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Approximate Analytical Orbital Functions for Second and Third-Row Transition Metals

By

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Approximate analytical functions for *s*, *p*, *d*, and *f* orbitals of the second and third-row transition metals have been constructed from the Herman-Skillman Hartree-Fock-Slater numerical wave functions. They consist of orthonormal linear combinations of Slater-type orbital functions, and depend on a weighted least-squares criterion to judge the accuracy of the fit. The option of using a single-μ (one orbital function per extremum) or double-μ representation for the outermost maximum of a given function is included. Whereas the latter basis set is more flexible, convergence problems in the fitting method as well as an inherent arbitrariness in choosing the fitting criterion result in derived parameters which are not uniquely determined by the least-squares criterion alone.

By relaxing the orthogonality requirement for orbitals of the same l and different n it is shown that the accuracy of the fit can be significantly improved. The importance of a proper choice for the fitting criterion is discussed.

Die numerischen Hartree-Fock-Slater-Funktionen von Herman-Skillman wurden für die *s*-, *p*-, *d*- und *f*-Zustände der Übergangsmetalle der zweiten und dritten Reihe durch analytische Funktionen (Linearkombinationen von Slaterfunktionen) angenähert. Die Annäherung an die vorgegebenen Funktionen wird besser, wenn man die Orthogonalitätsbedingungen für Zustände gleicher Nebenquantenzahl fallen läßt.

Par un critère des moindres carrés pesés, les fonctions d'onde numériques du procédé Hartree-Fock-Slater de Herman et Skillman pour les orbitales *s*, *p*, *d* et *f* des métaux de transition de la deuxième et troisième période, ont été approximées par des fonctions analytiques, soit de combinaisons linéaires orthonormées de fonctions de Slater. L'option d'employer une représentation simple-μ (une fonction de Slater) ou double-μ pour le maximum le plus éloigné d'une fonction est incluse. Quoique la seconde base soit plus flexible, des problèmes de convergence et un arbitraire inhérent de l'ajustage résultent en de paramètres non-uniques. L'ajustage s'améliore sensiblement quand l'orthogonalité des orbitales au même l est abandonnée. On discute le choix du critère d'ajustage.

Introduction

The investigation of the electronic structures of second and third-row transition metal complexes hitherto has proceeded mainly along experimental lines. The few calculations of electronic structure reported in the literature have had to rely on Slater's rules [*15*] or "reasonable estimates" to obtain the orbital exponents for the appropriate metal radial functions [*3*]. Recently, Burns has published [*4*] an improved set of rules for computing orbital exponents; these rules are claimed to be valid for all the elements in the periodic table. Unfortunately, the Burns' rules are based on published Hartree and Hartree-Fock radial functions, of which there is only an extremely small sampling for the second and third-row transition metals.

With the recent availability of reasonable semi-empirical methods [*1, 2*] for calculating the electronic structures of transition metal complexes, an extensive tabulation of analytical radial functions for the second and third-row transition metals is highly desirable. We present here such a tabulation.

Numerical Methods

The atomic functions presented here are analytical approximations to the numerical Hartree-Fock-Slater (HFS) radial functions computed using the Fortran program described by Herman and Skillman (HS) [*7*]. A fully automatic curve-fitting procedure was devised to obtain analytical functions from the computed numerical functions and attached directly to the slightly modified HS program. Curve-fitting methods previously described [*9, 10, 13, 16*] in the literature were considered unsuitable for use on a computer.

The basis set for an atomic orbital with principal n and azimuthal l quantum numbers consists of a normalized linear combination of $n - l$ or $n - l + 1$ Slater-type orbital functions. The former basis set has each extremum in the radial function represented by a single orbital function ("single-μ"); the latter basis set has one orbital function per extremum, except for the outermost maximum where two Slater-type functions are employed ("double-μ").

The radial part of a Slater-type orbital function is defined as follows:

$$R_n(\mu_n) = \frac{(2\mu_n)^{n+\frac{1}{2}}}{[(2n!)]^{\frac{1}{2}}} r^{n-1} \exp(-\mu_n r) . \tag{1}$$

The total radial function for a given n and l is expressed as in (2):

$$T_{n,l} = \sum_{k=l+1}^{n} C_{nk} \varphi_k . \tag{2}$$

In (2),

$$\begin{array}{lll} \varphi_k = R_k(\mu_k) & k = l+1, \cdots, n & \text{single-}\mu \\ \varphi_k = R_k(\mu_k) & k = l+1, \cdots, n-1 & \multirow{2}{*}{\left.\begin{array}{l}\\ \\ \end{array}\right\} \text{double-}\mu} \\ \varphi_k = N_k [R_k(\mu_k) + \lambda_k R_k(\mu'_k)] & k = n & \end{array} \tag{3}$$

$$T_{n,l} = C'_{nn} \varphi_n + \sum_{k=l+1}^{n-1} C'_{nk} T_{k,l} . \tag{4}$$

The functions of a given l and different n are orthonormal and the coefficients, C_{nk} (or C'_{nk}), are completely determined by the orthonormality constraints.

$$\langle T_{j,l} \mid T_{k,l} \rangle = \delta_{j,k} \tag{5}$$

from which follows:

$$C_{nn} = C'_{nn} \tag{6}$$

$$C_{nk} = \sum_{i=k}^{n-1} C'_{ni} C_{ik} \tag{7}$$

$$C'_{nn} = [1 - \sum_{k=l+1}^{n-1} \langle \varphi_n \mid T_{k,l} \rangle^2]^{-\frac{1}{2}} \tag{8}$$

$$C'_{nk} = - \langle \varphi_n \mid T_{k,l} \rangle C'_{nn} \tag{9}$$

$$N_k = [1 + \lambda_k^2 + 2\lambda_k \langle R_k(\mu_k) \mid R_k(\mu'_k) \rangle]^{-\frac{1}{2}} . \tag{10}$$

Eqs. (8) and (9) express the familiar Schmidt orthogonalization procedure.

In a single-μ representation there is only one variable parameter for each $T_{n,l}$; the orbital exponent μ_n. In the double-μ representation there are three variable parameters; μ_n, μ'_n and λ_n. As an example, the orthonormalization procedure for $Pt^+(5d^9)$ $3d$, $4d$, and $5d$ radial functions will now be described in detail.

The orbital exponent, μ_3 (see Tab. 5), for the $3d$ orbital function, uniquely determines T_{3d} in the single-μ representation (as it always will when $n = l + 1$); $T_{3d} = C_{33} R_3(\mu_3)$ with $C_{33} = C'_{33} = 1.000000$. After μ_4 (best) is found by the procedure outlined below, Eqs. (6) to (9) are used to find: $C_{44} = C'_{44} = 1.115290$, $C_{43} = C'_{43} = -0.493835$. Then, having obtained optimum values for μ_5, μ'_5, and λ_5 ($= 0.871324$), the values $N_5 = 0.633024$, $C_{55} = C'_{55} = 1.059568$, $C'_{54} = 0.349077$, $C_{54} = -0.389322$, $C'_{53} = -0.028787$, and $C_{53} = 0.143599$ are computed. The coefficients of $R_5(\mu_5)$ and $R_5(\mu'_5)$ are given by $C_{55} = C'_{55} N_5 = 0.670732$ and $C_{55'} = C_{55} \lambda_5 = 0.584424$, respectively. The radial functions are, therefore,

$$T_{3d} = 1.000000\, R_3(\mu_3)$$
$$T_{4d} = 1.115290\, R_4(\mu_4) - 0.493835\, R_3(\mu_3)$$
$$T_{5d} = 0.670732\, R_5(\mu_5) + 0.584424\, R_5(\mu'_5) - 0.389322\, R_4(\mu_4) + 0.143599\, R_3(\mu_3)\,.$$

The fitting procedure for finding the best μ_n [μ_n (best)] in the single-μ representation is based on finding a minimum value of S_n [S_n (min)] in the expression,

$$S_n = \sum_t [X_n^{(t)} - T_{n,l}^{(t)}]^2\, r^{(t)} \tag{11}$$

$X_n^{(t)}$ and $T_{n,l}^{(t)}$ are, respectively, values of the HFS numerical function and the analytical function at each radial point, $r^{(t)}$. The choice of this criterion will be discussed later.

In the curve-fitting program S_n is numerically differentiated at two points, μ_n (trial) and μ_n (trial) $+ \alpha$, to form $\Delta S_n/\Delta\mu_n$ and $\Delta S'_n/\Delta\mu_n$. The latter are then used to extrapolate linearly to $dS/d\mu = 0$:

$$\delta\mu_n = \alpha \frac{\Delta S_n}{\Delta \mu_n} \Bigg/ \left(\frac{\Delta S_n}{\Delta \mu_n} - \frac{\Delta S'_n}{\Delta \mu_n}\right) ;\ \mu_n\,(\text{best}) = \mu_n\,(\text{trial}) + \delta\mu_n\,. \tag{12}$$

If $|\delta\mu_n| >$ VALUE, a second iteration is tried using the fourth cycle of the previous iteration as the first cycle of the new iteration. The parameter value $\alpha = 0.05$ was found to give very rapid convergence with VALUE $= 0.0001$. When $|\delta\mu_n| <$ VALUE the procedure is halted.

The double-μ representation is more difficult to handle because the functional dependence of the radial function on any one of the three parameters (μ_n, μ'_n, and λ_n) is very weak and of a complicated nature; *i. e.*, different combinations of the three parameters will give essentially the same value of S_n. This is not to say that an absolute minimum does not exist for S_n as a function of μ_n, μ_n, and λ_n, but rather that either the minimum is extremely shallow or that the function consists of many closely-spaced minima. This ambiguity rules out linear extrapolation methods and requires that an additional criterion be used in choosing the specific set of orbital exponents and coefficients reported here.

The procedure adopted was to fit the parameters one at a time, the other two being held fixed. The chosen parameter is varied systematically in large steps (0.2) until a minimum is found in S_n. This point, $S_n^{(2)}$, together with two other points, one on each side of the minimum, $S_n^{(1)}$ and $S_n^{(3)}$, are used to describe a parabola and determine its minimum*. As before, if the S_n calculated from Eq. (11) using μ_n (best) is not satisfactory, another iteration is started using the calculated S_n as $S_n^{(2)}$.

The parameters are fitted successively in the order, λ_n, μ_n, and μ_n', for a pre-set number of cycles. Since a criterion other than an absolute minimum value of S_n is used, the iterations are not continued until the change in S_n is reduced to less than some predetermined small number, as in the single-μ method. This latter procedure, in fact, was found to be only slowly convergent. In practice, therefore, the parameters for only one metal in each row are optimized very carefully using the additional criterion discussed below. The results are then extended to the other atoms in that row as initial guess values. In this connection, the work of RICHARDSON et al. [*13*] on the first-row transition metals is very useful.

After all the orbitals of a given l are fitted, their orthonormality is tested. The $T_{n,l}$ reported here were invariably found to be orthonormal to better than $\pm$ 0.000001.

The time estimate given by HS [*7*] for calculating atomic numerical radial functions on an IBM 7090 is only slightly increased for calculating and fitting all the occupied atomic orbitals on an IBM 7094, on which these calculations were run.

Results

The fitted analytical functions are presented in Tab. 1 — 5. Tab. 6 compares the Cu$^+$ ($3d^{10}$) $3d$ analytical Hartree-Fock function [*5*] to the numerical HFS [*7*],

Table 1. *Analytical Functions for s Orbitals*[a]

orbital atom	exponents[b] n	μ_1	μ_2	μ_3	μ_4	μ_5
Zr	4	39.581	14.715	7.183	3.635	1.817
Nb	5	40.579	15.111	7.409	3.786	1.889
Mo	6	41.577	15.509	7.634	3.934	1.956
Tc	7	42.575	15.906	7.860	4.080	2.018
Ru	8	43.573	16.304	8.087	4.223	2.078
Rh	9	44.571	16.703	8.313	4.365	2.135
Pd	10	45.569	17.101	8.540	4.506	2.190
Ag	11	46.567	17.500	8.767	4.645	2.244
coefficients[c]		C_{51}	C_{52}	C_{53}	C_{54}	C_{55}
Zr		0.0230	−0.0836	0.2144	−0.4941	1.0930
Nb		0.0235	−0.0856	0.2190	−0.4958	1.0927
Mo		0.0230	−0.0871	0.2221	−0.4946	1.0916
Tc		0.0242	−0.0881	0.2240	−0.4917	1.0899
Ru		0.0244	−0.0887	0.2250	−0.4876	1.0879
Rh		0.0245	−0.0892	0.2255	−0.4829	1.0858
Pd		0.0246	−0.0894	0.2254	−0.4774	1.0835
Ag		0.0246	−0.0894	0.2249	−0.4718	1.0812

[a] Metal charge pf +1; configuration $4d^{n-3}\,5s^1\,5p^1$.

[b] Single-μ representation.

[c] $5s$ orbital.

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* Solution of the resulting simultaneous equations by direct expansion of the appropriate determinants led to an excessive loss of significant figures and an alternative method had to be used [*11*].

Table 2. *Analytical Functions for p and d Orbitals*[a]

orbital	exponents	*p* orbitals[b]				*d* orbitals[c]		
atom	n	μ_2	μ_3	μ_4	μ_5	μ_3	μ_4	μ_4'
Zr	4	17.990	8.334	3.955	1.776	8.731	3.835	1.505
Nb	5	18.481	8.611	4.140	1.852	9.068	4.080	1.637
Mo	6	18.973	8.888	4.321	1.921	9.404	4.542	1.901
Tc	7	19.465	9.164	4.498	1.984	9.738	4.900	2.094
Ru	8	19.957	9.441	4.673	2.043	10.072	5.378	2.303
Rh	9	20.449	9.718	4.845	2.099	10.404	5.542	2.398
Pd	10	20.941	9.994	5.015	2.152	10.735	5.983	2.613
Ag	11	21.434	10.271	5.183	2.202	11.065	6.070	2.663

coefficients	5*p* orbital[d]				4*d* orbital[e]		
	C_{52}	C_{53}	C_{54}	C_{55}	C_{43}	C_{44}	$C_{44'}$
Zr	−0.0463	0.1369	−0.3565	1.0522	−0.2186	0.6357	0.5933
Nb	−0.1476	0.1403	−0.3562	1.0516	−0.2382	0.6583	0.5673
Mo	−0.0484	0.1422	−0.3530	1.0503	−0.2611	0.6097	0.6097
Tc	−0.0489	0.1431	−0.3482	1.0486	−0.2790	0.5933	0.6241
Ru	−0.0492	0.1432	−0.3423	1.0467	−0.2986	0.5573	0.6642
Rh	−0.0492	0.1427	−0.3359	1.0447	−0.3086	0.5823	0.6405
Pd	−0.0491	0.1418	−0.3289	1.0427	−0.3246	0.5535	0.6701
Ag	−0.0488	0.1405	−0.3218	1.0407	−0.3308	0.5889	0.6370

[a] Metal charge of +1.

[b] Configuration $4d^{n-3}\,5s^1\,5p^1$.

[c] Configuration $4d^{n-1}$.

[d] Single-μ representation.

[e] Double-μ representation.

Table 3. *Analytical Functions for s Orbitals*[a]

orbital	exponents[b]						
atom	n	μ_1	μ_2	μ_3	μ_4	μ_5	μ_6
Hf	4	71.537	27.602	14.573	8.209	4.342	2.214
Ta	5	72.536	28.008	14.808	8.357	4.455	2.280
W	6	73.535	28.415	15.043	8.507	4.569	2.341
Re	7	74.535	28.821	15.279	8.657	4.682	2.398
Os	8	75.534	29.228	15.514	8.809	4.795	2.452
Ir	9	76.533	29.634	15.750	8.962	4.907	2.504
Pt	10	77.533	30.041	15.986	9.115	5.019	2.554
Au	11	78.532	30.447	16.220	9.269	5.131	2.602
Hg	12	79.531	30.853	16.458	9.424	5.243	2.649

coefficients[c]	C_{61}	C_{62}	C_{63}	C_{64}	C_{65}	C_{66}
Hf	−0.0129	0.0468	−0.1141	0.2245	−0.4681	1.0825
Ta	−0.0134	0.0483	−0.1177	0.2318	−0.4764	1.0846
W	−0.0137	0.0495	−0.1207	0.2376	−0.4816	1.0857
Rb	−0.0140	0.0505	−0.1232	0.2424	−0.4845	1.0860
Os	−0.0142	0.0513	−0.1252	0.2462	−0.4858	1.0858
Ir	−0.0144	0.0520	−0.1269	0.2494	−0.4859	1.0852
Pt	−0.0146	0.0526	−0.1284	0.2521	−0.4851	1.0843
Au	−0.0147	0.0531	−0.1296	0.2542	−0.4836	1.0832
Hg	−0.0148	0.0535	−0.1307	0.2560	−0.4815	1.0820

[a] Metal charge of +1; configuration $5d^{n-3}\,6s^1\,6p^1$.

[b] Single-μ representation.

[c] 6*s* orbital.

Table 4. *Analytical Functions for p Orbitals*[a]

orbital atom	exponents[b] n	μ_2	μ_3	μ_4	μ_5	μ_6
Hf	4	33.805	17.248	9.510	4.766	2.166
Ta	5	34.302	17.527	9.685	4.909	2.241
W	6	34.798	17.806	9.863	5.051	2.309
Re	7	35.294	18.084	10.041	5.191	2.372
Os	8	35.791	18.363	10.221	5.330	2.429
Ir	9	36.287	18.642	10.401	5.467	2.484
Pt	10	36.784	18.921	10.582	5.604	2.535
Au	11	37.280	19.200	10.764	5.739	2.584
Hg	12	37.777	19.479	10.947	5.872	2.631

coefficients[c]	C_{62}	C_{63}	C_{64}	C_{65}	C_{66}
Hf	0.0243	−0.0677	0.1394	−0.3204	1.0417
Ta	0.0254	−0.0708	0.1458	−0.3277	1.0431
W	0.0263	−0.0732	0.1508	−0.3318	1.0438
Re	0.0269	−0.0751	0.1546	−0.3338	1.0439
Os	0.0275	−0.0766	0.1577	−0.3341	1.0436
Ir	0.0279	−0.0778	0.1600	−0.3333	1.0430
Pt	0.0282	−0.0788	0.1618	−0.3317	1.0422
Au	0.0285	−0.0795	0.1631	−0.3293	1.0413
Hg	0.0287	−0.0800	0.1639	−0.3264	1.0403

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[a] Metal charge of +1; configuration $5d^{n-3}\,6s^1\,6p^1$.

[b] Single-μ representation.

[c] $6p$ orbital.

Table 5. *Analytical Functions for d and f Orbitals*[a]

orbital	exponents	*d*-orbitals				*f* orbitals	
atom	n	μ_3	μ_4	μ_5	μ_5'	μ_4	μ_4
Hf	4	19.279	9.794	4.360	1.709	11.798	5.241
Ta	5	19.604	9.997	4.762	1.938	12.199	5.534
W	6	19.929	10.202	4.982	2.068	12.358	5.673
Re	7	20.255	10.409	5.343	2.277	12.554	5.840
Os	8	20.580	10.617	5.571	2.416	12.738	5.982
Ir	9	20.905	10.826	5.796	2.557	12.982	6.168
Pt	10	21.230	11.035	6.013	2.696	13.184	6.324
Au	11	21.556	11.246	6.163	2.794	13.347	6.415
Hg[b]	12	21.881	11.457	6.436	3.032	13.495	6.504

coefficients	$5d$ orbital[c]				$4f$ orbital[c]	
	C_{53}	C_{54}	C_{55}	$C_{55'}$	C_{44}	$C_{44'}$
Hf	0.0934	−0.2507	0.7145	0.5458	0.5350	0.6239
Ta	0.1052	−0.2844	0.6815	0.5774	0.5273	0.6246
W	0.1139	−0.3077	0.6940	0.5631	0.5474	0.6015
Re	0.1230	−0.3342	0.6662	0.5910	0.5623	0.5826
Os	0.1304	−0.3541	0.6689	0.5877	0.5787	0.5632
Ir	0.1372	−0.3724	0.6698	0.5860	0.5872	0.5509
Pt	0.1436	−0.3893	0.6707	0.5844	0.6003	0.5343
Au	0.1492	−0.4030	0.6851	0.5696	0.6191	0.5140
Hg[b]	0.1598	−0.4322	0.6905	0.5593	0.6393	0.4915

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[a] Metal charge of +1; configuration $5d^{n-1}$.

[b] Configuration $5d^{n-2}\,6s^1$.

[c] Double-μ representation.

both for the original functions and for double-μ approximations to each. As noted by PRATT [*12*], the numerical HSF functions are very close to the analytical Hartree-Fock ones.

Finally, different analytical approximations, varying in the accuracy with which they reproduce the numerical functions, are compared in Tab. 7 for the Au^+ ($5d^8\,6s^1\,6p^1$) $6s$ function.

Discussion

The HFS numerical functions are approximate solutions to the non-relativistic Hartree-Fock equations for atomic systems [*17*]. A detailed account of the approximations involved and the consequences of invoking these approximations is given by HS [*7*] and others [*8, 17, 20*]. We restrict ourselves, therefore, to a discussion of the fitting procedure leading to the analytical functions.

Eq. (11) for S_n is familiar as the starting point for the usual least squares regression using the radial distance $r^{(t)}$ as a weighting factor at each point t. The choice of $r^{(t)}$ as a weighting factor over $[r^{(t)}]^2$ or a constant factor of unity is a compromise and introduces an element of arbitrariness into the fitted functions. It is to be noted that a minimum value of S_n using a constant weighting factor of unity will not come at the same value for the orbital exponent as a minimum value of S_n using $[r^{(t)}]^2$ as the weighting factor. The former corresponds to fitting the numerical function, $X_n^{(t)}$, whereas the latter corresponds to fitting $P_n^{(t)} = r^{(t)}\,X_n^{(t)}$, the radial-charge-distribution function. In fitting the radial function directly (constant weighting factor of unity), the inner parts of $X_n^{(t)}$ are faithfully reproduced at the expense of the "tail", since the largest contributions to S_n come from those places where $X_n^{(t)}$ has its largest amplitude, the innermost parts of the numerical function. In addition, the radial points chosen for fitting correspond to every eighth point on a 521 point integration mesh used in calculating $X_n^{(t)}$. These radial points (in atomic units) are not equally spaced; the smaller $r^{(t)}$ values are separated by smaller intervals than the larger $r^{(t)}$. This results in a larger number of small radial points over large radial points for any given distance from the nucleus. Thus, the innermost parts of $X_n^{(t)}$ are doubly favored; by the inherent nature of the radial function, and by the uneven intervals between the radial points chosen for the fitting procedure.

Alternatively, fitting $P_n^{(t)}$ (weighting factor of $[r^{(t)}]^2$) results in the reverse situation; the "tail" of the numerical function is faithfully reproduced while the inner portions are badly represented. This reflects a deficiency in the size of the basis set, not in the fitting method.

The compromise solution consists of using Eq. (11) to define the S_n used as the fitting criterion. Although fitting the innermost parts of an orbital would be desirable for energy considerations [*6, 14, 18*], since the largest contributions to the energy of an atom come from those electrons closest to the nucleus, the immediate uses envisioned for these analytical functions, in semi-empirical molecular orbital calculations, require that they accurately represent the extension of the radial function at large radial distances. For the purpose it is also important that the position of the outermost maximum of the radial charge density be accurately reproduced in the analytical function [*19*]. This is the additional criterion used in the double-μ representation in choosing among the various sets of parameters which give approximately the same value of S_n.

Examination of Tab. 6 and 7 shows that, with the orthogonality restrictions [Eq. (5)], both the single-μ and double-μ representations yield analytical functions which are not as accurate as might be desired. This is not unexpected in the single-μ representation, where only one variable parameter is used for each orbital. In fact, considering the limited size of the basis set, the fit must be considered remarkably good. The disappointment comes in the double-μ representation, where trebling the number of parameters does not proportionately increase the accuracy. However, the gross features of the numerical functions are followed very closely and certain inaccuracies may cancel each other in calculations of quantities such as overlap integrals, for example. Thus, the "tails" of the analytical functions presented here usually fall off too steeply at large $r^{(t)}$, whereas the outermost maximum peaks at a slightly larger value of the radial distance for the fitted analytical function than for the numerical function. In calculating diatomic overlap integrals, we may expect that these two small deviations will approximately cancel.

Table 6. *Comparison of Hartree-Fock and Hartree-Fock-Slater Functions for the* Cu^+ *3d Orbital*

$r^{(t)}$[a]	$X_3^{(t)}$[b]	$T_{3d}^{(t)}$[c]	CLEMENTI[d]	RICHARDSON[e]
0.0007	0.000	0.000	0.000	0.000
0.0122	0.036	0.023	0.032	0.019
0.0238	0.122	0.081	0.109	0.066
0.0418	0.320	0.224	0.288	0.182
0.0648	0.629	0.467	0.570	0.384
0.0893	0.971	0.764	0.883	0.632
0.1354	1.542	1.325	1.411	1.113
0.1815	1.955	1.801	1.799	1.535
0.2536	2.291	2.277	2.130	1.999
0.3458	2.338	2.450	2.204	2.205
0.4438	2.146	2.285	2.053	2.123
0.6282	1.612	1.652	1.579	1.623
0.8126	1.146	1.099	1.146	1.130
1.1008	0.672	0.615	0.689	0.653
1.4697	0.356	0.354	0.374	0.373
1.8616	0.193	0.214	0.205	0.221
2.5992	0.071	0.076	0.073	0.077
3.3370	0.028	0.023	0.028	0.023
4.4896	0.007	0.003	0.006	0.003
5.9651	0.001	0.000	0.001	0.000

[a] Radial points in atomic units.

[b] HFS numerical function.

[c] Fitted HFS numerical function; $T_{5d} = 0.6267\ R_3\,(6.2494) + 0.5566\ R_3\,(2.2824)$.

[d] Analytical Hartree-Fock from reference [*5*].

[e] Fitted analytical Hartree-Fock (double-μ representation) from reference [*13*].

The degree of accuracy of the fitted functions, within the same size basis set, can be improved by relaxing the orthogonality constraint for functions of the same l and different n. Then, for the single-μ representation, the $2n - 2l - 1$ parameters ($n - l$ orbital exponents and $n - l - 1$ coefficients) can be derived iteratively, one by one. This is easily extended to include a double-μ representation for the outermost maximum. The results, illustrated for the 6*s* orbital of Au^+ in Tab. 7, show that the size of the basis set is the limiting factor in obtaining a very accurate fit.

If each of the orbitals of a given and different *n* are fitted separately in this manner, the derived analytical functions will still be approximately orthogonal since the numerical functions being fitted are exactly orthogonal. The required machine time, however, is greatly increased. Considering the approximations involved in deriving the numerical functions [*7*, *17*], the time and effort required to improve the fit by optimizing the individual orbital exponents and coefficients for all the orbitals separately are probably not justified.

Table 7. *Comparison of Fitted and Numerical Orbital Functions for the* Au^+ 6*s* *Orbital*[a]

$r(t)$[b]	$X_6(t)$[c]	$T_{6s}(t)$[d]	$T_{6s}(t)$[e, g]	$T_{6s}(t)$[f, g]
0.0005	−16.556	−19.478	−18.447	−17.881
0.0088	− 7.773	− 8.227	− 8.064	− 8.019
0.0170	− 2.676	− 2.396	− 2.356	− 2.458
0.0299	1.208	1.318	1.438	1.367
0.0464	2.273	2.097	2.173	2.202
0.0640	1.572	1.457	1.352	1.420
0.0970	− 0.283	− 0.021	− 0.327	− 0.299
0.1300	− 1.067	− 0.739	− 0.944	− 0.970
0.1816	− 0.700	− 0.726	− 0.606	− 0.649
0.2476	0.260	− 0.108	0.203	0.199
0.3178	0.669	0.363	0.585	0.615
0.4498	0.268	0.413	0.297	0.333
0.5819	− 0.258	0.048	− 0.200	− 0.209
0.7882	− 0.452	− 0.328	− 0.464	− 0.484
1.0523	− 0.171	− 0.282	− 0.232	− 0.203
1.3329	0.132	− 0.012	0.092	0.149
1.8611	0.334	0.316	0.359	0.349
2.3893	0.296	0.334	0.331	0.278
3.2147	0.169	0.179	0.163	0.164
4.2711	0.070	0.048	0.040	0.077
5.3935	0.025	0.008	0.007	0.028
7.5064	0.003	0.000	0.000	0.002

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[a] Configuration $5d^8\,6s^1\,6p^1$.

[b] Radial points in atomic units.

[c] Numerical *HFS* function.

[d] Single-μ; orthogonal to 5*s*, 4*s*, etc.; from Tab. 3.

[e] Single-μ; no orthogonality constraints.

[f] Double-μ; no orthogonality constraints.

[g] Limit of accuracy has not been reached.

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References

[*1*] Ballhausen, C. J., and H. B. Gray: Molecular orbital theory. New York: Benjamin 1964.
[*2*] Basch, H., A. Viste, and H. B. Gray: J. chem. Physics, **44**, 10 (1966), and references therein.
[*3*] Buckingham, A. D., and P. J. Stevens: J. chem. Soc. 4583 (1964).
[*4*] Burns, G.: J. chem. Physics **41**, 1521 (1964).

[5] Clementi, E.: Tables of atomic functions, Supplement to IBM Journal of Res. and Dev. **9**, 2 (1965).
[6] —, and D. L. Raimondi: J. chem. Physics **38**, 2686 (1963).
[7] Herman, F., and S. Skillman: Atomic structure calculations. Englewood Cliffs, New Jersey: Prentice-Hall, Inc. 1963.
[8] Liberman, D., J. T. Waber, and D. T. Cromer: Physic. Rev. **137**, A 27 (1965).
[9] Løwdin, P. O.: Physic. Rev. **90**, 120 (1953); **94**, 1600 (1954).
[10] —, and K. Appel: Physic. Rev. **103**, 1746 (1956).
[11] Margenau, H., and G. M. Murphy: The mathematics of chemistry and physics, p. 497. Princeton, New Jersey: D. Van Nostrand Co. Inc. 1956.
[12] Pratt, Jr., G. W.: Physic. Rev. 88, 1217 (1952).
[13] Richardson, J. W., W. C. Nieupoort, R. R. Powell, and W. F. Edgell: J. chem. Physics **36**, 1057 (1962).
[14] —, R. R. Powell, and W. C. Nieupoort: J. chem. Physics **38**, 796 (1963).
[15] Slater, J. C.: Physic. Rev. **36**, 56 (1930).
[16] — Physic. Rev. **42**, 33 (1932).
[17] — Physic. Rev. **81**, 385 (1951).
[18] — Quantum theory of atomic structure, Vol. I, Chap. 15. New York: McGraw-Hill Co. Inc.
[19] — J. chem. Physics **41**, 3199 (1964).
[20] Snow, E. C., J. M. Canfield, and J. T. Waber: Physic. Rev. **135**, A 969 (1964).

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