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Improved generator coordinate Hartree–Fock method for molecular systems: application to H₂, Li₂ and LiH

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Abstract. The improved generator coordinate Hartree–Fock (GCHF) method is extended to molecular systems. The Griffin–Hill–Wheeler–HF equations were solved by an integral discretization technique. The method is then implemented with the use of the GAMESS program and applied to the H₂, Li₂, and LiH molecules. For these molecules, sequences of basis sets of atom-centred Gaussian-type functions are employed to explore the accuracy achieved with our approach. For all systems studied, our ground-state HF total energies are better than those obtained with basis sets generated with the original GCHF method for molecules and larger even-tempered basis sets. For H₂, Li₂, and LiH, the differences between our best energies and the corresponding numerical HF results are about 2×10^{-2}, 1, and 4×10^{-1} µhartree, respectively. The dipole, quadrupole, and octupole moments at the center of mass and electric field, the electric field gradient, the electrostatic potential, and the electron density at the nuclei were evaluated and compared with results reported in the literature.

Key words: Improved generator coordinate Hartree–Fock method – Molecular systems – Gaussian basis sets

1 Introduction

The use of finite expansions in analytic basis functions lies at the heart of computational molecular electronic structure theory [1, 2]. It is the choice of basis set that ultimately determines the accuracy of a calculation.

An approach for the selection of basis sets arises from the generator coordinate Hartree–Fock (GCHF) method [3]. In the GCHF method the one-electron functions are integral transforms, i.e.

$$\psi_i(1) = \int \phi_i(1, \alpha) f_i(\alpha) \mathrm{d}\alpha \ , \tag{1}$$

where ϕ_i are the generator functions (Slater- or Gaussian-type functions – STFs, GTFs – or other functions),

f_i are the unknown weight functions, and α is the generator coordinate. The application of the variational principle to calculate the energy expectation value built with such one-electron functions leads to the Griffin–Hill–Wheeler–HF (GHWHF) equations [3]. The GHWHF equations are solved through numerical integration. This is accomplished by discretization preserving the integral character of the GCHF method. The GCHF method [3] was successfully tested in the generation of universal basis sets [4, 5] and adapted Gaussian basis sets [6, 7] for light and heavy atoms.

Recently, Jorge and de Castro [8] developed the improved GCHF (IGCHF) method and it was applied to generate accurate Gaussian basis sets for first-row atoms [8] and second-row atoms and ions [9].

In 1991, the molecular GCHF (MGCHF) method was presented together with applications to the H₂, Li₂, and LiH molecules [10]. In the following years, this method was used to calculate some properties of the 14-electron diatomic molecules N₂, CO, and BF [11].

In this paper, we extend the IGCHF formalism to molecular systems and report first applications for the ground electronic states of H₂, Li₂, and LiH. The purpose of this work is to demonstrate the power of this new method when basis sets of atom-centred GTFs are employed. This is achieved by comparing our HF total energies of the diatomic molecules to those obtained with the original MGCHF method [10], with even-tempered basis sets [12], and numerical HF (NHF) calculations [13–15]. We also compare our results of some molecular properties with the corresponding ones obtained with other approaches.

2 Method

For a molecular orbital (MO) Eq. (1) has the explicit form

$$\psi_i(\gamma) = \sum_n^N \sum_p^P \int f_{inp}(\alpha_{np}) \phi_p(\alpha_{np}; \vec{r}_\gamma - \vec{R}_n) \mathrm{d}\alpha_{np} \ . \tag{2}$$

In Eq. (2) the index n runs for N atomic nuclei and p for the various $s, p, d, \ldots$ symmetries of the atomic functions ϕ_p, $\vec{r}_\gamma$ is the coordinate of the electron γ, and $\vec{R}_n$ is that of nucleus n. The indexes for α_{np} admit the possibility of different generator coordinates for different

atomic species and symmetries. For the case of the same atoms or universal basis sets one could write α_p only.

The variation of the total energy expectation value with respect to the weight function, f_{inp}, leads to the molecular GHWHF equations [10]

$$\sum_n^N \sum_p^P \int F_{np,n'p'}(\alpha_{np}, \alpha_{n'p'}) - \varepsilon_i S_{np,n'p'}(\alpha_{np}, \alpha_{n'p'}) f_{inp}(\alpha_{np})$$
$$\times \, \mathrm{d}\alpha_{np} = 0, \quad i = 1, ..., I \quad , \tag{3}$$

where ε_i are the orbital energies and the explicit forms of $F_{np,n'p'}$ and $S_{np,n'p'}$ are given in Ref. [10].

Equation (3) is solved through the integral discretization (ID) technique [16], in which case Eq. (2) becomes

$$\psi_i(\gamma, T) = \sum_n \sum_p \sum_t \int f_{inp}(\alpha_{npt}) \phi_p(\alpha_{npt}; \vec{r}_\gamma - \vec{R}_n) \Delta\alpha_{npt} \tag{4}$$

and one can interpret

$$C_{inpt} = \Delta\alpha_{npt} f_{inp}(\alpha_{npt}) \tag{5}$$

as the atomic linear combination coefficient in a MO. In order to make numerical integration through discretization efficient, a relabelling of the generator coordinate space was introduced [16] according to

$$\Omega = \ln(\alpha/A), \quad A > 1 \quad , \tag{6}$$

where A is a scaling parameter determined numerically. Thus, the coefficient that appear in Eq. (5) becomes

$$C_{inpt} = A\Delta\Omega_{npt} f_{inp}(\Omega_{npt}) \exp(A\Omega_{npt}) \quad .$$

The new generator coordinate space, Ω, is discretized for each s, p, d, ... symmetry of each atom in an equally spaced mesh Ω_{np}^k so that

$$\Omega_{np}^k = \Omega_{np}^{\min} + (k-1)\Delta\Omega_{np}, \quad k = 1, ..., N_{np} \quad . \tag{7}$$

In Eq. (7) N_{np} is the number of discretization points for atom n and symmetry p, and $\Omega_{np}^{\min}$ and $\Delta\Omega_{np}$ are the lowest value and the constant increment for the generator coordinate, respectively. The values of $\Omega_{np}^{\min}$ and N_{np} are chosen to embrace an adequate integration range for the weight function f_{inp}. From Eq. (7) we can see that the original MGCHF method [10] uses only one arithmetic sequence of equally spaced points $\{\Omega_{np}^k\}$ to generate basis sets.

One may wonder whether the results obtained with Eqs. (6) and (7) can be improved within the framework of the MGCHF method without adding more functions (GTF in our case), and we do this in analogy with the IGCHF method [8] by proposing a simple modification that may produce improvements in the HF wavefunctions. The idea is to use (when necessary) three arithmetic sequences with the same principal quantum number. This allows different distributions for small, intermediate, and large exponents of GTFs to be found.

In this new approach the generator coordinate space, Ω, is discretized for each s, p, d, f, ... symmetry in three independent arithmetic sequences:

$$\Omega_{np}^k = \begin{cases} \Omega_{np}^{\min} + (k-1)\Delta\Omega_{np}, & k = 1, ..., K_{np} \\ \Omega_{np}'^{\min} + (k-1)\Delta\Omega_{np}', & k = K_{np}+1, ..., M_{np} \\ \Omega_{np}''^{\min} + (k-1)\Delta\Omega_{np}'', & k = M_{np}+1, ..., N_{np} \quad . \end{cases} \tag{8}$$

For a given value of N_{np}, the number of parameters to be optimized for each symmetry of each atom is 3 times that of the original MGCHF method (see Eq. 7).

Here we call attention to the fact that when we use Eq. (8), we have no more equally spaced points $\{\Omega_{np}^k\}$ as occur in Eq. (7), because now three independent arithmetic sequences are used to generate the basis function exponents for each symmetry of each atom. We call this method to generate molecular basis sets the molecular IGCHF (MIGCHF) method. To test the performance of this method, we employ basis sets of primitive GTFs.

At each iteration of the self-consistent-field (SCF) procedure the integrations are implemented numerically. This approach leads formally to the Roothaan-HF (RHF) equations, with the advantage of allowing the use of available RHF codes. Nonetheless, the discretization points (exponents) are chosen to preserve the integral character of the molecular GHWHF equations (Eq. 3). Technically this procedure is implemented as follows. First, a test SCF run for a molecule is executed with arbitrary Gaussian basis sets generated with the IGCHF method [8] (or by another method). Then we use increments of 0.0001 first in the parameter, $\Omega_{np}^{\min}$, of Eq. (8), keeping all others fixed until the lowest HF total energy value is found. Next, we repeat the procedure for the parameter $\Delta\Omega_{np}$, now for the optimum value of $\Omega_{np}^{\min}$ and still keeping the remaining parameters with their initial values. The process is continued until the last parameter $\Delta\Omega_{np}''$ of the last p symmetry is reacted, and then it is successively repeated from the beginning until the total energy stabilizes within ten significant figures. Thus, at the end of this optimization process we have optimized all parameters of Eq. (8) of each symmetry that contributes to the ground state of each atom that forms the molecule.

3 Basis sets of atom-centred GTFs

We begin by generating Gaussian basis sets for the H_2 and Li_2 molecules using only symmetries of basis functions which contribute to the ground states of the H and Li atoms, i.e., using Eq. (8) we generate one $20s$ arbitrary basis set for each molecule (Tables 1, 2). Then, we optimize these basis sets for each molecule.

In the next step, we add polarization functions of p, d, and f symmetries. As the polarization functions have diffuse character, we use only one arithmetic sequence of Eq. (8) to generate these functions. Besides this, each set of polarization functions of symmetry $l \geq 1$ (l is the angular quantum number) is optimized from a previous choice of an exponent subset of the s symmetry. Finally, we search if it is necessary to add more functions of s, p, d, and f symmetries to improve the HF total energy results. For LiH, we start with $20s9p4d4f$ and $20s11p6d1f$ basis sets of H_2 and Li_2, respectively (Tables 1, 2). Then, we reoptimize these basis sets for LiH and, finally, we add more functions of s, p, d, and f symmetries when necessary to improve the energy value. The smaller basis sets of this molecule are subsets of the $21s11p6d1f$ (for Li) and $20s9p4d4f$ (for H) basis sets (Table 3) and they are not reoptimized.

In summary, the exponents of our atom-centred GTFs are generated using Eqs. (6) and (8). The scaling parameter A that appear in Eq. (6) has the same value (6.0) for all calculations. For H_2, Li_2, and LiH, the optimum discretization parameters used to generate our basis sets are shown in Tables 1, 2, and 4, respectively. Only four decimal places are given, although the discretization parameters were calculated to a machine accuracy of 10^{-9} for the energy calculations reported.

4 Results and discussion

By using sequences of primitive atom-centred GTFs, we calculated the ground-state HF total energies of the diatomic molecules H_2, Li_2, and LiH, where the internuclear distances of 1.400, 5.051, and 3.015 a.u., respectively, were used. The discretized MIGCHF method was implemented through the GAMESS program [17]. The calculation were performed with a Pentium II 300 MHz computer.

Table 1. Optimized discretization parameters for the H_2 molecule ($A = 6.0$, see Eq. 6). For s symmetry, the first, second, and third lines of the third column give the number of Gaussian-type functions (*GTFs*) and the discretization parameters for the first, second, and third arithmetic sequences of the Eq. (8). For p, d, and f symmetries, each line gives the number of GTFs and the discretization parameters for only one arithmetic sequence of Eq. (8)

N_{Hp}	Symmetry	GTF	$\Omega_{Hp}^{\min}$	$\Omega_{Hp}'^{\min}$	$\Omega_{Hp}''^{\min}$	$\Delta\Omega_{Hp}$	$\Delta\Omega_{Hp}'$	$\Delta\Omega_{Hp}''$
20	s	15	−0.6379			0.1149		
		3		−1.3049			0.1611	
		2			−1.5432			0.1737
21	s	15	−0.6379			0.1149		
		3		−1.3049			0.1611	
		3			−1.5432			0.1737
22	s	15	−0.6379			0.1149		
		3		−1.3049			0.1611	
		4			−1.5432			0.1737
9	p	9	−0.3194			0.1043		
10	p	10	−0.3194			0.1043		
11	p	11	−0.3194			0.1043		
13	p	13	−0.4237			0.1043		
4	d	4	−0.1765			0.1253		
5	d	5	−0.1765			0.1253		
6	d	6	−0.1765			0.1253		
7	d	7	−0.3018			0.1253		
4	f	4	−0.4000			0.1999		
5	f	5	−0.4000			0.1999		

Table 2. Optimized discretization parameters for the Li_2 molecule ($A = 6.0$, see Eq. 6). For s symmetry, the first, second, and third lines of the third column give the number of GTFs and the discretization parameters for the first, second, and third arithmetic sequences of Eq. (8). For p, d, and f symmetries, each line gives the number of GTFs and the discretization parameters for only one arithmetic sequence of Eq. (8)

N_{Lip}	Symmetry	GTF	$\Omega_{Lip}^{\min}$	$\Omega_{Lip}'^{\min}$	$\Omega_{Lip}''^{\min}$	$\Delta\Omega_{Lip}$	$\Delta\Omega_{Lip}'$	$\Delta\Omega_{Lip}''$
20	s	13	−0.6361			0.1355		
		3		−0.6225			0.1370	
		4			−0.5146			0.1370
23	s	13	−0.6361			0.1355		
		5		−0.8965			0.1370	
		5			−0.5146			0.1370
25	s	13	−0.6361			0.1355		
		5		−0.8965			0.1370	
		7			−0.9256			0.1370
11	p	11	−0.6118			0.1234		
6	d	6	−0.6904			0.1462		
7	d	7	−0.6904			0.1462		
1	f	1	−0.2170					
2	f	2	−0.3651			0.1481		

The total energies (E_0, in hartree) for H_2 for various basis sets of increasing size are presented in Table 5. Our results are compared with those obtained with the original MGCHF method [10], with even-tempered basis sets [12], and with NHF calculations [13]. The exponents of our GTFs are defined through the discretization parameters shown in Table 1.

From Table 5, we can see that only two basis sets ($20s$ and $20s9p4d$) generated with the MIGCHF method give energies larger than the corresponding values calculated with the larger basis sets ($23s$ and $23s9p4d$) presented in Refs. [10, 12]. The energy value (−1.133629409 hartree) calculated with our $20s9p4d4f$ is lower than the corresponding ones obtained with the $23s9p4d4f$ basis sets generated with the original MGCHF method (−1.133629397 hartree) and with the even-tempered

formula (−1.133629366 hartree). Besides this, the energy obtained with our $21s10p5d4f$ basis set is better than the energies calculated with the larger $23s9p4d4f2g1h$ and $30s15p5d4f$ even-tempered basis sets [12]. The main reasons for the better performance of the MIGCHF method presented here in comparison to the use of the basis sets reported in Ref. [12] are

1. The MIGCHF method has three independent arithmetic sequences to describe the symmetries (s symmetry in our case) contributing to the ground states of the atoms present in the molecules, thus we can describe independently the inner, intermediate, and outer electrons of these symmetries. We recall that the contribution of electrons of these symmetries to the total energy is more important than that of the other electrons. On the other hand, the even-tempered formula has only one

geometric sequence to describe these three different regions for these symmetries. This is also the reason why the energies calculated by us are better than the original MGCHF method [10].

2. Wells and Wilson [12] take the orbital exponents for basis functions with angular momentum quantum number l greater than zero to be a subset of those with $l = 0$. Furthermore, the orbital exponents for functions with angular momentum quantum number $l + 1$ are taken to be a subset of those with angular momentum quantum number l. On the other hand, we optimize the orbital exponents of all angular momentum quantum

numbers l. A similar procedure is used by da Costa et al. [10] in the MGCHF method. Our larger basis set ($22s13p7d5f$) gives a difference of 2×10^{-2} μhartree with respect to the NHF energy reported by Laaksonen et al. [13].

Here, it is important to say that in Ref. [10] the authors did not calculate the total energy (-1.133629570) of the H_2 molecule using the $33s16p6d4f$ basis set, because this basis set contains 278 functions, surpassing the capacity of the VAX program (255 functions). They estimated the $4f$ contribution from the difference between the $23s9p4d$ and the $23s9p4d4f$ calculations. Using the $33s16p6d4f$ basis set of Ref. [10] and the MGCHF method, we have found (with the GAMESS program) that this basis set is not fully linearly independent; thus, the total energy estimated in Ref. [10] is only a crude approximation.

Recently, universal basis sets for high-precision molecular electronic structure studies [18] and for accurate second-order many-body perturbation theory calculations [19] have been developed. Besides atom-centred basis sets, Moncrieff and Wilson [18, 19] used atom-centred plus bond-centred basis sets in their calculations.

The results for E_0 for Li_2 calculated with various basis sets generated with the MIGCHF and the original MGCHF [10] methods are shown in Table 6. This table also presents the NHF value reported by Sundholm et al. [14]. From this table, we can see that the HF total energies obtained with our Gaussian basis sets (except for $20s11p$) are always better than the corresponding ones calculated with larger basis sets generated with the original MGCHF method. The good performance of our basis sets is again attributed to the MIGCHF method presented here (see the previous discussion for the H_2

Table 3. Ground-state Hartree–Fock total energy, E_0 (hartree), of the LiH molecule. The internuclear distance is 3.015 a.u.

Basis set	E_0 (this work)	E_0 [10]
21s on Li		
20s on H	-7.971831332	–
23s on Li and H	–	-7.971851679
21s11p on Li		
20s9p on H	-7.987166334	–
23s11p on Li and H	–	-7.987172545
21s11p6d on Li		
20s9p4d on H	-7.987348184	–
23s11p6d on Li and H	–	-7.987348220
23s11p6d4f on Li		
23s11p6d1f on H	–	-7.987351678
21s11p6d1f on Li		
20s9p4d4f on H	-7.987351690	–
24s11p6d2f on Li		
20s9p4d4f on H	-7.987351899	–
25s12p8d2f on Li		
20s9p4d4f on H	-7.987352041	–
Numerical Hartree–Fock [15]	-7.9873524	

Table 4. Optimized discretization parameters for the LiH molecule ($A = 6.0$, see Eq. 6). For s symmetry, the first, second, and third lines of the third column give the number of GTFs and the discretization parameters for the first, second, and third arithmetic sequences of Eq. (8). For p, d, and f symmetries, each line gives the number of GTFs and the discretization parameters for only one arithmetic sequence of Eq. (8)

Atom	$N_{\text{LiH}p}$	Symmetry	GTF	$\Omega_{\text{LiH}p}^{\min}$	$\Omega_{\text{LiH}p}^{\prime\min}$	$\Omega_{\text{LiH}p}^{\prime\prime\min}$	$\Delta\Omega_{\text{LiH}p}$	$\Delta\Omega_{\text{LiH}p}^{\prime}$	$\Delta\Omega_{\text{LiH}p}^{\prime\prime}$
Li									
	21	s	13	-0.5006			0.1355		
			4		-0.6225			0.1370	
			4			-0.6516			0.1370
	24	s	14	-0.4873			0.1241		
			4		-0.6225			0.1370	
			6			-0.9256			0.1370
	25	s	14	-0.4873			0.1241		
			4		-0.6225			0.1370	
			7			-0.9256			0.1370
	11	p	11	-0.4885			0.1234		
	12	p	12	-0.6118			0.1234		
	6	d	6	-0.5477			0.1497		
	8	d	8	-0.6974			0.1497		
	1	f	1	-0.0615					
	2	f	2	-0.0615			0.1581		
H									
	20	s	15	-0.6374			0.1149		
			3		-0.6305			0.1179	
			2			-0.4248			0.1184
	9	p	9	-0.3194			0.1043		
	4	d	4	-0.2439			0.1605		
	4	f	4	-0.4293			0.2096		

Table 5. Ground-state Hartree–Fock total energy, E_0 (hartree), of the H_2 molecule. The internuclear distance is 1.400 a.u.

Basis set	E_0 (this work)	E_0 [10]	E_0 [12]
20s	−1.128541016	–	–
23s	–	−1.128542220	−1.128542094
23s9p	–	−1.133571853	−1.133571746
20s9p	−1.133572020	–	–
20s9p4d	−1.133628354	–	–
23s9p4d	–	−1.133628466	−1.133628387
23s9p4d4f	–	−1.133629397	−1.133629366
20s9p4d4f	−1.133629409	–	–
23s9p4d4f2g1h	–	–	−1.133629366
30s15p5d4f[a]	–	–	−1.13362948
21s10p5d4f	−1.133629514	–	–
21s11p6d4f	−1.133629538	–	–
22s13p7d5f	−1.133629548	–	–
33s16p6d4f[b]	–	−1.133629570	–
Numerical Hartree–Fock [13]	−1.13362957	–	–

[a] The 4f contribution is estimated from the 23s9p4d and 23s9p4d4f energy difference in Ref. [12]

[b] The 4f contribution is estimated from the 23s9p4d and 23s9p4d4f energy difference in Ref. [10]

Table 6. Ground-state Hartree–Fock total energy, E_0 (hartree), of the Li_2 molecule. The internuclear distance is 5.051 a.u.

Basis set	E_0 (this work)	E_0 [10]
20s	−14.8613561	–
20s11p	−14.8714608	–
23s11p	–	−14.8714650
23s11p6d	–	−14.8715587
20s11p6d	−14.8715588	–
23s11p6d2f	–	−14.8715602
20s11p6d1f	−14.8715608	–
23s11p6d2f	−14.8715612	–
25s11p7d2f	−14.8715615	–
Numerical Hartree-Fock [14]	−14.871563	–

molecule). The energy calculated with our largest basis set 25s11p7d2f differs by about 1 μhartree from the NHF value [14]. For Li_2, the corresponding discretization parameters (basis-set exponents) are shown in Table 2.

E_0 values for LiH obtained with basis sets generated with the MIGCHF and MGCHF [10] methods and with the NHF calculations [15] are presented in Table 3. Again, from this table we can see that the energy obtained with our basis set with 21s11p6d1f on Li and 20s9p4d4f on H is better than that obtained with the basis set with 23s11p6d4f on Li and 23s11p6d1f on H generated with the original MGCHF method [10]. We again draw attention to the fact that the MIGCHF method produces better energy values with smaller basis-set sizes. The reason why the smaller basis sets (subsets of the 21s11p6d1f on Li and 20s9p4d4f on H) give larger energies than the corresponding ones obtained with the MGCHF method is that when we gradually remove the polarization functions of the LiH molecule, these basis sets are not reoptimized with the new number of GTFs. The difference between the energies calculated with our

largest basis set and the NHF calculations [15] is about 4×10^{-1} μhartree.

Our results for dipole (μ), quadrupole (Q_{zz}), and octupole (O_{zzz}) moments at the center of mass and electric field (E), the electric field gradients (q_{zz}), the potential ($1/r$), and the electron density (ρ) at the nuclei for H_2, Li_2, and LiH, are listed in Table 7 and are compared with literature results. The symbols Q_{zz} and q_{zz} denote the zz component of the quadrupole moment and the electric field gradient tensors, respectively, and O_{zzz} denotes the zzz component of the octupole moment tensor. For all properties calculated for LiH, H_2, and Li_2, we have used our largest basis sets and the internuclear distances presented in Tables 3, 5 and 6 respectively. Our dipole moment value for LiH agrees with the NHF [15] result with five-figure accuracy. For H_2 and Li_2, our quadrupole moments and electric field gradients are in excellent agreement with the NHF [14, 20] results and, in general, are closer to the NHF ones than earlier results obtained with other basis sets [21–24]. Beside this, our $1/r$ values for H_2 and Li_2 agree with those calculated with the NHF [14, 20] method within the number of figures reported. Finally, the ρ values calculated with the MIGCHF method for H_2 and Li_2 are in

Table 7. Dipole (μ), quadrupole (Q_{zz}), and octupole (O_{zzz}) moments at the centre of mass and electric field (E), the electric field gradient (q_{zz}), the potential ($1/r$), and the electron density (ρ) at the nuclei (a.u.) of H_2, Li_2, and LiH. Q_{zz} and q_{zz} denote the zz components of the quadrupole moment and the electric field gradient tensors, respectively, O_{zzz} denotes the zzz component of the octupole moment tensor

Property	H_2[a]	Li_2[b]	LiH[c]
μ			2.3618175
			2.3618105 [15]
			2.3618056 [10]
Q_{zz}	0.4934196	10.6325292	−3.3700569
	0.4934223 [20]	10.632695 [14]	
	0.4934222 [21]		
O_{zzz}			−6.3276833
E(Li)		0.001116	0.000387
E(H)	0.005385		0.001328
q_{zz}(Li)		−0.004325	0.039996
		−0.00428 [14]	
		−0.00999 [24]	
q_{zz}(H)	0.341375		−0.052229
	0.341293 [20]		
	0.3416 [22]		
	0.3409 [23]		
$1/r_{Li}$		6.336750	−6.078026
		6.33675 [14]	
		6.3372 [24]	
$1/r_{H}$	1.816298		2.228033
	1.816298 [20]		
ρ(Li)		13.794467	13.769340
		13.82518 [14]	
ρ(H)	0.449546		0.372933
	0.450039 [20]		

[a] Properties calculated with our 22s13p7d5f basis set on H. The internuclear distance is 1.400 a.u.

[b] Properties calculated with our 25s11p7d2f basis set on Li. The internuclear distance is 5.051 a.u.

[c] Properties calculated with our 25s12p8d2f and 20s9p4d4f basis sets on Li and H, respectively. The internuclear distance is 3.015 a.u.

good agreement with those computed with the NHF [14, 20] method.

5 Conclusions

Using the ID technique we have presented a new scheme to integrate numerically the GHWHF equations, here called the MIGCHF method. In this method, the GTF exponents are not parameters to be variationally optimized as usual, but they are generated by some criterion (the ID technique) for integrating the GHWHF equations.

The present work shows, through basis sets generated with the MIGCHF method, that a careful numerical integration of the GHWHF equations is able to provide highly accurate atom-centred GTFs to be used in molecular HF calculations. The main advantage of the method presented here is that it can produce better energy values than the original MGCHF method [10] and the even-tempered formula [12] with a smaller basis-set size. For H_2, Li_2, and LiH, the differences between the HF energies obtained in this work (with our largest basis sets) and those calculated with NHF approaches are always lower than 1.5 µhartree. For all molecules studied, the results for some of the properties calculated here are in good agreement with the corresponding ones obtained with the NHF [14, 15, 20] method.

Work is now in progress to explore the accuracy of the MIGCHF method in calculations on molecules with more electrons than considered in the present study, including electron correlation effects.

References

1. Huzinaga S (1985) Comput Phys Rept 2: 279
2. Davidson ER, Feller D (1986) Chem Rev 86: 681
3. Mohallem JR, Dreizler RM, Trsic M (1986) Int J Quantum Chem Symp 20: 45
4. Jorge FE, Martins RF (1998) Chem Phys 233: 1
5. de Castro EVR, Jorge FE (1998) J Chem Phys 108: 5225
6. Jorge FE, Librelon PR, Canal Neto A (1998) J Comput Chem 19: 858
7. Jorge FE, Muniz EP (1999) Int J Quantum Chem 71: 307
8. Jorge FE, de Castro EVR (1999) Chem Phys Lett 302: 454
9. de Castro EVR, Jorge FE, Pinheiro JC (1999) Chem Phys 243:1
10. da Costa HFM, da Silva ABF, Mohallem JR, Simas AM, Trsic M (1991) Chem Phys 154: 379
11. da Costa HFM, Simas AM, Smith VH Jr, Trsic M (1992) Chem Phys Lett 192: 195
12. Wells BH, Wilson S (1989) J Phys B 22: 1285
13. Laaksonen L, Pyykkö P, Sundholm D (1983) Int J Quantum Chem 23: 319
14. Sundholm D, Pyykkö P, Laaksonen L (1985) Mol Phys 56: 1411
15. Laaksonen L, Sundholm D, Pyykkö P (1984) Chem Phys Lett 105: 573
16. Mohallem JR (1986) Z Phys D 3: 339
17. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14: 1347
18. Moncrieff D, Wilson S (1994) J Phys B 27: 1
19. Moncrieff D, Wilson S (1998) J Phys B 31: 3819
20. Pyykkö P, Sundholm D, Laaksonen L (1987) Mol Phys 60: 597
21. Wells BJ, Wilson S (1985) J Phys B 18: L731
22. Snyder LC (1974) J Chem Phys 61: 5032
23. Davidson ER, Feller D (1984) Chem Phys Lett 104: 54
24. Cade PE, Sales KD, Wahl AC, quoted in Kahn LR, Goddard WA III (1972) J Chem Phys 56: 2685