Theor Chem Acc (2001) 106: 297–300
DOI 10.1007/s002140100278

Theoretical
Chemistry Accounts

Regular article

Contracted polarization functions for the atoms Ca, Ga–Kr, Sr, and In–Xe

Masahiro Sekiya[1], **Takeshi Noro**[1], **You Osanai**[2], **Toshikatsu Koga**[3]

[1] Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan
[2] Aomori University, Aomori 030-0943, Japan
[3] Department of Applied Chemistry, Muroran Institute of Technology, Muroran 050-8585, Japan

Received: 23 February 2001 / Accepted: 19 April 2001 / Published online: 13 June 2001
© Springer-Verlag 2001

Abstract. Contracted Gaussian-type function sets are proposed for polarization functions of the atoms Ga–Kr and In–Xe. We also report polarization functions for Ca and Sr. A segmented contraction scheme is used for its compactness and computational efficiency. The contraction coefficients and orbital exponents are fully optimized to minimize the deviation from accurate atomic natural orbitals. The present polarization functions yield more than 99% of atomic correlation energies predicted by accurate natural orbitals of the same size.

Key words: Polarization functions – Correlating functions – Contracted Gaussian-type functions

1 Introduction

The inclusion of electron correlation effects is inevitable for a quantitative description of the electronic structure of molecules; therefore, highly correlated wave functions are often computed. Even when a sophisticated electron correlation technique is employed, however, the accuracy of the resultant wave function is largely dependent on the quality of the basis sets by which the molecular orbitals are approximated. In particular, the supplement of some basis functions which well describe both the correlation and polarization contributions is significant in molecular calculations. For this reason, we started to construct compact yet efficient correlating or polarization functions in a series of works [1, 2, 3]. In this study, we call them polarization functions.

In the first and second reports [1, 2], we proposed a new method for the construction of polarization function sets. Our method uses contracted (c) Gaussian-type functions (GTFs) in a segmented form to achieve both computational efficiency and compactness. The contraction coefficients and GTF exponents are determined so as to minimize the difference between the cGTFs and the accurate natural orbitals (NOs) in the polarization space. The method has been successfully applied to the atoms from He to Ar except Li and Na. The new polarization functions reproduce more than 99% of atomic correlation energies predicted by accurate NOs of the same size. These sets are superior to the correlation-consistent basis sets [4] and are more compact than the atomic NOs [5, 6]. In the third report [3] of this series, we applied the same method to the first transition-metal atoms from Sc to Zn and obtained the basis sets for both $4s$ and $3d$ valence functions as well as polarization functions. These new basis sets gave a well-balanced description for the two lowest states arising from the $4s^2 3d^n$ and $4s^1 3d^{n+1}$ configurations in Hartree–Fock calculations and yielded more than 97% of the atomic correlation energies predicted by accurate NOs of the same size.

When we go ahead in the periodic table, a few polarization sets are available for Ga–Kr [4, 7, 8]; however, their small sets are not expected to be sufficiently accurate as observed for light atoms. For In–Xe, Huzinaga et al. [7] prepared d polarization functions, but they did not give any f and g polarization functions, which are important for highly correlated molecular wave functions.

The current work is the fourth of our series, and we report here polarization basis functions for the atoms Ca, Ga–Kr, Sr, and In–Xe constructed by using the method proposed previously [1, 2]. In the next section, our computational procedure is outlined and the results for atomic polarization functions are summarized. In Sect. 3, test calculations of the present polarization function sets are given for the As_2, GeSe, and GaBr molecules in comparison with the correlation-consistent basis sets [4].

2 Atomic polarization functions

As in the previous work [1, 2, 3], both the contraction coefficients and the exponents of the GTFs were

Correspondence to: M. Sekiya

determined to minimize the difference between cGTFs and sufficiently accurate atomic NOs in the polarization space. We used the following functional:

$$\Delta = \sum_{k=1}^{N_f} n_k \int d\mathbf{r} |\lambda_k(\mathbf{r}) - \psi_k(\mathbf{r})|^2 w(\mathbf{r}) \ , \quad (1)$$

$$\psi_k(\mathbf{r}) = \sum_{i=1}^{N_f} C_{ki} \chi_i(\mathbf{r}) \ , \quad (2)$$

where $\{\lambda_k\}$ are accurate NOs, $\{n_k\}$ are their occupation numbers, $\{\chi_i\}$ is a polarization basis set, N_f is its size, and $w(\mathbf{r})$ is a weight function. In this functional, the occupation numbers $\{n_k\}$ incorporate the relative significance of NOs in the polarization space. For the weight function $w(\mathbf{r})$, we employed $1/r^2$, which was found [1] to give the most appropriate correlation energies among several forms of weight functions when atomic configuration interaction (CI) calculations were carried out. The conjugated direction algorithm [9] was used for nonlinear optimizations of the GTF exponents and contraction coefficients. We note that this optimization can be performed independently for each symmetry l of the polarization space.

To obtain sufficiently accurate NOs, we first performed CI calculations by using the program ATOMCI [10] on the ground states of the target atoms: Ca, Ga–Kr, Sr, and In–Xe. We considered all single and double excitations out of the valence s and p subshells with large, well-tempered basis sets [11]: (26s19p10d10f) for Ca, (26s20p16d10f10g) for Ga–Kr, (27s23p20d10f) for Sr, and (28s23p20d10f10g) for In–Xe. The NOs of the CI wave function were truncated by the criterion of the occupation number to form a contracted set of a desired size. We may expect these NOs are almost convergent to the exact ones and hereafter we refer to them as accurate NOs.

In the present study, we constructed [1p], [2p1d], [3p2d1f] for Ca and Sr, [1d], [2d1f], [3d2f1g] for Ga–Kr, and [1d], [2d1f], [2d2f1g] for In–Xe. The present exponent parameters and contraction coefficients are exemplified for Se and Te, respectively, in Table 1. In a segmented contraction form, we implicitly used two primitive GTFs for the first polarization function, and a single primitive for the remainder, of each symmetry. When there was no essential improvement, we used a single primitive GTF even for the first polarization function as in the case of the first d or f function of the [3d2f1g] set for the Se atom (Table 1). For In–Kr, we constructed the [2d2f1g] set, instead of [3d2f1g], because the occupation number of the third d NO is quite small and its contribution to the correlation energy is negligible.

The correlation energies obtained from the present cGTFs are summarized in Tables 2 and 3 along with those from the accurate NOs. The present basis sets reproduce more than 99% of atomic correlation energies obtained by the accurate NOs of the same size for all the atoms. We thus consider that these sets have a quality similar to that of the previous sets for lighter atoms [1, 2].

Table 1. The polarization contracted Gaussian-type function (cGTF) sets for Se and Te atoms. For each polarization set, the first line gives the exponents and the second line gives the contraction coefficients

Se	[1d]	d	0.565342	0.208212			
			0.525124	0.573169			
	[2d1f]	d	0.671107	0.469635	/	0.207030	
			0.431709	0.581749	/	1.000000	
		f	0.686542	0.264974			
			0.509292	0.603744			
	[3d2f1g]	d	0.662710		/	0.365754	/ 0.169769
			1.000000		/	1.000000	/ 1.000000
		f	0.691697		/	0.266128	
			1.000000		/	1.000000	
		g	0.706388	0.300643			
			0.611323	0.500399			
Te	[1d]	d	0.349678	0.139123			
			0.631674	0.450858			
	[2d1f]	d	0.382723		/	0.160813	
			1.000000		/	1.000000	
		f	2.290296	0.330054			
			0.088121	0.982286			
	[2d2f1g]	d	0.382723		/	0.160813	
			1.000000		/	1.000000	
		f	0.590821		/	0.209710	
			1.000000		/	1.000000	
		g	0.491952	0.216360			
			0.667487	0.432367			

Table 2. Comparison of correlation energies (in hartrees) from the present cGTF sets and the accurate natural orbitals (NOs) of the same size

Atom	Basis set	Present cGTFs	Accurate NOs	Reproduction percentage
Ca	[1p]	−0.027412	−0.027545	99.51
	[2p1d]	−0.028515	−0.028735	99.23
	[3p2d1f]	−0.028759	−0.028873	99.61
Ga	[1d]	−0.047546	−0.047588	99.91
	[2d1f]	−0.050366	−0.050420	99.89
	[3d2f1g]	−0.051111	−0.051142	99.94
Ge	[1d]	−0.061492	−0.061568	99.88
	[2d1f]	−0.068259	−0.068360	99.85
	[3d2f1g]	−0.069974	−0.070037	99.91
As	[1d]	−0.072709	−0.072809	99.86
	[2d1f]	−0.085706	−0.085862	99.82
	[3d2f1g]	−0.088827	−0.088935	99.88
Se	[1d]	−0.093540	−0.093671	99.86
	[2d1f]	−0.123196	−0.123478	99.77
	[3d2f1g]	−0.130834	−0.131054	99.83
Br	[1d]	−0.113597	−0.113760	99.86
	[2d1f]	−0.155707	−0.156104	99.75
	[3d2f1g]	−0.168945	−0.169275	99.80
Kr	[1d]	−0.132435	−0.132632	99.85
	[2d1f]	−0.182833	−0.183327	99.73
	[3d2f1g]	−0.202891	−0.203333	99.78

3 Molecular test calculations

To examine the quality of the present polarization functions for molecular systems, we calculated the

spectroscopic constants and total energies of diatomic As_2, GeSe, and GaBr molecules in their ground states. Both complete-active-space self-consistent field (CASSCF) and multireference single and double excitation (MRSD) CI calculations were performed with the program ALCHEMY II [12]. In the CASSCF calculations, we considered six electrons in six $4p$ orbitals as the active space. In the MRSDCI calculations, all double excitations from $(4p\sigma, 4p\pi)$ to $(4p\sigma^*, 4p\pi^*)$ were included in the reference space and two $4s$ electrons were also correlated. The *sp* set was taken from the minimal-type (7433/743/7) prepared by Koga et al. [13], and its valence $4s$ and $4p$ orbitals were decontracted into (21) and (111), respectively. The present [1d], [2d1f], and [3d2f1g] polarization sets were then added to the *sp* set. For comparison, we also tested the polarization functions of Dunning's cc-pVDZ, cc-pVTZ, and cc-pVQZ sets [4] by adding to the *sp* set described earlier.

Table 3. Comparison of correlation energies (in hartrees) from the present cGTF sets and the accurate NOs of the same size

Atom	Basis set	Present cGTFs	Accurate NOs	Reproduction percentage
Sr	[1p]	−0.024778	−0.024907	99.48
	[2p1d]	−0.026157	−0.026302	99.44
	[3p2d1f]	−0.026364	−0.026416	99.80
In	[1d]	−0.043143	−0.043159	99.96
	[2d1f]	−0.045690	−0.045758	99.85
	[2d2f1g]	−0.046301	−0.046365	99.86
Sn	[1d]	−0.054470	−0.054497	99.95
	[2d1f]	−0.060724	−0.060882	99.74
	[2d2f1g]	−0.062131	−0.062270	99.78
Sb	[1d]	−0.062804	−0.062840	99.94
	[2d1f]	−0.074920	−0.075356	99.42
	[2d2f1g]	−0.077759	−0.078002	99.69
Te	[1d]	−0.079530	−0.079579	99.94
	[2d1f]	−0.107760	−0.108940	98.92
	[2d2f1g]	−0.114903	−0.115549	99.44
I	[1d]	−0.095335	−0.095398	99.93
	[2d1f]	−0.135353	−0.137087	98.74
	[2d2f1g]	−0.147844	−0.148955	99.25
Xe	[1d]	−0.109761	−0.109841	99.92
	[2d1f]	−0.157039	−0.158848	98.86
	[2d2f1g]	−0.176289	−0.177515	99.31

The calculated equilibrium internuclear distances (R_e), the vibrational constants (ω_e), and the total energies (E_e) for the ground states of As_2, GeSe, and GaBr are shown in Table 4 along with previous theoretical and experimental results [14, 15, 16]. At both the CASSCF and MRSDCI levels of calculations, the present sets give better E_e values than the correlation-consistent sets for all three molecules. In particular, the E_e values given by the present [1d] sets are lower than those given by the correlation-consistent [1d] sets by 0.0015–0.003 hartrees in CASSCF and by 0.005 hartrees in MRSDCI. There are significant differences between the spectroscopic constants calculated with [1d] of the present and the correlation-consistent sets, although almost the same spectroscopic constants were predicted by the larger sets, [2d1f] and [3d2f1g]. The results with the largest sets, [3d2f1g], are in good agreement with the previous theoretical and experimental ones. We did not perform the molecular test calculations including the atoms In–Xe but we expect that the present sets have almost the same quality as those for the lighter atoms.

Table 4. Comparison of spectroscopic constants and total energies for the ground-state of As_2, GeSe, and GaBr molecules

Method/Set		As_2			GeSe			GaBr		
		R_e	ω_e	E_e	R_e	ω_e	E_e	R_e	ω_e	E_e
Complete-active-space self-consistent field										
[1d]	cc-pVDZ	4.081	398.8	−0.47255	4.121	389.3	−0.29148	4.533	261.9	−0.76489
	Present	4.074	400.1	−0.47382	4.113	385.7	−0.29298	4.537	260.4	−0.76718
[2d1f]	cc-pVTZ	4.063	404.0	−0.47754	4.091	392.8	−0.29847	4.513	263.5	−0.77262
	Present	4.063	403.9	−0.47768	4.091	392.5	−0.29867	4.514	262.9	−0.77290
[3d2f1g]	cc-pVQZ	4.059	405.3	−0.47872	4.087	394.3	−0.29980	4.511	262.0	−0.77377
	Present	4.060	405.0	−0.47874	4.087	394.0	−0.29981	4.511	262.0	−0.77379
Multireference single and double excitation configuration interaction										
[1d]	cc-pVDZ	4.060	416.4	−0.61465	4.127	402.7	−0.43551	4.549	262.5	−0.89585
	Present	4.057	414.8	−0.61915	4.129	407.8	−0.44034	4.552	260.7	−0.90137
[2d1f]	cc-pVTZ	4.024	430.9	−0.65880	4.103	401.2	−0.48313	4.526	268.0	−0.94847
	Present	4.025	429.8	−0.65974	4.105	399.7	−0.48415	4.532	266.0	−0.94989
[3d2f1g]	cc-pVQZ	4.012	436.9	−0.67290	4.092	404.4	−0.49889	4.525	266.5	−0.96723
	Present	4.013	436.3	−0.67353	4.093	404.2	−0.49946	4.526	266.1	−0.96790
SOCI + Q/8s6p4d2f1g[a]		4.03	429.6							
Second-order Møller-plesset/triple-zeta polarized[b]					4.057	406				
Experimental[c]		3.975	429.55		4.035	408.7		4.447	263.0	

Bond lengths and frequencies are given in bohrs and reciprocal centimeters, respectively. Total energies are given in hartrees and are shifted by +4468, +4475, and +4495 hartrees for As_2, GeSe, and GaBr, respectively

[a] Ref. [14]. SOCI + Q denotes second-order configuration interaction with the multireference analog of Davidson's correction

[b] Ref. [15]

[c] Ref. [16]

4 Summary

We developed cGTF polarization basis sets [1p], [2p1d], [3p2d1f] for Ca and Sr, [1d], [2d1f], [3d2f1g] for atoms Ga–Kr, and [1d], [2d1f], [2d2f1g] for atoms In–Xe. Despite their smallness, all these sets reproduce more than 99% of the atomic correlation energies predicted by the accurate NOs of the same size. Test calculations on the diatomic molecules As_2, GeSe, and GaBr showed that the present sets give better correlation energies than the correlation-consistent basis sets for all the cases, especially for [1d] sets.

All the present polarization basis sets are available through the internet at http://setani.sci.hokudai.ac.jp/qc/basis/.

Acknowledgement. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

References

1. Noro T, Sekiya M, Koga T (1997) Theor Chem Acc 98: 25
2. Sekiya M, Noro T, Koga T, Matsuyama H (1998) J Mol Struc (THEOCHEM) 451: 51
3. Noro T, Sekiya M, Koga T, Matsuyama H (2000) Theor Chem Acc 104: 146
4. (a) Dunning TH Jr (1989) J Chem Phys 90: 1007; (b) Woon DE, Dunning TH Jr (1993) J Chem Phys 98: 1358; (c) Woon DE, Dunning TH Jr (1994) J Chem Phys 100: 2975
5. (a) Almlöf J, Taylor PR (1987) J Chem Phys 86: 4070; (b) Bauschlicher CW Jr, Langhoff SR, Kormornicki A (1990) Theor Chim Acta 77: 263
6. Pou-Amérigo R, Merchán M, Nebot-Gil I, Widmark P-O, Roos BO (1995) Theor Chim Acta 92: 149
7. Huzinaga S, Andzelm J, Klobukowski M, Radio-Andzelm E, Sakai Y, Tatewaki H (1984) In: Huzinaga S (ed) Gaussian basis sets for molecular calculations. Elsevier, Amsterdam, pp 1
8. Binning RC Jr, Curtiss LA (1990) J Comput Chem 11: 1206
9. Powell MJD (1964) Comput J 7: 155
10. (a) Sasaki F (1974) Int J Quantum Chem 8: 605; (b) Sasaki F, Sekiya M, Noro T, Ohtsuki K, Osanai Y (1993) In: Clementi E (ed) Methods and techniques in computational chemistry: METECC-94, vol A. STEF, Caglilari, pp 163–219
11. (a) Huzinaga S, Miguel B (1990) Chem Phys Lett 175: 289; (b) Huzinaga S, Klobukowski M (1993) Chem Phys Lett 212: 260
12. (a) Lengsfield BH III (1980) J Chem Phys 73: 382; (b) Liu B, Yoshimine M (1981) J Chem Phys 74: 612; (c) Lengsfield BH III, Liu B (1981) J Chem Phys 75: 478
13. Koga T, Tatewaki H, Matsuyama H, Satoh Y (1999) Theor Chem Acc 102: 105
14. Mochizuki Y, Tanaka K (1997) Chem Phys Lett 274: 264
15. Leszczynski J, Kwiatkowski JS, Leszczynska D, Hale B (1994) Chem Phys Lett 226: 413
16. Huber K, Herzberg G (1979) Molecular spectra and molecular structure 4. Constants of diatomic molecules. Van Nostrand, Princeton, NJ