

Full CI benchmark calculations for molecular properties

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Full CI calculations of first- and second-order properties are presented to provide benchmark results for comparisons with other methods, such as multireference CI (MRCI). The full CI (FCI) polarizability of F^- is computed using a double zeta plus polarization plus diffuse basis set. These FCI results are compared to those obtained at other levels of theory; the CASSCF/MRCI with Davidson correction results are in excellent agreement with the FCI. Differences between the polarizability results computed as a (numerical) second derivative of the energy or as an induced dipole moment are also discussed. FCI calculations are presented for the dipole moment and polarizability of HF, CH_2 and SiH_2 using a DZP basis set. Again, the CASSCF/MRCI values are in excellent agreement with the FCI results, whereas SDCI values, whether computed as an expectation value or as an energy derivative, are much worse. The results obtained using the CPF approach are in considerably better agreement with the FCI results than SDCI, and are similar in quality to the SDCI energy derivative results with the inclusion of Davidson's correction.

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1. Introduction

Full CI (FCI) calculations provide important benchmarks for calibration of approximate methods of accounting for the effects of electron correlation. Until

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recently, such benchmark calculations were available [1, 2] in basis sets of only double zeta quality in general, owing to the rapid growth in the length of the CI expansion with increasing 1-particle basis set size. As these FCI calculations recovered only a limited fraction of the correlation energy it was not always possible to discriminate between different approximate methods.

As a result of recent improvements in FCI methodology [3, 4], the computer time required to perform FCI calculations has been reduced. Given also the very large central memory (256 Megawords) of the CRAY 2, these advances have enabled us to perform a new series of FCI benchmark calculations in which more realistic (double zeta plus polarization or better) basis sets have been used. Using the FCI method we have considered the calculation of T_e values [5-7], electron affinities [8, 9], the breaking of bonds [5, 7, 9] and barriers to reaction [10]. All of these calculations have focused on computed energies or energy differences. In this work we extend our benchmark FCI calculations to the dipole moment (μ) and the polarizability (α) of F^- , HF, CH_2 and SiH_2 . The FCI results are compared to those obtained at the SCF plus single and double excitation CI (SDCI) or coupled-pair functional (CPF) levels, and to those obtained using complete active space (CASSCF) MCSCF and multireference CI (MRCI) wave functions. For F^- the basis set used should be large enough to account for the important contributions to the polarizability, however, for the molecular systems the inclusion of diffuse valence and polarization functions would have made the FCI calculations intractable, and thus the results for the molecules should be regarded in the same light as the first series of FCI calculations [1, 2].

2. Computational methods

The basis set used for the calculation of the F^- polarizability is the Dunning (9s5p)/[4s3p] contraction [11] of fluorine. To this the diffuse p function needed to describe F^- is added [12], in addition to a tight d function optimized for the correlation energy [5, 13]. In order to describe the polarizability of F^- diffuse s and d functions are added. The final basis set is of the form (10s6p2d)/[5s4p2d] and is tabulated in Table 1. Note that the 3s combination of the 3d functions has been eliminated. For this basis set the polarizability at the SCF level is 9.9 a.u. compared to 10.6 obtained with a larger (11s7p4d)/[6s5p4d] basis set.

The basis sets for the HF, CH_2 and SiH_2 molecules are those used in our previous work. HF is described in [5] and CH_2 in [6]. The F and C basis sets are (9s5p1d)/[4s2p1d] contractions and H is (4s1p)/[2s1p]. The SiH_2 basis sets are described in [7]; Si and H are of the form (12s8p1d)/[6s4p1d] and (4s1p)/[2s1p], respectively. For HF we consider three geometries, r_e (1.733 a_0), $1.5 \times r_e$ (2.5995) and $2 \times r_e$ (3.466), for CH_2 and SiH_2 only the r_e geometries are considered. These geometries are summarized in Tables 2-4 together with the total energies; explicit Cartesian coordinates are given in the earlier publications [6, 7].

For CH_2 , SiH_2 and HF, the levels of treatment investigated are the same as those

Table 1. The basis set used for the calculation of the polarizability of F^-

	<i>s</i>		<i>p</i>	
	exp	coef	exp	coef
1	9994.79	0.002017	44.3555	0.020868
2	1506.03	0.015295	10.0820	0.130092
3	350.269	0.073110	2.9959	0.396219
4	104.053	0.246420	0.9383	0.620368
5	34.8432	0.612593	0.2733	1.000000
6	4.3688	0.242489	0.074	1.000000
7	12.2164	1.000000		
8	1.2078	1.000000		
9	0.3634	1.000000		
10	0.03	1.000000		
		<i>d</i> ^a		
1	1.60000	1.000000		
2	0.10000	1.000000		

^a The 3*s* combination has been eliminated**Table 2.** CH_2 total energies, in E_H

Field (a.u.)	0.000	0.005	-0.005
¹ <i>A</i> ₁ <i>r</i> (CH) = 2.1 a ₀ and ∠HCH = 102.4°			
SCF	-38.886296	-38.882388	-38.890458
FCI	-39.027182	-39.023736	-39.030896
SDCI	-39.018283	-39.014697	-39.022130
SDCI+Q	-39.027221	-39.023762	-39.030948
CPF	-39.025116	-39.021646	-39.028853
2CSF	-38.907659	-38.904211	-38.911371
2CSF+CI	-39.022155	-39.018704	-39.025873
2CSF+CI+Q	-39.027741	-39.024298	-39.031452
CASSCF	-38.945528	-38.942200	-38.949115
MRCI	-39.025803	-39.022371	-39.029502
MRCI+Q	-39.028479	-39.025033	-39.032192
³ <i>B</i> ₁ <i>r</i> (CH) = 2.045 a ₀ and ∠HCH = 132.4°			
SCF	-38.927946	-38.926817	-38.929244
FCI	-39.046259	-39.045025	-39.047662
SDCI	-39.041601	-39.040377	-39.042994
SDCI+Q	-39.046909	-39.045677	-39.048310
SDCI(1)	-39.041198	-39.039974	-39.042592
CPF	-39.044902	-39.043672	-39.046302
CASSCF	-38.965953	-38.964866	-38.967207
MRCI	-39.044871	-39.043645	-39.046266
MRCI+Q	-39.047262	-39.046027	-39.048667

Table 3. SiH₂ total energies, E_H

Field (a.u)	0.000	0.005	-0.005
1A_1 r (SiH) = 2.84 a ₀ \angle HSiH = 95°			
SCF	-290.016932	-290.016123	-290.018331
FCI	-290.133781	-290.133224	-290.134912
SDCI	-290.126239	-290.125639	-290.127410
SDCI+Q	-290.134375	-290.133842	-290.135484
CPF	-290.132321	-290.131768	-290.133447
2CSF	-290.036767	-290.036460	-290.037650
2CSF+CI	-290.129115	-290.128594	-290.130210
2CSF+CI+Q	-290.134198	-290.133639	-290.135332
CASSCF	-290.065632	-290.065053	-290.066789
MRCI	-290.132174	-290.131620	-290.133300
MRCI+Q	-290.134686	-290.134127	-290.135818
3B_1 r (SiH) = 2.77 a ₀ \angle HSiH = 118°			
SCF	-290.008187	-290.008814	-290.007913
FCI	-290.104550	-290.104862	-290.104694
SDCI	-290.100050	-290.100409	-290.100145
SDCI+Q	-290.105204	-290.105512	-290.105352
SDCI(1)	-290.099625	-290.099989	-290.099715
CPF	-290.103238	-290.103566	-290.103368
CASSCF	-290.038153	-290.038598	-290.038166
MRCI	-290.102997	-290.103318	-290.103131
MRCI+Q	-290.105442	-290.105747	-290.105595
1B_1 r (SiH) = 2.77 a ₀ \angle HSiH = 123°			
SCF	-289.951226	-289.951428	-289.951492
FCI	-290.059237	-290.059039	-290.059898
SDCI	-290.053538	-290.053396	-290.054142
SDCI+Q	-290.060318	-290.060114	-290.060987
CASSCF	-289.989650	-289.989500	-289.990272
MRCI	-290.057500	-290.057305	-290.058159
MRCI+Q	-290.060352	-290.060149	-290.061019

used in the earlier studies [5-7]. The simplest zeroth-order reference wave functions are based on the SCF configurations

$$(\text{HF } ^1\Sigma^+) 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 \quad (1)$$

$$(\text{CH}_2 \ ^3B_1) 1\alpha_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1 \quad (2)$$

$$(\text{CH}_2 \ ^1A_1) 1\alpha_1^2 2a_1^2 1b_2^2 3a_1^2 \quad (3)$$

$$(\text{SiH}_2 \ ^1B_1, \ ^3B_1) 1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 2b_2^2 1b_1^2 5a_1^1 2b_1^1 \quad (4)$$

and

$$(\text{SiH}_2 \ ^1A_1) 1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1b_2^2 2b_2^2 1b_1^2. \quad (5)$$

These configurations are used in SCF calculations to determine the orbitals for the FCI, SDCI and CPF [14] treatments. For the triplet states we also consider the effects of imposing the first-order interacting space restriction [15] in the

Table 4. HF total energies, E_H

Field (a.u.)	0.000	0.005	-0.005
		r_e 1.733 a_0	
SCF	-100.047086	-100.043070	-100.051207
FCI	-100.250968	-100.247199	-100.254847
SDCI	-100.241588	-100.237780	-100.245507
SDCI+Q	-100.249372	-100.245600	-100.253256
CPF	-100.247719	-100.243940	-100.251609
CASSCF	-100.070188	-100.066414	-100.074071
MRCI	-100.244725	-100.240957	-100.248604
MRCI+Q	-100.250863	-100.247102	-100.254735
		$1.5 \times r_e$ 2.5995 a_0	
SCF	-99.933228	-99.927557	-99.939184
FCI	-100.160392	-100.156064	-100.165026
SDCI	-100.145522	-100.140922	-100.150429
SDCI+Q	-100.158979	-100.154743	-100.163530
CPF	-100.156162	-100.151815	-100.160815
CASSCF	-99.986423	-99.982658	-99.990497
MRCI	-100.154120	-100.149823	-100.158724
MRCI+Q	-100.160276	-100.155947	-100.164911
		$2 \times r_e$ 3.466 a_0	
SCF	-99.817571	-99.810345	-99.825453
FCI	-100.081107	-100.078254	-100.084437
SDCI	-100.053534	-100.049765	-100.057874
SDCI+Q	-100.082399	-100.080415	-100.084922
CPF	-100.075803	-100.072826	-100.079273
CASSCF	-99.920994	-99.919077	-99.923253
MRCI	-100.075566	-100.072808	-100.078788
MRCI+Q	-100.080738	-100.077900	-100.084052

SDCI wavefunctions (denoted SDCI(1)); this constraint is always imposed in the CPF treatment.

An improved set of zeroth-order references is obtained by using CASSCF wave functions [16]. For HF, the active space comprises the bonding and anti-bonding orbitals; more extensive correlation is then included by adding all single and double excitations from the three CSF's in the CASSCF wave function. For CH_2 (and SiH_2) the zeroth-order reference space is improved in two different ways. In the first, only the treatment of the 1A_1 state is improved, by adding the $3a_1(5a_1)$ to $1b_1(2b_1)$ double excitation to the reference wave function (denoted 2CSF): single and double excitations from both reference configurations are included in the CI, which is denoted 2CSF+CI. The second improved treatment includes the C (Si) $2s(3s)$ and $2p(3p)$ orbitals and electrons and the H $1s$ orbitals and electrons in the CASSCF active space. All single and double excitations from all CSF's in the CASSCF wave function are then included in a multireference CI calculation, MRCI. The Davidson correction [17] or its multireference analog is added to all CI wave functions. The multireference Davidson correction

(denoted +Q) is defined as

$$\Delta E_{SD} \left(1 - \sum_R C_R^2 \right), \quad (6)$$

where ΔE_{SD} is the difference between the energy of the reference CSFs and the MRCI energy, and the C_R are the coefficients of the reference configurations in the MRCI wave function. For HF eight electrons are correlated, while for CH₂ and SiH₂ six electrons are correlated.

The polarizability and dipole moment are computed by including in the Hamiltonian an electric field of 0.005 or -0.005 a.u. along the HF bond axis or the C₂ axis in CH₂ and SiH₂. For a field of strength f , the change in energy to second order is

$$\Delta E = f \times \mu - \alpha \times f^2 / 2. \quad (7)$$

For the SCF and CASSCF wave functions (in which all parameters are variationally optimized) the dipole moment computed from (7) agrees with that computed as an expectation value to better than 0.001 a.u. The slight difference is a measure of errors associated with numerical precision and the importance of higher-order polarizabilities omitted from (7).

For the FCI calculations the dipole moment computed either from (7) or as an expectation value would also agree if all of the electrons were correlated, but we have only correlated the valence electrons. We can estimate the effect of this restriction by computing the dipole moment as an energy derivative with the core orbitals frozen in their field-free form and then with the core orbitals relaxed in the presence of the field. This approach is necessary since at present we do not obtain the first-order reduced density matrix or property expectation values from the FCI wave function. The difference arising from the use of field-free as opposed to relaxed core orbitals is only 0.0001 a.u. in the dipole moment for both CH₂ and SiH₂, and hence to the accuracy considered below we can regard the FCI energy derivative as agreeing perfectly with an expectation value. Interestingly enough, the same difference is seen in results at the SCF level when field-free core orbitals are used instead of relaxed MOs, which suggests that the slight difference in the FCI values results from polarization of the core.

For those wave functions where there is a formal difference between the expectation value and the energy derivative we report both values. Because of numerical precision the polarizability for the molecular systems is reported to only 0.1 a.u. Since the correlation correction to both μ and α is small, we report both the values and the fraction of the correlation contribution to the property, which, for a property x at level of treatment a , is defined as

$$frac = \frac{x(a) - x(\text{SCF})}{x(\text{FCI}) - x(\text{SCF})}. \quad (8)$$

For some systems the range of α is sufficiently small that a large part of the observed difference has its origin in numerical precision and for these systems

frac is not reported. Even where *frac* is reported, it is often the case that the correlation contribution to α is so small that *frac* considerably exaggerates the differences between methods. This problem does not arise for the dipole moment.

For the polarizability of F^- three different zeroth-order wave functions were used: SCF, CASSCF ($2p$) and CASSCF ($2s2p$). CASSCF ($2p$) has six $2p$ electrons active in the $2p$ orbital and a $2p'$ correlating orbital; in CASSCF ($2s2p$) the $2s$ electrons are included as active and the orbital space is expanded to include the $2s$ orbital and a $2s'$ correlating orbital. Correlated wave functions based on these zeroth-order references were then determined, correlating both six or eight electrons: the results are denoted FCI(6), FCI(8), etc. As noted above, the SDCl, CPF and FCI treatments are based on SCF orbitals. All single and double excitations away from all CSFs in the CASSCF ($2p$) comprise the MRCI(6) and MRCI(8) wave functions. The MRCIBIG(8) contains single and double excitations relative to the CASSCF ($2s2p$) reference. The Davidson correction is added to the SDCl and MRCI calculations. Total energies from these calculations are given in Table 5.

In the presence of an electric field, the polarizability of F^- can be computed either from the change in energy,

$$\alpha = 2 \times \Delta E / f^2 \quad (9)$$

or from the induced dipole moment

$$\alpha = \mu / f. \quad (10)$$

Using a small field (0.005 a.u.) eliminates the need to consider higher polarizability terms, but requires that high numerical precision be achieved. All wave functions

Table 5. F^- total energies, in E_H and induced dipole moment, in a.u.

Calculation	No field	0.005 field	Induced μ
SCF	-99.44446197	-99.44458565	0.04950
CASSCF($2p$)	-99.54401394	-99.54422523	0.08435
CASSCF($2s2p$)	-99.58264495	-99.58281877	0.06958
SDCl(6)	-99.59435181	-99.59452009	0.06902
SDCl(6)+Q	-99.60055040	-99.60073314	
CPF(6)	-99.59890878	-99.59909161	0.08154
MRCI(6)	-99.60252133	-99.60270311	0.08680
MRCI(6)+Q	-99.60310952	-99.60329256	
FCI(6)	-99.60292491	-99.60311695	
SDCl(8)	-99.64588785	-99.64606241	0.07009
SDCl(8)+Q	-99.65618271	-99.65637696	
CPF(8)	-99.65458417	-99.65478480	0.09163
MRCI(8)	-99.65774574	-99.65794741	0.08136
MRCI(8)+Q	-99.66027774	-99.66048207	
MRCIBIG(8)	-99.65858378	-99.65878421	0.07872
MRCIBIG(8)+Q	-99.65959347	-99.95979726	
FCI(8)	-99.65949320	-99.65969698	

have therefore been optimized to ensure convergence of the total energy to within 10^{-8} , and from our results it is clear that sufficient numerical precision has been achieved to give values of *frac* accurate to about 0.005. It is reasonable to assume, given our results for CH₂ and SiH₂, that the FCI(8) calculation would yield virtually the same α from (9) and (10), and we have used the FCI(8) results from (9) in all our comparisons. We have quoted results for the approximate methods from both (9) and (10) where six electrons are correlated, however, no FCI(6) result from (10) is available for comparison.

3. Results and discussion

The results are summarized in Tables 6–8. The 1A_1 state of CH₂ is poorly described by a single configuration: the difference between the SCF and FCI μ values is five times larger than for the 3B_1 state. The inclusion of correlation in the SDCI calculation improves the results for both states, but since the SCF is a better reference for the 3B_1 state, the 3B_1 SDCI μ is closer to the FCI value. The

Table 6. CH₂ properties, in atomic units

	α		μ^b		$\langle\mu\rangle^c$	
	Value	frac ^a	Value	frac ^a	Value	frac ^a
	1A_1					
SCF	10.2	0.00	0.807	0.00		
FCI	10.7	1.00	0.716	1.00		
SDCI	10.4	0.50	0.743	0.70	0.754	0.58
SDCI+Q	10.7	1.00	0.719	0.97		
CPF	10.7	1.00	0.721	0.95	0.726	0.89
2CSF	10.6	0.80	0.716	1.00		
2CSF+CI	10.7	1.00	0.717	0.99	0.723	0.92
2CSF+CI+Q	10.7	1.00	0.715	1.01		
CASSCF	10.4	0.50	0.691	1.27		
MRCI	10.7	1.00	0.713	1.03	0.715	1.01
MRCI+Q	10.7	1.00	0.716	1.00		
	3B_1					
SCF	6.8	—	0.243	0.00		
FCI	6.8	—	0.264	1.00		
SDCI	6.8	—	0.262	0.90	0.263	0.96
SDCI+Q	6.8	—	0.263	0.98		
SDCI(1)	6.8	—	0.262	0.91	0.262	0.92
CPF	6.8	—	0.263	0.97	0.268	1.19
CASSCF	6.7	—	0.234	-0.41		
MRCI	6.8	—	0.262	0.92	0.263	0.96
MRCI+Q	6.8	—	0.264	1.01		

^a The fraction of the correlation contribution to the property obtained, for level of treatment a, see Eq. (8)

^b μ computed as an energy derivative

^c μ computed as an expectation value

Table 7. SiH₂ properties, in atomic units

	α		μ^b		$\langle\mu\rangle^c$	
	Value	frac ^a	Value	frac ^a	Value	frac ^a
			¹ A ₁			
SCF	22.8	0.00	0.219	0.00		
FCI	23.0	1.00	0.169	1.00		
SDCI	22.8	0.00	0.177	0.83	0.189	0.59
SDCI+Q	23.0	1.00	0.164	1.09		
CPF	22.9	0.50	0.168	1.02	0.177	0.83
2CSF	23.0	1.00	0.119	2.00		
2CSF+CI	23.0	1.00	0.162	1.14	0.171	0.95
2CSF+CI+Q	23.0	1.00	0.169	0.99		
CASSCF	23.1	1.50	0.174	0.90		
MRCI	22.9	0.50	0.168	1.02	0.167	1.04
MRCI+Q	22.9	0.50	0.169	0.99		
			³ B ₁			
SCF	14.1	0.00	-0.090	0.00		
FCI	18.2	1.00	-0.017	1.00		
SDCI	18.2	1.00	-0.026	0.87	-0.020	0.96
SDCI+Q	18.2	1.00	-0.016	1.01		
SDCI(1)	18.2	1.00	-0.027	0.86	-0.017	1.00
CPF	18.3	1.02	-0.020	0.96	0.000	1.23
CASSCF	18.3	1.02	-0.043	0.64		
MRCI	18.2	1.00	-0.019	0.97	-0.018	0.98
MRCI+Q	18.3	1.02	-0.015	1.02		
			¹ B ₁			
SCF	18.7	0.00	0.006	0.00		
FCI	18.5	1.00	0.086	1.00		
SDCI	18.5	1.00	0.075	0.86	0.075	0.86
SDCI+Q	18.6	0.50	0.087	1.02		
CASSCF	18.9	-1.00	0.077	0.89		
MRCI	18.6	0.50	0.085	0.99	0.085	0.99
MRCI+Q	18.6	0.50	0.087	1.01		

^a The fraction of the correlation contribution to the property obtained, for level of treatment a, see Eq (8)

^b μ computed as an energy derivative

^c μ computed as an expectation value

interacting space restriction has little effect on the dipole moments. Formally, it might be expected that the SDCI energy derivative would be in better agreement with the FCI result than is the SDCI expectation value [see e.g. ref [18]], but this need not be the case for a truncated 1-particle space. In fact, for the ³B₁ state it is the expectation value that agrees best. For the ¹A₁ state, however, the SDCI energy derivative agrees best, possibly as a result of the poor description of this state at the SCF level. Accounting for higher excitations with either the Davidson correction or with the CPF approach improves the dipole moment results relative to FCI, and also produces an α value in good agreement with FCI. The CPF energy derivative results are superior to the CPF expectation value

Table 8. HF properties, in atomic units

	α		μ^b		$\langle\mu\rangle^c$	
	Value	frac ^a	Value	frac ^a	Value	frac ^a
			r_e			
SCF	4.2	—	0.814	0.00		
FCI	4.4	—	0.765	1.00		
SDCI	4.4	—	0.773	0.84	0.770	0.90
SDCI+Q	4.5	—	0.766	0.98		
CPF	4.4	—	0.767	0.96	0.759	1.13
CASSCF	4.4	—	0.766	0.98		
MRCI	4.4	—	0.765	1.00	0.767	0.95
MRCI+Q	4.4	—	0.763	1.03		
			$1.5 \times r_e$			
SCF	12.2	—	1.161	0.00		
FCI	12.2	—	0.896	1.00		
SDCI	12.3	—	0.951	0.79	0.969	0.72
SDCI+Q	12.6	—	0.879	1.07		
CPF	12.2	—	0.900	0.99	0.877	1.07
CASSCF	12.4	—	0.784	1.42		
MRCI	12.3	—	0.890	1.02	0.887	1.04
MRCI+Q	12.2	—	0.896	1.00		
			$2 \times r_e$			
SCF	26.2	0.00	1.511	0.00		
FCI	19.1	1.00	0.618	1.00		
SDCI	22.8	0.48	0.811	0.78	0.937	0.64
SDCI+Q	21.6	0.65	0.451	1.19		
CPF	19.7	0.92	0.645	0.97	0.602	1.02
CASSCF	13.7	1.76	0.418	1.22		
MRCI	18.6	1.07	0.598	1.02	0.591	1.04
MRCI+Q	19.0	1.01	0.615	1.00		

^a The fraction of the correlation contribution to the property obtained, for level of treatment a, see Eq (8)

^b μ computed as an energy derivative

^c μ computed as an expectation value

results; the latter are interesting since for 1A_1 (where SCF is poor) the estimate is too low, while for 3B_1 , where SCF is a good reference, the estimate is too high. Using a 2CSF treatment for the 1A_1 state yields essentially the same result for μ as does FCI, and the inclusion of correlation does not change this observation. However, the inclusion of correlation based on the 2CSF reference improves α . The CASSCF treatment, which yields a T_e value close to the 2CSF and FCI level, does not yield an accurate μ . For the 1A_1 state it overshoots the FCI result while for the 3B_1 state the CASSCF change is in the opposite direction to FCI. When the CASSCF is improved with the MRCI treatment the μ and α values are in very good agreement with FCI. The inclusion of the Davidson correction improves the MRCI results further. (For T_e , the inclusion of the Davidson correction in fact makes the computed separation marginally poorer [6].) The MRCI treatment

gives essentially the same result whether the energy derivative or expectation value is used.

The SiH₂ ¹A₁ and ³B₁ results are similar to those for CH₂. The results for the ¹B₁ state are very similar to those of ³B₁, which arises from the same occupation. The SCF is again a poor reference for the ¹A₁ state so that the error in the SDCI μ is larger than for ³B₁. The inclusion of the Davidson correction or the use of CPF improves the results, with the ³B₁ μ overshooting the FCI result when the CPF expectation value is used, just as in the case of CH₂. One difference between SiH₂ and CH₂ is observed in the 2CSF and CASSCF treatments. The 2CSF μ does not agree with the FCI, but the CASSCF values are superior to those for CH₂. On the other hand, CASSCF yields a poor polarizability for the ¹A₁ and ¹B₁ states. The inclusion of more extensive correlation leads to good results for both α and μ . The 2CSF+CI results overshoot the FCI values and it is only with the addition of the Davidson correction that agreement is reached. It is clear that higher than double excitations must be included to obtain agreement with the FCI.

For HF we also consider the properties as a function of the bond length. As the bond is stretched, the quality of the SCF reference becomes worse and thus correlation contributions become larger. In turn, the accuracy of the SDCI treatment decreases, and the difference in μ between the SDCI expectation value and energy derivative also becomes larger; in fact there is a change from the expectation value performing better (relative to FCI) near r_e to the energy derivative being superior at stretched HF geometries. The inclusion of the Davidson correction improves μ at r_e , but at $2 \times r_e$ it overshoots the FCI value by almost the same amount as the SDCI is low. Unlike SDCI or SDCI+Q, the accuracy of the CPF (energy derivative) μ is more consistent with HF bond length. The CPF expectation value is actually poorer at r_e than $2 \times r_e$. The CASSCF approach does not supply a consistent level of treatment for μ : the value is virtually equal to the FCI at r_e but overshoots by 1.42 at $1.5 \times r_e$ and then overshoots by only 1.22 at $2 \times r_e$. The CASSCF treatment does not provide a good description of α , either. As with the other systems, the inclusion of more extensive correlation, using either the MRCI or MRCI+Q methods, improves both α and μ and brings them into good agreement with FCI.

The F⁻ polarizability is summarized in Table 9. The difference between the SCF and FCI(8) levels is quite large - a factor of 1.65. CASSCF(2*p*) represents a major improvement over SCF, giving a result very similar to the FCI(8) value. If the CASSCF treatment is expanded to the CASSCF(2*s*2*p*) level, the value is actually in poorer agreement with the FCI (8) value. The inclusion of correlation at the SDCI level (SDCI(8)) gives only 63% of the correlation contribution to the polarizability even though it yields 94% of the FCI correlation energy. The value computed from (10) as an induced dipole moment, $\alpha(\mu)$, is virtually the same as that from the second difference (9). The addition of the Davidson correction makes a sizeable improvement, and the CPF(8) $\alpha(E)$ value is in excellent agreement, although the CPF(8) $\alpha(\mu)$ overshoots the FCI result by almost as much as the SDCI is too low. The MRCI(8) $\alpha(E)$ and $\alpha(\mu)$ values

Table 9. Polarizability of F^- in atomic units

Calculation	$\alpha(E)$		$\alpha(\mu)$	
	Value	frac ^a	Value	frac
	correlating $2s2p$			
SCF	9.894	0.000	9.900	0.000
FCI(8)	16.295	1.000	16.295 ^b	1.000
CASSCF($2p$)	16.903	1.095	16.869	1.090
CASSCF($2s2p$)	13.906	0.627	13.917	0.628
SDCI(8)	13.965	0.636	14.017	0.644
SDCI(8)+Q	15.540	0.882		
CPF(8)	16.050	0.962	18.327	1.317
MRCI(8)	16.134	0.975	16.272	0.996
MRCI(8)+Q	16.346	1.008		
MRCIBIG(8)	16.034	0.959	15.745	0.914
MRCIBIG(8)+Q	16.303	1.001		
	correlating $2p^c$			
SCF	9.894	0.000	9.900	
FCI(6)	15.363	1.000		
SDCI(6)	13.462	0.652	13.800	
SDCI(6)+Q	14.619	0.864		
CPF(6)	14.626	0.865	16.309	
MRCI(6)	14.542	0.850	17.360	
MRCI(6)+Q	14.643	0.868		

^a The fraction of the correlation contribution to the property obtained, for level of treatment a, see Eq (8). The FCI $\alpha(E)$ value is used for the calculation of frac for both $\alpha(E)$ and $\alpha(\mu)$

^b Assumed to be the same as the value computed as an energy difference

^c Note that the FCI(6) value is only 0.854 of the FCI(8) value

are very similar and both are in good agreement with the FCI. The inclusion of the Davidson correction causes a small overshoot, but is still in excellent agreement with the FCI result. The expansion of the reference space in the MRCIBIG calculation actually worsens the agreement with the FCI, this is perhaps a result of the fact that the CASSCF($2s2p$) value is in poorer agreement with the FCI than is that from CASSCF($2p$). The $\alpha(\mu)$ is affected more than is $\alpha(E)$. However, the inclusion of the Davidson correction overcomes any bias of the CASSCF($2s2p$) zeroth-order reference, and results in excellent agreement with the FCI. Overall, it appears that calculating the polarizability as an energy derivative yields better results than using the induced dipole moment: this is especially true if the Davidson correction is added.

We have also considered the calculation of α when only six electrons are correlated: the FCI(6) value is only 85% of the FCI(8) value. Clearly, an accurate computation of the polarizability requires that the $2s$ electrons be correlated. Overall, the trends in α using the various approximate methods when six electrons are correlated are similar to those of the 8-electron treatment, except that the MRCI(6) results do not agree as well with the FCI(6). Part of this difference

could arise from the different definition of the $2s$ (obtained from an SCF calculation for FCI but as an inactive CASSCF orbital for MRCI). As it is clear that the $2s$ must be correlated to obtain meaningful results the 6-electron treatment is not considered further.

4. Conclusions

The best agreement with the FCI, for the dipole moment and polarizability of CH_2 , SiH_2 and HF , is found at the CASSCF/MRCI level. The inclusion of the Davidson correction generally improves the results, although the difference between MRCI and MRCI+Q is small, as is the difference between computing the dipole moment as an expectation value or with the application of an electric field. A similar result is found for the calculation of the polarizability of F^- , where the values computed as an energy derivative and as the induced dipole moment are very similar at the CASSCF/MRCI level. However, the energy derivative has the advantage that with the inclusion of the Davidson correction the results are less sensitive to the choice of reference space. For the calculation of the dipole moment, the CPF energy derivative results are generally very good, while the CPF expectation values may overshoot FCI. Further, for the polarizability the CPF energy derivative is quite good, while the value computed from the induced dipole moment overshoots the FCI value. The accuracy of the different methods for the calculation of properties appears to be similar to that for calculating accurate energetics [5–10]; the single configuration-based techniques are markedly improved by using an estimate for the higher excitations, but to achieve high accuracy a CASSCF/MRCI approach must be used. Again, the MRCI results are generally improved with the addition of the Davidson correction. While this correction can make the MRCI results marginally poorer in some cases, it usually represents an improvement over the uncorrected results. Such an energy correction can, of course, only be included in an energy derivative calculation, but overall CASSCF/MRCI+Q seems to supply a very reliable approach.

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