

Serially improved GTOs for molecular applications (SIGMA): Basis sets from H to Ne

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ABSTRACT

A new approach for generating Gaussian basis sets is reported and tested for atoms from H to Ne. The basis sets thus calculated, named SIGMA basis sets, range from DZ to QZ sizes and have the same composition per shell as Dunning basis sets but with different treatment of the contractions. The standard SIGMA basis sets and their augmented versions have proven to be very suitable for providing good results in atomic and molecular calculations. The performance of the new basis sets is analyzed in terms of total, correlation, and atomization energies, equilibrium distances, and vibrational frequencies in several molecules, and the results are compared at several computational levels with those obtained with the corresponding Dunning and other basis sets.

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I. INTRODUCTION

In the theoretical study of chemical systems within the computational chemistry framework, the most commonly used procedures are based on the expansion of the wavefunction or density in terms of a set of one-electron functions, which is known as the basis set (BS). Therefore, in the application of these computational methods, two main decisions must be faced; namely, the choice of the computational method and the BS used to expand the orbitals and density. The ideal selection in each case implies a compromise between quality and cost so that the choice of a given method greatly determines the BS to be used, which should be feasible in terms of cost and suitable in terms of accuracy. Therefore, using highly accurate methods with poor BS or less accurate methods with high-quality BS is not usually a wise choice.

The importance of BS in the quality of the results can hardly be overemphasized, and a great effort has been devoted to the development of BS since the very beginning of computational chemistry.¹ This effort has been continued over time,^{1–9} and even today, BS incorporating new features is being reported. In fact, a large amount of BS is available (EMSL/PNNL,^{10,11} and BSE, <https://www.basisetexchange.org/>¹²) to meet a variety of different requirements.

BS are built as products of angular functions times radial factors (*orbitals*), where angular functions are usually taken as powers

of Cartesian coordinates or regular (real) spherical harmonics. For radial functions, most BS use either exponential functions (ETO) or Gaussian functions (GTO), the latter being much more common in molecular calculations than the former, mainly because of the easier-to-solve integrals they yield.¹³ In this respect, the usage of linear combinations of GTO (*contractions*) instead of single GTO (*primitives*) as basis functions has been decisive in their success, and all GTO BS currently used are built using contractions.

In the design of BS, several factors are usually taken into account, and depending on the relative importance assigned to each factor, BS with different features can be developed. Therefore, some BSs have been developed for good performance in simpler methods such as Hartree–Fock (HF) or density functional theory (DFT), whereas others have been developed to provide better performance in correlated methods. Likewise, in some cases, BSs originally developed to deal with ground states of neutral molecules have been augmented to deal with excited states or with anions, and more specialized BSs have been designed to provide good results in properties other than energy, as it happens with BSs aimed at yielding good NMR shift constants.¹⁴

The composition of the BS is determined in terms of the number of shells (values of the L quantum number in the angular part) and the number of functions per shell (contractions). Besides, the number and type of primitives (radial factors and parameters involved) included in each contraction are also characteristic of the

BS, so all these aspects must be considered when devising a BS. In particular, the number of shells and contractions per shell are often related to each other in BS families known as single-zeta (SZ), double-zeta (DZ), triple-zeta (TZ), and so forth. Once the composition in terms of the number of shells and contractions is decided, it remains the problem of selecting the number of primitives used to expand each contraction and the parameter values (exponents) in these primitives. To solve this problem, although most BSs are intended for molecular calculations, it is customary to select the number of primitives and exponents to meet some requirements at the atomic level. Therefore, a target function for different atomic properties is defined. The main goal is to achieve a good description of the atom ground state, but excited electronic states and ion states are also included to improve the BS performance in molecules and ions. The number of primitives and the exponents are chosen to provide the best attainable values of this function for a fixed composition of the BS, and the problem is mathematically formulated as a variational minimization process.

As can be readily seen, the optimization of the number of primitives and the exponents is a cumbersome non-linear problem that may lead to many different solutions characterized as local minima of the target function. Several techniques have been proposed to lighten this problem, like the use of even-tempered and well-tempered sequences of exponents^{15–19} or the usage of atomic natural orbitals (ANO).^{20–28} A largely used alternative is provided by the correlation-consistent BS for valence and core, and valence correlations. In these correlation-consistent BS, each correlation orbital is represented by a single GTO primitive chosen to maximize its contribution to the correlation energy, and all correlation orbitals making similar contributions to the correlation energy are added simultaneously.²⁹ Following this seminal work, Dunning reported the first family of correlation-consistent BS for the first-row elements and hydrogen. The members of this family are denoted as cc-pVXZ, where X (=D, T, Q, ...) represents the *cardinal number*, and cc and p stand for *correlation consistent* and *polarized*.^{29–37} The cc-BS are built upon a core of HF orbitals (a set of contracted functions) and are systematically supplemented with additional GTO primitives that describe polarization and valence shell correlation. Furthermore, the addition of diffuse functions has led to a derived family of augmented BS, noted as aug-cc-pVXZ. The addition of diffuse functions improves the flexibility of the BS in the outer valence region of atoms and molecules and is aimed at dealing with weak interactions and anions.

The design of BS for calculations including correlation is more demanding than in the case of HF or DFT calculations, as they must also provide a virtual space capable of recovering a large part of the correlation energy. In this regard, the proposal by Almlöf and Taylor²⁰ to construct a correlated systematic series of one-particle BS based on ANO deserves special attention. In ANO BS, all primitive GTOs of a given shell (with the same angular momentum) contribute to all the contractions of the shell. The result is that ANOs are among the best possible choices for atomic correlation calculations. In this spirit, we present a new way of building BS for molecular calculations. The new procedure named *Serially Improved GTOs for Molecular Applications* yields a new family of BS, named SIGMA BS (σ BS), and is characterized by the fact that the exponents of the primitives of a given shell are taken as a subset of a common set of exponents, so that, when an exponential appears in a shell corre-

sponding to a given angular momentum L , it also appears in all the shells with angular momentum $l < L$.

Another interesting feature is that, because of the structure of the SIGMA BS, for each member of the family, subsets of functions can be sequentially selected that are specially well suited for the calculation within the Gaussian- n (Gn) framework.^{38,39} This feature will be illustrated with an example in Sec. II.

Finally, the contractions are built to be orthogonal to each other and, in this way, a systematic expansion of the space spanned by the sets is accomplished, accompanied by high numerical stability in the calculations. This property is also present in other BSs, such as ANO. Nevertheless, unlike in ANO, in which the number of primitives per shell is the same for all the members of the family (DZ, TZ, ...), in SIGMA BS, the number of primitives per shell is lower the smaller the member.

The first σ BS were developed for He and tested in both the atom and its dimer,⁴⁰ and a preliminary study on other atoms was reported⁴¹ as the starting point for the development of BS suitable for the fulfillment of the Hellman–Feynman theorem.⁴² Here we report the completion of that work with the development of standard σ XZ and their augmented versions ($a\sigma$ XZ) ranging from double- ($X = D$) to quadruple-zeta ($X = Q$) for atoms from H to Ne. We find that, when compared with other BS of equivalent composition, σ BS yields better results than Dunning BS in variational calculations and overcomes the ANO relation quality/cost, especially for the smaller members of the family.

The article is organized as follows. In Sec. II, the procedure for developing σ BS is explained, and the contraction scheme and BS composition are described. The supplementary material is included, which contains a link for the full description and use of the σ BS as well as the BS in MOLPRO⁴³ format. The results on several atoms and molecules are reported in Sec. III, in which the precision attained in total energies as well as in equilibrium distances is discussed. The results on several atoms and molecules are reported in Sec. III, in which the precision attained in total, correlation, and atomization energies, as well as equilibrium distances, vibrational frequencies, and computational times, is discussed. Finally, conclusions are drawn from these results in Sec. IV.

II. METHODS

A. Criteria for basis set optimization and contraction scheme: Size and composition

The σ BS consists of linear combinations (contractions) of radial primitive Gaussians intended to provide highly accurate energies at different computational levels. In constructing σ BS, we have exploited our previous experience in the development of ETO BS.^{44–49}

Guided by this experience, we have decided to design σ BS with the characteristic that if a given primitive appears multiplied by a spherical harmonic of the quantum number $l = L$, all primitives with the same exponent and $l < L$ are also present in the set. For example, if there is a function d with the exponent α , then functions s and p with this exponent will appear in the σ BS. This feature was first intended to reduce the cost of computing integrals involving primitives, although most standard packages are usually not prepared to take advantage of it. It has also been exploited in the design and development of BS with a high degree of fulfillment of the

Hellmann–Feynman theorem.⁴⁰ Another feature of σ BS is that all primitives in a given shell, i.e., those with the same angular part, participate in all contractions of the same shell. The combination of both features makes it possible to systematically increase the number of primitives in the contractions and, therefore, to improve the quality of the BS functions without severely penalizing the computational cost. In short, the contractions in σ BS are built from the same set of exponentials combined with different angular functions. Furthermore, while polarization functions in Dunning BS consist of simple Gaussian functions (one primitive per polarization function), in SIGMA BS, they are true contractions, leading to significant improvements in energy results.

As a rule of thumb, the number of primitives included in each shell of polarization functions is equal to the number of contractions in the shell plus two. As mentioned before, the radial parts of the primitives used in the polarization functions are also present in the functions of the core shells. The choice of primitive exponents for polarization functions among those of core shell functions is not obvious and must be achieved by optimizing the exponents for both types of functions together. It is also noticeable that, although not specifically intended, the exponents of the primitives thus obtained follow an even tempered uniform sequence with slight variations and cover a wide range of values.

To simplify the notation in the following, XZ will be used as an abbreviation of Dunning's cc-pVXZ BS and aXZ for aug-cc-pVXZ BS. The equivalent σ BS will be denoted as σ XZ and $a\sigma$ XZ, respectively. In each of the SIGMA families, we have considered BS ranging from double-zeta (σ DZ) to quadruple-zeta (σ QZ). The procedure for developing σ BS is described in Sec. II B. That procedure, combined with the rule for the number of primitives, causes σ BS to tend to saturate one-electron space per shell yielding energies as close as possible to the best attainable values according to their size.

The composition of the BS from H up to Ne atoms is detailed in Table I, in which the numbers of exponentials, primitives, and contractions are quoted. Note that the composition is the same for both families, the only difference being the number of primitives, which is smaller in Dunning BS. On the other hand, the number of different exponentials is smaller in σ BS than in Dunning BS. This facilitates that, with a wise choice of the algorithm for integrals calculation, the cost of this step using σ BS can be kept comparable to the cost with Dunning or other widely used BS, despite the higher number of primitives in σ BS.

The electronic states chosen for the optimization of the BS are detailed in Table II for the atoms considered in this work. For H, He, F, and Ne atoms, the states used are the same as in Dunning. For C, N, and O atoms, all the states that belong to the electronic configuration containing the ground state are included, thus yielding a total of three states per atom (following an approach similar to the BS of Dunning's group for the transition elements⁵⁰). In the cases of Li and Be, the first states with electrons in the $2p$ shell were included due to their evident interest in the chemical bond. In the case of B, due to its peculiar chemical behavior, the optimization of the first excited state (4P) corresponding to the $2s^1 2p^2$ configuration was added, as it is very close in energy to the ground state (2P) belonging to the $2s^2 2p$ configuration. On the other hand, the first excited state of F (4P) lies quite far away from the ground state, and it does not seem appropriate to include it. In H and Li, as there

TABLE I. Composition of Dunning and SIGMA basis sets for H to Ne atoms. Number of exponents, primitives, and contracted functions.

BS	# σ Exp.	#	Primitives	#	Contractions
H and He atoms					
DZ	5	7	(4s, 1p)	5	[2s, 1p]
TZ	8	16	(5s, 2p, 1d)	14	[3s, 2p, 1d]
QZ	12	32	(6s, 3p, 2d, 1f)	30	[4s, 3p, 2d, 1f]
σ DZ	10	19	(10s, 3p)	5	[2s, 1p]
σ TZ	10	37	(10s, 4p, 3d)	14	[3s, 2p, 1d]
σ QZ	10	66	(10s, 5p, 4d, 3f)	30	[4s, 3p, 2d, 1f]
σ 5Z	10	108	(10s, 6p, 5d, 4f, 3g)	55	[5s, 4p, 3d, 2f, 1g]
aDZ	7	11	(5s, 2p)	9	[3s, 2p]
aTZ	11	25	(6s, 3p, 2d)	23	[4s, 3p, 2d]
aQZ	16	48	(7s, 4p, 3d, 2f)	46	[5s, 4p, 3d, 2f]
$a\sigma$ DZ	11	23	(11s, 4p)	9	[3s, 2p]
$a\sigma$ TZ	11	46	(11s, 5p, 4d)	23	[4s, 3p, 2d]
$a\sigma$ QZ	11	82	(11s, 6p, 5d, 4f)	46	[5s, 4p, 3d, 2f]
Li to Ne atoms					
DZ	14	26	(9s, 4p, 1d)	14	[3s, 2p, 1d]
TZ	19	42	(10s, 5p, 2d, 1f)	30	[4s, 3p, 2d, 1f]
QZ	24	68	(12s, 6p, 3d, 2f, 1g)	55	[5s, 4p, 3d, 2f, 1g]
σ DZ	15	60	(15s, 10p, 3d)	14	[3s, 2p, 1d]
σ TZ	15	86	(15s, 10p, 4d, 3f)	30	[4s, 3p, 2d, 1f]
σ QZ	15	125	(15s, 10p, 5d, 4f, 3g)	55	[5s, 4p, 3d, 2f, 1g]
aDZ	14	35	(10s, 5p, 2d)	23	[4s, 3p, 2d]
aTZ	19	58	(11s, 6p, 3d, 2f)	46	[5s, 4p, 3d, 2f]
aQZ	24	93	(13s, 7p, 4d, 3f, 2g)	80	[6s, 5p, 4d, 3f, 2g]
$a\sigma$ DZ	16	69	(16s, 11p, 4d)	23	[4s, 3p, 2d]
$a\sigma$ TZ	16	102	(16s, 11p, 5d, 4f)	46	[5s, 4p, 3d, 2f]
$a\sigma$ QZ	16	150	(16s, 11p, 6d, 5f, 4g)	80	[6s, 5p, 4d, 3f, 2g]

is no valence correlation due to the existence of a single electron in the outermost shell, the optimization of the diatomic molecule is taken at the equilibrium distance, as Dunning had already considered.

For augmented BS, we start from the corresponding non-augmented σ XZ BS and add a further exponent lower than the exponents present in the original set. Then we follow a process similar to that used in the non-augmented BS, selecting the subsets of exponents and the number of contractions to be used in each shell and optimizing the contraction coefficients to give the minimum sum of energies of the states selected for the neutral atom. Next, keeping those contractions unchanged, we add one more contracted function per shell optimized to yield the minimum energy of the ground state of the anion at the Configuration Interactions Single and Double (CISD) level. Finally, the exponents are refined by repeating this sequence of steps. As an example, Table III collects the exponents and shell composition thus achieved for the six σ BS of fluorine.

TABLE II. Reference states used for the optimization of SIGMA basis sets from hydrogen to neon.

States for optimization of basis sets σXZ									
H ² S	He ¹ S	Li ² S	Be ¹ S	B ² P	C ³ P	N ⁴ S	O ³ P	F ² P	Ne ¹ S
H ₂ ¹ Σ		Li ² P	Be ³ P	B ⁴ P	C ¹ D	N ² D	O ¹ D		
		Li ₂ ¹ Σ			C ¹ S	N ² P	O ¹ S		
States added for optimization of augmented basis sets $a\sigma XZ$									
H ⁻¹ S	He ₂ ¹ Σ	Li ⁻¹ S	Be ₂ ¹ Σ	B ⁻³ P	C ⁻⁴ S	N ⁻³ P	O ⁻² P	F ⁻¹ S	Ne ₂ ¹ Σ

TABLE III. Exponents and angular components for fluorine atom corresponding to σXZ and $a\sigma XZ$ with X = D, T, Q.

σDZ (ang) ^a		σTZ (ang)		σQZ (ang)		$a\sigma DZ$ (ang)		$a\sigma TZ$ (ang)		$a\sigma QZ$ (ang)	
2.714(+5)	(s)	2.834(+5)	(s)	2.850(+5)	(s)	2.704(+5)	(s)	2.817(+5)	(s)	2.964(+5)	(s)
4.059(+4)	(s)	4.235(+4)	(s)	4.259(+4)	(s)	4.045(+4)	(s)	4.217(+4)	(s)	4.400(+4)	(s)
9.211(+3)	(s)	9.565(+3)	(s)	9.612(+3)	(s)	9.160(+3)	(s)	9.540(+3)	(s)	9.916(+3)	(s)
2.594(+3)	(s)	2.672(+3)	(s)	2.680(+3)	(s)	2.583(+3)	(s)	2.669(+3)	(s)	2.773(+3)	(s)
8.349(+2)	(s)	8.473(+2)	(s)	8.459(+2)	(s)	8.303(+2)	(s)	8.475(+2)	(s)	8.761(+2)	(s)
2.942(+2)	(sp)	2.909(+2)	(sp)	2.885(+2)	(sp)	2.925(+2)	(sp)	2.909(+2)	(sp)	2.970(+2)	(sp)
1.126(+2)	(sp)	1.062(+2)	(sp)	1.047(+2)	(sp)	1.123(+2)	(sp)	1.061(+2)	(sp)	1.067(+2)	(sp)
4.670(+1)	(sp)	4.107(+1)	(sp)	4.032(+1)	(sp)	4.744(+1)	(sp)	4.114(+1)	(sp)	4.086(+1)	(sp)
2.041(+1)	(sp)	1.671(+1)	(sp)	1.640(+1)	(spd)	2.167(+1)	(sp)	1.693(+1)	(sp)	1.663(+1)	(spd)
9.136(+0)	(sp)	7.079(+0)	(spdf)	6.977(+0)	(spdfg)	1.019(+1)	(sp)	7.321(+1)	(spdf)	7.126(+1)	(spdfg)
4.015(+0)	(spd)	2.975(+0)	(spdf)	2.966(+0)	(spdfg)	4.684(+0)	(spd)	3.178(+0)	(spdf)	3.100(+0)	(spdfg)
1.728(+0)	(spd)	1.255(+0)	(spdf)	1.261(+0)	(spdfg)	2.074(+0)	(spd)	1.392(+0)	(spdf)	1.371(+0)	(spdfg)
7.316(-1)	(spd)	5.327(-1)	(spd)	5.334(-1)	(spdf)	8.987(-1)	(spd)	6.097(-1)	(spdf)	6.111(-1)	(spdfg)
3.088(-1)	(spd)	2.303(-1)	(sp)	2.290(-1)	(sp)	3.837(-1)	(spd)	2.685(-1)	(spd)	2.737(-1)	(spdf)
1.269(-1)	(sp)	9.985(-2)	(sp)	9.883(-2)	(sp)	1.615(-1)	(sp)	1.185(-1)	(sp)	1.207(-1)	(sp)
						6.090(-2)	(sp)	4.700(-2)	(sp)	4.582(-2)	(sp)

^aAngular functions with the same exponential.

In the case of N, albeit the anion is unstable, we keep the optimization based on the anion's ³P state,⁵¹ as we have found that this procedure yields satisfactory results. For He, Be, and Ne, however, the anions (also unstable) are replaced by the corresponding dimers at their experimental equilibrium distances. It can be noticed that, in the case of atoms with stable anions, the criterion is common in the SIGMA and Dunning BSs.

B. Generation of basis sets: Fluorine atom

To understand the optimization of the σ BS, we analyze here in detail the construction of the σ BS of fluorine. In this atom, the states considered by Dunning are taken into account in the optimization of the σXZ and $a\sigma XZ$ BS, but the optimization approach is different. The σ BS differs from Dunning's BS not only in the number and type of primitives but also in the contraction scheme selected, which keeps the orthogonality of the BS functions, and in the energies optimized for each BS. In the case of σ BS, a general contraction is performed with a different and sequential optimization process to achieve the best atomic energies.

The fluorine atom is the simplest case of the σ BS optimization, in which only one state is considered. Therefore, it is a good example to illustrate the process of σXZ developing. The BS optimization consists of the following steps:

1. A set of primitive functions (exponents and angular factors) is selected for the shells to be considered. This set will remain fixed in the following steps. For the fluorine atom, the initial set of primitives consists of 15 *s* and 10 *p* functions. This initial set has two purposes: it will be used to build the core functions using HF calculations, and it will provide suitable primitive exponents to build the polarization functions. This initial set of primitives is usually larger than the set used by Dunning to describe the core functions because, in the case of σ BS, it needs to be large enough to meet other goals. Therefore, it can be seen in Table III that the first five exponents are taken only for *s* functions. These exponents are significantly higher than those appearing in the remaining shells and are related to the cusp of the density at the nucleus. The next ten exponents (from positions 6 to 15 in the table) also appear in *p* functions,

and so forth. A criterion to decide the number of primitives used in the polarization has been heuristically determined and consists of taking a number of primitives per shell equal to the number of contractions in the shell plus two. For instance, in the σ DZ, there is one contraction in the d shell, so there will be three d primitives; in the σ TZ, there are two d and one f contractions, which will come from four d and three f primitives, and so forth.

- Contraction coefficients for core functions are optimized by minimizing HF energy. Therefore, the 15 s and 10 p primitives are contracted to two s plus one p basis functions with the criterion of optimizing the HF energy. The subsequent s and p contractions will be orthogonal to those already present, and they will only slightly improve the HF result, which is sufficiently well described with the initial contraction: $2s + 1p$ ([21] for short).
- Next, in σ DZ, a new shell and a new contraction per shell are added and optimized by minimizing the CISD energy (keeping all primitives unchanged). Therefore, in the case of fluorine, the 15 s and 10 d primitives are kept unchanged, as are the two s and one p contractions of the previous step, and two new contractions (one s and one p) orthogonal to them are added to the set. These new contractions are built with the same set of primitives. Furthermore, three d primitives are added, with exponents taken from those available in the s primitives and used to build a d contraction. The exponents of the d primitives and the contraction coefficients are determined by minimizing the CISD energy. In this particular case, the exponents chosen are those of rows 11, 12, and 13 in the first column of Table III. In this regard, it is noticeable that in BS, in which single primitives are added to enlarge the BS, the resultant set is not orthogonal.
- The previous step is performed as many times as necessary to arrive at the desired σ XZ (once for σ DZ, twice for σ TZ, and so forth). Therefore, for the σ DZ, the optimization ends with the step described earlier, i.e., when the set of contracted functions is extended from [21] to [321].

For σ TZ, we proceed in the same way, first generating the contracted functions [21] with the HF of fluorine and then optimizing one s , one p , and one d contractions with the CISD of fluorine to obtain the contracted functions [321]. To complete the optimization

of the σ TZ, one more stage is required, which corresponds to the addition of one further shell, like in Dunning BS, as well as new contractions, s , p , d , and f , at a rate of one new contraction per shell. The addition of new contractions gives rise to a new CISD energy value that is considered in the optimization process. Therefore, for σ TZ optimization, the energies corresponding to HF[21], CISD[321], and CISD[4321] are taken into account. The exponents of σ TZ are collected in the second column of Table III.

In summary, for σ DZ, σ TZ, and σ QZ, there are two, three, and four energy values to consider, respectively. These energies define the function that is sought to be minimized with the optimization of the different contracted functions, and different weights will be applied to the energy values in this function. It is worth mentioning that, to have a good starting HF result, the HF energy value is weighted with a factor 10 times larger than the weights of the CISD energy values. As each optimization step proceeds keeping unchanged the contractions built in the previous steps, new contractions are obtained, keeping the orthogonality between all of them. This way of building the BS limits its flexibility, as it would be possible to improve the final energy with a complete optimization of all the contractions in a single step. However, partial and successive optimization has been chosen as it allows us a more systematic approach by analyzing the energy saturation at each step.

In the case of atoms in which more than one electronic state is considered, the sum of their energies would be used, taking the same weight for the energies of all the states taken into account.

- Steps 2–4 are repeated, varying the exponents of the primitive functions until convergence.

Calculations of the electronic structure of atoms and molecules have been carried out at the HF and CISD levels using the MOLPRO⁴³ suite.

In Table IV, the angular components associated with each primitive exponent are quoted in parentheses. The exponents of the primitives used in polarization functions are grouped in the central part of the available set. The changes in exponents when passing from σ DZ to σ TZ or from σ TZ to σ QZ mainly correspond to exponents associated with a higher number of angular components.

For the $a\sigma$ BS, one diffuse primitive is added to each core shell (sp), with a common exponent smaller than those available in the corresponding σ BS. This is necessary to improve the descrip-

TABLE IV. Optimized energies (E_n) for fluorine atom using SIGMA basis sets.

Basis subset	[21]	[321]	[4321]	[54321]	
Basis set	$E_{HF} F (^2P)$		$E_{CISD} F (^2P)$		$E_{CISD} F^- (^1S)$
σ DZ[321]	−99.409 244	−99.581 864			
σ TZ[4321]	−99.409 202	−99.582 237	−99.629 454		
σ QZ[54321]	−99.409 201	−99.582 295	−99.629 660	−99.645 019	
$a\sigma$ DZ[432]	−99.409 233	−99.582 155			−99.705 131
$a\sigma$ TZ[5432]	−99.409 222	−99.582 305	−99.629 698		−99.745 334
$a\sigma$ QZ[65432]	−99.409 213	−99.582 339	−99.629 737	−99.645 144	−99.759 065

tion of the anion F^- , whose CISD energy is incorporated into the optimization procedure.

Table IV shows the intermediate results of each optimization step. The last values of each row are the energies that result at the end of the optimization process and are the ones that are compared with the Dunning values. Intermediate values for each optimization stage are included to understand the process and illustrate the previously mentioned possibility of choosing suitable subsets to carry out efficient calculations within the $G-n$ framework.

It should be noted that with this approach, each successive BS can serve as a better solution for the BS of a smaller size. For example, with an σQZ , a σDZ better than the current one can be obtained since the augmented BS contains more primitives. Therefore, it would suffice to keep the subset of the σQZ corresponding to the σDZ within it, i.e., the first [321] contractions. In this case, the energy is improved by 0.4 millihartree with respect to the proper σDZ . Due to this contraction scheme, any unconventional set can be selected and will be valid. Therefore, a basis of contractions [532] can be taken as a subset of a larger BS like the σQZ , which consists of contractions [54321] optimized for the energy of the atom. Alternatively, one could also take the unconventional set [532] from the σQZ , keeping in mind that the latter consists of contractions [65432] in which the subset [54321] is optimized for the neutral atom and the remaining contractions are added to also describe the anion.

The HF calculations for different BS are not all equally saturated, but they are observed to be reasonably well converged (contrary to what happens with the Dunning BS). It happens that, in general, as in this case of fluorine, the HF energy attained with the σDZ is usually slightly better than that of larger BS. This is so because the exponents have been optimized mostly to yield good HF energy values, whereas on larger BS, exponents are used in a greater number of primitives aimed at providing good results in energies computed at HF and CISD levels, and this affects especially the primitives related to polarization functions.

III. RESULTS AND DISCUSSION

A. Atoms

In Table V, the states and species considered in the optimization of σBS are reported together with the difference between their average energies and those computed with Dunning BS of the same composition. Details on the raw energies attained for atoms from H to Ne are given in Tables S1–S10 of the supplementary material.

As it can be seen in Tables S1–S10 of the supplementary material, optimization starts with calculations at a lower level, sometimes taken as HF and other times as a small multiconfigurational (MC). The latter is preferred when excited states exist close to the ground state. For example, in the Be atom, two states (1S and 3P) with electrons in $2s$ and $2p$ orbitals are optimized. This is so because it is more realistic and gives a better balance to the final contractions in the configurations generated in the CISD of both states. Using a single determinant as a reference, the possible participation of $2s$ and $2p$ contractions in both states would not be taken into account.

In particular, HF is used for H, He, F, and Ne, and MC calculations for the remaining ones, with two configurations for Li, Be, and B and three configurations for C, N, and O. The HF or MC and

CISD results are collected in the tables. It can be mentioned that the MC results are very close to those of HF.

In addition, in these tables, the energy differences (in mE_h) with respect to the equivalent Dunning BS are given in parenthesis. These differences are taken as $\Delta E = E_{Dunning} - E_{\sigma}$, so positive values mean that σBS outperforms the equivalent Dunning BS. This happens in all cases. Furthermore, it is worth noticing that even in these cases, in which more than one state is considered together, the sum of the energies of the states, which is taken into account in the optimization, is lower in the σBS . It is also noticeable that the improvement of σBS with respect to Dunning BS is achieved both in the HF and in the correlation energies at the CISD level. On the other hand, as would be expected, the improvement is higher for the smaller BS, which is farther from the complete BS.

Figure 1 contains a graphical summary of Table V in four panels. They show the energy differences in mE_h of Table V for atoms from H to Ne, which is equivalent to the difference between the energy computed with Dunning BS and that computed with the equivalent SIGMA BS. In panels *a* and *b*, ΔE for the standard BS is plotted for HF/MC and CISD calculations, respectively, and panels *c* and *d* contain similar plots for augmented BS.

When comparing the panels on the left side [(a) and (c)] with those on the right side [(b) and (d)], it is observed that the energy differences are greater for CISD calculations because the SIGMA BS improves the correlation energy with respect to the equivalent Dunning BS (see raw energies in Tables S1–S10 of the supplementary material). When comparing the upper panels [(a) and (b)] with the lower ones [(c) and (d), i.e., standard BS with the augmented BS], it can be observed how the improvement is higher for the augmented BS both at the HF/MC and CISD calculation levels. In summary, SIGMA BS overcomes Dunning BS in all cases studied. Furthermore, details can be found in the file *asTZ.molpro.out.tar* of the supplementary material.

From Table V and Fig. 1, we can conclude that: (i) the smallest differences between both kinds of BS (Dunning and SIGMA) are given for the Li atom. These differences increase with atomic number and become greatest for the Ne atom. (ii) For each atom, energy differences are higher for augmented BS than for standard BS, i.e., the improvement achieved with SIGMA BS is even greater with augmented BS than with standard BS. (iii) For a given family of BS (standard or augmented), differences decrease with the size of the BS, and both Dunning and SIGMA BS tend to yield results of similar quality as the BS size increases.

B. Molecules

The thermochemical properties of a system are based on the differences in the values of those properties between the reactants and the products. Something similar occurs with other properties related to transition states, excited states, etc. Theoretical calculations should provide good values for these properties, allowing reasonable values to be reached for the necessary differences. Dunning's BS and, in general, most common BS usually give good differences, although, in absolute terms, the values can be far from a valid reference. For this reason, in the analysis of these new bases, we will focus both on the absolute values of energies and on the internuclear distances obtained upon geometry optimization in molecules.

This section begins with a first study of the quality of the variational values of the energy of several systems and their impact on the optimization of the geometry. To do this, the results on molecules that illustrate the performance of the SIGMA BS will be discussed. First, the results of the C–O interatomic distance in the ground state of the CO₂ linear molecule are presented as an example of the study carried out on other molecules. Table S20 of the supplementary material shows the variational energies of CO₂ at the optimized equilibrium distance computed both at the HF and CISD levels using SIGMA XZ ($X = 2-4$) and Dunning XZ ($X = 2-6$) and their corresponding augmented versions. Similarly, Tables S11–S19 of the supplementary material contain the raw results of energies and distances for the diatomic molecules B₂, BN, BF, C₂, CO, N₂, NF, O₂, and F₂. In the case of CO₂, the calculations reported with σ DZ involve 69 contracted functions and yield lower HF energies than those attained with Dunning DZ, TZ, aDZ, and aTZ. It is noteworthy that the computation using aTZ requires 138 contracted functions, which doubles the number of contractions in σ DZ. In addition, the correlation energy is greater for the σ BS than for the Dunning BS. The convergence toward the reference value of the C–O distance is also better with the σ BS, both at HF and CISD levels. This trend is general and occurs in most diatomic molecules studied (see Tables S11–S19 of the supplementary material). It must be

noticed that, whereas Dunning BSs are aimed at correlated wavefunction methods, σ BSs are optimized for both HF and correlated methods. In general, optimized BSs for correlated methods have different compositions than those optimized for independent particle methods, such as HF and DFT.⁸ However, the ideal goal is to have a BS that provides a good reference both at the HF and CISD levels simultaneously. This is the case of the SIGMA BS, which starts with a better HF energy compared to the Dunning BS and yields better values for the CISD energies and more correlation energy. This idea is supported by the results on CO₂ shown in Table VI, which also apply to other molecules (see Table VII). Table VI contains the percentages of HF, CISD, and correlation energies and the equilibrium distance differences (in mÅ) with respect to the cc-pV6Z and aug-cc-pV6Z Dunning BS, which are taken as references. (Raw values can be found in Table S20 of the supplementary material.) Figure 2 shows the improvement of the correlation energy that SIGMA BS provides with respect to their equivalent Dunning BS for the CO₂ molecule (at CISD equilibrium distance) both for standard and augmented BS. It is noticeable that not only is the starting HF value of the SIGMA BS better than the HF value of the Dunning BS, but the correlation energy is also significantly better, which implies an even better improvement in the CISD energy.

TABLE V. HF or MC and CISD average energy differences between XZ and σ XZ basis sets.

Species	Method	$\Delta E/mE_h$			Species	Method	$\Delta E/mE_h$		
		σ DZ	σ TZ	σ QZ			σ DZ	σ TZ	σ QZ
H/H ₂	HF	2.7	0.4	0.1	H/H ₂ /H [−]	HF	2.0	0.3	0.0
	CISD	3.6	0.6	0.2		CISD	3.0	0.6	0.2
He	HF	6.5	0.5	0.2	He/He ₂	HF	9.0	0.7	0.2
	CISD	9.9	1.5	0.4		CISD	15.6	2.8	0.9
Li/Li ₂	HF	1.0	0.2	0.0	Li/Li ₂ /Li [−]	HF	0.8	0.2	0.1
	CISD	0.7	0.2	0.0		CISD	1.3	0.3	0.1
Be	MC	1.5	0.4	0.1	Be/Be ₂	MC	1.7	0.5	1.0
	CISD	2.1	0.8	0.3		CISD	2.5	0.7	1.9
B	MC	2.8	1.2	0.2	B/B [−]	MC	2.8	1.0	0.2
	CISD	5.9	1.9	0.4		CISD	5.8	1.9	0.4
C	MC	6.7	2.0	0.4	C/C [−]	MC	5.2	1.7	0.2
	CISD	12.9	4.3	1.1		CISD	10.4	3.8	1.0
N	MC	13.3	3.8	0.8	N/N [−]	MC	10.4	3.1	0.6
	CISD	23.3	6.4	1.4		CISD	20.1	6.7	1.9
O	MC	23.8	6.4	1.4	O/O [−]	MC	19.6	5.6	1.2
	CISD	39.4	12.3	3.5		CISD	34.8	12.0	3.7
F	HF	38.2	10.0	2.2	F/F [−]	HF	32.1	8.8	1.9
	CISD	58.4	17.8	5.1		CISD	53.2	18.0	5.7
Ne	HF	58.1	15.0	3.4	Ne/Ne ₂	HF	75.8	20.4	4.7
	CISD	85.4	25.2	7.6		CISD	132.5	42.4	14.0

TABLE VI. Comparison of the SIGMA and Dunning basis sets for CO₂ molecule.

Size	% E _{HF}		% E _{CISD}		% E _{corr}		ΔR_{eHF} (mÅ)		ΔR_{eCISD} (mÅ)	
	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning
DZ	99.986 0	99.959 8	99.918 4	99.878 0	78.42	73.91	3.40	6.19	9.62	13.93
TZ	99.997 0	99.990 2	99.974 0	99.961 3	92.66	90.78	1.10	1.81	3.46	4.68
QZ	99.999 0	99.998 1	99.991 5	99.988 3	97.60	96.87	0.11	0.11	0.75	0.92
BS	E _{HF}		E _{CISD}		E _{corr}		R _{eHF}		R _{eCISD}	
cc-pV6Z	−187.728 388		−188.314 647		−0.586 889		1.134 376		1.145 823	

Size	% E _{HF}		% E _{CISD}		% E _{corr}		ΔR_{eHF} (mÅ)		ΔR_{eCISD} (mÅ)	
	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning
aDZ	99.992 1	99.965 9	99.938 3	99.893 6	82.84	77.00	3.39	7.45	7.49	15.52
aTZ	99.998 8	99.991 3	99.981 6	99.966 3	94.53	92.03	0.36	1.87	1.74	4.80
aQZ	99.999 8	99.998 3	99.994 3	99.989 9	98.24	97.32	0.02	0.20	0.37	1.13
BS	E _{HF}		E _{CISD}		E _{corr}		R _{eHF}		R _{eCISD}	
aug-cc-pV6Z	−187.728 403		−188.315 556		−0.587 788		1.134 377		1.145 865	

It is quite obvious that the better performance of SIGMA BS over Dunning BS comes from the use of true contractions (more than one primitive per GTO) in all basis functions. This idea is not new, and other families of BS like ANO BS have already used it,²⁶ but while in ANO BS, different exponents are taken from the primitives of each shell, in SIGMA BS, the exponents are shared among shells. This feature is intended to reduce the cost of the molecular integrals' computation, provided it is taken into account in the corresponding algorithms. This is an important point, as better performance is attained at the expense of a

noticeable increase in the number of primitives involved in the calculation.

As mentioned before, these results attained for CO₂ are confirmed for other molecules, as shown in Tables VII–X. In these tables, some statistics are reported on different types of systems (raw data are collected in Tables S11–S20 of the supplementary material). In Table VII, results attained on a set of diatomic molecules (B₂, BN, BF, C₂, CO, N₂, NF, O₂, and F₂) plus a triatomic molecule, CO₂, are analyzed by comparison with the corresponding results using Dunning cc-pV6Z and aug-cc-pV6Z BS. The first three columns show

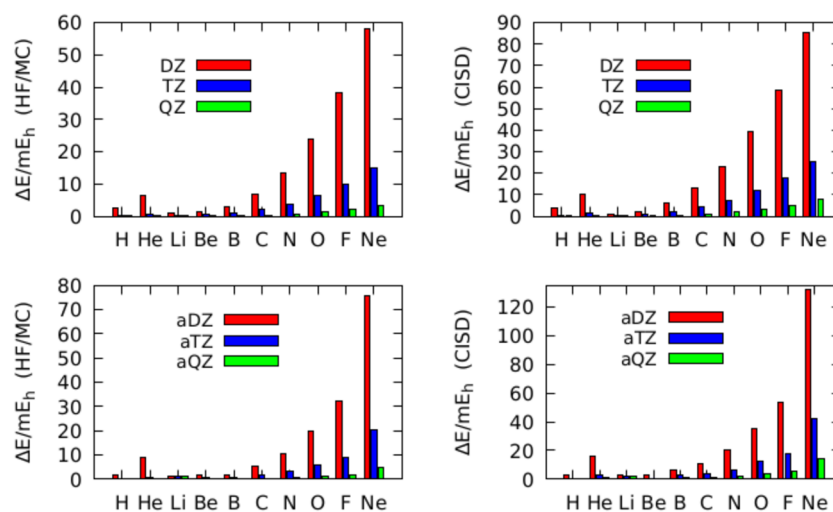
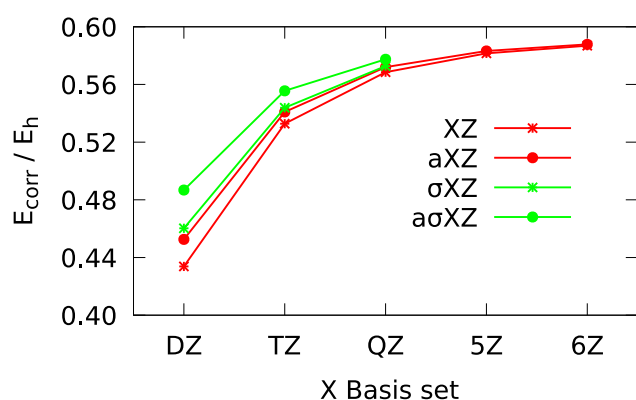
**FIG. 1.** Energy differences (mEh) between Dunning and SIGMA BS (the former minus the latter) for atoms from H to Ne using standard and augmented BS at HF/MC and CISD levels.

TABLE VII. Comparison of the SIGMA and Dunning basis sets: average values for the ground states of molecules: B₂, BN, BF, C₂, CO, N₂, NF, O₂, F₂, and CO₂. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	% E _{HF}		% E _{CISD}		% E _{corr,CISD}		$\Delta R_{e,HF}$ (mÅ)		$\Delta R_{e,CISD}$ (mÅ)	
	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning
DZ	99.9866	99.9634	99.9251	99.8881	81.06	76.74	14.05	12.12	23.51	22.90
TZ	99.9969	99.9909	99.9765	99.9648	93.68	91.93	3.27	2.43	6.47	6.04
QZ	99.9987	99.9981	99.9920	99.9893	97.94	97.27	1.17	0.36	2.13	1.44
aDZ	99.9934	99.9689	99.9443	99.9020	84.91	79.51	6.31	12.52	13.47	25.07
aTZ	99.9987	99.9920	99.9835	99.9694	95.31	93.05	1.11	2.33	3.49	6.35
aQZ	99.9997	99.9984	99.9948	99.9909	98.51	97.68	0.22	0.32	0.88	1.59

**FIG. 2.** Correlation energies for CO₂ molecule for Dunning and SIGMA BS.

the percentage of HF, CISD, and correlation energies obtained with SIGMA and Dunning BS with respect to this reference. As happens with CO₂, the results of SIGMA BS overcome those of Dunning BS of equivalent composition, both for the standard and augmented BS. It is noteworthy to discuss the differences of the equilibrium distances with respect to the reference, which are displayed (in mÅ) in columns 4 and 5 of this Table VII. In general, as expected, the results improve with the BS size for both families of BS and at both computation levels. In the case of standard BS, the results obtained with Dunning BS are similar to those obtained with SIGMA BS, but in the case of augmented BS, the results of SIGMA BS significantly improve, whereas those of Dunning BS remain almost unchanged (even worsen in some cases), so that augmented SIGMA BS overcomes those of Dunning BS in all cases. This illustrates the importance of the diffuse functions for accurate geometry optimization and the better performance of these functions in SIGMA BS. Table VIII contains the same analysis for several hydrides with a single bond length (mostly triatomic nonlinear molecules with a fixed angle) and displays trends that are similar to those of Table VII, with an improvement in standard SIGMA BS performance in equilibrium distance calculations and an even higher superiority in the case of results with augmented BS (raw data in Tables S21–S26 of the supplementary material). Likewise, Tables IX and X summarize the results for some molecular cations and anions. In the case of anions,

only augmented BSs have been considered, as diffuse functions are mandatory in this type of system. It is noticeable that in these ions, equilibrium distances computed with SIGMA BS overcome those of Dunning BS with both standard and augmented BS (raw data in Tables S27–S30 of the supplementary material for cations and S31 to S37 for anions).

To visualize the relative performance of SIGMA BS vs that of Dunning BS, we present in Fig. 3 the statistics in the percentage of the correlation energy and the difference in the equilibrium distance of diatomics with respect to the reference. It is interesting to notice the better performance in these properties (on average) of standard SIGMA BS over augmented Dunning BS, with this difference being more noticeable in the smallest BS.

As a last test, we analyzed the performance of these BS in molecules with two equilibrium distances to be optimized. We have considered five molecules, ranging from HCN to benzene. The results of energies and distances are summarized in Tables S38 and S39 of the supplementary material, and the raw data are collected in Tables S40–S49 of the supplementary material. Again, the results attained with Dunning cc-pV6Z and aug-cc-pV6Z BS have been taken as a reference, except in the case of benzene, in which the cc-pV5Z has been used. Results are visualized in Fig. 4, where statistics on the correlation energy and distance differences are plotted for the augmented BS. Raw data are collected in Tables S38–S49 of the supplementary material. The same trends as before can also be observed here, and SIGMA BS outperforms Dunning BS in these systems too.

Finally, we want to notice that, although the results shown are reduced to a set of 32 molecules, we are currently carrying out tests in more complex systems, reaching the same conclusions for the moment: a substantial and evident variational improvement with the use of SIGMA BS with respect to Dunning BS and the suitability of the augmented SIGMA BS for geometry optimization. This last observation is the most novel since the general belief is that augmented BS are useful in energy calculations in systems with changes in electronic density, but they are not usually considered for the optimization of the geometries of any system.

C. Additional tests

To confirm the good performance of the SIGMA BS, further comparisons have been made with other popular BS and

TABLE VIII. Comparison of the SIGMA and Dunning basis sets: average values for the ground states of molecules: BeH₂ ($\alpha = 180^\circ$), BH₃, CH₄, NH₃ ($\alpha = 112.94^\circ$), H₂O ($\alpha = 104.48^\circ$), and FH. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	% E _{HF}		% E _{CISD}		% E _{corr} CISD		ΔR_{eHF} (mÅ)		ΔR_{eCISD} (mÅ)	
	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning
DZ	99.9863	99.9525	99.9026	99.8549	80.43	77.07	3.26	8.04	4.99	11.91
TZ	99.9972	99.9887	99.9732	99.9590	94.27	92.89	0.47	1.12	0.63	1.81
QZ	99.9991	99.9975	99.9919	99.9886	98.27	97.82	0.07	0.10	0.33	0.27
aDZ	99.9953	99.9628	99.9322	99.8805	85.30	80.79	1.31	5.98	3.05	11.37
aTZ	99.9994	99.9912	99.9826	99.9667	96.00	94.14	0.30	1.23	0.74	2.72
aQZ	99.9999	99.9982	99.9950	99.9908	98.83	98.21	0.05	0.19	0.19	0.56

TABLE IX. Comparison of the SIGMA and Dunning basis sets: average values for the ground states of molecules: NH₄⁺, CH₃⁺, H₃O⁺ ($\alpha = 109.00^\circ$), and NO⁺. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	% E _{HF}		% E _{CISD}		% E _{corr} CISD		ΔR_{eHF} (mÅ)		ΔR_{eCISD} (mÅ)	
	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning
DZ	99.9832	99.9576	99.9102	99.8712	80.87	77.35	1.57	7.49	4.25	12.95
TZ	99.9950	99.9905	99.9729	99.9629	94.17	92.69	0.70	1.17	1.43	2.60
QZ	99.9987	99.9980	99.9920	99.9920	98.22	97.69	0.12	0.15	0.28	0.51
aDZ	99.9931	99.9626	99.9338	99.8839	84.45	79.39	1.02	6.47	2.89	12.19
aTZ	99.9984	99.9912	99.9819	99.9665	95.61	93.48	0.22	1.12	0.74	2.91
aQZ	99.9997	99.9981	99.9947	99.9904	98.66	97.93	0.03	0.19	0.12	0.70

TABLE X. Comparison of the SIGMA and Dunning basis sets: average values for the ground states of molecules: BeH₃[−], BH₄[−], CN[−], NO₂[−], NO₃[−], and OH[−] y OF[−]. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	% E _{HF}		% E _{CISD}		% E _{corr} CISD		ΔR_{eHF} (mÅ)		ΔR_{eCISD} (mÅ)	
	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning
aDZ	99.9934	99.9663	99.9327	99.8875	85.10	80.46	3.79	9.08	9.00	17.94
aTZ	99.9989	99.9915	99.9818	99.9818	95.62	93.72	0.63	1.42	2.29	4.28
aQZ	99.9997	99.9983	99.9947	99.9947	98.71	98.04	0.15	0.25	0.60	1.11

using other computational methods, in particular, CCSD(T) and DFT. To complement the information in Table I, The composition of ANO, ANO-R, pcseg, aug-ANO, and aug-pcseg BS used in this analysis is reported in Table S50 (taking nitrogen as a representative atom because, for these BS, there are different numbers of primitive functions depending on the particular atom in the period).

To begin this analysis, the performance of ANO²⁶ BS and the most recent version of them, the ANO-R,^{27,28} has been compared with that of SIGMA and Dunning BS. In Table XI, which is equivalent to Table VII, statistics is reported on the performance of these BS in different properties for diatomic molecules plus CO₂. The percentage of energy at CCSD(T) level retrieved with respect to the reference (cc-pV6Z and aug-cc-pV6Z) is collected in the upper

panel. As it can be seen, both the SIGMA and ANO BSs have a parallel behavior and display better percentages (greater than 99.99% in QZ) than the corresponding ANO-R and Dunning BSs. In the second panel of Table XI, the percentage of the correlation energy retrieved at this computational level (with respect to the reference) is shown. In this case too, the performance of SIGMA and ANO overcomes that of ANO-R and Dunning BS, except in the case of TZ, in which ANO-R is slightly better. The percentage error in atomization energies is reported in the third panel. In this regard, for standard (non-augmented) BS, ANO-R and Dunning BS perform better than SIGMA and ANO BS, but in augmented BS (no ANO-R in this case), this difference is reversed. Finally, the errors in the equilibrium distance, displayed in the fourth panel, are rather similar for non-augmented BS, but in the case of augmented BS, a significant

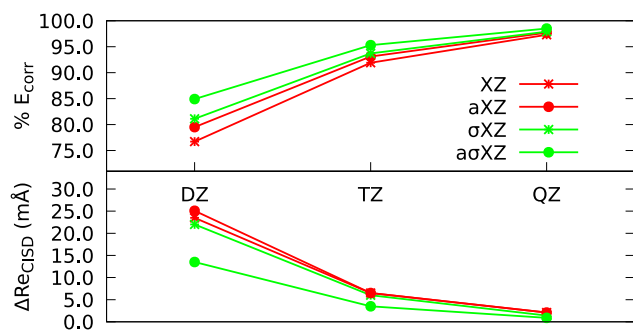


FIG. 3. Average percentage of correlation energy and error in the optimization of the internuclear distance (mÅ) using Dunning and SIGMA BS for diatomic molecules.

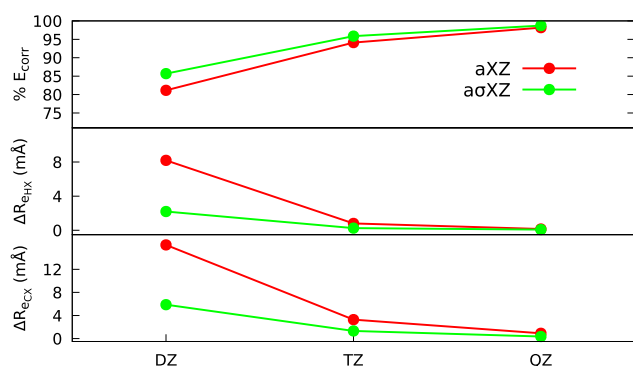


FIG. 4. Average percentage of correlation energy and error in the optimization of the equilibrium distances (mÅ) using Dunning and SIGMA BS for larger molecules.

improvement is found in SIGMA and ANO BS, unlike Dunning BS, which do not improve the results and even worsen them in some cases.

Similar tests have been carried out on molecules containing hydrogen, and the pertaining statistics are collected in Table S51 of the supplementary material. The results of the percentages of the CCSD(T) and correlation energies are very close to those of diatomic molecules for all four BS. Meanwhile, the errors in the atomization energies and the equilibrium distances are significantly reduced for all BS when compared to those reported for diatomics, with a notable improvement in the case of SIGMA and ANO BSs, which in these systems overcome Dunning BS and yield results comparable to those of ANO-R. This effect of going from Table XI to Table S51 is similar to the changes that occur in energy and equilibrium distance at the HF and CISD levels in Tables VII and VIII for the same compounds. Furthermore, tests on charged molecules have been performed, and the results reported in Tables S52 (cations) and S53 (anions) of the supplementary material are very similar to those obtained for neutral molecules. In the case of Table S53, as in Table X, calculations have been made only with augmented BS. For this reason, there are no calculations for the ANO-R BS. The results attained in this analysis at CCSD(T) level illustrate the satisfactory performance of the

TABLE XI. Comparison of the SIGMA, ANO, ANO-R, and Dunning basis sets: total energy and correlation energy, and errors in atomization energy and equilibrium distance. Average values for ground states of B₂, BN, BF, C₂, CO, N₂, NF, O₂, F₂, and CO₂ at the CCSD(T) level. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	σ	ANO	ANO-R	Dunning
% E_{total}				
DZ	99.9141	99.9132	99.8914	99.8741
TZ	99.9732	99.9729	99.9670	99.9606
QZ	99.9910	99.9912	99.9795	99.9880
aDZ	99.9399	99.9466		99.8911
aTZ	99.9816	99.9840		99.9664
aQZ	99.9943	99.9950		99.9900
% E_{corr}				
DZ	80.77	80.39	76.94	76.19
TZ	93.68	93.47	93.71	91.89
QZ	97.94	97.87	96.06	97.27
aDZ	85.04	87.15		79.46
aTZ	95.44	95.94		93.21
aQZ	98.56	98.71		97.74
% ΔE_{atom}				
DZ	21.46	21.34	12.60	17.60
TZ	7.26	6.75	5.76	5.94
QZ	2.62	2.11	3.53	2.05
aDZ	12.90	12.87		15.56
aTZ	4.20	4.08		4.61
aQZ	1.32	1.33		1.35
ΔR_e (mÅ)				
DZ	24.92	28.85	24.29	22.73
TZ	6.39	7.56	8.04	5.63
QZ	1.99	2.19	4.31	1.30
aDZ	14.22	10.55		26.17
aTZ	3.66	2.94		6.66
aQZ	0.90	0.80		1.66

new SIGMA BS, which is generally better than that of Dunning BS and comparable to ANO BS.

A second aspect that has been considered is the performance of SIGMA BS in DFT calculations. Although there are specific BS for DFT methods, BS designed for *ab initio* methods are also used in this type of calculation. In this regard, given the excellent results obtained by the SIGMA BS in HF calculations, with a performance close to the complete BS even for the smaller members, and considering the monodeterminant character of the DFT methods, the SIGMA BS seems to be well suited for DFT calculations too. To test this possibility, we have selected four functionals of different types:

TABLE XII. Comparison of the SIGMA, ANO, pcseg, and Dunning basis sets: total energy, errors in atomization energy, and equilibrium distance. Average values for ground states of B₂, BN, BF, C₂, CO, N₂, NF, O₂, F₂, and CO₂ for several DFT methods. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	% E _{total}				ΔR _e (mÅ)				% Δ E _{atom}			
	σ	ANO	pcseg	Dunning	σ	ANO	pcseg	Dunning	σ	ANO	pcseg	Dunning
B3LYP												
DZ	99.9855	99.9855	99.9351	99.9585	14.43	17.34	10.52	12.72	6.55	6.90	4.01	3.17
TZ	99.9961	99.9964	99.9925	99.9890	3.43	3.52	1.20	2.24	1.67	1.61	0.47	0.61
QZ	99.9981	99.9986	99.9997	99.9969	1.30	0.78	0.12	0.42	0.58	0.36	0.12	0.18
aDZ	99.9923	99.9946	99.9385	99.9663	6.54	4.58	9.52	12.55	2.97	3.04	3.04	3.83
aTZ	99.9980	99.9986	99.9928	99.9906	1.13	0.77	1.11	2.18	0.55	0.38	0.38	0.54
aQZ	99.9994	99.9995	99.9998	99.9975	0.15	0.15	0.06	0.32	0.27	0.12	0.12	0.09
M06-2X												
DZ	99.9857	99.9861	99.9358	99.9623	13.18	16.16	8.70	11.29	9.00	9.26	8.04	7.22
TZ	99.9956	99.9961	99.9927	99.9899	3.17	3.12	1.06	2.34	3.53	3.01	1.69	2.63
QZ	99.9977	99.9983	99.9992	99.9957	1.34	0.57	0.06	0.26	0.41	0.64	0.54	0.92
aDZ	99.9920	99.9941	99.9396	99.9689	5.82	3.92	7.88	11.40	5.93	6.65	3.26	5.36
aTZ	99.9976	99.9983	99.9931	99.9912	0.85	0.70	1.09	2.16	2.90	2.10	1.50	2.96
aQZ	99.9990	99.9993	99.9992	99.9961	0.25	0.28	0.10	0.23	1.13	0.61	0.87	1.19
TPSS												
DZ	99.9877	99.9878	99.9356	99.9622	14.74	17.12	9.32	12.55	5.94	5.98	3.04	2.59
TZ	99.9966	99.9968	99.9914	99.9896	3.57	3.60	1.13	1.90	1.90	1.58	0.35	0.52
QZ	99.9984	99.9989	99.9990	99.9976	1.42	0.95	0.17	0.44	0.44	0.34	0.15	0.20
aDZ	99.9941	99.9952	99.9368	99.9655	6.41	5.61	10.16	12.83	3.38	3.11	2.77	4.25
aTZ	99.9982	99.9988	99.9920	99.9904	1.27	1.10	1.17	1.91	0.78	0.43	0.23	0.59
aQZ	99.9994	99.9995	99.9993	99.9980	0.16	0.38	0.08	0.44	0.09	0.15	0.09	0.12
PBE												
DZ	99.9858	99.9858	99.9354	99.9591	14.30	17.05	9.97	12.55	6.65	6.71	3.83	2.98
TZ	99.9959	99.9962	99.9925	99.9887	3.33	3.36	1.19	2.06	1.77	1.52	0.41	0.64
QZ	99.9979	99.9985	99.9985	99.9967	1.27	0.73	0.12	0.43	0.76	0.51	0.11	0.27
aDZ	99.9922	99.9942	99.9397	99.9670	6.49	4.56	8.62	12.09	2.30	2.00	2.29	3.01
aTZ	99.9975	99.9982	99.9928	99.9900	1.05	0.78	1.10	2.03	0.40	0.31	0.21	0.37
aQZ	99.9992	99.9994	99.9998	99.9971	0.78	0.20	0.06	0.34	0.39	0.17	0.09	0.12

B3LYP,^{52,53} M06-2X,⁵⁴ TPSS,⁵⁵ and PBE,^{56,57} and replaced the ANO-R by the pcseg BS⁵⁸ that has been specifically developed for DFT methods. Table XII compares the results attained with the four considered DFT functionals and the SIGMA, ANO, pcseg, and Dunning BS. In all cases, the results with Dunning cc-pV6Z and aug-cc-pV6Z, respectively, are taken as references. In the case of energy retrieval, the results are quite similar for all BS except for the smaller members, in which the superiority of the SIGMA and ANO BS over the pcseg and Dunning is appreciable. The atomization energies at the DFT level show very similar behavior for all the non-augmented BS with the four functionals, with a slightly favorable result for pcseg BS, which are specially designed for this type of calculation (notice that QZ BS are a little bigger in pcseg than the other three BS).

On the contrary, for the augmented versions, a significant improvement is observed for SIGMA and ANO BS, which does not occur for pcseg and Dunning BS. This improvement for augmented BS is also observed in the rightmost panel of Table XII, where the error in the equilibrium distance is reported. In this case, the non-augmented Dunning BS and pcseg yield lower errors, whereas the errors in the augmented versions are more evenly distributed among all the BSs as a consequence of the mentioned significant improvement achieved in the SIGMA and ANO BS.

Another test has been performed by computing the vibration frequencies of several diatomic molecules. The results are reported in Tables XIII and XIV for *ab initio* and DFT calculations, respectively. In Table XIII, where the errors in the frequencies with respect

TABLE XIII. Percentage of error in vibrational frequency, ω_e , with SIGMA, ANO, ANO-R, and Dunning basis sets at CISD and CCSD(T) levels. Average values for the ground states of B₂, BN, BF, C₂, CO, N₂, NF, O₂, and F₂. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	σ	ANO	ANO-R	Dunning	σ	ANO	ANO-R	Dunning
CISD					CCSD(T)			
DZ	4.26	4.76	2.73	3.86	5.01	5.44	2.91	3.99
TZ	1.16	1.31	1.37	0.79	1.27	1.43	1.48	0.87
QZ	0.49	0.48	0.86	0.27	0.45	0.48	0.99	0.25
aDZ	2.63	2.50		4.79	2.97	2.74		5.14
aTZ	0.88	0.75		1.16	0.98	0.83		1.31
aQZ	0.26	0.22		0.35	0.30	0.26		0.38

TABLE XIV. Percentage of error in vibrational frequency, ω_e , with SIGMA, ANO, pcseg, and Dunning basis sets for several DFT methods. Average values for the ground states of B₂, BN, BF, C₂, CO, N₂, NF, O₂, and F₂. Referred to the values obtained with Dunning cc-pV6Z and aug-cc-pV6Z BS.

BS	σ	ANO	pcseg	Dunning	σ	ANO	pcseg	Dunning
B3LYP					M06-2X			
DZ	1.70	2.02	0.85	1.23	2.10	2.30	1.37	1.59
TZ	0.46	0.42	0.10	0.27	0.55	0.54	0.25	0.32
QZ	0.17	0.13	0.04	0.08	0.29	0.12	0.12	0.11
aDZ	0.85	0.85	1.12	1.77	0.90	0.94	1.43	1.68
aTZ	0.21	0.13	0.11	0.31	0.29	0.30	0.24	0.48
aQZ	0.07	0.05	0.04	0.05	0.10	0.10	0.11	0.07
TPSS					PBE			
DZ	1.93	2.15	1.17	1.16	1.75	2.04	0.88	1.16
TZ	0.50	0.48	0.21	0.44	0.48	0.41	0.11	0.28
QZ	0.19	0.13	0.07	0.11	0.20	0.14	0.04	0.09
aDZ	0.74	0.80	1.11	1.53	0.85	0.82	1.09	1.72
aTZ	0.22	0.15	0.19	0.32	0.19	0.15	0.11	0.28
aQZ	0.04	0.07	0.09	0.09	0.12	0.06	0.04	0.05

to the reference are reported for CISD and CCSD(T) calculations, it can be seen that among non-augmented BS, Dunning BS yields the lower errors, except in the case of DZ, in which ANO-R performs better. However, in the augmented BS, the results worsen in the case of Dunning BS. On the other hand, in the DFT calculations illustrated in Table XIV, the errors in the frequencies for the four functionals considered in this work are in general smaller than those corresponding to the *ab initio* calculations. For non-augmented BS, the pcseg and Dunning BS perform slightly better than SIGMA and ANO BS, but for the augmented versions, the errors are quite evenly distributed among the four BS.

To complement the tests on the quality of the results, we report in Table XV the computational cost of HF and CCSD(T) calculations of benzene using SIGMA and Dunning BS, both for the standard and the augmented versions. In the left column, the BS types are quoted with the number of contractions between parentheses. The upper half of Table XV shows the number of primitives

of each BS, the time required by MOLPRO for the different steps, and the total time, measured on a system with an Intel(R) Xeon(R) Gold 6252 CPU at 2.10 GHz processor. The HF and CCSD(T) energies are displayed at the lower part of the table. It can be readily observed that the computational time required for HF and CCSD(T) steps is essentially the same for Dunning and SIGMA BS of the same composition. This is not surprising, as the cost of these steps depends on the number of contracted functions, which are the same for both BS. The time spent in the computation of the integrals is smaller for Dunning BS than for SIGMA BS of the same size. However, the results of the SIGMA BS overcome those of the equivalent Dunning BS.

On the other hand, comparing the timing for BS with a similar number of primitives shows that the integrals with SIGMA BS are much less expensive to compute. For instance, the σ TZ, which involves 738 primitive functions (p.f.) and 264 contracted functions (c.f.), spends ~85 s, whereas the cc-pVQZ (600 p.f., 510 c.f.) spends

TABLE XV. Time^a in s for C₆H₆ single point evaluation ($r_{C-C} = 1.3793 \text{ \AA}$, $r_{C-H} = 1.0721 \text{ \AA}$). Boldface is intended to facilitate comparisons, see text for details.

BS (# Contr)	# Primitives		Time integrals		Time HF		Time CCSD(T)		Time total	
	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ	Dunning	σ
DZ(114)	198	474	2.8	9.3	0.1	0.3	4.8	4.7	7.7	14.3
TZ(264)	348	738	22.8	83.9	2.1	2.4	101.1	73.0	126.0	159.3
QZ(510)	600	1146	217.7	770.4	21.5	23.2	999.2	947.7	1 239.4	1741.3
5Z(876)	996		2163.5		388.8		7836.0		10 388.3	
aDZ(192)	276	552	6.2	23.8	0.7	0.8	22.8	19.6	29.7	44.2
aTZ(414)	498	888	92.5	272.9	10.3	10.9	403.1	432.6	506.0	716.4
aQZ(756)	846	1392	1142.1	3065.1	158.8	174.7	4874.8	4599.4	6 175.7	7839.2
Energy HF					Energy CCSD(T)					
Dunning			σ		Dunning			σ		
DZ(114)	-230.721 343 07		-230.772 560 40		-231.574 469 91		-231.659 365 48			
TZ(264)	-230.780 433 25		-230.792 429 89		-231.803 540 02		-231.828 073 62			
QZ(510)	-230.794 822 35		-230.797 277 41		-231.869 989 21		-231.876 228 47			
5Z(876)	-230.798 276 39				-231.889 992 86					
aDZ(192)	-230.727 375 01		-230.782 732 21		-231.608 502 69		-231.718 146 69			
aTZ(414)	-230.782 265 53		-230.796 082 59		-231.817 949 78		-231.852 357 87			
aQZ(756)	-230.795 488 66		-230.798 352 24		-231.875 629 46		-231.884 930 48			

^aTime measured on a system with an Intel(R) Xeon(R) Gold 6252 CPU at 2.10 GHz processor.

~220 s, and in their augmented versions, the $a\sigma TZ$ (888 p.f., 414 c.f.) spends ~270 s, whereas the aug-cc-pVQZ (846 p.f., 756 c.f.) spends ~1140 s, and something analogous happens for the σDZ and σQZ BSs. This performance suggests that MOLPRO is able to take some advantage of the exponent sharing in SIGMA BS. Moreover, as expected, it can be observed that the contribution of the integral computation to the total time is quite significant for the smaller BS, whereas for the large BS, the largest contribution comes from the CCSD(T) process.

Finally, regarding energy, it can be seen that σTZ (264 c.f.) yields better HF and CCSD(T) values than aug-cc-pVTZ (414 c.f.) at a much lower cost (~160 s for the former and ~500 s for the latter), and the same holds for the corresponding DZ and QZ BS.

IV. CONCLUSIONS

A new family of GTO BS named SIGMA (Serially Improved GTOs for Molecular Applications), or σBS , has been presented. The new BS reported here for atoms from H to Ne ranges from DZ to QZ sizes and has the same composition as the corresponding Dunning BS. The σXZ contractions are designed to provide highly accurate energies in atomic and molecular calculations at different computational levels. For this purpose, like in other BS such as ANO and ANO-R, a higher number of primitives per contraction are used in σBS than in Dunning BS, especially in the polarization functions, which improves the results both at HF and CISD levels.

Energies for atoms ranging from H to Ne computed with SIGMA BS both at HF and CISD levels lie below those attained

with the Dunning BS of the same composition. The differences are smaller for the Li atom and increase with the atomic number, becoming largest for the Ne atom. Furthermore, differences are higher for augmented BS than for standard ones. In the case of molecules, it is noticeable the significant improvement in total energies and other properties like equilibrium distances, atomization energies, and vibrational frequencies when passing from the SIGMA non-augmented to the augmented BS. This also happens in the case of ANO BS, but it is not so for Dunning and pcseg BS. In Dunning BS, one possible source of this poorer performance in the augmented version is the insufficient convergence at the HF level.

On the other hand, the reduced number of exponents in SIGMA BS and the lower number of primitives for the smaller members than for the equivalent ANOs give the former some advantage from a computational point of view, although the effect of the number of exponents certainly depends on the ability of the codes for two-electron integrals calculation to exploit this feature. In this regard, we note that developing and modifying efficient codes for molecular integral calculations is far from an easy task.⁵⁹ Nevertheless, the current design of some existing packages, like MOLPRO, which can efficiently deal with general contractions, seems to be pretty well fitted for this purpose. This is also the case with the SHARK system⁶⁰ implemented in the ORCA⁶¹ suite, in which a modification of E matrices to cover more than one shell when required could do the job.

In summary, the results reported in this work demonstrate that SIGMA BS performs satisfactorily at very different levels of computation like HF, DFT, CISD, and CCSD(T) is competitive, and exhibits some advantages over other customarily used BS.

SUPPLEMENTARY MATERIAL

See the supplementary material for Additional Tables (S1–S56): supplementary_tables.pdf. SIGMA BS from H to Ne in MOLPRO format: basis_SIGMA_1680605602_2.txt. MOLPRO output files for augmented TZ SIGMA BS: asTZ.molpro.out_1680605602_3.zip.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ignacio Ema López: Conceptualization (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Guillermo Ramírez Moreno:** Conceptualization (equal); Methodology (equal); Software (equal); Writing – original draft (equal); Writing – review & editing (equal). **Rafael López Fernández:** Methodology (equal); Software (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **José Manuel García de la Vega:** Conceptualization (equal); Methodology (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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