (5) and the $^1\Sigma^+$ coupling of occupation (6) are also very important CSFs in the $X\ ^1\Sigma^+$ CASSCF wave function, having coefficients of greater than 0.2. The $A\ ^1\Pi$ state is very ionic and well characterized by the occupation

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3, \tag{7}$$

where the orbitals are localized; the 1σ and 2σ are the O and Be $1s$ orbitals, the 3σ is the O $2s$, while the 4σ and 1π are the O $2p$ orbitals. The open-shell 5σ is a Be $2s$-$2p$ hybrid orbital polarized away from the oxygen. The $X\ ^1\Sigma^+$ state contains some O–Be covalent bonding in addition to the ionic component.

For the $1d$ basis set calculations on BeO, the orbitals are determined from a state-averaged CASSCF calculation for the $X\ ^1\Sigma^+$, $B\ ^1\Sigma^+$, and $(1)\ ^1\Delta$ states (three lowest roots of $^1A_1$ symmetry in C_{2v}), and the A $^1\Pi$ state. In the $2d$ basis set we focus on the $X\ ^1\Sigma^+$-$A\ ^1\Pi$ moment, so only these two states are included in the state-averaged CASSCF treatment. While the calculations are performed in C_{2v}

symmetry, full symmetry and equivalence restrictions are imposed on the CASSCF (or SCF) orbitals. The CASSCF calculations have the O $2p$ and the Be $2s$ and $2p$ orbitals and electrons as active. In C_{2v} symmetry, there are three active a_1, one active b_1 and one active b_2 orbitals, denoted [322]. In the $2d$ basis set we add either an extra π orbital [333] or an extra δ orbital [4221] to the active spaces. SOCI calculations are carried out from each of these active spaces. In the $1d$ basis set we also consider separate CASSCF optimizations of the orbitals for the $X\ ^1\Sigma^+$ and $A\ ^1\Pi$ states and compute a nonorthogonal transition moment. To minimize the differential effect of $2s$ correlation, we determine the 1σ–3σ orbitals at the CASSCF level and freeze them in this form for all other calculations.

We use SCF or average SCF orbitals for the single reference SDCI, MCPF or CPF approaches. An SCF calculation for the $A^1\Pi$ state defines the 1–5σ and 1π occupied orbitals, and thus can be used as a reference for either the $^1\Pi$ or $^1\Sigma^+$ states. We also optimize average SCF orbitals for the occupations given by Eqs. (4) and (5). Note that the 1σ–3σ orbitals are taken from the [322] CASSCF.

The FCI calculations have been performed using a modified version of the Knowles and Handy FCI program [4]. The original FCI program has been interfaced into the MOLECULE-SWEDEN [18, 19] codes. Details of our implementation of FCI transition moments and some timings on the CRAY 2 are given in the Appendix. All FCI calculations were performed on the NAS CRAY 2, while all other calculations were performed on the NASA Ames CRAY X-MP/48. The CPF and MCPF calculations were performed using the Blomberg-Siegbahn code [15], while the remaining calculations were performed using the MOLECULE-SWEDEN codes.

3. Results and discussion

First consider the state separations and electronic transition moments for CH_2 in Table 2. When the $\tilde{b}^1B_1$ SCF orbitals are used, the $\tilde{a}^1A_1$–$\tilde{b}^1B_1$ separation at the SCF level is only half that of the FCI, and the transition moment is too large. However, the SCF separation is significantly improved if state-averaged SCF orbitals are used. Both the separation and moment are significantly improved at the SDCI level. The Davidson correction leads to an overshoot of the total energies, especially for the $\tilde{a}^1A_1$ state, which is poorly described by a single reference configuration. The MCPF treatment does quite well for both the separation and the transition moment. Also, since the MCPF accounts for higher excitations, the separation and transition moment are less sensitive to the choice of the molecular orbital basis. It is interesting that the $\tilde{a}^1A_1$–$\tilde{b}^1B_1$ separation in CH_2 varies more with level of treatment than does the transition moment, which is opposite to the trend observed for the $A\ ^2\Sigma^+$–$X\ ^2\Pi$ transition in OH [1].

The state-averaged CASSCF treatments yield a $\tilde{a}^1A_1 - \tilde{b}^1B_1$ separation and transition moment that are about as accurate as the SDCI treatment based on $\tilde{b}^1B_1$ orbitals, whether just the $\tilde{b}^1B_1$ and $\tilde{a}^1A_1$ states are averaged or the $(2)^1A_1$ state is included in the averaging as well. The addition of single and double excitations

Table 2. Variation of the energy E(a.u.), the energy separations Δ (kcal/mole), and electronic moments (a.u.) for the $\tilde{a}\,^1A_1$, $(2)^1A_1$, and $\tilde{b}\,^1B_1$ states of CH_2 with level of correlation treatment

Calculation	$E(\tilde{a}\,^1A_1)$	$E(\tilde{b}\,^1B_1)$	Δ	Moment
A. $\tilde{b}\,^1B_1$ SCF orbitals				
SCF	−38.867180	−38.834419	20.56	0.404447
SDCI	−39.016341	−38.956323	37.66	0.336080
SDCI+Q	−39.028684	−38.962878	41.29	
MCPF	−39.025248	−38.960585	40.58	0.312686
FCI	−39.027130	−38.962058	40.83	0.303082
B. State-averaged SCF for the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ states				
SCF	−38.884442	−38.830398	33.91	0.439670
SDCI	−39.018048	−38.955792	39.07	0.339950
MCPF	−39.025100	−38.960654	40.44	0.316723
C. State-averaged CASSCF for the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ states				
CASSCF	−38.933251	−38.872359	38.21	0.333272
SOCI	−39.025378	−38.960205	40.90	0.303743
SOCI+Q	−39.028954	−38.963619	41.00	
CCI	−39.023153	−38.958078	40.83	0.300501
D. State-averaged CASSCF for the $\tilde{a}\,^1A_1$, $(2)^1A_1$ and $\tilde{b}\,^1B_1$ states				
CASSCF	−38.932957	−38.870189	39.39	0.338749
SOCI[a]	−39.025333	−38.960121	40.92	0.304155
SOCI+Q	−39.028936	−38.963665	40.96	
Calculation	$E(\tilde{a}\,^1A_1)$	$E((2)^1A_1)$	Δ	Moment
$\tilde{b}\,^1B_1$ SCF orbitals				
FCI	−39.027130	−38.858439	105.85	0.179223
A. State-averaged CASSCF for the $\tilde{a}\,^1A_1$ and $(2)^1A_1$ states				
CASSCF	−38.936608	−38.763090	108.88	0.192631
SOCI	−39.025461	−38.856372	106.10	0.177474
SOCI+Q	−39.028764	−38.860449	105.62	
B. State-averaged CASSCF for the $\tilde{a}\,^1A_1$, $(2)^1A_1$ and $\tilde{b}\,^1B_1$ states				
CASSCF	−38.932957	−38.762884	106.72	0.194419
SOCI[b]	−39.025333	−38.856333	106.05	0.177545
SOCI+Q	−39.028936	−38.860404	105.75	

[a] If the C 1s like orbital is fixed in the form found in the $\tilde{b}\,^1B_1$ SCF, i.e. that used in the FCI calculations, the separation and moment change by 0.02 kcal and 0.000040 a.u., respectively

[b] If the C 1s like orbital is fixed in the form found in the $\tilde{b}\,^1B_1$ SCF, i.e. that used in the FCI calculations, the separation and moment change by 0.02 kcal and 0.000109 a.u., respectively

from the CASSCF reference gives nearly perfect agreement with the FCI for both the separation and the moment. The moment and separation are therefore not significantly degraded at this level by including a third state of considerably higher energy in the orbital optimization procedure. Note that excellent agreement between the SOCI and FCI calculations is achieved without the need to add any additional orbitals to the active space. This is consistent with the rapid increase in the importance of d orbitals in going from carbon to fluorine. Adding the multireference Davidson correction worsens the results slightly, as is often the case when a CASSCF/SOCI treatment is employed. The CCI treatment is in

Table 3. Total energies (a.u.) for BeO

Calculation	$E(X\,^1\Sigma^+)$	$E(B\,^1\Sigma^+)$	$E(^1\Delta)$	$E(A\,^1\Pi)$
1d basis[c]				
State-averaged [322] CASSCF orbitals				
CASSCF	−89.519714	−89.420594	−89.263864	−89.475431
SOCI	−89.597290	−89.499485	−89.373284	−89.547643
SOCI+Q	−89.599436	−89.501734	−89.383664	−89.549455
CCI	−89.595949			−89.546226
FCI	−89.598571	−89.500670	−89.377325	−89.548524
$^1\Pi$ SCF orbitals[a]				
SCF	−89.264218			−89.440887
SDCI	−89.559543			−89.544443
SDCI+Q	−89.630424			−89.549198
MCPF	−89.708188			−89.547897
Average SCF orbitals[a]				
SCF	−89.389920			−89.403096
SDCI	−89.578694			−89.538297
SDCI+Q	−89.601393			−89.547015
CPF	−89.603457			−89.544889
MCPF	−89.605675			−89.545497
Separate CASSCF orbitals[a]				
CASSCF	−89.543288			−89.500882
2d basis[c]				
Two-state-averaged CASSCF orbitals				
FCI	−89.613306			−89.562748
[322]SOCI	−89.611916			−89.561844
[333]SOCI[b]	−89.612700			−89.562274
[4221]SOCI[b]	−89.612478			−89.563305

[a] The 1-3σ orbitals are taken from the state-averaged CASSCF wave functions

[b] The 1-3σ orbitals are taken from the [322] state-averaged CASSCF wave functions - the orbitals are optimized using a CASSCF with the same active space as the SOCI

[c] See basis description in Sect. 2

good agreement with the SOCI, which is generally the case when the CASSCF wave function is a good zeroth-order representation of both states. Taking the 1*s* orbital from the $\tilde{b}^1B_1$ SCF calculation, as in the FCI, has little effect on either the separation or moment - see footnote to Table 2.

Many of these same observations apply to the $\tilde{a}^1A_1$-$(2)^1A_1$ transition in CH_2, where the errors are comparable at the CASSCF level. Again the results are not significantly different whether two or three states are included in the CASSCF treatment. The inclusion of more extensive correlation via the SOCI procedure reduces the errors in both the separation and transition moment to less than 1%.

The total energies for the $X\,^1\Sigma^+$, $A\,^1\Pi$, $B\,^1\Sigma^+$ and (1) $^1\Delta$ states of BeO at various levels of correlation treatment are compared with the FCI in Table 3. The energies are given explicitly since the principal focus of this work is the calibration of methods. Since the $A\,^1\Pi$-$X\,^1\Sigma^+$ transition can be treated by all the methods considered in this work we consider it first - see Table 4. The single reference

Table 4. Theoretical results for the $A\,^1\Pi$–$X\,^1\Sigma^+$ transition in BeO

Calculation	Δ(cm^{-1})	Moment[a]
A. 1d basis		
SCF($^1\Pi$)	−38 777	0.326692
SDCI	3 314	0.624918
SDCI+Q	17 828	
MCPF	35 182	0.517892
SCF(avg)	−2 892	0.527602
SDCI	8 867	0.661624
SDCI+Q	11 935	
CPF	12 855	0.657268
MCPF	13 208	0.677409
CASSCF(non)	9 308	0.676009
CASSCF	9 720	0.778689
SOCI	10 897	0.691018
SOCI+Q	10 970	
CCI	10 914	0.697299
FCI	10 985	0.683427
B. 2d basis		
FCI	11 097	0.650468
[322]SOCI	10 990	0.644273
[333]SOCI	11 068	0.652108
[4221]SOCI	11 034	0.646267

[a] The moment is computed in C_{2v} as $\langle ^1A_1|y|^1B_1\rangle$

methods are very sensitive to the molecular orbital basis. The results are significantly better using average SCF orbitals rather than $A\,^1\Pi$ orbitals. Using $A\,^1\Pi$ orbitals, the separation is almost 50 000 cm^{-1} in error and the transition moment is in error by a factor of two. Since the $A\,^1\Pi$ is well described by a single configuration, most of the error arises from the description of the $^1\Sigma^+$ state. Note that the MCPF reference CSF comprises only about 20% of the $X\,^1\Sigma^+$ state, but about 94% of the $A\,^1\Pi$ state wave function. A further consequence of this is that the total energy of the $X\,^1\Sigma^+$ state is lower than the FCI at the SDCI+Q and MCPF levels. The single reference descriptions are dramatically improved using state-averaged SCF orbitals, and the SDCI, CPF and MCPF results are now in reasonably good agreement with the FCI. Interestingly, the MCPF moment is an improvement over the SDCI, while the CPF is actually slightly poorer than the SDCI. This is consistent with the contention [14] that MCPF should perform better than CPF when the reference contains a smaller percent of the final wave function. These results clearly demonstrate the importance of choosing the best possible compromise set of molecular orbitals when single-reference based CI methods are used to compute transition moments.

If separate CASSCF optimizations are performed for the $X\,^1\Sigma^+$ and $A\,^1\Pi$ states, the separation and the nonorthogonal transition moment are in good agreement with the FCI. If the state-averaged CASSCF orbital are used, the separation is hardly changed, but the transition moment is significantly poorer. However, the

Table 5. Separations and moments, in cm^{-1} and a.u., respectively, for selected transitions in BeO

Calculation	$B\,^1\Sigma^+$-$X\,^1\Sigma^+$		$^1\Delta$-$X\,^1\Sigma^+$	
	Δ	moment[a]	Δ	moment[b]
CASSCF	21 756	0.760886	56 156	1.24953
SOCI	21 467	0.811836	49 167	1.06725
SOCI+Q	21 445		47 360	
FCI	21 488	0.814204	48 561	1.03436
	$B\,^1\Sigma^+$-$A\,^1\Pi$		$^1\Delta$-$A\,^1\Pi$	
	Δ	moment[c]	Δ	moment[c]
CASSCF	12 036	0.308471	46 437	0.770785
SOCI	10 570	0.265031	38 270	0.861471
SOCI+Q	10 474		36 389	
FCI	10 503	0.260892	37 576	0.866565
	$^1\Delta$-$B\,^1\Sigma^+$			
	Δ	moment[b]		
CASSCF	34 401	0.30350		
SOCI	27 700	0.37625		
SOCI+Q	25 915			
FCI	27 073	0.37318		

[a] The moment is computed in C_{2v} as $\langle (1)^1A_1|z|(2)^1A_1\rangle$

[b] The moment is computed in C_{2v} as $\langle (n)^1A_1|(x^2-y^2)/2|(3)^1A_1\rangle$

[c] The moment is computed in C_{2v} as $\langle (n)^1A_1|y|^1B_1\rangle$

inclusion of correlation in the SOCI approach yields a separation and transition moment in good agreement with the FCI. Even in this case where extensive correlation in the SOCI approach is needed to correct for the limitations of the CASSCF reference, the CCI approach is in good agreement with the SOCI results.

In previous studies [1] of the A-X ultraviolet system of OH, we found that quantitative agreement with the FCI required adding a δ orbital to the CASSCF active space. However, to observe the full impact of this effect required having an adequate d basis. To study the impact on the $A\,^1\Pi$-$X\,^1\Sigma^+$ transition moment of expanding the active space, we therefore employed the oxygen $2d$ basis. The difference between the [322] CASSCF/SOCI and the FCI results is about the same in the two basis sets - see Table 4. Adding a δ orbital to the active space to give a [4221] CASSCF/SOCI reduces the error by only one third. The natural orbitals for the $X\,^1\Sigma^+$ and $A\,^1\Pi$ SOCI (or FCI) wave functions show that the third π orbital has a larger occupation number than the first δ orbital. If this π orbital is added to the active space instead of the δ orbital, the error is further reduced, but changed in sign. Hence for both BeO and OH the importance of adding an orbital to the active space parallels the magnitude of its natural orbital occupation number. These results suggest that the natural orbital occupation numbers of the SOCI wave function should be a good guide for choosing the CASSCF active space for the calculation of transition moments, as they are for single-state energy related properties.

Since the remaining transitions involve upper states of the same symmetry as the ground state, we limit ourselves to the CASSCF and SOCI approaches (see Table 5). Overall we find that the state-averaged CASSCF supplies a reasonable zeroth order description of the transition and that the inclusion of more extensive correlation improves the results. This is true even though the averaging contains states that differ in energy by up to 50 000 cm^{-1}.

4. Conclusions

For CH_2 where the three states considered are well described in a common molecular orbital basis, single reference-based methods such as MCPF do rather well for both the separation and transition moment. The CCI method also works rather well, but still the best results are obtained using the CASSCF/SOCI approach.

The BeO molecule provides a more critical test of various methods, since in particular the $X\ {}^1\Sigma^+$ state is poorly described by a single reference configuration. Nonetheless, the MCPF method still gives qualitatively correct results when state-averaged SCF orbitals are employed for the MO basis. The state-averaged CASSCF/SOCI approach gives quantitative agreement with the FCI even when higher lying states are included in the orbital determination. For the $A\ {}^1\Pi$-$X\ {}^1\Sigma^+$ transition in BeO, the transition moment using state-averaged orbitals differs by about 15% from that obtained in a nonorthogonal calculation using the individually state optimized orbitals. Overall, the results indicate that state-averaged CASSCF/SOCI is capable of accounting for all of the correlation effects on the transition moment. Also, the FCI results are particularly useful in delineating the correct active space for the CASSCF and the reference configurations for the SOCI.

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Appendix

The FCI program originally written by Knowles and Handy has been vectorized for the CRAY XMP and CRAY 2. Most of the work has been organized as matrix multiply using the MXM subroutine (see CRAY library reference manual). On the CRAY 2, the MXM routine can achieve 420 MFLOPS. Since the memory on the CRAY 2 is large relative to the available disk space, we generally fold the current set of vectors (Cs) and Hamiltonian matrix times vector (HCs) down to a single C and HC using an eigenvector of the small matrix [20]. Higher roots are obtained using the Liu simultaneous root extension [21] of the original Davidson approach [20]. The calculation of the transition moments or density matrices over FCI wave functions is a straightforward extension of the original method. As noted in appendix 1 of the paper [4] of Knowles and Handy, the program loops over all α and all β strings, and thereby over all determinants in the wave function. For each determinant, all single replacements are generated. Since the method contains a sum over intermediate states, the singles are of all possible symmetries. Using only the single excitations of the same symmetry as the wave function, it is straightforward to construct the density matrix by modifying the processing of the one-electron contribution to HC. The transition density matrix can be constructed similarly by generating single excitations that have the symmetry of the second wave function. The transition density can be generated at only a small fraction of the cost of generating the FCI wave functions. For example, the OH $X\,^2\Pi$ and $A\,^2\Sigma^+$ FCI wave functions, which contain about 12.8 million determinants and 51.3 million intermediate states, require about one hour per iteration in the FCI, but only 86 seconds is required for the calculation of the transition density matrix.

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