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Double Zeta *d* Radial Wave Functions for Transition Elements

NOEL J. FITZPATRICK and GEORGE H. MURPHY

Department of Chemistry, University College, Belfield, Dublin 4, Ireland

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Abstract

A consistent double zeta set of exponents and coefficients for neutral and +1 charged transition metals is presented. The results were calculated by fitting analytical functions to numerical Herman–Skillman calculations.

Results and Discussion

Recently [1] a consistent set of single zeta wave functions for all elements of the periodic table has been published. The single zeta Slater Type Orbitals (STO) were represented by:

$$R(r) = Nr^{n-1}e^{-\zeta r}$$

The exponents were calculated by maximising the overlap between the analytical functions and numerical Herman–Skillman [2] results. These single zeta STOs are adequate for many uses. However, it has been shown [3] that double zeta radial wave functions of the type:

$$R(r) = \sum_{1}^{2} C_i N_i r^{n-1} \exp(-\zeta_i r_i)$$

are preferable.

Single zeta relativistic ($Z = 1-120$) and non-relativistic functions ($Z = 1-100$) have been given by

TABLE I. 3d Exponents and Coefficients for the First Transition Series; Neutral Atoms

	ζ_1	ζ_2	C_1	C_2
Sc	3.807	1.455	0.460	0.702
Ti	4.218	1.664	0.469	0.686
V	4.600	1.846	0.474	0.677
Cr	4.978	2.022	0.475	0.673
Mn	5.318	2.176	0.481	0.666
Fe	5.653	2.325	0.485	0.661
Co	5.996	2.476	0.486	0.659
Ni	6.339	2.625	0.486	0.658
Cu	6.676	2.768	0.487	0.657
Zn	7.015	2.911	0.487	0.656

TABLE II. 3d Exponents and Coefficients for the First Transition Series; +1 Ions

	ζ_1	ζ_2	C_1	C_2
Sc	3.816	1.465	0.459	0.701
Ti	4.231	1.673	0.468	0.686
V	4.617	1.858	0.472	0.678
Cr	4.975	2.024	0.477	0.671
Mn	5.314	2.178	0.483	0.664
Fe	5.656	2.331	0.485	0.660
Co	6.002	2.484	0.486	0.659
Ni	6.343	2.632	0.486	0.657
Cu	6.684	2.777	0.486	0.657
Zn	7.024	2.921	0.486	0.656

TABLE III. 4d Exponents and Coefficients for the Second Transition Series; Neutral Atoms

	ζ_1	ζ_2	C_1	C_2
Y	2.554	1.068	0.602	0.578
Zr	2.769	1.224	0.650	0.508
Nb	2.955	1.333	0.686	0.462
Mo	3.126	1.408	0.717	0.426
Tc	3.293	1.468	0.743	0.399
Ru	3.429	1.453	0.780	0.368
Rh	3.577	1.452	0.805	0.348
Pd	3.746	1.501	0.815	0.338
Ag	3.912	1.545	0.825	0.329
Cd	4.094	1.640	0.824	0.325

TABLE IV. 4d Exponents and Coefficients for the Second Transition Series; +1 Ions

	ζ_1	ζ_2	C_1	C_2
Y	2.574	1.146	0.597	0.563
Zr	2.764	1.249	0.657	0.493
Nb	2.976	1.379	0.678	0.462
Mo	3.137	1.435	0.715	0.423
Tc	3.330	1.482	0.744	0.394
Ru	3.428	1.450	0.785	0.362
Rh	3.584	1.466	0.805	0.346
Pd	3.747	1.497	0.818	0.334
Ag	3.921	1.565	0.823	0.328
Cd	4.101	1.657	0.823	0.324

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TABLE V. 5d Exponents and Coefficients for the Third Transition Series; Neutral Atoms

	ζ_1	ζ_2	C_1	C_2
La	3.153	1.338	0.594	0.612
Hf	3.337	1.505	0.637	0.546
Ta	3.478	1.606	0.674	0.496
W	3.609	1.683	0.705	0.456
Re	3.734	1.742	0.732	0.424
Os	3.851	1.782	0.758	0.395
Ir	3.968	1.813	0.780	0.371
Pt	4.084	1.840	0.798	0.352
Au	4.200	1.861	0.814	0.336
Hg	4.353	1.979	0.810	0.332

TABLE VI. 5d Exponents and Coefficients for the Third Transition Series; +1 Ions

	ζ_1	ζ_2	C_1	C_2
La	3.236	1.468	0.571	0.610
Hf	3.373	1.572	0.628	0.542
Ta	3.500	1.652	0.670	0.492
W	3.622	1.713	0.705	0.451
Re	3.739	1.759	0.735	0.417
Os	3.857	1.797	0.760	0.390
Ir	3.974	1.828	0.781	0.367
Pt	4.094	1.862	0.797	0.349
Au	4.211	1.886	0.813	0.334
Hg	4.350	1.969	0.815	0.327

Pyykkö and Lohr [4]. Pyykkö *et al.* [5–7] have also calculated double zeta functions. Clementi and Roetti [8] have reported double zeta Roothaan–Hartree–Fock atomic wavefunction for $Z \leq 54$, while McLean and McLean [9] have given corresponding functions for $Z = 55$–92. Both groups consider the $d^{n-2}s^2$ configurations for the transition series fully and $d^{n-1}s^1$ partially. The exponents of Clementi and Roetti for the first transition series are slightly larger than those now reported. Thus the present set, being less contracted, is preferable to discuss the bonding in transition metal complexes, where the $d^{n-2}s^2$ functions, as opposed to the $d^{n-1}s^1$ ones, have a tendency not to be sufficiently diffuse. Similarly, in the other two transition series the exponents now reported are smaller than the Roothaan–Hartree–Fock ones, previously published [8, 9].

Using the double zeta form of the radial wave function and again getting the best fit with the Herman–Skillman numerical results, the exponents and coefficients for d radial wave function for neutral and +1 charged transition metals, shown in the tables, were calculated. The configurations considered for the neutral atoms were $d^{n-2}s^2$ for the s and d orbitals and $d^{n-2}s^1p^1$ for the p orbitals. For the ions the configurations corresponding to the removal of an s electron were considered.

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