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Accurate Gaussian Basis Sets for the Ground State of the CS Molecule

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Sequences of increasing size atom centered basis sets of Gaussian-type functions for the ground state of the CS molecule are generated with the molecular improved generator coordinate Hartree-Fock (HF) method. At the HF level, total and orbital energies and electric dipole moment and, at the second-order Mϕller-Plesset (MP2) level, correlation and dissociation energies and electric dipole moment were calculated and compared with the results obtained with other Gaussian basis sets reported in the literature. Considering our largest basis set, the HF energy is in error by 56.2 μhartree and the second order correlation energy corresponds to $\sim$ 80% of an estimate of the limiting value. At the MP2 level, the dipole moment and the dissociation energy computed with our largest basis set are in good agreement with the corresponding experimental values. The CS molecule is considered a prototype for systems containing atoms from different rows of the periodic table.

I. INTRODUCTION

In the vast majority of contemporary quantum chemical calculations, basis set truncation is a significant, and frequently dominant, source of error. Early many-body perturbation theory calculations on molecules [1, 2] pointed to basis set truncation as the largest source of error in accurate electronic structure calculations. This observation has been confirmed by configuration interaction studies [3, 4]. There has, therefore, been considerable interest in the construction of basis sets for precision calculation [5, 6]. The growth of central processing power, in uniprocessor and multiprocessor environments, and memory in high-performance computers facilitates the use of increasingly large and flexible basis sets in molecular electronic structure calculations which in turn allows calculations of increasing accuracy by reducing the error associated with basis set truncation.

There are procedures for approaching the complete basis set limit by systematically enlarging a basis set (e.g. even-tempered basis set [7]). In 1979, Schmidt and Ruedenberg [8] proposed a practical scheme for systematically extending basis sets of even-tempered Gaussian functions so as to approach the complete basis set limit. Wilson et al. have used with success the even-tempered formula, where the parameter values of the formula were determined through the empirical formula of the Ref. [8], to generate Gaussian basis sets (GBSs) for various diatomic systems [9, 10]. For the CS molecule [9], these authors, using a distributed basis set centered not only on the atomic nuclei but also on the C-S center, claim to have obtained a total HF energy below any value previously reported in the literature. The idea of using bond functions in molecular structure calculations is an old one [11]. Such functions were introduced to provide the same effects as the addition of a set of polarization functions but at a lower cost [12]. More recently the correlation-consistent polarized valance (cc-pVXZ, X = D, T, Q, 5) and augmented cc-pVXZ (aug-cc-pVXZ, X = D, T, Q, 5) basis sets developed by Dunning et al. [13, 14] have been employed extensively as hierarchical basis sets for systematically reducing the basis set truncation error. Some successful recent applications of these basis sets can be found in Refs. [15, 16]. The cc-pVXZ basis sets have been developed for calculating the valence correlation energy in a systematic fashion. On the basis of a suitable number of s and p functions, the number and types of higher angular momentum functions, as well as their exponents, are selected from correlated calculations on atoms.

An other procedure to select basis sets, where the one electron functions are written as integral transform, arose from the generator coordinate Hartree-Fock (GCHF) method [17]. In the last seventeen years, this method has been applied with success in the generation of basis sets for atomic and molecular systems [18–23].

Da Costa et al. [24] developed the molecular GCHF (MGCHF) method and it was used to calculate some properties of diatomic molecules [24, 25].

In 1999, Jorge and de Castro [26] presented the improved GCHF (IGCHF) method, and it was applied in the generation of GBSs for the first-row atoms [26] and for second-row atoms and ions [27].

Recently, Jorge et al. [28] extended the IGCHF method for molecular systems and it was called molecular IGCHF (MIGCHF) method. Previous paper [29] examined the accuracy with which ground state HF energies of diatomic molecules containing first-row atoms can be calculated with the MIGCHF method by using atom centered basis sets of primitive Gaussian-type functions (GTFs). In Ref. [28], it was demonstrated that accuracy of 1 μhartree or less can be achieved for H_2, HLi, and Li_2 molecules. In Ref. [29], it was shown that accuracy smaller than 77 μhartree can be achieved for the total HF energies of fourteen electron diatomic systems.

When a molecule contains atoms from different rows of the periodic table the importance of using a balanced basis set has been recognized for many years [30]. In this work, we consider the CS molecule as a prototype system containing atoms from different rows of the periodic table. In particular, at the HF and Mϕller-Plesset second order (MP2) levels, the accurate atom centered GBSs generated with the MIGCHF [28] method were used to calculate energies, electric dipole moment, and dissociation energy for the ground state of the CS molecule. A comparison with results obtained with other approaches [9, 13, 14] and with experimental values [31, 32] is done.

II. MOLECULAR IMPROVED GENERATOR COORDINATE HARTREE-FOCK METHOD

In the MGCHF method [24] the molecular orbitals (MO) are integral transform, i.e.,

$$\psi_i(\gamma) = \sum_n^N \sum_p^P \int \mathrm{f_{inp}}(\alpha_{np}) \phi_p(\alpha_{np}; \vec{r}_\gamma - \vec{R}_n) d\alpha_{np}, \qquad (1)$$

where the index n runs for N atomic nuclei and p for the various s, p, d, ... symmetries of the atomic functions ϕ_p; $\vec{r}_\gamma$ is the coordinate of the electron γ and $\vec{R}_n$ 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 equal atoms or universal basis set one could write α_p only.
The variation of the total energy expectation value with respect to the weight function $\mathrm{f_{inp}}$ leads to the molecular Griffin-Hill-Wheeler-HF (GHWHF) equations [24]

$$\sum_n^N \sum_p^P \int \mathrm{F_{np,n'p'}}(\alpha_{np}, \alpha_{n'p'}) - \varepsilon_i \mathrm{S_{np,n'p'}}(\alpha_{np}, \alpha_{n'p'}) \times \mathrm{f_{inp}}(\alpha_{np}) d\alpha_{np} = 0, \quad i = 1, ..., I, \qquad (2)$$

where the ε_i are the orbital energies and the explicit forms of $\mathrm{F_{np,n'p'}}$ and $\mathrm{S_{np,n'p'}}$ are given in Ref. [24].
The Eqs. (2) are solved through integral discretization (ID) technique [33], in such case Eq. (1) becomes

$$\psi_i(\gamma, T) = \sum_n \sum_p \sum_t \mathrm{f_{inp}}(\alpha_{npt}) \phi_p(\alpha_{npt}; \vec{r}_\gamma - \vec{R}_n) \Delta\alpha_{npt} \qquad (3)$$

and one can interpret

$$\mathrm{C_{inpt}} = \Delta\alpha_{npt} \mathrm{f_{inp}}(\alpha_{npt}) \qquad (4)$$

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 [33] according to

$$\Omega = \ln(\alpha/A), \qquad \mathrm{A} > 1, \qquad (5)$$

where A is a scaling parameter determined numerically. Thus, the coefficient that appear in Eq. (4) becomes

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

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

$$\Omega_{np}^k = \Omega_{np}^{min} + (\mathrm{k}-1)\Delta\Omega_{np}, \quad \mathrm{k} = 1, \ldots, \mathrm{N}_{np}. \qquad (7)$$

In Eq. (6) N_{np} is the number of discretization points for atom n and symmetry p, Ω_{np}^{min} and $\Delta\Omega_{np}$ are respectively the lowest value and the constant increment for the generator coordinate. The values of Ω_{np}^{min} and N_{np} are chosen to embrace adequate integration range for the weight function $\mathrm{f_{inp}}$. From Eq. (6) we can see that the original MGCHF method [24] uses only one arithmetic sequence of equally spaced points $\{\Omega_{np}^k\}$ to generate basis sets.
One may wonder whether the results obtained with the Eqs. (5) and (6) can be improved within the framework of the MGCHF method without adding more functions (GTFs in our case). We did this in analogy with the IGCHF method [26] by proposing a simple modification that may produce improvements in the HF wave functions. The idea is to use (when necessary) three arithmetic sequences with the same principal quantum number. This allows form different distributions for small, intermediate, and large exponents of GTFs.
In this new approach the generator coordinate space, Ω, is discretized for each s, p, d, f, ... symmetry in three independent arithmetic sequences:

$$\Omega_{np}^k = \begin{cases} \Omega_{np}^{min} + (\mathrm{k}-1)\Delta\Omega_{np}, & \mathrm{k} = 1, \ldots, \mathrm{K}_{np} \\ \Omega_{np}^{'min} + (\mathrm{k}-1)\Delta\Omega_{np}^{'}, & \mathrm{k} = \mathrm{K}_{np}+1, \ldots, \mathrm{M}_{np} \\ \Omega_{np}^{''min} + (\mathrm{k}-1)\Delta\Omega_{np}^{''}, & \mathrm{k} = \mathrm{M}_{np}, \ldots, \mathrm{N}_{np}. \end{cases} \qquad (8)$$

For a given value of N_{np}, the number of parameters to be optimized for each symmetry of each atom is three times that of the original MGCHF method [see Eq. (6)].
Here, we call attention to the fact that when one uses Eq. (7), one does not have equally spaced points $\{\Omega_{np}^k\}$ anymore as occur in Eq. (6), because now three independent arithmetic sequences are used to generate the basis functions exponents for each symmetry of each atom. This methodology to generate primitive GTF exponents in molecular environment was called MIGCHF method [28].
At each iteration of the self-consistent field procedure the integrations are implemented numerically. This approach leads formally to the HF Roothaan (HFR) equations, with the advantage of allowing the use of available HFR codes. Nonetheless, the discretization points (exponents) are chosen to preserve the integral character of the molecular GHWHF equations (2).

III. ATOM CENTERED BASIS SETS OF PRIMITIVE GAUSSIAN-TYPE FUNCTIONS

As start point to construct accurate basis sets for CS, the GBSs generated by Librelon and Jorge [34] with the IGCHF method [26] for C(23s14p) and S(26s18p) were used. To improve the molecular HF energy, two and three functions of s symmetry for C and S, respectively, were added and, then, all s and p exponents were reoptimized through the Eq. (7). Next, 7d polarization functions for each atom were included in the basis set and, then, optimized in the molecular environment using only one arithmetic sequence of the Eq. (7), since the number of exponents of d symmetry is small. The last step was repeated for higher angular momentum functions and sequences of optimized larger basis sets were constructed (see Table I). It is important to say that only the additional basis functions with respect to the previous entry were optimized using the minimum energy criterion. Besides this, all basis functions were centered on the nuclei, and only the spherical components of the polarization functions were used. For all

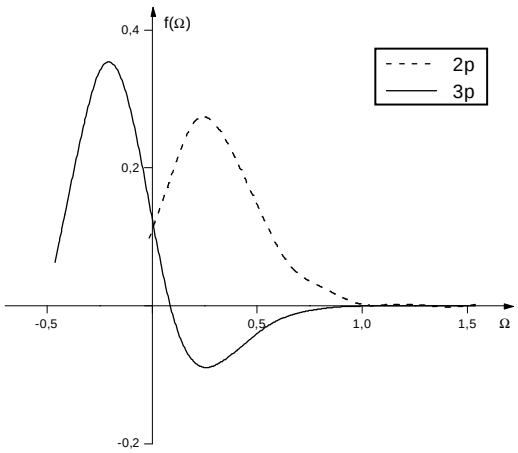

FIG. 1: The 2p and 3p Gaussian weight functions for C and S atoms, respectively.

calculations, the scaling parameter of the Eq. (5) has the same value (6.0).

Since the GHWHF equations were obtained from the minimization of the energy functional with respect to the weight functions (f_i), the description of the f_i governs the quest for the total energies for any atomic or molecular system. Achieving the best HF energy for an atomic or molecular system means obtain the best description of f_i. Gaussian 2p and 3p weight functions for C(23s14p) and S(26s18p) atoms have been plotted in Fig. 1. The forms of the 2p weight functions of fluorine (see Ref. [21]) and carbon (this work), which were obtained respectively from the GCHF [17] and IGCHF [26] methods, are very similar.

IV. RESULTS AND DISCUSSION

Using the MIGCHF method presented above, GBSs for the CS molecule (for an internuclear separation of 2.89964 a.u.) were constructed. The majority of the calculations reported in this work were carried out with the GAUSSIAN 94 program [35], and the correlation calculations include all electrons. It is known that the computational linear dependence can be measured by the smallest eigenvalue of the overlap matrix. As all the basis sets generated in this work have overlap matrix with smallest eigenvalues in the range $3x10^{-5}$-$8x10^{-6}$, this suggests that the difference between the total energies is attributed to basis set truncation errors and not to problems associated with computational near linear dependence.

Table I displays the ground state total HF energies (in hartree) evaluated with our GBSs, with the basis sets [9] of even-tempered GTFs centered not only on the atomic nuclei but also on the C-S bond centered (bc), with the aug-cc-pV5Z basis sets of Dunning et al. [13, 14], and with a NHF method [9]. The second-order correlation energies (E_2) were also calculated and compared with the result obtained with the aug-cc-pV5Z basis sets [13, 14]. Besides this, the PSI3 code [36] was used for the MP2 perturbation theory calculations with linear terms r_{12} (MP2-R12/A) [37, 38]. For the MP2-R12/A calculations, the cc-pV6Z basis set of Wilson et al. [39] in a fully uncontracted form, denoted in the present work as cc-pV6Z(uc), was used to estimate a 'limiting' value of the second-order correlation energy of -0.925936 hartree (see the last row of Table I).

From Table I, one can see that the total HF energies calculated with the MIGCHF method [28] decrease monotonically with increasing size of basis set, that is, the energy is found to decrease monotonically on adding the higher harmonic basis functions with the largest decrease of $\sim$ 69 mhartree resulting from the addition of the atom centered d functions. Besides this, one can observe that the energy obtained with the C(44s22p);S(44s22p);bc(44s) basis set [9] is better and worse than those computed with our smaller C(25s14p);S(29s18p) and C(25s14p7d);S(29s18p7d) basis sets, respectively. For the basis sets designated aug-cc-pV5Z (372 primitive GTFs contracted to 258 functions) and C(25s14p7d1f);S(29s18p7d1f) (234 GTFs) the HF energies are -435.3618841 and -435.3619846 hartree, respectively. These results show that our basis set give better result at a lower cost than the widely used correlation consistent basis sets of Dunning et al. [13, 14]. The main difference between these two approaches is that the aug-cc-pV5Z basis sets are atom specific, whereas the exponents of our basis set are optimized in the molecular environment with the MIGCHF method. The C(44s22p22d);S(44s22p22d);bc(44s22p) basis set [9] and the smaller C(25s14p7d4f);S(29s18p7d4f) and C(25s14p7d4f2g);S(29s18p7d4f2g) basis sets generated with the MIGCHF method [28] have associated errors of 80.4, 254.6, and 69.4 μhartree, respectively. From these results, it is clear that the GBS of the Ref. [9] needs twice more GTFs than that constructed by us to provide better energy. The HF energy obtained with our largest basis set C(25s14p7d4f2g1h);S(29s18p7d4f2g1h) is in error by 56.2 μhartree, whereas the larger basis sets C(32s16p16d16f);S(32s16p16d16f);bc(28s12p13d) and C(44s22p22d22f);S(44s22p22d22f);bc(39s18p19d17f) [9], which include functions centered on both the atomic and bond centers, are in errors by 46.5 and 2.1 μhartree, respectively. Again, these two GBSs of the Ref. [9] have at least twice more GTFs than our largest basis set. Kobus et al. [9] claim to have obtained the lowest matrix HF energy (-435.3624177 hartree) reported in the literature, whose difference is only 54.1 μhartree of the best result obtained here (-435.3623636 hartree) at a much reduced cost (our largest basis set contain 334 GTFs vs the 1055 GTFs contained in the basis set of the Ref. [9]). We recall that the number of two electron integrals, which consumes a major part of the time needed in a SCF molecular orbital calculation, increases as $(N_{np})^4$.

The first two E_2 results presented in Table I show clearly that the addition of d-type polarization functions yields the largest energy decrease in the correlation energy. The next two studies summarized in this Table indicate that the second-order correlation energy evaluated with the MIGCHF method [28] is $\sim$ 0.15 hartree lower than the result obtained with the larger aug-cc-pV5Z basis set [13, 14]. We recall that all the GTF exponents of our C(25s14p7d1f);S(29s18p7d1f) basis

TABLE I: Ground state total HF energies (E_{HF}) and second-order correlation energies (E_2) for the CS molecule. All energies are in hartree.

Basis set	Number of GTFs	-E_{HF}	-E_2	Reference
C(25s14p);S(29s18p)	150	435.2902407	0.370830	this work
C(44s22p);S(44s22p);bc(44s)	264	435.3192503	-	[9]
C(25s14p7d);S(29s18p7d)	220	435.3592617	0.674629	this work
aug-cc-pV5Z	258	435.3618841	0.543462	calculated in this work
C(25s14p7d1f);S(29s18p7d1f)	234	435.3619846	0.695092	this work
C(25s14p7d4f);S(29s18p7d4f)	276	435.3621652	0.721751	this work
C(44s22p22d);S(44s22p22d);bc(44s22p)	550	435.3623394	-	[9]
C(25s14p7d4f2g);S(29s18p7d4f2g)	312	435.3623504	0.734334	this work
C(25s14p7d4f2g1h);S(29s18p7d4f2g1h)	334	435.3623636	0.737929	this work
C(32s16p16d16f);S(32s16p16d16f);bc(28s12p13d)	673	435.3623733	-	[9]
C(44s22p22d22f);S(44s22p22d22f);bc(39s18p19d17f)	1055	435.3624177	-	[9]
HF limit	-	435.3624198	-	[9]
MP2-R12/A cc-pV6Z(uc)	339	-	0.925936	calculated in this work

set were optimized at the HF level, and that the aug-cc-pV5Z basis set (which contains up to h functions) is designed for valence correlation calculations. Even so, it is notable that the basis set generated with the MIGCHF method reproduces all electron correlation energy better than aug-cc-pV5Z. Helgaker et al. [40] investigating the basis set convergence of the correlation energy in the water molecule verified that the correlation-consistent polarized core-valence (cc-pCVXZ) basis sets [41] give all electron correlation energies closer to the MP2-R12 results than the corresponding values calculated with the cc-pVXZ basis sets. One knows that for calculations of electron correlation effects it is necessary to include functions of higher angular symmetry in the basis set. The best E_2 value (-0.737929 hartree) presented in Table I is obtained with our C(25s14p7d4f2g1h);S(29s18p7d4f2g1h) atom centered basis set, which corresponds to $\sim 80\%$ of the limiting value. The results of the second order correlation energies confirm the good accuracy that can be achieved with the MIGCHF method [28] in the generation of total wave functions for diatomic molecules containing atoms from different rows of the periodic table.

Table II shows the convergence pattern for the ground state CS molecule. From this Table, one can see that increasing the number of points in each s and p symmetries rapidly favor the convergence of the total HF to the value of -435.2902407 hartree, and that the difference between the C(24s14p);S(28s18p) and C(25s14p);S(29s18p) energies is very small (12.1 μhartree). Even if we go beyond the C(25s14p);S(29s18p) basis set, there is no substantial improvement in the HF energy.

A comparison of the occupied MO energies calculated with the largest basis set reported in this work with the corresponding ones obtained with the largest basis set and a NHF method of the Ref. [9] is made in Table III. When compared with the corresponding NHF results, the MO energies obtained with our basis set are slightly worse than those computed with the very large basis set of Kobus et al. [9].

The main differences between the MIGCHF method [28] and the algebraic approximation used in Ref. [9] are:
(i) The MIGCHF method has three independent arithmetic sequences [see Eq.(7)] to describe each occupied atomic orbital (s and p in our case) of the ground state of each atom present in the molecule. Thus, one can describe independently the inner, intermediate, and outer electrons of these orbitals. We recall that the electrons of these subshells give the largest contribution to the total HF energy. On the other hand, the even-

TABLE II: Convergence pattern for the ground state of the CS molecule (in hartree). E_{HF} represents the total HF energy.

Basis set	E_{HF}
C(22s11p);S(26s15p)	-434.8516794
C(22s12p);S(26s16p)	-435.2306421
C(23s12p);S(27s16p)	-435.2535167
C(23s13p);S(27s17p)	-435.2881600
C(24s13p);S(28s17p)	-435.2889832
C(24s14p);S(28s18p)	-435.2902286
C(25s14p);S(29s18p)	-435.2902407

TABLE III: Comparison of the occupied molecular orbital (MO) energies (in hartree) calculated with Gaussian basis sets (GBSs) and with a numerical HF (NHF) method.

Orbital	-$\varepsilon(GBS)^a$	-$\varepsilon(GBS)^b$	-$\varepsilon(NHF)^c$
1σ	92.00112	92.00114	92.00114
2σ	11.35392	11.35391	11.35391
3σ	9.00704	9.00705	9.00705
4σ	6.68728	6.68732	6.68733
5σ	1.10033	1.10032	1.10032
6σ	0.69250	0.69252	0.69253
7σ	0.47052	0.47052	0.47052
1π	6.68657	6.68657	6.68657
2π	0.46309	0.46309	0.46309

[a] MO energies obtained with our largest GBS C(25s14p7d4f2g1h);S(29s18p7d4f2g1h).
[b] MO energies obtained with the largest GBS of the Ref. [9] C(44s22p22d22f);S(44s22p22d22f);bc(39s18p19d17f).
[c] MO energies obtained with the NHF method of the Ref. [9].

TABLE IV: Electric dipole moment (μ) and dissociation energy (D_e) for the ground state of the CS molecule. The correlation calculations include all electrons.

Method	Basis set	N[a]	-μ[b](Debye)	D_e[c](kJ/mol)	Reference
Expt.	-	-	1.958	714.1±1.2	[31, 32]
HF	aug-cc-pV5Z	258	1.631	435.1	calculated in this work
	C(25s14p7d4f2g1h);S(29s18p7d4f2g1h)	334	1.631	436.3	this work
MP2	aug-cc-pV5Z	258	2.272	752.7	calculated in this work
	C(25s14p7d4f2g1h);S(29s18p7d4f2g1h)	334	2.195	748.3	this work

[a]Number of GTFs.
[b]The dipole moments were calculated using the experimental nuclear distance (2.89964 a.u.).
[c]The dissociation energies were calculated using the experimental nuclear distance (2.89964 a.u.).

tempered formula [7] has only one geometric sequence to describe the three different regions of s and p orbitals. This is one of the reasons why our smaller atom centered basis sets are more accurate than the corresponding ones of the Ref. [9].
(ii)For each s, p, d, f , g, and h symmetry of the C and S atoms, we have optimized the primitive GTF exponents in the molecular environment (CS molecule), using the MIGCHF method [28], whereas Kobus et al. [9] have used a universal basis set developed previously for the N_2 ground state [10]. Thus, it is another reason that our atom centered basis sets for CS to be more accurate than the corresponding ones of the Ref. [9].
(iii) As discussed above, Kobus et al. [9] developed a universal sequence of GBSs which can be easily extended to include more functions of each symmetry type and more symmetry types, and also an extended distribution of expansion centers. In our case, if it is desired to add a new set of exponents of a given symmetry, it is necessary to optimize this set in the molecular environment with the MIGCHF method [28].
At the HF level, our μ and D_e results, when compared with the corresponding experimental values [31, 32], are respectively as good as and better than those evaluated with the aug-cc-pV5Z basis set (see Table IV). As is widely recognized, HF theory with any basis set gives poor results for direct calculation of the energy of a homolytic dissociation process A-B $\rightarrow$ A+B. The correlation energy correction for the electron forming the bond is a significant fraction of the total bond energy. If correlation is omitted, the error will be greater for the bonded system A-B than for separated A and B, and calculated dissociation energies will be too small. From Table IV, one can verify that when the electron correlation is taken into account (MP2 calculations), the dissociation energies evaluated with both basis sets improve significantly. Besides this, at this level of approximation, our μ and D_e results are closer to the experimental values than those obtained with the aug-cc-pV5Z basis set, and they are in good agreement with the corresponding experimental values.

V. CONCLUSIONS

We used the MIGCHF method to generate accurate GBSs of atom centered GTFs for the CS molecule. In this method, the GHWHF equations are integrated through the ID technique.

Previous HF calculations realized with the MIGCHF method showed that accuracies smaller than 1.1 and 77 μhartree can be achieved for the H_2, LiH, and Li_2 molecules and for diatomic systems containing first-row atoms, respectively. For the carbon monosulphide molecule, which we consider as a prototype system containing atoms from different rows of the periodic table, we have estimated the accuracy of the present energy calculations to be 56.2 μhartree. Besides this, from the results presented in Tables I and III, one can observe that in general the basis sets constructed by Kobus et al. [9] need at least twice more GTFs than those generated by us to provide better total HF energies, and that the differences among the occupied MO energies evaluated with the largest GBSs reported here and in Ref. [9] are in the last figure.

At the MP2 level, the correlation energy obtained by us with the C(25s14p7d1f);S(29s18p7d1f) basis set is better than the result obtained with the widely used larger aug-cc-pV5Z basis sets [13, 14], and the E_2 computed with our largest basis set (-0.737929 hartree) accounts for $\sim$ 80% of the limiting value.
Thus, employing only atom centered basis sets of GTFs, we believe that it is the first time that this level of accuracy has been achieved at the HF and MP2 levels for the ground state of the CS molecule.

Finally, at the MP2 level, calculated C(25s14p7d4f2g1h);S(29s18p7d4f2g1h) electric dipole moment and dissociation energy are in good agreement with the experimental data.

It is in progress studies of electronic structures of small polyatomic molecules with the MIGCHF method [28].

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