A set of d-polarization functions for pseudo-potential basis sets of the main group elements Al–Bi and f-type polarization functions for Zn, Cd, Hg

A. Höllwarth, M. Böhme, S. Dapprich, A.W. Ehlers, A. Gobbi, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking [1]

Fachbereich Chemie, Universität Marburg, Hans-Meerwein-Strasse, W-3550 Marburg, Germany

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A set of five-component d-type polarization functions has been optimized for the main group elements Al–Bi at the energetically lowest lying s^2p^n electronic states for use with the effective core potentials of Hay and Wadt at the CISD level of theory. Also a set of f-type polarization functions is suggested for the elements Zn, Cd and Hg.

1. Introduction

Recently we reported [1] a set of f-type polarization functions for use in conjunction with the small-core effective-core potentials (ECP) of Hay and Wadt [2] for the transition metals Sc–Cu, Y–Ag and La–Au. The same authors have also presented optimized ECPs and s, p valence orbitals for the main group elements [3]. In this Letter, we report the results of optimizing a set of five-component d-type polarization functions for ECP valence orbitals [3] of the main group elements Al–Bi using the same procedure as described in the previous Letter [1]. The d-type polarization functions for the alkaline and earth alkaline elements K, Rb, Cs, Ca, Sr, Ba, have been optimized in conjunction with the small-core ECPs [2], which do not replace the $(n-1)s^2$ and $(n-1)p^6$ electrons by a core potential. We also optimized sets of seven-component f-type polarization functions for the elements Zn, Cd and Hg which formally belong to the group of transition metals, but behave chemically as main group elements because the d shell is completely filled. ECPs for Zn, Cd and Hg are also optimized by Hay and Wadt [4].

[1] To whom correspondence should be addressed.

2. Theoretical methods

The calculations have been performed using the Convex version of GAUSSIAN 92 [5]. The valence basis sets for the main group elements are derived from the (3/3) minimal basis sets optimized by Hay and Wadt [3]. We used the valence double-zeta contraction scheme (21/21) augmented by a set of d-type functions, i.e. (21/21/1). For alkaline and earth-alkaline metals the (55/5) minimal basis set [2] was split into (441/2111). In case of the transition metals the minimal basis sets are split (3/2/5)→(21/11/41) for Zn, (3/3/4)→(21/21/31) for Cd, (3/3/3)→(21/21/21) for Hg and then augmented by a set of f-type functions.

The optimization of the polarization functions was carried out in two steps similar to the method used for the calculations of f-polarization functions of the transition metals [1]. First, the HF energies were calculated for the lowest lying electronic state of the configuration s^2p^n. For the alkaline elements K, Rb and Cs, the ^2S state with the configuration s^1p^0 was

Table 1
Optimized d exponents for the main group elements Al–Bi

		Al	Si	P	S	Cl	Ar
		0.190	0.284	0.387	0.503	0.640	0.786
K	Ca	Ga	Ge	As	Se	Br	Kr
1.000	1.245	0.185	0.230	0.303	0.364	0.428	0.499
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.491	0.699	0.143	0.180	0.218	0.252	0.289	0.326
Cs	Ba	Tl	Pb	Bi			
0.306	0.438	0.147	0.172	0.202			

Table 2
HF energies (au) without and with d functions

		Al	Si	P	S	Cl	Ar
		−1.86947	−3.67570	−6.31523	−9.87464	−14.68131	−20.67321
		−1.87298	−3.69529	−6.31523	−9.87863	−14.68547	−20.67321
K	Ca	Ga	Ge	As	Se	Br	Kr
−27.85216	−36.21537	−1.94526	−3.59814	−5.95615	−9.01108	−12.91872	−17.86551
−27.85216	−36.21537	−1.94812	−3.61566	−5.95615	−9.01460	−12.92241	−17.86551
Rb	Sr	In	Sn	Sb	Te	I	Xe
−23.58341	−30.09938	−1.78307	−3.23323	−5.25996	−7.85673	−11.15731	−15.22433
−23.58341	−30.09938	−1.78584	−3.24838	−5.25996	−7.85990	−11.16061	−15.22433
Cs	Ba	Tl	Pb	Bi			
−19.60690	−24.85736	−1.75897	−3.16590	−5.30858			
−19.60690	−24.85739	−1.76025	−3.16590	−5.30858			

calculated. For Zn, Cd and Hg, the ^1S state with the configuration s^2d^{10} was calculated.

The desired spin state was controlled by Mulliken population analysis [6]. Then the energy was computed by configuration interaction [7] with all single and double substitutions (CISD) from the HF reference determinant. The optimal d exponents were obtained by numerical interpolation of the calculated atomic energies at the CISD level using the (441/2111/1) valence basis set for the alkaline and earth-alkaline elements and the (21/21/1) valence basis set for the other main group elements. For the transition metals the basis sets are (21/11/41/1) for Zn, (21/21/31/1) for Cd and (21/21/21/1) for Hg.

3. Results and discussion

The optimized d exponents for the main group elements are shown in table 1. The HF energies of the atoms calculated with and without the d functions are summarized in table 2. The CISD energies are listed in table 3. The HF energy does not change by including the d functions if the p shell is empty, half occupied or fully occupied.

The optimized f exponents for Zn, Cd and Hg are

Table 3
CISD energies (au) without and with d functions

		Al	Si	P	S	Cl	Ar
		−1.89676	−3.67962	−6.32447	−9.89019	−14.70351	−20.70193
		−1.91920	−3.74238	−6.39308	−9.97566	−14.80453	−20.81757
K	Ca	Ga	Ge	As	Se	Br	Kr
−27.87544	−36.26192	−1.97119	−3.60145	−5.96264	−9.02204	−12.93321	−17.88295
−28.00675	−36.34349	−1.99139	−3.65739	−6.02508	−9.09899	−13.02541	−17.98831
Rb	Sr	In	Sn	Sb	Te	I	Xe
−23.60032	−30.13593	−1.80606	−3.23627	−5.26597	−7.86507	−11.16767	−15.23695
−23.66310	−30.26326	−1.82482	−3.28648	−5.32119	−7.93445	−11.25064	−15.33164
Cs	Ba	Tl	Pb	Bi			
−19.61924	−24.92023	−1.94077	−3.34002	−5.31458			
−19.67364	−25.03233	−1.956719	−3.38306	−5.36199			

Table 4
Optimized f exponents for the elements Zn, Cd and Hg

Zn	Cd	Hg
3.031	1.495	1.002

shown in table 4. The HF and CISD energies calculated with and without f functions for these elements are summarized in table 5.

Fig. 1 shows graphically the trend in the d exponents for the main group elements. The exponents become smaller for heavier atoms within a group, with exception of Tl, which has a slightly larger exponent (0.147) than In (0.143). There is a steady increase in the value of the exponents within a row with increasing number of valence electrons. Note that the $(n-1)$s and $(n-1)$p electrons are treated explicitly only for the alkaline and earth-alkaline elements. This may be the reason for the hump in the curve from Kr to Rb and from Xe to Cs. The ECPs have nine electrons for the atoms of main group I and ten electrons for the atoms of main group II.

It is interesting to compare the d exponents for the polarization functions of the ECP valence orbitals with all-electron values. This is shown in fig. 2. Note that the d exponents for the all-electron wavefunctions are optimized at the HF level of theory [8]. The d exponents for the ECP valence orbitals and the all-electron values are quite similar, in particular for the elements of the fourth, fifth and sixth rows of the period system. Slightly larger differences are found for the heavier elements of the third row. The ECP-polarization functions are in most cases a little larger than the all-electron functions. It may be concluded that in cases where polarization functions for ECPs are not available, it is justified to use exponents optimized for all-electron wavefunctions.

Table 5
HF and CISD energies (au) for Zn, Cd and Hg without and with f functions

HF			CISD		
Zn	Cd	Hg	Zn	Cd	Hg
−63.52056	−46.57144	−41.41183	−63.68709	−46.65965	−41.50598
−63.52056	−46.57144	−41.41183	−63.79996	−46.84132	−41.69834

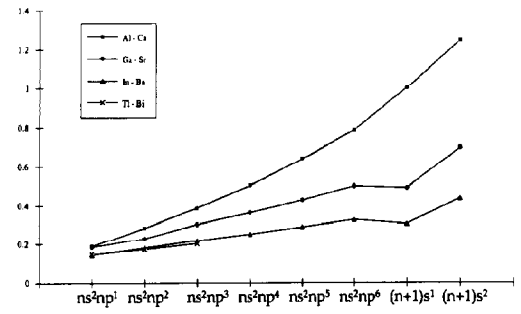

Fig. 1. Optimized d exponents for the main group elements Al–Bi.

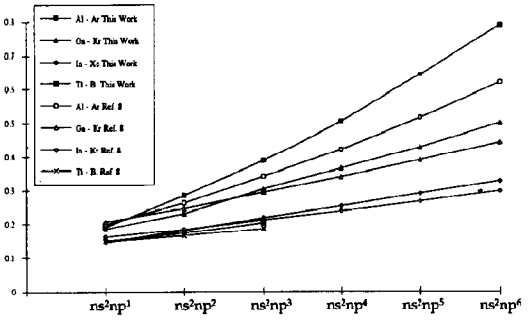

Fig. 2. Optimized d exponents for the main group elements Al–Bi compared to all-electron calculations [8].

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