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The Scalar Relativistic Contribution to the Atomization Energies of CF, CF_4, and SiF_4

Charles W. Bauschlicher, Jr.*

Mail Stop 230-3, NASA Ames Research Center, Moffett Field, California 94035

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The one-electron Douglas Kroll (DK) approach and perturbation theory, accounting for the mass-velocity and Darwin (MVD) terms, are used to compute the scalar relativistic contribution to the atomization energies of CF, CF_4, and SiF_4. The difference between these two approaches is studied as a function of basis set and level of correlation treatment.

I. Introduction

Recently Feller and Peterson reported[1] on obtaining accurate atomization energies for first-row systems. They concluded that it is important to include scalar relativistic effects, which is consistent with our studies[2] and those of Martin and co-workers.[3] While there seems to be agreement about the need to include the scalar relativistic effects, the exact approach has varied. Feller and Peterson used configuration interaction wave functions and perturbation theory, including only the mass-velocity and Darwin (MVD) terms.[4,5] Martin also accounted for the MVD terms, but used a size consistent averaged coupled pair functional (ACPF)[6] wave function. We have used modified coupled pair functional (MCPF)[7] wave functions in conjunction with the one-electron Douglas Kroll (DK) approach.[8] We should note that Pople and co-workers[9] have also investigated the scalar relativistic contribution to the atomization energy using a second-order perturbation treatment of the Dirac-Coulomb-Hartree-Fock method.

Given the small size of the scalar relativistic effects on the atomization energy of compounds containing first- and second-row elements, it might have been expected that all of the approaches would yield similar results. However, we noted that the scalar relativistic effects cited by Feller and Peterson for the atomization energies of CF_4 and SiF_4 (−1.5 and −2.5 kcal/mol, respectively) seemed larger than what we have been observing using the DK approach. The SiF_4 result is also larger than that (−2.18 kcal/mol) found by Pople and co-workers or the value (−1.88 kcal/mol) found by Martin and Taylor.[10] Therefore, we have investigated the scalar relativistic effect on the atomization energies of CF, CF_4, and SiF_4 at several levels of theory.

II. Methods

The experimental geometries are used for CF, CF_4, and SiF_4, namely X−F bond lengths of 1.2718, 1.319, and 1.552 Å, respectively. The scalar relativistic effect is computed at the following levels of theory: the self-consistent field (SCF), the singles and doubles configuration interaction (SDCI), modified coupled pair functional (MCPF),[7] average coupled pair functional (ACPF),[6] and coupled cluster singles and doubles,[11] including a perturbational estimate of triples (CCSD(T)).[12] For the SDCI approach, the effect of higher excitations is estimated using the Davidson correction, which is denoted +Q. We use both the one-electron DK approach and perturbation theory, accounting for the MVD terms. In some calculations, the basis set superposition error (BSSE) is computed.

For C and Si, we use the correlation-consistent polarized-valence (cc-pV) basis sets, while for F we use the augmented (aug) cc-pV set.[13−16] The triple zeta (TZ), quadruple zeta (QZ), and quintuple zeta (5Z) sets are used. Finally we note that we add a tight d function (1.44) to Si. To simplify the notation, we give the C or Si basis set first, followed by the F set. The cc-pVNZ and aug-cc-pVNZ sets are denoted as NZ and ANZ, respectively. We perform calculations in which these basis sets are completely uncontracted as well as those using the published contractions. In the DK calculations, the basis sets are contracted to the same size as in the nonrelativistic calculations, but the contraction coefficients are taken from DK atomic SCF calculations. The CCSD(T) calculations are performed using MOLCAS4,[17] while the remaining calculations are performed using Molecule-Sweden.[18] The DK integrals are computed using a modified version of the program written by Hess.[8]

III. Results and Discussion

We first consider CF since it is possible in that case to use the largest basis sets, and our results are summarized in Table 1. We first note that electron correlation reduces the size of the scalar relativistic effect on the atomization energy. It is therefore not surprising that the CCSD(T) approach yields a slightly smaller value than does the MCPF approach. The second observation is that the DK values are almost unaffected by contraction of the basis set or by improving the basis set beyond TZ/ATZ. The BSSE at the nonrelativistic and DK levels is essentially the same for all basis sets and all levels of theory, hence correcting for BSSE does not affect the computed relativistic contribution to the dissociation energy. The MVD MCPF results are stable excluding the TZ/ATZ set. The MVD MCPF TZ/ATZ results are improved if the BSSE is accounted for. That is, for the TZ/ATZ basis set, the BSSE at the nonrelativistic and MVD levels differs enough to affect the computed relativistic contribution to the dissociation energy. Clearly, this basis set, without calculation of the BSSE, is not appropriate for this property; either a larger basis set must be used, or it must be contracted more flexibly. Excluding this basis set, the MVD and DK results are in good agreement. This is

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* Corresponding author. Tel.: 650-604-6231. Fax: 650-604-0350. E-mail: bauschli@pegasus.arc.nasa.gov.

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TABLE 1: Summary of the Scalar Relativistic Effect on the CF Atomization Energy, in kcal/mol

	contracted				uncontracted	
	SCF	MCPF	CCSD	CCSD(T)	SCF	MCPF
			TZ/ATZ[a]			
non-rel	82.957	124.663	123.396	128.002	83.141	124.616
MVD	82.661	124.449			82.899	124.472
Δ	−0.296	−0.213			−0.242	−0.145
DK	82.716	124.494	−123.224	127.842	82.900	124.448
Δ	−0.241	−0.168	−0.172	−0.160	−0.241	−0.169
			TZ/ATZ−BSSE			
non-rel	82.806	123.259			82.969	123.585
MVD	82.529	123.083			82.727	123.442
Δ	−0.277	−0.176			−0.242	−0.143
DK	82.565	123.092			82.727	123.417
Δ	−0.241	−0.167			−0.241	−0.168
			QZ/AQZ			
non-rel	83.542	127.203			83.565	127.094
MVD	83.300	127.059			83.323	126.948
Δ	−0.241	−0.144			−0.242	−0.146
DK	83.300	127.034			83.323	126.924
Δ	−0.242	−0.169			−0.242	−0.170
			QZ/AQZ−BSSE			
non-rel	83.490	126.586			83.512	126.621
MVD	83.244	126.437			83.270	126.475
Δ	−0.246	−0.149			−0.242	−0.145
DK	83.248	126.417			83.270	126.451
Δ	−0.242	−0.169			−0.242	−0.169
			5Z/A5Z			
non-rel	83.671	127.952			83.677	127.917
MVD	83.432	127.810			83.435	127.771
Δ	−0.238	−0.142			−0.242	−0.146
DK	83.429	127.782			83.435	127.747
Δ	−0.242	−0.170			−0.242	−0.170

[a] The carbon basis set is given first; NZ indicates the cc-pVNZ set, while ANZ indicates the aug-cc-pVNZ set.

TABLE 2: The Effect of Basis Set Contraction on the MVD Contribution to the CF Atomization Energy, in kcal/mol

basis[a]	SCF	MCPF
(10s5p)/[4s3p] (11s6p)/[5s4p] TZ/ATZ	−0.296	−0.213
(10s5p)/[5s3p] (11s6p)/[6s4p] TZ/ATZ+1s	−0.230	−0.128
(10s5p)/[6s3p] (11s6p)/[7s4p] TZ/ATZ+2s	−0.281	−0.173
(10s5p)/[7s3p] (11s6p)/[8s4p] TZ/ATZ+3s	−0.253	−0.150
(10s5p)/[8s3p] (11s6p)/[9s4p] TZ/ATZ+4s	−0.260	−0.157
(10s5p)/[9s3p] (11s6p)/[10s4p]TZ/ATZ+5s	−0.255	−0.152
(10s5p)/[10s3p] (11s6p)/[11s4p]uncontracted s	−0.257	−0.154
(10s5p)/[5s4p] (11s6p)/[6s5p] TZ/ATZ+1s1p	−0.222	−0.125
(10s5p)/[7s4p] (11s6p)/[8s5p] TZ/ATZ+3s1p	−0.240	−0.142
(10s5p)/[8s4p] (11s6p)/[9s5p] TZ/ATZ+4s1p	−0.245	−0.148
(10s5p) (11s6p) uncontracted TZ/ATZ	−0.242	−0.145

[a] The carbon basis set is given first. The polarization set is fixed at 2d1f for carbon and 3d2f for fluorine.

TABLE 3: Summary of the Scalar Relativistic Effects on the CF$_4$ Atomization Energy, in kcal/mol

TZ/TZ[a]	SCF	MCPF	SDCI[b]	SDCI(sup[c])	SDCI+Q(sup)
non-rel	329.19	453.29	366.67	429.55	448.05
MVD	327.75	452.10	364.21	428.22	
Δ	−1.44	−1.20	−1.46	−1.33	
DK	328.07	452.41	364.64	428.56	447.12
Δ	−1.12	−0.88	−1.03	−0.99	−0.93

TZ/ATZ	SCF	MCPF	ACPF
non-rel	329.68	455.53	454.90
MVD	328.41	454.50	453.88
Δ	−1.27	−1.02	−1.02
DK	328.56	454.64	454.02
Δ	−1.13	−0.89	−0.88

QZ/AQZ	SCF	MCPF
non-rel	330.30	462.57
MVD	329.18	461.78
Δ	−1.12	−0.79
DK	329.18	461.69
Δ	−1.13	−0.88

[a] The carbon basis set is given first; NZ indicates the cc-pVNZ set, while ANZ indicates the aug-cc-pVNZ set. [b] The infinitely separated atoms energy is obtained by summing the atomic results. [c] Indicates that a supermolecule approach is used, where the four fluorines are 100 Å from the carbon atom. A septet state is used.

consistent with the work of Davidson et al.,[19] who concluded that for first-row systems, perturbation theory should work well. However, this conclusion clearly depends on using the appropriate basis set for this property.

For the MVD approach, the results obtained using the TZ basis set are not accurate; however, the calculation of the BSSE can lead to very time consuming calculations for large molecules with high symmetry, and use of the uncontracted TZ basis set can also result in very large calculations. Therefore, we test other basis set contractions for the MVD approach—these results are summarized in Table 2. We first note that uncontracting an additional *s* function leads to a value that is too small, while uncontracting two additional *s* functions gives a result that is too large, but in much better agreement with the uncontracted basis set than the original TZ/ATZ contraction. Uncontracting additional *s* functions yields values that are close to the result obtained when all *s* functions are uncontracted, but this is not the same value as that obtained for the completely uncontracted basis set. Uncontracting three additional *s* functions and one additional *p* function yields a MVD effect that is very similar to that of the completely uncontracted basis set. It is not clear how general this result is, but it does make the case that caution must be shown in picking a basis set for the MVD approach.

Our CF$_4$ results are summarized in Table 3. At the MCPF level, the difference between the MVD and DK approaches decreases from the TZ/TZ to the TZ/ATZ and on to the QZ/AQZ basis set. The relativistic effect on the atomization energy is larger at the SDCI level than at the MCPF level. If the SDCI value is computed as the difference between CF$_4$ and the sum of atomic SDCI calculations, the SDCI MVD value is actually larger than the SCF value. This SDCI MVD value is similar to that reported by Feller and Peterson. If a supermolecule approach is used, the SDCI MVD value is marginally smaller than the result at the SCF level of theory. The SDCI results using the DK approach are also larger than the MCPF results; however, if the supermolecule approach is used, the DK SDCI+Q result is close to the DK MCPF result. This clearly shows that the 1.5 kcal/mol result cited by Feller and Peterson is about 0.6 kcal/mol too large as a result of their using an SDCI wave function and a basis set that is inappropriate for this property. Thus, it is clear that a size-consistent method should be used to compute the scalar relativistic effects, and caution must be used in picking a basis set for the MVD approach. This latter point was also made by Blomberg and Wahlgren.[20]

The ACPF results obtained using the TZ/ATZ basis set are very similar to the MCPF result. Combining this result with the effect of uncontracting the TZ/ATZ basis set for CF leads us to conclude that Martin's use of the MVD ACPF approach in an uncontracted basis set should yield similar results to our DK MCPF approach for first-row (and probably second-row) compounds.

On the basis of the CF and CF$_4$ results, we expect that the DK MCPF results using the TZ/ATZ basis set will yield a very good estimate of the scalar relativistic effect on the atomization

TABLE 4: Summary of the Scalar Relativistic Effect on the SiF_4 Atomization Energy, in kcal/mol

TZ/ATZ[a]	SCF	MCPF
non-rel	443.82	549.39
MVD	441.51	547.52
Δ	−2.31	−1.88
DK	441.54	547.49
Δ	−2.28	−1.91

[a] The Si cc-pVTZ and F aug-cc-pVTZ basis sets are used.

energy of SiF_4. The results of these calculations are summarized in Table 4. We have also included the MVD results, and unlike for CF and CF_4, the MVD results agree with the DK results for SiF_4. Our best estimate of the scalar relativistic effect on the atomization energy of SiF_4 is −1.91 kcal/mol. This is 0.6 kcal/mol smaller than the value reported by Feller and Peterson, which we attribute to their use of CI wave functions. Pople and co-workers[9] compute an effect of −2.18 kcal/mol; we suspect that their result would be in better agreement with ours if they included electron correlation, which reduces the scalar relativistic effect on atomization energies. Our computed value is in excellent agreement with that reported (−1.88 kcal/mol) by Martin and Taylor,[10] as expected on the basis of the CF_n results.

IV. Conclusions

We find that the scalar relativistic effect on the atomization energies computed using the DK approach, in conjunction with the MCPF wave function, converges rapidly with basis set. The MVD results are similar to the DK results if a large basis set is used or if the TZ basis sets are more flexibly contracted. Even though the scalar relativistic effect is very small, we find that using a SDCI approach introduces a sizable error.

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