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Gaussian Basis Set for Molecular Wavefunctions Containing Second-Row Atoms

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A Gaussian basis set consisting of 12*s*-type and 9*p*-type functions has been optimized for the second-row atoms. Energy values are also reported for different contractions of this basis set.

Es wird ein Basissatz von 12*s*- und 9*p*-Gaußfunktionen für die Atome der zweiten Periode optimiert. Für verschiedene Kontraktionen dieser Basis werden die Energiewerte angegeben.

On presente un ensemble optimal de fonctions de base gaussiennes pour les atomes de la seconde ligne. Cet ensemble comprend 12 fonctions du type *s* et 9 fonctions du type *p*. On etudie egalement l'effet de differentes contractions de cet ensemble sur l'energie totale.

Most of *ab initio* calculations for molecules of general geometry resort to gaussian orbitals for the expansion of the wavefunction. In this respect, the basis set optimized by Huzinaga for the first row atoms [1] has proved extremely useful, since the sets used for molecules are usually too large to allow any optimization of the orbital exponents. The work of Huzinaga was restricted to the first-row atoms. We report here an optimized basis set for the second-row atoms. Optimization of the basis set was achieved through minimization of the SCF atomic energy with respect to the gaussian orbital exponents. Other methods can also be used, such as a least-square fitting of Hartree-Fock orbitals expanded with respect to Slater-type orbitals [2].

Table 1. *Total energy (in a.u.)*

	GTO[a]	CGTO[b]	STO[c]
Na(^2S)	−161.85259	−161.84160	−161.85889
Mg(^1S)	−199.60777	−199.59312	−199.61458
Al(^2P)	−241.87118	−241.85580	−241.87665
Si(^3P)	−288.84857	−288.83328	−288.85426
P(^4S)	−340.71213	−340.69578	−340.71866
S(^3P)	−397.49776	−397.48183	−397.50475
Cl(^2P)	−459.47405	−459.45557	−459.48187
Ar(^1S)	−526.80828	−526.78325	−526.81734

[a] Uncontracted basis set 12*s*, 9*p*.
[b] Best result from Table 5.
[c] Best result with Slater orbitals from Ref. [5].

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Table 2. *Orbital exponents*

	Na(^2S)	Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
1*s*	36631.1	43643.6	55112.7	69989.3	77718.0	94181.1	105747.	118186.
	5385.07	6585.89	8204.66	10380.2	11609.3	13921.8	15855.3	17688.8
	1216.20	1510.32	1863.56	2330.01	2644.29	3168.04	3615.32	4027.30
	339.529	431.833	530.195	657.466	753.328	901.843	1030.03	1144.96
	109.563	142.071	174.895	214.004	248.525	296.954	339.691	376.954
	38.7834	51.4089	64.0090	77.6064	91.0698	108.669	124.497	138.070
	14.5790	19.9361	25.3231	30.6395	36.1916	43.1579	49.5143	54.9540
	5.27901	8.04158	10.5639	12.8156	15.2063	18.1168	20.8138	23.1650
	1.82902	2.50948	3.21260	3.92714	4.71378	5.57096	6.46497	7.37688
	0.620535	0.871939	1.15432	1.45221	1.78316	2.14287	2.52567	2.92369
	0.058065	0.108819	0.178128	0.257644	0.343249	0.434389	0.538139	0.650663
	0.024617	0.040455	0.065885	0.094404	0.125204	0.157093	0.193558	0.232877
2*p*	148.928	192.644	259.307	337.495	385.322	494.274	587.622	660.901
	34.5149	45.7493	60.9263	78.6871	90.6269	116.981	139.745	157.219
	10.6045	14.2558	19.3113	24.9351	28.7788	37.4960	44.7900	50.0639
	3.67106	4.99324	6.99747	9.21515	10.6643	13.8938	16.5885	18.6119
	1.28490	1.78234	2.66879	3.61526	4.24361	5.50267	6.60076	7.43692
	0.430941	0.615100	1.03447	1.45199	1.73769	2.24291	2.71409	3.08857
			0.307591	0.503992	0.595843	0.773628	0.950083	1.10267
			0.113877	0.186040	0.228550	0.291781	0.358271	0.414763
			0.041397	0.065432	0.083760	0.102867	0.124986	0.145449

Table 3. *Orbital energies and expansion coefficients*

	Na(^2S)	Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
1*s*	−40.4758	−49.0290	−58.4999	−68.8110	−79.9684	−92.0028	−104.882	−118.608
	0.00038	0.00038	0.00035	0.00031	0.00032	0.00030	0.00030	0.00030
	0.00305	0.00293	0.00275	0.00249	0.00255	0.00240	0.00236	0.00238
	0.01599	0.01496	0.01418	0.01303	0.01314	0.01235	0.01220	0.01233
	0.06427	0.05863	0.05585	0.05227	0.05195	0.04909	0.04844	0.04908
	0.19481	0.17661	0.16789	0.16151	0.15809	0.15099	0.14902	0.15104
	0.40099	0.37113	0.35419	0.34767	0.34099	0.33176	0.32876	0.33177
	0.39267	0.40079	0.40028	0.40445	0.40463	0.40836	0.40884	0.40780
	0.08282	0.12384	0.15029	0.16243	0.17114	0.18573	0.19018	0.18556
	−0.00265	0.00375	0.00759	0.00914	0.01040	0.01235	0.01310	0.01259
	0.00177	0.00052	−0.00032	−0.00067	−0.00095	−0.00145	−0.00165	−0.00152
	−0.00031	−0.00003	0.00017	0.00025	0.00031	0.00042	0.00045	0.00038
	0.00017	0.00001	−0.00008	−0.00011	−0.00014	−0.00018	−0.00020	−0.00017
2*s*	−2.79516	−3.76584	−4.90963	−6.15531	−7.51002	−9.00301	−10.6060	−12.3208
	−0.00009	−0.00009	−0.00009	−0.00008	−0.00008	−0.00008	− 0.00008	− 0.00008
	−0.00074	−0.00073	−0.00071	−0.00066	−0.00069	−0.00066	− 0.00066	− 0.00067
	−0.00396	−0.00384	−0.00374	−0.00352	−0.00362	−0.00346	− 0.00347	− 0.00355
	−0.01613	−0.01514	−0.01482	−0.01419	−0.01440	−0.01382	− 0.01384	− 0.01422
	−0.05310	−0.04979	−0.04859	−0.04764	−0.04757	−0.04609	− 0.04614	− 0.04740
	−0.12776	−0.11832	−0.11480	−0.11479	−0.11473	−0.11260	−0.11321	−0.11644
	−0.19952	−0.20111	−0.19991	−0.20269	−0.20438	−0.20578	− 0.20794	−0.21140
	0.03427	−0.02310	−0.05228	−0.06623	−0.07669	−0.09047	− 0.09603	− 0.09415
	0.59803	0.57420	0.55218	0.54349	0.53543	0.52974	0.52772	0.53045
	0.48579	0.53517	0.56269	0.57276	0.58178	0.58890	0.59131	0.58860
	0.01663	0.02118	0.02743	0.03119	0.03476	0.03739	0.03956	0.04085
	−0.00762	−0.00801	−0.00885	−0.00869	−0.00872	−0.00861	− 0.00833	− 0.00785
3*s*	−0.18174	−0.25270	−0.39313	−0.53936	−0.69592	−0.87879	−1.07195	−1.27634
	0.00001	0.00001	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002
	0.00011	0.00014	0.00016	0.00016	0.00019	0.00019	0.00020	0.00021

Table 3 (continued)

	$Na(^2S)$	$Mg(^1S)$	$Al(^2P)$	$Si(^3P)$	$P(^4S)$	$S(^3P)$	$Cl(^2P)$	$Ar(^1S)$
3*s*	0.00060	0.00074	0.00086	0.00090	0.00099	0.00100	0.00104	0.00110
	0.00241	0.00291	0.00342	0.00365	0.00397	0.00404	0.00422	0.00448
	0.00822	0.00971	0.01132	0.01228	0.01311	0.01340	0.01396	0.01481
	0.01915	0.02298	0.02696	0.03007	0.03239	0.03370	0.03541	0.03773
	0.03311	0.04123	0.04861	0.05434	0.05851	0.06196	0.06515	0.06838
	−0.01052	0.00306	0.01273	0.01926	0.02488	0.03162	0.03558	0.03699
	−0.09898	−0.13501	−0.16340	−0.18536	−0.20193	−0.21687	−0.23035	−0.24463
	−0.20686	−0.25490	−0.30809	−0.34190	−0.36596	−0.38535	−0.39972	−0.40856
	0.59948	0.59531	0.60750	0.60651	0.61259	0.63458	0.64197	0.64828
	0.48401	0.52058	0.53539	0.55734	0.56627	0.55752	0.56122	0.56446
2*p*	−1.51611	−2.28022	−3.21727	−4.25486	−5.39985	−6.68128	−8.07086	−9.57015
	0.00513	0.00475	0.00407	0.00354	0.00370	0.00313	0.00294	0.00299
	0.03791	0.03462	0.03048	0.02754	0.02858	0.02423	0.02290	0.02364
	0.15341	0.14372	0.12689	0.11649	0.12149	0.10600	0.10216	0.10589
	0.35313	0.34665	0.31355	0.29330	0.30214	0.28302	0.27867	0.28567
	0.45550	0.46489	0.43981	0.43275	0.43369	0.43808	0.43849	0.44322
	0.24372	0.24109	0.28558	0.30572	0.29089	0.31509	0.31892	0.30458
			0.03353	0.04573	0.03897	0.04567	0.04728	0.04162
			−0.00564	−0.00389	−0.00423	−0.00430	−0.00378	−0.00368
			0.00192	0.00151	0.00138	0.00177	0.00195	0.00116
3*p*			−0.20972	−0.29670	−0.39125	−0.43673	−0.50558	−0.59016
			−0.00073	−0.00075	−0.00088	−0.00080	−0.00080	−0.00084
			−0.00549	−0.00593	−0.00682	−0.00619	−0.00618	−0.00662
			−0.02361	−0.02566	−0.03000	−0.02806	−0.02864	−0.03088
			−0.05845	−0.06608	−0.07568	−0.07600	−0.07927	−0.08458
			−0.08897	−0.10235	−0.11780	−0.12805	−0.13676	−0.14528
			−0.05068	−0.07229	−0.06422	−0.07442	−0.07645	−0.06726
			0.22619	0.20252	0.26816	0.27867	0.29440	0.32467
			0.54403	0.56412	0.56239	0.55806	0.55450	0.55074
			0.37439	0.38465	0.31943	0.32395	0.31609	0.28994

The number of gaussian functions was chosen so that the basis set could be used in conjunction with the $10s-6p$ set reported by Huzinaga for the first-row atoms. By inspection from Huzinaga's set, this implies that eight $1s$ functions are used to describe the $1s$ atomic orbital, two $1s$ functions for the $2s$ atomic orbital and six $2p$ functions for the $2p$ atomic orbital. One can expect that the $3s$ atomic orbital will be adequately represented with two additional $1s$ functions. As to the $3p$ atomic orbital, we found that a fair representation could be obtained by using three additional $2p$ functions. This makes a total of twelve $1s$ functions and nine $2p$ functions. No attempt was made to include some $3s$ type gaussian orbitals.

Orbital exponent optimization was performed using a program written for atomic calculations [3], which in its main lines is similar to the one described by Roothaan and Bagus [4]. We first proceeded by optimizing a $10s-6p$ basis set for the Si^{4+} ion. Then two $1s$ functions were added to this set to represent the $3s$ orbital and exponent optimization was performed again for the Si^{2+} ion. Last, the three $2p$ functions describing the $3p$ atomic orbital were added and the optimization process was repeated this time for the Si atom. Once this was completed, a fairly good guess could be derived for the orbital exponents of the Al and P atoms, since there is a roughly constant ratio between the orbital exponents of two consecutive atoms. This ratio can be easily inferred from previously reported results with Slater orbitals [5].

Table 1 shows the optimized energy values together with the best results obtained with Slater orbitals. The orbital exponents are reported in Table 2, the orbital energies and expansion coefficients in Table 3. Because of the existence of multiple minima, it is not claimed that the orbital exponents and energy values are fully optimized. However, it seems reasonable that any further optimization would not change more than the last two figures given for the total energy. Since these basis sets are intended for molecular calculations which usually depart from the Hartree-Fock limit by at least 0.01 a.u., this seems of little importance.

In order to make molecular calculations feasible despite the large number of gaussian functions which are needed, one usually turns to a "contraction" which replaces the individual basis functions with some appropriate linear combinations

Table 4. *Contraction of the orbitals*

Contraction No.	Grouping of the Gaussian basis orbitals[a]
1	(1 2 3 4) (5 6 7 8) (9) (10) (11) (12)/(13 14 15 16) (17 18) (19 20) (21)
2	(1 2 3 4 5) (6 7 8) (9) (10) (11) (12)/(13 14 15 16) (17 18) (19 20) (21)
3	(1 2 3 4 5 6) (7 8) (9) (10) (11) (12)/(13 14 15 16) (17 18) (19 20) (21)
4	(1 2 3 4 5 6 7) (8) (9) (10) (11) (12)/(13 14 15 16) (17 18) (19 20) (21)
5	(1 2 3 4 5 6) (7 8) (9) (10) (11) (12)/(13 14 15) (16 17 18) (19 20) (21)
6	(1 2 3 4 5 6) (7 8) (9) (10) (11) (12)/(13 14 15 16 17) (18) (19 20) (21)
7	(1 2 3 4 5 6) (7 8) (9) (10) (11) (12)/(13 14 15 16 17) (18) (19) (20 21)
8	(1 2 3 4 5 6) (7 8) (9) (10) (11) (12)/(13 14 15 16) (17 18) (19) (20 21)
9	(1 2 3 4 5 6) (7 8) (9) (10) (11) (12)/(13 14 15) (16 17 18) (19) (20 21)

[a] The notation (1 2 3 4) ... means that the first contracted orbital is a linear combination of the first four orbitals reported in Table 2, with the coefficients equal to the first four expansion coefficients of the $1s$ orbital in Table 3.

Table 5. *Atomic energy (in a.u.) from the contracted calculations*

Contraction No.	Na[a]	Mg[a]	Al	Si	P	S	Cl	Ar
1	−161.79699	−199.52636	−241.75649	−288.69398	−340.52738	−397.26468	−459.19633	−526.49026
2	−161.84160	−199.59312	−241.84474	−288.80654	−340.66319	−397.42848	−459.38887	−526.71345
3	−161.82278	−199.58930	−241.85214	−288.82393	−340.68892	−397.46987	−459.44045	−526.76843
4	−161.75252	−199.50752	−241.75978	−288.71529	−340.56263	−397.32710	−459.27626	−526.57570
5			−241.85185	−288.82283	−340.68846	−397.46915	−459.43984	−526.76832
6			−241.85300	−288.82675	−340.69077	−397.47313	−459.44493	−526.77462
7			−241.85576	−288.83316	−340.69546	−397.48130	−459.45498	−526.78325
8			−241.85579	−288.83328	−340.69560	−397.48148	−459.45491	−526.78162
9			−241.85580	−288.83325	−340.69578	−397.48183	−459.45557	−526.78264

[a] For the Na and Mg atoms, the energy does not depend on the contraction used for the *p*-type orbitals.

[6]. A previous paper dealt with the choice of these contracted functions and the effect of the contraction on the total energy for the first row atoms [7]. We now report the results obtained when the optimized basis set of 12*s* and 6*p* gaussian functions is contracted to 6*s*-type and 4*p*-type linear combinations, namely two contracted functions describe each atomic orbital. Given this number of contracted functions, one can think of many different groupings of the basis functions. Of course, we did not consider all the possible contractions and we report in Table 4 only the nine groupings which appear as the most plausible from an energy point of view. The coefficients of the linear combinations are taken equal to the expansion coefficients of Table 3. The corresponding total energies are reported in Table 5 and the lowest value for each atom is also given in Table 1 together with the energy for the uncontracted set.

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