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Generation, contraction, and polarisation of Gaussian basis sets for atomic and molecular calculations using the generator coordinate method with polynomial discretisation: atoms from Na through Cl†

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The polynomial Generator Coordinate Hartree–Fock Gaussian basis sets, pGCHF, for the atoms Na, Mg, Al, Si, P, S, and Cl were generated using the generator coordinate method based on polynomial integral expansion to discretise the Griffin–Wheeler–Hartree–Fock equations. The pGCHF basis sets were contracted with the CONTRACT program based on the Davidson contraction model through which a set of 9s8p functions for the atoms Na through Cl were obtained. Polarisation exponents generated using the POLARIZATION program were added to the contracted pGCHF Gaussian basis sets. Molecular calculations at the DFT level of theory showed that the pGCHF basis sets can be used to calculate the atomisation energy with accuracy comparable to the well-established pcseg-3, def2-QZVP, and Sapporo-QZP basis sets; also, the complete basis set (CBS) limit estimate was obtained with the pcseg-3/pcseg-4 basis sets.

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Introduction

One of the approximations required by *ab initio* methods to solve the Schrödinger equation is the introduction of basis sets. Using a set of known functions to expand the molecular orbitals plays an important role in the investigation of electronic structure systems because the computational cost and overall accuracy of the results are directly related to the basis sets.^{1,2}

Ideal basis sets should be composed of an infinite number of functions, but this is impossible to achieve owing to computational limitations. Thus, the main aim to design basis sets is to find a set of functions that represents the unknown molecular orbital with as small computational cost as possible. In this context, Gaussian-type orbitals (GTOs),³

where N is the normalization function, $Y_{l,m}$ are the spherical harmonic functions, r is the nuclear distance, and α is the exponent providing the radial extent of the function, are preferred for molecular calculations because of, for example, the easiness in solving multicentre two-electron integrals, which results in a significant decrease in the computational cost.

The advantages of GTOs have encouraged many researchers to find the best set of α exponents to perform *ab initio* calculations. Some basis sets have become very popular in theoretical research, such as the Pople's basis sets ($k\text{-lmnG}$),^{4–8} the cc-pVXZ ($X = \text{D, T, Q, 5, and 6}$) basis sets developed by Dunning,^{9–14} ANO,^{15,16} Jensen's pcseg- n ($n = 0, 1, 2, 3, \text{ and } 4$) basis sets,^{17–19} Sapporo-nZP ($n = \text{D, T, Q}$)^{20,21} and def2-XZVP(P)^{22,23} (where $X = \text{S, T and Q}$ and the label P and PP represent the polarisation functions which the former is recommended in DFT and HF calculations and the later for post-HF calculations).¹ These basis sets were generated by either minimizing the energy as a function of the α exponents using an optimisation method^{24,25} (using a parameterised formula to generate the exponents^{26–28}) or choosing the GTO exponents and coefficients by fitting to Slater-type orbitals (STOs).²⁹

Mohallem *et al.*³⁰ proposed an alternative method to generate the α exponents called the generator coordinate Hartree–Fock (GCHF) method by using the Griffin–Hill–Wheeler³¹ version of the Hartree–Fock (HF) equations, which is a new way to obtain the GTOs and STOs³² of atoms. In this method the Griffin–Wheeler–HF (GWHF) equations are numerically integrated using

$$\chi_{\alpha,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{2n-2-l}e^{-\alpha r^2} \quad (1)$$

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a discretisation technique that preserves the integral character of the GCHF method, which is known as integral discretisation (ID).³³

Through ID, the GWHF equations are numerically integrated relabelling the generator coordinate (α) space for new coordinate space Ω :

$$\Omega = \frac{\ln \alpha}{A}, \quad A > 1 \quad (2)$$

where A is a numerically determined scaling factor and Ω is discretised for each w atomic orbital (e.g., $w = s, p, d, f$, and g) in an equally spaced numerical mesh:

$$\Omega_k^{(w)} = \frac{\ln \alpha_k^{(w)}}{A} = \Omega_{\min}^{(w)} + (k-1)\Delta\Omega^{(w)}, \quad k = 1, \dots, N \quad (3)$$

where $\Omega_{\min}^{(w)}$ and $\Delta\Omega^{(w)}$ are the initial point of the mesh and the increment used to obtain the subsequent points of the mesh, respectively.

This method has been used to generate Gaussian and Slater^{34–37} basis sets applying the concept of universal basis sets proposed by Silver and co-workers.^{38,39} However, the equally spaced mesh has serious consequences in the GCHF method because the accuracy of the generated basis sets is at the expense of large number of exponents irrespective of the atom size.³⁶

De Castro and co-workers^{40,41} proposed another discretization form to the GWHF equations, named as “Improved Generator Coordinate Hartree–Fock (IGCHF) method,” where the new coordinate space Ω is also discretised for each w atomic orbital, but in two or three independent arithmetic sequences. This procedure results in a non-equally spaced mesh, which reduces the size of the basis set generated using this approach.

Barbosa and da Silva⁴² subsequently proposed a new way to discretise the GWHF equations known as “polynomial ID (pID)”. In addition to providing more flexible optimisation of the $\alpha_k^{(w)}$ exponents, the basis sets generated by pID are smaller than those obtained by the original GCHF method without loss of accuracy.

Here, we report the pGCHF basis sets generated by the GCHF method and discretised by pID for second-row atoms ($Z = 11–17$). Generation, contraction, and the choice of the polarisation exponents are discussed, as well as the accuracy of the pGCHF basis sets through molecular calculations using the criteria of the Atomisation Energy, and computational cost. To evaluate the quality of the results, molecular calculations were performed using standard basis sets at DFT level of theory with M062X exchange–correlation functional. Furthermore, a complete basis set (CBS) limit estimate was obtained with the pcseg-3/pcseg-4 basis sets.

Theory

The GCHF method was developed by applying the generator coordinate (GC)³¹ to the independent particle model. The equation

$$\psi_i(1) = \int \phi_i(1, \alpha) f_i(\alpha) d\alpha, \quad i = 1, 2, \dots, n \quad (4)$$

is taken as the spatial one-electron function in the Hartree–Fock approximation, where n is the number of particles, $f_i(\alpha)$

are unknown weight functions, and $\phi_k(1, \alpha)$ are the generator functions (either GTOs or STOs), which depend on the generator coordinate α . The trial function is expressed as a Slater determinant as in eqn (4).

The energy functional

$$E[f_i(\alpha)] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (5)$$

is minimised with respect to the weight functions $f_k(\alpha)$, which leads to the GWHF equations

$$\int [F(\alpha, \beta) - \varepsilon_i S(\alpha, \beta)] f_i(\beta) d\beta = 0, \quad i = 1, 2, \dots, n. \quad (6)$$

The overlap ($S(\alpha, \beta)$) and Fock ($F(\alpha, \beta)$) kernels are

$$S(\alpha, \beta) = \langle \phi_i(1, \alpha) | \phi_i(1, \beta) \rangle \quad (7)$$

and

$$F(\alpha, \beta) = h(\alpha, \beta) + \sum_j^n [2J_j(\alpha, \beta) - K_j(\alpha, \beta)], \quad (8)$$

where the one electron kernel $h(\alpha, \beta)$ is defined as

$$h(\alpha, \beta) = \langle \phi_i(1, \alpha) | h(1) | \phi_i(1, \beta) \rangle \quad (9)$$

and

$$h(1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \quad (10)$$

The Coulomb ($J_i(\alpha, \beta)$) and exchange ($K_i(\alpha, \beta)$) integrals are expressed as

$$J_j(\alpha, \beta) = \int d\alpha' \int d\beta' f_j(\alpha') f_j(\beta') V(\alpha, \alpha'; \beta', \beta) \quad (11)$$

and

$$K_j(\alpha, \beta) = \int d\alpha' \int d\beta' f_j(\alpha') f_j(\beta') V(\alpha, \alpha'; \beta, \beta'), \quad (12)$$

where $V(\alpha, \alpha'; \beta', \beta)$ and $V(\alpha, \alpha'; \beta, \beta')$ are

$$V(\alpha, \alpha'; \beta', \beta) = \left\langle \phi_i(1, \alpha) \phi_j(2, \alpha') \left| \frac{1}{r_{12}} \right| \phi_j(2, \beta') \phi_i(1, \beta) \right\rangle \quad (13)$$

$$V(\alpha, \alpha'; \beta, \beta') = \left\langle \phi_i(1, \alpha) \phi_j(2, \alpha') \left| \frac{1}{r_{12}} \right| \phi_i(2, \beta) \phi_j(1, \beta') \right\rangle. \quad (14)$$

The GWHF equations are solved by an iterative procedure starting from an initial guess for $f_i(\alpha)$, resulting in the orbital energies ε_i and $f_i(\alpha)$. In each iteration, the integrals are solved by a discretisation technique.

In the original formulation proposed by Mohallem *et al.*,³⁰ the monoelectronic eigenvalue equations are discretised by ID, providing coefficients which oscillate between positive and negative values without any definite pattern of convergence.³³ The pID proposed by Barbosa and da Silva⁴² was applied in this work, and, as previously mentioned provided more flexible optimisation of the $\alpha_k^{(w)}$ exponents.

The coordinate space in eqn (2) ($\Omega_k^{(w)}$) is now discretised by a polynomial expansion:

$$\Omega_k^{(w)} = \frac{1}{A} \ln \alpha_k^{(w)} = \Omega_{\min}^{(w)} + \Delta\Omega_1^{(w)}(k-1) + \Delta\Omega_2^{(w)}(k-1)^2 + \Delta\Omega_3^{(w)}(k-1)^3 + \dots + \Delta\Omega_q^{(w)}(k-1)^q, \quad (15)$$

where w is the symmetry of the atomic orbital (e.g., s, p, d, f, and g), A is the scaling factor, q is the polynomial degree, and $\Omega_{\min}^{(w)}$ and $\Delta\Omega^{(w)}$ are defined as in eqn (3).

The $\Omega_k^{(w)}$ increment is discretised for each w atomic orbital, and all of the $\alpha_k^{(w)}$ GTO exponents are now determined by

$$\alpha_k^{(w)} = \exp A \{ \Omega_{\min}^{(w)} + \Delta\Omega_1^{(w)}(k-1) + \Delta\Omega_2^{(w)}(k-1)^2 + \Delta\Omega_3^{(w)}(k-1)^3 + \dots + \Delta\Omega_q^{(w)}(k-1)^q \}. \quad (16)$$

By a relabelling procedure, the discretisation interval is now $[-\infty, +\infty]$ and the weight function becomes narrow, and also susceptible to discretisation and the expansion coefficients converge to $f_i(\alpha)$ regardless of the orbital symmetry (Fig. 1 and 2). The right-hand side of eqn (15) guarantees that the exponents are generated through a numerical mesh $\Omega_k^{(w)}$, rather than equally spaced $\Delta\Omega_q^{(w)}$ intervals.

The relabelling procedure and the condition of a non-equally spaced mesh give some advantages to the GCHF

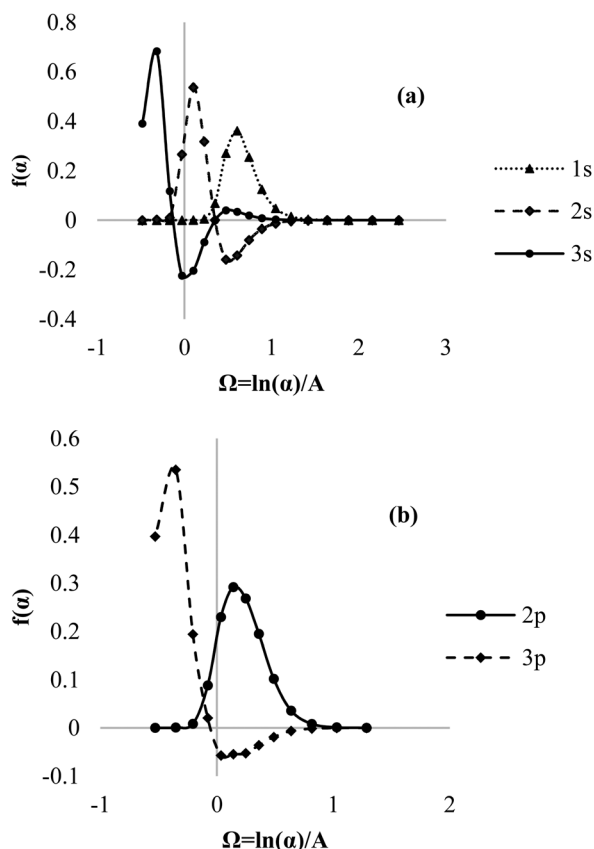


Fig. 1 Weight functions for (a) 1s, 2s, and 3s. (b) 2p and 3p states of the Al atom. In this work, $A = 6$ was used.

Si 0	
s 10 1.0	
7.143E+05	1.634E-05
1.423E+05	8.706E-05
3.336E+04	4.921E-04
9.059E+03	2.205E-03
2.804E+03	8.458E-03
9.745E+02	2.629E-02
3.741E+02	6.707E-02
1.562E+02	1.140E-01
6.985E+01	9.621E-02
3.291E+01	1.397E-01
s 7 1.0	
2.804E+03	-4.682E-06
9.745E+02	-1.602E-04
3.741E+02	-1.038E-03
1.562E+02	-6.333E-03
6.985E+01	-2.189E-02
3.291E+01	-5.256E-02
1.609E+01	-2.364E-02
s 5 1.0	
1.562E+02	-1.267E-05
6.985E+01	4.175E-05
3.291E+01	2.974E-04
1.609E+01	1.256E-03
8.035E+00	-1.841E-03
s 1 1.0	
4.03416200	1.0
s 1 1.0	
2.00456238	1.0
s 1 1.0	
0.97045371	1.0
s 1 1.0	
0.45059931	1.0
s 1 1.0	
0.19753231	1.0
s 1 1.0	
0.08048021	1.0

Fig. 2 pGCHF basis set for the Si atom (s functions).

method. For example, economy of computational time because the non-linear parameters are not optimised, good representation of various excited states by a single diagonalization, the possibility of segmentation of eqn (15) in different sets of $\Omega_k^{(w)}$ and $\Delta\Omega_q^{(w)}$ to describe different atomic regions (inner, intermediate, and outer shells),⁴² and generation of accurate basis sets that are smaller than those generated by the original GCHF method.^{33,42}

Results and discussion

Basis set generation

The basis sets in this work were generated in the same way as reported by Celeste *et al.*⁴³ The way in which the pGCHF basis sets were generated, contracted, and polarised in this work will be explained in detail next. All of the calculations were performed with a modified version of the ATOMSCF code.⁴⁴ The choice of the exponents was made through discretisation points according to pID principles and the simplex method⁴⁵ was incorporated in the program to optimise the parameter

Table 1 $\Omega_{\min}$ and the $\Delta\Omega_n^{(w)}$ increments for atoms Na–Cl

Atom	w	$\Omega_{\min}$	$\Delta\Omega_1$	$\Delta\Omega_2$	$\Delta\Omega_3$
Na	s	−0.60673	0.17317	−0.00733	0.00040
	p	−0.40557	0.13947	−0.00752	0.00065
Mg	s	−0.55004	0.16685	−0.00645	0.00037
	p	−0.24184	0.13682	−0.00792	0.00067
Al	s	−0.48252	0.17243	−0.00865	0.00051
	p	−0.52983	0.19247	−0.01756	0.00118
Si	s	−0.42970	0.16740	−0.00777	0.00044
	p	−0.49025	0.17151	−0.01187	0.00082
P	s	−0.42970	0.16740	−0.00777	0.00044
	p	−0.49025	0.17151	−0.01187	0.00082
S	s	−0.35033	0.15028	−0.00547	0.00034
	p	−0.42341	0.16979	−0.01200	0.00087
Cl	s	−0.34377	0.14966	−0.00571	0.00031
	p	−0.43041	0.15206	−0.00862	0.00054

Table 2 Ground state energies (in Hartree) for second-row atoms compared with the numerical values

Atoms	States	Energy (E_h) (this work)	HF numerical (E_h)	Sizes
Na	2S	−161.8588439	−161.8589116	18s13p
Mg	1S	−199.6145626	−199.6146363	
Al	2P	−241.8764874	−241.8767072	
Si	3P	−288.8541910	−288.8543624	
P	4S	−340.7186567	−340.7187808	20s15p
S	3P	−397.5047145	−397.5048958	
Cl	2P	−459.4820388	−459.4820721	

sets. The polynomial was truncated using three segments for each w orbital symmetry. In other words, a three-degree polynomial was used, resulting in a set containing the starting point, $\Omega_{\min}^{(w)}$, and the increments $\Delta\Omega_1^{(w)}$, $\Delta\Omega_2^{(w)}$, and $\Delta\Omega_3^{(w)}$ for each w. The starting point and increments were determined variationally from a trial set of $\Omega_{\min}^{(w)}$, $\Delta\Omega_1^{(w)}$, $\Delta\Omega_2^{(w)}$, and $\Delta\Omega_3^{(w)}$ using Dunning's cc-pV5Z basis exponents (the exponents adopted by Celeste *et al.*⁴⁴ were taken from Partridge basis sets^{46,47}).

The size of the basis set is related to the number of α primitive exponents generated for each w orbital symmetry. Increasing the number of α primitive exponents lowers the energy, and it approaches the energy numerical value. A set of 10s6p primitive functions were initially generated for each atom studied in this work, by which a set of optimised $\Omega_{\min}^{(w)}$, $\Delta\Omega_1^{(w)}$, $\Delta\Omega_2^{(w)}$, $\Delta\Omega_3^{(w)}$, α exponents, expansion coefficients and energy values were obtained. The previously generated mesh was reoptimised until there was no significant change in the energy value. The procedure was repeated while the number of α exponents was gradually increased.

The final optimised values of $\Omega_{\min}^{(w)}$ and the three increments $\Delta\Omega_1^{(w)}$, $\Delta\Omega_2^{(w)}$, and $\Delta\Omega_3^{(w)}$ for describing the inner, intermediate, and outer electrons of the second-row atoms are given in Table 1. The basis set sizes and energy values in Hartree (E_h), at the atomic level, are given in Table 2. The process led to a set of 18s13p primitive functions for atoms Na–S. The total energies obtained by polynomial expansion were no more than 0.2 m E_h (for Al and Si) higher than the numerical values.⁴⁸ Similar accuracy was not achieved with 18s13p for Cl so, the number of primitive functions of chlorine atom was increased to 20s15p resulting in an energy only 0.03 m E_h higher than the HF numerical.

Contraction

Although the sizes 18s13p and 20s15p approached the energy values of the numerical HF, it is computationally inefficient to use all of these primitive functions in a calculation. Contraction of the basis sets reduces the number of functions by grouping certain primitive functions by linear combination.

Regarding the energetic importance, the inner-shell orbitals considerably contribute to the total electronic energy, so many functions must be used to describe that atomic region. Contraction of these many primitive functions results in only one function to be computed, making two-electron integral evaluation faster and reducing the computational time. **However, contraction increases the energy because the basis set becomes less flexible owing to the reduction in the number of variational parameters.** The goal in contraction is to find the proper balance between reducing the number of primitives and preserving the accuracy.

The pGCHF basis sets were contracted by Gaussian Elimination (GE) to make some coefficients zero, as suggested by Davidson.⁴⁹ To explain how GE works, 18s exponents and three sets of the corresponding coefficients generated for Si (Table 3) are used as a model, but the same procedure can be applied to any orbital symmetry.

Initially, the most diffuse exponents whose corresponding coefficients were separated because they will not take part in the GE. The number of separated exponents will define the quality of the basis set. In the present work, a total of six exponents were removed to form 7Z-like basis sets. By 7Z-like we refer to the six s and p primitive exponents left uncontracted but, it is not energetically equivalent to the 7 zeta quality basis sets known in the literature. The six exponents removed from the set of primitive functions of the Si atom are highlighted in bold in the second column in Table 3 ($n = 13$ –18).

Contraction starts by choosing the coefficients to be eliminated. In our example, these coefficients are highlighted in bold in the fourth row ($n = 4$) of columns C_n and D_n in Table 3.

Table 3 The set of the α exponents and the expansion coefficients C_{1s} , C_{2s} , and C_{3s} for the Si atom

n	α	C_{1s}	C_{2s}	C_{3s}
	A	B_n	C_n	D_n
1	$7.143 \times 10^{+05}$	1.493×10^{-05}	-3.970×10^{-06}	1.020×10^{-06}
2	$1.423 \times 10^{+05}$	8.590×10^{-05}	-2.287×10^{-05}	5.860×10^{-06}
3	$3.336 \times 10^{+04}$	4.851×10^{-04}	-1.292×10^{-04}	3.310×10^{-05}
4	$9.059 \times 10^{+03}$	2.205×10^{-03}	-5.881×10^{-04}	1.507×10^{-04}
5	$2.804 \times 10^{+03}$	8.498×10^{-03}	-2.277×10^{-03}	5.839×10^{-04}
6	$9.745 \times 10^{+02}$	2.777×10^{-02}	-7.543×10^{-03}	1.935×10^{-03}
7	$3.741 \times 10^{+02}$	7.660×10^{-02}	-2.147×10^{-02}	5.525×10^{-03}
8	$1.562 \times 10^{+02}$	1.723×10^{-01}	-5.177×10^{-02}	1.339×10^{-02}
9	$6.985 \times 10^{+01}$	2.963×10^{-01}	-1.027×10^{-01}	2.690×10^{-02}
10	$3.291 \times 10^{+01}$	3.366×10^{-01}	-1.548×10^{-01}	4.149×10^{-02}
11	$1.609 \times 10^{+01}$	1.920×10^{-01}	-1.272×10^{-01}	3.566×10^{-02}
12	$8.035 \times 10^{+00}$	3.654×10^{-02}	6.699×10^{-02}	-2.083×10^{-02}
13	$4.034 \times 10^{+00}$	2.777×10^{-03}	3.656×10^{-01}	-1.192×10^{-01}
14	$2.005 \times 10^{+00}$	4.449×10^{-04}	5.033×10^{-01}	-2.396×10^{-01}
15	9.705×10^{-01}	2.248×10^{-04}	2.118×10^{-01}	-2.133×10^{-01}
16	4.506×10^{-01}	-7.477×10^{-05}	8.813×10^{-03}	2.017×10^{-01}
17	1.975×10^{-01}	2.091×10^{-05}	1.724×10^{-03}	6.337×10^{-01}
18	8.048×10^{-02}	-8.390×10^{-06}	-1.773×10^{-04}	3.913×10^{-01}

Table 4 Coefficients after the first stage of contraction (elimination of C_4 and D_4 in Table 3)

n	α	C_{1s}	C_{2s}	C_{3s}
	A	B	$C_x = -(X \times B_n - C_n)$	$D_y = -(Y \times B_n - D_n)$
1	$7.143 \times 10^{+05}$	1.000×10^{-05}	1.000×10^{-08}	$0.000 \times 10^{+00}$
2	$1.423 \times 10^{+05}$	9.000×10^{-05}	4.000×10^{-08}	-1.000×10^{-08}
3	$3.336 \times 10^{+04}$	4.900×10^{-04}	2.200×10^{-07}	-5.000×10^{-08}
4	$9.059 \times 10^{+03}$	2.200×10^{-03}	$0.000 \times 10^{+00}$	$0.000 \times 10^{+00}$
5	$2.804 \times 10^{+03}$	8.500×10^{-03}	-1.077×10^{-05}	3.160×10^{-06}
6	$9.745 \times 10^{+02}$	2.777×10^{-02}	-1.350×10^{-04}	3.719×10^{-05}
7	$3.741 \times 10^{+02}$	7.660×10^{-02}	-1.038×10^{-03}	2.906×10^{-04}
8	$1.562 \times 10^{+02}$	1.723×10^{-01}	-5.805×10^{-03}	1.612×10^{-03}
9	$6.985 \times 10^{+01}$	2.963×10^{-01}	-2.363×10^{-02}	6.657×10^{-03}
10	$3.291 \times 10^{+01}$	3.367×10^{-01}	-6.495×10^{-02}	1.848×10^{-02}
11	$1.609 \times 10^{+01}$	1.920×10^{-01}	-7.602×10^{-02}	2.254×10^{-02}
12	$8.035 \times 10^{+00}$	3.654×10^{-02}	7.674×10^{-02}	-2.332×10^{-02}

Each of the numbers is divided by the corresponding number in column B_n :

$$X = \frac{C_4}{B_4} = \frac{-5.881 \times 10^{-04}}{2.205 \times 10^{-03}} = -0.2667 \quad (17)$$

$$Y = \frac{D_4}{B_4} = \frac{1.507 \times 10^{-04}}{2.205 \times 10^{-03}} = 0.068 \quad (18)$$

In eqn (17) and (18), X and Y are multiplied by all of the elements in column B_n and the results are subtracted from all of the elements in columns C_n and D_n , respectively, to make the fourth line in those columns zero, as shown in Table 4.

The elimination process finishes after all of the columns are manipulated. The number of contraction stages is $z - 1$ coefficient columns, that is, a total of two stages of contraction were performed in our example. The next coefficient to be eliminated must be at least one line under the previously chosen coefficient.

Making a coefficient zero means that the corresponding exponent will no longer exist in the basis set to represent an orbital. Because the exponents represent the radial extent of a function and their numeric range describes a specific atomic region, it is reasonable to relate the choice of the coefficient to be eliminated to the numeric value of the corresponding exponent and the orbital, which that coefficient represents to avoid a significant increase in the energy.

Large exponents provide tight functions that can describe the shapes of the orbitals near the nucleus, whereas small exponents describe the orbitals far from the nuclear region. Therefore, if coefficients related to the most diffuse exponents are removed from the 1s orbital and the major exponents are removed from the 3s orbital, the increase in the energy value will be minimised. The exponents and coefficients for the Si atom, after contraction, are given in Table 5 and the s functions to be used in computational chemistry codes (in this example, Gaussian software package format) are shown in Fig. 2.

In total, two exponents were removed from the 1s orbital, five were removed from the 2s orbital, and seven were removed from the 3s orbital (Table 5). The label s 10 1.0 in Fig. 2 means

Table 5 Expansion coefficients after two stages of the GE

n	α	C_{1s}	C_{2s}	C_{3s}
	A	B	C	D
1	$7.143 \times 10^{+05}$	1.634×10^{-05}	1.462×10^{-07}	3.208×10^{-09}
2	$1.423 \times 10^{+05}$	8.706×10^{-05}	1.218×10^{-07}	1.883×10^{-09}
3	$3.336 \times 10^{+04}$	4.921×10^{-04}	7.436×10^{-07}	1.263×10^{-08}
4	$9.059 \times 10^{+03}$	2.205×10^{-03}	$0.000 \times 10^{+00}$	$0.000 \times 10^{+00}$
5	$2.804 \times 10^{+03}$	8.458×10^{-03}	-4.682×10^{-06}	1.461×10^{-07}
6	$9.745 \times 10^{+02}$	2.629×10^{-02}	-1.602×10^{-04}	-6.052×10^{-07}
7	$3.741 \times 10^{+02}$	6.707×10^{-02}	-1.038×10^{-03}	$0.000 \times 10^{+00}$
8	$1.562 \times 10^{+02}$	1.140×10^{-01}	-6.333×10^{-03}	-1.267×10^{-05}
9	$6.985 \times 10^{+01}$	9.621×10^{-02}	-2.189×10^{-02}	4.175×10^{-05}
10	$3.291 \times 10^{+01}$	-1.397×10^{-01}	-5.256×10^{-02}	2.974×10^{-04}
11	$1.609 \times 10^{+01}$	$0.000 \times 10^{+00}$	-2.364×10^{-02}	1.256×10^{-03}
12	$8.035 \times 10^{+00}$	$0.000 \times 10^{+00}$	$0.000 \times 10^{+00}$	-1.841×10^{-03}

that 10s primitive GTOs (PGTOs) will become one contracted GTO (CGTO) by linear combination as in eqn (19):

$$\chi_{1s}(\text{CGTO}) = \sum_{i=1}^{10} a_i \chi_i(\text{PGTO}). \quad (19)$$

The same definition applies to s 7 1.0 and s 5 1.0:

$$\chi_{2s}(\text{CGTO}) = \sum_{i=1}^7 a_i \chi_i(\text{PGTO}) \quad (20)$$

$$\chi_{3s}(\text{CGTO}) = \sum_{i=1}^5 a_i \chi_i(\text{PGTO}), \quad (21)$$

where a_i are the expansion coefficients and χ_i are the i primitive functions.

By describing the orbitals through a fixed linear combination, the expansion coefficients become constant and are no longer parameters to be determined by the variational principle, which decreases the computational time.⁵⁰

The exponents, previously removed from the primitive set, are finally included in the s basis set (exponents highlighted in bold in Fig. 2). After contraction, the Na, Mg, Al, Si, P, and S atoms decreased from 18s13p to 9s8p primitive functions. The Cl atom with an original size of 20s15p primitive functions was also reduced to 9s8p primitive functions.

Polarisation functions and molecular calculations

Polarisation functions were generated by using a polarisation program developed in our research group that optimises a preselected set of functions using CISD calculations.

The arising polarisation exponents, added to the set of the previously contracted pGCHF basis sets, were optimised at the atomic level. Because the atoms investigated in this study only contain s and p orbitals, the pGCHF basis sets were polarised by adding higher angular momentum exponents to the 9s8p contracted set of functions. For each atom, some primitive p exponents (the functions that did not take part in the contraction process) were chosen from the pGCHF set to use as initial guesses to generate the optimised polarisation functions.

The exponents chosen as initial guesses are highlighted in bold in Fig. 3. For the 2d1f set, the last two p exponents (Fig. 3)

p 6 1.0	
2.291E+03	1.382E-04
5.576E+02	1.317E-03
1.663E+02	8.055E-03
5.886E+01	3.249E-02
2.393E+01	6.793E-02
1.083E+01	8.733E-02
p 3 1.0	
2.393E+01	-4.392E-04
1.083E+01	-1.692E-03
5.274E+00	-4.303E-03
p 1 1.0	
2.67931413	1.0
p 1 1.0	
1.37446446	1.0
p 1 1.0	
0.68934022	1.0
p 1 1.0	
0.32727056	1.0
p 1 1.0	
0.14240869	1.0
p 1 1.0	
0.05499273	1.0

Fig. 3 p exponents for the Si atom.

were used as guesses for the 2d functions. The initial guess for the 1f function was obtained by simply repeating the last p function (0.05499273).

This procedure was inspired by the work of Sadlej *et al.*⁵¹ and also follows the rules proposed in our recently published work.⁵² However, in this study, the functions were optimised until there was no significant change in the polarisation exponent. The initial guesses for any other combination of d, f, g, *etc.* polarisation functions followed the same pattern as previously described.

It is worth mentioning that this is not the only efficient way to obtain polarisation functions for incorporation in GCHF basis sets. For example, Ratuchne *et al.*⁵³ showed that numerical interpolation of the least-squares fitting of GCHF exponents can also provide polarisation exponents that are as accurate as those obtained with explicit optimisation.

Sets of polarisation functions were generated for each atom to identify the number of exponents that best fits the final pGCHF basis set. Molecular calculations were performed to evaluate the quality of the contracted sets along with the polarisation exponents. We chose a set of 26 molecules (Table 6) which were optimised at DFT level of theory using the M062X exchange–correlation functional⁵⁴ without dispersion corrections. This Minnesota functional was selected because it was demonstrated to have suitable accuracy⁵⁵ for describing properties such as atomisation energy, ionisation potentials, and electron affinity among the fourth-rung functionals in Jacob's ladder.⁵⁶ The molecular calculations were run in the Gaussian 09⁵⁷ suite performed in an Intel® Core™ i7-2600, 3.40GHZ CPU model.

For comparison purposes, the calculations were also carried out at the same level of theory using the standard basis sets pcseg-3,¹⁹ def2-QZVP,²² and Sapporo-QZP.^{20,21}

The CBS limit for the atomisation energies was estimated by the extrapolation scheme proposed by Jensen⁵⁸ and later on refined by Karton and Marting.⁵⁹ More details of this procedure are found in the Section S5 of the ESI† where it is also found extrapolations to the CBS limit calculated with Dunning's cc-pVQZ and cc-pV5Z.

Bauschlicher Jr. and Partridge,⁶⁰ while studying the SO₂ molecule, singled out that the absence of tight d exponent on sulphur's basis set results in inaccurate extrapolation of the atomisation energies. The finds reported by Bauschlicher Jr. and Partridge inspired other authors to revise their second-row basis sets. Dunning *et al.*⁶¹ and Jorge *et al.*,⁶² for example, added an extra d exponent in their respective cc-pVXZ (X = T, Q, 5 and 5) and XZP (X = D, T, Q, 5 and 6) basis sets for the second-row atoms which are known as cc-pV(X + d)Z (X = T, Q, 5 and 6) and XZP + 1d (X = D, T, Q, 5 and 6). In this work, the accuracy of the polarised version of the pGCHF was evaluated and special attention was paid on the d exponents as recommended by Bauschlicher Jr. and Partridge.

The number of polarisation exponents added to the pGCHF contracted set were 2d1f, 3d2f, 3d2f+d, 4d2f, 3d2f1g, pGCHF-4d2f1g_(not contracted) and 4d2f1g_(contracted)⁵¹ (Table S2 in the in the ESI† contains all the pGCHF polarisation exponents). The label 3d2f+d refers to the 3d2f exponents generated *via* optimisation as previously described plus an extra tight d exponent “pinched”⁵² from the set of p exponent left uncontracted.

The label 4d2f refers to the tight d exponent optimized along with the 3d2f functions. In the 4d2f1g_(contracted), two of the d exponents as well as the f exponents were grouped to form linear combinations. The 4d2f1g_(not contracted) is the set of polarisation exponents with no linear combinations.

Table 7 contains the root mean square deviation (RMSD) of the atomisation energies calculated with the well-established basis sets pcseg-3, def2-QZVP, Sapporo-QZP and our pGCHF basis sets containing 2d1f, 3d2f, 3d2f+d, 4d2f, 3d2f1g, 4d2f1g_(not contracted) and 4d2f1g_(contracted) polarisation exponents. Tables S3–S6 in the ESI† contains more details of all the calculations which resulted in the and RMSD values in Table 7.

The RMSD shows that pGCHF-2d1f has the lowest accuracy among the pGCHF sets. By adding one more d and f exponents, the error of 3.21 drops to 1.39 with the pGCHF-3d2f set. The adding of one d exponent decreases the error in both cases pGCHF-3d2f+d and pGCHF-4d2f. However, the optimized version has higher impact (RMSD = 1.00) compared with the “pinched” version (RMSD = 1.26).

The inclusion of one g function in both pGCHF-3d2f and pGCHF-4d2f to form the sets pGCHF-3d2f1g and pGCHF-4d2f1g_(not contracted), respectively, also improves the results shown in Table 7. In fact, adding one more d function to get the pGCHF-4d2f1g_(not contracted)

Table 6 The 26 molecules studied in this work

Al₂, AlCl, AlCl₃, AlP, AlS, PCl, Cl₂, Na₂ Mg₂, MgCl MgCl₂, MgS, P₂, P₄, PCl₃, PCl₅, S₂, S₂Cl₂, S₃, SCl, SiCl₂, SCl₂, Si₂, SiCl, SiP and SiS

Table 7 Calculated RMSD for the Atomisation Energy using the functional M062X

Atomisation energy (kcal mol ⁻¹)	
Basis sets	RMSD CBS _{pcseg-3/pcseg-4}
pGCHF-4d2f1g _(not contracted)	0.72
pGCHF-4d2f	1.00
pGCHF-3d2f+d	1.26
pGCHF-3d2f1g	1.31
pGCHF-3d2f	1.39
pGCHF-4d2f1g _(contracted)	1.62
pGCHF-2d1f	3.21
Sapporo-QZP	1.28
def2-QZVP	1.56
pcseg-3	1.96

drops the RMSD to 0.72 which is the best result amongst the pGCHF basis sets. In fact, the pGCHF-4d2f1g_(not contracted) basis sets have the smallest RMSD value of atomisation energies compared with the basis sets pcseg-3, def2-QZVP and Sapporo-QZP (the same tendencies are found when the results are compared with CBS_{cc-pvQZ/cc-pv5Z} – see Table S6 in the ESI†).

Lastly, the computational time of the basis sets pGCHF-3d2f+d, pGCHF-4d2f, pGCHF-3d2f1g, pGCHF-4d2f1g_(contracted), pGCHF-4d2f1g_(not contracted), Sapporo-QVP, pcseg-3 and def2-QZVP were assessed. Fig. 4 contains the mean CPU times (in seconds) spent in the optimisation of the total energy of the 26 molecules at the ground state studied in this work.

From Fig. 4, it is observed that both pGCHF-3d2f+d and pGCHF-4d2f optimise the 26 molecules with lower computational cost when compared with those well-established basis sets. This is expected due to the absence of g exponents in both sets.

According to Fig. 4, the pGCHF-4d2f1g_(contracted) takes 293.1 seconds to optimize the 26 molecules which is only 1.9 seconds higher than def2-QZVP and 13.1 seconds lower than Sapporo-QZP. Contracting higher angular momentum exponents brings advantage to the computational time (Fig. 4), that is, the pGCHF-4d2f1g_(contracted) optimises the 26 molecules studied 88 seconds faster than the pGCHF-4d2f1g_(not contracted). However, the RMSD on Table 7 prove that the contraction drives the AE away from the CBS limit. It is also worth mentioning that the pGCHF-4d2f1g_(contracted) basis sets behaves similarly to the

well-established def2-QZVP basis sets, according to Table 7 and Fig. 4, but further analyses are necessary to confirm if such tendency is maintained in other circumstances.

Although the pGCHF-4d2f1g_(not contracted) set claims for 398 seconds to optimise the 26 molecules, which is the highest value amongst all of the evaluated basis sets, it is noteworthy that the accuracy achieved by this basis sets, while describing the atomisation energies, is substantial specially when compared with the standard basis sets here reported.

Considering both the accuracy in describing atomisation energies and the corresponding computational costs, we can summarise our findings as follows:

(a) The pGCHF-4d2f1g_(not contracted) gave the lowest RMSD value while describing atomisation energies among all of the basis sets studied in this work, especially when compared with the well-established basis sets Sapporo-QVP, pcseg-3 and def2-QZVP.

(b) In fact, adding a tight d polarisation exponent to the set improves the atomisation energies in agreement with Bauschlicher Jr. and Partridge.⁶⁰

(c) Contracting higher angular momentum exponents in the pGCHF basis sets brings advantages to computational cost, but it is not energetically favourable.

(d) pGCHF-4d2f1g_(not contracted) has shown the best accuracy while describing atomisation energies amongst all the basis sets here analysed, but such achievement is followed by an increasing in the computational cost.

Based on the above conclusions, we recommend the pGCHF-4d2f1g_(not contracted) basis sets to calculate atomisation energies of molecules containing second-row atoms based on its good accuracy while describing such a property.

Conclusions

This paper has reported and discussed the generation, contraction, and polarisation of the pGCHF Gaussian basis sets.

The functions were generated using the GCHF method, in which the GWHF equations are solved by a pID. A set of 18s13p primitive functions for the atoms Na-S and 20s15p primitive functions for Cl atom were contracted, resulting in 7Z-like Gaussian basis sets. Polarisation exponents generated at the CISD level of theory were incorporated into the set of contracted functions.

Atomic energy calculations revealed the good accuracy of the pGCHF basis sets, and they gave energy values close to those obtained from atomic numerical HF calculations. DFT calculations of 26 molecules using the M062X exchange–correlation functional demonstrated that our pGCHF-4d2f1g_(not contracted) basis set can reproduce atomisation energies with superior accuracy than the well-established pcseg-3, def2-QZVP, and Sapporo-QZP basis sets. However, attention should be paid on the computational cost penalty that comes with such accuracy.

The results reported in this paper are promising for future theoretical molecular calculations. The pGCHF basis sets discussed in this work can be found in the ESI† as well as

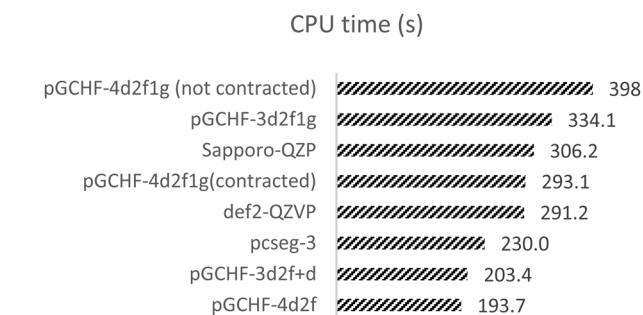


Fig. 4 Mean CPU time (in seconds) of the total energies for the pGCHF-3d2f+d, pGCHF-4d2f, pGCHF-3d2f+d, pGCHF-4d2f1f, Sapporo-QVP, pcseg-3 and def2-QZVP basis sets.

at <http://quanta.iqsc.usp.br/basis-sets>, <https://www.basissetexchange.org>.

Conflicts of interest

There are no conflicts to declare.

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