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Commentationes

Gaussian Basis Sets for Molecular Wavefunctions Containing Third-Row Atoms

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A Gaussian basis set consisting of 12*s*-type, 6*p*-type and 4*d*-type functions has been optimized for the third row atoms, together with a 9*s*, 5*p*, 3*d* set for the corresponding dipositive ion. The applicability of these atomic sets for molecular calculation is discussed.

Ein Basissatz von 12*s*-, 6*p*- und 4*d*-Funktionen für die Atome der dritten Reihe des periodischen Systems ist optimalisiert worden; das gleiche gilt für einen entsprechenden Satz für die zweifach positiven Ionen aus 9*s*-, 5*p*- und 3*d*-Funktionen. Ferner wird ihre Anwendbarkeit bei Rechnungen an Molekülen diskutiert.

On présente un ensemble optimal de fonctions de base gaussiennes pour les atomes et les ions de la troisième ligne. Cet ensemble est constitué de 12 fonctions du type *s*, 6 fonctions du type *p* et 4 fonctions du type *d* pour l'atome neutre et de 9 fonctions *s*, 5 fonctions *p* et 3 fonctions *d* pour l'ion M^{2+}. On discute l'emploi de ces bases pour des calculs moléculaires.

To day, *ab-initio* calculations of the LCAO-MO-SCF type are fairly common for molecules of arbitrary geometry including first-row and second-row atoms. This has been made possible through the use of Gaussian-type functions as basis orbitals and the availability of various gaussian basis sets for the first-row and second-row atoms [1]. The situation appears less favourable for the molecules or ions involving third-row atoms. The lack or scarcity of gaussian basis sets for the third-row atoms might have a retarding effect on molecular orbital calculations. So far, two basis sets have been reported for this region of the periodic table. The first one, for the first-row transition metal atoms, consists of 15*s*-type, 8*p*-type and 5*d*-type Gaussian functions [2]. The second one, for the third-row atoms up to Zn, consists of 14*s*-type, 9*p*-type and 5*d*-type functions [3]. These are large basis sets which yield a value of the total energy close to the Hartree-Fock limit. The set reported by Wachters [3] is an extension of the 10*s*,6*p* set optimized by Huzinaga for the first-row atoms [4] and of the 12*s*,9*p* set optimized by Veillard for the second-row atoms [5]. Basis sets of this size are used in order to get accurate wavefunctions. However, useful qualitative information has been obtained from less accurate wavefunctions for molecules including first-row atoms. These wavefunctions were built from medium-size basis

sets ranging from $7s,3p$ to $9s,5p$ [6–8]. We feel that there is a need to obtain medium-size basis sets for the third-row atoms, especially if molecular calculations are to be performed for transition metal complexes with a relatively large number of ligand atoms.

We report here two optimized basis sets for the third row atoms and ions. The Gaussian-type functions used in the present paper are defined as

$$Nr^l \exp(-\xi r^2)\, Y_{lm}(\theta, \varphi)$$

where N is an appropriate normalizing factor [4]. Optimization of the basis set was achieved through minimization of the SCF atomic energy with respect to the gaussian orbital exponents. The first basis set is a $9s,5p,3d$ set optimized for the ground state of the dipositive ion M^{2+} (see below the discussion). Five $1s$ functions are used to describe the $1s$ atomic orbital, two $1s$ functions for the $2s$ and $3s$ atomic orbitals, three $2p$ functions for the $2p$ atomic orbital, two $2p$ functions for the $3p$ atomic orbital and three $3d$ functions for the $3d$ atomic orbital. This set can be used in conjunction with a $7s$, $3p$ set for the first-row atoms [6–8]. The second basis set is a $12s,6p,4d$ set optimized for the lowest state of the $3d^n4s^2$ neutral atom configuration. Respectively six, two, two and two $1s$ functions are used for the $1s$, $2s$, $3s$ and $4s$ atomic orbitals, four and two $2p$ functions for the $2p$ and $3p$ atomic orbitals and four $3d$ functions for the $3d$ atomic orbital. This set should be used in conjunction with a $8s,4p$ set for the first-row atoms [7] and a $10s$, $6p$ set for the second-row atoms [8].

Orbital exponent optimization was performed using a program written for atomic calculations [9]. Tables 1 and 2 show the optimized energy values together with the best results obtained with Slater orbitals. The orbital exponents are reported in Tables 3 and 5, the orbital energies and expansion coefficients in Tables 4 and 6. Since one usually turns to a contraction of the basis functions for molecular calculations, we also report in Tables 1 and 2 the energy values obtained for some contracted basis sets. For the $9s,5p,3d$ set we considered a minimal contracted basis set except for the $3d$ valence shell which uses split orbitals. For the $12s,6p,4d$ set we considered also a minimal contracted basis set with split orbitals for the $3d$ and $4s$ valence shells together with the result of a "double-zeta" contracted basis set (*id est* with two contracted orbitals for each atomic shell).

Some questions can be raised in connection with the use of these basis sets for molecular calculations. The first one is relative to the use of orbital exponents optimized for the neutral atom in the calculation of wavefunction for ionic species. For instance, it was found that in the cluster NiF_6^{4-} the total population for each atom is very close to that for the free ion [11]. We have found that this problem is relatively unimportant since exponents optimized respectively for the neutral atom and the dipositive ion, using a similar basis set, are very close one to another. We performed an exponent optimization for the Cu^{++} ion with a $10s,6p,4d$ set similar to the $12s,6p,4d$ set used for the Cu atom. The lower s exponent for Cu^{++} was 1.04 while the corresponding value for Cu^0 was 1.12. The lower d exponent was 0.66 for Cu^{++} and 0.70 for Cu^0. The energy value for Cu^{++} was -1637.570 a.u. with the exponents optimized for Cu^{++} and -1637.563 a.u. with the exponents optimized for Cu^0.

Table 1. *Total energy (in a.u.) for the ground state of the dipositive ion* M^{2+}

Ion 2+	GTO[a]	CGTO[b]	STO[c]
Sc (^2D)	− 758.3988	− 755.7181	− 759.0921
Ti (^3F)	− 846.9318	− 843.9241	− 847.7303
V (^4F)	− 941.2578	− 937.9868	− 942.1784
Cr (^5D)	−1041.5147	−1038.0051	−1042.5740
Mn (^6S)	−1147.8887	−1144.0971	−1149.1080
Fe (^5D)	−1260.2498	−1256.1510	−1261.6556
Co (^4F)	−1378.9888	−1374.5666	−1380.5991
Ni (^3F)	−1504.1888	−1499.4044	−1506.0286
Cu (^2D)	−1635.9879	−1630.8975	−1638.0832
Zn (^1S)	−1774.5847	−1769.1266	−1776.9579

[a] Uncontracted basis set 9*s*, 5*p*, 3*d*.
[b] Contracted basis set (1, 2, 3, 4, 5)(6, 7)(8, 9)/(1, 2, 3)(4, 5)/(1, 2)(3).
[c] Best result with Slater orbitals from Ref. [10].

Table 2. *Total energy (in a.u.) for the lowest state of the* $3d^n4s^2$ *neutral atom configuration*

Atom	GTO[a]	CGTO[b]	CGTO[c]	STO[d]
K (^2S)	− 599.0184	− 597.9619	− 598.9541	− 599.1645
Ca (^1S)	− 676.6038	− 675.3369	− 676.5295	− 676.7580
Sc (^2D)	− 759.5574	− 758.1174	− 759.4754	− 759.7356
Ti (^3F)	− 848.2001	− 846.6108	− 848.1138	− 848.4052
V (^4F)	− 942.6456	− 940.8640	− 942.5516	− 942.8829
Cr (^5D)	−1043.0370	−1041.0634	−1042.9370	−1043.3061
Mn (^6S)	−1149.5527	−1147.3974	−1149.4433	−1149.8651
Fe (^5D)	−1262.0818	−1259.7272	−1261.9615	−1262.4425
Co (^4F)	−1381.0004	−1378.4145	−1380.8693	−1381.4136
Ni (^3F)	−1506.3969	−1503.6356	−1506.2619	−1506.8690
Cu (^2D)	−1638.4121	−1635.3810	−1638.2576	−1638.9491
Zn (^1S)	−1777.2409	−1773.9511	−1777.0784	−1777.8470

[a] Uncontracted basis set 12*s*, 6*p*, 4*d*.
[b] Contracted basis set (1, 2, 3, 4, 5, 6)(7, 8)(9, 10)(11)(12)/(1, 2, 3, 4)(5, 6)/(1, 2, 3)(4).
[c] Contracted basis set (1, 2, 3, 4)(5, 6)(7)(8)(9)(10)(11)(12)/(1, 2, 3)(4)(5)(6)/(1, 2, 3)(4).
[d] Best result with Slater orbitals from Ref. [10].

Another question is relative to the adequacy of the valence shell exponents optimized for the atom in molecular calculations. Examination of the exponent values reported in Table 1 indicate that, for the 3*d* orbitals with optimized exponents, the maximum of charge density will be too close to the nucleus for effective participation to the molecular bonding (assuming average bond length values between 1.5 and 2 Å). On the contrary, the orbitals representative of the 4*s* valence shell appear too diffuse, they extend too far away from the bond region. We conclude that an additional 3*d* orbital with a low exponent value should be used for molecular calculations. Simultaneously, the gaussian functions representative of the 4*s* atomic orbital should be discarded and replaced with some functions of higher exponent. In studies on nickel and copper complexes, we have

Table 3. *Orbitals exponents of the basis set 9s,5p,3d*

	Sc	Ti	V	Cr	Mn
s	17487.1	19809.7	21477.0	23362.7	25500.4
	2696.22	3001.54	3269.53	3532.00	3867.12
	623.042	694.487	755.634	813.124	891.241
	177.784	197.865	215.795	232.991	254.726
	56.8455	63.1946	69.1219	74.9245	81.8517
	13.0699	14.7130	15.9141	17.6791	19.3196
	5.33459	6.03959	6.62739	7.35570	8.07486
	1.31421	1.52294	1.65690	1.81811	2.01652
	0.534775	0.610241	0.667203	0.732528	0.804589
p	137.556	154.885	172.998	190.658	208.602
	31.5338	35.4886	39.6735	43.7183	47.8430
	9.06937	10.2433	11.4782	12.6785	13.9565
	2.43994	2.75855	3.09164	3.40004	3.72356
	0.690628	0.787131	0.886824	0.983839	1.08448
d	6.19207	7.32670	8.60073	10.0091	11.3265
	1.47409	1.78745	2.11541	2.47334	2.80948
	0.364773	0.447528	0.526129	0.610535	0.698108
	Fe	Co	Ni	Cu	Zn
s	27196.3	30165.2	32260.2	34677.9	38011.5
	4120.56	4573.53	4907.01	5275.88	5747.45
	952.534	1052.72	1131.78	1217.27	1319.99
	273.711	300.528	323.739	348.010	376.889
	88.5642	96.6770	104.201	111.982	121.439
	21.1774	23.3569	25.0693	26.9098	29.3363
	8.88725	9.77620	10.5734	11.3757	12.4537
	2.24366	2.46579	2.68849	2.86660	3.14422
	0.888434	0.971807	1.06449	1.12305	1.22736
p	227.314	246.223	269.005	291.007	313.159
	52.2324	56.8510	62.1403	67.1702	72.3356
	15.3017	16.6867	18.2558	19.7789	21.3328
	4.07755	4.43121	4.85357	5.25234	5.63023
	1.19594	1.30369	1.42726	1.54758	1.66578
d	12.7344	14.0830	15.5038	17.0869	18.6112
	3.15947	3.49960	3.86506	4.26917	4.66051
	0.774040	0.850434	0.932390	1.02366	1.11441

used an additional 3*d* function of exponent 0.2 and two 1*s* functions of exponent 0.32 and 0.08 [12].

For a similar reason, we found that orbital exponents representative of the 4*p* atomic orbital cannot be obtained from energy optimization for some excited configurations. They should also be chosen in order to get a maximum of the charge density in the bonding region. A rather similar conclusion has already been obtained for the 3*d* orbital exponents of second-row atoms [8].

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Table 4. *Orbital energies and expansion coefficients (basis set 9s,5p,3d)*

	Sc	Ti	V	Cr	Mn
1*s*	−166.410	−183.800	−202.049	−221.138	−241.129
	− 0.00482	− 0.00469	− 0.00472	− 0.00474	− 0.00471
	− 0.03510	− 0.03461	− 0.03478	− 0.03531	− 0.03488
	− 0.15784	− 0.15537	− 0.15626	− 0.15827	− 0.15694
	− 0.42479	− 0.42244	− 0.42232	− 0.42380	− 0.42297
	− 0.47157	− 0.47468	− 0.47413	− 0.47051	− 0.47219
	− 0.07526	− 0.07794	− 0.07824	− 0.07617	− 0.07750
	0.02372	0.02446	0.02553	0.02354	0.02426
	− 0.00800	− 0.00818	− 0.00841	− 0.00758	− 0.00777
	0.00333	0.00331	0.00343	0.00310	0.00314
2*s*	− 19.5991	− 21.9591	− 24.4304	− 26.9928	− 29.7039
	− 0.00141	− 0.00138	− 0.00140	− 0.00142	− 0.00142
	− 0.01051	− 0.01044	− 0.01058	− 0.01082	− 0.01075
	− 0.04956	− 0.04920	− 0.04983	− 0.05088	− 0.05076
	− 0.16196	− 0.16196	− 0.16381	− 0.16603	− 0.16667
	− 0.26843	− 0.27236	− 0.27324	− 0.27441	− 0.27689
	0.30782	0.29596	0.31035	0.30657	0.30866
	0.75670	0.76454	0.75442	0.76000	0.75883
	0.09842	0.10228	0.09866	0.09988	0.09862
	− 0.01976	− 0.01926	− 0.01923	− 0.02006	− 0.01908
3*s*	− 3.08782	− 3.41120	− 3.73837	− 4.05790	− 4.40257
	0.00049	0.00049	0.00050	0.00051	0.00052
	0.00370	0.00374	0.00383	0.00394	0.00395
	0.01757	0.01770	0.01815	0.01870	0.01881
	0.05868	0.05958	0.06090	0.06226	0.06299
	0.10241	0.10557	0.10767	0.10947	0.11159
	− 0.14545	− 0.14256	− 0.15621	− 0.15779	− 0.16235
	− 0.56482	− 0.57827	− 0.57633	− 0.58089	− 0.58442
	0.40335	0.39725	0.44213	0.46155	0.47429
	0.80714	0.81764	0.78022	0.76295	0.75511
2*p*	− 16.1326	− 18.2690	− 20.5148	− 22.8494	− 25.3326
	0.06752	0.06637	0.06541	0.06532	0.06559
	0.34909	0.34726	0.34565	0.34711	0.34850
	0.61991	0.62127	0.62279	0.62362	0.62321
	0.17393	0.17427	0.17416	0.17102	0.16920
	− 0.01757	− 0.01770	− 0.01774	− 0.01787	− 0.01830
3*p*	− 2.07903	− 2.31527	− 2.55419	− 2.78695	− 3.04201
	− 0.02367	− 0.02372	− 0.02374	− 0.02397	− 0.02431
	− 0.12755	− 0.12990	− 0.13179	− 0.13455	− 0.13712
	− 0.25123	− 0.25603	− 0.26000	− 0.26192	− 0.26302
	0.26906	0.27909	0.28843	0.30235	0.31500
	0.83892	0.83145	0.82454	0.81367	0.80357
3*d*	− 0.84808	− 0.95774	− 1.03768	− 1.09841	− 1.18598
	0.14338	0.14803	0.14972	0.14962	0.15319
	0.47896	0.48532	0.49012	0.49183	0.49679
	0.63479	0.62312	0.61838	0.61787	0.60978

Table 4 (continued)

	Fe	Co	Ni	Cu	Zn
1*s*	−261.951	−283.665	−306.231	−329.640	−353.943
	− 0.00480	− 0.00463	− 0.00466	− 0.00465	0.00453
	− 0.03551	− 0.03437	− 0.03444	− 0.03435	0.03375
	− 0.15860	− 0.15529	− 0.15521	− 0.15491	0.15322
	− 0.42283	− 0.42092	− 0.42042	− 0.42041	0.41726
	− 0.46934	− 0.47396	− 0.47446	− 0.47491	0.47776
	− 0.07791	− 0.07957	− 0.07991	− 0.07979	0.08339
	0.02423	0.02406	0.02470	0.02470	− 0.02595
	− 0.00771	− 0.00759	− 0.00779	− 0.00766	0.00803
	0.00307	0.00301	0.00308	0.00302	− 0.00315
2*s*	− 32.5207	− 35.4709	− 38.5313	− 41.6876	− 44.9933
	− 0.00145	− 0.00141	− 0.00143	− 0.00143	− 0.00140
	− 0.01101	− 0.01070	− 0.01078	− 0.01080	− 0.01065
	− 0.05165	− 0.05080	− 0.05100	− 0.05111	− 0.05076
	− 0.16800	− 0.16734	− 0.16819	− 0.16907	− 0.16800
	− 0.27746	− 0.28153	− 0.28269	− 0.28401	− 0.28624
	0.30512	0.29445	0.30086	0.30688	0.29240
	0.76132	0.77056	0.76528	0.76255	0.77213
	0.10058	0.10251	0.10169	0.09877	0.10362
	− 0.01895	− 0.01916	− 0.01884	− 0.01841	− 0.01928
3*s*	− 4.75197	− 5.11734	− 5.48749	− 5.85194	− 6.24573
	0.00054	0.00052	0.00053	0.00053	0.00052
	0.00408	0.00399	0.00403	0.00406	0.00402
	0.01929	0.01909	0.01928	0.01940	0.01934
	0.06400	0.06413	0.06477	0.06534	0.06523
	0.11280	0.11526	0.11666	0.11789	0.11924
	− 0.16263	− 0.15867	− 0.16574	− 0.17189	− 0.16449
	− 0.58986	− 0.59763	− 0.59515	− 0.59420	− 0.60174
	0.47175	0.47413	0.47542	0.50864	0.49468
	0.75993	0.75879	0.75898	0.73043	0.74296
2*p*	− 27.9176	− 30.6355	− 33.4623	− 36.3813	− 39.4498
	0.06572	0.06589	0.06507	0.06501	0.06510
	0.34929	0.34994	0.34833	0.34925	0.35034
	0.62297	0.62371	0.62478	0.62468	0.62520
	0.16774	0.16540	0.16604	0.16466	0.16262
	− 0.01838	− 0.01836	− 0.01825	− 0.01819	− 0.01843
3*p*	− 3.30034	− 3.57325	− 3.84816	− 4.11821	− 4.41456
	− 0.02459	− 0.02485	− 0.02473	− 0.02484	− 0.02499
	− 0.13932	− 0.14121	− 0.14188	− 0.14347	− 0.14520
	− 0.26433	− 0.26570	− 0.26794	− 0.26854	− 0.26878
	0.32365	0.33541	0.33894	0.34606	0.35650
	0.79652	0.78734	0.78489	0.77927	0.77053
3*d*	− 1.18552	− 1.21596	− 1.24512	− 1.26478	− 1.31211
	0.15472	0.15811	0.16075	0.16185	0.16462
	0.49782	0.50171	0.50432	0.50524	0.50842
	0.61056	0.60637	0.60355	0.60303	0.59873

Table 5. *Orbital exponents of the basis set 12s,6p,4d*

	K	Ca	Sc	Ti	V	Cr
1*s*	35793.1	41913.6	45822.6	48680.0	50281.3	55643.4
	5582.95	6177.05	6824.96	7144.04	7424.64	8240.33
	1266.93	1398.88	1539.60	1638.02	1716.55	1876.03
	357.820	396.028	433.931	465.527	492.456	537.177
	115.311	128.244	140.439	152.394	163.130	177.239
	40.0442	44.7503	49.2303	54.0349	58.2952	63.3965
	9.39581	10.7175	12.0090	13.2356	14.8239	16.2072
	3.76564	4.35046	4.92315	5.47417	6.09769	6.73669
	0.811518	1.03222	1.21920	1.38870	1.57364	1.74645
	0.320545	0.436709	0.515736	0.583370	0.650938	0.717674
	0.040000	0.063625	0.076408	0.080663	0.088861	0.094109
	0.018000	0.026995	0.031836	0.032828	0.035435	0.036848
2*p*	197.376	229.840	259.687	284.565	311.142	357.615
	45.6830	53.7651	60.9968	66.8999	73.2585	83.6031
	13.9463	16.5150	18.8155	20.7458	22.8156	25.9210
	4.69104	5.58088	6.40111	7.13330	7.91458	8.97595
	1.14343	1.41714	1.65914	1.87140	2.10690	2.41609
	0.344210	0.447944	0.527407	0.596298	0.674850	0.766685
3*d*			13.1089	13.7482	15.9635	18.3628
			3.16767	3.50857	4.14158	4.79639
			0.896721	1.04080	1.23818	1.44225
			0.239050	0.287729	0.343496	0.400287

	Mn	Fe	Co	Ni	Cu	Zn
1*s*	60370.5	63509.8	71283.9	73850.4	76569.1	82831.3
	8910.51	9344.59	10328.7	10939.2	11944.7	12711.4
	2008.93	2156.66	2363.30	2504.61	2726.44	2919.19
	579.251	627.320	677.873	720.706	785.697	836.851
	192.434	208.380	224.950	240.114	261.625	277.916
	69.0690	74.8588	81.0468	86.8503	94.3546	100.822
	17.7053	19.2876	21.0939	22.4686	24.5815	26.4643
	7.39915	8.09403	8.87011	9.50508	10.4216	11.2290
	1.94442	2.14813	2.36802	2.57910	2.80706	3.03908
	0.791057	0.868997	0.953468	1.02958	1.12010	1.20441
	0.101306	0.110224	0.118259	0.125776	0.131029	0.140711
	0.039118	0.041854	0.044273	0.046377	0.047955	0.050700
2*p*	383.732	424.039	459.697	493.637	537.269	595.547
	90.5004	98.9427	109.051	116.498	127.621	140.104
	28.2205	30.8593	33.9790	36.5669	39.9997	43.8249
	9.82707	10.7975	11.8744	12.8762	14.0748	15.4003
	2.64911	2.91785	3.24082	3.54585	3.88005	4.24035
	0.839238	0.924889	1.02446	1.12160	1.22287	1.33289
3*d*	21.0880	23.2006	25.5415	27.9859	30.5295	33.6927
	5.51882	6.13066	6.78969	7.47243	8.19102	9.05781
	1.66192	1.84927	2.04924	2.25654	2.47533	2.73823
	0.461264	0.505755	0.555999	0.608474	0.664120	0.731228

Table 6. *Orbital energies and expansion coefficients (basis set 12s,6p,4d)*

	K	Ca	Sc	Ti	V	Cr
1s	−133.519	−149.347	−165.877	−183.254	−201.483	−220.548
	0.00152	0.00147	0.00147	0.00156	0.00167	0.00162
	0.01136	0.01152	0.01150	0.01212	0.01284	0.01268
	0.05704	0.05723	0.05763	0.05931	0.06201	0.06209
	0.20106	0.20098	0.20300	0.20638	0.21113	0.21149
	0.44186	0.43967	0.44087	0.43848	0.43933	0.44136
	0.40033	0.40069	0.39696	0.39326	0.38528	0.38312
	0.04980	0.05183	0.05161	0.05224	0.04915	0.04897
	−0.01448	−0.01559	−0.01555	−0.01623	−0.01400	−0.01409
	0.00480	0.00577	0.00578	0.00598	0.00502	0.00494
	−0.00245	−0.00303	−0.00298	−0.00298	−0.00243	−0.00235
	0.00074	0.00086	0.00083	0.00078	0.00062	0.00058
	−0.00041	−0.00044	−0.00042	−0.00039	−0.00031	−0.00029
2s	−14.4791	−16.8121	−19.0645	−21.4099	−23.8597	−26.4073
	−0.00044	−0.00042	0.00043	−0.00046	−0.00050	−0.00049
	−0.00326	−0.00334	0.00337	−0.00358	−0.00383	−0.00380
	−0.01706	−0.01728	0.01757	−0.01826	−0.01925	−0.01941
	−0.06307	−0.06385	0.06522	−0.06704	−0.06948	−0.07005
	−0.17780	−0.17861	0.18150	−0.18326	−0.18625	−0.18906
	−0.22914	−0.23289	0.23379	−0.23336	−0.23333	−0.23322
	0.41444	0.40268	−0.40219	0.40991	0.40817	0.41245
	0.68408	0.68964	−0.68902	0.68258	0.68804	0.68376
	0.06953	0.07874	−0.08107	0.07917	0.07785	0.07899
	−0.01992	−0.02155	0.02076	−0.01888	−0.01716	−0.01738
	0.00537	0.00527	−0.00499	0.00428	0.00383	0.00380
	−0.00298	−0.00268	0.00249	−0.00214	−0.00189	−0.00188
3s	−1.74142	−2.23914	−2.55591	−2.86214	−3.16870	−3.47597
	−0.00014	−0.00014	0.00015	0.00016	0.00018	0.00017
	−0.00107	−0.00115	0.00119	0.00128	0.00138	0.00139
	−0.00562	−0.00597	0.00620	0.00653	0.00697	0.00709
	−0.02104	−0.02229	0.02327	0.02431	0.02551	0.02597
	−0.06030	−0.06355	0.06602	0.06768	0.06965	0.07137
	−0.08309	−0.08845	0.09106	0.09275	0.09429	0.09546
	0.19114	0.19479	−0.20123	−0.21232	−0.21551	−0.22286
	0.48397	0.51725	−0.52904	−0.53210	−0.54162	−0.54120
	−0.59406	−0.52034	0.50544	0.51778	0.52716	0.53963
	−0.60899	−0.68702	0.70719	0.70295	0.70088	0.69240
	−0.01574	−0.02716	0.03173	0.03118	0.02939	0.02773
	0.00620	0.01062	−0.01219	−0.01235	−0.01142	−0.01085
4s	−0.14538	−0.19371	−0.20684	−0.21732	−0.22640	−0.23439
	−0.00002	−0.00003	−0.00003	−0.00003	−0.00004	−0.00003
	−0.00020	−0.00027	−0.00027	−0.00029	−0.00031	−0.00030
	−0.00106	−0.00140	−0.00144	−0.00149	−0.00155	−0.00153
	−0.00402	−0.00527	−0.00545	−0.00558	−0.00571	−0.00567
	−0.01138	−0.01496	−0.01540	−0.01546	−0.01553	−0.01552
	−0.01620	−0.02126	−0.02173	−0.02166	−0.02152	−0.02124
	0.03926	0.04898	0.05035	0.05198	0.05156	0.05198
	0.09527	0.13140	0.13331	0.13173	0.13086	0.12755
	−0.12670	−0.15406	−0.14789	−0.15112	−0.15044	−0.15123
	−0.31094	−0.38536	−0.38542	−0.36946	−0.35861	−0.34437
	0.53654	0.62049	0.54754	0.59386	0.57645	0.59049
	0.57530	0.52455	0.59410	0.54329	0.55776	0.54012

Table 6 (continued)

	K	Ca	Sc	Ti	V	Cr
2p	− 11.4966	− 13.6065	− 15.6392	− 17.7639	− 19.9923	− 22.3171
	0.02729	0.02565	0.02513	0.02568	0.02609	0.02440
	0.17150	0.16202	0.15943	0.16259	0.16498	0.15873
	0.46263	0.45201	0.44943	0.45281	0.45557	0.45090
	0.48292	0.49482	0.49653	0.48977	0.48402	0.49165
	0.06648	0.07505	0.07704	0.07452	0.07286	0.07690
	− 0.01108	− 0.01218	− 0.01193	− 0.01119	− 0.01052	− 0.01055
3p	− 0.94367	− 1.33054	− 1.55878	− 1.77867	− 1.99914	− 2.21963
	− 0.00853	− 0.00856	− 0.00865	− 0.00904	− 0.00935	− 0.00886
	− 0.05354	− 0.05421	− 0.05503	− 0.05734	− 0.05921	− 0.05783
	− 0.16223	− 0.16905	− 0.17377	− 0.18011	− 0.18534	− 0.18554
	− 0.13760	− 0.15686	− 0.16232	− 0.15929	− 0.15664	− 0.16496
	0.49820	0.49487	0.49878	0.51488	0.52186	0.51491
	0.63250	0.63421	0.63185	0.61696	0.61010	0.61979
3d			− 0.33005	− 0.42391	− 0.48847	− 0.54001
			0.05103	0.06175	0.06286	0.06341
			0.25099	0.27291	0.27687	0.27995
			0.51110	0.51483	0.51745	0.51777
			0.49986	0.46154	0.45268	0.44846

	Mn	Fe	Co	Ni	Cu	Zn
1s	−240.552	−261.345	−283.032	−305.584	−328.995	−353.285
	0.00162	0.00169	0.00163	0.00168	0.00170	0.00170
	0.01284	0.01320	0.01286	0.01307	0.01270	0.01277
	0.06309	0.06284	0.06242	0.06348	0.06257	0.06254
	0.21138	0.21100	0.21218	0.21402	0.21049	0.21289
	0.43976	0.44009	0.43912	0.43926	0.43768	0.43842
	0.38319	0.38283	0.38282	0.38017	0.38499	0.38157
	0.04951	0.04966	0.05008	0.04951	0.05115	0.05138
	− 0.01444	− 0.01452	− 0.01445	− 0.01479	− 0.01503	− 0.01520
	0.00501	0.00500	0.00492	0.00503	0.00503	0.00509
	− 0.00233	− 0.00230	− 0.00223	− 0.00224	− 0.00222	− 0.00223
	0.00057	0.00055	0.00052	0.00051	0.00049	0.00049
	− 0.00028	− 0.00027	− 0.00025	− 0.00025	− 0.00024	− 0.00024
2s	− 29.1028	− 31.9117	− 34.8393	− 37.8852	− 41.0478	− 44.3239
	− 0.00049	− 0.00051	− 0.00049	− 0.00051	− 0.00052	− 0.00053
	− 0.00388	− 0.00401	− 0.00393	− 0.00400	− 0.00391	− 0.00395
	− 0.01986	− 0.01990	− 0.01985	− 0.02031	− 0.02009	− 0.02016
	− 0.07052	− 0.07080	− 0.07164	− 0.07262	− 0.07169	− 0.07292
	− 0.18996	− 0.19139	− 0.19201	− 0.19416	− 0.19328	− 0.19497
	− 0.23446	− 0.23557	− 0.23729	− 0.23570	− 0.24002	− 0.23937
	0.41573	0.41810	0.41417	0.43029	0.41804	0.42031
	0.68116	0.67946	0.68329	0.66975	0.68014	0.67925
	0.07839	0.07829	0.07948	0.07607	0.07939	0.07845
	− 0.01650	− 0.01601	− 0.01588	− 0.01446	− 0.01534	− 0.01477
	0.00356	0.00341	0.00332	0.00300	0.00309	0.00296
	− 0.00175	− 0.00167	− 0.00162	− 0.00145	− 0.00150	− 0.00143

Table 6 (continued)

	Mn	Fe	Co	Ni	Cu	Zn
3s	− 3.79754	− 4.14354	− 4.49282	− 4.85110	− 5.21841	− 5.59028
	0.00018	− 0.00019	0.00018	− 0.00019	− 0.00019	0.00020
	0.00143	− 0.00149	0.00146	− 0.00150	− 0.00147	0.00149
	0.00731	− 0.00738	0.00740	− 0.00761	− 0.00756	0.00762
	0.02636	− 0.02667	0.02716	− 0.02769	− 0.02746	0.02804
	0.07228	− 0.07340	0.07411	− 0.07536	− 0.07534	0.07631
	0.09693	− 0.09836	0.09986	− 0.10002	− 0.10233	0.10266
	− 0.22878	0.23400	− 0.23450	0.24831	0.24297	− 0.24682
	− 0.54275	0.54470	− 0.54912	0.54260	0.54888	− 0.54910
	0.54551	− 0.55185	0.55092	− 0.56554	− 0.56194	0.56878
	0.69103	− 0.68840	0.69116	− 0.68233	− 0.68482	0.68061
	0.02721	− 0.02683	0.02699	− 0.02564	− 0.02591	0.02512
	− 0.01067	0.01042	− 0.01050	0.00992	0.01023	− 0.00978
4s	− 0.24202	− 0.25138	− 0.25945	− 0.26716	− 0.27450	− 0.28114
	− 0.00003	− 0.00004	− 0.00003	− 0.00003	− 0.00003	− 0.00003
	− 0.00030	− 0.00031	− 0.00030	− 0.00030	− 0.00029	− 0.00029
	− 0.00154	− 0.00153	− 0.00151	− 0.00152	− 0.00148	− 0.00146
	− 0.00561	− 0.00559	− 0.00558	− 0.00559	− 0.00543	− 0.00544
	− 0.01533	− 0.01532	− 0.01518	− 0.01514	− 0.01485	− 0.01474
	− 0.02105	− 0.02102	− 0.02094	− 0.02058	− 0.02064	− 0.02031
	0.05213	0.05248	0.05164	0.05365	0.05146	0.05130
	0.12467	0.12318	0.12179	0.11814	0.11725	0.11480
	− 0.14901	− 0.14888	− 0.14569	− 0.14736	− 0.14401	− 0.14241
	− 0.33402	− 0.32623	− 0.31949	− 0.30964	− 0.30196	− 0.29507
	0.57759	0.56505	0.55589	0.55362	0.56196	0.54128
	0.54945	0.56030	0.56694	0.56761	0.55605	0.57546
2p	− 24.7912	− 27.3714	− 30.0718	− 32.8883	− 35.8203	− 38.8684
	0.02506	0.02472	0.02447	0.02496	0.02448	0.02351
	0.16096	0.16155	0.15854	0.16147	0.15879	0.15575
	0.45387	0.45455	0.45458	0.45551	0.45462	0.45184
	0.48700	0.48537	0.48696	0.48263	0.48509	0.48964
	0.07424	0.07401	0.07460	0.07352	0.07453	0.07643
	− 0.01004	− 0.00991	− 0.00953	− 0.00909	− 0.00909	− 0.00927
3p	− 2.45322	− 2.70864	− 2.96638	− 3.23188	− 3.50479	− 3.78135
	− 0.00921	− 0.00920	− 0.00919	− 0.00945	− 0.00934	− 0.00903
	− 0.05926	− 0.06015	− 0.05963	− 0.06130	− 0.06070	− 0.05987
	− 0.18997	− 0.19314	− 0.19498	− 0.19767	− 0.19882	− 0.19886
	− 0.16070	− 0.15959	− 0.16233	− 0.15992	− 0.16198	− 0.16536
	0.52949	0.53686	0.53594	0.53944	0.54123	0.54031
	0.60584	0.59877	0.60106	0.59777	0.59697	0.59865
3d	− 0.61089	− 0.61095	− 0.63228	− 0.65667	− 0.68268	− 0.71810
	0.06333	0.06540	0.06700	0.06848	0.06979	0.06952
	0.28294	0.28749	0.29198	0.29628	0.29980	0.30021
	0.52016	0.51785	0.51733	0.51699	0.51670	0.51677
	0.44272	0.44311	0.44043	0.43736	0.43471	0.43510

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