Theoret. Chim. Acta (Berl.) 65, 215–218 (1984)

**THEORETICA CHIMICA ACTA**

# Gaussian basis sets for transition metals of the second series

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A Gaussian basis set consisting of (15*s*, 9*p*, 8*d*) Gaussian functions has been optimized for the transition metal atoms of the second series (fourth-row atoms).

**Key words:** Gaussian basis set—transition metals

## 1. Introduction

Three different basis sets are available in the literature for the second transition series (fourth-row atoms Y–Ag):

i) the (17, 11, 8) basis set by Huzinaga [1] corresponding to a (10, 6) basis set for the first-row atoms [2, 3];

ii) the (14, 8, 7) basis set by Hyla-Kryspin et al [4] corresponding to a (8, 4) basis set for the first-row atoms [5];

iii) the (12, 8, 7) basis set by Friedlander et al [6], corresponding also to a (8, 4) basis set for the first-row atoms.

A basis set which is commonly used for the first-row atoms is the (9, 5) basis set [2, 3] and its counterparts for the second- and third-row atoms, respectively (11, 7) [3] and (13, 7, 5) [4]. We report here the counterpart for the fourth-row atoms, a (15, 9, 8) basis set.

## 2. Computational details

Orbital exponent optimization was performed using an improved version of a program designed for atomic calculations [7], with the SCF energy minimized for the $5s^1 4d^{n-1}$ configuration rather than for the ground state configuration [8].

**Table 1.** Orbital exponents

| | Y($^4$F) | Zr($^5$F) | Nb($^6$D) | Mo($^7$S) | Tc($^6$D) | Ru($^5$F) | Rh($^4$F) | Pd($^3$D) | Ag($^2$S) |
|---|---|---|---|---|---|---|---|---|---|
| 1s | 374493. | 395824. | 418254. | 445063. | 468949. | 498641. | 529043. | 553700. | 591567. |
| | 56210.9 | 59421.2 | 62796.4 | 66291.5 | 69948.1 | 74529.5 | 79287.7 | 83544.6 | 88767.4 |
| | 12822.1 | 13552.7 | 14327.7 | 15103.8 | 15936.8 | 16968.1 | 18071.1 | 19097.6 | 20216.0 |
| | 3644.92 | 3851.54 | 4072.79 | 4294.28 | 4529.16 | 4813.81 | 5122.75 | 5422.66 | 5723.93 |
| | 1194.29 | 1262.04 | 1334.42 | 1407.04 | 1483.30 | 1573.69 | 1672.37 | 1768.75 | 1863.66 |
| | 432.029 | 456.780 | 482.754 | 508.972 | 536.285 | 567.844 | 602.052 | 635.532 | 668.873 |
| | 165.877 | 175.528 | 185.457 | 195.484 | 205.891 | 217.563 | 230.048 | 242.381 | 254.847 |
| | 48.6088 | 51.8145 | 54.8260 | 57.9477 | 61.1720 | 64.7058 | 68.4977 | 72.2608 | 76.2401 |
| | 21.3732 | 22.8934 | 24.3452 | 25.7723 | 27.2729 | 28.9645 | 30.7801 | 32.5785 | 34.4583 |
| | 7.08176 | 7.78507 | 8.41912 | 8.96508 | 9.57435 | 10.3276 | 11.1335 | 11.9430 | 12.7964 |
| | 3.25305 | 3.58155 | 3.90743 | 4.18102 | 4.48242 | 4.83745 | 5.22261 | 5.57815 | 5.93991 |
| | .827319 | .965443 | 1.10518 | 1.15939 | 1.25294 | 1.37461 | 1.51547 | 1.61182 | 1.72810 |
| | .397135 | .454413 | .521731 | .547877 | .583251 | .639721 | .705768 | .747893 | .776428 |
| | .102034 | .103369 | .131698 | .123139 | .117961 | .135109 | .136677 | .124876 | .119263 |
| | .035601 | .038075 | .042607 | .043231 | .042448 | .044914 | .045322 | .043909 | .042559 |
| 2p | 2357.22 | 2530.75 | 2704.67 | 2877.75 | 3051.22 | 3222.59 | 3409.10 | 3596.49 | 3780.06 |
| | 557.996 | 598.809 | 640.048 | 681.115 | 722.242 | 762.956 | 807.084 | 851.448 | 894.994 |
| | 178.789 | 191.774 | 205.010 | 218.251 | 231.495 | 244.662 | 258.867 | 273.104 | 287.166 |
| | 66.2022 | 71.0051 | 75.9311 | 80.8912 | 85.8599 | 90.8281 | 96.1553 | 101.479 | 106.784 |
| | 26.4595 | 28.3887 | 30.3739 | 32.3873 | 34.4149 | 36.4561 | 38.6218 | 40.7975 | 42.9810 |
| | 9.35168 | 10.0901 | 10.8526 | 11.6348 | 12.4271 | 13.2295 | 14.0693 | 14.9218 | 15.7806 |
| | 3.65889 | 3.98693 | 4.32658 | 4.67659 | 5.03468 | 5.39976 | 5.78045 | 6.16894 | 6.56329 |
| | .980921 | 1.09477 | 1.21234 | 1.33390 | 1.46010 | 1.58909 | 1.72236 | 1.85962 | 1.99958 |
| | .341948 | .384369 | .427486 | .471335 | .517777 | .564570 | .612681 | .661905 | .711799 |
| 3d | 214.062 | 229.701 | 245.941 | 261.731 | 277.813 | 295.409 | 313.108 | 329.835 | 347.579 |
| | 63.6321 | 68.2590 | 73.0679 | 77.8523 | 82.6562 | 87.9438 | 93.1723 | 98.3554 | 103.7120 |
| | 23.5322 | 25.2088 | 26.9880 | 28.7827 | 30.5901 | 32.5967 | 34.6090 | 36.5875 | 38.6386 |
| | 9.48360 | 10.1181 | 10.8282 | 11.5556 | 12.3002 | 13.1403 | 13.9978 | 14.8358 | 15.7090 |
| | 3.87463 | 4.10396 | 4.38937 | 4.69548 | 5.01829 | 5.39204 | 5.77972 | 6.16683 | 6.57046 |
| | 1.50949 | 1.55312 | 1.62869 | 1.72243 | 1.82958 | 1.97189 | 2.12882 | 2.28639 | 2.45686 |
| | .432088 | .490998 | .544927 | .598024 | .644858 | .703286 | .765709 | .828989 | .897191 |
| | .109057 | .133882 | .155739 | .177638 | .193130 | .213002 | .234079 | .255751 | .279442 |

The exponents of a Gaussian basis set are usually requested to minimize the SCF atomic energy of the reference state. However this criterion applied without discrimination may result in an overrepresentation of the inner shells to the detriment of the valence shells [4]. The solution consists of constraining the number of Gaussian functions used for the description of each atomic orbital (AO). These numbers were fixed to seven and five functions for the $1s$ and $2p$ AO's respectively, two functions for the others $ns$ and $np$ AO's, five and three functions for the $3d$ and $4d$ AO's respectively.

## 3. Results and discussion

Orbitals exponents are given in Table 1 for the atoms Y to Ag. For the sake of brevity, the corresponding expansion coefficients are not reported since they can be easily reproduced. The total energies for the lowest state of the $4d^{n-1}5s^1$ configuration are compared in Table 2 with the best results from Slater orbital calculations [9].

In order to use this basis set in SCF and CI calculations for organometallics of Tc and Mo we have introduced some supplemental basis functions:
i) Schaefer noticed that, in one of the basis sets for the first transition series, the basis functions describing the $3s$ and $4s$ shells are widely separated [10]. A similar situation is found here for the $4s$ and $5s$ shells, this being especially true at the end of the series. Therefore we tentatively added an additional $s$ function with an exponent $\alpha_s = 0.2597$ for Mo and 0.2623 for Tc chosen according to the even-tempered criterion of Raffenetti and Ruedenberg [11] (namely the chosen $s$ function is equidistant from the functions describing the outer part of the $3s$ and inner part of the $4s$ orbitals).
ii) Two new $p$ functions were added corresponding to the $5p$ shells, with their exponents (0.1665 and 0.0588 for Mo, 0.1836 and 0.0651 for Tc) determined following the even-tempered criterion.

**Table 2.** Total energy (in a.u.) for the lowest state of the $4d^{n-1}5s^1$ neutral configuration

| | GTO[a] | STO[b] |
|---|---|---|
| Y($^4$F) | −3331.5220 | −3331.6550 |
| Zr($^5$F) | −3538.8561 | −3538.9957 |
| Nb($^6$D) | −3753.4378 | −3753.5845 |
| Mo($^7$S) | −3975.3833 | −3975.5338 |
| Tc($^6$D) | −4204.6077 | −4204.7669 |
| Ru($^5$F) | −4441.3585 | −4441.5264 |
| Rh($^4$F) | −4685.6930 | −4685.8833 |
| Pd($^3$D) | −4937.6966 | −4937.8815 |
| Ag($^2$S) | −5197.4933 | −5197.6852 |

[a] Uncontracted basis set (15, 9, 8) (this work).
[b] Best results with Slater orbitals from Ref. [9].

iii) The need for an additional diffuse *d* function has been emphasized by several authors [8, 12, 13]. Here too the basis set was augmented with a diffuse *d* function according to the even-tempered criterion (the exponents of 0.0528 for Mo and 0.0578 for Tc are close to the respective values of 0.0432 and 0.0658 reported by Walch et al. [13]).

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Received January 6, 1984