Volume 208, number 1,2 CHEMICAL PHYSICS LETTERS 4 June 1993

A set of f-polarization functions for pseudo-potential basis sets of the transition metals Sc–Cu, Y–Ag and La–Au

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Received 2 December 1992

A set of seven-component f-type polarization functions has been optimized for use with the pseudo-potentials of Hay and Wadt at the CISD level of theory for the transition metals Sc–Cu, Y–Ag, La–Au in the energetically lowest-lying s^1d^n electronic state.

1. Introduction

Because the computational efforts of ab initio calculations increase rapidly with the number of electrons, the core functions are often replaced by an effective core potential (ECP) and in particular for heavy atoms [1]. Several sets of ECPs have been developed by various authors [2–9]. We have recently published [10] a systematic test of the accuracy of theoretically predicted geometries for transition metal complexes using various ECPs with differently contracted valence shell basis sets. In this [10] and in other [11] studies we found that the geometries of transition metal complexes in high oxidation states can be calculated in good agreement with experiment at the Hartree-Fock (HF) level of theory using the $(441/41/(N-1)1)$ or $(441/2111/(N-1)1)$ valence basis set developed by Hay and Wadt [3]. For the calculation of energies, however, it was found that additional f-type polarization functions may become important [12]. Since f functions were not available for the ECPs used in our studies [10–12], we optimized the exponents for seven-component f-type polarization functions for calculations using configuration interaction with single and double substitution (CISD) in conjunction with the $(441/2111/(N-1)1)$ valence basis set for the transition metals Sc–Cu, Y–Ag and La–Au. The results are reported in this study.

2. Theoretical methods

The calculations have been performed using the Convex version of GAUSSIAN 92 [13]. The valence basis sets of the transition metals are derived from the $(55/5/N)$ minimal basis sets [#1] optimized by Hay and Wadt [3]. We used the contracting scheme $(441/2111/(N-1)1)$ with $N=5$ for the first, $N=4$ for the second and $N=3$ for the third row of the transition metals.

The calculation of the f-polarization functions was carried out in two steps. First, the UHF [14] energy was calculated for the s^1d^n state with the highest possible spin state which was monitored by Mulliken population analysis [15]. Then the energy was computed using configuration interaction [16] with all CISD from the UHF reference determinant. The optimal f exponents were obtained by numerical interpolation of the calculated atomic energies at the CISD

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[#1] This is not identical with LANL2MB implemented in GAUSSIAN 92 [13]. The latter has an additional p function for the second- and third-row transition metals which is not given in ref. [3].

level using the (441/2111/($N-1$)1/1) valence basis set.

3. Results and discussion

The optimized f exponents are summarized in table 1. The values of the f exponents increase exponentially within one period with increasing atomic number. This trend is shown graphically in fig. 1. The curve shows a hump for the first members of the third-row transition metals because there is a jump in the atomic numbers between the first element La (57) and the second element Hf (72). It is obvious that the "lanthanide-contraction" induces less diffuse f functions for the elements Hf–Au. The values for the f exponents decrease with increasing atomic number within one group.

The UHF energies of the atoms at the electronic state of highest multiplicity calculated with and without additional f functions are summarized in table 2. For the elements of the fourth and ninth triads (Cr, Mo, W, Cu, Ag, Au) the calculated energies at the HF level do not change with an additional f function. For the other elements the maximum energy lowering at the HF level is obtained for states with three unpaired and two unoccupied d electrons (Ti triad), and three paired and two unpaired d elec-

Table 1
f exponents for the first-, second- and third-row transition metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
1.335	1.506	1.751	1.941	2.195	2.462	2.780	3.130	3.525
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
0.835	0.875	0.952	1.043	1.134	1.235	1.350	1.472	1.611
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
0.591	0.784	0.790	0.823	0.869	0.886	0.938	0.993	1.050

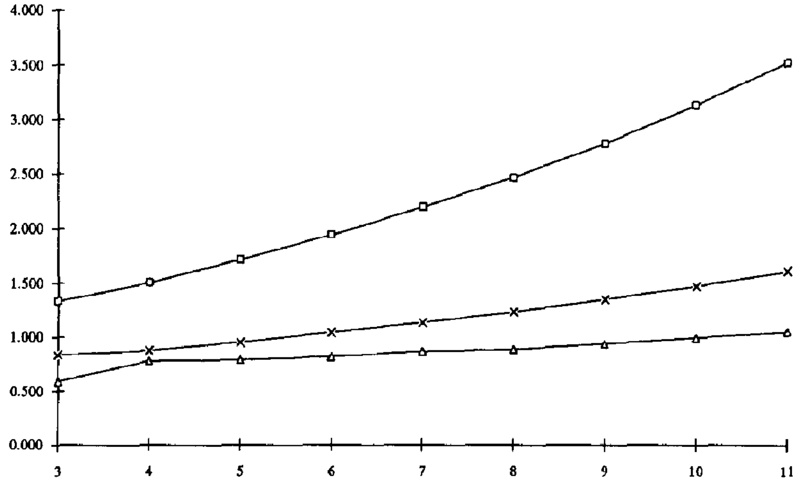

Fig. 1. f exponents for the (□) first-, (×) second- and (△) third-row transition metals.

Table 2
UHF energies (au) with and without an f function for the lowest-lying s^1d^n state

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
−45.92331	−57.48098	−70.67968	−85.65794	−103.11747	−122.53943	−144.08356	−168.21291	−194.99177
−45.92640	−57.48486	−70.68219	−85.65794	−103.11983	−122.54446	−144.08868	−168.21582	−194.99177
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
−37.43105	−45.98220	−55.68176	−66.90180	−79.34132	−93.11322	−108.68830	−125.86224	−144.89151
−37.43349	−45.98580	−55.68432	−66.90180	−79.34416	−93.11925	−108.69464	−125.86588	−144.89151
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
−30.77160	−48.23880	−57.09645	−67.09190	−78.27144	−90.18086	−103.79734	−118.22716	−134.53145
−30.77492	−48.24134	−57.09836	−67.09190	−78.27366	−90.18545	−103.80232	−118.23013	−134.53145

Table 3
CISD energies (au) with and without an f function for the lowest-lying s^1d^n state

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
−46.06083	−57.62669	−70.83266	−85.81021	−103.28311	−122.71083	−144.27048	−168.41605	−195.20820
−46.92640	−57.70846	−70.93393	−85.92820	−103.41409	−122.85344	−144.42268	−168.57324	−195.36717
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
−37.51863	−46.07988	−55.78320	−66.99514	−79.44223	−93.21408	−108.78809	−125.97978	−145.00627
−37.57517	−46.15996	−55.88836	−67.12259	−79.59296	−93.38607	−108.97758	−126.17735	−145.21811
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
−30.85191	−48.32218	−57.18262	−67.17273	−78.36669	−90.28353	−103.89817	−118.31693	−134.61516
−30.91870	−48.38541	−57.26766	−67.27877	−78.50017	−90.43856	−104.07542	−118.51081	−134.82628

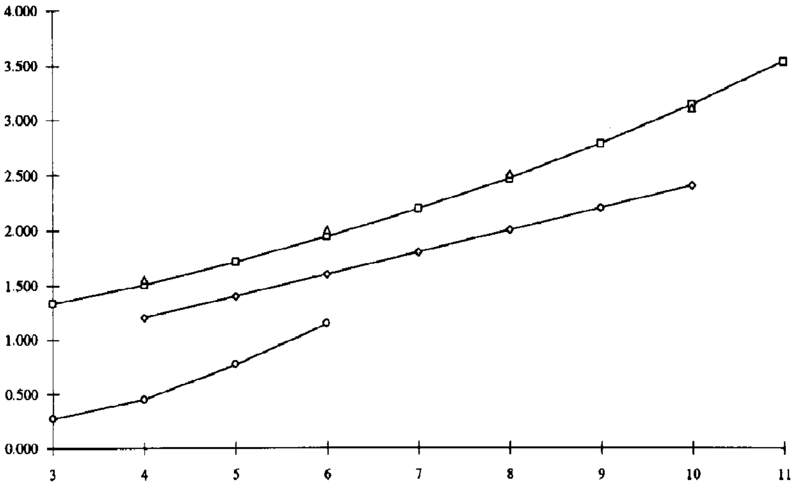

Fig. 2. f exponents for the first-row transition metals compared to all-electron calculations. (□) This work, (△) ref. [16], (◇) ref. [19], (○) ref. [20].

trons (Co triad). The difference between the CISD energies with and without f functions listed in table 3 increases steadily from the early to the late transition metals, La being an exception.

It is interesting to compare the optimal f exponents for ECP wavefunctions with all-electron basis sets. Bauschlicher and Walch [17] optimized a set of f functions for Ti, Cr, Fe and Ni. They used a Wachters [18] basis with two additional p functions and a diffuse d function by Hay [19] contracted to (14s11p6d)/[6s6p3d]. These authors optimized the f functions by correlating the 4s, 3s, 3p and 3d electrons at the CISD level. The values for the f exponents obtained in this manner are similar to our values for the pseudopotential basis set (fig. 2).

The same authors [20] developed another set of f functions for the same basis set contracted to (14s11p6d)/[5s4p3d] by optimizing the values of Fe and Ni and selecting the values for the other elements by linear extrapolation. These values are smaller than those of the less contracted basis set (fig. 2). Dunning and co-workers [21] also developed a set of f functions for the early transition metals of the first period using the same basis set contracted to (14s11p6d)/[5s4p3d]. These values are considerably smaller, but the exponential increase is steeper.

Acknowledgement

This work has been supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. Additional support was provided by the HLRZ Jülich, HHLR Darmstadt and the computer companies Convex and Silicon Graphics.

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