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New Relativistic ANO Basis Sets for Transition Metal Atoms

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New basis sets of the atomic natural orbital (ANO) type have been developed for the first, second, and third row transition metal atoms. The ANOs have been obtained from the average density matrix of the ground and lowest excited states of the atom, the positive and negative ions, and the atom in an electric field. Scalar relativistic effects are included through the use of a Douglas−Kroll−Hess Hamiltonian. Multiconfigurational wave functions have been used with dynamic correlation included using second order perturbation theory (CASSCF/CASPT2). The basis sets are applied in calculations of ionization energies, electron affinities, and excitation energies for all atoms and polarizabilities for spherically symmetric atoms. These calculations include spin−orbit coupling using a variation−perturbation approach. Computed ionization energies have an accuracy better than 0.2 eV in most cases. The accuracy of computed electron affinities is the same except in cases where the experimental values are smaller than 0.5 eV. Accurate results are obtained for the polarizabilities of atoms with spherical symmetry. Multiplet levels are presented for some of the third row transition metals.

1. Introduction

This work is part of an ongoing effort to develop a new set of AO basis sets for molecular calculations. The aim is to cover the entire periodic system with basis sets of the same quality. We have recently presented results for the group Ia (Li−Fr) and group IIa (Be−Ra) elements,[1] the main group (IIIa−VIIa), rare gas elements (VIIIa),[2] and the actinides (Ac−Cm).[3] The basis sets are of the atomic natural orbital (ANO) type as was originally suggested by Almlöf and Taylor in 1987.[4] They can be considered as extensions of the ANO-L basis sets developed by Widmark and co-workers[5−7] for the atoms H−Kr. Those basis sets were constructed using average density matrices obtained from CI calculations on ground and excited states of the atom, the positive and negative ions, and the atom in an electric field (to obtain polarization functions).

The extension to heavy elements in the new basis sets makes it necessary to include relativistic effects also in the basis set generation. This has been done using the Douglas−Kroll−Hess Hamiltonian,[8,9] which makes it possible to include the scalar relativistic effects in a basically nonrelativistic formulation. Another feature that needs to be taken into account for heavier elements is correlation of the semicore electrons. Consequently, these electrons are included in the correlation treatment, and ANOs, which include such effects, are generated. Polarization functions for the ANO-L basis sets were constructed by including a density matrix obtained from calculations on the atom in an external electric field. Such a procedure leads to polarization functions that are somewhat diffuse. Calculations on the homonuclear diatomics were instead used to generate polarization functions for the alkaline, alkaline earth, and main group elements. Calculations on the dimers were straightforward for these elements. In the present work, we extend the ANO−RCC basis sets to the transition metals. It is not equally straightforward to perform calculations for the dimers of these atoms, and we have therefore returned to use the atom in an electric field for the generation of polarization functions.

Multiconfigurational wave functions have been used (CASSCF) with the most important orbitals in the active space and dynamic correlation treated using second-order perturbation theory (CASPT2).[10−12] This approach was used because it is general and can be applied to all electronic states without loss of accuracy. The experience gained also shows that the approach works well, and it generates ANOs which are well suited for correlated calculations in the relativistic regime. For the heavier transition metals it is also important to include the effects of spin−orbit coupling in the calculations. The basis sets were generated without such effects, but test calculations performed on third row transition metal atoms and ions with the new basis sets include spin−orbit coupling. The RAS state interaction (RASSI−SO) method was used for this purpose.[13] It has been described in detail in a recent review.[14]

Below, we shall present the general features of the new basis sets and some results obtained for the atoms with emphasis on spectroscopic data. It is well-known by now that the calculation of excitation energies for transition metal atoms is not trivial, in particular when the MRCI or CASPT2 methods are used.[15−17] The basis sets will be available in the MOLCAS basis set library under the heading ANO−RCC.[23]

2. Primitive Basis Sets and Density Averaging

The sets of primitive Gaussian functions are presented in Table 1. The ANO-L primitives were used for the first row transition metals (TMs).[7] The primitives for the other atoms were based on the Faegri primitive sets.[18] They were extended with more diffuse functions in an even-tempered way. Angular momentum functions up to h-type were added and exponents were optimized for the ground-state atoms (at the CASPT2 level of theory) using an even-tempered extension with a scale factor of 0.4.

Calculations with the primitive basis set was performed for the following: each atom in its ground state; one excited state

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TABLE 1: Size of the Primitive Basis Sets and the Contraction Range

atoms	primitive	contraction range
Sc−Zn	21s15p10d6f4g2h	MB-DZP-TZP-QZP-10s9p8d5f4g2h
Y−Cd	21s18p13d6f4g2h	MB-DZP-TZP-QZP-10s9p8d5f4g2h
Hf−Hg	24s21p15d11f4g2h	MB-DZP-TZP-QZP-11s10p9d8f4g2h

(normally corresponding to the excitation $(n + 1)\mathrm{s} \rightarrow n\mathrm{d}$ or the reverse); the positive ion; for atoms with positive electron affinity, the negative ion. In addition, calculations were performed for the atom in an electric field of strength 0.01 au. An average density matrix was constructed as

$$\rho_{\mathrm{av}} = \sum_i \omega_i \rho_i \tag{1}$$

where ρ_i are the density matrices obtained from the different CASPT2 wave functions. Equal weights, ω_i were used for all states. The final ANO's were obtained as the eigenfunctions of ρ_{av}. All orbitals with occupation number larger than 10^{-6} were kept in the final basis set. This give the maximum sizes given in Table 1. The calculations were performed using the GENANO utility of the MOLCAS program system.[19]

Correlation of semicore electrons was applied as follows: Sc−V(3s, 3p), Cr−Cu(3p), Zn(3d), Y−Rh(4s, 4p), Pd−Ag(4p), Cd(4d), Hf−Re(4f, 5s, 5p), Os−Au(5p), Hg(5d). Because the basis sets have been constructed including such correlation effects, these should also be included when the basis set is used. In particular, one should note that correlation functions of f-, g-, and h-type include primitives with large exponents. Other core-electrons are described with minimal basis set quality and should not be included in any correlation treatment, because that could cause large basis set superposition errors.

The choice of the active space is crucial for transition metal atoms when CASPT2 or MRCI is used to obtain dynamic correlation effects. For more than half filled d shells it is necessary to include an extra set of d-type orbitals (the *double shell* effect[15]) that describe radial correlation effects of the d shell. This is especially important when studying processes where the number of d electrons changes. It may be noted that these strong correlation effects are in general well described with the coupled cluster (CCSD(T)) method, as a recent study of $(n + 1)\mathrm{s} \rightarrow n\mathrm{d}$ excitations in all transition metals has shown.[17] The chosen active space is therefore in general nd, nd′, $(n + 1)$s, $(n + 1)$p, that is, 14 orbitals. The d orbitals were left inactive for the atoms Zn, Cd, and Hg, and the second d shell (nd′) was omitted for transition metals with less than five d electrons. It is likely that this shell becomes of less importance for the second and, in particular, for the third row atoms, but this was not systematically investigated.

The CASSCF/CASPT2 calculations were performed in D_{2h} symmetry, and the orbital rotations were restricted such that mixing between different angular momenta did not occur. This does not completely ensure spherical symmetry because orbitals in different irreps may have different radial shape, but the deviations should be small. In most cases, separate calculations were made for each of the two electronic states. In some cases, this was not possible because the two states have components in the same irreps and have the same spin. State average calculations were then made. The final ANOs are of course spherically averaged. The CASPT2 calculations used the new level shift technique that shifts active orbital energies in order to simulate ionization energies for orbitals excited out of and electron affinities for orbitals excited into. This technique has recently been shown to reduce the systematic error in the CASPT2 approach for processes where the number of closed shell electron pairs changes.[20]

TABLE 2: Ground State Electronic Configuration for the Transition Metal Atoms and the 1+ Ions

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Electronic Configuration, Neutral									
d^1s^2	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$	$d^{10}s^2$
d^1s^2	d^2s^2	d^4s^1	d^5s^1	d^5s^2	d^7s^1	d^8s^1	d^{10}	$d^{10}s^1$	$d^{10}s^2$
d^1s^2	d^2s^2	d^3s^2	d^4s^2	d^5s^2	d^6s^2	d^7s^2	d^9s^1	$d^{10}s^1$	$d^{10}s^2$
Electronic Configuration, 1+ Ion									
d^1s^1	d^2s^1	d^4s^0	d^5s^0	d^5s^1	d^6s^1	d^8s^0	d^9s^0	$d^{10}s^0$	$d^{10}s^1$
d^0s^2	d^2s^1	d^4s^0	d^5s^0	d^5s^1	d^7s^0	d^8s^0	d^9s^0	$d^{10}s^0$	$d^{10}s^1$
d^2s^0	d^1s^2	d^3s^1	d^4s^1	d^5s^1	d^6s^1	d^7s^1	d^9s^0	$d^{10}s^0$	$d^{10}s^1$

3. Results

We present in this section the results obtained for the ionization energies (IP), electron affinities (EA) and some of the spectroscopic data. Most of these calculations have been performed without including spin−orbit coupling (SOC). Comparison is therefore made to *J*-averaged experimental data, when available. We expect the effect of SOC to be small for first and second row TMs. For third row TMs, the effect may be somewhat larger. We shall return to this issue below. All results presented have been obtained with the primitive basis sets. Contracted basis sets of QZP quality give results that differ with less than 0.1 eV.

3.1. Ionization Energies. Intuitively, one might assume that the first ionization energy would originate in the removal of one electron from an $(n + 1)$s orbital, but this is often not the case. We present in Table 2 the ground-state electronic configuration for all atoms and the positive ions.

The ground-state configuration for first row atoms is d^ns^2 for all atoms except Cr and Cu where exchange stabilization favors the half (Cr) or completely (Cu) filled d shell. The electron repulsion is weaker for the second row atoms, which favors configurations with only one s electron (or even zero for Pd). One might expect this tendency to be even more pronounced for the third row atoms. This is not the case. Instead the trend reverses. This is due to the relativistic contraction of the s shell and a corresponding destabilization and slight expansion of the d shell. For example, both Cr and Mo have the ground-state configuration d^5s^1 but W has d^4s^2 with the lowest multiplet of d^5s^1 0.37 eV above (the order is, however, reversed if *J*-averaged energies are used).

The same trends are found for the positive ions. As a result, the first ionization energy may correspond to a nontrivial change in the electronic configuration. The s electron is first ionized in all atoms except seven (V, Co, Ni, Y, Pd, La, and Hf). In these cases, either a d electron is ionized first or a more extensive change of configuration takes place. One example is V where the neutral d^3s^2 configuration changes to d^4s^0 in the ion.

One might expect that the error in computed IPs would be larger when the number of d electron changes, but this does not seem to be the case. The computed RMS error is 0.12 eV for all three rows. The errors vary in the range −0.18 to +0.19 eV for first row atoms, −0.15 to +0.28 eV for second row atoms, and −0.17 to +0.17 eV for the third row. These are typical error ranges for the CASPT2 method, maybe with the exception of the error for Tc (0.28 eV), which is surprisingly large considering that the ionization is from d^5s^2 to d^5s^1. Attempts were made to decrease this error by increasing the size of the AO basis set but this had not effect on the IP. The

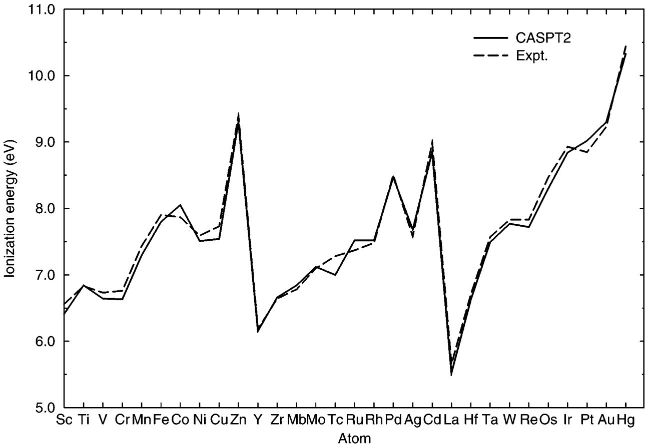

Figure 1. Calculated and experimental ionization energies for all transition metal atoms. The experimental values have been *J*-averaged.

TABLE 3: Atomic Ionization Energies (in eV), Where the Values Have Been Obtained without Inclusion of Spin−Orbit Coupling and Experimental Values Are in the Second Row[a]

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
6.47	6.84	6.64	6.63	7.29	7.80	8.05	7.51	7.54	9.30
6.56	6.83	6.73	6.76	7.43	7.90	7.87	7.59	7.73	9.39
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
6.15	6.66	6.84	7.12	7.00	7.52	7.52	8.47	7.68	8.85
6.18	6.64	6.78	7.10	7.28	7.37	7.48	8.50	7.58	8.99
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
5.52	6.63	7.49	7.77	7.72	8.30	8.84	9.02	9.30	10.33
5.65	6.71	7.57	7.83	7.83	8.47	8.93	8.85	9.23	10.44

[a] Experimental data (*J*-averaged) from the ref 22.

ground state of Tc is ^{6}S and that of Tc$^+$ ^{7}S, so the effect of SOC is expected to be small. The size of the error therefore remains unexplained. The effect of spin−orbit coupling was studied for some of the third row atoms. These calculations used the variation-perturbation method described in Ref. 14. State average CASSCF/CASPT2 calculations were performed for terms arising from the d^{n}s^2, d^{n+1}s^1, and d^{n+2}s^0 configurations. These wave functions formed the basis for the SO Hamiltonian. CASPT2 energies were used in the diagonal. Calculations were performed for the atoms La, Hf, Ta, and W with the results: 5.43 (5.58), 6.83 (6.83), 7.55 (7.60), and 7.86 (7.90), respectively. Experimental data are given within parentheses. Notice that they are different from those of Table 3, which are *J*-averaged values. The effect of SOC varies between −0.1 and +0.2 eV for these atoms. The errors in computed IPs are not affected.

3.2. Electron Affinities. Negative ions were also used in the construction of the average density matrix in the cases where the electron affinity (EA) is positive. Only five of the TMs have zero EA: Mn, Zn, Cd, Hf, and Hg. It is interesting to note that while Ti and Zr have positive EAs, Hf has not. This must be due to the relativistic destabilization of the 5d shell.

In Table 4, we present results obtained for the EAs with the primitive basis set. The errors (experiment − theory) are here much larger than they were for the IPs. For the first row they vary between −0.06 and +0.39 eV, being largest for Fe. The RMS error is 0.22 eV. The errors vary between +0.02 and +0.40 eV for the second row with the largest error for Y. Finally, we obtain errors ranging from −0.45 to +0.34 eV for the third row TMs. What is the reason for these larger errors?

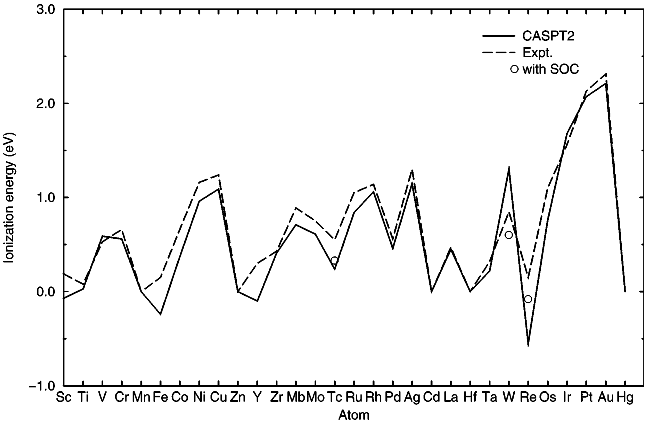

Figure 2. Calculated and experimental electron affinities for all transition metal atoms. No *J*-averaging of experimental values. The dots for the atoms Tc, W, and Re show results obtained including spin−orbit coupling.

A more detailed inspection of the results gives some clues: If we only consider EAs larger than 0.5 eV, we find errors smaller than 0.2 eV for all first and second row TMs. It is thus clear that we have difficulties in computing the small EAs. A typical example is Fe, which has an experimental EA of 0.15 eV. The computed value (corresponding to Fe$^-$ d^{7}s^2, ^4F) is −0.24 eV. It is not absolutely certain that the right ground state for the ion has been selected, but no alternative was studied. One more electron in the 3d shell will increase the electron repulsion and make the orbitals more diffuse. The basis set needs to be extended in order to cover such effects. To accurately compute the small EAs for the TMs seems to be a challenge for quantum chemistry. The experimental values have been taken from the tabulation in ref 21 and should be treated with a critical mind. A more careful analysis of the experimental data would be necessary in a comprehensive study of the transition metal EAs. Such a study is, however, outside the scope of this work. For third row TMs there is one further complication: spin−orbit coupling. While the effects were small for IPs, they are substantial here. We have computed the effect of SOC for the two atoms which have the largest errors: W and Re. Without SOC, the computed EA is 1.30 eV for W, which is 0.45 eV larger than experiment. For Re, we obtain −0.55 eV, 0.70(!) smaller than the experimental value. With the inclusion of SOC we obtain the values: 0.60 eV for W and −0.08 eV for Re, a considerable improvement. The computed values have decreased 0.70 eV for W and increased 0.45 eV for Re. It seems clear that the positive value for the EA of Re is due to spin−orbit coupling.

3.3. Excitation Energies. One excited state was included for the construction of the average density matrix. This state was normally chosen to have a different number of d electrons than the ground state, either one more or one less depending on the s population in the ground state. We shall not report all the computed excitation energies here. Some of them were discussed in detail in a recent publication where they were compared to results obtained using restricted open shell coupled cluster theory.[17] The RMS error for 33 excited states (excitations between d^{10}, d^{9}s^1, and d^{8}s^2 were included for Ni, Pd, and Pt) was 0.14 eV with the largest error, 0.29 eV, for the ^{1}S d^{10}s^0 → ^{3}F d^{8}s^2 excitation in Pd. The corresponding RMS error for the CCSD(T) method was 0.11 eV. We refer to ref 17 for more details. The CASPT2 and CCSD(T) results are similar, with one striking exception. The CASPT2 method seem to overestimate the effect of *n*p correlation for atoms with five or less *n*d electrons.

TABLE 4: Atomic Electron Affinities (in eV), Where the Values Have Been Obtained without Inclusion of Spin−Orbit Coupling and Experimental Values Are Given in the Second Row[a] (no *J*-Averaging)[a]

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$d^1s^2p^1\ {}^3F$	$d^3s^2\ {}^1F$	$d^4s^2\ {}^5D$	$d^5s^2\ {}^6S$		$d^7s^2\ {}^4F$	$d^8s^{2\,3}F$	$d^9s^2\ {}^2D$	$d^{10}s^2\ {}^1S$
−0.07	0.03	0.59	0.56		−0.24	0.37	0.96	1.09
0.19	0.08	0.53	0.66	0.00	0.15	0.66	1.16	1.24
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**
$d^2s^2\ {}^3F$	$d^3s^2\ {}^4F$	$d^4s^2\ {}^5D$	$d^5s^2\ {}^6S$	$d^6s^2\ {}^5D$	$d^7s^2\ {}^4F$	$d^8s^{2\,3}F$	$d^{10}s^1\ {}^2S$	$d^{10}s^2\ {}^1S$
−0.10	0.41	0.71	0.61	0.24	0.84	1.06	0.46	1.15
0.30	0.43	0.89	0.75	0.55	1.05	1.14	0.56	1.30
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**
$d^2s^2\ {}^3F$		$d^4s^2\ {}^5D$	$d^5s^2\ {}^6S$	$d^6s^2\ {}^5D$	$d^7s^2\ {}^4F$	$d^8s^{2\,3}F$	$d^9s^2\ {}^2D$	$d^{10}s^2\ {}^1S$
0.45		0.22	1.30	−0.55	0.76	1.68	2.07	2.21
0.47	0.00	0.32	0.85	0.15	1.10	1.56	2.13	2.31

[a] Experimental data from ref 21.

TABLE 5: Excitation Energies (CASPT2/RASSI−SO) for Some Third Row Transition Metal Atoms Including Spin−Orbit Coupling[a]

Hf	Ta	W	Pt
$d^2s^2\ {}^3F_2$ 0.00 (0.00)	$d^3s^2\ {}^4F_{3/2}$ 0.00	$d^4s^2\ {}^5D_0$ 0.00	$d^9s^1\ {}^3D_3$ 0.00 (0.00)
$d^2s^2\ {}^3F_3$ 0.34 (0.29)	$d^3s^2\ {}^4F_{5/2}$ 0.27 (0.25)	$d^4s^2\ {}^5D_1$ 0.23 (0.21)	$d^9s^1\ {}^1D_2$ 0.05 (0.10)
$d^2s^2\ {}^3F_4$ 0.64 (0.57)	$d^3s^2\ {}^4F_{7/2}$ 0.54 (0.49)	$d^5s^1\ {}^7S_3$ 0.21 (0.37)	$d^8s^2\ {}^3F_4$ 0.06 (0.10)
$d^2s^2\ {}^1D_2$ 0.73 (0.70)	$d^3s^2\ {}^4P_{1/2}$ 0.74 (0.75)	$d^4s^2\ {}^5D_2$ 0.46 (0.41)	$d^9s^1\ {}^3D_2$ 0.76 (0.81)
$d^2s^2\ {}^3P_0$ 0.77 (0.69)	$d^3s^2\ {}^4F_{9/2}$ 0.75 (0.70)	$d^4s^2\ {}^5D_3$ 0.66 (0.60)	$d^{10}s^0\ {}^1S_0$ 0.90 (0.76)
$d^2s^2\ {}^3P_1$ 0.91 (0.82)	$d^3s^2\ {}^4P_{3/2}$ 0.75 (0.75)	$d^4s^2\ {}^5D_4$ 0.85 (0.77)	$d^8s^2\ {}^3F_3$ 1.23 (1.25)
$d^2s^2\ {}^3P_2$ 1.20 (1.11)	$d^3s^2\ {}^4P_{5/2}$ 1.20 (1.15)	$d^4s^2\ {}^3P_0$ 1.24 (1.18)	$d^9s^1\ {}^3D_1$ 1.27 (1.26)
$d^2s^2\ {}^1G_4$ 1.39 (1.31)	$d^3s^2\ {}^2G_{7/2}$ 1.26 (1.20)	$d^4s^2\ {}^3P_1$ 1.75 (1.65)	$d^8s^2\ {}^3P_2$ 1.71 (−)
$d^3s^1\ {}^5F_1$ 1.85 (1.75)	$d^4s^1\ {}^6D_{1/2}$ 1.11 (1.21)	$d^4s^2\ {}^3H_4$ 1.62 (1.51)	$d^8s^2\ {}^3F_2$ 1.92 (1.92)
$d^3s^1\ {}^5F_2$ 1.94 (1.83)	$d^4s^1\ {}^6D_{3/2}$ 1.15 (1.24)	$d^4s^2\ {}^3G_3$ 1.77 (1.66)	$d^8s^2\ {}^3P_0$ 2.09 (2.11)
$d^3s^1\ {}^5F_3$ 2.08 (1.94)	$d^4s^1\ {}^2G_{9/2}$ 1.39 (1.33)	$d^4s^2\ {}^3F_2$ 1.83 (1.71)	$d^8s^2\ {}^3P_1$ 2.30 (2.30)
$d^3s^1\ {}^5F_4$ 2.23 (2.08)	$d^4s^1\ {}^6D_{5/2}$ 1.32 (1.39)	$d^4s^2\ {}^3H_5$ 1.86 (1.87)	$d^8s^2\ {}^1G_4$ 2.81 (2.72)
$d^3s^1\ {}^5F_5$ 2.40 (2.22)	$d^3s^2\ {}^2P_{1/2}$ 1.45 (1.46)	$d^4s^2\ {}^3D_2$ 1.98 (1.87)	$d^8s^2\ {}^1D_2$ 3.30 (3.30)
$d^2s^2\ {}^1S_0$ 2.41 (2.52)	$d^4s^1\ {}^6D_{7/2}$ 1.43 (1.52)	$d^4s^2\ {}^3G_5$ 2.01 (−)	$d^8s^2\ {}^1S_0$ 6.02 (−)
$d^3s^1\ {}^5P_1$ 2.64 (2.58)	$d^3s^2\ {}^2D_{5/2}$ 1.71 (1.60)	$d^4s^2\ {}^3D_3$ 2.05 (−)	
$d^3s^1\ {}^5P_2$ 2.65 (2.59)	$d^4s^1\ {}^6D_{9/2}$ 1.60 (1.66)	$d^4s^2\ {}^3H_4$ 2.20 (−)	
$d^3s^1\ {}^5P_3$ 2.86 (2.75)	$d^3s^2\ {}^2D_{3/2}$ 1.39 (1.97)		

[a]Experimental values[22] are given in parentheses.

TABLE 6: Atomic Polarizabilities (in au^3)[a]

Cr	Mn	Cu	Zn	Mo	Tc
78.4	66.8	40.7	38.4	72.5	80.4
78.3 ± 19.6	63.44 ± 15.8	41.2 ± 10.3	38.8 ± 0.81	86.4 ± 21.6	76.9 ± 19.2

Ag	Cd	Re	Au	Hg
36.7	46.9	61.1	27.9	33.3
57.5 ± 14.4	49.7 ± 1.6	65.5 ± 16.4	39.1 ± 9.8	33.9 ± 0.3

[a] Experimental values are given in the second row. Experimental data were taken from ref 21 for Zn, Cd, and Hg. The others are estimates with 25% accuracy.

Any detailed study of the electronic spectrum has to include SOC. A number of such calculations have been done and a few examples are given in Table 5 for the third row atoms Hf, Ta, W, and Pt. The agreement between computed and experimental multiplet values is better than 0.2 eV, in most cases actually better than 0.1 eV. There is one striking exception in the table: the $^2D_{3/2}$ level in Ta is computed to lie at 1.24 eV, but ref 22 gives 1.97 eV. This must certainly be an error in the assignment. More examples of multiplet levels can be found in the basis set library of MOLCAS-6.[19]

3.4. Atomic Polarizabilities. Finally, we present in Table 6 the computed polarizabilities for the atoms with spherical symmetry. Accurate experimental information seems to be available only for the elements Zn, Cd, and Hg. The experimental data are for these atom accurately reproduced by the calculations. There is no reason to believe that the results obtained for the other atoms should be less accurate. Thus, we can conclude that the generated basis sets are flexible enough to describe the polarization of the atoms in an external field or in a molecular environment.

4. Conclusions

We have presented a new set of atomic basis functions for the transition metal atoms. They are of the ANO type and include scalar relativistic effects using the Douglas−Kroll−Hess Hamiltonian. The CASSCF/CASPT2 method was used to generate correlated wave functions, from which average density matrices were constructed. The ANOs were obtained as the eigenfunctions of these matrices. Results have been presented for ionization, energies, electron affinities, multiplet levels, and atomic polarizabilities. The agreement with experiment is within the limits expected for the quantum chemical method applied. It was difficult to obtain accurate results for electron affinities smaller than 0.5 eV. The main reason is probably the lack of enough diffuse functions in the basis set and an incomplete treatment of dynamic electron correlation. It was found that for third row atoms it is essential to include spin−orbit coupling in the calculation of the EAs. Indeed, it is spin−orbit coupling that makes the EA for Re positive. We have also presented atomic polarizabilities for all spherically symmetric atoms. The errors are small in the three cases where accurate experimental information is available. For the other atoms, the presented results represents accurate predictions.

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