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Slater Functions for Y to Cd Atoms by the Distance between Subspaces

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Slater functions for the atoms Y–Cd have been formulated by the distance between subspaces method. Basis sets proposed here are single- and double-zeta size and have been constructed using numerical Hartree–Fock functions as reference. A comparative study with Clementi and Roetti basis sets of the same size has been carried out, obtaining a uniform criterion for the behavior of the series of atoms Y–Cd when the number of *d* electrons is varied. The new basis sets provide a better simulation of some atomic properties and appear to be appropriate for molecular and solid state calculations. © 1995 Academic Press, Inc.

INTRODUCTION

Most quantum-mechanical calculations on atoms and molecules are carried out within the framework of an expansion method. The one-electron orbitals are expressed in terms of a basis set and the expansion coefficients are chosen by minimization of the total energy. Calculations of molecules containing elements beyond the second-row transition metal atoms represent an enormous computational effort when the size of the basis set used is increased and thus few calculations have been reported. A compromise must be struck between the optimization of the quality of variables and the computational difficulty required.

While a great amount of effort has been devoted to the construction of Slater-type orbital (STO) basis sets (1–10), consistency in the choice of basis sets used in ab initio studies of transition metal compounds is still lacking. However, the progress experienced in the development of new techniques for computing the multicenter molecular integrals of STOs (4, 11) has renewed interest in the design of STO basis sets to perform molecular calculations. In fact, the generation of STO basis sets of adequate size and quality represents an appropriate tool for molecular calculations. The need for sets of STOs to be used as basis orbitals for the metal atoms is also increasing, because calculations performed on transition metal complexes are becoming more and more common.

In practice, such large basis sets can only be used for relatively small systems. This represents a severe limitation in the area of transition metal chemistry. However, experience has shown that accurate information concerning structural and chemical problems may also be obtained from medium-size basis sets. This occurs when the valence shells (and especially the *nd* shell) are granted enough flexibility to mimic the electronic relaxation involved in chemical bonding.

In regards to the second row transition elements, Clementi and Roetti (2) have carried out a very extensive study of STO basis sets using the minimization of the total atomic energy, whereby one can find small-size-type basis sets (single-zeta), intermediate-size-type basis sets (double-zeta), and very accurate large-size-type basis sets (limit Hartree–Fock). In addition, Richardson *et al.* (12) have reported STO basis sets (double zeta in the $3d$ and $4d$ orbitals) for atoms and ions of the second-transition elements in the ground states of the configurations [Kr] $4d^n$. In particular, double-zeta and larger size basis sets yielded results almost matching the corresponding HF solutions (2, 13). Recently, high-quality STO basis sets have become available (6–8). However, in problems with a large number of electrons or in processes requiring repetitive calculations, smaller basis sets are needed.

An interesting alternative approach is to prepare practical basis sets (expanded over a small basis set) that accurately reproduce the desired characteristics of a given set of high-quality basis sets (expanded over a large basis set). This idea has been fruitfully applied by us (14–16). We are interested in practical basis sets that reproduce in a satisfactory manner the characteristics of the high-quality basis sets presently available. Generation of small basis sets that optimally reproduce some desired characteristics of a larger, high-quality basis sets have been considered in the literature (12, 17). The use of small basis sets is extended as starting points in density of functional theory (18) and pseudopotential methods (19). Different criteria of simulation have been discussed and applied, all of them directed toward making molecular calculations feasible.

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BACKGROUND THEORY

In a previous paper, we extended the initial study of light atoms to the first-row transition metals (16), optimizing the distance between subspaces for the ground states of atoms Sc–Zn by using limit Hartree–Fock (LHF) as reference functions. In the present work we have obtained functions of single-zeta (SZ) and double-zeta (DZ) size from numerical Hartree–Fock (NHF) (13) as reference for the 10 atoms of the second series of transition with electronic structure [Kr] $4d^n5s^2$.

In the application of the method of the distance between subspaces to multielectronic wavefunctions (14), we define the corresponding equations for the distance between two orbitals d_i and for the distance between two multielectronic wavefunctions d_D as

$$d_i = (2 - 2p_i^{1/2})^{1/2} \quad [1]$$

and

$$d_D = 2\left(1 - \prod_{i=1}^{N} p_i\right), \quad [2]$$

where N is the number of electrons and p_i are the eigenvalues of the matricial equation,

$$\mathbf{P} = \mathbf{C}^+\mathbf{M}^+\rho\mathbf{M}\mathbf{C}, \quad [3]$$

TABLE 1
Exponents for Optimized SZ Basis Sets of Y–Cd Atoms

	Y (^2D)	Zr (^3F)	Nb (^4F)	Mo (^5D)	Tc (^6S)
1s	37.78781	38.76204	39.72876	40.70769	41.68048
2s	15.04830	15.44820	15.84290	16.24646	16.64558
3s	7.92290	8.20135	8.47998	8.75846	9.03808
4s	3.63789	3.84241	4.03783	4.22627	4.40877
5s	1.29347	1.35982	1.41718	1.46772	1.51148
2p	17.27238	17.76225	18.25190	18.71614	19.22542
3p	7.70681	8.00222	8.29695	8.59366	8.88585
4p	3.13021	3.33007	3.52120	3.69786	3.88500
3d	7.51808	7.93810	8.35678	8.74908	9.12509
4d	1.89999	2.18984	2.42280	2.63191	2.83399
	Ru (^5D)	Rh (^4F)	Pd (^3F)	Ag (^2D)	Cd (^1S)
1s	42.65297	43.62523	44.59740	45.56973	46.54161
2s	17.04454	17.44315	17.84208	18.24077	18.63929
3s	9.31737	9.59736	9.87769	10.15844	10.44017
4s	4.59317	4.77248	4.94870	5.12219	5.29351
5s	1.56261	1.60737	1.64883	1.68761	1.72263
2p	19.71999	20.21773	20.71981	21.21492	21.66843
3p	9.17818	9.46783	9.76886	10.06065	10.35423
4p	4.06595	4.24772	4.41963	4.58993	4.72638
3d	9.49155	9.84985	10.20217	10.54987	10.89383
4d	2.99733	3.16710	3.33559	3.50252	3.67046

TABLE 2
Exponents for Optimized DZ Basis Sets of Y–Cd Atoms

	Y (^2D)	Zr (^3F)	Nb (^4F)	Mo (^5D)	Tc (^6S)
1s	40.08016	41.10547	42.07157	43.04876	43.93758
1s	28.87248	29.65697	30.13625	30.50621	31.11497
2s	16.70737	16.79628	16.98062	18.11895	18.92889
2s	16.53732	17.06938	17.40227	17.95674	18.72720
3s	10.83169	11.31312	11.76450	12.22594	12.67117
3s	7.48592	7.79236	8.05652	8.46948	8.74502
4s	4.32781	4.49358	4.69700	4.89257	5.13156
4s	2.94683	3.07377	3.20935	3.37352	3.50249
5s	1.64145	1.75288	1.82798	1.89626	1.94773
5s	0.96934	1.02514	1.06053	1.09265	1.11037
2p	27.41114	28.19304	28.50994	29.26357	29.74614
2p	16.49394	16.99401	17.43996	17.92527	18.25042
3p	8.90835	9.10516	9.44099	9.76358	10.00751
3p	6.41543	6.64728	6.98834	7.29208	7.55658
4p	3.85978	4.08209	4.31096	4.55111	4.65765
4p	2.40392	2.55171	2.69895	2.84866	2.91119
3d	11.58909	12.36544	12.80483	13.14460	13.89653
3d	6.20156	6.62701	6.98602	7.28004	7.67860
4d	2.85597	3.10710	3.34902	3.57195	3.86303
4d	1.35077	1.52862	1.68551	1.82895	1.98914
	Ru (^5D)	Rh (^4F)	Pd (^3F)	Ag (^2D)	Cd (^1S)
1s	45.10781	46.06824	47.16369	48.02604	49.23722
1s	31.51667	32.06164	32.62741	33.75929	34.71929
2s	19.94432	20.74419	21.06030	21.96653	22.16630
2s	19.16555	19.72461	20.51693	21.07024	21.89491
3s	13.47783	14.12507	14.83470	15.36794	15.83970
3s	9.15216	9.23329	9.82030	10.14772	10.41585
4s	5.30583	5.47209	5.68933	5.86895	6.09660
4s	3.62125	3.73775	3.87374	3.98866	4.14092
5s	2.04345	2.08005	2.16529	2.22883	2.27982
5s	1.15256	1.17439	1.20647	1.23332	1.26487
2p	30.18881	30.81327	31.18938	31.64007	32.09252
2p	18.83944	19.17740	19.75887	20.21485	20.62987
3p	10.29451	10.51002	10.85084	11.07347	11.30686
3p	7.84644	8.01400	8.43406	8.68348	8.92969
4p	4.98229	5.18625	5.41436	5.60608	5.81585
4p	3.11799	3.24315	3.38380	3.50197	3.62911
3d	14.30278	14.37533	15.23683	15.65030	16.06598
3d	8.01817	8.23314	8.68626	9.00420	9.31716
4d	4.01415	4.19845	4.41147	4.61807	4.84893
4d	2.05057	2.13953	2.25294	2.35609	2.46524

where $\mathbf{C}$ is the matrix of coefficients for the trial basis set, $\mathbf{M}$ is the mixed overlap matrix between trial and reference basis sets and ρ is the density matrix of the reference basis set. The total distance d_D is the optimized variables of the method.

The coefficient matrix $\mathbf{C}$ of the trial basis set is unknown and it is modified in the optimization process and we can write Eq. (3) as

$$\mathbf{P} = \mathbf{S}^{1/2}\mathbf{M}^+\rho\mathbf{M}\mathbf{S}^{-1/2}, \quad [4]$$

where $\mathbf{S}$ is the overlap matrix of the trial basis set.

TABLE 3
Orbital (d_{4d}) and Total (d_D) Distances for Optimized SZ and DZ Basis Sets of Y–Cd Atoms

	SZ_{opt}		DZ_{opt}	
	d_{4d}	d_D	d_{4d}	d_D
Y (^2D)	0.11131223	0.72076998	0.00804795	0.04598338
Zr (^3F)	0.10432787	0.66589626	0.00729237	0.04631095
Nb (^4F)	0.09863740	0.64400855	0.00666204	0.04720189
Mo (^5D)	0.09407802	0.63248086	0.00589977	0.04773511
Tc (^6S)	0.09009901	0.62111896	0.00527535	0.04842307
Ru (^5D)	0.08672089	0.63419085	0.00543452	0.05352492
Rh (^4F)	0.08360353	0.63916715	0.00485444	0.05407395
Pd (^3F)	0.08073588	0.64242513	0.00521228	0.05904121
Ag (^2D)	0.07808428	0.64477659	0.00494960	0.06237170
Cd (^1S)	0.07560571	0.64519529	0.00445672	0.06371982

When NHF functions are used as the reference basis set, the radial part $P_{nl}(r)$ of the wave function is obtained for different values of r. We have calculated the radial part of Y–Cd atoms with the MCHF72 program (13).

Using the NHF functions Eq. (4) is transformed into

$$\mathbf{P} = \mathbf{S}^{-1/2}\mathbf{M}^{+}\mathbf{M}\mathbf{S}^{-1/2}. \quad [5]$$

The solution of this equation requires the calculation of the elements of mixed-overlap matrix **M** between numerical orbitals and trial orbitals STOs and the overlap matrix **S** of this last basis set. The calculation of elements of matrix **M** has been carried out with a cubic spline interpolation and integration (20).

RESULTS AND DISCUSSION

Exponents summarized in Tables 1 and 2 correspond to basis sets of size SZ and DZ for Y–Cd atoms. All calculations have been carried out for the lower states associated with the configuration [Kr] s^2d^n. This selection of states has been done because only these configurations are defined for NHF by Froese Fischer (13); nonetheless, other configurations for these atoms can been found. If we compare these optimized exponents with Clementi and Roetti's (2), then our functions generally prove to be more contracted. The variation is greater for 1s and 4d functions than all other functions. Optimized exponents for 1s and 4d functions show greater variation than Clementi and Roetti's exponents.

In this series the optimized orbital exponents of basis sets exhibit a linear dependence with the atomic number, as has been found previously for the first row of transition metals (16). This correlation is good in the inner orbitals, but some deviations from the linear shape appear in the DZ basis sets (see Table 2). This regular behavior of atomic orbitals with nuclear charge is also shown in the Richardson *et al.* basis sets (12).

The distance is a function of the exponents and not of the coefficients. In Table 3, 4d orbital and total distances are given for atoms Y–Cd. Wavefunctions of double-zeta size present total distances lower than those of single-zeta functions for all atoms. The most important contribution to the change of the total distance d_D is produced by the 4d orbital distance.

In Table 4, we show that Clementi and Roetti's basis sets give lower energies than those of the corresponding optimized SZ and DZ. Calculations of total energies with these new basis sets give an error of less than 0.1 and 0.01% for SZ and DZ sizes respectively, defining the error with respect to Clementi and Roetti's basis sets.

On the other hand, Y and Zr atoms give positive orbital energies with SZ Clementi and Roetti's basis sets that only have one 4d function. In Table 5, we present 4d orbital energies for these atoms obtained with Clementi and Roetti's and our basis sets. Optimized basis sets with respect to the distance give 4d orbital energies lower than those of the corresponding basis set of the same size SZ and DZ given by Clementi and Roetti. For some atoms the

TABLE 4
Total Energies (au) for SZ, SZ_{opt}, DZ, DZ_{opt}, and LHF Basis Sets of Y–Cd Atoms

	SZ	SZ_{opt}	DZ	DZ_{opt}	LHF
Y (^2D)	−3324.7806	−3322.9283	−3331.6538	−3331.6251	−3331.6712
Zr (^3F)	−3531.3181	−3529.6774	−3538.9632	−3538.9360	−3538.9821
Nb (^4F)	−3745.4826	−3744.0864	−3753.5211	−3753.4978	−3753.5394
Mo (^5D)	−3967.0398	−3965.6744	−3975.4131	−3975.3967	−3975.4280
Tc (^6S)	−4196.0536	−4194.7198	−4204.7590	−4204.7153	−4204.7753
Ru (^5D)	−4432.3604	−4430.9896	−4441.4569	−4441.4282	−4441.4746
Rh (^4F)	−4676.2637	−4674.8389	−4685.7699	−4685.7244	−4685.7892
Pd (^3F)	−4927.8059	−4926.3060	−4937.7504	−4937.7174	−4937.7709
Ag (^2D)	−5187.0705	−5185.4706	−5197.4836	−5197.4014	−5197.5029
Cd (^1S)	−5454.1908	−5452.3973	−5465.0971	−5465.0035	−5465.0722

TABLE 5
4*d* Orbital Energies (au) for SZ, SZ_{opt}, DZ, DZ_{opt}, and LHF Basis Sets of Y–Cd Atoms

	SZ	SZ_{opt}	DZ	DZ_{opt}	LHF
Y (^2D)	+0.742747	−0.178694	−0.246362	−0.247663	−0.249866
Zr (^3F)	+0.007466	−0.262621	−0.333411	−0.334725	−0.336541
Nb (^4F)	−0.176494	−0.325522	−0.401706	−0.404255	−0.405599
Mo (^5D)	−0.252331	−0.384934	−0.465155	−0.467974	−0.469921
Tc (^6S)	−0.319138	−0.451146	−0.539626	−0.542879	−0.543716
Ru (^5D)	−0.313875	−0.458452	−0.562487	−0.567339	−0.568211
Rh (^4F)	−0.327662	−0.484896	−0.604028	−0.608769	−0.611133
Pd (^3F)	−0.341351	−0.517533	−0.649053	−0.653695	−0.657171
Ag (^2D)	−0.360996	−0.553600	−0.696432	−0.700936	−0.706374
Cd (^1S)	−0.386210	−0.611129	−0.752369	−0.757802	−0.763570

differences between the orbital energies are remarkably large. For example, the Y atom gives a positive orbital energy with SZ; however with SZ_{opt} the sign is correct and the value only differs 0.06 au with respect to the DZ basis set. In Table 5, we can observe that *d* orbital energies increase along the series, and the lowest energy is obtained for Cd.

Minimal basis sets of STO functions are not efficient for transition metals as they need more functions to describe the valence atomic orbitals. STO basis sets obtained by minimization of atomic energy give poor results for 3*d* and 4*d* orbital energies of transition metals of first and second series respectively, particularly for Cu and Zn, and Y and Zr, where positive values are obtained. We note that the 4*d* orbital energies calculated with our new SZ basis sets are lower than those recently obtained by Koga and Thakkar (10). For the 4*d* orbital of the Y atom they report a positive energy (0.70769), compared with our value in (−0.178694) Table 5.

Some atomic properties for 4*d* orbitals for analyzing these new basis sets have been considered: Condon-Shortley parameters, average values of $\langle r^n \rangle$ and $\langle p^n \rangle$, $n = -2, -1, 1$, and 2. First, we analyze Condon-Shortley parameters in Fig. 1 for Y to Cd atoms. We have represented values of $[F_i(4d, 4d) - F_{LHF}(4d, 4d)] \times 100$ versus atoms, where $F_i(4d, 4d)$ and $F_{LHF}(4d, 4d)$ are the corresponding Condon-Shortley parameters of the determined basis set and LHF basis set for the 4*d* orbital. Better results are obtained for optimized basis sets (SZ_{opt}) than for Clementi and Roetti's sets, except for Y, Zr, and Nb where the SZ basis set gives higher values. However the DZ_{opt} always gives a smaller error than DZ, and for some atoms the difference is remarkable.

Using the wavefunction expanded in the SZ, SZ_{opt}, DZ, and DZ_{opt} basis set, average values of powers of $\langle r^n \rangle$ ($n = -2, -1, 1, 2, 3, 4$) and $\langle p^n \rangle$ ($n = -2, -1, 1, 2, 3, 4$) have been calculated using the recently published formulas (21). In the present work only some of these powers are presented. In Fig. 2, the relative error of $\langle r^1 \rangle$ property is plotted. The relative errors have been defined using LHF as the reference basis set. The results demon-

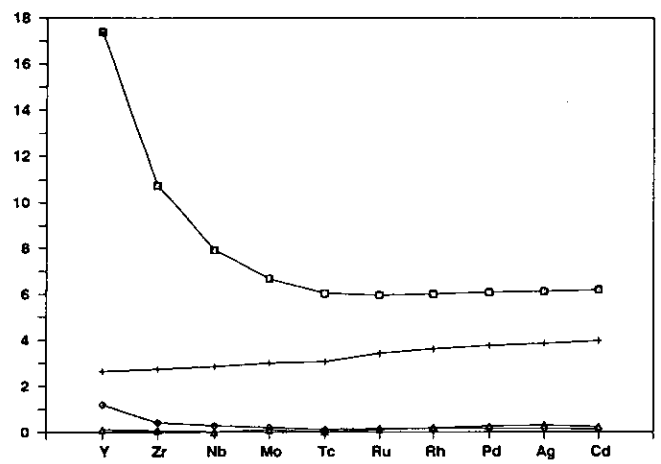

FIG. 1. Condon-Shortley parameters for 4*d* orbitals of Y–Cd atoms: □, SZ; +, SZ_{opt}; ◇, DZ; △, DZ_{opt}.

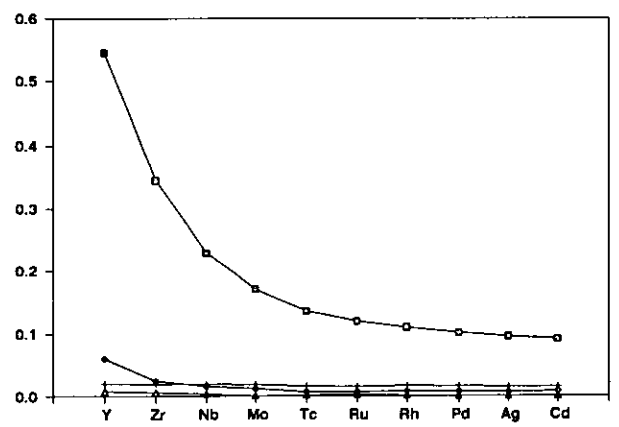

FIG. 2. Relative error $\langle r^1 \rangle$ for 4*d* orbitals of Y–Cd atoms: □, SZ; +, SZ_{opt}; ◇, DZ; △, DZ_{opt}.

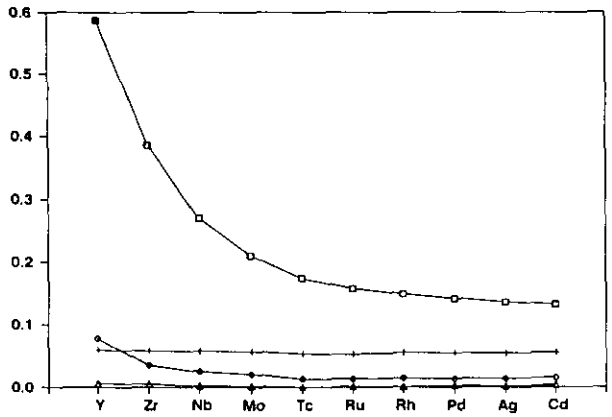

FIG. 3. Relative error $\langle p^{-1} \rangle$ for $4d$ orbitals of Y–Cd atoms: □, SZ; +, SZ_{opt}; ◇, DZ; △, DZ_{opt}.

strate a lineal dependence with the atomic nuclear charge, except for Y, Zr, Nb, and Mo atoms when the SZ basis set is employed.

Relative error of $\langle p^{-1} \rangle$ is shown in Fig. 3. For positive powers of r and negative powers of p the optimized basis sets give lower error than Clementi and Roetti's basis sets; similar results are obtained for the first row of transition metals (16). For negative powers of r and positive powers of p the two types of DZ basis sets give similar errors. For all average values of powers of r and p, SZ basis sets of Y, Zr, and Nb atoms give an error higher than that for the rest of the elements of the series. This behavior agrees with orbital energies of Table 5. Thus Y and Zr atoms give the maximum error for powers of r and p and present positive orbital energies $4d$.

SZ and DZ basis sets give better results for $\langle p^2 \rangle$ and $\langle r^{-1} \rangle$ since, in both cases, the energy is the optimization criterion, and thus they are indirectly optimized. However SZ basis sets for this series do not have the same degree of accuracy for all atoms; the higher errors are given by the first atoms of the series and the error decreases as the nuclear charge increases.

In order to prove those new exponents in molecular integrals we expand every STO function as a linear combination of three Gaussian functions. These expansions of STOs have been obtained with the criterion previously published by us (15, 16). We have chosen three Gaussian functions in order to compare them with STO-3G basis sets, because they are the most simple basis sets and are used in calculations with transition metals (22), and also because STO-3G basis sets and those obtained with the distance between subspaces are not optimized with respect to the atomic energy.

We have constructed Gaussian expansions minimal basis sets for second-row transition metals using the distance between subspaces as we have previously described (15). Exponents and coefficients are optimized for the minimal distance between the subspace generated by our optimized STO and the subspace generated by the three Gaussians for the lowest state of the [Kr] $5s^2\,4d^n$ configuration.

In order to compare our results we have constructed a linear combination of Gaussian functions similar to how Pietro and Hehre (23) prepared their basis sets. The $1s$, $2s$, $3s$, $4s$, and $5s$, the $2p$, $3p$, and $4p$, and the $3d$ and $4d$ STO functions are expanded in the $1s$, $2p$, and $3d$ Gaussian functions, respectively. In molecular calculations the Slater functions of a given principal quantum number are expanded in the same set of Gaussian functions, giving different coefficients for different l numbers. In this series of atoms, the set of exponents used has been ζ_{1s}, $\zeta_{2s} = \zeta_{2p}$, $\zeta_{3s} = \zeta_{3p}$, ζ_{3d}, $\zeta_{4s} = \zeta_{4p}$, ζ_{4d}, and ζ_{5s}. The ζ_{3d} and ζ_{4d} exponents have not been considered equal to ζ_{3s} and ζ_{4s}, respectively.

We have calculated the molecular energies of four molecules that contain Zr, Nb, and Ag atoms using our expansions for the heavy element and the STO-3G for the lighter element. The molecular energies and the optimized bond lengths are given in Table 6 which also includes the experimental bond lengths. Energies and bond lengths, for $ZrCl_4$ and NbF_5 molecules, obtained with the STO-3G basis set are lower than those obtained with our functions. However, the values of axial and radial bond lengths for NbF_5 obtained with our Gaussians fit better with the ex-

TABLE 6
Energies (au) and Geometries (Å) for Compounds with Second-Row Transition Metal

Molecule	Point group	This work		Other[a]		Experimental[a] bond length
		Energy	Bond length	Energy	Bond length	
$ZrCl_4$	T_d	−5323.6077	2.261	−5324.2197	2.316	2.32
NbF_5	D_{3h}	−4208.2656	1.761/1.753	−4208.9564	1.804/1.788	1.88/1.88
AgF	$C_{\infty v}$	−5248.0231	1.735	−5247.9023	1.633	1.983
AgCl	$C_{\infty v}$	−5604.6789	2.181	−5604.4933	2.083	2.281

[a] Ref. (23).

perimental ones. In the case of AgF and AgCl molecules, the energies obtained with our expansions are lower than those obtained with STO-3G while the bond lengths are more similar to the experimental values.

We have developed new STO functions of small (SZ) and middle (DZ) size, optimized with a mathematical criterion for the second row of transition metals. These basis sets improve some atomic properties (average values of r^n and p^n, and orbital energies of $4d$ orbitals) with respect to the Clementi and Roetti's STOs. In molecular calculations, the proposed basis sets produce values as accurate as those obtained with basis sets of the same size used in standard molecular programs.

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