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Optimum Gaussian Basis Set for the Bromine Atom. *Ab initio* Calculations on the HBr Molecule

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An optimum ($15^s12^p2^d$) Gaussian basis set was obtained for the Bromine atom by minimizing the open shell energy functional. In the minimization procedure the method of conjugate gradients was applied. The optimum ($15^s12^p2^d$) basis set was contracted to an [$8^s6^p2^d$] "double zeta" quality basis set and this contracted set was tested on the HBr molecule.

Key words: Bromine, optimized Gaussian basis for ~ – HBr

1. Introduction

Though the theoretical study of simple Bromine compounds via *ab initio* calculations is of considerable interest, (e.g. in studying the electrophilic addition of halogenes to a carbon-carbon double bond [1]) so far no optimized Gaussian basis set has been proposed for bromine. The recently developed technique of direct optimization of Gaussian basis sets [2, 3] proved to be effective in locating optimum basis sets to any desired accuracy. In this paper the first application of the direct optimization for a remarkably large basis is reported and an optimized ($15^s12^p2^d$) Gaussian basis is proposed for the bromine atom.

It was felt necessary to obtain as well balanced a basis set as possible yet provide an adequate representation to both the core and valance electron shell. In addition to these motivations, economy dictated the reduction of the number of primitive functions as far as possible. In choosing a ($15^s12^p2^d$) basis set the d subshell of the M shell seemed to be the least adequately represented by using a (2^d) primitive set only. However, this choice was felt to be fairly consistent with the general representational requirement since the critical regions are the K (core) and the N (valence) shells and the $3d$ subshell is located in between these two extremes. On the other hand, our aim was to obtain a double zeta quality contracted basis set, and this is the reason why the (2^d) functions remained uncontracted. Test calculation was performed on the HBr molecule using the "double zeta" [$8^s6^p2^d$] contraction of the optimum ($15^s12^p2^d$) primitive set. Both the optimization of the ($15^s12^p2^d$) Br basis set and the test calculation on HBr were carried out on an IBM 370/165 computer.

2. Results and Discussion

The initial guess for the *s* and *p* exponent subsets of the $(15^s12^p2^d)$ primitive basis was obtained by extrapolation based on Huzinga's fluorine [4] and Veillard's chlorine [5] exponents. The initial *d* orbital exponents were guessed on the basis of the *d* exponent sets of Roos, Veillard and Vinot for the third row atoms from K to Zn [6].

The total dimension of the exponent space $\{\alpha_i\}$ of the $(15^s12^p2^d)$ basis set is 63. However, the original 63 dimensional optimization problem is equivalent to a 29 dimensional problem due to the symmetry of the basis.

In Fig. 1 the variation of the total energy is shown in the course of the iterative optimization procedure. The length of the logarithmic energy gradient vector,

$$|G| = (\sum G_i^2)^{1/2}, \tag{1}$$

where

$$G_i = \frac{1}{\sqrt{n}} \frac{\partial E}{\partial \ln \alpha_i} \tag{2}$$

belonging to the initial point $\{\alpha_i\}$ in the exponent space was rather large, $|G| = 0.793$, indicating that this basis set was far from the optimum. In the first iteration the total energy improved by more than one hartree unit, and we maintained a relatively rapid convergence by further iterations. Though the change in total energy in the subsequent iterations became less than 0.0003 hartree from iteration 19, we performed five full additional iterations. In the last step the gradient length $|G|$ became 6.79×10^{-3}, better by two orders of magnitude than the initial value. Since $|G|$ was still greater than zero the final exponent set was not the exact optimum, nevertheless, the stability of the energy value in the first seven significant figures

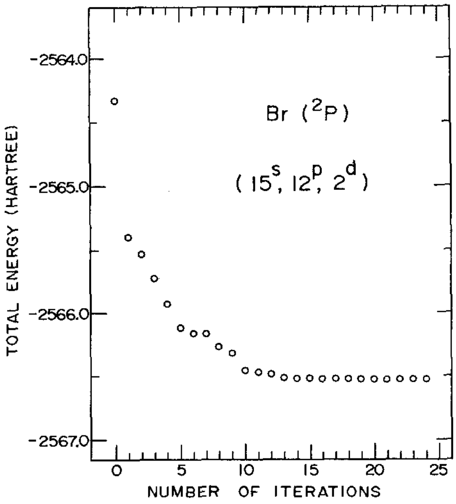

Fig. 1. Convergent series of calculated total energy values in the optimization of the $(15^s12^p2^d)$ bromine basis set

Table 1. Exponents of the optimized ($15^s12^p2^d$) basis set and specification of [$8^s6^p2^d$] contracted gaussian basis set for bromine atom

Contracted	Primitive	Exponent	Coefficient	Contracted	Primitive	Exponent	Coefficient
1*s*	s_1	6.96178*E*+5	2.7228493*E*−4	2*p*	p_1	2.28361*E*+3	4.9654796*E*−3
	s_2	1.03934*E*+5	2.1224534*E*−3		p_2	5.40112*E*+2	3.9314814*E*−2
	s_3	2.36182*E*+4	1.1048684*E*−2		p_3	1.74376*E*+2	1.7101837*E*−1
	s_4	6.77817*E*+3	4.3506264*E*−2		p_4	6.59986*E*+1	4.2141253*E*−1
	s_5	2.29304*E*+3	1.3615935*E*−1		p_5	2.74705*E*+1	5.0418482*E*−1
	s_6	8.69090*E*+2	3.3099763*E*−1				
	s_7	3.54913*E*+2	5.7604098*E*−1	2*p*′	p_6	1.18580*E*+1	1.0000000*E*+0
1*s*′	s_8	1.51604*E*+2	1.0000000*E*+0	3*p*	p_7	5.28930*E*+0	5.5075474*E*−1
					p_8	2.32941*E*+0	4.9883191*E*−1
2*s*	s_9	7.07366*E*+1	8.7095038*E*−2				
	s_{10}	2.54774*E*+1	9.2661399*E*−1	3*p*′	p_9	9.66848*E*−1	1.0000000*E*+0
2*s*′	s_{11}	1.07763*E*+1	1.0000000*E*+0	4*p*	p_{10}	3.75683*E*−1	5.9202855*E*−1
					p_{11}	1.55198*E*−1	4.6431616*E*−1
3*s*	s_{12}	3.38575*E*+0	1.0000000*E*+0				
				4*p*′	p_{12}	6.00665*E*−2	1.0000000*E*+0
3*s*′	s_{13}	1.25322*E*+0	1.0000000*E*+0				
4*s*	s_{14}	3.25379*E*−1	1.0000000*E*+0	3*d*	d_1	1.57389*E*+1	1.0000000*E*+0
4*s*′	s_{15}	9.95463*E*−2	1.0000000*E*+0	3*d*′	d_2	3.51592*E*+0	1.0000000*E*+0

and the improved value of the virial coefficient, as well, as the final gradient length suggested, that this set is rather close to the true optimum.

The exponents of the optimized ($15^s12^p2^d$) basis set are listed in Table 1. The magnitudes of the resulted SCF coefficient matrix elements belonging to the optimum exponent set $\{\alpha_i\}$ suggested a particular grouping and contraction of the primitive functions. This grouping into subsets is illustrated in detail by Table 1. The numerical values of the contraction coefficients were obtained by renormalizing the original SCF coefficient matrix elements belonging to each particular subset in the corresponding SCF orbital. These contraction coefficients are collected in Table 1.

The atomic SCF results, obtained with our optimized GTF basis set are comparable with those reported earlier by Straub and McLean [7] using two different quality STO basis sets as shown in Table 2. Clearly the accuracy of our results falls between those of their minimal STO and DZ+ polarization STO bases. Although, in absolute terms the calculated total energy is well above the Hartree-Fock limit, the comparison of the 3d orbital energy to that obtained with the superior STO basis suggests that the difference in total energy is due mainly to the restrictions imposed on the dimension of the *d*-subset. Though orbital energies do not measure unambiguously the quality of basis functions, the fact that most calculated orbital energies are comparable or even lower, than the corresponding value with the ($8^s6^p4^d2^f$) STO basis suggests that the chemically more important *s* and *p* symmetry types are adequately represented.

To compare the qualities of Huzinaga's (9^s5^p) fluorine basis [4] and Veillard's (12^s9^p) chlorine basis [5] to our optimized ($15^s12^p2^d$) basis for bromine, we also evaluated the G_i gradient components for the above fluorine and chlorine bases.

Table 2. Calculated orbital energies, total energy and virial coefficient of bromine atom

		STO[a]		GTO[b]
Orbital		($8^s6^p4^d2^f$)	($4^s3^p3^d2^f$)	($15^s12^p2^d$)
Orbital Energies				
	1*s*	−490.0251	−489.5194	−490.4120
	2*s*	− 65.1508	− 63.7984	− 65.3242
	3*s*	− 9.8350	− 9.0972	− 9.7614
	4*s*	− 0.9757	− 0.8552	− 0.9717
	2*p*	− 58.5048	− 58.1141	− 58.7158
	3*p*	− 7.4417	− 7.0051	− 7.3839
	4*p*	− 0.4430	− 0.3675	− 0.4511
	3*d*	− 3.1766	− 2.3323	− 2.5284
Total energy		−2572.316774	−2564.265888	−2566.527220
Virial coefficient		−1.99987	−1.97512	−2.000123

[a] Reference [7]. [b] Present work.

The gradient lengths obtained,

$$\begin{aligned}|G|_{\mathrm{F}}&=2.85\times 10^{-3}\\ |G|_{\mathrm{Cl}}&=6.36\times 10^{-4}\\ |G|_{\mathrm{Br}}&=6.79\times 10^{-3},\end{aligned}\tag{3}$$

indicate that the basis sets approximate the corresponding optima by about the same accuracy.

Test calculations have been performed on the HBr molecule using the $[8^s6^p2^d]$ "double zeta" contraction of the optimized $(15^s12^p2^d)$ basis for bromine as specified in Table 1 and Huzinaga's (4*s*) basis for hydrogen [4]. In these calculations the H–Br bond distance was taken as 2.6576 Bohr a.u. which is the same as that Straub and McLean assumed in their *ab initio* calculation using $(8^s6^p4^d2^f)$ Slater basis [7]. The calculated SCF energy is −2566.79606 a.u. which compares favourably to the −2572.95156 a.u. result of Straub and McLean, particularly when it is realized that these latter SCF calculations employed twice as many 3*d* AO on Br supplemented with *f*-type polarization functions.

In Table 3 the calculated one-electron properties are presented, including the results of Straub and McLean obtained using STO basis set. The present results do not show considerable deviations from the corresponding STO results. This favourable comparison suggests that for the purpose of molecular calculations

Table 3. Calculated one-electron properties for the HBr molecule

		This Work		STO result[a]		Exp
		Electronic	Total	Electronic	Total	
Potential	Br	−175.91528	−175.53901	−176.2174		
	H	− 14.07864	− 0.90886	− 14.1387		
Electric Field Z component	Br	0.08187	− 0.05972			
	H	− 4.80917	0.14634			
Field Gradient	Br	− 7.71738	− 7.82392		−7.5842	
	H	3.39788	− 0.33143		−0.240	
Dipole Moment	CM	− 0.85500	0.62144		0.931	0.834[b]
Quadrupole Moment	CM	− 3.90739	3.01981		3.784	
Third Moment	CM	− 17.55926	0.52305			
Second Moment	CM	− 18.99275	− 12.06555			
Charge Density	Br	29148.88823	29148.88823			
	H	0.34114	0.34114			

[a] Ref. [7]. [b] W.H. Robinette, R.B. Sanderson: Appl. Optics **8**, 711 (1969).

the optimized Bromine ($15^s12^p2^d$) Gaussian basis set, contracted to [$8^s6^p2^d$] "double zeta" set represents a good compromise between the opposing requirements of accuracy and economy.

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