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Gaussian Basis Sets for the First and Second Row Atoms

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Gaussian basis sets consisting for first row atoms of 7 *s*-type and 3 *p*-type and for second row atoms of 10 *s*-type and 6 *p*-type functions with optimized exponents are reported. These basis sets consists of at least two functions per atomic orbital.

Es werden für die Atome der ersten und zweiten Reihe Basissätze aus Gaußfunktionen mitgeteilt, die aus 7 Funktionen vom *s*-Typ und 3 Funktionen vom *p*-Typ für die Elemente der ersten Reihe und 10 Funktionen vom *s*-Typ und 6 Funktionen vom *p*-Typ für die Elemente der zweiten Reihe mit optimierten Exponenten bestehen. Diese Basissätze bestehen aus wenigstens zwei Funktionen pro Atomorbital.

Une base de 7 gaussiens du type *s* et 3 du type *p* est presenté pour les éléments du premier rang et de 10 gaussiens du type *s* et 6 du type *p* pour des éléments du deuxième rang; les exposants sont optimisés. Les bases consistent au moins en deux fonctions par orbital atomique.

Several large computer program systems are today available for large scale all electron MO-SCF calculations on molecules, using Gaussian functions as basis orbitals. Atomic basis sets for use in such calculations are available in the literature [1–12]. The basis sets with fully optimized exponents for the separate atoms are at the Hartree-Fock limit. In order to achieve this many

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

Atom	GTO	STO
Li (^2S)	− 7.429	− 7.433
Be (^1S)	− 14.567	− 14.573
B (^2P)	− 24.514	− 24.529
C (^3P)	− 37.656	− 37.689
N (^4S)	− 54.339	− 54.401
O (^3P)	− 74.700	− 74.809
F (^2P)	− 99.234	− 99.409
Ne (^1S)	−128.284	−128.547
Na (^2S)	−161.787	−161.859
Mg (^1S)	−199.534	−199.615
Al (^2P)	−241.811	−241.877
Si (^3P)	−288.773	−288.854
P (^4S)	−340.630	−340.719
S (^3P)	−397.400	−397.505
Cl (^2P)	−459.358	−459.482
Ar (^1S)	−526.673	−526.817

Table 2. *Orbital exponents for the atoms* Li–Ne

GTO	Li	Be	B	C	N	O	F	Ne
1*s*	284.399	547.083	992.490	1412.29	2038.41	2714.89	3373.81	4095.18
	42.3482	81.6023	147.330	206.885	301.689	415.725	495.323	619.634
	9.37924	18.2378	31.7359	45.8498	66.4630	91.9805	110.303	139.810
	2.50578	4.94019	8.38942	12.3887	17.8081	24.4515	29.9871	38.0736
	0.733345	1.47438	2.48651	3.72337	5.30452	7.22296	9.05545	11.4502
	0.073733	0.177797	0.325501	0.524194	0.764993	1.06314	1.40327	1.79556
	0.029787	0.059381	0.104399	0.163484	0.234424	0.322679	0.419736	0.532277
2*p*			2.70937	4.18286	5.95461	7.75579	10.3347	12.9564
			0.532831	0.851563	1.23293	1.62336	2.15444	2.72012
			0.125188	0.199206	0.286752	0.365030	0.472793	0.591654

Table 3. *Orbital exponents for the atoms* Na–Ar

GTO	Na	Mg	Al	Si	P	S	Cl	Ar
1*s*	9387.07	13222.1	17011.1	19237.2	22566.5	25506.3	28656.3	31867.6
	1415.03	1983.12	2550.77	2885.41	3380.80	3812.82	4299.00	4780.92
	326.160	449.711	578.256	655.111	766.417	860.556	976.335	1086.32
	94.0976	126.311	162.093	184.413	214.964	242.940	274.415	305.908
	31.2957	40.6081	51.7073	59.2516	68.9703	97.0448	89.0063	99.7541
	11.1802	14.0488	17.7035	20.4626	23.9195	27.5705	31.2371	35.2510
	2.26229	2.83014	3.65079	4.41116	5.26929	6.49476	7.76951	9.08941
	0.723387	0.946932	1.28635	1.61479	1.96297	2.41078	3.07933	3.65762
	0.074103	0.104438	0.192347	0.291392	0.350435	0.469815	0.651038	0.808670
	0.032716	0.040018	0.086448	0.140147	0.131021	0.173396	0.240798	0.293273
2*p*	39.1856	51.0503	71.062677	95.7865	109.959	129.088	150.436	173.059
	8.75009	11.4895	16.323969	21.9200	25.1292	29.6305	34.7101	40.0236
	2.42775	3.24676	4.890113	6.43988	7.51127	8.84715	10.4071	12.0613
	0.661647	0.917529	1.579507	1.98998	2.39583	2.85576	3.37330	3.95842
			0.467637	0.482930	0.531089	0.626108	0.748495	0.894152
			0.091675	0.122840	0.150160	0.175233	0.207855	0.248681

Table 4. *Orbital energies and expansion coefficients for the atoms* Li–Ne

	Li	Be	B	C	N	O	F	Ne
1*s*	-2.47534	-4.72932	-7.69230	- 11.3227	- 15.6271	- 20.6667	- 26.3751	- 32.7620
	0.005889	0.005504	0.004627	0.004813	0.004479	0.004324	0.004545	0.004596
	0.044471	0.041496	0.036157	0.037267	0.034581	0.032265	0.035130	0.034256
	0.194745	0.184411	0.173653	0.172403	0.164263	0.156410	0.164336	0.159910
	0.474138	0.466399	0.463934	0.459261	0.453898	0.447813	0.451030	0.446842
	0.428081	0.441496	0.455348	0.456185	0.468979	0.481602	0.467475	0.474669
	0.024888	0.026916	0.031233	0.034215	0.038039	0.042157	0.040793	0.043169
	-0.010571	-0.009633	-0.009995	- 0.009977	- 0.010577	- 0.011360	- 0.010225	- 0.010552
2*s*	-0.19622	-0.30893	-0.49323	- 0.70230	- 0.93969	- 1.23430	- 1.55390	- 1.90409
	-0.000936	-0.001003	-0.000930	- 0.001020	- 0.000981	- 0.000975	- 0.001046	- 0.001073
	-0.006993	-0.007696	-0.007457	- 0.008141	- 0.007822	- 0.007518	- 0.008360	- 0.008277
	-0.032973	-0.035477	-0.036667	- 0.038437	- 0.037808	- 0.037030	- 0.039811	- 0.039300
	-0.085931	-0.105550	-0.118763	- 0.126098	- 0.128928	- 0.130541	- 0.136263	- 0.136706
	-0.166643	-0.174139	-0.185588	- 0.190474	- 0.197084	- 0.204753	- 0.202501	- 0.206704
	0.523078	0.521417	0.535204	0.522342	0.513598	0.504708	0.503917	0.497024
	0.556303	0.580040	0.575574	0.594186	0.605721	0.616743	0.621272	0.629452
2*p*			-0.30368	- 0.42171	- 0.54900	- 0.60187	- 0.68452	- 0.78874
			0.101016	0.112194	0.119664	0.129373	0.129667	0.133080
			0.453693	0.466227	0.474629	0.481269	0.481296	0.483546
			0.639975	0.622569	0.611142	0.604484	0.608133	0.605240

Table 5. *Orbital energies and expansion coefficients for the atoms* Na–Ar

	Na	Mg	Al	Si	P	S	Cl	Ar
1*s*	−40.4681	−49.0234	−58.4965	−68.7918	−79.9534	−91.9874	−104.866	−118.590
	0.002089	0.001699	0.001518	0.001570	0.001531	0.001546	0.001558	0.001576
	0.015809	0.013047	0.011687	0.012066	0.011793	0.011973	0.011941	0.012070
	0.075278	0.064729	0.058316	0.059960	0.058861	0.059943	0.059685	0.060275
	0.242519	0.223459	0.206651	0.210054	0.208183	0.207528	0.208871	0.209731
	0.457550	0.459832	0.449346	0.449954	0.447369	0.442977	0.444010	0.442296
	0.338911	0.366056	0.394128	0.387533	0.390968	0.392193	0.388159	0.386563
	0.026512	0.030647	0.040279	0.040624	0.043349	0.044891	0.046877	0.048238
	− 0.005779	− 0.007114	− 0.010799	− 0.011270	− 0.011793	− 0.011027	− 0.011362	− 0.011239
	0.001828	0.001924	0.003786	0.004430	0.003554	0.003370	0.003299	0.003174
	− 0.001051	− 0.000996	− 0.002035	− 0.002374	− 0.001599	− 0.001458	− 0.001374	− 0.001281
2*s*	− 2.78680	− 3.75984	− 4.90162	− 6.13564	− 7.49670	− 8.98913	− 10.5912	− 12.3048
	− 0.000514	− 0.000433	− 0.000397	− 0.000421	− 0.000418	− 0.000429	− 0.000439	− 0.000450
	− 0.003841	− 0.003277	− 0.003030	− 0.003204	− 0.003198	− 0.003315	− 0.003351	− 0.003433
	− 0.019381	− 0.017159	− 0.015818	− 0.016657	− 0.016657	− 0.017197	− 0.017414	− 0.017810
	− 0.064634	− 0.061133	− 0.058188	− 0.060794	− 0.061593	− 0.062990	− 0.064228	− 0.065492
	− 0.166205	− 0.167922	− 0.163687	− 0.168984	− 0.170839	− 0.170675	− 0.174983	− 0.176810
	− 0.160243	− 0.179532	− 0.201230	− 0.203996	− 0.210723	− 0.220562	− 0.220246	− 0.223304
	0.513513	0.510833	0.459566	0.450911	0.441137	0.406937	0.350098	0.328002
	0.608276	0.611988	0.651492	0.654968	0.667165	0.700363	0.730327	0.744768
	0.033881	0.028140	0.048411	0.057665	0.050092	0.055594	0.090502	0.100514
	− 0.015885	− 0.011701	− 0.019168	− 0.020912	− 0.014299	− 0.013599	− 0.022487	− 0.023062

3*s*	– 0.18013	– 0.25168	– 0.38640	– 0.52638	– 0.68869	– 0.87033	– 1.06206	– 1.26463
	0.000078	0.000083	– 0.000092	0.000108	0.000115	0.000125	0.000134	0.000141
	0.000573	0.000625	– 0.000699	0.000824	0.000878	0.000962	0.001015	0.001074
	0.002968	0.003308	– 0.003671	0.004285	0.004588	0.005011	0.005320	0.005626
	0.009587	0.011697	– 0.013495	0.015763	0.017038	0.018436	0.019584	0.020629
	0.026421	0.033227	– 0.038911	0.044475	0.048294	0.051125	0.055213	0.057799
	0.023237	0.035485	– 0.048986	0.056417	0.062103	0.068969	0.071284	0.074701
	– 0.081078	– 0.115456	0.130198	– 0.149734	– 0.156549	– 0.152708	– 0.131777	– 0.126743
	– 0.222549	– 0.268771	0.327596	– 0.356066	– 0.398961	– 0.438273	– 0.471889	– 0.495551
	0.250182	0.603707	– 0.385202	0.247058	0.557322	0.524282	0.390248	0.373092
	0.813964	0.503337	– 0.727449	0.869970	0.609385	0.655507	0.782082	0.804744
2*p*	– 1.50028	– 2.26550	– 3.20329	– 4.22812	– 5.37823	– 6.65830	– 8.04532	– 9.54268
	0.042125	0.039917	0.032726	0.027444	0.028840	0.028414	0.027887	0.027555
	0.228398	0.221590	0.187152	0.168160	0.175866	0.175840	0.173468	0.172648
	0.509629	0.512935	0.453082	0.458069	0.461765	0.467398	0.469717	0.469939
	0.452569	0.447666	0.467017	0,499275	0.490526	0.485545	0.485035	0.483633
			0.091982	0.076630	0.069031	0.063619	0.060237	0.058981
			– 0.003696	– 0.009179	– 0.012273	– 0.010985	– 0.009462	– 0.010211
3*p*			– 0.20076	– 0.28370	– 0.38412	– 0.42740	– 0.49389	– 0.57617
			– 0.005959	– 0.005988	– 0.007013	– 0.007411	– 0.007695	– 0.007896
			– 0.036624	– 0.038083	– 0.043400	– 0.045940	– 0.047638	– 0.049065
			– 0.083067	– 0.105304	– 0.121526	– 0.134234	– 0.144101	– 0.150933
			– 0.121981	– 0.129242	– 0.124617	– 0.120902	– 0.121294	– 0.121419
			0.185755	0.289739	0.391025	0.450422	0.485239	0.503641
			0.914682	0.823106	0.729140	0.678482	0.648858	0.632661

GTO's had to be used for each of the individual atomic orbitals. Even if the contraction technique is used, these basis sets cannot be used in molecular wavefunction calculations for larger molecules. The computational times would be too long. Calculations on molecules consisting of more than around five atoms (hydrogen atoms not counted) therefore have to use basis sets of more limited size. Many such calculations have been reported, but a collection of atomic orbitals with fully optimized exponents seems to be missing.

This paper reports Gaussian type orbitals for first and second row atoms. A limited size basis should be constructed in a way which permits some flexibility in the valence orbitals. This is necessary in order to obtain a basis which can be used in MO-SCF calculations, without further optimization of orbital exponents. For this reason each atomic orbital should be composed of at least two Gaussian functions. This is achieved for first row atoms with 7*s*-type and 3*p*-type functions, and for second row atoms with 10*s*-type and 6*p*-type functions.

The orbital exponent optimization was performed by means of an atomic SCF program written by one of us [13]. All exponents were optimized simultaneously, using a combined method of one and many dimensional exponent variations, together with a scaling procedure.

It is not claimed that the exponents reported here are completely optimal in all cases. Further optimization might decrease the total energy somewhat. The energy improvement will for first and second row atoms certainly be less than 0.01 a.u. This is clearly of little importance in MO-SCF calculations, where these basis sets are used.

Table 1 gives the total energy obtained with the present GTO basis. Comparison is made to the HF energies obtained by Clementi [14]. The GTO energies are for first and second row atoms in most cases less than 0.1 a.u. above the HF limit.

GTO exponents and atomic orbital expansion coefficients are presented in Tables 2–5.

In another paper the addition of polarization functions for first and second row atoms will be discussed. 3*d*-orbitals with exponents optimized in molecules will be reported [15].

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