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## Relativistic and correlation effects on molecular properties. II. The hydrogen halides HF, HCl, HBr, HI, and HAt

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# Relativistic and correlation effects on molecular properties.

## II. The hydrogen halides HF, HCl, HBr, HI, and HAt

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A benchmark study of a number of four-component relativistic correlation methods is presented. Bond lengths, harmonic frequencies, and dissociation energies of the molecules HF, HCl, HBr, HI, and HAt are calculated at various levels of theory, using both the Schrödinger and the Dirac–Coulomb–(Gaunt) Hamiltonian. The inclusion of relativity leads to a weakening of the bond, giving a decrease in the calculated harmonic frequencies and dissociation energies of the hydrogen halides. The effect on the bond length is small. These trends are explained by considering the relativistic change in hybridization induced by the spin–orbit coupling. © 1996 American Institute of Physics. [S0021-9606(96)02229-5]

### INTRODUCTION

In a previous paper,<sup>1</sup> hereafter called paper I, one of the present authors studied the effect of relativistic and correlation effects on spectroscopic constants in the series  $X_2$  with ( $X=F, Cl, Br, I, At$ ). The methods used were Hartree–Fock (HF), second-order Møller–Plesset perturbation theory (MP2), configuration interaction with single and double substitutions (CISD), coupled cluster with single and double substitutions (CCSD) and the latter method, perturbatively corrected for the effect of triple excitations (CCSD(T)). This gives a range of correlation treatments, from no electron correlation in the HF method to a fairly high level of correlation in the CCSD(T) method.

In the present paper a complementary study is made for the series HX. In these calculations we furthermore estimate the effect of basis set superposition errors (BSSE) by means of the counterpoise method<sup>2</sup> and present CI–SD results that are corrected for size-extensivity errors by means of the Davidson correction.<sup>3</sup>

### COMPUTATIONAL DETAILS

All calculations were performed using MOLFDIR.<sup>4,5</sup> We used a Gaussian distribution to represent the spatial extent of the nucleus in both the relativistic and the nonrelativistic calculations. The exponents used in this description are given in Table I. The speed of light in atomic units was taken to be 137.035 9895.

All molecular calculations were performed using  $C_{4v}$  symmetry. The atomic calculations were carried out in  $O_h$ . To prevent spurious discrepancies between the nonrelativistic and relativistic dissociation energies, we calculated both the nonrelativistic and the relativistic atomic asymptotes in a

basis of spinors optimized for the spherical average of the four  $^2P_{3/2}$  states.

Spectroscopic constants were obtained by fitting the potential energy curve to a fourth-order polynomial in the internuclear distance. BSSE corrections to the dissociation energy  $D_e$  were calculated using the counterpoise method at the optimized values of  $r_e$  for each method.

### Basis sets

The basis sets for the halogens used were the same as described in paper I, but extended with sets of diffuse functions to describe the electronegativity of the halogen atom in the molecule. This extension is denoted aug-cc-pVXZ<sup>6–8</sup> for F and Cl, we will use the notation aug-pVXZ for the Br, I, and At basis sets that do not originate from the correlation consistent sets. In astatine the set of  $s$  and  $p$  exponents was reoptimized, because an error in the basis set optimization program was detected. This reoptimization did not give rise to significant changes in the calculated spectroscopic constants. The list of diffuse functions added to the original bases is given in Table II.

### RESULTS AND DISCUSSION

The hydrogen halides have been a sample case for many relativistic approaches. Molecules consisting of a hydrogen bounded to a heavy atom present a feasible computational problem to most methods, yet giving insight to the relativistic changes that occur in the bonding. The changes are usually interpreted as arising from both scalar relativistic effects and spin–orbit coupling.

The relativistic effects on the hydrogen atom are negligible, while the effect on the halogen atom is determined by the relativistic contraction of the  $s$  and  $p$  shell and the spin–

TABLE I. Exponents used in the Gaussian nuclear model.

Nucleus	Exponent
<sup>1</sup> H	2118 265 473.0
<sup>19</sup> F	535 493 007.4
<sup>35</sup> Cl	384 827 492.2
<sup>79</sup> Br	243 199 191.6
<sup>127</sup> I	184 523 891.6
<sup>210</sup> At	136 902 770.0

orbit splitting of the  $p$  shell. The latter effect causes a relativistic hybridization energy which will make the bond intermediate between  $\sigma$  and  $\pi$  character.

The three atomic  $p$  orbitals and the hydrogen  $s$  orbital form four combinations that may be labeled  $\sigma_{1/2}$ ,  $\pi_{1/2}$ ,  $\pi_{3/2}$ , and  $\sigma_{1/2}^*$ . The  $\pi$  orbitals are degenerate and nonbonding in the nonrelativistic limit, but in the relativistic case the  $\pi_{1/2}$  can mix with the  $\sigma_{1/2}$  and  $\sigma_{1/2}^*$  orbitals. This makes the bonding and antibonding orbitals partly  $\sigma$  and partly  $\pi$  with the amount of mixing determined by the spin-orbit splitting. If the energy difference between the  $p_{1/2}$  and  $p_{3/2}$  is small, the three occupied linear combinations will be a pure  $\sigma$  bond ( $\sigma_{1/2}$ ) and two pure  $\pi$  nonbonding orbitals ( $\pi_{1/2}$  and  $\pi_{3/2}$ ). The LUMO is the pure  $\sigma$  antibonding  $\sigma_{1/2}^*$  orbital and the total bond order is one  $\sigma$  bond. This is the case for HF. On the other hand, if the spin-orbit splitting is large the hybridization energy will make the formation of pure  $\sigma$  or  $\pi$  bonds less favorable. In the hyper-relativistic limit no hybridization will occur and the atomic  $p_{1/2}$  orbital remains nonbonding. The bonding orbital is then formed solely from the halogen  $p_{3/2}$  and the hydrogen  $s_{1/2}$ . Since the halogen  $p_{3/2,1/2}$  is one-third  $\pi$  and two-thirds  $\sigma$  in character the bond is weakened to a bond order of  $2/3 \sigma$ . This hyper-relativistic limit is observed in Dirac-Fock calculations by Saue, Faegri, and

TABLE II. Diffuse exponents added to the original basis sets. The hydrogen, fluorine and chlorine primitive basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory. See also "http://www.emsl.pnl.gov:2080/forms/basisform.html".

	Fluorine	Chlorine	Bromine	Iodine	Astatine
$dz\ s$	0.098 63	0.0608	0.0620	0.033 35	0.0550
$dz\ p$	0.085 02	0.0466	0.0470	0.045 36	0.0350
$dz\ d$	0.464 00	0.1960	0.1120	0.280 00	0.0550
$tz\ s$	0.091 58	0.0591	0.0580	0.024 57	0.0500
$tz\ p$	0.073 61	0.0419	0.0380	0.040 00	0.0300
$tz\ d$	0.292 00	0.1350	0.0880	0.095 80	0.0500
$tz\ f$	0.724 00	0.3120	0.2000	0.169 80	0.0861

Gropen<sup>9</sup> on HUus (Uus=element 117), where a dramatic increase of the bond distance relative to the nonrelativistic limit is found. In the lighter systems treated here we find a gradual increase of  $\pi$  character in the first ( $\omega=1/2$ ) orbital. Using a Mulliken population analysis we find that in hydrogenfluorine this contribution is only 0.01%, this increases through 0.02% in HCl, 0.34% in HBr, 1.6% in HI to 18.0% in HAt. In the latter case the amount of hydrogen character is still considerable (31%), so the bonding is in-between the nonrelativistic and hyper-relativistic scheme.

Results of the calculations are given in Tables III–VII. Table VIII gives the difference between the outcome of the relativistic and the nonrelativistic calculations. We will first discuss the results for each molecule and summarize the trends at the end of this section. These trends are also graphically represented in Figs. 1–3.

TABLE III. Properties of HF calculated at various levels of theory. Columns with the header BSSE give results that are corrected for the basis set superposition error.

Method	$r_e(\text{\AA})$		$\omega_e(\text{cm}^{-1})$		$D_e(\text{kcal mol}^{-1})$			
	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVDZ BSSE	pVTZ	pVTZ BSSE
NR–HF	0.900	0.899	4472	4466	99.5	99.1	101.4	101.2
DC–HF	0.900	0.899	4470	4464	98.9	98.5	100.7	100.5
DC+G–HF	0.900	0.899	4469	4464	98.9	98.5	100.7	100.5
NR–MP2	0.924	0.922	4086	4123	138.7	136.7	144.4	142.9
DC–MP2	0.924	0.922	4083	4121	138.1	136.1	143.8	142.3
NR–CCSD	0.922	0.918	4120	4169	133.5	131.9	137.4	136.1
DC–CCSD	0.922	0.918	4117	4168	132.9	131.3	136.8	135.5
NR–CISD	0.919	0.915	4170	4223	131.1	129.4	134.7	133.4
DC–CISD	0.919	0.915	4168	4222	130.5	128.8	134.1	132.8
NR–CISD+Q	0.923	0.919	4093	4145	133.6	131.9	137.5	136.2
DC–CISD+Q	0.923	0.919	4090	4144	133.0	131.3	136.9	135.6
NR–CCSD(T)	0.924	0.921	4084	4124	134.6	132.9	139.3	138.0
DC–CCSD(T)	0.924	0.921	4082	4123	134.0	132.3	138.7	137.4
Ref. 10, HF	0.9002	0.8991	4466.3	4464.9	98.8		100.1	
Ref. 10, CI–SD	0.9192	0.9149	4165.8	4222.9	130.9		134.6	
Experiment (Ref. 22)	0.9168		4138.3		141.2			

TABLE IV. Properties of HCl calculated at various levels of theory. Columns with the header BSSE give results that are corrected for the basis set superposition error.

Method	$r_e(\text{\AA})$		$\omega_e(\text{cm}^{-1})$		$D_e(\text{kcal mol}^{-1})$			
	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVDZ BSSE	pVTZ	pVTZ BSSE
NR-HF	1.277	1.267	3128	3136	78.6	78.4	81.2	81.1
DC-HF	1.277	1.267	3124	3132	77.4	77.2	80.0	79.9
DC+G-HF	1.277	1.267	3123	3132	77.4	77.2	80.0	79.9
NR-MP2	1.288	1.275	3023	3044	100.4	98.2	105.6	104.1
DC-MP2	1.288	1.275	3019	3041	99.3	97.0	104.5	103.0
NR-CCSD	1.291	1.277	2989	3014	100.0	97.6	103.7	102.2
DC-CCSD	1.290	1.277	2985	3011	98.9	96.6	102.6	101.1
NR-CISD	1.288	1.274	3018	3049	98.2	96.0	101.5	100.1
DC-CISD	1.288	1.273	3014	3046	97.1	94.9	100.4	99.0
NR-CISD+Q	1.292	1.278	2972	2999	100.3	97.9	103.8	102.3
DC-CISD+Q	1.292	1.278	2967	2995	99.3	96.9	102.8	101.2
NR-CCSD(T)	1.292	1.279	2971	2991	100.9	98.4	105.0	103.4
DC-CCSD(T)	1.292	1.279	2967	2988	99.9	97.3	103.9	102.3
Ref. 11, HF	1.2772	1.2674	3128.3	3135.4	78.3		80.1	
Ref. 12, MBPT(4)+R		1.282	3009					
Experiment (Ref. 22)		1.2746	2991.0				106.5	

## HF and HCl

The nonrelativistic values differ slightly from the benchmark values calculated by Peterson, Kendall, and Dunning<sup>10</sup> and Woon and Dunning<sup>11</sup> in the same basis sets. For the hydrogenfluorine aug-cc-pVDZ results this is mainly due to the extra tight  $p$  function that was added to the basis. The rather large discrepancy that is found in the dissociation energies is due to the atomic calculation of fluorine. In our case this was done in double group symmetry. This gives different orbitals than found in a single group symmetry calculation,

affecting the calculated energies slightly. As expected the choice of orbitals becomes less important as we go to a higher level of correlation. In the hydrogenfluorine aug-cc-pVTZ results the discrepancy in the dissociation energy at the HF level is 1.3 kcal mol<sup>-1</sup>, while it is only 0.1 kcal mol<sup>-1</sup> at the CISD level of theory.

In these light molecules relativistic effects are negligible for most purposes. The relativistic effect on the frequency does not depend on the method used, but does depend slightly on the quality of the basis set used. The relativistic

TABLE V. Properties of HBr calculated at various levels of theory. Columns with the header BSSE give results that are corrected for the basis set superposition error.

Method	$r_e(\text{\AA})$		$\omega_e(\text{cm}^{-1})$		$D_e(\text{kcal mol}^{-1})$			
	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVDZ BSSE	pVTZ	pVTZ BSSE
NR-HF	1.412	1.408	2807	2795	67.7	67.2	69.3	69.2
DC-HF	1.409	1.406	2798	2784	63.5	62.9	65.0	64.9
DC+G-HF	1.410	1.406	2796	2783	63.5	62.9	65.0	64.9
NR-MP2	1.423	1.415	2717	2724	87.2	84.8	91.5	89.7
DC-MP2	1.421	1.413	2707	2711	83.4	80.7	87.5	85.7
NR-CCSD	1.427	1.419	2673	2679	88.1	85.3	90.8	89.1
DC-CCSD	1.425	1.417	2661	2664	84.3	81.5	86.9	85.2
NR-CISD	1.425	1.415	2699	2711	86.5	83.9	88.9	87.2
DC-CISD	1.422	1.414	2687	2697	82.7	80.0	84.9	83.2
NR-CISD+Q	1.429	1.421	2655	2662	88.6	85.7	91.1	89.3
DC-CISD+Q	1.427	1.419	2641	2646	84.8	81.9	87.2	85.5
NR-CCSD(T)	1.429	1.421	2659	2660	89.0	86.0	92.0	90.2
DC-CCSD(T)	1.427	1.419	2646	2645	85.2	82.2	88.1	86.3
Ref. 12, MBPT(4)+R		1.421	2693					
Ref. 13, CISD+Q		1.398					84.9	
Ref. 14, RCI		1.455	2645				85.8	
Ref. 15, KRMP2		1.411	2702				83.5	
Experiment (Ref. 22)		1.414	2648				90.4	

TABLE VI. Properties of HI calculated at various levels of theory. Columns with the header BSSE give results that are corrected for the basis set superposition error.

Method	$r_e(\text{Å})$		$\omega_e(\text{cm}^{-1})$		$D_e(\text{kcal mol}^{-1})$			
	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVDZ BSSE	pVTZ	pVTZ BSSE
NR-HF	1.611	1.611	2470	2457	56.4	56.0	58.0	58.0
DC-HF	1.605	1.603	2439	2429	48.0	47.4	49.7	49.4
DC+G-HF	1.606	1.604	2437	2427	48.1	47.4	49.7	49.4
NR-MP2	1.619	1.616	2405	2404	74.0	71.2	78.0	76.0
DC-MP2	1.614	1.610	2371	2373	66.3	63.2	70.4	68.2
NR-CCSD	1.625	1.623	2353	2351	76.1	72.9	78.4	76.5
DC-CCSD	1.621	1.617	2313	2314	68.5	65.3	70.9	68.8
NR-CISD	1.622	1.619	2375	2382	74.6	71.6	76.4	74.6
DC-CISD	1.618	1.613	2336	2347	67.1	63.9	68.9	66.9
NR-CISD+Q	1.627	1.625	2333	2334	76.7	73.4	78.6	76.7
DC-CISD+Q	1.624	1.620	2291	2295	69.2	65.8	71.2	69.2
NR-CCSD(T)	1.626	1.625	2341	2334	77.0	73.5	79.4	77.4
DC-CCSD(T)	1.623	1.620	2301	2297	69.5	66.0	72.0	69.9
Ref. 12 MBPT(4)+R	1.608		2368					
Ref. 13 CISD+Q	1.593					70.3		
Ref. 16 RCI	1.66		2305			70.9 <sup>a</sup>		
Ref. 15 KRMP2	1.598		2358			67.1		
Ref. 17 DC-HF	1.601		2410			46.8		
Ref. 9 DC-HF	1.602		2436					
Experiment (Ref. 22)	1.609		2309			73.6		

<sup>a</sup>Calculated using the  $D_0^0$  and  $\omega_e$  given in this paper.

effects on the bond length and on the dissociation energy are consistent in all calculations.

The relativistic effect on the dissociation energy is mainly due to the spin-orbit splitting of the  $H(1S) + X(2P)$  asymptote. This leads to a correction to the nonrelativistic dissociation energy by 1/3 of the atomic  $p$ -shell spin-orbit splitting. This atomic spin-orbit only (ASO only) correction

is  $-0.39$  and  $-0.84$  kcal mol<sup>-1</sup> for HF and HCl, respectively. The calculated values are larger ( $-0.6$  and  $-1.1$  kcal mol<sup>-1</sup>), indicating an additional scalar or molecular spin-orbit effect. The small basis set superposition error does not influence the relativistic shift in the  $D_e$ .

Two-electron relativistic effects are estimated by adding the Gaunt operator as a perturbation to the two-electron op-

TABLE VII. Properties of HAt calculated at various levels of theory. Columns with the header BSSE give results that are corrected for the basis set superposition error.

Method	$r_e(\text{Å})$		$\omega_e(\text{cm}^{-1})$		$D_e(\text{kcal mol}^{-1})$			
	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVDZ BSSE	pVTZ	pVTZ BSSE
NR-HF	1.713	1.713	2302	2306	49.6	49.4	53.0	52.0
DC-HF	1.710	1.715	2098	2112	29.7	28.6	32.1	30.7
DC+G-HF	1.712	1.716	2097	2112	29.8	28.6	32.2	30.8
NR-MP2	1.723	1.719	2234	2258	66.7	64.2	72.2	69.1
DC-MP2	1.723	1.723	2028	2070	48.3	45.5	53.1	49.9
NR-CCSD	1.730	1.727	2176	2198	69.4	66.5	73.0	70.0
DC-CCSD	1.736	1.737	1938	1983	51.4	48.6	54.7	51.6
NR-CISD	1.727	1.723	2198	2228	68.1	65.3	71.1	68.2
DC-CISD	1.732	1.731	1965	2017	50.1	47.2	52.8	49.7
NR-CISD+Q	1.732	1.730	2154	2179	70.1	67.1	73.3	70.2
DC-CISD+Q	1.741	1.741	1904	1955	52.3	49.3	55.4	52.3
NR-CCSD(T)	1.731	1.730	2165	2182	70.2	67.1	74.0	70.8
DC-CCSD(T)	1.738	1.739	1925	1966	52.3	49.2	55.8	52.6
Ref. 21, DGCI	1.732		2094			61.8		
Ref. 21, CIPSO	1.705		2202			54.9		
Ref. 17, DC-HF	1.675		2343			39.6		
Ref. 9, DC-HF	1.712		2116					

TABLE VIII. Relativistic effects on the properties of the hydrogen halides at various levels of theory. Columns with the header BSSE give results that are corrected for the basis set superposition error.

Molecule	Method	$\Delta r_e(\text{\AA})$		$\Delta \omega_e(\text{cm}^{-1})$		$\Delta D_e(\text{kcal mol}^{-1})$			
		pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVDZ BSSE	pVTZ	pVTZ BSSE
HF	HF	0.000	0.000	-2	-1	-0.6	-0.6	-0.6	-0.6
	HF+G	0.000	0.000	-3	-2	-0.7	-0.7	-0.6	-0.6
	MP2	0.000	0.000	-3	-2	-0.6	-0.6	-0.6	-0.6
	CCSD	0.000	0.000	-3	-2	-0.6	-0.6	-0.6	-0.6
	CISD	0.000	0.000	-2	-1	-0.6	-0.6	-0.6	-0.6
	CISD+Q	0.000	0.000	-3	-2	-0.6	-0.6	-0.6	-0.6
	CCSD(T)	0.000	0.000	-3	-2	-0.6	-0.6	-0.6	-0.6
HCl	HF	0.000	0.000	-4	-3	-1.2	-1.2	-1.2	-1.2
	HF+G	0.000	0.000	-5	-4	-1.2	-1.2	-1.2	-1.2
	MP2	0.000	0.000	-4	-3	-1.1	-1.2	-1.1	-1.1
	CCSD	0.000	0.000	-4	-3	-1.1	-1.1	-1.1	-1.1
	CISD	0.000	0.000	-4	-3	-1.1	-1.1	-1.1	-1.1
	CISD+Q	0.000	0.000	-4	-3	-1.1	-1.0	-1.1	-1.1
	CCSD(T)	0.000	0.000	-4	-3	-1.1	-1.0	-1.1	-1.1
HBr	HF	-0.003	-0.002	-9	-12	-4.2	-4.3	-4.4	-4.4
	HF+G	-0.002	-0.002	-10	-13	-4.2	-4.3	-4.4	-4.3
	MP2	-0.002	-0.002	-11	-13	-3.8	-4.0	-4.0	-4.0
	CCSD	-0.002	-0.002	-12	-14	-3.8	-3.9	-4.0	-3.9
	CISD	-0.002	-0.002	-12	-14	-3.8	-3.9	-4.0	-3.9
	CISD+Q	-0.002	-0.002	-13	-15	-3.7	-3.8	-3.9	-3.9
	CCSD(T)	-0.002	-0.002	-13	-15	-3.7	-3.8	-3.9	-3.9
HI	HF	-0.006	-0.007	-31	-29	-8.3	-8.6	-8.4	-8.6
	HF+G	-0.005	-0.006	-33	-30	-8.3	-8.6	-8.4	-8.6
	MP2	-0.004	-0.006	-34	-31	-7.7	-8.1	-7.6	-7.9
	CCSD	-0.004	-0.006	-40	-37	-7.5	-7.6	-7.5	-7.6
	CISD	-0.004	-0.006	-39	-35	-7.6	-7.7	-7.5	-7.7
	CISD+Q	-0.003	-0.005	-42	-39	-7.5	-7.5	-7.4	-7.5
	CCSD(T)	-0.004	-0.005	-40	-37	-7.5	-7.5	-7.4	-7.5
HAt	HF	-0.003	0.002	-204	-194	-19.9	-20.9	-20.9	-21.3
	HF+G	-0.002	0.003	-205	-194	-19.9	-20.8	-20.8	-21.2
	MP2	0.001	0.004	-206	-188	-18.4	-18.8	-19.1	-19.3
	CCSD	0.007	0.009	-238	-215	-18.0	-18.0	-18.3	-18.4
	CISD	0.006	0.008	-233	-211	-18.0	-18.1	-18.4	-18.5
	CISD+Q	0.009	0.011	-249	-224	-17.8	-17.7	-17.9	-18.0
	CCSD(T)	0.007	0.010	-240	-216	-17.9	-17.9	-18.1	-18.2

erator. This gives only a marginal change in the calculated properties with as most notable effect an enhanced relativistic decrease of the harmonic frequency of  $-0.9 \text{ cm}^{-1}$  for HF and  $-0.7 \text{ cm}^{-1}$  for HCl.

### HBr

All methods give a relativistic decrease of the bond length by 0.2 pm. The effect on the frequency is more pronounced than in HF and HCl and varies from  $-9 \text{ cm}^{-1}$  at the HF-aug-pVDZ level to  $-15 \text{ cm}^{-1}$  at the CCSD(T)/aug-pVTZ level of theory. The effect on the dissociation energy is  $-4 \text{ kcal mol}^{-1}$ , again somewhat larger than the ASO-only estimate of  $-3.5 \text{ kcal mol}^{-1}$ . The DC-CCSD(T)/aug-pVTZ values give good agreement with experiment. The basis set superposition error is somewhat larger than in HF and HCl. The BSSE corrected relativistic shifts in the  $D_e$  show less basis set dependence than the uncorrected values but the dif-

ferences are small. Two-electron relativistic effects are not important, the results with and without a perturbational estimate of the magnetic part of the Breit interaction are almost identical ( $-1.2 \text{ cm}^{-1}$  effect on the frequency).

We can compare our results with previous theoretical work as well. Kello and Sadlej<sup>12</sup> used many-body-perturbation theory, including electron correlation through the fourth order in perturbation theory and representing the relativistic effects in first order via the Cowan-Griffin operator (MBPT+R). On basis of a minimal three point fit they give an approximate bond length of 1.421 Å and a frequency of  $2693 \text{ cm}^{-1}$ , which is in line with our correlated results.

Schwerdtfeger *et al.*<sup>13</sup> used a semiempirically adjusted relativistic pseudopotential in CI-SD+Q calculations and included spin-orbit effects using the ASO only approximation. Chapman, Balasubramanian, and Lin<sup>14</sup> used relativistic effective core potentials (RECP), followed by CI calcula-

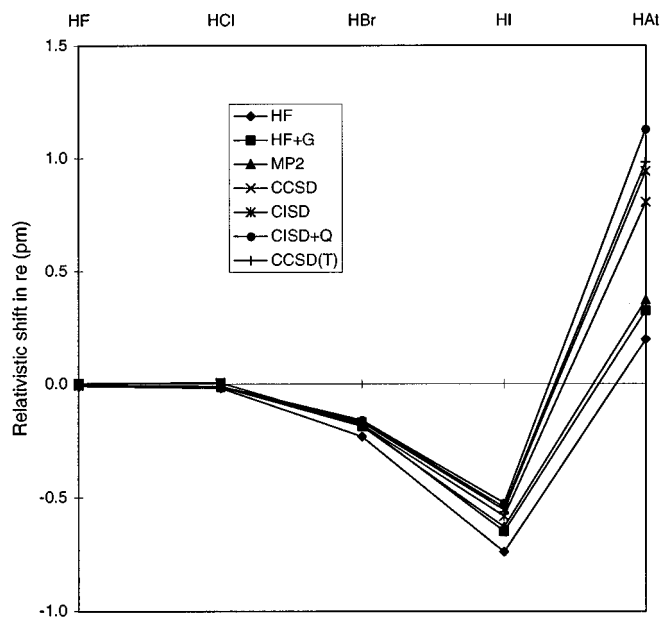


FIG. 1. Relativistic effects on the equilibrium bondlength of the hydrogen halides at various levels of theory.

tions that include spin-orbit effects. Lee and Lee<sup>15</sup> also used an RECP but included the spin-orbit operator in the HF process and treated electron correlation using Kramers-restricted MP2 (KRMP2) theory. All these authors used basis sets that include one or two polarization  $d$  functions but no  $f$  function. The results should therefore be comparable to our aug-pVDZ results.

The bond length calculated by Schwerdtfeger *et al.* is 1.398 Å, significantly smaller than the other calculated values and experiments. This is probably due to the preliminary pseudopotentials that they used at the time. The dissociation energy is 84.9 kcal mol<sup>-1</sup>, which is close to our DC-CISD

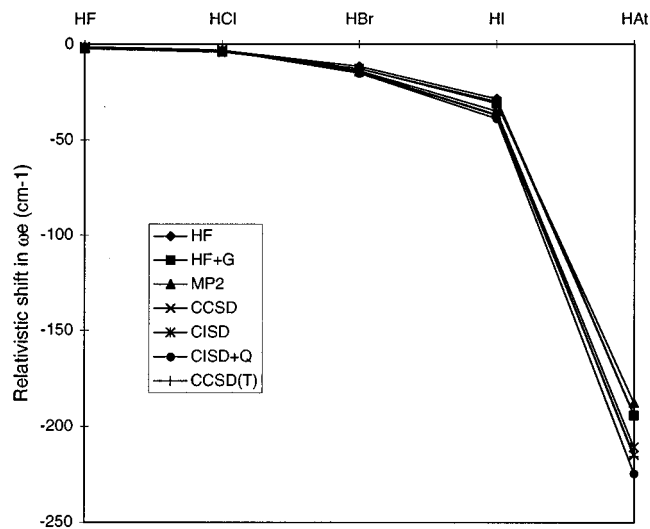


FIG. 2. Relativistic effects on the vibrational frequency of the hydrogen halides at various levels of theory.

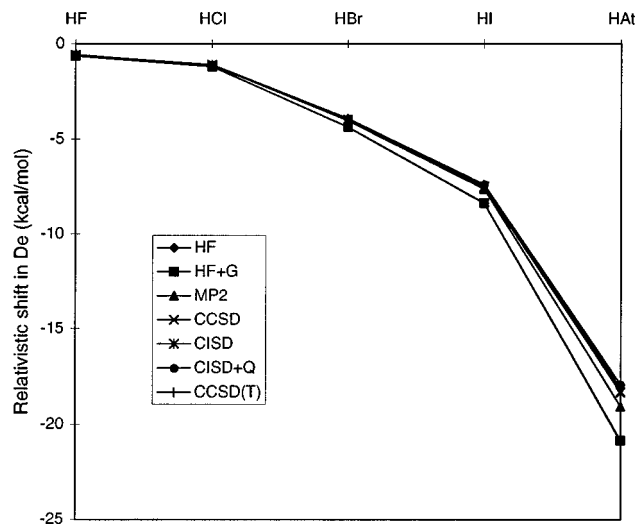


FIG. 3. Relativistic effects on the dissociation energies of the hydrogen halides at various levels of theory. Results are not corrected for basis set superposition errors.

+Q/aug-pVDZ value. The KRMP2 results of Lee and Lee are in quite good agreement with our DC-MP2/aug-pVDZ results, except for the bond length that is smaller by one picometer. Chapman *et al.* use the same RECP but find a bond length of 1.455 Å, significantly longer than all other calculated results. The origin of this discrepancy is not clear. Their calculated frequency and dissociation energy are in line with our results.

## HI

As the relativistic corrections becomes larger, some dependence on the choice of method begins to appear. DHF theory overestimates the relativistic bondlength contraction and dissociation energy decrease relative to what is found in the correlated calculations. The effect on the frequency is on the other hand smaller at the DHF level than in the correlated calculations. The CCSD(T)/aug-pVTZ calculation gives, as should be expected, the best overall agreement with experiment. The bondlength is somewhat too long. This may either be due to strong basis set contraction used for all but the valence orbitals or to core-valence correlation effects. Correcting for the BSSE error gives more consistent relativistic shifts in the  $D_e$ . These are still reasonably well estimated by the ASO-only value of  $-7.3$  kcal mol<sup>-1</sup>. The effect of the Breit interaction is small.

We can again compare with other theoretical work. The bondlength calculated via MBPT(4)+R method by Kellö and Sadlej<sup>12</sup> is somewhat shorter than the one calculated at the DC-MP2/aug-pVTZ level or with other correlated methods. This is probably due to neglect of spin-orbit coupling in the MBPT(4)+R method. Kellö and Sadlej also performed MBPT(2) calculations that included the halogen core electrons. From these calculations they estimate an effect on the bondlength due to core-core and core-valence correlation of  $-0.01$  Å.



The ECP type calculations of the authors mentioned in the discussion about HBr again give the same general picture as for HBr. The bond length as calculated by Lee and Lee<sup>15</sup> and Schwerdtfeger *et al.*<sup>13</sup> are shorter than the ones calculated by us, while the bond length calculated by Chapman *et al.*<sup>16</sup> is much longer. The frequencies and dissociation energies are in good agreement with the values obtained by us.

There are also two calculations on the DHF level of theory. The calculation by Matsuoka<sup>17</sup> is done using the same primitive basis<sup>18</sup> as we used for the aug-pVDZ calculations. We, however, extended this basis with a tight *s* and *p* function plus extra diffuse (one *s*, one *p*, and two *d*) functions and used *relativistic* contraction coefficients in a general contraction scheme. Matsuoka added one diffuse *d* function and contracted some exponents with *nonrelativistic* contraction coefficients in a segmented contraction scheme. The use of a nonrelativistic contraction coefficients combined with a minimal kinetic balance to generate the small component functions is questionable,<sup>19</sup> since the relativistic core functions deviate significantly from the nonrelativistic core functions. In this case no serious problems seem to arise and the results are in good agreement with our DC-HF/aug-pVDZ results.

Very recently Saue, Faegri, and Gropen<sup>9</sup> also calculated the frequency and bond length using an uncontracted (20*s*17*p*11*d*) basis. Their results are in very good agreement with our DC-HF/aug-pVDZ results.

## HAt

Both at the DHF level and at the correlated levels of theory we see a small relativistic extension of the bond. As was seen in the other compounds, the relativistic decrease of dissociation energy is overestimated at the DHF level. The Breit interaction has a small effect on the bond length, but does not affect the calculated frequency and  $D_e$  much. The ASO-only approximation for the relativistic shift in the  $D_e$  now breaks down, the calculated shifts are 18–21 kcal mol<sup>-1</sup>, 2–5 kcal mol<sup>-1</sup> smaller than the ASO-only value of 23 kcal mol<sup>-1</sup>.

When the relativistic effects become large the calculated relativistic corrections become more basis set dependent. With the medium-sized basis sets that are used in this work deviations from the basis set limit are non-negligible and may be different in size for the nonrelativistic and relativistic case. This makes it essential to use nonrelativistic and relativistic basis sets that have the same accuracy and size. The importance of such a balanced approach can be seen from the following observation.

In the construction of the relativistic contracted aug-pvtz basis set it was found that the core region of the 6*s* spinor was almost completely spanned by the other 5 contracted *s* functions (total overlap was 0.9999). To avoid numerical instability due to linear dependencies this function was not included in the basis. The 6*s* function was thus considered to be described by the five other contracted functions plus the three uncontracted outermost primitive functions. In the non-relativistic case this near-linear dependency was one order

smaller (total overlap 0.9981) and the core part of the 6*s* was retained in the initial calculations. The calculated relativistic effects differed more than expected from the aug-pvdz results. For instance the calculated relativistic frequency shifts were 10%–20% smaller and the relativistic bond length shifts were about 0.3 pm smaller. Recalculation of the aug-pvtz relativistic shifts after deletion of the nonrelativistic 6*s* function gave frequency shifts and bond length shifts that were more consistent with the aug-pvdz results. These results are given in Tables VII and VIII. HF and CCSD results in the other nonrelativistic aug-pvtz basis (with the 6*s* function) are given in Ref. 20.

Experimental data is very scarce for this molecule. DGCI and CIPSI calculations including spin-orbit operators and using energy adjusted *ab initio* pseudopotentials were done by Dolg *et al.*<sup>21</sup> The DGCI method is in this case used with a single reference determinant and gives good agreement with our CISD bond length. The harmonic frequency and  $D_e$  values, however, are in between our relativistic and nonrelativistic results. The multireference CIPSO approach gives quite good agreement with our calculated dissociation energies, but differs in the frequency and bond length.

DC-HF calculations were done by Matsuoka<sup>17</sup> and Saue, Faegri, and Gropen.<sup>9</sup> Our DC-HF/aug-pVTZ bond length and frequency agree very well with the values calculated by Saue *et al.* Their calculations also predict similar relativistic shifts as found by us, a small change of bond length and a large frequency shift of about -200 cm<sup>-1</sup>. Matsuoka's results are quite different. He gets a much shorter bond length, giving a relativistic effect of -0.027 Å. His calculated relativistic frequency shift is much smaller than calculated by us and has the opposite sign, while he finds a dissociation energy of 39.6 kcal mol<sup>-1</sup>, about 10 kcal mol<sup>-1</sup> larger than our DC-HF/aug-pVDZ value. These discrepancies from the other two DC-HF calculations are probably due to the small primitive basis that he employed, combined with the use of a nonrelativistic contraction scheme that further degrades the quality of the relativistic basis set. This further illustrates the point made above, that one needs large basis sets, or medium basis sets of comparable accuracy, to compare relativistic and nonrelativistic results.

## Trends

Summarizing the trends, we see that the  $D_e$  of the HX molecules is decreased by relativity. Up to iodine, this effect can be modeled by considering the spin-orbit coupling as completely quenched in the molecule and correcting only the atomic asymptote. For astatine this simple model fails and scalar relativistic and molecular spin-orbit effects should be taken into account. The influence of spin-orbit coupling and other relativistic effects on the bond length is somewhat less consistent. In bromine and iodine we find a contraction of the bond length relative to the nonrelativistic result, while in astatine we find a relativistic expansion. In all cases the effect is rather small, of the order of 0.01 Å. This is probably due to the cancellation of scalar relativistic and spin-orbit effects. The overall contraction of the *p* shell will decrease

the bond length but the increasing hybridization energy due to spin-orbit coupling weakens the bond and increases the bond length. This weakening of the bond is also seen in the relativistic decrease of the harmonic frequency that we observe for all molecules.

In all cases the relativistic corrections on the  $r_e$  and  $\omega_e$  are more pronounced when we allow for a higher level of electron correlation. These relativistic corrections are fairly independent of the basis set employed, provided that the nonrelativistic and relativistic basis set are of comparable accuracy and size.

The remaining errors, when comparing our highest level CCSD(T)/aug-pVTZ results with experiment, are probably mainly due to the one-particle basis set incompleteness and the neglect of  $d$  shell core-valence correlation for the heavier elements. Higher-order relativistic effects are likely to be small, as can be seen from the magnitude of the Gaunt interaction corrections.

## CONCLUSIONS

For all hydrogen halides the calculated bond lengths show only little change upon inclusion of relativity. The relativistic bond length contraction due to the relativistic contraction of the  $p$  shell, that is often observed in  $p$ -block elements, is counteracted by the spin-orbit coupling. This leads to a mixing of the occupied  $\pi$  orbitals with the antibonding  $\sigma^*$  orbital which weakens the bond and increases the bond length. The two effects nearly cancel each other, for HI the net effect is a bond contraction, for HAt we find an extension.

The weakening of the bond is also seen in the relativistic decrease of the harmonic frequency and the dissociation energy that is observed. The large relativistic effect on the dissociation energy is mostly due to the spin-orbit splitting of the  $^2P$  atomic asymptote. Only for the heaviest hydrogen halide, HAt, a significant molecular contribution to this relativistic effect is apparent.

The similarity of the relativistic corrections, obtained with different four-component methods to treat electron correlation, that was found in paper I, is to some extent also present here. The difference between the relativistic shifts calculated at the MP2 and CCSD(T) level in HAt may, however, be too large to be neglected.

The effect of two-electron relativistic corrections, i.e., the Gaunt interaction, is found to be unimportant at the level of accuracy reached in the calculated spectroscopic constants. It may be of interest for highly accurate calculations on the lighter elements since the effect on the frequency of HF and HCl is of the order of a wave number.

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