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Electronic Structure of Linear Halogen Compounds

I. The Diatomic Halides, Interhalogens and Halogen Hydrides

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Self consistent field molecular orbital calculations have been carried out for the ground electronic states for diatomic molecules XY, with X, Y = H, F, Cl, Br or I. Basis sets are critically discussed, and computed properties compared with experiment. The correlation between experimental ionization energies and those estimated through the use of *Koopmans'* theorem is given.

Key words: Interhalogens, SCF-MO calculations on ~

Introduction

Several studies of the diatomic halogen-halogen and halogen hydride molecules have been reported where the halogen is limited to fluorine or chlorine [1]. Until rcently *ab initio* calculations on polyatomic molecules involving heavier halogens have been prohibitively expensive. This paper reports a systematic determination of single configuration self consistent field wave functions for the entire series through iodine using extended (double zeta plus polarization) basis sets for all calculations, with the exception of the two heaviest molecules IBr and I_2. For these last two molecules single zeta plus polarization basis sets were used to bring the calculations into more manageable limits. In particular this restriction was necessary because these calculations on diatomics are used as a guide for setting up the halogenated acetylene calculations to be reported in a subsequent paper, and larger basis sets would have exceeded reasonable computational limits in the four atom systems.

Use of "equivalent" basis sets for the several molecules reported in this study permits an assessment of the accuracy of computed molecular properties over a range covering light to heavy halogens. Those properties which depend predominantly on the valence shell structure are expected to be computed with equal reliability over the whole range. Binding energies and electric moments can be anticipated to fall in this class. The total energy of the molecule will be increasingly in error the heavier atoms are, because of the neglect of correlation and relativistic effects, which become large for the inner electrons, but are not expected to affect energy differences of chemical interest. The reliability of properties such as the electric field and its gradients at the various nuclei in the molecule must be assessed with considerable caution because of the importance of inner shell polarization contributions. A basis set not flexible enough to be able to describe these inner shell polarizations will not lead to stable computed electric fields and field gradients at the atomic nuclei. Thus, in the present calculations, where only the valence shell is treated with adequate flexibility, we might expect computation of these properties at the heavier nuclei to be less reliable than at the light ones. The definitive testing of these assertions would involve a careful study of computed properties as a function of basis set. This study, however, is outside the scope of the present work.

1. Basis Sets and Wave Functions

All calculations were done with the ALCHEMY computer program which was used to construct single configuration closed shell wave functions for the dihalogen and interhalogen ground states from a *Slater*-type basis [2]. These one particle basis sets contain two components, an atomic component taken

Table 1. Atomic basis sets for wave functions of this paper

	Double zeta + polarization basis orbital exponents[a]					Reduced basis orbital exponents[a]	
	H	F	Cl	Br	I	Br	I
1s	1.23739	11.0110	17.6501	37.0647	59.214	35.2471	51.9391
1s	0.98226	7.91788	12.0587	28.3638	49.376		
2s		3.09603	6.98333	18.8031	34.527	12.8217	19.5335
2s		1.94665	4.92606	15.3161	24.856		
3s			3.34163	9.5189	15.726	6.7395	11.5958
3s			2.00905	6.6824	13.218		
4s				4.0670	8.4393	2.6382	6.3243
4s				2.3318	6.0467		
5s					3.4180		2.6807
5s					2.0959		
2p	1.66827*	4.170990	8.90262	28.3336	33.205	15.5282	24.4237
2p		1.845390	4.90727	15.06109	20.653		
3p			2.33358	9.00371	15.653	6.5236	11.6138
3p			1.32171	6.2067	11.467		
4p				3.5888	8.2310	2.2570	6.0074
4p				1.8959	5.5025		
5p					3.1906		2.3223
5p					1.8139		
3d	1.5*	3.5*	2.5*	9.92066	19.960	6.5197	12.9669
3d		2.2*	1.8*	4.8816	11.490		
4d				3.5*	6.7820	3.5*	5.2335
4d				2.0*	4.0631	2.0*	
5d					3.0*		3.0*
5d					2.0*		2.0*
4f		4.0*	4.0*	4.0*		4.0*	
4f		2.0*	2.0*	2.0*		2.0*	
5f					4.0*		4.0*
5f					1.8*		1.8*

[a] Polarization functions are indicated with an asterik.

Table 2. Atomic electronic energies and virial ratios with basis sets of Table 1

Atom	$E_{\text{electronic}}$	V^a
H^b	−0.499995	−2.00110
F^b	−99.401166	−1.99991
Cl^b	−459.473791	−2.00017
Br^b	−2572.316774	−1.99987
I^b	−6917.900626	−1.99999
Br^c	−2564.265888	−1.97512
I^c	−6905.946212	−2.00003

[a] $V = E_{\text{potential}}/E_{\text{kinetic}}$.

[b] Double zeta + polarization basis of Table 1.

[c] Reduced basis of Table 1.

Table 3. Atomic orbital energies, ε_J, in atomic units for the atoms in their lowest electronic configurations. Basis sets used are given in Table 1

	Orbital energies ε_J obtained from the "double zeta + polarization" basis set					Orbital energies obtained from the reduced basis set	
	H	F	Cl	Br	I	Br	I
1s	−0.5000	−26.3745	−104.8779	−490.0251	−1177.1836	−489.5194	−1177.0790
2s		−1.5670	−10.6008	−65.1508	−180.9313	−63.7984	−178.6468
3s			−1.0655	−9.8350	−37.9095	−9.0972	−36.7050
4s				−0.9757	−7.2275	−0.8552	−6.7755
5s					−0.8125		−0.6920
2p		−0.7244	−8.0646	−58.5048	−169.6373	−58.1141	−169.3266
3p			−0.4999	−7.4417	−33.0974	−7.0051	−32.7335
4p				−0.4430	−5.4571	−0.3675	−5.2326
5p					−0.3960		−0.3156
3d				−3.1766	−24.2591	−2.3323	−23.5381
4d					−2.3857		−2.0906

from variational calculations on isolated atoms [3], and a polarization component necessary for describing distortion of atomic valence shells in the electric field present in the molecule. The atomic component used in the present calculations is double zeta [4] for all molecules except IBr and I_2. This means that the occupied shells on the separate atoms are essentially described by two *Slater*-functions with basis function exponents optimized to give a minimum atomic energy. It is generally recognized that this offers close the most compact description of atomic shells suitable for quantitative prediction. For the two largest molecules a less satisfactory optimized "single zeta" representation was used for the atomic component. Atomic components of the basis sets used in these calculations were taken from existing tabulations [4] and [5], and for iodine from atomic variational calculations carried out for this paper. The polarization components have radial dependences with large overlap with the radial part of the basis functions used to describe the atomic valence shells; thus they span the

Table 4. Molecular basis set populations and ground state electronic configurations

Molecule	Number of basis functions[a]			Number of filled shells in ground electronic configuration[b]		
	σ	π	δ	σ	π	δ
H_2	8			1		
FH	14	8		3	1	
ClH	18	10		5	2	
BrH	24	15	7	8	4	1
IH	30	18	9	11	6	2
F_2	20	12		5	2	
ClF	24	14		7	3	
BrF	30	18	10	10	5	1
IF	36	22	12	13	7	2
Cl_2	28	16		9	4	
BrCl	34	20	10	12	6	1
ICl	40	24	12	15	8	2
Br_2	40	24	12	15	8	2
IBr[a]	27	18	11	18	10	3
I_2[a]	30	20	12	21	12	4

[a] All basis sets expect for IBr, I_2 are constructed from the "double zeta + polarization" entries of Table 1. IBr, I_2 basis sets are from "reduced basis" entries of Table 1.

[b] All ground state configurations of these molecules are closed shell.

space of the valence shell motions and are appropriate for describing the valence electronic motions in the molecule. For all atoms in the molecule, except hydrogen, two polarization functions of each atomic symmetry type are used, as shown in Table 1. This reduces the sensitivity of computed results to change in the polarization component of the basis set to a point where exponent optimization is unwarranted. Indeed, two unoptimized functions are generally superior to one single optimized function [6]. For example, all that need be done if two 3*d* polarization functions are included in an atomic basis set in a molecule, is to try two or three exponent pairs with these functions to make sure that valence shell properties are stabilized. This was the procedure adopted in the present calculations, resulting in the two basis sets specified in Table 1, which yield the atomic electronic energies and virial ratios of Table 2, and atomic orbital energies of Table 3. The population of the molecular basis sets constructed from Table 1, broken down into the axial symmetry classes of diatomic molecule are given in Table 4.

2. Population Analysis and Energies

Table 5 lists the results of *Mulliken* population analysis of wave functions described in the previous section, along with total energies of the diatomic molecules. Table 6 lists orbital energies.

The comparable quality of "double zeta + polarization" basis sets for the different halogen atoms can be studied by computing heats of reaction for

Table 5. Internuclear distances R, *Mulliken* gross atomic populations Q, and total energies E_{total}, for the calculations on the diatomic molecules, XY, with basis sets from Table 1 and 4

XY[a]	R[b]	Q(X)[c]	Q(Y)[c]	E_{total}[b]
H_2	1.3891[d]	1.0000	1.0000	− 1.133373
FH	1.6970[d]	9.3188	0.6812	− 100.058005
ClH	2.3641[d]	17.2017	0.7983	− 460.10252
BrH	2.6576[d]	35.2096	0.7904	− 2572.95156
IH	3.04[e]	53.1266	0.8734	− 6918.50434
F_2	2.5276[d]	9.0000	9.0000	− 198.76126
ClF	2.9960[d]	16.6416	9.3584	− 558.90277
BrF	3.2488[d]	34.6227	9.3773	− 2671.77361
IF	3.45[e]	52.4950	9.5050	− 7017.35937
I_2	3.7619[d]	17.0000	17.0000	− 918.99012
BrCl	4.0389[d]	34.9632	17.0368	− 3031.85918
ICl	4.38[e]	52.7403	17.2597	− 7377.43248
Br_2	4.3315[e]	35.0000	35.0000	− 5144.72606
IBr	4.66[e]	52.9286	35.0714	− 9472.44401
I_2	5.04[e]	53.0000	53.0000	−13813.46354

[a] All calculations except IBr, I_2 use "double zeta + polarization" basis sets. IBr, I_2 use reduced basis of Table 1.

[b] Atomic units.

[c] Q(X) is gross atomic population for left hand atom, X, as written in the first column. Y stands for right hand atom.

[d] Computed as minimum in a calculated potential energy curve; the calculation was done at this R value.

[e] Internuclear distance at which the lowest total energy was obtained. The interpolated R value is not given in this table.

formation of the interhalogens from the homopolar diatomics, that is for the following bimolecular gas-phase reaction

$$1/2X_2(g)+1/2Y_2(g)\xrightarrow{\Delta H_0}XY(g). \tag{1}$$

In Eq. (1) the energy ΔH_0 refers to the enthalpy of reaction at 0 °K, and an exothermic reaction has a negative ΔH_0. In terms of dissociation energies, D_0^0, from the zero point vibrational level of the diatomic reactants into separated atoms, ΔH_0 can be expressed as [7]

$$\Delta H_0=1/2D_0^0(X_2)+1/2D_0^0(Y_2)-D_0^0(XY) \tag{2}$$

while in terms of total energies E the expression for ΔH_0, neglecting contributions from rotational and translation energies is:

$$\begin{aligned}\Delta H_0 &= E(XY)-1/2E(X_2)-1/2E(Y_2)\\ &\quad+\tfrac{1}{2}\omega_e(XY)-1/4\omega_e(X_2)-1/4\omega_e(Y_2).\end{aligned} \tag{3}$$

In Eq. (3) $\frac{1}{2}\omega_e$ is the zero point energy for the diatomic molecule. Equation (3) would give exact results if true total energies E and true vibrational quanta ω_e are used. The zero point energy contribution is small enough, so that approximate values ω_e, obtained from computed potential curves, will introduce no error.

Table 6. Molecular orbital energies, ε_J, in atomic units. The symmetric and the antisymmetric orbitals in homonuclear diatomics X_2 are indicated by g and u. Internuclear distances are given in Table 5. Basis sets from Tables 1 and 4

Orbital	H_2	FH	ClH	BrH	IH
1σ	−0.5963g	−26.2683	−104.8380	−490.0439	−1177.1902
2σ		− 1.590	− 10.5637	− 65.1738	− 180.9392
3σ		− 0.7569	− 8.0304	− 58.5283	− 169.6459
4σ			− 1.1118	− 9.8440	− 37.9129
5σ			− 0.6222	− 7.4549	− 33.1033
6σ				− 3.1914	− 24.2657
7σ				− 1.0228	− 7.2257
8σ				− 0.5731	− 5.4604
9σ					− 2.3912
10σ					− 0.8626
11σ					− 0.5248
1π		− 0.6370	− 8.0282	− 58.5272	− 169.6450
2π			− 0.4693	− 7.4484	− 33.1001
3π				− 3.1870	− 24.2645
4π				− 0.4242	− 5.4528
5π					− 2.3859
6π					− 0.3832
1δ				− 3.1787	− 24.2612
2δ					− 2.3766

Orbital	F_2	ClF	BrF	IF
1σ	−26.4206g	−104.9275	−490.1196	−1177.2374
2σ	−26.4203u	− 26.3487	− 65.2467	− 180.9850
3σ	− 1.8057g	− 10.6466	− 58.6023	− 169.6923
4σ	− 1.4761u	− 8.1134	− 26.3131	− 37.9582
5σ	− 0.7801g	− 1.6515	− 9.9155	− 33.1508
6σ		− 1.0979	− 7.5297	− 26.2929
7σ		− 0.7080	− 3.2688	− 24.3136
8σ			− 1.6037	− 7.2708
9σ			− 1.0212	− 5.5101
10σ			− 0.6627	− 2.4445
11σ				− 1.5902
12σ				− 0.8693
13σ				− 0.6346
1π	− 0.8261u	− 8.1094	− 58.5994	− 169.6905
2π	− 0.6498g	− 0.7304	− 7.5168	− 33.1440
3π		− 0.4815	− 3.2614	− 24.3111
4π			− 0.6929	− 5.4948
5π			− 0.4398	− 2.4344
6π				− 0.6805
7π				− 0.3877
1δ			− 3.2439	− 24.3043
2δ				− 2.4153

Table 6 (continued)

Orbital	Cl_2	BrCl	ICl	Br_2	IBr	I_2
1σ	−104.8943*u*	−490.0977	−1177.2309	−490.0849*u*	−1178.0566	−1178.0453*u*
2σ	−104.8943*g*	−104.8777	−180.9791	−490.0849*g*	−491.0908	−1178.0453*g*
3σ	−10.6168*u*	−65.2258	−169.6862	−65.2135*u*	−179.5573	−179.5468*u*
4σ	−10.6167*g*	−58.5809	−104.8620	−65.2135*g*	−170.2574	−179.5451*g*
5σ	−8.0831*g*	−10.6006	−37.9522	−58.5685*g*	−65.2467	−170.2461*u*
6σ	−8.0828*u*	−9.8949	−33.1443	−58.5685*u*	−59.6002	−170.2459*g*
7σ	−1.2141*g*	−8.0668	−24.3068	−9.8825*g*	−37.3884	−37.3762*u*
8σ	−1.0109*u*	−7.5076	−10.5857	−9.8825*u*	−33.4355	−37.3762*g*
9σ	−0.5936*g*	−3.2449	−8.0518	−7.4949*g*	−24.2962	−33.4231*u*
10σ		−1.1570	−7.2643	−7.4948*u*	−9.8320	−33.4231*g*
11σ		−0.9685	−5.5022	−3.2330*g*	−7.7547	−24.2846*g*
12σ		−0.5579	−2.4332	−3.2307*u*	−7.1442	−24.2831*u*
13σ			−1.1121	−1.0920*g*	−5.5954	−7.1319*u*
14σ			−0.8358	−0.9406*u*	−3.1791	−7.1309*g*
15σ			−0.5268	−0.5241*g*	−2.4418	−5.5824*u*
16σ					−0.9816	−5.5806*g*
17σ					−0.7597	−2.4299*g*
18σ					−0.4606	−2.4251*u*
19σ						−0.8485*g*
20σ						−0.7092*u*
21σ						−0.4253*g*
1π	−8.0801*g*	−58.5787	−169.6846	−58.5665*u*	−170.2565	−170.2453*g*
2π	−8.0801*u*	−8.0641	−33.1383	−7.4852*g*	−59.5984	−170.2453*u*
3π	−0.5654*u*	−7.4971	−24.3048	−7.4851*u*	−33.4308	−33.4190*g*
4π	−0.4398*g*	−3.2397	−8.0496	−3.2271*u*	−24.2944	−33.4190*u*
5π		−0.5321	−5.4888	−3.2268*g*	−7.7451	−24.2838*u*
6π		−0.4152	−2.4265	−0.4969*u*	−5.5811	−24.2814*g*
7π			−0.5087	−0.3984*g*	−3.1751	−5.5695*g*
8π			−0.3820		−2.4359	−5.5686*u*
9π					−0.4348	−2.4231*u*
10π					−0.3300	−2.4216*g*
11π						−0.3952*u*
12π						−0.3098*g*
1δ		−3.2255	−24.2988	−3.2139*u*	−24.2901	−24.2792*u*
2δ			−2.4101	−3.2138*g*	−3.1645	−24.7785*g*
3δ					−2.4200	−2.4088*g*
4δ						−2.4086*u*

Use of computed single configuration energies E^{HF} instead of the true energies E will be correct in Eq. (3) if the correlation energies E^{corr}

$$E^{corr} = E^{exact} - E^{HF} \tag{4}$$

are independent of the type of bond in the diatomic molecule. Therefore one might expect that for the diatomic halogen compounds

$$E^{corr}(XY) - 1/2\,E^{corr}(X_2) - 1/2\,E^{corr}(Y_2)$$

is only a very small energy compared to the enthalpy of reaction ΔH_0. *Snyder* [8] has shown that Eq. (3) with computed energies E and frequencies ω_e is a good

Table 7. Dissociation energies D_0^0 for the diatomic XY and enthalpies of reaction, ΔH_0, for $1/2X_2(g) + 1/2Y_2(g) \rightarrow XY(g)$ at 0 °K for heteropolar molecules

Molecule	D_0^0	ΔH_0 (exp)		ΔH_0 (calc)	
XY	(eV)	(eV)	(kcal)	(eV)	(kcal)
H_2	4.476[a]				
FH	5.74[b]	−2.83	−65.3	−2.92	−67.3[c]
ClH	4.43[a]	−0.95	−21.9	−1.04	−24.0
BrH	3.75[a]	−0.53	−12.3	−0.58	−13.4
IH[d]	3.056[a]	−0.05	− 1.2		
F_2	1.34[b]				
ClF	2.616[a]	−0.71	−16.4	−0.72	−16.6
BrF	2.6[a]	−0.95	−21.9	−0.81	−18.7
IF[d]					
Cl_2	2.475[a]				
BrCl	2.26[a]	−0.04	− 0.9	−0.03	− 0.7
ICl[d]	2.152[a]	−0.14	− 3.2		
Br_2	1.971[a]				
IBr[d]	1.817[a]	−0.06	− 1.4		
I_2	1.5417[a]				

[a] See Ref. [12].

[b] Dibeler, V. H., Walker, J. A., McCulloh, K. E.: J. Chem. Phys. **50**, 4230 (1969); **53**, 4414 (1970).

[c] Snyder [8] calculated for ΔH_0 (calc) a value of −72.8 kcal/Mol using a (10,6) basis set of Gaussian functions to represent the orbitals on F and four Gaussians for represent the 1s-functions on H.

[d] As for the molecule I_2 no calculation with the double zeta + polarization basis set of Table 1 was available the ΔH_0 (calc) for the diatomics containing I are not given in this table.

approximation in cases where (a) basis sets used for computed energies of reactants are of comparable quality and (b) reactants are in closed shell ground states so that the number of valence shell electron pairs on both sides of Eq. (1) is constant. This latter condition is certainly met, and therefore agreement between observed heats of reaction and those computed from Eq. (3) using our computed total energies is a measure of basis set quality. Table 7 gives the comparisons for the interhalogens for which "double zeta + polarization" results were available, and the agreement shown is excellent. This means that valence shell properties of all diatomics reported in this paper which used "double zeta + polarization" basis sets are of comparable quality.

3. The Internuclear Distances and Spectroscopic Constants

Several points on the potential curve $E(R)$ of each molecule were calculated at distance separations $\Delta R = 0.2$ atomic units. A parabolic fit to the calculated points nearest the energy minimum yields a calculated minimum R_{calc}, given in Table 8. For the lighter molecules, all except Br_2, IH, IF, ICl, IBr and I_2, a final SCF calculation was carried out at a separation of R_{calc} and results shown in Table 5. For the heavier molecules, listed above, the entries in Table 5 are those for the initially chosen separation which yielded the lowest energy. This separation must be within 0.1 atomic units of R_{calc}.

Table 8. Internuclear separation R_{calc} in Å units interpolated from calculated points on the potential energy curve and vibrational frequencies ω_e in cm^{-1} for the diatomic molecules XY. The experimental internuclear distances R_{exp} as well the observed frequencies ω_e are taken from [14]

XY	Interpolated values		Spectroscopic values	
	R_{calc} (Å)	ω_e (cm^{-1})	R_{exp} (Å)	ω_e (cm^{-1})
H_2	0.7351	4599.8	0.7416	4395.2
FH	0.8980	4493.8	0.9171	4138.52
ClH	1.2510	3661.4	1.2746	2989.74
BrH	1.4063	2775.3	1.413	2649.67
IH	1.61[a]	2462.4	1.604	2309.5
F_2	1.3375	1259.2	1.417	923.1
ClF	1.5854	912.4	1.62813	793.2
BrF	1.7192	769.8	1.7555	671.
IF	1.86[a]	711.1		
Cl_2	1.9907	603.7	1.988	564.9
BrCl	2.1373	481.6	2.138	430.
ICl	2.33[a]	421.07	2.32069	384.18
Br_2	2.29[a]	358.4	2.283	323.2
IBr	2.40[a]	341.9	2.47	268.4
I_2	2.59[a]	289.8	2.666	214.57

[a] Values obtained from the potential energy curve given by 3 or 4 aequidistant points in steps of 0.2 atomic units. These values give the minima of the energy curve only in the case of a parabolic potential.

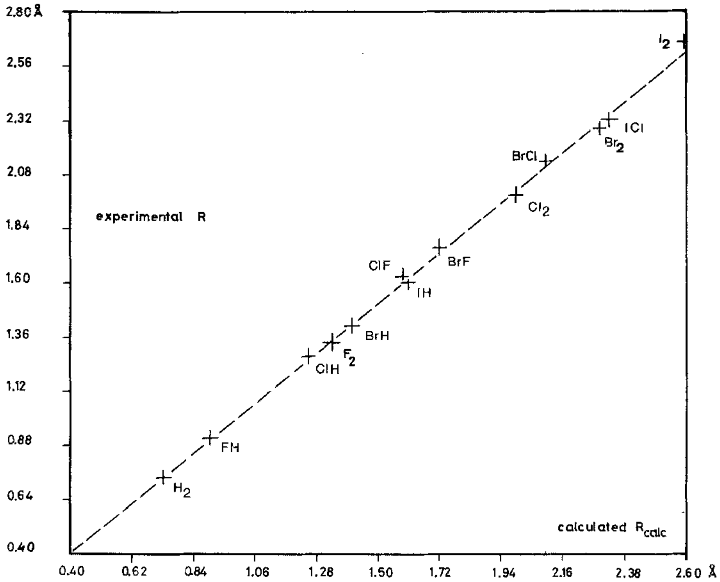

Fig. 1. Internuclear distances R from Table 8 as function of the internuclear distance of the SCF calculation with minimum total electronic energy

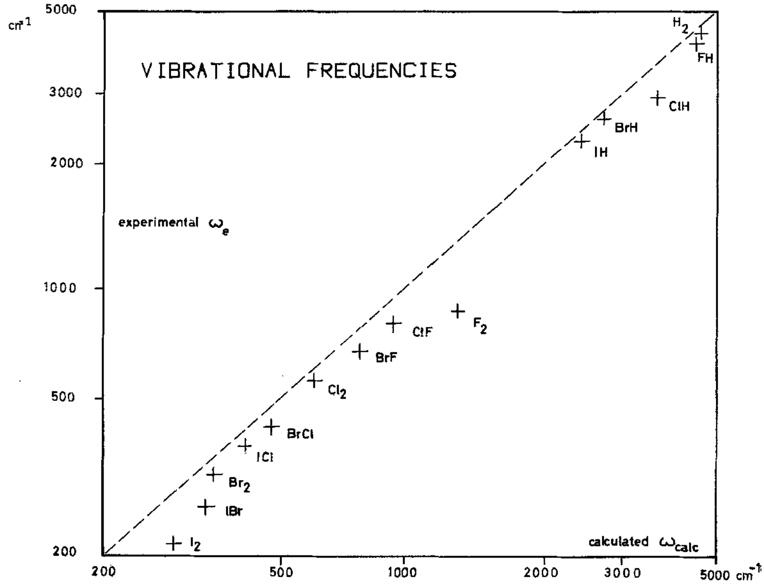

Fig. 2. Vibrational frequencies ω_e from Table 8 as a function of the calculated frequency obtained from the potential energy curve

As the total energy $E(R)$ for the points R close to the internuclear distances R_0 are supposed to fit a parabolic curve, the failure $\Delta E = |E(R) - E(R_0)|$ may be estimated from the curvature of $E(R)$. The absolute value of ΔE for the diatomics IH, IF, ICl, IBr, I_2 and Br_2 are calculated for $R\_R_0 = 0.1$ a.u. to 0.2, 0.36, 0.50, 0.29, 0.4 and 0.32 kcal/mol showing that the failure ΔE from the minimal energy must be less than 0.5 kcal/mol.

Interpolated values R_{calc} from the parabolic fit can be compared with the experimental values R_{exp} and show a satisfactory agreement (Fig. 1). The deviations in the cases of I_2 and IBr can be explained by the use of the reduced basis set which is not sufficient for the prediction of equilibrium separations. Force constants and vibrational frequencies ω_e are obtained from the curvature of $E(R)$ for $R = R_{\text{calc}}$. The calculated frequencies ω_{calc} are presented in Table 8 and compared with experiment in Fig. 2. It is obvious that all calculated frequencies are larger than the corresponding spectroscopic vibrational frequencies ω_e, indicating that the true energy curvature $E(R)$ must be flatter at the equilibrium position $R = R_{\text{calc}}$. This behaviour of $E(R)$ of a diatomic molecule is typical for a single configuration SCF calculation for large internuclear separations $R \gg R_{\text{calc}}$ where the wavefunction has a large ionic component. The simplest well known example of this property was carefully discussed [9] by using two configurations to represent the ground state wavefunction of H_2. Again the failure of the points refering to IBr and I_2 is explained by the insufficient basis set used for the inner shells of these compounds.

The value of ω_{calc} for F_2 is significantly out of the general trend. In fact, the calculated total electronic energy E_{total} of the bound state F_2 is larger than the

Table 9. Orbital energies ε_J of the highest occupied molecular orbital in eV and averaged vertical ionization potentials $\bar{I}_J$

XY	Calculated orbital energies			Vertical ionization potentials		
	$\varepsilon_m(\pi)^a$	$\varepsilon_{m-1}(\pi)^a$	$\varepsilon_n(\sigma)^a$	$\bar{I}_1(^2\Pi)^b$	$\bar{I}_2(^2\Pi)^b$	$I_1(^2\Sigma)^b$
H_2			−16.22			15.45
FH	−17.33		−20.60	16.27		
ClH	−12.77		−16.93	12.80		16.28
BrH	−11.54		−15.59	11.87		15.31
IH	−10.43		−14.28	10.75		14.03
F_2	−17.68	−22.47	−21.23	15.63	17.35	18.46
Cl_2	−11.87	−15.39	−16.15	11.50	14.11	15.94
Br_2	−10.84	−13.52	−14.26	10.70	12.52	14.44
I_2	− 8.43	−10.75	−11.57	9.64	11.28	12.79
ICl	−10.39	−13.84		10.55	12.16	
IBr	− 8.98	−11.83		10.23	11.64	

[a] The highest molecular orbital energies $\varepsilon_m(\pi)$, $\varepsilon_{m-1}(\pi)$, $\varepsilon_n(\sigma)$ for each molecule XY are taken from Table 6.

[b] The lowest three observed ionization potentials $\bar{I}_1(^2\pi)$, $\bar{I}_2(^2\pi)$, $I_1(^2\pi)$ are characterized by the assigned symmetry of the wavefunction of the ionic state. The experimental values are taken from Ref. [15].

Table 10. Expectation values for one electron operators. These values have been obtained by numerical integration over the charge distribution of the wavefunction ψ. All values are given in atomic units. The indices of the operators in the first row refer to the origin of the coordinate system on the nuclei X, Y. M represents the center of mass of the molecule XY

XY	r_X^{-1}	r_Y^{-1}	z_M	z_M^2	$x_M^2+y_M^2$	z_X/r_X^3	z_Y/r_Y^3	$\frac{3z_X^2-r_X^2}{2r_X^5}$	$\frac{3z_Y^2-r_Y^2}{2r_Y^5}$
H_2	1.8226	1.8226	0.0000	2.0163	3.0372	0.5170	−0.5170	0.1869	0.1869
FH	23.1232	6.2606	0.1217	5.1085	8.0307	0.2874	−3.1199	−1.2128	1.5214
ClH	65.9588	8.1616	0.7488	12.9373	20.2304	0.1546	−3.0362	−1.7609	1.1202
BrH	176.2174	14.1387	1.0988	18.4501	28.6752	0.1294	−4.9572	−3.7388	1.7446
IH	311.2302	18.4132	1.4881	28.2339	44.5645	0.0937	−5.7420	−5.2086	1.7982
F_2	30.0351	30.0351	0.0000	35.2508	13.8330	1.3544	−1.3544	−2.7312	−2.7312
ClF	67.3063	32.2059	0.1405	64.6095	25.4748	0.9553	−1.8437	−3.6747	−1.4567
BrF	178.5188	37.3351	2.3485	91.9727	33.6841	0.8369	−3.2689	−7.3590	−0.8611
IF	312.7297	41.9525	3.7669	115.6932	49.1899	0.7299	−4.4091	−9.5417	−0.0714
Cl_2	68.8755	68.8755	0.0000	136.4851	37.4108	1.1644	−1.1644	−2.7725	−2.7725
BrCl	180.0122	73.0200	4.3485	207.2491	45.7712	1.0247	−2.1128	−5.9501	−2.2861
ICl									
Br_2	183.8979	183.8979	0.0000	351.9080	54.2567	1.8498	−1.8498	−5.3206	−5.3206
IBr	316.2375	184.0139	4.9030	487.8166	66.3538	1.5952	−2.4057	−4.2409	−2.1206
I_2	319.2882	319.2882	0.0000	709.5897	81.2378	2.0723	−2.0723	−3.5452	−3.5452

calculated total energy of the two atoms F in their lowest electronic states. This discrepancy of the theory with the experimental dissociation energy is an artefact of the single determinant approximation of the SCF theory, in which the correlation energy of F_2 is assumed to be larger than in the open shell system of two independent fluorine atoms.

Table 11. Properties of the ground state configuration of the molecule XY

XY	Calculated				Experimental			
	DM^a	Θ^b	$q_X{}^c$	$q_Y{}^c$	DM^a	Θ^b	$e^2Qq_X{}^d$	$e^2Qq_Y{}^d$
H_2	0.0	0.628	0.3724	0.3724				
FH	−1.829	2.111	2.8348	0.6404	1.8195[h]	2.34[f]		
ClH	−1.114	3.409	3.6732	0.3328	1.12[i]	3.84[f]	− 53.0	
BrH	−0.931	3.784	7.5842	0.2401	0.834[k]		535.44	
IH	−0.654	4.271	10.4884	0.1766	0.445[i]		−1831.07	
F_2	0.0	0.558	6.5771	6.5771	0.881[l]			
ClF	0.901	1.278	8.0187	4.1777	1.20[l]	1.35[g]	− 146.0	
BrF	1.440	0.677	15.2429	3.7636		0.91[g]	1089.0	
IF	1.448	0.860	19.5217	2.7242				
Cl_2	0.0	3.378	6.1836	6.1836			− 108.95	− 108.95
BrCl	0.588	3.520	12.4162	5.6347	0.57[l]		876.8	− 103.6
ICl					0.65[l]		−2944.0	− 82.50
Br_2	0.0	4.779	11.5026	11.5026			765.86	765.86
IBr[e]	0.645	4.520	9.1735	5.2887	1.26[l]		−2731.0	722.0
I_2[e]	0.0	5.611	7.9184	7.9184			−2156.0	−2156.0

[a] *DM* is the dipolmoment of the charge distribution in the molecule XY in the Debye units. Computed polarity is X^+Y^-.

[b] Θ is the quadrupolement of the charge distribution in the molecule given 10^{-6} esu · cm^2.

[c] q_X, q_Y are the calculated electrostatic field gradients on the nuclei in the molecule XY. The field gradients are given in atomic units.

[d] e^2Qq_X, e^2Qq_Y are experimental nuclear quadrupole coupling constants in Mc/sec taken from [14]. These constants refer to the isotopic nuclei of Cl^{35}, Br^{79}, and J^{127}.

[e] The ground state properties of JBr and J_2 are calculated from the reduced basis set wavefunction of Table 4.

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The molecular wave function ψ^{SCF} determined from the SCF-MO calculations was used to calculate the multipole moments of the charge distribution and the electrostatic field gradients q_X and q_Y along the z-axis at the nuclei of the atoms X and Y in the molecule XY. These values were obtained by numerical integration over the charge distribution in the molecule XY with the appropriate one electron operator. The expectation values of these operators are given in Table 10. The lower indices X, Y, M of these operators refer to the origin of the coordinate system, which may be chosen on the nuclei of X or Y or at the center of mass M of the diatomic molecule XY. Using the expectation values of Table 10 the multipole moments and the field gradients on the nuclei may be obtained by adding the charges of the nuclei of X and Y to the charge distribution of the electronic wave function. The resulting expectation values are given in Table 11.

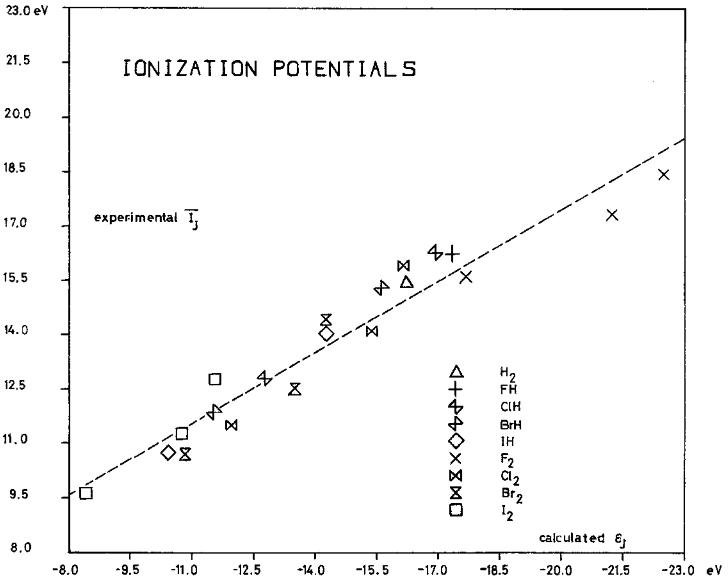

Fig. 3. Vertical ionization potentials $\bar{I}_J$ from Table 9 as function of the calculated orbital energy. The dashed line corresponds to the best linear fit of Eq. (5)

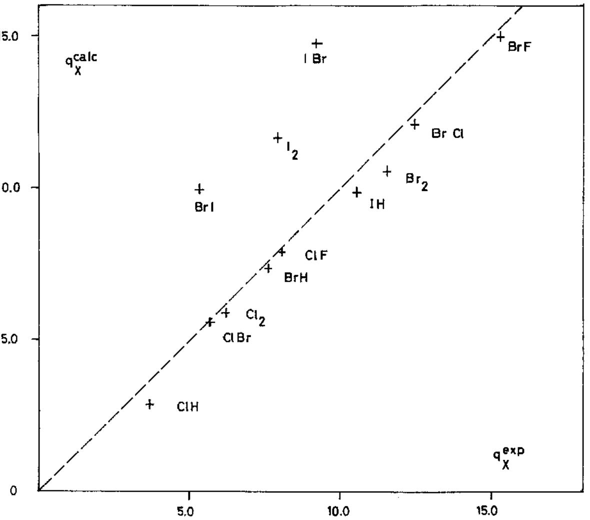

Fig. 4. Calculated electric-field gradients q_X^{calc} of Table 11 for the diatomic molecules XY are plotted against q_X^{exp} obtained from the nuclear coupling constants e^2qQ_X of Table 11 and the nuclear quadrupole moments Q_X for the isotopes X = ^{35}Cl, ^{79}Br or ^{127}I of Table 12

The quadrupole moments in the heteronuclear compounds with non vanishing dipole moments are given for the center of mass of these molecules.

The experimental nuclear quadrupole coupling constants e^2Qq_X and e^2Qq_Y for the diatomic molecules XY containing the isotopes ^{35}Cl, ^{79}Br or ^{127}I are

Table 12. Nuclear quadrupole moments Q and $\hat{Q}$ for the isotope nuclei ^{35}Cl, ^{79}Br and ^{127}I in 10^{-24} cm^2

	$Q^a * 10^{24}$	$\hat{Q}^b * 10^{24}$
^{35}Cl	-0.079	-0.073 ± 0.0079
^{79}Br	0.31	0.297 ± 0.0093^c
^{127}I	-0.79	-0.74^c

[a] Averaged quadrupole moments form different experimentalists by Fuller, G., Cohen, V. W.: Nuclear Data A5, 433 (1969).

[b] $\hat{Q}$ are nuclear qudrupole moments obtained from the calculated field gradients and the experimental coupling constants of Table 10. The standard deviation is obtained from 4 values.

[c] The calculations for IBr and I_2 with the reduced basis set of Table 4 are not considered in these results.

given in Table 11. From these constants we may compute experimental field gradients q_X^{exp}, q_Y^{exp} by dividing the coupling constants by the corresponding nuclear quadrupole moment of Table 12 and a constant factor of 234.97 Mc/cm^2. Figure 4 shows a comparison of the calculated field gradients q_X^{calc} of Table 11 with the experimental field gradients q_X^{exp}. The three points obtained from the calculations of IBr and I_2 clearly do not follow the general trend which proves that the reduced basis of Table 4 cannot be used safely to predict nuclear quadrupole coupling constants.

If we trust the calculated field gradients one may also estimate the nuclear quadrupole moments from the experimental coupling constants of Table 11 and the calculated field gradients. Table 12 shows the averaged nuclear quadrupole moments $\hat{Q}$ obtained by these calculations for the three isotopes ^{35}Cl, ^{79}Br and ^{127}I. As we do not believe that the reduced basis set of Table 4 for the two molecules IBr and I_2 is sufficient for computation of field gradients, these calculations are not taken into account for the $\hat{Q}$ values of Table 12.

We also computed the residual electrostatic forces on the nuclei in the molecule XY. These forces ideally should be zero if the nuclei are in their equilibrium positions. The numerical calculations show that these forces can be quite large (1.16 atomic units in Cl_2) which is probably due to the insufficient basis set for describing the polarization of the inner shell electrons. The magnetic susceptibilities, the rotational magnetic g factors as well as the electrostatic polarizabilities of the diatomic molecules may easily be compiled by using Table 10.

4. The Ionization Potentials

Using *Koopmans'* theorem [10] the ionization potentials I_J of the diatomic compounds XY should be equal to the negative *Hartree Fock* energies ε_J of the orbitals ϕ_J (Table 9). The vertical ionization potentials I_J are known from photo ionization and photo electron spectroscopy [11] for energies $I_J < 21$ eV. For the linear molecules XY containing Cl, Br or I there is a significant splitting of the doublet ionic state $^2\Pi$ which has a non vanishing total angular momentum 3/2. This splitting can be interpreted by the coupling of the orbital angular momentum associated with the wavefunction $\psi(XY^+)$ and the corresponding spin momentum of the unpaired electron. Because spin orbit coupling leads to a symmetric splitting of the two ionic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ with angular momentum 1/2 and 3/2 the arithmetic mean $\overline{I_J}$ of the two experimental vertical ionization potentials $I_{1/2}$ and $I_{3/2}$ is given in Table 9 for the known halogen hydrides, the diatomic halides and some interhalogens. Figure 3 shows a plot of the averaged vertical ionization potentials I_J taken from Table 9 to their correspondant calculated orbital energies ε_J. The regression line for these points:

$$I_J = -m\varepsilon_J + \text{const} \tag{5}$$

has a gradient $m = 0.66 \pm 0.04$ and intersects the $\overline{I_J}$-axis at a positive value (const = 4,3 eV). According to (5) *Koopmans*' theorem happens to be correct for orbital energies $\varepsilon_J \sim -10$ eV. The higher ionization potentials are predicted at larger values than the experimental ones. Similar behaviour of the theoretical *Koopmans*' theorem was observed in semi empirical calculations on organic compounds [13].

5. Conclusions

The SCFMO wavefunctions for the diatomic molecules XY with X, Y = H, F, Cl, Br, I can be used to obtain satisfactory expectation values for quantities describing the ground state of these molecules. All calculations performed on these molecules are close to the *Hartree Fock* limit of SCF-MO calculations with exception of those for the two molecules IBr and I_2 where a strongly restricted basis set was used. The high accuracy obtained for some of the properties of these molecules is clearly shown. Deviation from experimental constants are either inherent in the simple SCF model or due to numerical difficulties such as in the case of IBr and I_2.

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