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ABSTRACT

The generator coordinate Hartree-Fock method is used to generate adapted Gaussian basis sets for the atoms from Li (Z=3) through Xe (Z=54). In this method the Griffin-Hill-Wheeler-Hartree-Fock equations are integrated through the integral discretization technique. The wave functions generated in this work are compared with the widely used Roothaan-Hartree-Fock wave functions of Clementi and Roetti (1974), and with other basis sets reported in the literature. For all atoms studied, the errors in our total energy values relatively to the numerical Hartree-Fock limits are always less than 7.426 mhartree.

Key words: generator coordinate Hartree-Fock method, Gaussian basis sets, atomic total energy values.

1 INTRODUCTION

Hartree-Fock (HF) wave functions for atoms may be computed numerically by standard methods (Froese Fischer 1977). Algebraic approximations to HF wave functions in which the radial orbitals are expanded by the Roothaan procedure (Roothaan 1960) in a set of basis functions such as Slater-type functions (STFs) or Gaussian-type functions (GTFs), are known as Roothaan-HF wave functions. Roothaan-HF wave functions are convenient for many purposes, as indicated by the large impact of the work of Clementi and Roetti (CR) (1974).

An alternative to the Roothaan-HF method is the generator coordinate HF (GCHF) method developed by Mohallem et al. (1986). In the last years, this method has been used with success to gener-

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ate atomic and molecular wave functions (Jorge et al. 1998, Jorge and Martins 1998, Jorge and Fantin 1999, Jorge and Franco 2000, Jorge and Aboul Hosn 2001, Centoducatte et al. 2001, de Castro and Jorge 1998, Pinheiro et al. 1997a, b, da Costa et al. 1991, Custodio et al. 1992a, b).

In this paper we present accurate adapted Gaussian basis sets (AGBSs – a specific basis set for each atom studied here) for the atoms from Li through Xe, generated with the GCHF method (Mohallem et al. 1986). These basis sets are appropriate to be contracted and enriched with polarization functions and, then, can be used in nonrelativistic molecular calculations.

2 METHOD

The GCHF method (Mohallem et al. 1986) is based in choosing the one-electron functions as the continuous superpositions

$$\Phi_i(1) = \int \phi_i(1, \alpha) f_i(\alpha) d\alpha \,, \tag{1}$$
$$i = 1, \dots, n,$$

where n is the number of one-electron functions of the system, ϕ_i are the generator functions (GTFs – in our case), f_i are the weight functions and α is the generator coordinate. Using Eq. (1) to build a Slater determinant for the multi-electronic wave functions, and minimizing the total energy E with respect to the $f_i(\alpha)$, one arrives at the Griffin-Hill-Wheeler-HF (GHWHF) equations (Mohallem et al. 1986)

$$\int [F(\alpha, \beta) - \varepsilon_i S(\alpha, \beta)] f_i(\beta) d\beta = 0 \,, \tag{2}$$
$$i = 1, \dots, n,$$

where F and S are Fock and overlap kernels, respectively (for more details about these kernels see Mohallem et al. (1986)).

The GHWHF equations are integrated using a procedure known as integral discretization (ID) (Mohallem 1986). The ID technique is implemented through a relabelling of the generator coordinate space, i.e.,

$$\Omega = ln\frac{\alpha}{A} \,, \qquad A > 1, \tag{3}$$

where A is a scaling factor determined numerically. In the new generator coordinate space Ω, an equally spaced N-point mesh $\{\Omega_i\}$ is selected, and the integration range is characterized by a starting point Ω_{min}, an increment $\Delta\Omega$, and the number of discretization points N. The highest value (Ω_{max}) for the generator coordinate is given by

$$\Omega_{max} = \Omega_{min} + (N - 1)\Delta\Omega \,. \tag{4}$$

The choice of the discretization points determines the exponents of the GTFs.

3 RESULTS AND DISCUSSION

Self-consistent-field ground state total energy calculations are performed for the atoms from Li (Z=3) through Xe (Z=54), using the GCHF method (Mohallem et al. 1986) presented in the last section.

Throughout the calculations we used the scaling factor A [see Eq. (3)] equal to 6.0. For all atoms studied here, we searched the best discretization parameters (Ω_{min} and $\Delta\Omega$) values for each s, p and d symmetry. The AGBS exponents generated in this work for the above atoms can be easily reproduced by using Eqs. (3) and (4) and the discretization parameters showed in Table I. All calculations were carried out using a modified version of the ATOMSCF program (Chakravorty et al. 1989). For each atom, the optimization process is repeated until the total energy stabilize within ten significant figures.

Table II shows the ground state total energies (in hartree) for Li-Xe calculated by us with the GCHF method (Mohallem et al. 1986), by CR (1974) and Koga et al. (1993) using a fully-optimized basis sets of STFs, and by a numerical HF (NHF) (Bunge et al. 1992) method.

From Table II we can see that our total energies for Li, Be, and Na-Kr are worse than the CR (1974) results, while for the fourth-row atoms the opposite occurs. For B, C and Ne the two approaches give the same energy values. These results are surprising since the CR wave functions have been regarded for a long time as having near NHF quality. It is known that STFs have the correct functional forms to describe the nonrelativistic wave functions of atomic species at the origin, but they are not particularly suitable for self-consistent field molecular calculations. On the other hand, GTFs are useful in the evaluation of multicenter integrals in molecules, but they do not possess the correct functional behavior at the origin. Thus, for an atomic system, to obtain equivalent results for any physical or chemical property it is necessary to use GTFs basis set greater in size than STFs basis set. The CR (1974) result for Rh is wrong, because it is below the HF limit.

Koga et al. (1993) improved the widely used wave functions of CR (1974) by reoptimization of the STF exponents. They used exactly the same number and type of STFs (see the discussion about STFs and GTFs presented in the last paragraph) as CR. However, for Sr and Zr-Cd our energy results

TABLE I

Discretization parameters of the adapted Gaussian basis sets (AGBSs).

Z	Atom	N	$\Omega_{min}(s)$	$\Delta\Omega(s)$	$\Omega_{min}(p)$	$\Delta\Omega(p)$	$\Omega_{min}(d)$	$\Delta\Omega(d)$
3	Li	18s	–0.6330	0.1380				
4	Be	18s	–0.5490	0.1380				
5	B	20s11p	–0.4790	0.1320	–0.5290	0.1380		
6	C	20s11p	–0.4150	0.1320	–0.4630	0.1380		
7	N	20s11p	–0.3640	0.1320	–0.4110	0.1390		
8	O	20s11p	–0.3190	0.1320	–0.384	0.1400		
9	F	20s11p	–0.2810	0.1320	–0.3530	0.1410		
10	Ne	20s11p	–0.2460	0.1320	–0.3200	0.1410		
11	Na	18s11p	–0.6000	0.1521	–0.2507	0.1390		
12	Mg	18s11p	–0.5475	0.1506	–0.2021	0.1370		
13	Al	18s11p	–0.4858	0.1485	–0.5459	0.1420		
14	Si	18s11p	–0.4338	0.1470	–0.4917	0.1400		
15	P	18s11p	–0.3915	0.1460	–0.4459	0.1390		
16	S	18s11p	–0.3545	0.1415	–0.4247	0.1380		
17	Cl	18s11p	–0.3228	0.1446	–0.4004	0.1380		
18	Ar	18s11p	–0.2929	0.1440	–0.3719	0.1370		
19	K	20s13p	–0.6523	0.1479	–0.3108	0.1350		
20	Ca	21s13p	–0.5902	0.1422	–0.2678	0.1340		
21	Sc	20s13p10d	–0.5696	0.1456	–0.2430	0.1334	–0.4499	0.1390
22	Ti	20s13p10d	–0.5546	0.1456	–0.2209	0.1331	–0.4072	0.1370
23	V	20s13p10d	–0.5416	0.1456	–0.2017	0.1326	–0.3788	0.1370
24	Cr	20s13p10d	–0.5250	0.1455	–0.1958	0.1330	–0.4119	0.1400
25	Mn	20s13p10d	–0.5194	0.1455	–0.1639	0.1322	–0.3354	0.1360
26	Fe	20s13p10d	–0.5075	0.1454	–0.1501	0.1320	–0.3232	0.1360
27	Co	20s13p10d	–0.4996	0.1452	–0.1357	0.1316	–0.3128	0.1370
28	Ni	20s13p10d	–0.4916	0.1450	–0.1202	0.1315	–0.2998	0.1370
29	Cu	20s13p10d	–0.5162	0.1456	–0.1198	0.1316	–0.3340	0.1400
30	Zn	20s13p10d	–0.4900	0.1449	–0.0930	0.1312	–0.2720	0.1370
31	Ga	22s14p10d	–0.4594	0.1366	–0.4757	0.1430	–0.2241	0.1340
32	Ge	22s14p9d	–0.4244	0.1357	–0.4410	0.1417	–0.1630	0.1400
33	As	22s14p9d	–0.3843	0.1350	–0.4078	0.1404	–0.1297	0.1380
34	Se	22s14p9d	–0.3493	0.1344	–0.3927	0.1401	–0.1025	0.1370
35	Br	22s14p9d	–0.3250	0.1345	–0.3724	0.1396	–0.0784	0.1360
36	Kr	22s14p9d	–0.3016	0.1341	–0.3513	0.1390	–0.0571	0.1350
37	Rb	22s16p11d	–0.6080	0.1431	–0.3316	0.1282	–0.0728	0.1220
38	Sr	23s16p11d	–0.5827	0.1390	–0.3009	0.1270	–0.0454	0.1212
39	Y	24s16p12d	–0.5839	0.1341	–0.2788	0.1262	–0.4176	0.1350
40	Zr	24s16p13d	–0.5694	0.1336	–0.2608	0.1256	–0.4090	0.1280
41	Nb	23s16p13d	–0.5266	0.1375	–0.2483	0.1253	–0.4290	0.1290
42	Mo	23s16p13d	–0.5141	0.1373	–0.2338	0.1250	–0.4037	0.1280
43	Tc	23s16p13d	–0.5578	0.1281	–0.2111	0.1242	–0.3463	0.1262
44	Ru	25s16p13d	–0.5429	0.1300	–0.2034	0.1242	–0.3733	0.1274
45	Rh	25s17p14d	–0.5280	0.1300	–0.2140	0.1270	–0.4200	0.1270
46	Pd	24s17p13d	–0.1484	0.1240	–0.1961	0.1200	–0.3873	0.1280
47	Ag	25s17p13d	–0.5440	0.1307	–0.1713	0.1195	–0.3268	0.1250

TABLE I (continuation)

Z	Atom	N	$\Omega_{min}(s)$	$\Delta\Omega(s)$	$\Omega_{min}(p)$	$\Delta\Omega(p)$	$\Omega_{min}(d)$	$\Delta\Omega(d)$
48	Cd	25s16p14d	−0.5229	0.1301	−0.1458	0.1226	−0.3289	0.1200
49	In	25s17p14d	−0.4687	0.1287	−0.4859	0.1307	−0.2702	0.1170
50	Sn	25s18p13d	−0.4284	0.1281	−0.4785	0.1260	−0.2255	0.1210
51	Sb	25s18p13d	−0.4040	0.1280	−0.4521	0.1251	−0.2074	0.1206
52	Te	24s18p13d	−0.3825	0.1302	−0.4431	0.1248	−0.1873	0.1200
53	I	25s18p13d	−0.3668	0.1270	−0.4238	0.1241	−0.1733	0.1192
54	Xe	26s18p13d	−0.3479	0.1237	−0.4103	0.1236	−0.1554	0.1190

are better than those obtained by them (see Table II). Clearly, greater number of STFs are needed to improve the wave function (Koga et al. 1993) accuracy for Sr and Zr-Cd.

In summary, the AGBSs generated in this work are appropriate to be used in nonrelativistic atomic and molecular calculations of physical and chemical properties. An application of these basis sets in HF calculations of some properties of third- and fourth-row diatomic molecules is in progress. We recall that AGBSs generated with the GCHF method (Mohallem et al. 1986) were used with success to calculate various properties of first- and second-row diatomic molecules (Pinheiro et al. 1997a, b).

For the atoms from Li to Ar, the error in our total energies is not more than 1 mhartree. For the third- and fourth-row atoms the error is always larger than 1 mhartree (see Table II). The largest error (7.426 mhartree) occurs for In.

4 CONCLUSIONS

The present work shows that a specific and careful numerical evaluation of the GHWHF equations for each of those atoms studied here, is capable of generating accurate AGBSs to be used in HF atomic and molecular calculations.

When we compare our ground state total energies with the benchmark results obtained by CR (1974), who used fully-optimized basis sets of STFs, we find that the results for first-, second- ant third-row atoms are in general worse, while those for fourth-row atoms are better than theirs. Besides this, the largest difference between our energy re-

sults and the corresponding values computed with a NHF method (Bunge et al. 1992) is equal to 7.426 mhartree for In.

RESUMO

Utiliza-se o método coordenada geradora Hartree-Fock para gerar bases Gaussianas adaptadas para os átomos de Li (Z=3) até Xe (Z=54). Neste método, integram-se as equações de Griffin-Hill-Wheeler-Hartree-Fock através da técnica de discretização integral. Comparam-se as funções de ondas geradas neste trabalho com as funções de ondas Roothaan-Hartree-Fock de Clementi e Roetti (1974) e com outros conjuntos de bases relatados na literatura. Para os átomos estudados aqui, os erros em nossas energias totais relativos aos limites numéricos Hartree-Fock são sempre menores que 7,426 milihartree.

Palavras-chave: método coordenada geradora Hartree-Fock, conjuntos de bases de Gaussianas, energias totais atômicas.

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CHAKRAVORTY SJ, CORONGIU G, FLORES JR, SONNAD V,

TABLE II

Ground state HF total energies in hartree (sign reversed) for the atoms from Li (Z=3) through Xe (Z=54).

Z	Atom	State	AGBS Size	AGBS[a]	STFs number	Clementi-Roetti[b]	Koga et al.[e]	NHF[d]
3	Li	^{2}S	18s	7.432723753	6s	7.4327257	7.4327258	7.432726927
4	Be	^{1}S	18s	14.57301688	6s	14.573021	14.573021	14.57302316
5	B	^{2}P	20s11p	24.52905706	6s4p	24.529057	24.529058	24.52906072
6	C	^{3}P	20s11p	37.68861213	6s4p	37.688612	37.688616	37.68861895
7	N	^{4}S	20s11p	54.40092241	6s4p	54.400924	54.400931	54.40093419
8	O	^{3}P	20s11p	74.80937867	6s4p	74.809370	74.809395	74.80939845
9	F	^{2}P	20s11p	99.40931821	6s4p	99.409300	99.409344	99.40934933
10	Ne	^{1}S	20s11p	128.5470516	6s4p	128.54705	128.54709	128.5470980
11	Na	^{2}S	18s11p	161.8585712	8s5p	161.85890	161.85891	161.8589116
12	Mg	^{1}S	18s11p	199.6142530	8s5p	199.61461	199.61463	199.6146363
13	Al	^{2}P	18s13p	241.8762264	8s8p	241.87668	241.87670	241.8767072
14	Si	^{3}P	18s13p	288.8538207	8s8p	288.85431	288.85436	288.8543624
15	P	^{4}S	18s13p	340.7181628	8s8p	340.71869	340.71877	340.7187808
16	S	^{3}P	18s13p	397.5041636	8s8p	397.50485	397.50489	397.5048958
17	Cl	^{2}P	18s13p	459.4812242	8s8p	459.48187	459.48207	459.4820721
18	Ar	^{1}S	18s13p	526.8165421	8s8p	526.81739	526.81751	526.8175126
19	K	^{2}S	20s13p	599.1634498	11s6p	599.16453	599.16470	599.1647865
20	Ca	^{1}S	21s13p	676.7572344	11s6p	676.75803	676.75810	676.7581857
21	Sc	^{2}D	20s13p10d	759.7341836	11s6p5d	759.73552	759.73563	759.7357178
22	Ti	^{3}F	20s13p10d	848.4042367	11s6p5d	848.40575	848.40592	848.4059967
23	V	^{4}F	20s13p10d	942.8823196	11s6p5d	942.88420	942.88426	942.8843374
24	Cr	^{7}S	20s13p10d	1043.353979	11s6p5d	1043.3552	1043.3563	1043.356376
25	Mn	^{6}S	20s13p10d	1149.863619	11s6p5d	1149.8657	1149.8662	1149.866251
26	Fe	^{5}D	20s13p10d	1262.440683	11s6p5d	1262.4432	1262.4436	1262.443665
27	Co	^{4}F	20s13p10d	1381.411190	11s6p5d	1381.4142	1381.4145	1381.414553
28	Ni	^{3}F	20s13p10d	1506.867139	11s6p5d	1506.8705	1506.8709	1506.870908
29	Cu	^{2}S	20s13p10d	1638.959169	11s6p5d	1638.9628	1638.9637	1638.963742
30	Zn	^{1}S	20s13p10d	1777.843481	11s6p5d	1777.8477	1777.8481	1777.848116
31	Ga	^{2}P	22s14p10d	1923.255079	10s9p5d	1923.2604	1923.2609	1923.261009
32	Ge	^{3}P	22s14p9d	2075.353405	10s9p5d	2075.3591	2075.3597	2075.359733
33	As	^{4}S	22s14p9d	2234.232429	10s9p5d	2234.2382	2234.2386	2234.238654
34	Se	^{3}P	22s14p9d	2399.861092	10s9p5d	2399.8658	2399.8676	2399.867611
35	Br	^{2}P	22s14p9d	2572.434622	10s9p5d	2572.4408	2572.4413	2572.441332
36	Kr	^{1}S	22s14p9d	2752.048102	10s9p5d	2752.0546	2752.0549	2752.054977
37	Rb	^{2}S	22s16p11d	2938.352546	11s7p3d	2938.3470	2938.3531	2938.357453
38	Sr	^{1}S	23s16p11d	3131.542302	11s7p3d	3131.5379	3131.5417	3131.545686
39	Y	^{2}D	24s16p12d	3331.680503	11s7p5d	3331.6712	3331.6807	3331.684169
40	Zr	^{3}F	24s16p13d	3538.992004	11s7p5d	3538.9821	3538.9914	3538.995064
41	Nb	^{6}D	23s16p13d	3753.593465	11s7p5d	3753.5845	3753.5917	3753.597727
42	Mo	^{7}S	23s16p13d	3975.545002	11s7p5d	3975.5338	3975.5430	3975.549499
43	Tc	^{6}S	26s16p13d	4204.786484	11s7p5d	4204.7753	4204.7839	4204.788736
44	Ru	^{5}F	25s16p13d	4441.536271	11s7p5d	4441.5264	4441.5310	4441.539487

TABLE II (continuation)

Z	Atom	State	AGBS Size	AGBS[a]	STFs number	Clementi-Roetti[b]	Koga et al.[e]	NHF[d]
45	Rh	^{4}F	25s17p14d	4685.878637	11s7p5d	(4685.8833)	4685.8726	4685.881703
46	Pd	^{1}S	24s17p13d	4937.918470	9s7p5d	4937.9071	4937.9091	4937.921023
47	Ag	^{2}S	25s17p13d	5197.695075	11s7p5d	5197.6852	5197.6890	5197.698472
48	Cd	^{1}S	25s16p14d	5465.129785	11s7p5d	5465.0722	5465.1253	5465.133141
49	In	^{2}P	25s17p14d	5740.161728	11s9p5d	5740.1570	5740.1638	5740.169154
50	Sn	^{3}P	25s18p13d	6022.926898	11s9p5d	6022.9220	6022.9271	6022.931694
51	Sb	^{4}S	25s18p13d	6313.480742	11s9p5d	6313.4755	6313.4813	6313.485319
52	Te	^{3}P	24s18p13d	6611.778554	11s9p5d	6611.7748	6611.7803	6611.784058
53	I	^{2}P	25s18p13d	6917.976264	11s9p5d	6917.9727	6917.9773	6917.980895
54	Xe	^{1}S	26s18p13d	7232.134224	11s9p5d	7232.1302	7232.1350	7232.138363

[a]HF total energies obtained by using our adapted Gaussian basis sets (AGBSs). [b]HF total energies obtained by using fully-optimized STFs basis sets (Clementi and Roetti 1974). [c]HF total energies obtained by using fully-optimized STFs basis sets (Koga et al. 1993). [d]Numerical HF (NHF) total energies for Li to Xe obtained by Bunge et al. (1992).

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