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Generation of Basis Sets for Accurate Molecular Calculations: Application to Helium Atom and Dimer

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Abstract: A new approach for basis set generation is reported and tested in helium atom and dimer. The basis sets thus computed, named sigma, range from DZ to 5Z and consist of the same composition as Dunning basis sets but with a different treatment of contractions. The performance of the sigma sets is analyzed for energy and other properties of He atom and He dimer, and the results are compared with those obtained with Dunning and ANO basis sets. The sigma basis sets and their extended versions up to triple augmented provide better energy values than Dunning basis sets of the same composition, and similar values to those attained with the currently available ANO. Extrapolation to complete basis set of correlation energy is compared between the sigma basis sets and those of Dunning, showing the better performance of the former in this respect.

Keywords: He atomic basis sets; helium dimer; He₂ potential well; correlation energy; complete basis set; sigma basis set



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1. Introduction

The study of weak van der Waals (vdW) interactions has always been one of the most challenging applications of theoretical calculations of electron structure. Thus, methods based on Kohn–Sham (KS) density functional theory (DFT) have shown limitations for including weak and long-range interactions in the exchange-correlation term of the KS equation. In particular, standard functionals of DFT fail to explain these interactions because the stabilization is determined by dispersion interactions, and is not explained by these functionals. Exchange-correlation potentials, derived from local and semi-local models, often exhibit artifacts when applied to systems with large non-local correlation effects. Nevertheless, there is a continuous effort to include vdW interactions within the framework of KS theory [1], and remarkable progress on corrections to this fact has been made, such as the exchange-hole dipole moment (XDM) model [2,3].

In the long range, vdW interactions are dominated by dispersion and permanent multipole moment interaction and include superposition and exchange contributions. The behavior of an exchange functional in the region of small density and large density gradients plays a very important role. From a topological point of view, the presence of vdW interactions can be identified by reduced density gradient (RDG) analysis. In this respect, a novel procedure for studying van der Waals interactions has been developed as an extension of Bader's QTAIM in combination with RDG analysis in which a volumetric source function is used for describing the atomic composition of vdW interactions [4].

The above considerations reinforce that the well known fact is that to reliably study vdW interactions, not only large basis sets (BS) are needed, but also fine electron correlation treatments are required to reproduce experimental data. In particular, noble gases have been the focus of much research as a starting point for the study of rare gas dimer interactions [5], a criterion for the performance of basis sets and correlation methods in vdW studies.

Among the systems linked by vdW dispersion interactions, helium occupies an outstanding position. The properties of gaseous helium are close to those of the ideal gas

because the interactions between helium atoms are extremely weak, and its behavior at very low temperatures makes helium a paramount system on its own, with unusual physico-chemical properties under these conditions. Furthermore, vdW interaction in helium dimer, He_2 , is a touchstone for testing the capabilities of the most precise theoretical procedures available [6], as its existence is due to purely electronic correlation effects.

The accurate computation of the He_2 potential energy curve is a big challenge, and a great amount of work has been devoted to this task. Ab initio studies on He_2 interactions have been published by Van Mourik et al., who report dimer calculations using different methods and computational levels (MPn, CCSD(T), FCI, ...) with large basis sets, including polarization [7–9]. In the late 20th and 21st centuries, many other authors have published works on He_2 , using various sets of a consistent basis for correlation and a high level of theory: SAPT [10], CCSD(T) [11], r12-MR-ACPF [12–14], MRCI [15], CCSD(T) [16], Monte Carlo [17], Compton profiles [18] and Gaussian geminal theory [19]. The most accurate results were obtained with BS supplemented with an additional set of bond functions [20], obtaining better results when compared with larger BS without bond functions.

Because of the high accuracy intended and the feeble interaction involved, the question about the full elimination of basis set superposition error (BSSE) in the calculations of He_2 energy has been a matter of discussion [21], which still remains today. This problem comes from the difficulty of saturating the dispersion energy in calculations with conventional basis sets, and it is especially relevant in weakly interacting species. A good representation of the dispersion energy requires polarization functions with small exponents, and extrapolation methods from the raw energies without Counterpoise (CP) correction have been proposed to reduce the BSSE [22–24]. In particular, extrapolation to complete basis set (CBS) limit for the helium dimer was studied by A. Varandas [22,25], who carried out calculations with size-consistent methods such as Hartree–Fock (HF) and full configuration interaction (FCI) using Dunning BS.

As a consequence of this extraordinary effort, the accuracy achieved is certainly impressive and, according to the best estimations, the potential energy curve of He_2 has a minimum at a distance $R_e = 2.9676 \text{ \AA}$, with an energy of $-34.82 \mu E_h$ with respect to the limit of separated atoms [20,26]. This minimum in the potential energy curve is remarkably shallow and has been found to admit only one vibrational state, the mean distance between nuclei in this state being ca. ten times the equilibrium distance [27].

In this work, we report a way of constructing new basis sets for molecular calculations which overcome the variational performance of the existing ones of equivalent composition. Furthermore, we apply the procedure to the development of basis sets, hereafter named sigma (σ BS), for helium atoms and use them for the study of helium atom and dimer.

The article is organized as follows. In Section 2, the procedure for developing sigma BS is explained, and the contraction scheme and composition are described. Supplementary Materials are included, which contain the link for the sigma basis sets for He. In Section 3, a brief summary of computational procedures, methods, bases and programs is given. The results on the He atom and the He_2 dimer are reported in Section 4, in which the the precision of the total and dissociation energies as well as the equilibrium distances is discussed. Results on the CBS extrapolation of correlation energies are included in a subsection of Section 4. Finally, conclusions are drawn from these results in Section 5.

2. Criteria for Basis Set Optimization and Contraction Scheme: Size and Composition

The σ BS consists of linear combinations (contractions) of radial primitive Gaussians aimed at providing highly accurate energy values at different computational levels. In the construction of σ BS, we have exploited our previous experience in the development of exponential type BS [28–31]. Guided by this experience, we have decided to design σ BS with the characteristic that, if a given primitive contains a spherical harmonic of quantum number $l = L$, all the primitives with the same exponent and $l < L$ are also present in the set. For instance, if there is a d function with exponent α_i , then s and p functions with this exponent will appear in the BS. This characteristic was thought to reduce the

computation cost of integrals involving primitives, although most standard packages are usually not prepared to profit from it. Another feature of σ BS is that all primitives in a given shell, i.e., with the same angular part, participate in all contractions of the same shell. The combination of both features makes it possible for the number of primitives in the contractions can be increased, and the quality of the BS functions is thus improved, without penalizing the computational cost. In summary, contractions in σ BS are built from the same set of exponentials combined with different angular functions. Furthermore, whereas polarization functions of Dunning BS consist of single Gaussian functions (one primitive per function without contraction), in sigma basis sets they are true contractions, yielding significant improvements in the results on energy.

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 primitives for polarization functions, among those of core shells functions, is not obvious and must be accomplished by optimizing the exponents together for both types of functions. It is also noticeable that, albeit not specifically intended, the exponents of the primitives thus obtained almost follow an even tempered sequence, with slight variations and covering a wide range of values.

To simplify the notation, XZ will be used in the following as an abbreviation of cc-pVXZ, and aXZ of aug-cc-pcVXZ families. The equivalent Atomic Natural Orbitals (ANO) and σ BS will be denoted as anoXZ, aanoXZ, σ XZ and a σ XZ, respectively. In each of the six families, we have considered basis sets ranging from X = 2 (DZ) up to 5 (5Z).

The optimization of helium σ BS follows the general lines of Dunning's procedure which relies on the minimization of CISD energy in He atoms. Starting with a given set of exponents in the primitives, the contractions are constructed in a stepwise way. In the case of He, the (1s) contraction of the σ DZ is determined by minimizing the HF energy for the ground state. Next, the CISD is used to add a new shell and one more contraction per shell, but keeping unchanged the contraction previously optimized. These two steps yield the σ DZ basis set. This procedure is repeated, changing the primitive exponents until their optimum values are obtained.

To build the σ TZ, we proceed as in the case of the σ DZ. After optimizing the 2(s) + 1(p) contractions, a new shell and a new contraction per shell, 1(s) + 1(p) + 1(d), are added and optimized with CISD of the He atom. The scheme for all σ BS follows the procedure described but repeating the steps of contraction/optimization as many times as required according to the BS level. Proceeding in this way, and taking into account that the number of primitives is increased according to the rule mentioned, σ BS tend to saturate one-electron space per shell, yielding energies as close as possible to the best attainable values according to their size.

In general, these σ BS give energy values for He atoms lower than those of Dunning BS and similar to those of ANO BS, as we will see the next section. Unlike in Dunning and ANO BS, in the case of the augmented σ BS (a σ BS), the CISD energy of the dimer at the best available equilibrium distance (BED) $R_e = 2.9676 \text{ \AA}$ [26] is considered for the optimization of σ BS exponents.

3. Computational Details

As it is well known, basis sets augmented with polarization and diffuse functions can adequately reproduce weak dispersion interactions [9,25,32]. Bearing this in mind, to study He₂ interactions in a systematic way, we have carried out calculations using atom-centered basis sets. In particular, in this work we use correlation consistent basis sets developed by Dunning et al. [32–35] as a reference for testing the performance of σ BS reported herein. Dunning BS are widely used, and they are especially well suited for our purposes because they incorporate polarization functions and, in the case of augmented versions, diffuse functions. In addition, it has been shown that correlation-consistent basis sets doubly augmented with diffuse functions can be used to nearly saturate the radial contribution

to the dispersion energy in rare gas dimers [8,9,36]. Furthermore, these basis sets are grouped in families whose members are ranked in size (and quality), and this facilitates the extrapolation of results to the CBS limit.

For testing the accuracy of energy values attained with the σ BS, we have also used the ANO BS, which have proved to be able to exhaust the capabilities of the underlying Gaussian expansion basis (to minimize the contraction error) and provide a highly accurate reference [37,38].

Electronic structure calculations of He and He₂ have been carried out at HF, CISD and FCI levels, using MOLPRO suite [39].

4. Results and Discussion

4.1. Sigma Basis Sets vs. Dunning and ANO Basis Sets

The composition of the basis sets for the He atom is detailed in Table 1, in which the numbers of exponentials, primitives and contractions are quoted. Notice that the composition is the same for the three families, the only difference being the number of primitives, smaller in Dunning BS and similar in ANO and σ BS. On the other hand, the number of exponentials is smaller in σ BS than in the other two.

Table 1. Composition of Dunning, ANO and sigma basis sets.

Basis Sets	# Exponentials	#	Primitives	#	Contracted
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]
5Z	17	57	(7s, 4p, 3d, 2f, 1g)	55	[5s, 4p, 3d, 2f, 1g]
anoDZ	15	25	(10s, 5p)	5	[2s, 1p]
anoTZ	19	45	(10s, 5p, 4d)	14	[3s, 2p, 1d]
anoQZ	23	66	(10s, 5p, 4d, 3f)	30	[4s, 3p, 2d, 1f]
ano5Z	25	84	(10s, 5p, 4d, 3f, 2g)	55	[5s, 4p, 3d, 2f, 1g]
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]
a5Z	22	82	(8s, 5p, 4d, 3f, 2g)	80	[6s, 5p, 4d, 3f, 2g]
aanoDZ	15	25	(10s, 5p)	9	[3s, 2p]
aanoTZ	19	45	(10s, 5p, 4d)	23	[4s, 3p, 2d]
aanoQZ	23	66	(10s, 5p, 4d, 3f)	46	[5s, 4p, 3d, 2f]
aano5Z	25	84	(10s, 5p, 4d, 3f, 2g)	80	[6s, 5p, 4d, 3f, 2g]
a σ DZ	11	23	(11s, 4p)	9	[3s, 2p]
a σ TZ	11	46	(11s, 5p, 4d)	23	[4s, 3p, 2d]
a σ QZ	11	82	(11s, 6p, 5d, 4f)	46	[5s, 4p, 3d, 2f]
a σ 5Z	11	133	(11s, 7p, 6d, 5f, 4g)	80	[6s, 5p, 4d, 3f, 2g]

In Table 2, some properties computed at HF and FCI levels are reported. As can be appreciated, FCI energies computed with σ BS are lower than those computed with their equivalent partners of the other two families. In the case of He₂, energies have been calculated at the equilibrium distance optimized at each computational level, and no result is displayed in the case of HF calculations with ANO or σ BS because no minimum is found in these cases.

Table 2. He and He₂ energies (E_h), dissociation energies and equilibrium distances at HF and FCI levels.

	He Atom		He ₂ Dimer		$D_e(\mu\text{H})$		$R_e(\text{\AA})$	
	HF	FCI	HF	FCI	HF	FCI	HF	FCI
DZ	-2.85516048	-2.88759483	-5.71032241	-5.77519594	1.47	6.28	3.209	3.090
TZ	-2.86115334	-2.90023217	-5.72230756	-5.80047345	0.87	9.11	3.637	3.296
QZ	-2.86151423	-2.90241088	-5.72302886	-5.80483479	0.40	13.03	3.806	3.236
5Z	-2.86162483	-2.90315188	-5.72324982	-5.80632032	0.15	16.55	4.005	3.155
anoDZ	-2.86165583	-2.89748229	—	-5.79496717	—	2.60	—	3.623
anoTZ	-2.86166988	-2.90170267	—	-5.80341360	—	8.26	—	3.335
anoQZ	-2.86167139	-2.90282021	—	-5.80565442	—	13.99	—	3.194
ano5Z	-2.86167205	-2.90324192	—	-5.80650279	—	18.95	—	3.112
σ DZ	-2.86166454	-2.89755779	—	-5.79511772	—	2.13	—	3.645
σ TZ	-2.86166897	-2.90175275	—	-5.80351122	—	5.73	—	3.426
σ QZ	-2.86167087	-2.90283439	—	-5.80567817	—	9.39	—	3.301
σ 5Z	-2.86167106	-2.90324791	—	-5.80651300	—	17.17	—	3.141
aDZ	-2.85570467	-2.88954849	-5.71141075	-5.77914013	1.41	43.16	3.417	2.998
aTZ	-2.86118343	-2.90059792	-5.72236734	-5.80122808	0.49	32.22	3.806	3.007
aQZ	-2.86152200	-2.90253360	-5.72304429	-5.80510033	0.30	33.13	4.057	2.979
a5Z	-2.86162693	-2.90320053	-5.72325393	-5.80643456	0.07	34.96	4.131	2.981
aanoDZ	-2.86166988	-2.89996594	—	-5.79993919	—	7.31	—	3.378
aanoTZ	-2.86167139	-2.90245288	—	-5.80490575	—	13.88	—	3.197
aanoQZ	-2.86167205	-2.90312610	—	-5.80627113	—	18.93	—	3.113
aano5Z	-2.86167282	-2.90339507	—	-5.80681090	—	20.76	—	3.088
$a\sigma$ DZ	-2.86167614	-2.89997789	—	-5.79996081	—	5.02	—	3.464
$a\sigma$ TZ	-2.86167722	-2.90245411	—	-5.80491755	—	9.33	—	3.300
$a\sigma$ QZ	-2.86167716	-2.90313545	—	-5.80628469	—	13.84	—	3.197
$a\sigma$ 5Z	-2.86167707	-2.90340070	—	-5.80681741	—	16.02	—	3.143

Dissociation energies of He₂, D_e have been computed as the difference between the energies of the separated atoms and that in the minimum of the curve, R_e . In the case of Dunning BS, a shallow minimum is obtained at the HF level at a distance that increases with the BS size. As mentioned above, this minimum does not appear in HF calculations with the two other families, suggesting that the improvements in the core zone with respect to those of Dunning should prevent the presence of a minimum at the HF level.

The convergence of D_e and R_e towards the currently best available values ($D_e = 34.82 \mu E_h$ and $R_e = 2.9676 \text{\AA}$) [26] has been analyzed in FCI calculations, and the results are depicted in Figures 1 and 2. In Figure 1, D_e is plotted vs. the BS size for the three types of BS, including the augmented versions. It is observed that non-augmented BS have a slow convergence towards the exact result, and they are far away from it even at the 5Z level. Augmented ANO and σ BS improve the results slightly, but the convergence is still far from the reference. On the other hand, Dunning augmented BS, although not optimized for CISD energy of He₂ at R_e , yield astonishing precise depth values of the well.

In the case of equilibrium distance, displayed in Figure 2, the behavior is quite similar to that of D_e , with Dunning augmented BS giving a very good agreement even with the smallest set (aDZ).

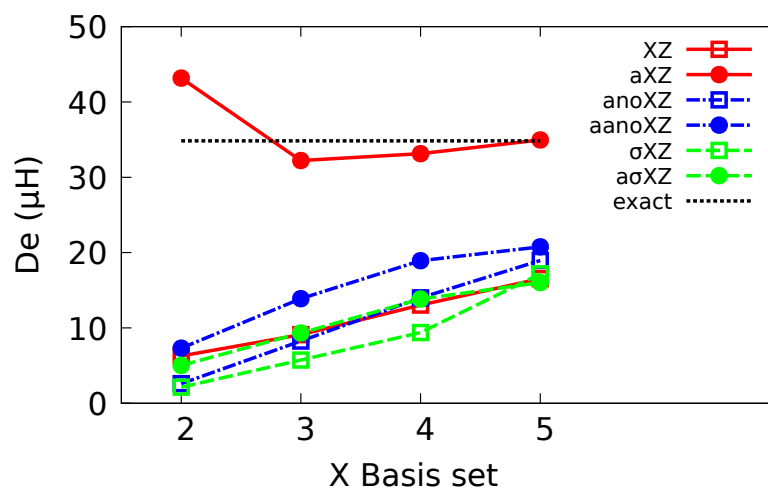


Figure 1. Dissociation energy, D_e (μE_h).

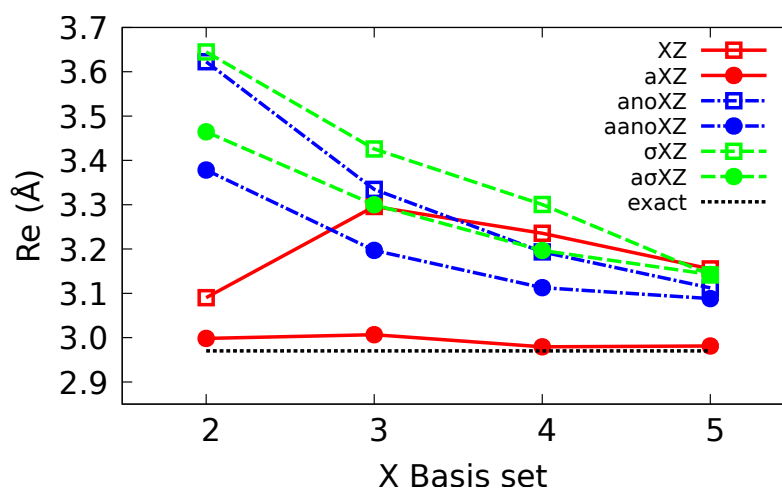


Figure 2. Equilibrium distance, R_e (angstrom).

4.2. Multiple Augmented Basis Sets

Given the excellent performance of Dunning BS with regard to the dissociation energy of He_2 , and in an attempt to understand why this is not so in the case of σ BS, we decided to explore the performance of multiple augmented basis sets in both families.

We developed double and triple augmented σ BS but, unlike in Dunning BS, which were designed to improve the polarizability of the He atom, we followed the methodology based only on energy. Thus, we obtained double and triple augmented σ BS (da σ XZ and ta σ XZ) to compare with the corresponding Dunning BS (daXZ and taXZ, for short). These multiply augmented BS are described in Table 3. In analogy with Table 1, the number of exponentials, primitives and contracted functions are given, and the same comments on the composition, size and characteristics mentioned before also hold for the new multiple augmented σ BS.

Table 3. Composition of double and triple augmented Dunning and σ BS.

Basis Sets	# Exponentials	#	Primitives	#	Contracted
daDZ	9	15	(6s, 3p)	13	[4s, 3p]
daTZ	14	34	(7s, 4p, 3d)	32	[5s, 4p, 3d]
daQZ	20	64	(8s, 5p, 4d, 3f)	62	[6s, 5p, 4d, 3f]
da5Z	27	107	(9s, 6p, 5d, 4f, 3g)	105	[7s, 6p, 5d, 4f, 3g]
da σ DZ	12	27	(12s, 5p)	13	[4s, 3p]
da σ TZ	12	55	(12s, 6p, 5d)	32	[5s, 4p, 3d]
da σ QZ	12	98	(12s, 7p, 6d, 5f)	62	[6s, 5p, 4d, 3f]
da σ 5Z	12	158	(12s, 8p, 7d, 6f, 5g)	105	[7s, 6p, 5d, 4f, 3g]
taDZ	11	19	(7s, 4p)	17	[5s, 4p]
taTZ	17	43	(8s, 5p, 4d)	41	[6s, 5p, 4d]
taQZ	24	80	(9s, 6p, 5d, 4f)	78	[7s, 6p, 5d, 4f]
ta5Z	32	132	(10s, 7p, 6d, 5f, 4g)	130	[8s, 7p, 6d, 5f, 4g]
ta σ DZ	13	31	(13s, 6p)	17	[5s, 4p]
ta σ TZ	13	64	(13s, 7p, 6d)	41	[6s, 5p, 4d]
ta σ QZ	13	114	(13s, 8p, 7d, 6f)	78	[7s, 6p, 5d, 4f]
ta σ 5Z	13	183	(13s, 9p, 8d, 7f, 6g)	130	[8s, 7p, 6d, 5f, 4g]

Results obtained with multiple augmented BS are summarized in Table 4, whose structure is identical to that of Table 2. Regarding the atomic calculations at HF and FCI levels, it is observed again that energies computed with σ BS are always better than those of the equivalent Dunning sets. In fact, ta σ XZ, albeit not directly intended, yields a good agreement with the HF limit ($-2.861679995 E_h$) [40,41] even for the smallest set of the series, with an error ca. $10^{-6} E_h$ in all cases.

Table 4. He and He₂ energies (E_h), dissociation energies and equilibrium distances at HF and FCI levels for double and triple augmented BS.

	He Atom		He ₂ Dimer		D _e (μ H)		R _e (\AA)	
	HF	FCI	HF	FCI	HF	FCI	HF	FCI
daDZ	-2.85570939	-2.88959436	-5.71142686	-5.77924689	8.09	58.17	3.288	2.964
daTZ	-2.86118387	-2.90060812	-5.72237146	-5.80126097	3.72	44.72	3.837	2.995
daQZ	-2.86152234	-2.90253661	-5.72304596	-5.80511435	1.28	41.13	4.045	2.958
da5Z	-2.86162717	-2.90320194	-5.72325487	-5.80644187	0.52	37.98	3.882	2.965
da σ DZ	-2.86167803	-2.90035561	—	-5.80072031	—	9.08	—	3.320
da σ TZ	-2.86167821	-2.90265038	—	-5.80531813	—	17.37	—	3.136
da σ QZ	-2.86167822	-2.90323388	—	-5.80648926	—	21.52	—	3.080
da σ 5Z	-2.86167816	-2.90343963	—	-5.80690928	—	30.02	—	3.002
taDZ	-2.85571146	-2.88960188	-5.71143417	-5.77926374	11.22	59.92	3.351	2.984
taTZ	-2.86118406	-2.90061002	-5.72237488	-5.80128012	6.76	60.33	3.654	2.996
taQZ	-2.86152247	-2.90253721	-5.72304861	-5.80511936	3.67	44.93	3.973	2.957
ta5Z	-2.86162726	-2.90320225	-5.72325624	-5.80644560	1.72	41.10	3.850	2.960
ta σ DZ	-2.86167928	-2.90046500	—	-5.80094227	—	12.26	—	3.247
ta σ TZ	-2.86167885	-2.90272428	—	-5.80546977	—	21.21	—	3.087
ta σ QZ	-2.86167886	-2.90328593	—	-5.80659710	—	25.24	—	3.037
ta σ 5Z	-2.86167829	-2.90344482	—	-5.80692585	—	32.21	—	2.982

With respect to the dimer, Dunning BS (daXZ and taXZ) again give minima at the HF level, the well depth being greater than that obtained with the smaller XZ and aXZ, and the equilibrium distances range from 3.2 to 4.0 \AA . Again, the σ BS (da σ XZ and ta σ XZ) give no minimum. In all cases, the FCI energies for the diatom tend to the exact value $-5.80748357 E_h$, estimated from the best available values for the He energy

($2.903724377 \dots E_h$) [42] and for the well depth ($34.82 \mu E_h$) [26]. Notice that energy values computed with $da\sigma XZ$ y $ta\sigma XZ$ are significantly lower than those obtained with the equivalent Dunning BS.

Regarding the dissociation energy, Figure 3 shows that in Dunning BS, the inclusion of new polarization functions in the sequence aXZ , $daXZ$, $taXZ$ tends to worsen the results, whereas in σ BS, a regular improvement in the value of D_e is observed. In the case of equilibrium distance, R_e , Dunning BS produce results closer to the exact than those of σ BS, but the results attained with the latter also exhibit a regular approach to the right value, as shown in Figure 4.

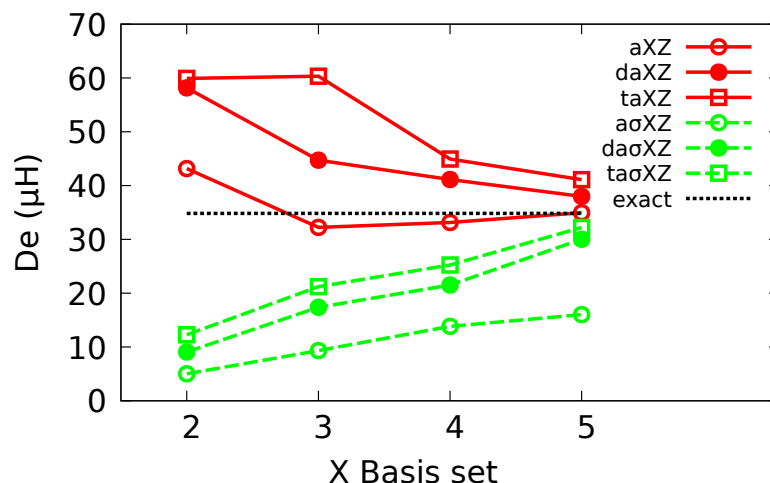


Figure 3. Dissociation energy, D_e (μE_h), multiple augmented BS.

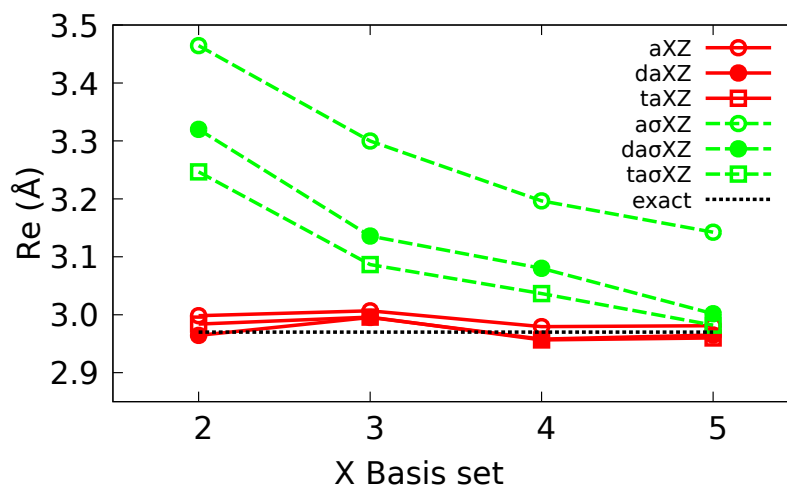


Figure 4. Equilibrium distance, R_e (angstrom), multiple augmented BS.

4.3. Extrapolation to CBS

The performance of the basis sets in extrapolations to CBS has been analyzed in the case of correlation energy both for the atom and for the dimer at BED. Although there are many extrapolation schemes, we have taken one due to Helgaker [43]:

$$E_{XZ} = E_{CBS} + \alpha/X^\beta.$$

The correlation energy of the atom has been calculated as the difference between the exact value [42] and the HF limit energy [40] and that of the dimer with the HF value at BED and adding the energy of the well ($34.82 \mu E_h$).

Correlation energy values thus computed plus the extrapolated CBS energies obtained for the Dunning and σ BS are collected in Table 5 and depicted in Figures 5 and 6. The best available correlation energies appear at the top of Table 5, with values of $0.0420444 E_h$ and $0.0841528 E_h$ for the atom and the dimer, respectively. To facilitate comparisons, figures coincident with reference values are displayed in bold type.

Table 5. Correlation energy (E_h) for He and He₂ dimer at the equilibrium distance (2.97 Å).

Limit	He Atom		He ₂ Dimer	
	0.0420444		0.0841528	
BS	Dunning	Sigma	Dunning	Sigma
DZ	-0.0324343	-0.0358932	-0.0648756	-0.0717958
TZ	-0.0390788	-0.0400838	-0.0781781	-0.0801879
QZ	-0.0408967	-0.0411635	-0.0818256	-0.0823559
5Z	-0.0415271	-0.0415768	-0.0830947	-0.0831955
CBS ^a	-0.0423430	-0.0420352	-0.0847403	-0.0841253
aDZ	-0.0338438	-0.0383018	-0.0677448	-0.0766221
aTZ	-0.0394145	-0.0407769	-0.0788879	-0.0815831
aQZ	-0.0410116	-0.0414583	-0.0820829	-0.0829540
a5Z	-0.0415736	-0.0417231	-0.0832083	-0.0834887
CBS ^a	-0.0423532	-0.0420496	-0.0847687	-0.0841510
daDZ	-0.0338850	-0.0386776	-0.0678307	-0.0773832
daTZ	-0.0394242	-0.0409722	-0.0789168	-0.0819873
daQZ	-0.0410143	-0.0415557	-0.0820937	-0.0831597
da5Z	-0.0415748	-0.0417615	-0.0832142	-0.0835811
CBS ^a	-0.0423531	-0.0419952	-0.0847654	-0.0840554
taDZ	-0.0338904	-0.0385857	-0.0678420	-0.0776054
taTZ	-0.0394260	-0.0410454	-0.0789302	-0.0821388
taQZ	-0.0410147	-0.0416071	-0.0820963	-0.0832671
ta5Z	-0.0415750	-0.0418099	-0.0832159	-0.0836765
CBS ^a	-0.0423526	-0.0420285	-0.0847545	-0.0841117

^a Extrapolation to complete basis set with $E_{XZ} = E_{CBS} + \alpha/X^\beta$.

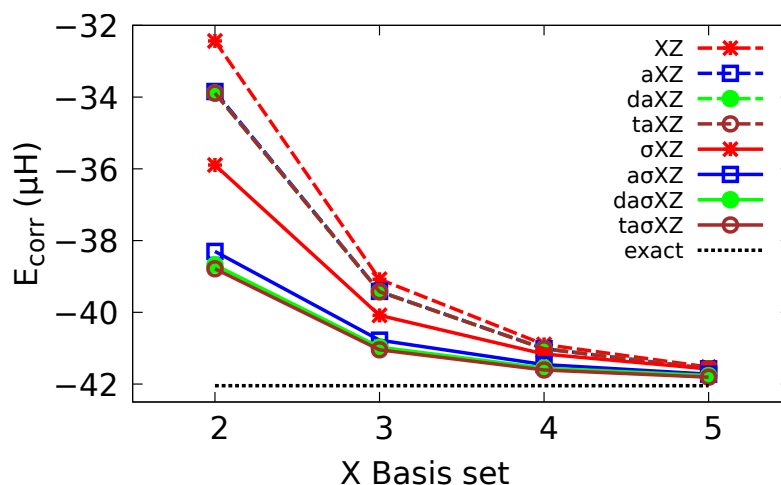


Figure 5. He: correlation energy.

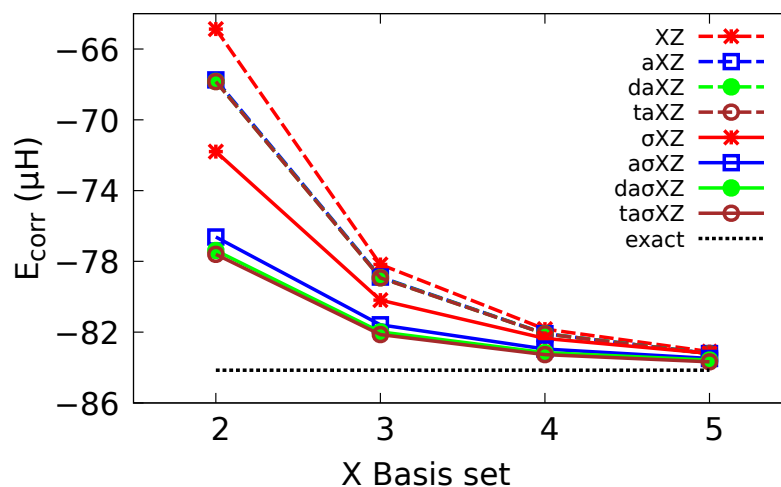


Figure 6. He₂: correlation energy.

The better performance of σ BS over Dunning BS is evident. CBS extrapolation yields a gain of at least two figures in the former, while scarcely one figure is gained in the latter. The case of σaXZ is specially noticeable, as three figures are gained in the CBS extrapolation both in the atom and in the diatom. Furthermore, CBS extrapolation in Dunning BS lies below the exact value, whereas it converges to the right value in the case of σ BS. This behavior is clearly visible in Figures 7 and 8.

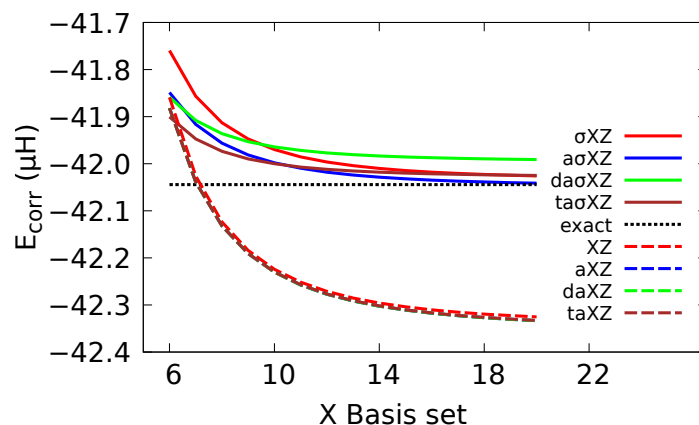


Figure 7. He: CBS extrapolation of correlation energy.

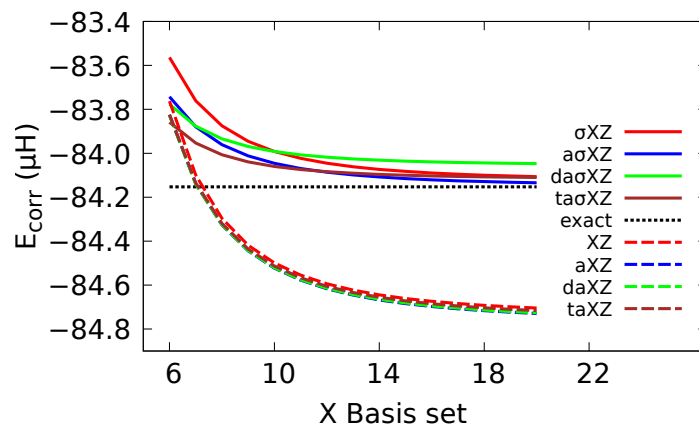


Figure 8. He₂: CBS extrapolation of correlation energy.

5. Conclusions

A new scheme for developing basis sets is reported and applied to helium atom and dimer. The σ BS thus developed are configured by combining the same set of exponentials with different angular functions and saturating the corresponding one-electron spaces. The new family ranges from DZ to 5Z, with the same composition as Dunning BS, and also includes, simply, double and triple augmented versions. Energy values for helium atom and diatom computed with the σ BS are lower than those obtained with their partners in Dunning BS, and similar to ANO BS, both at HF and FCI levels.

The analysis of the energy of He₂ reveals the presence of a minimum in the curve at the HF level in the case of Dunning BS that does not appear with σ or ANO BS. In the case of FCI, all calculations yield a well whose depth tends to the reference value as the BS quality improves. Augmented σ BS display a good convergence which, in the case of multiple augmented BS, is even more regular than in the corresponding Dunning BS.

CBS extrapolation of the correlation energy of He₂ at BED has also been examined, proving that the results with σ BS are clearly superior to those attained with Dunning BS. Especially remarkable is the result with the $a\sigma XZ$, which shows an agreement of five decimal figures with the best available result. Furthermore, it can be noticed that the CBS extrapolation with Dunning BS falls below the exact value, while the sigma converges to the right value.

Supplementary Materials: The σ BS used in this work can be found online in MOLPRO format at <https://www.mdpi.com/article/10.3390/computation10050065/s1>.

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Abbreviations

The following abbreviations are used in this manuscript:

ANO	Atomic Natural Orbitals
aANO	Augmented ANO
aXZ	aug-cc-pVXZ
$a\sigma$ BS	Augmented Sigma Basis Set
BED	Best Available Equilibrium Distance of He ₂
BS	Basis set(s)
BSSE	Basis Set Superposition Error
CBS	Complete Basis Set
CC	Coupled Clusters
CCSD(T)	Coupled Clusters Singles Doubles (Triples)
CISD	Configuration Interactions Singles and Doubles
CP	Cunterpoise
daXZ	aug-aug-cc-pVXZ
$da\sigma$ BS	Double Augmented Sigma Basis Set
FCI	Full Configuration Interaction
HF	Hartree-Fock
MP	Möller-Plesset
MR-ACPF	Multi-Reference Averaged Coupled-Pair Functional
MRCI	Multi-Reference Configuration Interaction

SAPT	Symmetry-Adapted Intermolecular Perturbation Theory
σ BS	Sigma Basis Set
taXZ	aug-aug-aug-cc-pVXZ
ta σ BS	Triple Augmented Sigma Basis Set
vdW	van der Waals
XZ	cc-pVXZ

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