Compact Contracted Gaussian-Type Basis Sets for Halogen Atoms. Basis-Set Superposition Effects on Molecular Properties.

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Compact, contracted Gaussian basis sets for halogen atoms are generated and tested in *ab initio* molecular calculations. These basis sets have similar structure to that of Huzinaga and co-workers' (HTS) sets; however, they give both better atomic total energies and better properties of atomic valence orbitals. These sets, after splitting of valence orbitals and augmenting with polarization functions, provide molecular results that agree well with those given by extended calculations. Basis set superposition error (BSSE) is calculated using the counterpoise method. BSSE has only slight influence on calculated equilibrium geometry, shape of potential curve, and electric properties (dipole and quadrupole moments) of molecules. However, atomization energies may be significantly changed by the BSSE.

I. INTRODUCTION

A variety of compact, contracted Gaussian-type (CGTO) basis sets have been prepared for Li through Cd[1-4] by Huzinaga and co-workers (HTS). Their method guarantees that an appropriate number of Gaussian functions is used for description of outer atomic orbitals, unlike those in uncontracted Gaussian basis sets where most functions tend to be spent for the innermost orbitals. Therefore properties of valence atomic orbitals obtained in the HTS method are close to those produced by more extended sets like Slater-type-orbital double-zeta (STO-DZ) functions. This feature remains valid even for smallest HTS basis set (MINI-1), although the total energy of an atom for that set is worse than the energy obtained by using a Slater-type-orbital single-zeta (STO-SZ) set.

The HTS MINI and MIDI basis sets have been recently compared[1,4,5] with widely used STO-3G and split valence basis sets (44-31G, 3-21G*) of Pople et al. Since in the bases of Pople et al. the constraint of identical exponents within each shell is imposed, these basis sets require less computer time for integral evaluation than the HTS basis sets. The equilibrium structures and spectroscopic constants produced by MIDI* and 3-21G* sets are of similar quality.[5] However, the

MIDI*-type sets reproduce better near Hartree–Fock (HF) atomization energies and especially orbital energies.[1,3,4]

In the present work we have examined HTS basis sets using least-squares fitting technique,[6] and we have found new basis sets that have better atomic total energies and properties of atomic valence orbitals. The structure of the newly prepared sets is similar to that of HTS sets, but the number of Gaussians may be smaller, e.g., one of our basis sets (called here M2) for heavier atoms has smaller number of Gaussians than MINI-1 does; however, it produces considerably better atomic energy than the energy obtained with STO-SZ basis.

The aim of this article is to present new basis sets for halogen atoms (up to I) and to test their usefulness in self-consistent-field (SCF) molecular calculations.[†] For halogen atoms our new basis sets differ most from the previously published MINI-1 and MINI-4 sets. On the other hand, halogen molecules seem to be a severe test for our close-to-minimal basis sets since the halogen atoms have almost completely filled atomic shells.

Total energies, atomization energies, equilibrium geometries, vibrational frequencies, and the multipole moments are calculated using two kinds of minimal (M2, M4), split valence (SV2,

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[†] Basis sets for other atoms (up to Rn) prepared according to the method presented here will be published in book form by Elsevier in 1984.

SV4), and split valence plus one (SV2P, SV4P) or two (SV2PP, SV4PP) polarization functions.

Whenever small basis sets are used, the basis set superposition error (BSSE) may influence the calculated results. In the case of interactions between open shell atoms, which result in formation of chemical bond, only few attempts were made[1,7,8] to elucidate that problem. The role of BSSE in the case of intermolecular weak interactions is already well-established.[9,10]

In the present article, systematic studies of the BSSE given by the basis sets presented here are performed using the counterpoise (CP) method.[11]

II. ATOMIC WAVE FUNCTIONS

A. Method of Basis-Set Preparation

In the minimal basis sets, the radial functions of the atomic orbitals are expressed as[1-3]

$$R_{ns}(r) = \sum_{i=1}^{N_s} C_{ns,i} s_i(r)$$

$$R_{np}(r) = \sum_{i=1}^{N_p} C_{np,i} p_i(r) \qquad (1)$$

$$R_{nd}(r) = \sum_{i=1}^{N_d} C_{nd,i} d_i(r)$$

where N_s, N_p, N_d denote the number of s-, p-, d-type atomic orbitals. The contracted functions (CGTO) $s_i(r)$, $p_i(r)$, $d_i(r)$ are composed of primitive, normalized $1s$-type (g_{s_i}), $2p$-type (g_{p_i}), and $3d$-type (g_{d_i}) Gaussian functions (GTO), respectively:

$$s_i(r) = \sum_{k=1}^{k_{s_i}} d_{s_i,k} g_{s_i}(\alpha_{s_i,k}, r)$$

$$p_i(r) = \sum_{k=1}^{k_{p_i}} d_{p_i,k} g_{p_i}(\alpha_{p_i,k}, r) \qquad (2)$$

$$d_i(r) = \sum_{k=1}^{k_{d_i}} d_{d_i,k} g_{d_i}(\alpha_{d_i,k}, r)$$

The following shorthand notation will be used to denote the basis sets (see Table I):

$$\left(k_{s_1}, k_{s_2} \cdots / k_{p_1}, k_{p_2} \cdots / k_{d_1} \cdots \right)$$

The optimization procedure consists of two steps. In the first step, the t_i ($t = s, p, d$) CGTOs are obtained using least-squares fitting technique.[6] In that method an analytical representation $F_{nl}(r_i; p)$ of the numerical Hartree–Fock (NHF) radial function $R_{nl}^{NHF}(r_i)$ is found by minimizing the sum of deviations:

$$\sigma = \sum_{i=1}^{N} r_i^2 \left[F_{nl}(r_i; p) - R_{nl}^{NHF}(r_i) \right]^2 \qquad (3)$$

where p denotes both linear and exponential parameters. This step provides the initial estimates of the basis-set parameters.

In the second step, all the parameters are changed so as to give the minimal atomic energy according to the HTS method.[12,13]

In the first step, particular attention has been paid to obtaining good representation of the valence orbitals. The details of the procedure are explained in Table II for the case of bromine.

It is seen that for M4 basis, the set no. 3 should be taken to give (4333/433/4) basis set. Similarly, the set no. 5 can serve as M2, (4322/422/3) basis set. The sets no. 1 and 7 from Table II produce MINI-4 and MINI-1,[3] respectively, accord-

Table I. Shorthand description for minimal (M) and split valence (SV) contracted Gaussian basis sets for halogen atoms.[a]

Basis set	F	Cl	Br	I
M2	(42/3)	(432/42)	(4322/422/3)	(43222/4222/42)
SV2	(411/21)	(4311/411)	(43211/4211/3)	(432211/42211/42)
M4	(43/4)	(433/43)	(4333/433/4)	(43333/4333/43)
SV4	(421/31)	(4321/421)	(43321/4321/4)	(433321/43321/43)

[a]The numbers in parentheses represent the expansion terms of each contracted Gaussian-type orbital. A slash separates the different symmetries.

Table II. The root mean square deviations $\delta = \sqrt{\sigma/N}\,(\times 10^3)$ for valence orbitals of $Br(^2P)$ for various patterns of s and p part of minimal basis functions. The total energy TE (in a.u.) and orbital energies ε (in a.u.) obtained after the second step of optimization of given patterns are also shown.

set:[a] s	p	d	δ_{4s}	δ_{4p}	TE	ε_{4s}	ε_{4p}
1	(4333)[b]	(433)	(4)	1.2	4.5	-2570.0301	-0.9831	-0.4496
2	(4333)	(433)	(4)	1.2	2.1	-2570.0351	-0.9866	-0.4535
3	(4333)	(433)	(4)	1.2	1.6	-2570.0691	-0.9881	-0.4542
4	(4322)	(422)	(3)	9.9	5.6	-2568.9626	-0.9660	-0.4394
5	(4322)	(422)	(3)	4.3	5.6	-2568.9688	-0.9729	-0.4461
6	(4322)	(422)	(3)	7.2	5.6	-2568.8918	-0.9659	-0.4472
7	(3333)	(333)	(3)	1.2	4.5	-2562.1269	-0.9759	-0.4465

[a](4333) and (422) patterns are unstable in least squares fitting technique.

[b]The N symbol indicates that this CGTO is interconnected with the previous one; i.e., the first GTO in this CGTO has exponent larger than the smallest one of previous CGTO, and the first coefficient d (e.g., 2) has opposite sign to the remaining one(s) in this CGTO.

ing to the HTS nomenclature. The MINI-4 set differs from presently introduced M4 in p part only, but the latter one gives lower total energy and better valence orbital energies for both $4p$ and $4s$ orbitals. The MINI-1 set can be compared with our M2 set with respect to quality of va-

lence orbitals; however, M2 has far better total energy and is more economical in applications since it contains smaller number of GTOs.

The orbital exponents α_k and contraction coefficients d_k of the CGTOs for M2 and M4 sets of Cl, Br, and I are presented in Table III.

Table III. Exponents (α_k) and expansion coefficients (d_k) for M2 and M4 sets of chlorine, bromine, and iodine.[a] Exponents of one (P) and two (PP) polarization functions are enclosed in braces.

Cl   M4   (433/43)

ORB SYM	s_1	s_2	s_3	p_1	p_2
α_1	3956.9449	54.204785	3.3569590	135.73073	1.0435196
α_2	597.04304	5.5388018	.47131854	31.266981	.12718497
α_3	135.00230	2.1607950	.17079619	9.2933166	.37377535
α_4	36.118053			2.9555541	
d_1	0.0181683	-.0984629	0.1910550	0.0329938	0.2717692
d_2	0.1265480	0.6052887	-.6944812	0.1987182	0.3191056
d_3	0.4494831	0.4663727	-.4235268	0.5079065	0.5513821
d_4	0.5419488			0.4513245	

P = {0.514}   PP = {0.220, 0.797}

Cl   M2   (432/42)

ORB SYM	s_1	s_2	s_3	p_1	p_2
α_1	3933.9590	54.082124	.42711768	134.74118	.77426997
α_2	593.95377	5.4690537	.15202345	31.050769	.20956838
α_3	134.46574	2.2047612		9.2285701	
α_4	36.014945			2.9388546	
d_1	0.0182938	-.0979813	0.7201012	0.0333393	0.4788181
d_2	0.1271767	0.6078227	0.3192423	0.2002516	0.6342001
d_3	0.4503559	0.4610292		0.5090444	
d_4	0.5404361			0.4485645	

P = {0.511}   PP = {0.248, 0.839}

Table III. (continued)

Br   M4   (4333/433/4)

ORB SYM	s_1	s_2	s_3	s_4
α_1	17914.012	247.33791	21.472689	2.3397075
α_2	2700.8820	27.825882	3.6072844	.38832539
α_3	612.63764	11.692350	1.5510670	.14562498
α_4	165.04835			
d_1	0.0170373	-.1103867	-.2389743	-.2266599
d_2	0.1195879	0.6460753	0.7433529	0.7202304
d_3	0.4370146	0.4264025	0.3921021	0.4183848
d_4	0.5587696			

ORB SYM	p_1	p_2	p_3	d_1
α_1	769.88290	8.6662920	.62509542	61.699454
α_2	180.60286	3.4372753	.23852551	17.176489
α_3	56.012187	1.4102279	.08924869	5.5706174
α_4	19.108991			1.7383942
d_1	0.0270082	0.3301375	0.3662229	0.0584980
d_2	0.1771929	0.5621199	0.5323300	0.2795209
d_3	0.5034818	0.2118896	0.2245335	0.5311305
d_4	0.4607090			0.4006201

P = {0.389}   PP = {0.162, 0.548}

Br   M2   (4322/422/3)

ORB SYM	s_1	s_2	s_3	s_4
α_1	17840.505	248.00953	23.708456	.32003940
α_2	2691.2016	27.526132	2.7585310	.11588670
α_3	611.13589	11.715350		
α_4	164.90248			
d_1	0.0171207	-.1098522	0.2265015	0.7758375
d_2	0.1200286	0.6547674	-1.088207	0.2574600
d_3	0.4373105	0.4162174		
d_4	0.5579592			

Table III. (*continued*)

ORB SYM	P_1	P_2	P_3	d_1
α_1	758.27698	7.3705425	.15503558	34.040909
α_2	178.02877	2.4432082	.51810540	8.9190786
α_3	55.250877			2.4312513
α_4	18.832923			
d_1	0.0276604	0.4764098	0.5890892	0.1492732
d_2	0.1801918	0.6082355	0.5110602	0.5112273
d_3	0.5076756			0.5768366
d_4	0.4537059			

$$P = \{0.384\} \quad PP = \{0.176, 0.562\}$$

I   M4   (43333/4333/43)

ORB SYM	s_1	s_2	s_3	s_4	s_5
α_1	42297.957	582.20124	54.589064	8.8441340	1.5207770
α_2	6375.1354	67.838092	10.070202	2.0968138	.27302449
α_3	1447.6218	29.640666	4.5676679	.98611692	.10795603
α_4	390.94964				
d_1	0.0165457	-.1144000	-.2773274	0.3569170	0.2698431
d_2	0.1164656	0.6457644	0.8671635	-.8254301	-.7625119
d_3	0.4309597	0.4265016	0.2890370	-.3901444	-.3948624
d_4	0.5667813				

ORB SYM	P_1	P_2	P_3	P_4	d_1	d_2
α_1	1997.5692	158.66544	3.5785818	.41515416	238.44881	5.9337495
α_2	470.17426	21.085556	1.6034530	.17098833	69.545921	2.2186322
α_3	147.12001	8.3903226	.70343694	.06856211	24.677895	.80937642
α_4	51.632190				9.0881485	
d_1	0.0239358	-.0253934	0.4341764	0.3908686	0.0382347	0.2777183
d_2	0.1641003	0.4791351	0.5290721	0.5190582	0.2205252	0.5733560
d_3	0.4915455	0.5879478	0.1113815	0.1955209	0.5210939	0.3207317
d_4	0.4795349				0.4279063	

$$P = \{0.266\} \quad PP = \{0.105, 0.334\}$$

In the case of fluorine, the M4 set is exactly the same as MINI-4 set, already published in ref. 1. For M2 set of F, we have found poor description of $2s$ orbital, and therefore we do not recommend such a small basis set for fluorine. Comparison of the M4 and MINI-4 sets for Cl and Br clearly shows that essential difference between the two kinds of sets arises from description of p-type orbitals. The M4 sets contain, in valence orbitals, p-type GTOs with exponents smaller than in MINI-4 sets.

The split valence (SV) sets are derived from minimal sets by splitting the outer s- and p-type CGTOs. Next, they are augmented with polarization functions composed of one or two d-type GTOs. The exponents and coefficients of the polarization function are determined by maxi-mizing the overlap[1] defined as

$$\text{OVLP} = \left\langle n_{vs} R_{ns} + n_{vp} R_{np} \middle| \sum_{i=1}^{M} d_i g_{d_i} \right\rangle \middle/ (n_{vs} + n_{vp}) \quad (4)$$

$n_{vs} = 2$, $n_{vp} = 5$, and $M = 1$ or 2, where polarization function is assumed to be normalized, and R_{ns}, R_{np} (e.g., 1) are outer shell radial functions. In molecular calculations we always use uncontracted polarization functions, and therefore only exponents of g_{d_i} are given in Table III.

The values of OVLP for one (two) polarization functions are equal to 0.91 (0.98) for F atom, 0.94 (0.97) for Cl, 0.94 (0.96) for Br, and 0.94 (0.95) for I. It is seen that when replacing one polariza-tion

Table III. (*continued*)

I   M2   (43222/4222/42)

ORB SYM	s_1	s_2	s_3	s_4	s_5
α_1	42266.826	582.86273	57.250293	10.483810	.25202067
α_2	6368.9032	67.149142	8.7070787	1.6008452	.10179444
α_3	1446.3305	29.525350			
α_4	390.81324				
d_1	0.0165616	-.1139990	0.2693426	-.2990509	-.7005152
d_2	0.1166092	0.6562478	-1.124697	1.1356832	-.3311117
d_3	0.4310917	0.4150787			
d_4	0.5664940				

ORB SYM	p_1	p_2	p_3	p_4	d_1	d_2
α_1	1992.3665	21.768159	3.2832108	.36083912	231.32048	4.3190775
α_2	468.56379	8.4911166	1.2925537	.11611492	67.568313	1.3136428
α_3	146.91838				23.975172	
α_4	51.246483				8.7532774	
d_1	0.0241407	0.4703671	0.5423730	0.5234426	0.0403619	0.4897892
d_2	0.1643372	0.5930526	0.5207944	0.5666575	0.2275587	0.6409330
d_3	0.4926577				0.5293632	
d_4	0.4788374				0.4133308	

P = {0.262}   PP = {0.117, 0.341}

[a] The M4 sets for F and H are given in ref. 1 as MINI-4 and MINI-3 sets, respectively: for F atom, P = {1.496} and PP = {0.682, 3.559}; for H atom, P = {0.479} and PP = {0.259, 1.814}.

function by two of them, the largest improvement in matching valence s, p part of the atomic function occurs for fluorine. This suggests that molecular results obtained using SVP and SVPP sets for F may differ from each other more than those obtained for other atoms.

B. TOTAL ATOMIC ENERGIES

The total energies (TE) of the Mi ($i = 2, 4$) and SVi ($i = 2, 4$) sets are given in Table IV together with those of STO-SZ, STO-DZ and previously published MINI-i basis sets.[1-3]

As we already pointed out, the Mi sets have always better TE than both STO-SZ and the corresponding MINI-i sets. The relative differences between TE of MINI-1 and MINI-4 sets are equal to $\sim 0.4\%$ and reflect difference in description of inner region by 3 and 4 GTOs, respectively. For F and Br the differences between M2 and M4 sets are equal to 0.2 and 0.04%, respectively. They are mostly due to different representation of $2p$ (in F) and $3d$ (in Br) orbitals by the two basis sets. For Cl and I the different description of valence orbitals results in much smaller ($\sim 0.01\%$) distinction between M2 and M4 sets.

In our molecular SCF calculations, the six-membered d-type GTO set is used, which contains

one $3s$-type function in addition to five genuine d-type functions. Therefore whenever we use the d-type function in molecular calculations we should know atomic energies corrected by the additional $3s$ function. These reference atomic energies are given in Table IV.

It can be seen (Table IV) that the $3s$ effect is more important for the smaller B2 set than for the B4 set. For sets of F and Cl the second polarization function changes the TE more than the first one, since, being more compact, it contributes more to the inner atomic orbitals (mostly $1s$). In the case of Br and I the polarization functions cause not only the $3s$ effect but also improve original atomic d-type orbitals. The orbital energy of the $3d$ (for Br) and the $4d$ (for I) orbital for SV2P set changes about 4.4 and 3.0%, respectively, in comparison with SV2 set. In the case of SV4P and SV4 sets the valence d-orbital energies are lowered by 2.0 and 0.6%, respectively.

This indicates that description of $3d$ shell of Br by only 3 GTOs and $4d$ shell of I by 2 GTOs, desirable from computational point of view, is rather poor. Fortunately, d orbitals of both Br and I belong to the inner shell of the atom, which we believe play minor role in formation of molecules considered here. However, for the first

Table IV. Total energies (in a.u.) of the B2, B4, MINI, STO-SZ, and STO-DZ sets.[a]

Atom\ $^{-TE}$	M2	M4	MINI-1	MINI-4	STO SZ	STO DZ
F	99.07454	99.25567	98.77655	99.25567	98.94211	99.40131
Cl	458.92873	458.96279	457.25788	458.94611	458.52369	459.47960
Br	2568.9688 (2568.9951)	2570.0691 (2570.0758)	2562.1269	2570.0301	2565.1131	2572.3415
I	6912.2930 (6912.4510)	6912.8649 (6913.0062)	–	–	6905.9462	6917.9602

Atom\ $^{-TE}$	SV2	SV2P	SV2PP	SV4	SV4P	SV4PP
F	–	–	–	99.26408	(99.26449)	(99.27161)
Cl	458.94161	(458.95078)	(458.96405)	458.97489	(458.98320)	(458.99218)
Br	(2569.0249)	(2569.2063)	(2569.2748)	(2570.0804)	(2570.1217)	(2570.1381)
I	(6912.4678)	(6912.5826)	(6912.5924)	(6913.0174)	(6913.0397)	(6913.0527)

[a]Total energy corrected by additional $3s$ function is given in parentheses. For convenience, set of the M2, SV2, SV2P, SV2PP (M4, SV4, SV4P, SV4PP) bases will be called B2(B4) set.

transition metal atoms one should use at least 5 GTOs for description of the $3d$ orbital.[14] The fact that the B2 set seems to be rather unsaturated suggests that BSSE for that set will be of great importance.

C. ORBITAL ENERGIES

The essential feature of HTS[12,13] method of basis set optimization is that the good quality of valence orbitals obtained in the least-squares fitting of the NHF functions deteriorates only slightly during energy optimization. The errors defined as

$$\text{Error} = (\epsilon_{NHF} - \epsilon_i)/\epsilon_{NHF} \times 100\% \qquad (5)$$

where i – M2, M4, STO-DZ, MINI-1, MINI-4, and ϵ stands for valence orbital energy and shown in Figure 1.

One can see that the valence shell description on the M4 level is close to that of the STO-DZ set. For Br and especially for F, the peaks on M4, M2, and STO-DZ curves appear (see Fig. 1). They reflect insufficient description of the "new" shell: $2p$ for F and $3d$ for Br. The error for $2p$ orbital of F can be significantly diminished if one takes five GTOs of p-type instead of four GTOs. Then the error becomes equal to 0.45%. The influence of the quality of description of the new shell on the properties of the valence orbitals is seen
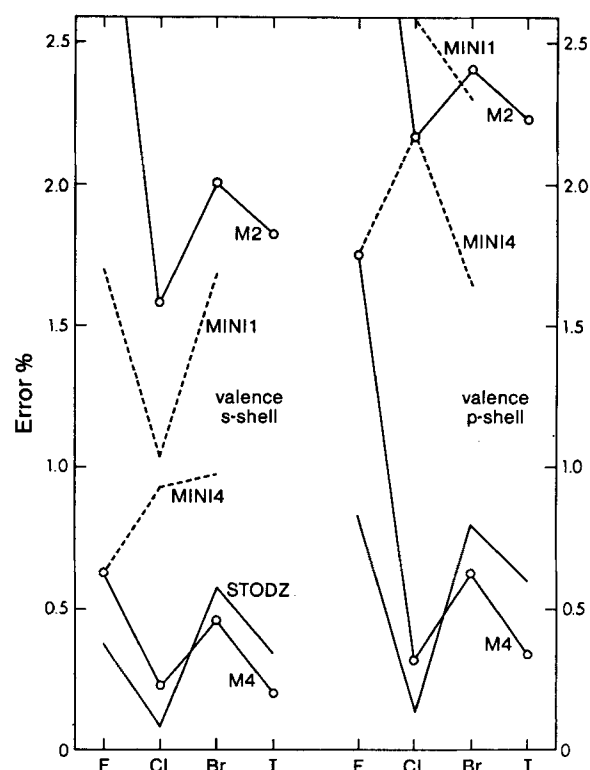

Figure 1. Errors of the valence orbital energies for several minimal type basis sets in comparison with the errors for STO-DZ sets.

particularly well when comparing the valence s shells in MINI-1 and MINI-4 basis sets. The valence CGTOs in both sets have the same number of GTOs, and the only serious differences exist in description of the $2p$ or $3d$ orbitals. The changes

in inner orbitals like $1s$ and $2p$ of Cl influence the valence properties in smaller degree.[1] Our smallest set M2 has similar quality of valence orbitals as MINI-1 set.

III. MOLECULAR CALCULATIONS

Ten diatomic molecules containing halogen atoms and four halogen hydride molecules are the subject of the present investigation.

The basis sets described in section II have been used. For fluorine atom the better set B4 is used, but for iodine only B2 is used because of economical reasons. In the case of Br_2 we have found that using the M2 set instead of M4 reduces time of computations by a factor of two. Following Huzinaga and co-workers[1,4] the scale factor of 1.2 has been used for M4 set of hydrogen.

It is well-known that if two polarization functions are used instead of one then the computed results are less sensitive to any changes in the polarization component of the basis set.[15] Therefore whenever our molecular results change considerably when one polarization function is replaced by two functions we should reoptimize this one polarization function. This is the case mostly for molecules containing fluorine atom, particularly when SV2P set is used. For this atom, the single polarization function with exponent equal to 0.9 has been also used. This value is close to that of Pople et al. (0.8) and of Dunning and Hay (0.9),[16] or that found in ref. 1 (0.938) by taking into account molecular environment of the fluorine atom. We did not perform more advanced studies in that direction because our aim here is to construct atomic basis sets that are fully determined by atomic properties only.

The total energies are calculated for all molecules at four internuclear separations (the difference between two consecutive separations is $\simeq$ 0.2 a.u.). The equilibrium distance R_e (Å) and vibrational frequencies ω_e (cm^{-1}) are found using the third-degree polynomial fitting procedure.[17] The atomization energies D_e (eV) are calculated from interpolated total energies.

We have used GAUSSIAN 80 program[18(a)] for lighter molecules up to Cl_2; SPDFG program[19] has been used for larger molecules because the limited accuracy of integrals in GAUSSIAN 80 package[18(b)] has appeared to be insufficient for calculations on systems of heavy atoms where the interatomic interactions are fairly weak. For Br_2

molecule using M4 set, we found essential differences in results using these two programs.* The calculations of dipole moments, μ, (in Debye units D) and quadrupole moments, Θ, (in Buckingham units B) are done using MOLECULE program.[20]

The errors involved in these calculations seem to be[1] $|\Delta D_e| \leq 0.01$ eV, $|\Delta R_e| \leq 0.005$ Å, $\Delta\omega_e \leq 2\%$, $|\Delta\mu| \leq 0.01$ D, and $\Delta\Theta \leq 0.01$ B. The results of the calculations and the pertinent discussions are presented in the following sections.

A. GEOMETRIES

The calculated R_e values are given in Table V. The mean of absolute errors defined as follows:

$$\text{Error} = \sum_{1}^{N} \left(|R_e^{\text{cal}} - R_e^{\text{exp}}|/R_e^{\text{exp}} \right)/N \times 100 \ (\%)$$

$$(6)$$

where R_e^{cal} and R_e^{exp} stand for calculated and experimental equilibrium internuclear distances, respectively, N denotes all available molecular data; these are also presented in Table V.

It is clearly seen from Table V that for both B2 and B4 sets splitting of the valence orbitals and subsequent addition of polarization functions makes bond lengths shorter, so that the computed R_e values approach the experimental ones. It is sufficient to use only one polarization function as the changes produced by the second one are negligible, except for molecules containing fluorine. It suggests that our fluorine function may be inferior to those of other halogen atoms and/or our choice of one polarization function for F is improper. For ClF molecule the calculations using SV2P′ set (polarization function for fluorine has exponent equal to 0.9) have been done giving R_e equal to 1.624 Å, slightly closer to that obtained using SV2PP set.

The errors shown in Table V for SViP and SViPP $(i = 2, 4)$ sets almost coincide with those obtained using extended SCF results.

Our minimal set M4 gives R_e larger (by about 1%) than both MINI-1 set[4] and M2 set. This is due to the fact that M4 function is more diffuse,

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*The equilibrium distances obtained using GAUSSIAN 80 and SPDFG programs are equal to 2.449 and 2.478 Å, respectively. The atomization energies and vibrational frequencies calculated with GAUSSIAN 80 and SPDFG programs differ by 0.04 eV and $\sim$ 9%, respectively.

Table V. Calculated equilibrium distances R_e (in Å) with various kinds of basis sets.[a] The R_e results from extended SCF calculations (ext) and experimental values[b] (exp) are also included.

	exp[b]	ext[c]	M4[d]	SV4	SV4P	SV4PP	M2[d]	SV2	SV2P	SV2PP
HF	0.917	0.897[e]	1.027(0.983)	0.935	0.899	0.904	-	-	-	-
HCl	1.275	1.264[e]	1.434(1.365)	1.306	1.288	1.276	1.430(1.359)	1.301	1.281	1.268
HBr	1.414	1.406	1.563(1.488)	1.438	1.422	1.413	1.561(1.484)	1.420	1.417	1.407
HI	1.609	1.608[f]					1.742(1.699)	1.610	1.613	1.610
F$_2$	1.412	1.323[g]	(1.429)[h]	1.418[h]	1.338	1.342	-	-	-	-
ClF	1.628	1.588[i]	1.767	1.718	1.632	1.615	1.766	1.720	1.632	1.603
BrF	1.759	1.719	1.874	1.821	1.760	1.738	1.873	1.791	1.751	1.728
IF	1.910	1.86	-	-	-	-	2.024	1.938	1.918	1.891
Cl$_2$	1.988	2.000[j]	2.200	2.155	2.008	1.999	2.191	2.183	2.022	2.013
BrCl	2.136	2.137	2.336	2.285	2.148	2.144	2.328	2.301	2.151	2.144
ICl	2.321	2.33	-	-	-	-	2.513	2.461	2.354	2.339
Br$_2$	2.281	2.287[k]	2.478	2.422	2.288	2.286	2.479	2.455	2.278	2.286
IBr	2.469	2.40	-	-	-	-	2.680	2.644	2.489	2.487
I$_2$	2.666	2.678[l]	-	-	-	-	2.904	2.871	2.705	2.700
Error[m]	1.5(1.0)	9.8		4.1	1.2(0.7)	1.1(0.6)	8.8	4.8	0.7	0.8

[a]For H and F only B4 set is used in connection with B2 set for other atoms.

[b]Experimental values are taken from K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Vol. IV, Constants of Diatomic Molecules, Van Nostrand-Reinhold Co., New York, 1979.

[c]Results of extended calculations are from P. A. Straub and A. D. McLean [15] unless otherwise marked. For IF, ICl, IBr assumption of parabolic potential was made. For IBr molecule SZ + P function was used and presently obtained total energy of IBr is better than that in [15].

[d]Values in parentheses are obtained using scale factors [1].

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[h]H. Tatewaki and S. Huzinaga [1].

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[j]O. Gropen, S. Huzinaga and A. D. McLean [23]

[k]Y. Sakai, H. Tatewaki and S. Huzinaga [4].

[l]A. D. McLean, O. Gropen and S. Huzinaga, J. Chem. Phys., 73, 396 (1980).

[m]Values in parentheses are obtained neglecting the errors of F$_2$. The error for extended results is found without values for IF, ICl and IBr molecules because these results cannot be regarded as extended ones.

especially in the p part. But when the function becomes more flexible (sv$i$, sv$i$P; $i = 2, 4$), then the differences between R_e obtained with the present sets and with MIDI or MIDI* sets appear to be negligible.

Comparison of R_e obtained by Huzinaga and co-workers (see Table XVIII, ref. 4) for various molecules indicates that for molecules containing atoms other than halogens our minimal sets will give generally shorter R_e than for molecules considered here.

Recently R_e values for most of the molecules presented in Table V have been calculated[21, 22] using STO-3G basis set. The error calculated according to formula (6) for STO-3G results, excluding F$_2$ case, is very small and equal to 1.7%. In improved calculations, polarization functions are usually added, resulting in STO-3G* set. For HCl, ClF, Cl$_2$ molecules,[21] STO-3G* sets produce shortening of bond lengths by about 4%. If the same trend holds for heavier molecules, we can expect that the mean of errors for STO-3G* re-

sults will reach about −2%. It seems that such short bond lengths are caused by large BSSE for these sets, and we plan to study this problem in the near future.

B. SPECTROSCOPIC CONSTANTS

The vibrational frequencies ω_e have been calculated from the curvature of the potential curves and are displayed in Table VI, together with experimental and extended SCF results. The errors of ω_e (in %) defined similarly as in Eq. (6) are also given in Table VI.

One can see in Table VI that ω_e^{ext} is always larger than ω_e^{exp}, and the mean error is equal to 11.7%. The discrepancy between SCF theory and experiment is largest for F$_2$ molecule. Since it is not an artifact of basis sets, but rather of SCF theory, we excluded this case from calculation of error in Table VI.

The mean errors both for SV4P, SV4PP, and SV2P, SV2PP sets are close to each other and they

Table VI. Vibrational frequencies ω_e (in cm^{-1}).[a]

	exp[b]	ext[c]	M4[d]	SV4	SV4P	SV4PP	M2[d]	SV2	SV2P	SV2PP
HF	4138	4469[e]	3697(4225)	4142	4590	4532	–	–	–	–
HCl	2991	3181[e]	2716(3035)	3037	3190	3213	2750(3074)	2949	3181	3235
HBr	2649	2775	2473(2743)	2705	2848	2864	2481(2762)	2710	2856	2870
HI	2309	2462	–	–	–	–	2202(2319)	2421	2507	2485
F_2	917	1257[g]	(1270)[h]	1140[h]	1243	1261	–			
ClF	786	926[i]	860	850	906	925	859	812	895	934
BrF	671	770	715	736	769	795	712	742	776	801
IF	610	711					623	696	698	730
Cl_2	560	564[j]	559	523	620	603	573	537	597	569
BrCl	444	482	442	422	492	479	451	423	488	474
ICl	384	421	–	–	–	–	385	375	417	424
Br_2	325	352[k]	323	311	362	355	326	306	366	343
IBr	269	342	–	–	–	–	266	253	296	291
I_2	214	236[l]	–	–	–	–	211	200	236	230
Error[m]		11.7(8.9)	5.5	6.9(4.7)	13.7(10.8)	13.7(10.7)	3.6	5.5	10.4	10.2

[a–l] See footnotes to Table V.
[m] Error (in %) for extended results obtained without HI, IF, ICl, IBr molecules because of approximations involved in their calculations (ref. 15). Values in parentheses obtained with neglect of F_2 errors.

approach within ~ 2% the errors of extended SCF calculations. Addition of polarization functions is essential since minimal sets differ from extended ones by ~ 9%, and splitting of valence shells does not reduce much (~ 7%) this deficiency.

The largest differences between our SV4PP results and extended ones are for Cl_2 molecule where, surprisingly, the ω_e^{ext} value[23] is very close to the ω_e^{exp} one. The ω_e^{ext} value reported by Gropen, Huzinaga, and McLean[23] has been obtained by recalculation data of Straub and McLean[15]. Our SV4PP results agree very well with the original value of ω_e^{ext} given in ref. 15 (equal to 604 cm^{-1}). Except for Cl_2 molecule, SV4P and SV4PP sets produce more uniform distribution of errors than SV2P or SV2PP sets. The root-mean-square deviations between our and extended SCF results (omitting Cl_2, HI, FI, ClI, and BrI molecules) are equal to 2.0, 1.8, 2.3, 2.4(%) for SV4P, SV4PP, SV2P, SV2PP sets, respectively.

C. TOTAL ENERGIES AND ATOMIZATION ENERGIES

Total energies calculated at the computed geometries from potential curves for SV4P and SV2P sets are given in Table VII, and the atomization energies (AE) for all basis sets are displayed in Table VIII.

The atomization energies are very sensitive to the quality of basis function used.

Our minimal and split valence sets for most examined molecules are not able to predict a

Table VII. Total energies (in a.u.) at the calculated equilibrium internuclear distances for SV4P and SV2P sets.

	SV4P	SV2P
HF	− 99.91284	−
HCl	− 459.60520	− 459.57241
HBr	−2570.72783	−2569.81556
HI	−	−6913.17209
F_2	− 198.47959	
ClF	− 558.25517	− 558.22346
BrF	−2669.39920	−2668.48783
IF	−	−7011.87437
Cl_2	− 917.99797	− 917.93366
BrCl	−3029.13701	−3028.27410
ICl	−	−7371.56973
Br_2	−5140.27555	− 5138.44963
IBr	−	− 9481.82409
I_2	−	−13825.19629

stable molecular state. The first acceptable basis set is split valence plus polarization function set. The influence of the second polarization function is important only for molecules containing fluorine. The SV2P′ set ($d_F = 0.9$) gives considerably better atomization energy for ClF, equal to 0.36 eV, instead of 0.22 eV produced by SV2P set ($d_F \simeq 1.5$).

The BSSE effect influences seriously the calculated AE, and it also partially explains the differences between SViP and SViPP ($i = 2, 4$) results. We will discuss this problem in section IV.

Finally we compare our results with experimental ones and those from extended SCF calculations (see Table VIII).

Table VIII. Atomization energies D_e (in eV).[a]

	exp[b]	ext[c]	M4[d]	SV4	SV4P	SV4PP	M2[d]	SV2	SV2P	SV2PP
HF	6.13	4.38[e]	2.05(2.77)	3.25	4.06	4.14				
HCl	4.61	3.48[e]	1.86(2.33)	2.65	3.34	3.41	1.93(2.33)	2.60	3.33	3.42
HBr	3.92	3.67	1.64(2.02)	2.30	2.91	2.95	1.71(2.06)	2.34	2.99	2.96
HI	3.19	–	–	–	–	–	1.44(1.62)	1.98	2.45	2.45
F$_2$	1.66	−1.37[g]	(−2.10)[h]	−2.04[h]	−1.34	−1.20				
ClF	2.67	0.76	−1.09	−0.66	0.20	0.50	−0.98	−0.66	0.22	0.61
BrF	2.59	1.51	−0.92	−0.28	0.35	0.67	−0.81	−0.10	0.46	0.73
IF	2.92	–	–	–	–	–	−0.64	0.18	0.74	1.13
Cl$_2$	2.51	1.16	−0.39	−0.31	0.86	0.92	−0.12	0.12	0.87	0.93
BrCl	2.26	1.87	−0.27	−0.12	0.87	0.91	−0.04	0.03	0.96	0.96
ICl	2.17	–	–	–	–	–	0.07	0.17	0.99	1.13
Br$_2$	1.99	0.81[k]	−0.20	−0.06	0.87	0.91	−0.01	0.04	1.00	0.83
IBr	1.84	–[l]	–	–	–	–	0.04	0.15	0.95	0.91
I$_2$	1.55	0.96[l]	–	–	–	–	0.01	0.10	0.84	0.81

[a-l] See footnotes to Table V. D_e^{exp} values have been corrected by taking into account the zero-point energy. The D_e^{ext} results for HI, IF, ICl, IBr are not given by P. A. Straub and A. D. McLean (ref. 15).

The SViPP ($i = 2, 4$) results are similar to D_e^{ext} ones except for results for molecules containing Br, HBr, BrF, and BrCl. These molecules were calculated in ref. 15 using DZ + P sets. Recently[4] extended SCF calculations for Br$_2$ molecule have been performed, and AE has been found to be 0.81 eV instead of 2.51 eV given in ref. 15. Therefore it seems that the published results[15] for HBr, BrF, and BrCl should be taken with caution.

The calculated AE differ considerably from experimental ones because correlation effects are different in open-shell atoms and closed-shell molecules composed of these atoms. It is believed[16] that in some chemical processes (e.g., for hydrogenation reactions) correlation effects can be disregarded. For hydrogenation reaction:

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}X_2 = HX \qquad X: F, Cl, Br, I$$

both reactants and product have the same num-

ber of valence shell electron pairs, and correlation effects to some extent are mutually cancelled.

The enthalpy of hydrogenation reaction at 0 K is calculated according to formula:

$$\Delta H_0 = \tfrac{1}{2}D_e(H_2) + \tfrac{1}{2}D_e(X_2) - D_e(HX)$$
$$+ \tfrac{1}{2}\omega_e(HX) - \tfrac{1}{4}\omega_e(H_2) - \tfrac{1}{4}\omega_e(X_2) \quad (7)$$

where D_e and ω_e stand for atomization energies, and vibrational frequencies taken from Table VIII and Table VI, respectively. The ΔH_0 results are compared with experimental ones and are shown in Table IX.

It is seen that split valence and split valence plus polarization sets provide ΔH_0, which is in qualitative agreement with experimental values.

D. ORBITAL ENERGIES

In Table X orbital energies of Cl$_2$ calculated using various basis sets are given for comparison.

Table IX. Hydrogenation energies ΔH_0 (in eV) at 0 K experimental (exp) and calculated using various basis sets.[a]

	exp[b]	M4[c]	SV4	SV4P	SV4PP	M2[c]	SV2	SV2P	SV2PP
HF	−2.83	−2.02	−2.48	−2.87	−2.87	–	–	–	–
HCl	−0.95	−0.78	−1.06	−1.12	−1.14	−0.64	−0.93	−1.11	−1.15
HBr	−0.53	−0.38	−0.60	−0.70	−0.70	−0.33	−0.59	−0.71	−0.75
HI	−0.05	–	–	–	–	0.10	−0.22	−0.27	−0.27

[a] For H$_2$ molecule the values of D_e are equal to 3.54, 3.51, 3.43, 3.49 (eV) and the values of ω_e are equal to 4692, 4686, 4741, 5382 (cm^{-1}) for M4, SV4, SV4P, SV4PP sets, respectively.
[b] The experimental values of D_e and ω_e are the same as in Tables VIII and VI and are taken from reference given in Table V, footnote b.
[c] Minimal basis set for hydrogen with scale factor (1.2) was used.

Table X. Orbital energies of Cl_2 (in a.u.).[a]

Basis sets	$1\sigma_u$	$1\sigma_g$	$2\sigma_u$	$2\sigma_g$	$3\sigma_g$	$3\sigma_u$
Extended I[b]	-104.8943	-104.8943	-10.6168	-10.6167	-8.0831	-8.0828
M4	-104.7458	-104.7453	-10.6339	-10.6339	-8.1000	-8.1006
SV4	-104.7783	-104.7782	-10.6362	-10.6363	-8.1047	-8.1048
SV4P	-104.7752	-104.7748	-10.6246	-10.6247	-8.0934	-8.0933
SV4PP	-104.7838	-104.7836	-10.6241	-10.6242	-8.0930	-8.0930
M2	-104.7620	-104.7616	-10.6350	-10.6350	-8.1016	-8.1022
SV2	-104.8284	-104.8283	-10.6547	-10.6547	-8.1243	-8.1243
SV2P	-104.8272	-104.8271	-10.6430	-10.6431	-8.1142	-8.1140
SV2PP	-104.8444	-104.8444	-10.6463	-10.6464	-8.1186	-8.1184

Basis sets	$1\pi_g$	$1\pi_u$	$4\sigma_g$	$4\sigma_u$	$5\sigma_g$	$2\pi_u$	$2\pi_g$
Extended I	-8.0801	-8.0801	-1.2141	-1.0109	-0.5936	-0.5654	-0.4398
Extended II[c]			-1.2201	-1.0209	-0.5903	-0.5681	-0.4493
M4	-8.0950	-8.0946	-1.1898	-1.0509	-0.5546	-0.5595	-0.4784
SV	-8.0990	-8.0989	-1.1967	-1.0421	-0.5581	-0.5595	-0.4705
SV4P	-8.0882	-8.0882	-1.2176	-1.0184	-0.5984	-0.5675	-0.4468
SV4PP	-8.0879	-8.0878	-1.2194	-1.0170	-0.5972	-0.5681	-0.4448
M2	-8.0962	-8.0959	-1.1778	-1.0350	-0.5487	-0.5515	-0.4675
SV2	-8.1183	-8.1183	-1.1793	-1.0342	-0.5476	-0.5508	-0.4659
SV2P	-8.1084	-8.1084	-1.2047	-1.0106	-0.5846	-0.5604	-0.4426
SV2PP	-8.1126	-8.1126	-1.2072	-1.0099	-0.5868	-0.5605	-0.4400

[a] The values are calculated at the optimized geometries which are given in Table V.
[b] See ref. 15. The values were calculated at the R_e = 1.9907 Å.
[c] See ref. 23. The values were calculated at the R_e = 1.9995 Å.

It is seen from Table X that B4 and even B2 sets give reasonable orbital energies if compared with extended SCF calculations. Again, addition of polarization functions appears to be important, and SV4P or SV4PP results almost coincide with extended SCF results for valence orbitals of Cl_2. Smaller basis sets (Mi or SVi, $i = 2, 4$) cannot reproduce the correct orbital ordering of $5\sigma_g$ and $2\pi_u$ given by the extended calculations.

The core orbitals of Cl_2 are "deeper" for the B2 set than for the B4 one as a consequence of lower atomic core energies for the B2 set. Moreover, the poorer (B2) set has tendency to excessive lowering of the molecular core orbitals.[25] For example, the $1\sigma_u$ and $1\sigma_g$ orbital energies are lower than 1s orbital of Cl by 0.05, 0.04, 0.02, and 0.02 a.u. for M2, SV2, SV2P and SV2PP, respectively. For B4 set the corresponding values are equal to 0.04, 0.02, 0.01, and 0.01 a.u. These results suggest that BSSE corrections should be larger for the B2 set than for the B4 one.

E. CHARGE DISTRIBUTION

The dipole moments and quadrupole moments have been calculated and the results are displayed in Table XI.

It is known that the extended SCF results can be reproduced in a rather cumbersome way, using DZ set plus two polarization functions or DZ plus one diffuse polarization function.[26] Our results obtained using split valence set augmented with two d functions approach quite well the extended values. It should be noticed that splitting of the valence orbitals does not bring simultaneous improvement in both dipole and quadrupole moments in comparison with Mi ($i = 2, 4$) results. Similar behavior of the split basis sets 4-31G was discussed by Ditchfield.[27] Addition of one polarization function brings considerable improvement in both electric moments. The SViPP ($i = 2, 4$) sets reproduce extended results within $\sim$ 0.1 D and $\sim$ 0.5 B.

Using SV2P' set (see section IIIA) with more diffuse d exponent on F for ClF molecule we have obtained slightly better value of dipole moment, equal to 1.250 D.

The dipole moments for HF and BrCl molecules obtained using SViPP ($i = 2, 4$) sets are smaller than the experimental values. This result is slightly surprising since SCF method tends to overestimate ionic contribution to the wave function at the expense of covalent ones. However, this lowering of dipole moments is caused

Table XI. Dipole moments μ (D) in the XY molecule (X^+Y^-) and quadrupole moments Θ (B) calculated at equilibrium distances of XY molecule.[a] The experimental (exp) and extended SCF results (ext) are also included.

	exp[b]	ext[c]	M4[d]	SV4	SV4P	SV4PP	M2[d]	SV2	SV2P	SV2PP
μ:										
HF	1.826[e]	1.888[f]	1.992(2.022)	2.251	1.861	1.773				
HCl	1.109	1.186[f]	1.524(1.847)	1.908	1.334	1.189	1.551(1.861)	1.864	1.310	1.176
HBr	0.788	0.931	1.105(1.610)	1.534	1.078	0.965	1.093(1.586)	1.495	1.078	0.961
ClF	0.888	0.901	0.936	1.672	1.318	1.007	1.056	1.717	1.346	1.050
BrF	1.29	1.440	1.454	2.386	1.907	1.472	1.536	2.370	1.887	1.440
BrCl	~0.57	0.588	0.696	1.069	0.623	0.524	0.723	1.013	0.566	0.417
Θ:										
F_2	0.881[c]	0.558	0.460	0.300	0.404	0.691	-	-	-	-
Cl_2	-	3.378	2.49	2.12	3.29	3.73	2.41	2.34	3.36	3.86

[a] See footnote a, Table V.
[b] See footnote b, Table V, unless otherwise marked.
[c] P. A. Straub and A. D. McLean (ref. 15), unless otherwise marked.
[d] Values in parentheses were obtained using scale factors (1.2 for H).
[e] Reference 29.
[f] Reference 30.

by BSSE error and will be explained in the next section.

IV. BASIS-SET SUPERPOSITION ERROR

The basis-set superposition corrections to calculated geometry, shape of potential curve, atomization energy, and electric properties of the molecules are estimated using the standard counterpoise method (CP).[11] This method results in an over-estimation of the BSSE because both occupied and virtual orbitals from the second center are used to compensate incompleteness of the investigated atomic basis set. This overestimation seems to be around 10–20%[7,8] above the true BSSE corrections caused exclusively by the virtual space from the other center.

A. METHOD

The CP corrected atomization energy (D_e^c) of XY molecule can be written as

$$D_e^c = E_{X(Y)} + E_{Y(X)} - E_{XY} \qquad (8)$$

where E_{XY} denotes the total energy of XY, and $E_{X(Y)}$, $E_{Y(X)}$ stand for total energies of atoms X and Y, respectively, calculated using molecular basis set. The net BSSE correction can be obtained by subtracting from the previously reported atomization energy D_e (see Table VIII) the corrected one, D_e^c:

$$\Delta^{BSSE} = D_e - D_e^c = E_X + E_Y - E_{X(Y)} - E_{Y(X)}$$
$$(9)$$

where E_X and E_Y is atomic energy of the isolated X and Y atom, respectively.

The degeneracy of open shell (p) of halogen atoms is lowered when linear symmetry $C_{\infty v}$ of XY molecule is imposed. It brings the new $^2\Sigma$ and $^2\Pi$ states of the atom in $C_{\infty v}$ symmetry which correspond to $\sigma^1\pi^4$ and $\sigma^2\pi^3$ configurations, respectively:

$$p^5 \rightarrow \sigma^1\pi^4 + \sigma^2\pi^3$$

We can define atomic energy $E_{X(Y)}$ in terms of the total energies of the $^2\Sigma(^2\Sigma E_{X(Y)})$ and $^2\Pi(^2\Pi E_{X(Y)})$ states, taking into account degeneracy of open valence orbitals of these states,

$$E_{X(Y)} = \tfrac{1}{3}\left({}^2\Sigma E_{X(Y)} + 2\,{}^2\Pi E_{X(Y)} \right) \qquad (10)$$

Δ^{BSSE} value [e.g. eq. (9)] should approach zero when distance R between X and Y increases. However, this does not happen since even for $R = \infty$, we still keep $C_{\infty v}$ symmetry constraint, which causes difference between p_σ and p_π orbitals. To exclude this relatively small effect we recalculated the atomic energy E_X according to formula (10) with the linear symmetry $C_{\infty v}$ imposed, thus providing the proper asymptotic properties of the Δ^{BSSE} correction.

The total atomic energies for $^2\Sigma$ and $^2\Pi$ states are calculated using the open-shell package of ALIS[28] or MOLECULE[20] programs. The corrected equilibrium distances R_e^c and vibration frequencies ω_e^c are recalculated from potential curve corrected for BSSE.

For light molecules, up to Cl_2, full basis sets on both centers are used for calculation of $E_{X(Y)}$. For heavier molecules we take only valence

orbitals and polarization functions (if necessary) for the role of ghost orbitals on the second center. It has a minor effect on computed BSSE, but considerably decreases computational time. For example, Δ^{BSSE} for Br calculated using M2 set is equal to 0.087 eV when $3s$ and $3p$ orbitals are ghost orbitals, and it is equal to 0.096 eV when full basis set is used.

The method of calculation of the basis set superposition (BSS) corrections to electric properties [$\Delta^{BSS}(P)$] is essentially the same as described above. The $\Delta^{BSS}(P)$ correction is expressed as

$$\Delta^{BSS}(P) = P_{X(Y)} + P_{Y(X)} - P_X - P_Y \quad (11)$$

and

$$P_{X(Y)} = \frac{1}{3}\left({}^{2\Sigma}P_{X(Y)} + 2\,{}^{2\Pi}P_{X(Y)} \right)$$

where P stands for μ or Θ and other symbols have the same meaning as those in eqs. (8)–(10).

When calculating quadrupole moment of the atom using ghost orbitals located nearby, the dipole moment inevitably appears. It causes the dependence of the calculated $\Theta_{X(Y)}$ on the choice of coordinates. In order to get consistent results, the same origin of the coordinate system (at the center of mass of XY molecule) is kept throughout all calculations of Θ_{XY}, $\Theta_{X(Y)}$, and Θ_X.

B. INFLUENCE OF BSSE ON ATOMIZATION ENERGIES, GEOMETRIES, AND SPECTROSCOPIC CONSTANTS

The Δ^{BSSE} corrections to atomization energies at equilibrium distances for several molecules are given in Table XII. These corrections should be subtracted from D_e values (Table VIII) to obtain atomization energies without BSSE.

At first sight one could expect that Δ^{BSSE} will increase as we are passing from minimal set to split valence one with polarization functions, since virtual space on the second atom will increase. One could expect also that the poorer basis set B2 will produce larger BSSE corrections than better B4 set. These predictions, however, do not always hold.

For ClF molecule, Δ^{BSSE} corrections obtained using B4 set are larger than those using B2 set. To elucidate this phenomenon we collected in Table XII contributions to Δ^{BSSE} from particular atoms. One can see that Δ^{BSSE} correction for fluorine (Δ_F^{BSSE}) dominates the error for ClF molecule. The Δ_F^{BSSE} for B4 set is even larger than the corresponding error for F_2 molecule. This indicates that the fluorine basis set is rather poor and the relatively better set of Cl placed nearby seeps considerably into the fluorine orbitals. On the other hand, atomic total energy of chlorine cannot be improved as efficiently as in the case of Cl_2 molecule.

When we replace the B4 set of Cl by the more compact B2 set, then the overlap with fluorine

Table XII. BSSE corrections to atomization energies (in eV) calculated at equilibrium distances.

		M4	SV4	SV4P	SV4PP	M2	SV2	SV2P	SV2PP
HF		0.039	0.023	0.026	0.037	–	–	–	–
F_2		0.035	0.044	0.047	0.059	–	–	–	–
ClF[a]	F	0.034	0.052	0.056	0.071	0.033	0.040	0.042	0.057
	Cl	0.016	0.007	0.012	0.015	0.017	0.013	0.018	0.025
	Σ	0.050	0.059	0.068	0.086	0.050	0.053	0.060	0.082
Cl_2		0.041	0.020	0.035	0.036	0.063	0.061	0.072	0.103
BrCl	Cl	0.020	0.011	0.018	0.019	0.033	0.038	0.045	0.056
	Br	0.012	0.028	0.030	0.048	0.043	0.082	0.130	0.044
	Σ	0.032	0.039	0.048	0.067	0.076	0.120	0.175	0.100
Br_2		0.023	0.036	0.066	0.100	0.087	0.129	0.248	0.090
I_2		–	–	–	–	0.054	0.134	0.110	0.078

[a] Contributions to Δ^{BSSE} from particular atoms and total (Σ) value of Δ^{BSSE}. The Δ_H^{BSSE} correction for HF molecule is negligibly small.

orbitals decreases, and as a consequence Δ_F^{BSSE} becomes smaller.

This example shows that basis sets of similar quality should be used for atoms in heteronuclear molecules because otherwise BSSE can be substantial.

To emphasize this problem calculations have been carried out for ClF with unbalanced basis sets: M4 and SV4 for F and Cl, respectively. The Δ_F^{BSSE} and Δ_{Cl}^{BSSE} are then equal to 0.087 and 0.004 eV, respectively.

In the case of BrCl molecule, it seems that both sets (B2 and B4) for Br and Cl are well balanced.

For some molecules and basis sets the enlargement of the virtual space does not cause increase of the Δ^{BSSE}, since at the same time the atomic basis set under investigation is improved.

This is the case, e.g., for Br_2 molecule, when one passes from SV2P set to SV2PP one. The ghost orbitals of the second center improve mainly the 3d orbital of Br. The orbital energy of 3d for SV2P set decreases by ~ 1.5% when the ghost orbitals are placed nearby. The SV2PP set is much more saturated (see section II), and the decrease of 3d orbital energy caused by the second center is equal only to ~ 0.5%.

Now let us compare the BSSE corrections for homonuclear molecules from F_2 to I_2. For most basis sets one can notice tendency that Δ^{BSSE} are large for F_2, then are smaller for Cl_2, next reach maximum for Br_2, and, finally, in the case of I_2 Δ^{BSSE}, diminish. This tendency indicates that the presence of the new shells: 2p for F and 3d for Br and quality of their description has significant influence on the BSSE (see also sections IIB and IIC). Similar conclusions have been already reported in refs. 1, 8, and 14.

BSSE affects seriously the atomization energies given in Table VIII, and for Br_2 it can amount to 25% of the calculated atomization energy. We compare only the results obtained using SViP or SViPP ($i = 2, 4$) since they produce reasonable atomization energies (see section IIIC).

Taking into account the Δ^{BSSE} corrections brings about smaller differences between results obtained using SViP and SViPP sets ($i = 2, 4$) for all molecules. Especially for Br_2, exclusion of BSSE is important, and it brings about quite good agreement with the extended SCF results. However, the BSSE corrections only partially explain large differences between SViP and SViPP ($i = 2, 4$) results for molecules containing F.

Exclusion of the BSSE results in longer equilibrium distances R_e^c and flatter potential curves (ω_e^c is smaller than ω_e). The BSSE effect is almost negligible for lighter molecules and becomes more important for heavier ones. For Cl_2, R_e increases by only 0.005 Å, and ω_e decreases by less than 1%. For Br_2 molecule and SV2P set, elongation of R_e is equal to 0.01 Å and decrease of the ω_e is about 2%. For I_2 molecule, elongation of R_e is largest, but it is around 0.5% of the calculated R_e, given in Table V.

C. THE INFLUENCE OF BASIS-SET SUPERPOSITION ON ELECTRIC PROPERTIES

BSS influence on the dipole moments for HF, ClF, and quadrupole moments for F_2, Cl_2 molecules is analyzed here using CP method described in section IVA.

The changes in total atomic energies caused by BSSE, examined in the previous section, depend mostly on the changes in the core orbitals. On the other hand, BSS effects on the electric moments are mainly related to influence of BSS on the valence orbitals.

In Table XIII, corrections $\Delta^{BSS}(P)$ ($P = \mu, \Theta$) [see eq. (11)] are collected. For heteronuclear molecules $\Delta_F^{BSS}(\mu)$ [$\Delta_{Cl}^{BSS}(\mu)$] from particular atoms are also given. It is seen that $\Delta^{BSS}(\mu)$ corrections increase the value of dipole moment, given in Table XI, by at most 8% for ClF and 4% for HF molecule.

The $\Delta^{BSS}(\mu)$ can be regarded as a measure of mutual balance between the valence atomic orbitals of atoms composing the molecule. If valence orbitals of these atoms are of different quality, then fictitious charge transfer appears which changes the dipole moment of the molecule. The $\Delta_F^{BSS}(\mu)$ corrections are larger for the B4 set than for the B2 set, and in the case of B2 set they are partly compensated by $\Delta_{Cl}^{BSS}(\mu)$ values. This shows again (see the previous section) that in ClF the basis sets of fluorine are better balanced by the chlorine B2 bases than by the B4 set. This can be also deduced from comparison of orbital energies in Figure 1. The calculations with highly unbalanced sets, i.e. M4 for F and SV4 for Cl, give decrease of the $\Delta_F^{BSS}(\mu)$ from -0.033 D (see Table XIII) up to -0.081 D.

The dipole moment of HF calculated using SV4PP basis set and corrected for BSS is equal to 1.842 D. This value agrees much better with the

Table XIII. Basis set superposition corrections to dipole moment μ (in D) and quadrupole moment Θ (in B) calculated at equilibrium distances.

		M4	SV4	SV4P	SV4PP	M2	SV2	SV2P	SV2PP
$\Delta^{BSS}(\mu)$:									
HF[a]	F	-0.033	-0.046	-0.050	-0.068	-	-	-	-
	H	0.000	+0.003	+0.001	-0.001	-	-	-	-
	Σ	-0.033	-0.043	-0.049	-0.069	-	-	-	-
ClF	F	-0.033	-0.088	-0.073	-0.081	-0.033	-0.078	-0.064	-0.065
	Cl	0.003	-0.003	-0.000	-0.001	-0.014	-0.005	0.010	0.016
	Σ	-0.030	-0.091	-0.073	-0.082	-0.047	-0.083	-0.054	-0.049
$\Delta^{BSS}(\Theta)$:									
F_2		-0.002	0.002	0.001	0.003	-	-	-	-
Cl_2		0.001	-0.022	-0.016	-0.012	0.003	0.106	0.070	0.038

[a]Contributions to $\Delta^{BSS}(\mu)$ from particular atoms and total (Σ) value of $\Delta^{BSS}(\mu)$.

extended SCF result than the uncorrected one and is consistently larger than experimental value.

The quadrupole corrections $\Delta^{BSS}(\Theta)$ are almost negligible for the better set B4 and for the poorer B2 set; they result in decrease of the Θ moment by at most 5%.

In general the values of μ^c calculated with B2 or B4 sets are closer to each other than those from Table XI, obtained without taking into account the BSS effects. The same conclusion holds for the Θ moment.

CONCLUSIONS

The basis sets introduced here produce molecular results similar to those given by extended SCF calculations. We do not expect to achieve agreement with experimental results from the calculations on the SCF level. In fact, even the results of extended SCF calculations frequently differ from the experimental measurements, as we reported above.

The basis sets and polarization functions presented here are determined entirely from atomic calculations. For minimal type sets the scale factors determined in molecular environment seem to be useful. For small atoms like F and H adjustment of polarization function to molecular conditions could also improve obtained results.

The split valence basis sets are sufficient to obtain reasonable results for molecular geometries and hydrogenation energies. The addition of a single polarization function allows to get

results of high quality for molecular geometry, spectroscopic constants, and orbital energies. Two polarization functions are required if one desires to obtain good values for electric moments.

The set SV2P is recommended for molecular calculations. The SV4P set provides more reliable results than SV2P does; however, it is more expensive. The better fluorine function should be used in connection with SV4P set for other atoms to provide better balance of functions.

It is found that BSSE has little influence on calculated geometry, spectroscopic constants, and dipole and quadrupole moments. Taking into account the BSS effects is necessary if one aims at getting reasonable results for the atomization energies.

The BSSE calculated here represents an upper bound to the true BSSE. The lower bound can be estimated by taking into account only polarization functions as ghost orbitals (see also ref. 8). This approach gives much smaller value of BSSE; about one-third of the values reported in section IVB. Therefore we can say that BSSE connected with the basis sets presented here may change atomization energies within range 10–30%.

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