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ORIGINAL PAPER

On polarization functions for Gaussian basis sets

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Abstract
In this work, we introduce a technique to choose polarization functions directly from the primitive set of Gaussian exponent without the necessity to optimize or even reoptimized them. For this purpose, initially, we employed Gaussian basis sets generated by using the Polynomial Generator Coordinate Hartree-Fock (PGCHF) method, and later we extended our technique to the cc-pVQZ and pc-3 Gaussian basis sets in order to show how our technique works and how good it is. Using the new polarized basis sets, from our technique, total electronic energies, equilibrium geometries, and vibrational frequencies were calculated for a set of molecules containing atoms from H($Z = 1$) to Ba($Z = 56$). The technique presented here can be used with any Gaussian basis set flexible (large) enough and also can be used to choose Gaussian basis set exponents from one basis set to another as polarization functions.

Keywords Gaussian basis sets · Polarization functions · Polarization exponents · GBS

Introduction

The Generator Coordinate Hartree-Fock (GCHF) method [1] was introduced in 1986, and since then, it was basically used in the generation of universal Slater and Gaussian basis sets [2, 3].

The main interest in the generation of universal basis sets, that time, laid on the idea that one could transfer the molecular integrals from one molecular calculation to another when using universal basis sets [4]. In fact, the idea of using universal basis set never became practical, and afterwards, it was completely abandoned. The main challenge of the GCHF method is how the integral equation of the method is discretized. Actually, this equation was always discretized through the Integral Discretization [5] (ID) instead of the Variational Discretization (VD) that is more commonly used. Later on, in 2003, Barbosa and da Silva [6] modified the way of discretizing the integral equation of the GCHF method with the aim to generate more flexible nonrelativistic and relativistic Gaussian basis sets [7–10] to be used in molecular calculations.

There are three steps to be followed in order to attain a Gaussian basis set ready to be used in molecular calculation: (a) the construction of the primitive set of exponents, (b) the contraction of the primitive set, and (c) the addition of polarization functions.

In the generation of an atomic basis set, one of the most import requirements is the size of it, as the generated primitive set is not adequate to be used in molecular calculation since the description of the molecular electron density distribution is generally poor. Thus, the addition of higher angular moment functions (exponents) in the body of the primitive set of exponents improves the performance of a basis set as a whole [11]. Generally, the atomic polarization exponents are found by optimizing the total energy for a small set of molecules, for example, employing the HF and DFT levels of theory [11–14].

Actually, the quality of a basis set is generally related to the polarization degree of the primitive set and how it can approach the basis set limit. Here, we would like to mention two families of basis sets that provide a systematic hierarchy

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for approaching the basis set limit; they are the correlation consistent Gaussian basis sets by Dunning [15–20], known as cc-pVXZ (with $X = D, T, Q, 5, \ldots$), in which the polarization functions were optimized in an electronic correlated environment and the polarization consistent Gaussian basis sets by Jensen, known as pc-*n* [11, 13, 14], in which the polarization functions were chosen through an energetical analysis for a set of selected molecules. In both cases, the polarization exponents were explicitly optimized, however, while the polarization exponents in the cc-pVXZ basis sets decreases in an arithmetic form and in the pc-n basis sets the polarization exponents decrease geometrically [11].In this work, we will show that when the Polynomial Generator Coordinate Hartree-Fock (PGCHF) method [6] is used to generate primitive sets of Gaussian exponents, we are always able to add polarization functions to the basis set just taking them directly from the body of the primitive set of exponents, without the need of optimizing them by explicit optimization (one does not need to optimize the polarization exponents individually).

A similar methodology that can be compared with our is used in the polarization of the property-oriented basis sets by Sadlej [21–24], which proved to be quite successful in calculation of molecular dipole moments and polarizability. In this work, we also show that our methodology can be extended to other Gaussian basis sets.

Computational details

Here, we have used the PGCHF method [6] to generate primitive Gaussian basis sets for some atoms from H($Z = 1$) to Ba ($Z = 56$). The size of the primitive basis sets has been chosen to be able to reproduce the HF energy with the precision of mH or less when compared with the atomic numerical HF energies from Ref. [25]. Afterwards, the primitive sets of Gaussian exponents were contracted through the general contraction scheme [26].

The main reason why we generated PGC basis sets was to increase the number of Gaussian basis sets to be tested with our technique.

The choice of polarization exponents

In order to show when one is handling with flexible (large) Gaussian basis sets (as those generated with the PGCHF method) [6], it is always possible to choose the polarization functions direct from the primitive set of Gaussian exponents; we will present a set of examples with the aim to show how one can do it. For this purpose, we have performed a study using a sample of several combinations of Gaussian exponents taken directly from PGC primitive basis sets that we have generated for the atoms nitrogen (N), oxygen (O), and fluorine (F). Initially, we have taken the outer exponents from the set of primitive functions related to the *s* symmetry and created six combinations with those exponents with the aim to obtain a set of $2d1f$ polarization functions to be added in the contracted PGC basis sets. To illustrate how we did the different combinations, polarization sets with $2d1f$ functions for N, O, and F atoms are shown in Table 1. The same procedure was performed using primitive functions taken from the *p* symmetry as shown in Table 2.

Table 1 Combination of polarization exponents from the *s* symmetry exponents for atoms of the first row of the periodic table

Atom	Symmetry	s_1	s_2	s_3	s_4	s_5	s_6
N	1*d*	2.2913	2.2913	2.2913	5.4815	5.4815	5.4815
	2*d*	0.9378	0.9378	0.9378	2.2913	2.2913	2.2913
	1*f*	0.3758	0.9378	2.2913	0.9378	2.2913	5.4815
O	1*d*	2.3843	2.3843	2.3843	5.6545	5.6545	5.6545
	2*d*	0.9581	0.9581	0.9581	2.3843	2.3843	2.3843
	1*f*	0.3542	0.9581	2.3843	0.9581	2.3843	5.6545
F	1*d*	4.1243	4.1243	4.1243	9.7741	9.7741	9.7741
	2*d*	1.6804	1.6804	1.6804	4.1243	4.1243	4.1243
	1*f*	0.6611	1.6804	4.1243	1.6804	4.1243	9.7741

The combinations displayed in Tables 1 and 2 were added to the contracted PGC basis sets for N, O, and F. The polarized basis sets were then tested in the minimization of the total energy for the homonuclear diatomic molecules (N_2, O_2, and F_2). Several theory levels of calculation (B3LYP, MP2, CISD, and CCSD) were used with the purpose of considering both charge distribution and correlation electronic effects. The results are displayed in Table 3 and Table 4, along with other molecular property calculations by employing the Gaussians09 program [27].

Additionally, we have also used the same strategy for the atoms of the second row and the 3*d* series of the transition

Table 2 Combination of polarization exponents from the *p* symmetry exponents for atoms of the first row of the periodic table

Atom	Symmetry	p_1	p_2	p_3	p_4	p_5	p_6
N	1*d*	1.5968	1.5968	1.5968	4.3425	4.3425	4.3425
	2*d*	0.6152	0.2483	0.6152	0.6152	0.6152	0.6152
	1*f*	0.2483	0.2483	1.5968	1.5968	0.6152	4.3425
O	1*d*	2.0621	2.0621	2.0621	5.1397	5.1397	5.1397
	2*d*	0.8605	0.8605	0.8605	0.8605	0.8605	0.8605
	1*f*	0.3513	0.8605	2.0621	2.0621	0.8605	5.1397
F	1*d*	2.7170	2.7170	2.7170	7.4346	7.4346	7.4346
	2*d*	1.0229	1.0229	1.0229	1.0229	1.0229	1.0229
	1*f*	0.3967	1.0229	2.7170	2.7170	1.0229	7.4346

Table 3 Total energies at different levels of theory obtained by using the combinations of polarization exponents from the *s* symmetry exponents of Table 1 for atoms of the first row of the periodic table

	s_1	s_2	s_3	s_4	s_5	s_6
N_2						
B3LYP	− 109.5745	− 109.5759	− 109.5766	− 109.5559	− 109.5558	− 109.5535
MP2	− 109.6484	− 109.3646	− 109.3604	− 109.2973	− 109.2918	− 109.2750
CISD	− 109.3461	− 109.3353	− 109.3317	− 109.2792	− 109.2621	− 109.2461
CCSD	− 109.2656	− 109.3605	− 109.3560	− 109.2823	− 109.2893	− 109.3453
O_2						
B3LYP	− 150.3315	− 150.3339	− 150.3337	− 150.3157	− 150.3143	− 150.3114
MP2	− 150.0522	− 150.1234	− 150.1226	− 150.0045	− 150.0035	− 149.9812
CISD	− 150.0126	− 150.0951	− 150.0942	− 149.9682	− 149.9664	− 149.9443
CCSD	− 149.9723	− 150.1244	− 150.1226	− 149.9955	− 149.9980	− 150.0471
F_2						
B3LYP	− 199.6041	− 199.6052	− 199.6029	− 199.5954	− 199.5930	− 199.5924
MP2	− 199.2608	− 199.3079	− 199.2822	− 199.1829	− 199.1775	− 199.1579
CISD	− 199.2309	− 199.2526	− 199.2369	− 199.1576	− 199.1505	− 199.1321
CCSD	− 199.2640	− 199.2866	− 199.2696	− 199.1850	− 199.1778	− 199.1583

metals. An energetical analysis was used for defining a rule to choose the polarization functions to be added in the PGC basis sets.

The exponents for the polarization functions added to the basis sets were determined by finding the minimum energy of the diatomic molecules as a function of the exponents.

Results and discussion

We have performed molecular calculations carried out with diatomic homonuclear molecules using PGC-contracted Gaussian basis sets added with polarization functions reported in Tables 1 and 2, and the results are shown in Tables 3 and 4, respectively. A deep analysis of the total energy values obtained shows how the magnitude of the exponents "pinched" from the primitive set interferes in the total energy results when we combine them in different ways. The poorest (highest) energy values (E_h) were obtained when the magnitude of the second *d* polarization function is higher than the first *f* (s_1 and p_1 combinations) and also for those combinations with very different exponents (s_4, s_5, s_6, p_4, p_5, and p_6 combinations) which provide the highest values for the total energy.

Although the combinations with the same polarization functions for the second *d* and first *f* do not present good

Table 4 Total energies at different levels of theory obtained by using the combinations of polarization exponents from the *p* symmetry exponents of Table 2 for atoms of the first row of the periodic table

	p_1	p_2	p_3	p_4	p_5	p_6
N_2						
B3LYP	− 109.5759	− 109.5762	− 109.5781	− 109.5734	− 109.5695	− 109.5721
MP2	− 109.3495	− 109.3628	− 109.3721	− 109.3510	− 109.3315	− 109.3462
CISD	− 108.9898	− 109.3340	− 109.3428	− 108.9861	− 108.9811	− 108.9841
CCSD	− 109.3404	− 109.3596	− 109.3686	− 109.3473	− 109.3272	− 109.3429
O_2						
B3LYP	− 150.3320	− 150.3953	− 150.3343	− 150.3336	150.3311	150.3340
MP2	− 150.0528	− 150.0753	− 150.0797	− 150.0688	− 150.0469	− 150.0682
CISD	− 150.0130	− 150.0937	− 150.0981	− 150.0276	− 150.0055	− 150.0265
CCSD	− 150.0477	− 150.1232	− 150.1260	− 150.0629	− 150.0393	− 150.0625
F_2						
B3LYP	− 199.6069	− 199.6089	− 199.6079	− 199.6078	− 199.6064	− 199.6088
MP2	− 199.2676	− 199.2940	− 199.3003	− 199.2751	− 199.2501	− 199.2740
CISD	− 199.3282	− 199.2613	− 199.2672	− 199.3282	− 199.3282	− 199.3282
CCSD	− 199.2703	− 199.2997	− 199.3034	− 199.2768	− 199.2497	− 199.2761

Table 5 Molecular properties for the combinations s_2, s_3, p_2, and p_3 at different levels of theory

		s_2			s_3			p_2			p_3		
		E	R_e	w_e	E	R_e	w_e	E	R_e	w_e	E	R_e	w_e
N_2	B3LYP	− 109.575856	1.09	2447	− 109.576620	1.089	2454	− 109.576029	1.09	2440	− 109.578120	1.09	2450
	MP2	− 109.364602	1.11	2200	− 109.360366	1.105	2240	− 109.362650	1.11	2172	− 109.372069	1.11	2221
	CISD	− 109.335271	1.08	2516	− 109.331732	1.082	2545	− 109.333867	1.89	2493	− 109.342853	1.08	2530
	CCSD	− 109.360472	1.09	2432	− 109.356016	1.088	2464	− 109.359646	1.10	2405	− 109.368609	1.09	2446
	Exp [28]		*1.10*	*2359*									
O_2	B3LYP	− 150.333986	1.20	1622	− 150.333687	1.203	1625	− 150.395313	1.02	1633	− 150.334317	1.203	1623
	MP2	− 150.123457	1.22	1467	− 150.122645	1.214	1491	− 150.122068	1.22	1461	− 150.125587	1.215	1493
	CISD	− 150.095106	1.19	1754	− 150.094239	1.178	1770	− 150.093742	1.19	1750	− 150.098106		
	CCSD	− 150.124419	1.20	1670	− 150.122590	1.193	1688	− 150.123158	1.20	1666	− 150.126042	1.194	1690
	Exp [28]		*1.21*	*1580*									
F_2	B3LYP	− 199.605208	1.40	1030	− 199.602900	1.40	1019	− 199.608872	1.40	1043	− 199.607950	1.39	1041
	MP2	− 199.307865	1.39	999	− 199.282210	1.40	966	− 199.294053	1.40	1007	− 199.300259	1.39	1002
	CISD	− 199.252563	1.37	1103	− 199.236915	1.37	1075	− 199.261319	1.37	1107	− 199.267169	1.37	1104
	CCSD	− 199.286605	1.39	998	− 199.269582	1.39	965	− 199.299674	1.39	1008	− 199.303451	1.39	1003
	Exp [29]		*1.41*	*917*									

E_h (Hartree), R_e (Å), ω_e (cm^{-1})

The experimental values are presented in italic

Table 6 Polarization functions from the PGC primitive exponents for the N, Cl, and Fe atoms

N (2*d*1*f*)	**Cl (3*d*2*f*)**	**Fe (3*f*2*g*1*h*)**
p 4 1.0	p 5 1.0	d 7 1.0
115.55547	101.9464	579.820368
36.941014	45.26703	185.411563
12.373476	21.60780	69.4832194
4.3424940	10.87366	29.6315687
p 1 1.0	5.657112	13.9634512
1.596803	p 1 1.0	7.06034842
p 1 1.0	2.983912	3.71951706
0.6152166	p 1 1.0	d 1 1.0
p 1 1.0	1.564831	1.9824665
0.2483529	**p 1 1.0**	d 1 1.0
p 1 1.0	**0.8001226**	**1.03804424**
0.1050449	**p 1 1.0**	d 1 1.0
d 1 1.0	0.3911754	0.51849956
1.596803	**p 1 1.0**	d 1 1.0
d 1 1.0	0.1793207	0.23990277
0.6152166	p 1 1.0	d 1 1.0
f 1 1.0	0.0755876	0.0984086
1.596803	**d 1 1.0**	d 1 1.0
	0.8001226	0.03629103
	d 1 1.0	**f 1 1.0**
	0.3911754	**1.03804424**
	d 1 1.0	**f 1 1.0**
	0.1793207	0.51849956
	f 1 1.0	**f 1 1.0**
	0.8001226	0.23990277
	f 1 1.0	**g 1 1.0**
	0.3911754	**1.03804424**
		g 1 1.0
		0.51849956
		h 1 1.0
		1.03804424

The orbital symmetry in bold letter stands for the polarization exponent, and the color of the exponent is just to indicate where from we have chosen the polarization exponent

results, if the polarization functions are very different (p_5 combination) or even when the exponents are near (s_2 and p_2 combinations), slight variations are observed in the energy results when compared with those obtained with the p_3 combination. For the case of the p_3 combination, the first f polarization function is always equal to the first d, and this is the best combination. We also tested combinations using more diffuse exponents (valence region) for the p symmetry, but the results were not so good as the p_3 combination.

On the other hand, the best (lowest) E_h were obtained with the combinations s_2, s_3, p_2, and p_3 for all of the levels of theory tested, and only the molecular results for these combinations are presented in Table 5. Once more, the p_3 combination provides, in general, the best results. So, the p_3 combination is the best one to "pinch" (choose) polarization functions from a primitive set.

In fact, after comparing the s_2, s_3, p_2, and p_3 combinations, we came out with a rule to choose polarization functions from a primitive basis set generated by the PGC method, that is, for all the atoms of the periodic table, the polarization exponents are always chosen from the highest valence symmetry.

Our rule can be easily seen from Table 6, where the coefficients and exponents of the valence symmetry for the atoms N, Cl, and Fe are shown, and we have highlighted the primitive exponents used as polarization exponents in each case.

More specifically, for a polarization set (2d1f) for the N atom, we need two exponents from the p symmetry. An

analysis of the exponents for this symmetry (see Table 6) shows that the most diffuse exponent is 0.1050449. Following our rule, this exponent should not be considered, and the more external ones 1.596803 and 0.6152166 will be the polarization functions 2*d* and 1*d*, respectively, and the exponent for the polarization function 1f will be then 1.596803 (equal to the exponent of the 2*d* function).

For the (3*f*2*g*1*h*) polarization, the 3*f* polarization exponents are always taken from the *d* symmetry. For the *d* exponents of the Fe atom (Table 6), we can see that there are two exponents with values lesser than 0.1 (0.0984086 and 0.03629103) which cannot be considered according to our rule. The next outer exponents are 1.03804424, 0.51849956, and 0.23990277, and they will be the exponents for the polarization functions 3*f*, 2*f*, and 1 *f*. The exponents for the 2*g* and 1*g* functions will be 1.03804424 and 0.51849956, respectively (equal to the two first *f* exponents), and the 1*h* will be 1.03804424 (equal to the 2*g*) and so on.

With the aim to show that our rule is efficient to be used in molecular calculations, we will show other molecular tests for atoms of the second row and the 3*d* series of the transition metals. Besides, we have applied also our rule to the cc-pVQZ and pc-3 basis sets and performed calculations for a set of selected molecules.

Molecular properties

In order to assess the accuracy of the polarized PGC basis sets, by choosing the polarization exponents directly from the PGC primitive basis sets, we performed calculations of some molecular properties, such as R_e and ω_e, employing the DFT/B3LYP for a set of 24 molecules.

We have used the PGC(5Z)2*d*1*f* basis sets for the atoms from B through F, PGC(6Z)3*d*2*f* for the atoms from Al through Cl, PGC(7Z)3*f*2*g*1*h* for the 3d transition metal

Table 7 Total electronic energies DFT-B3LYP calculated with basis sets with original polarization exponents and with polarization exponents chosen from its primitive exponents of the valence symmetry

Molecules	DFT-B3LYP				
	cc-pVQZ	cc-pVQZ/Pin*	pc-3	pc-3/Pin*	PGC/Pin
CO	− 113.36676	− 113.36544	− 113.36991	− 113.36932	− 113.36753
NO	− 129.95141	− 129.95081	− 129.95545	− 129.95518	− 129.95283
Si_2	− 578.87435	− 578.87467	− 578.88241	− 578.87467	− 578.87901
P_2	− 682.76082	− 682.76119	− 682.77046	− 682.76794	− 682.76794
$AlCl_3$	− 1623.39671	− 1623.39672	− 1623.41312	− 1623.40908	− 1623.40978
FeO	− 1338.98901	− 1338.98913	− 1338.98934	− 1338.98913	− 1338.98523
$GaCl_3$	− 3305.79324	− 3305.82716	− 3305.85272	− 3305.85152	− 3305.77506
AsN	− 2290.57652	− 2290.68268	− 2290.69598	− 2290.68983	− 2290.77527
TiCl	− 1309.71903	− 1309.70953	− 1309.71561	− 1309.71489	− 1309.71143
VCl	− 1404.27998	− 1404.27732	− 1404.28494	− 1404.28451	− 1404.28236
CrCl	− 1504.79411	− 1504.79421	− 1504.80245	− 1504.80132	− 1504.79805
MnCl	− 1611.34003	− 1611.33832	− 1611.34561	− 1611.34560	− 1611.34344
FeCl	− 1723.08162	− 1724.08134	− 1724.04115	− 1724.04055	− 1724.03114
CoCl	− 1843.09912	− 1843.11302	− 1843.12086	− 1843.12017	− 1843.11693
NiCl	− 1968.68102	− 1968.67721	− 1968.68452	− 1968.68378	− 1968.67999
CuCl	− 2100.89861	− 2100.89762	− 2100.90492	− 2100.90470	− 2100.90178
ScH	− 761.23526	− 761.23529	− 761.24000	− 761.23997	− 761.23885
TiH	− 849.96855	− 849.96852	− 849.97287	− 849.97230	− 849.97067
CrH	− 1045.06569	− 1045.06570	− 1045.06962	− 1045.06969	− 1045.06734
MnH	− 1151.59874	− 1151.59875	− 1151.60197	− 1151.60199	− 1151.60040
FeH	− 1264.30416	− 1264.30388	− 1264.30768	− 1264.30720	− 1264.29794
CoH	− 1383.39674	− 1383.39648	− 1383.40019	− 1383.39998	− 1383.39754
NiH	− 1508.96622	− 1508.96603	− 1508.96941	− 1508.96909	− 1508.96621
CuH	− 1641.19230	− 1641.19244	− 1641.19561	− 1641.19569	− 1641.19350

Pin* = Basis sets with polarization functions "pinched" from the primitive set of Gaussian exponents

All total energy values are given in a.u

atoms, and PGC(5Z)2*d*1*f* for the atoms from Ga through Ba.

In order to show as our technique can be applied to other Gaussian basis sets, we have taken the cc-pVQZ basis sets of Dunning [17–20] without polarization, that is, we have removed their original polarization exponents and added new polarization exponents applying now our technique. The polarization degree used is the same with that in the original basis sets (3*f*2*g*1*h*). Afterwards, we have tested the performance of these basis sets in molecular calculations, and the results were compared with those obtained with the original cc-pVQZ basis sets.

We have also applied our technique to the pc-3 basis set of Jensen in the same way we did with the cc-pVQZ basis sets (see Tables 7 and 8).

In Tables 7 and 8, we can see how good is the performance of our technique using PGC, cc-pVQZ [18–20], and pc-*3* [11] Gaussian basis sets. In all cases, we can notice that for all polarized basis sets, using our technique, the results for total electronic energies, equilibrium geometries (R_e), and vibrational frequencies (ω_e) are very close.

In fact, our technique can always be used with any Gaussian basis set flexible (large) enough as, for example, the Dunning's [17–20] and Jensen's basis sets [11–14].

Table 8 Molecular properties DFT-B3LYP calculated with basis sets with original polarization exponents and with polarization exponents chosen from its primitive exponents of the valence symmetry

Molecules	*Re*/(DFT/B3LYP)					ω_e/(DFT/B3LYP)				
	cc-pVQZ	cc-pVQZ/Pin*	pc-3	pc-3/Pin*	PGC/Pin	cc-pVQZ	cc-pVQZ/Pin*	pc-3	pc-3/Pin*	PGC/Pin*
CO	1.2370	1.1250	1.1236	1.1243	1.1202	2213.9357	2216.8273	2213.3633	2211.6010	2216.12
NO	1.1452	1.1457	1.1440	1.1447	1.1432	1975.3031	1972.1945	1973.9001	1972.8517	1976.25
Si_2	2.0586	2.0569	2.0574	2.0619	1.9071	600.0850	601.0785	600.1440	598.6053	599.4815
P_2	1.8904	1.8894	1.8878	1.8899	1.8903	807.5779	808.0659	809.5450	807.9715	806.4216
$AlCl_3$	2.0798	2.0774	2.0765	2.0808	2.0810	146.1732 202.7128 379.1536 611.1372	146.5571 202.5856 379.8353 611.7309	146.3419 202.1354 379.4616 611.4739	145.8152 202.0151 378.5053 610.2439	145.9436 202.2044 378.4952 610.2436
FeO	1.6110	1.6113	1.6111	161,112	1.6048	904.62	904.9286	904.8517	904.8252	906.2030
$GaCl_3$	2.1274	2.1277	2.1272	2.129	2.1272	125.9932 136.3712 365.7723 452.3358	124.4490 136.7270 366.0827 451.8683	124.3916 136.9813 366.7766 452.6227	124.2432 137.2508 365.6026 451.4163	125.04236 137.2123 366.8636 453.2832
AsN	1.5951	1.6092	1.6097	1.6099	1.6087	1173.161	1141.8675	1139.6307	1139.6660	1140.813
TiCl	2.2442	2.3043	2.3032	2.3056	2.3071	406.4836	378.7878	378.8332	378.0132	377.9718
VCl	2.2269	2.2456	2.24316	2.2467	2.2466	392.4324	391.9569	392.4346	390.6581	391.7144
CrCl	2.2175	2.2171	2.2151	2.2182	2.2188	382.0072	381.7527	382.9539	381.5944	381.4162
MnCl	2.2541	2.2539	2.2531	2.2556	2.2559	366.8860	366.5530	366.7527	365.9665	366.2034
FeCl	2.1949	2.1946	2.1936	2.1959	2.1912	384.8777	385.7323	386.3379	385.3562	390.3315
CoCl	2.1092	2.1140	2.1111	2.1143	2.1152	390.1681	391.8788	393.0897	391.8445	391.5585
NiCl	2.0902	2.0921	2.0897	2.0924	2.0930	398.4848	406.9986	407.7040	406.7129	407.0712
CuCl	2.0880	2.0870	2.0853	2.0881	2.0888	395.1770	395.0615	395.5761	394.1571	394.1700
ScH	1.7518	1.7514	1.7522	1.7523	1.7551	1616.3559	1617.2931	1615.1418	1615.2461	1615.2461
TiH	1.7495	1.7492	1.7492	1.7490	1.7489	1546.0225	1547.0073	1547.0164	1546.7859	1546.7859
CrH	1.6618	1.6620	1.6617	1.6619	1.6619	1632.9951	1632.6677	1633.6788	1632.8742	1633.3326
MnH	1.7333	1.7335	1.7342	1.7343	1.7366	1515.0542	1514.8087	1512.4028	1512.285	1517.7379
FeH	1.5550	1.5551	1.5545	1.5541	1.5516	1759.7102	1760.2727	1758.7936	1760.1729	1759.7186
CoH	1.5378	1.5382	1.5375	1.5372	1.5373	1767.6472	1768.0706	1766.2369	1766.5869	1767.9025
NiH	1.5163	1.5167	1.5161	1.5158	1.5156	1794.4606	1795.5335	1793.0429	1793.2568	1795.7409
CuH	1.4816	1.4818	1.4813	1.4813	1.4813	1872.8322	1874.0262	1872.6602	1872.8668	1873.0609

Pin* = Basis sets with polarization functions "pinched" from the primitive set of Gaussian exponents

R_e (Å), ω_e (cm^{-1})

Also, it is interesting to mention that the technique presented here was already used in a set of papers that one of us published recently when generating relativistic Gaussian basis sets [8–10].

Additionally, this technique can be used to choose Gaussian exponents from one basis set to another (as a "grafting") in order to polarize it without the necessity of any exponent optimization or reoptimization.

Conclusions

In this paper, we present a technique that can be used to choose Gaussian polarization functions (exponents) directly from a primitive basis set. This technique is really valid for those that work with the Generator Coordinate Hartree-Fock method in the development of Gaussian basis set to be used in quantum chemistry atomic and molecular calculations.

The technique presented here can be also employed with any Gaussian basis set that is flexible enough, i.e., those that the primitive set of exponents is large enough, as the Gaussian basis sets of Dunning cc-pVQZ [18–20] and cc-pV5Z [17] and other ones [11–14].

Another important thing to mention is that our technique can be also used to choose Gaussian exponents from one basis set and transfer them to another one as polarization functions, as a "grafting."

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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