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The general Gaussian product theorem

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Abstract The Gaussian Product Theorem between two 1s Gaussian Type Orbitals (GTOs) is extended to an arbitrary number of s-type functions, giving a compact formula which permits to express the condensed GTO result. Then, this new formulation is combined with the product of arbitrary GTO Cartesian angular parts, obtaining a finite expansion expressing this product as a multilinear combination of such functions sharing a common center. The combination of both results constitutes the General Gaussian Product Theorem (GGPT), a final compact expression for the product of an arbitrary number of Cartesian GTOs. The notation provides an easy way to express algebraically any general multicenter GTO product expression. It is also shown how by means of Nested Summation Symbols the computational implementation can be easily and elegantly achieved. Computational parallelizable schemes of the GGPT are provided.

Keywords Gaussian type orbital (GTO) functions product · General GTO product theorem (GGPT) · Nested summation symbols · Cartesian GTO angular part

1 Introduction

From the early days of quantum mechanics applied to chemistry, a major progression has been made in the field of molecular integrals and basis sets expressions. From the pioneering work of Boys regarding the use of Gaussian functions [1], Gaussian Type Orbitals (GTOs) have been extensively used, see for example references [2,3] and a review on the algorithms for computing the usual integrals used in quantum chemistry up to four GTO in different centers [4]. More recently, and contemporaneously

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with the gestation of the Quantum Molecular Similarity Theory [5–9], has appeared the need to deal with overlap-like multicenter integrals, sometimes involving up to six or even more centers [10,11], a kind of computational structures which have not been studied in the current literature. The actual interest is even greater, due to the many applications of the Atomic Shell Approximation (ASA) [12–15], which allows to expand the molecular density along an arbitrary number centers by means of linear combinations of 1s-type Gaussians, see references [9,16,17] for modern applications of ASA to quantum similarity problems. Moreover, this paper has to be connected with earlier studies on GTO products related to nested summation symbols [18] and recent work on GTO properties [19].

The need and possibility to go beyond the two Gaussian product theorem (TGPT) due to the computational needs of future work on quantum similarity measures, has lead the present authors to revise the previous work [18]. The effort of the present paper will be mainly devoted to extend the well-known TGPT [20–22] up to a product of an arbitrary number GTO functions. This will permit to describe a general algorithmic platform, as a first step towards the parallel implementation of overlap-like integral evaluation, involving an indefinite number of GTO basis functions. The general formula which will be deduced here will deal with the product of N Cartesian Gaussian functions and will express it in terms of a multilinear expansion of GTO centerd at a common point. The final formula will constitute a general algebraic expression from which many scientific fields can take benefit, especially molecular quantum mechanics and related fields see, for example, reference [20]. Additionally, it will be shown how the computational implementation of the final formula it is easily achieved within a Nested Summation Symbol (NSS) algorithmic framework [23–28], constructed from a general point of view and involving any number of GTO's. The practical use of these ideas will be developed in several studies, like the triple density integral measure evaluation [29]. On the other hand, the present paper can be also considered a first step to obtain a tensorial description of molecular structures via multiple density quantum similarity measures.

2 A convenient GTO description

A unnormalized Cartesian Gaussian function with quantum numbers $n_1,\ n_2$ and n_3, centerd at point $\boldsymbol{A} = (A_1,\ A_2,\ A_3)$ and with a unique exponential parameter α can be conveniently defined as the symbolic function:

$$\gamma_A = \gamma\left(\boldsymbol{A}, \boldsymbol{n}, \alpha\right) = H\left(\boldsymbol{A}, \boldsymbol{n}, \boldsymbol{r}\right) e^{-\alpha|\boldsymbol{r}-\boldsymbol{A}|^2}, \tag{1}$$

where the angular part has been defined in turn with the term

$$H\left(\boldsymbol{A}, \boldsymbol{n}, \boldsymbol{r}\right) = \prod_{q=1}^{3} \left(x_q - A_q\right)^{n_q}. \tag{2}$$

In the present notation, the vector $\boldsymbol{n} = (n_1,\ n_2,\ n_3)$ assembles the GTO quantum numbers, while $x_1,\ x_2$ and x_3 are the Cartesian position coordinates, which can be collected into the vector $\boldsymbol{r} = (x_1,\ x_2,\ x_3)$.

In general, the symbol $\langle \boldsymbol{v}_n \rangle$, will be used along this text in order to express the complete sum of the elements of any n-dimensional vector $\boldsymbol{v}_n = (v_1,\ v_2, \ldots, v_n)$, in the following way:

$$\langle \boldsymbol{v}_n \rangle = \sum_{i=1}^{n} v_i . \tag{3}$$

Now, using the complete sum definition over the vector $\boldsymbol{n} : \langle \boldsymbol{n} \rangle = n_1 + n_2 + n_3$, the normalization factor of function (1) can be written as:

$$\chi\left(\boldsymbol{n}, \alpha\right) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} \left(\frac{(4\alpha)^{\langle \boldsymbol{n} \rangle}}{\prod_{i=1}^{3}\left[(2n_i - 1)!!\right]}\right)^{\frac{1}{2}} \tag{4}$$

The parameter $\langle \boldsymbol{n} \rangle$ appearing in Eq. (4) above is the *order* of the GTO. For simplicity sake, in this text only unnormalized functions will be considered. If needed, normalization elements can be considered as an extra multiplicative factor in the final expressions.

GTOs are separable along the three Cartesian coordinates:

$$\gamma\left(\boldsymbol{A}, \boldsymbol{n}, \alpha\right) = \prod_{q=1}^{3} \gamma_q\left(A_q, n_q, \alpha\right), \tag{5}$$

where

$$\forall q : \gamma_q\left(A_q, n_q, \alpha\right) = H_q\left(A_q, n_q, x_q\right)\ e^{-\alpha\left(x_q - A_q\right)^2}, \tag{6}$$

being the angular part defined as:

$$\forall q : H_q\left(A_q, n_q, x_q\right) = \left(x_q - A_q\right)^{n_q} . \tag{7}$$

This property is particularly useful for algebraic purposes and will be taken frequently into account along the present development.

3 The two s-type Gaussian product theorem (TsGPT)

Any 1s-type function is a GTO bearing zeroes as quantum numbers, that is: $\boldsymbol{n} =^3 \boldsymbol{0} = (0, 0, 0)$, thus any 1s-type GTO is of order zero coinciding with a bare Gaussian function over three dimensional position space:

$$s_A = s\left(\boldsymbol{A}, \alpha\right) = \gamma\left(\boldsymbol{A}, {}^3\boldsymbol{0}, \alpha\right) = e^{-\alpha|\boldsymbol{r} - \boldsymbol{A}|^2}, \tag{8}$$

being its normalization factor: $\chi\left({}^3\boldsymbol{0}, \alpha\right) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}}$.

As it is well known, the TGPT states that the product of two GTOs of order a and b with centers at points $\boldsymbol{A}$ and $\boldsymbol{B}$ is a finite linear combination of other Gaussian functions up to order $a+b$ and centered on a point lying somewhere along the axis connecting the centers $\boldsymbol{A}$ and $\boldsymbol{B}$ [20–22]. In particular, the product of two 1s-type GTOs is another scaled 1s-type Gaussian:

$$s_A s_B = s(\boldsymbol{A}, \alpha)\, s(\boldsymbol{B}, \beta) = \kappa e^{-(\alpha+\beta)|\boldsymbol{r}-\boldsymbol{P}|^2} = \kappa s(\boldsymbol{P}, \alpha+\beta), \tag{9}$$

being the coefficient κ defined as:

$$\kappa = e^{-\frac{\alpha\beta}{\alpha+\beta}|\boldsymbol{A}-\boldsymbol{B}|^2}, \tag{10}$$

the intermediate point $\boldsymbol{P}$ being defined through the weighted mean as well:

$$\boldsymbol{P} = \frac{\alpha\boldsymbol{A} + \beta\boldsymbol{B}}{\alpha+\beta}. \tag{11}$$

Expression (9) constitutes the Two 1s-type Gaussian Product Theorem (TsGPT). As a simple rule, one can express the TsGPT as an equality involving the exponential terms implicit within expression (9):

$$\alpha|\boldsymbol{r}-\boldsymbol{A}|^2 + \beta|\boldsymbol{r}-\boldsymbol{B}|^2 = \frac{\alpha\beta}{\alpha+\beta}|\boldsymbol{A}-\boldsymbol{B}|^2 + (\alpha+\beta)|\boldsymbol{r}-\boldsymbol{P}|^2. \tag{12}$$

4 The general s-type Gaussian product theorem (GsGPT)

The previous TsGPT can be extended to an arbitrary number of 1s-type GTOs product. Let be a set of N 1s-type GTOs placed at the respective centers $\{\boldsymbol{A}_i\,|i=1,N\}$ with scale factors collected as a vector:

$$\boldsymbol{a}_N = (\alpha_1, \alpha_2, \ldots, \alpha_N). \tag{13}$$

The General 1s-type Gaussian Product Theorem (GsGPT) states that a 1s-type GTO product is another scaled 1s-type GTO, which can be shortly written as:

$$\prod_{i=1}^{N} s(\boldsymbol{A}_i, \alpha_i) = \kappa s\left({}^{N}\boldsymbol{P}, \langle \boldsymbol{a}_N \rangle\right), \tag{14}$$

where, according to definition (3), $\langle \boldsymbol{a}_N \rangle = \sum_{i=1}^{N} \alpha_i$, while the point ${}^{N}\boldsymbol{P}$ is defined by the weighted mean:

$${}^{N}\boldsymbol{P} = \langle \boldsymbol{a}_N \rangle^{-1} \sum_{i=1}^{N} \alpha_i \boldsymbol{A}_i. \tag{15}$$

The constant κ being a simple exponential:

$$\kappa = e^{-\langle {}^{N}\boldsymbol{C} \rangle} \tag{16}$$

where the scalar exponent $\langle {}^{N}\boldsymbol{C} \rangle$ is defined as:

$$\left\langle {}^{N}\boldsymbol{C} \right\rangle = \langle \boldsymbol{a}_N \rangle^{-1} \sum_{i<j}^{N} \alpha_i \alpha_j \left| \boldsymbol{A}_i - \boldsymbol{A}_j \right|^2 ; \tag{17}$$

an expression which in turn arises from the definition of the three-component vector:

$${}^{N}\boldsymbol{C} = \left\{ {}^{N}C_q \right\}_{q=1,3} = \langle \boldsymbol{a}_N \rangle^{-1} \left\{ \sum_{i<j}^{N} \alpha_i \alpha_j \left(A_{iq} - A_{jq} \right)^2 \right\}_{q=1,3} . \tag{18}$$

The previous Eqs. (17) and (18) use the elements of the rectangular matrix $\boldsymbol{A}_{N\times 3}$ which collects the original centers of each Gaussian function ordered as follows:

$$\boldsymbol{A}_{N\times 3} = \begin{pmatrix} \boldsymbol{A}_1 \\ \boldsymbol{A}_2 \\ \vdots \\ \boldsymbol{A}_N \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ \vdots & \vdots & \vdots \\ A_{N1} & A_{N2} & A_{N3} \end{pmatrix}, \tag{19}$$

where the generic matrix element A_{iq} stands for the coordinate q of the i-th GTO center.

For convenience, in order to better represent the relationship (14), the rule which could be associated to Eq. (12), can be generalized into the following one:

$$\sum_{i=1}^{N} \alpha_i \left| \boldsymbol{r} - \boldsymbol{A}_i \right|^2 = \left\langle {}^{N}\boldsymbol{C} \right\rangle + \langle \boldsymbol{a}_N \rangle \left| \boldsymbol{r} - {}^{N}\boldsymbol{P} \right|^2 \tag{20}$$

applying to each dimension of the position space as well:

$$\sum_{i=1}^{N} \alpha_i \left(x_q - A_{iq} \right)^2 = {}^{N}C_q + \langle \boldsymbol{a}_N \rangle \left(x_q - {}^{N}P_q \right)^2 ; \quad \forall q = 1, 2, 3. \tag{21}$$

In fact, the sum of the three terms appearing into Eq. (21) leads to the general expression (20).

5 Proof of the GsGPT

In this section, the GsGPT will be proved by recurrent construction, or what is the same: by the iterative application of the TsGPT. At each step of the process, one GTO has to be multiplied by the former product of GTO's which, in turn, became another GTO. Here it will be presented a mathematical treatment via the manipulation of the exponential terms which are implicit in Eq. (14) and appear in expression (20). Due to the separability of all these terms with respect to each Cartesian coordinate, it is only necessary to work out a generic coordinate q only, by means of deducing Eq. (21) for a particular value of q. The proof relies on the induction method:

Step 1. The GsGPT holds for the trivial case $N = 1$, if it is assumed that ${}^1C_q = 0$. Also, GsGPT formulation is true for $N = 2$, since Eq. (15) gives, for an specific coordinate q,

$$\forall q : \; {}^2P_q = \frac{\alpha_1 A_{1q} + \alpha_2 A_{2q}}{\alpha_1 + \alpha_2} \tag{22}$$

and, by Eq. (18),

$$\forall q : \; {}^2C_q = \frac{\alpha_1\alpha_2 \left(A_{1q} - A_{2q}\right)^2}{\alpha_1 + \alpha_2} \tag{23}$$

which is coincident with the same result as the one given by the TGPT [20–22], when applied over two 1s-type GTOs. In fact, in this manner the rule associated to Eq. (12) has been found out again, although here is written for the dimension q as follows:

$$\begin{aligned}\forall q : \; & \alpha_1 \left(x_q - A_{1q}\right)^2 + \alpha_2 \left(x_q - A_{2q}\right)^2 \\ &= {}^2C_q + (\alpha_1 + \alpha_2)\left(x_q - {}^2P_q\right)^2 .\end{aligned} \tag{24}$$

In other words, expression (24) is the particular case of Eq. (21) for $N = 2$.

Step 2. Assuming that the GsGPT theorem is valid for $N = k$, that is: for a product of k 1s-type GTOs; then, the rule of Eq. (21) holds for k functions, using the fact that the following equality will hold:

$$\forall q : \sum_{i=1}^{k} \alpha_i \left(x_q - A_{iq}\right)^2 = {}^kC_q + \langle \boldsymbol{a}_k \rangle \left(x_q - {}^kP_q\right)^2 \tag{25}$$

where, according to Eq. (18),

$$\forall q : {}^kC_q = \langle \boldsymbol{a}_k \rangle^{-1} \sum_{i<j}^{k} \alpha_i \alpha_j \left(A_{iq} - A_{jq}\right)^2 \tag{26}$$

and

$$\forall q : {}^kP_q = \langle \boldsymbol{a}_k \rangle^{-1} \sum_{i=1}^{k} \alpha_i A_{iq}. \tag{27}$$

Step 3. It is necessary to prove now that equivalent relationships, as the ones expressed in the preceding step, hold when a new GTO enters into the product. The product of $N = k+1$ functions can be build, according to the TsGPT, by means of the resulting product of the former k functions by the new added one. Due to expression (25), the following equality holds:

$$\forall q : \sum_{i=1}^{k+1} \alpha_i \left(x_q - A_{iq}\right)^2 = {}^{k}C_q + \langle \boldsymbol{a}_k \rangle \left(x_q - {}^{k}P_q\right)^2 + \alpha_{k+1} \left(x_q - A_{k+1,q}\right)^2, \tag{28}$$

and by application of rule (24) to the two rightmost terms, it is obtained

$$\forall q : \sum_{i=1}^{k+1} \alpha_i \left(x_q - A_{iq}\right)^2 = {}^{k}C_q + \langle \boldsymbol{a}_{k+1} \rangle^{-1} \alpha_{k+1} \langle \boldsymbol{a}_k \rangle \left(A_{k+1,q} - {}^{k}P_q\right)^2 + \langle \boldsymbol{a}_{k+1} \rangle \left(x_q - {}^{k+1}P_q\right)^2 \tag{29}$$

where relationship (26) has been taken into account. Then, according to Eq. (11) the new center coordinates can be written as:

$$\forall q : {}^{k+1}P_q = \langle \boldsymbol{a}_{k+1} \rangle^{-1} \langle \boldsymbol{a}_k \rangle {}^{k}P_q + \alpha_{k+1} A_{k+1,q} \tag{30}$$

or, due to expression (27),

$$\forall q : {}^{k+1}P_q = \langle \boldsymbol{a}_{k+1} \rangle^{-1} \sum_{i=1}^{k+1} \alpha_i A_{iq}. \tag{31}$$

In all preceding equations it has been also used the trivial relationship:

$$\langle \boldsymbol{a}_{k+1} \rangle = \langle \boldsymbol{a}_k \rangle + \alpha_{k+1}. \tag{32}$$

Equation (31) presents the same structure as the former Eq. (27), although with one more GTO. Similarly, the rightmost part of expression (29) constitutes the generalization for $k+1$ functions of the exponential Cartesian dependent part of the GTO product. In order to conclude the demonstration, it remains to check that the expression:

$$\forall q : M_q = {}^{k}C_q + \langle \boldsymbol{a}_{k+1} \rangle^{-1} \alpha_{k+1} \langle \boldsymbol{a}_k \rangle \left(A_{k+1,q} - {}^{k}P_q\right)^2, \tag{33}$$

which appears as the pre-exponential scaling factor in Eq. (29), results equal to ${}^{k+1}C_q$, the generalized term homologous to expression (26). This property can be obtained after some straightforward algebra, as follows.

Making explicit some auxiliary mathematical relationships first, like the general term:

$$\forall q : \sum_{i<j}^{k} \alpha_i \alpha_j \left(A_{iq} - A_{jq}\right)^2 = \sum_{i<j}^{k} \alpha_i \alpha_j \left(A_{iq}^2 + A_{jq}^2\right) - 2\sum_{i<j}^{k} \alpha_i \alpha_j A_{iq} A_{jq} \quad (34)$$

and taking also into account the general equality:

$$\forall q : \sum_{i<j}^{k} \alpha_i \alpha_j \left(A_{iq}^2 + A_{jq}^2\right) = \sum_{i=1}^{k} A_{iq}^2 \alpha_i \left(\langle \boldsymbol{a}_k \rangle - \alpha_i\right), \quad (35)$$

then Eq. (34) becomes:

$$\forall q : \sum_{i<j}^{k} \alpha_i \alpha_j \left(A_{iq} - A_{jq}\right)^2 = \langle \boldsymbol{a}_k \rangle \sum_{i=1}^{k} \alpha_i A_{iq}^2 - \left(\sum_{i=1}^{k} \alpha_i A_{iq}\right)^2 \quad (36)$$

where it has been employed the multinomial formula

$$\forall q : \left(\sum_{i=1}^{k} \alpha_i A_{iq}\right)^2 = \sum_{i=1}^{k} \alpha_i^2 A_{iq}^2 + 2\sum_{i<j}^{k} \alpha_i \alpha_j A_{iq} A_{jq}. \quad (37)$$

Substituting Eqs. (26), (27) and (36) into expression (33), performing the sum and arranging terms it is obtained

$$\forall q : M_q = \langle \boldsymbol{a}_{k+1} \rangle^{-1} \left(\langle \boldsymbol{a}_{k+1} \rangle \sum_{i=1}^{k} \alpha_i A_{iq}^2 + \langle \boldsymbol{a}_k \rangle^{-1} \left(\alpha_{k+1} - \langle \boldsymbol{a}_{k+1} \rangle\right) \left(\sum_{i=1}^{k} \alpha_i A_{iq}\right)^2 \right.$$
$$\left. + \langle \boldsymbol{a}_k \rangle \alpha_{k+1} A_{k+1,q}^2 - 2\alpha_{k+1} A_{k+1,q} \sum_{i=1}^{k} \alpha_i A_{iq} \right) \quad (38)$$

Due to the relationship (32), the equality $\langle \boldsymbol{a}_k \rangle = \langle \boldsymbol{a}_{k+1} \rangle - \alpha_{k+1}$ holds. Substituting it twice in (38) and rearranging terms again, it follows that:

$$\forall q : M_q = \langle \boldsymbol{a}_{k+1} \rangle^{-1} \left(\langle \boldsymbol{a}_{k+1} \rangle \sum_{i=1}^{k+1} \alpha_i A_{iq}^2 \right.$$
$$\left. - \left[\left(\sum_{i=1}^{k} \alpha_i A_{iq}\right)^2 + \alpha_{k+1}^2 A_{k+1,q}^2 + 2\alpha_{k+1} A_{k+1,q} \sum_{i=1}^{k} \alpha_i A_{iq} \right] \right) \quad (39)$$

The square-bracketed term constitutes the multinomial expansion (37), though attached to $k+1$ terms instead of k. Substituting it in Eq. (39) and considering the general expression (36) but applied to $k+1$ terms, it is obtained the desired result:

$$\forall q : M_q = \langle \boldsymbol{a}_{k+1} \rangle^{-1} \left(\langle \boldsymbol{a}_{k+1} \rangle \sum_{i=1}^{k+1} \alpha_i A_{iq}^2 - \left(\sum_{i=1}^{k+1} \alpha_i A_{iq} \right)^2 \right)$$
$$= \langle \boldsymbol{a}_{k+1} \rangle \sum_{i<j}^{k+1} \alpha_i \alpha_j \left(A_{iq} - A_{jq} \right)^2 = {}^k C_q . \tag{40}$$

Therefore the GsGPT is proved in this way.

6 Cartesian angular parts product

It is of interest to describe a procedure to deal with the product of several angular parts as those appearing in the GTO definition in Eq. (1). The combination of this result with the previous GsGPT will permit to demonstrate the GGPT.

The angular part of a GTO is a polynomial expression in x_1, x_2 and x_3 and the same can be said for the product of N angular parts involved in a product of N GTOs. It has to be noted that, in practice, the product of the angular parts must be generated after that the product of the exponential ones is known. This is so because, for convenience, the angular binomial terms will be expanded at the point defined by the vector described in Eq. (15), whose three components can be written as:

$${}^N\boldsymbol{P} = \left({}^N P_1, {}^N P_2, {}^N P_3 \right) . \tag{41}$$

For instance, the Cartesian angular component for the i-th ($i = 1, N$) GTO within the Cartesian position component number q ($q = 1, 3$) can be expressed according to the convenient Newton binomial expansion at the point ${}^N P_q$:

$$\forall q : H_q \left(A_{iq}, n_{iq}, x_q \right) = \left(x_q - A_{iq} \right)^{n_{iq}} = \left(x_q - {}^N P_q + {}^N P_q - A_{iq} \right)^{n_{iq}}$$
$$= \left({}^P x_q + B_{iq} \right)^{n_{iq}} = \sum_{k=0}^{n_{iq}} \binom{n_{iq}}{k} B_{iq}^{n_{iq}-k} \, {}^P x_q^k , \tag{42}$$

where the new coordinate variable ${}^P x_q = x_q - {}^N P_q$ is centered at the coordinate of the common center point ${}^N P_q$, while it has been defined the extra auxiliary term: $B_{iq} = {}^N P_q - A_{iq}$. As the notation in expression (42) suggests, for computational purposes the pool of GTO quantum numbers can be collected into a rectangular matrix:

$$\boldsymbol{n}_{N\times 3} = \begin{pmatrix} n_{11} & n_{12} & n_{13} \\ n_{21} & n_{22} & n_{23} \\ \vdots & \vdots & \vdots \\ n_{N1} & n_{N2} & n_{N3} \end{pmatrix} = \left({}^N\boldsymbol{n}_1, {}^N\boldsymbol{n}_2, {}^N\boldsymbol{n}_3 \right) . \tag{43}$$

Here, the element n_{iq} stands for the quantum number n_q $(q = 1, 3)$ of the i-th $(i = 1, N)$ GTO. For practical purposes, the rectangular matrix $\boldsymbol{n}_{N\times 3}$ is constructed by three column vectors, $\left\{{}^N\boldsymbol{n}_q\right\}_{q=1,3}$ of dimension N. It is also convenient to define the $N \times 3$ matrix which collects the set of B_{iq} terms:

$$\boldsymbol{B}_{N\times 3} = \begin{pmatrix} {}^N\boldsymbol{P} \\ \vdots \\ {}^N\boldsymbol{P} \end{pmatrix} - \boldsymbol{A}_{N\times 3} = \left({}^N\boldsymbol{B}_1, {}^N\boldsymbol{B}_2, {}^N\boldsymbol{B}_3\right), \tag{44}$$

where ${}^N\boldsymbol{P}$ is the vector defined in Eq. (41). Again, the matrix $\boldsymbol{B}_{N\times 3}$ is constructed from three column vectors of dimension N, $\left\{{}^N\boldsymbol{B}_q\right\}_{q=1,3}$, each one attached to a Cartesian coordinate.

Following Eq. (42), the product of angular factors (2) for the i-th GTO is the same as:

$$H\left(\boldsymbol{A}_i, \boldsymbol{n}_i, \boldsymbol{r}\right) = \prod_{q=1}^{3}\left[\sum_{k=0}^{n_{iq}} \binom{n_{iq}}{k} B_{iq}^{n_{iq}-k}\, {}^P x_q^k\right]. \tag{45}$$

As the previous equation shows, the angular functions are separable into three terms, each one attached to every space coordinate. Hence, it is more convenient to express the product of N angular parts in a partitioned fashion along the three coordinates. For a particular dimension q, the product of the angular parts of N GTOs can be written as:

$$\forall q : {}^N H_q = \prod_{i=1}^{N} H_q\left(A_{iq}, n_{iq}, x_q\right) = \prod_{i=1}^{N}\left[\sum_{k_i=0}^{n_{iq}} \binom{n_{iq}}{k_i} B_{iq}^{n_{iq}-k_i}\, {}^P x_q^{k_i}\right], \tag{46}$$

where each summation index k is now associated to an extra identification label using the subindex i. Next, it will be made clear the usefulness to define such a labelling. Rearranging terms in Eq. (46) one obtains:

$$\forall q : {}^N H_q = \sum_{k_1=0}^{n_{1q}} \sum_{k_2=0}^{n_{2q}} \cdots \sum_{k_N=0}^{n_{Nq}} c\left(\boldsymbol{k}, {}^N\boldsymbol{n}_q, {}^N\boldsymbol{B}_q\right)\, {}^P x_q^{k_1+k_2+\cdots+k_N}. \tag{47}$$

In the previous expression, the numerical coefficients attached to the coordinate powers are defined by means of the expression:

$$\forall q : c\left(\boldsymbol{k}, {}^N\boldsymbol{n}_q, {}^N\boldsymbol{B}_q\right) = \prod_{i=1}^{N}\left[\binom{n_{iq}}{k_i} B_{iq}^{n_{iq}-k_i}\right] \tag{48}$$

and it is also implicitly defined the vector: $\boldsymbol{k} = (k_1, k_2, \ldots, k_N)$. Expression (47) can now be written more compactly as follows:

$$\forall q : {}^N H_q = \sum\nolimits_N \left(\boldsymbol{k}, {}^N\boldsymbol{0}, {}^N\boldsymbol{n}_q\right)\, c\left(\boldsymbol{k}, {}^N\boldsymbol{n}_q, {}^N\boldsymbol{B}_q\right)\, {}^P x_q^{\langle \boldsymbol{k}\rangle} \tag{49}$$

where ${}^{N}\boldsymbol{0}$ is a N dimensional zero vector and the sum symbol definition (3) has been employed in order to express the coordinate powers.

In the previous Eq. (49), the operator: $\sum_N \left(\boldsymbol{k}, {}^{N}\boldsymbol{0}, {}^{N}\boldsymbol{n}_q\right)$ stands for a Nested Summation Symbol (NSS) [18,23–28] of dimension N. The NSS operator expresses the product of an arbitrary number of summation symbols. In the present application it is the same as to write:

$$\forall q : \sum_N \left(\boldsymbol{k}, {}^{N}\boldsymbol{0}, {}^{N}\boldsymbol{n}_q\right) = \prod_{i=1}^{N} \left(\sum_{k_i=0}^{n_{iq}}\right). \tag{50}$$

The NSS definition allows obtaining compact algebraic expressions, which are related to the possibility to compute the involved expression in a fully parallel way.

7 Complete expressions: the general Gaussian product theorem (GsGPT)

According to the results of the preceding sections, regarding a particular dimension q ($q = 1, 3$), the product of N unnormalized Cartesian GTOs with quantum numbers collected in matrix (43), centered at the points specified in matrix (19) and with the exponential parameters appearing in vector (13) can be expressed like:

$$\begin{aligned}\forall q : &\prod_{i=1}^{N} \gamma_q \left(A_{iq}, n_{iq}, \alpha_i\right) \\ &= e^{-{}^{N}C_q} \sum_N \left(\boldsymbol{k}, {}^{N}\boldsymbol{0}, {}^{N}\boldsymbol{n}_q\right)\ c\left(\boldsymbol{k}, {}^{N}\boldsymbol{n}_q, {}^{N}\boldsymbol{B}_q\right)\ \gamma_q\left({}^{N}P_q, \langle\boldsymbol{k}\rangle, \langle\boldsymbol{a}_N\rangle\right).\end{aligned} \tag{51}$$

The product of terms in all the three dimensions is obtained by means of relationships (5) and (51), therefore it can be written:

$$\begin{aligned}\prod_{i=1}^{N} \gamma\left(\boldsymbol{A}_i, \boldsymbol{n}_i, \alpha_i\right) &= \prod_{i=1}^{N}\left[\prod_{q=1}^{3} \gamma_q\left(A_{iq}, n_{iq}, \alpha_i\right)\right] = \prod_{q=1}^{3}\left[\prod_{i=1}^{N} \gamma_q\left(A_{iq}, n_{iq}, \alpha_i\right)\right] \\ &= \kappa \sum_N \left(\boldsymbol{k}_1, {}^{N}\boldsymbol{0}, {}^{N}\boldsymbol{n}_1\right) \sum_N \left(\boldsymbol{k}_2, {}^{N}\boldsymbol{0}, {}^{N}\boldsymbol{n}_2\right) \sum_N \left(\boldsymbol{k}_3, {}^{N}\boldsymbol{0}, {}^{N}\boldsymbol{n}_3\right) \\ &\quad \times c\left(\boldsymbol{k}_1, {}^{N}\boldsymbol{n}_1, {}^{N}\boldsymbol{B}_1\right)\ c\left(\boldsymbol{k}_2, {}^{N}\boldsymbol{n}_2, {}^{N}\boldsymbol{B}_2\right)\ c\left(\boldsymbol{k}_3, {}^{N}\boldsymbol{n}_3, {}^{N}\boldsymbol{B}_3\right) \\ &\quad \times \gamma\left({}^{N}\boldsymbol{P}, \left(\langle\boldsymbol{k}_1\rangle, \langle\boldsymbol{k}_2\rangle, \langle\boldsymbol{k}_3\rangle\right), \langle\boldsymbol{a}_N\rangle\right).\end{aligned} \tag{52}$$

This result constitutes a convenient expression to be computationally implemented. Basically, three NSSs hyperloops are to be codified, as it will be shown below, each one being attached to a specific position space coordinate and carrying the computation of the associated coefficients c.

The GTO collection appearing in Eq. (52) above: $\gamma\left({}^{N}\boldsymbol{P}, \left(\langle\boldsymbol{k}_1\rangle, \langle\boldsymbol{k}_2\rangle, \langle\boldsymbol{k}_3\rangle\right), \langle\boldsymbol{a}_N\rangle\right)$, which successively arise while the associated terms within the three NSSs are being generated, sweep all the combinatorial variations of quantum numbers by means of the three dimensional vector $(\langle \boldsymbol{k}_1 \rangle, \langle \boldsymbol{k}_2 \rangle, \langle \boldsymbol{k}_3 \rangle)$. This is so, because the expansion covers all the GTO orders from zero up to the sum of all the orders of the original N functions. If an explicit multilinear combination of functions has to be generated, it is possible to cumulate terms sharing the same sets of quantum numbers; that is: grouping the terms according to the order of the generated GTOs: s-type, p-type,... and so on.

Such a procedure is described in the following *Algorithm 1*:

Algorithm 1

1) Construct matrices (43) and (44) with the related column vectors.
2) Clear accumulator $C\left(0 : \left\langle {}^N\boldsymbol{n}_1 \right\rangle, 0 : \left\langle {}^N\boldsymbol{n}_2 \right\rangle, 0 : \left\langle {}^N\boldsymbol{n}_3 \right\rangle\right) = 0$.
3) Loop NSS #1: $\sum_N \left(\boldsymbol{k}_1, {}^N\boldsymbol{0}, {}^N\boldsymbol{n}_1\right)$
    4) Compute coefficient $c_1 = c\left(\boldsymbol{k}_1, {}^N\boldsymbol{n}_1, {}^N\boldsymbol{B}_1\right)$
    5) Loop NSS #2: $\sum_N \left(\boldsymbol{k}_2, {}^N\boldsymbol{0}, {}^N\boldsymbol{n}_2\right)$
        6) Compute coefficient $c_2 = c\left(\boldsymbol{k}_2, {}^N\boldsymbol{n}_2, {}^N\boldsymbol{B}_2\right)$
        7) Loop NSS #3: $\sum_N \left(\boldsymbol{k}_3, {}^N\boldsymbol{0}, {}^N\boldsymbol{n}_3\right)$
            8) Compute coefficient $c_3 = c\left(\boldsymbol{k}_3, {}^N\boldsymbol{n}_3, {}^N\boldsymbol{B}_3\right)$
            9) $C(\langle \boldsymbol{k}_1 \rangle, \langle \boldsymbol{k}_2 \rangle, \langle \boldsymbol{k}_3 \rangle) \leftarrow C(\langle \boldsymbol{k}_1 \rangle, \langle \boldsymbol{k}_2 \rangle, \langle \boldsymbol{k}_3 \rangle) + c_1 c_2 c_3$
        10) End Loop #3
    11) End Loop #2
12) End Loop #1
13) $C(:, :, :) \leftarrow \kappa C(:, :, :)$

As it is shown in references [23–28], the product of three NSSs of dimension N, results in another NSS of dimension $3N$. The new NSS is constructed by the direct sum of all the involved vector arguments. Thus, expression (52) can be written in an even more compact fashion as:

$$\prod_{i=1}^{N} \gamma(\boldsymbol{A}_i, \boldsymbol{n}_i, \alpha_i) = \kappa \sum\nolimits_{3N} \left(\boldsymbol{k}_1 \oplus \boldsymbol{k}_2 \oplus \boldsymbol{k}_3, {}^{3N}\boldsymbol{0}, {}^N\boldsymbol{n}_1 \oplus {}^N\boldsymbol{n}_2 \oplus {}^N\boldsymbol{n}_3\right) \\ \times c\left(\boldsymbol{k}_1, {}^N\boldsymbol{n}_1, {}^N\boldsymbol{B}_1\right) c\left(\boldsymbol{k}_2, {}^N\boldsymbol{n}_2, {}^N\boldsymbol{B}_2\right) c\left(\boldsymbol{k}_3, {}^N\boldsymbol{n}_3, {}^N\boldsymbol{B}_3\right) \\ \times \gamma\left({}^N\boldsymbol{P}, (\langle \boldsymbol{k}_1 \rangle, \langle \boldsymbol{k}_2 \rangle, \langle \boldsymbol{k}_3 \rangle), \langle \boldsymbol{a}_N \rangle\right). \tag{53}$$

Equation (53) constitutes the algebraic expression of the GGPT: *an arbitrary product of Cartesian GTOs is a multilinear combination of a GTOs collection*, centered at the same point of space:${}^N\mathbf{P}$, with common exponential scaling factor $\langle \boldsymbol{a}_N \rangle$, and sweeping all the possible orders from zero up to $\sum_{i=1}^{N} \langle \boldsymbol{n}_i \rangle$.

Taking into account the body of the GGPT and the *Algorithm 1*, once the coefficients set $\{C(i, j, k)\}$ is computationally known, the practical way to implement expression (53) will simply consist into setting up three summation symbols, which can be written by means of the simplified expression:

$$\prod_{i=1}^{N} \gamma\left(\boldsymbol{A}_i, \boldsymbol{n}_i, \alpha_i\right) = \kappa \sum_{i=0}^{\langle^N \boldsymbol{n}_1\rangle} \sum_{j=0}^{\langle^N \boldsymbol{n}_2\rangle} \sum_{k=0}^{\langle^N \boldsymbol{n}_3\rangle} C\left(i, j, k\right)\ H\left({}^N\boldsymbol{P}, (i, j, k), \boldsymbol{r}\right) e^{-\langle \boldsymbol{a}_N\rangle \left|\boldsymbol{r}-{}^N\boldsymbol{P}\right|^2} \quad (54)$$

8 Implementation of the involved NSSs

In references [18,23–28] it is indicated how to easily implement a NSS in high level programming languages. This feature allows the codification of expression (49) in a compact manner. For the sake of completeness and in order to provide with an example the present GGPT formulation, the following pseudocode describes how to codify in Fortran 90 a NSS like: $\sum_N \left(\boldsymbol{k}, {}^N\boldsymbol{0}, {}^N\boldsymbol{n}\right)$. The code asks for the dimension N, generates the needed vectors (here, the considered quantum numbers are given as an example) and launches the application which, in turn, can have as parameters the same aforementioned vectors.

```
integer Ng ! Number of Gaussian functions
integer, allocatable :: k(:),n(:)
integer L
read(*,*) Ng
allocate(k(Ng),n(Ng))
! Quantum numbers. An example:
n(:) = 2 ! All are d-functions in one dimension
! NSS procedure
L = Ng
k(:) = 0
k(Ng) = −1
do while (L > 0)
   k(L) = k(L) + 1
   if (k(L) > n(L)) then
      k(L) = 0
      L = L − 1
   else ! Executes the application
      call Application(k,n,Ng)
      L = Ng
   end if
end do
deallocate(k,n)
END
```

The nest of three NSSs, like the one needed to codify *Algorithm 1* as defined above, can be schematically programmed as follows:

```
integer Ng ! Number of Gaussian functions
integer, allocatable :: k1(:),k2(:),k3(:)
integer, allocatable :: n1(:),n2(:),n3(:)
integer L1,L2,L3

read(*,*) Ng

allocate(k1(Ng),k2(Ng),k3(Ng))
allocate(n1(Ng),n2(Ng),n3(Ng))

! Quantum numbers
n1(:) = 1 ! An example:
n2(:) = 1 ! All are f-type GTO functions
n3(:) = 1 !

! NSS1 procedure
L1 = Ng
k1(:) = 0
k1(Ng) = −1
do while (L1 > 0)
   k1(L1) = k1(L1) + 1
   if (k1(L1) > n1(L1)) then
      k1(L1) = 0
      L1 = L1 − 1
   else ! Executes the application inside NSS1

      ! NSS2 procedure
      L2 = Ng
      k2(:) = 0
      k2(Ng) = −1
      do while (L2 > 0)
         k2(L2) = k2(L2) + 1
         if (k2(L2) > n2(L2)) then
            k2(L2) = 0
            L2 = L2 − 1
         else ! Executes the application inside NSS2

            ! NSS3 procedure
            L3 = Ng
            k3(:) = 0
            k3(Ng) = −1
            do while (L3 > 0)
               k3(L3) = k3(L3) + 1
               if (k3(L3) > n3(L3)) then
                  k3(L3) = 0
                  L3 = L3 − 1
               else ! Executes the application inside NSS3

                  call Application(k1,k2,k3,n1,n2,n3,Ng)

                  L3 = Ng ! Closes NSS3
               end if
            end do
```

```
            L2 = Ng ! Closes NSS2
         end if
      end do

      L1 = Ng ! Closes NSS1
   end if
end do

deallocate(k1,k2,k3,n1,n2,n3)

END
```

9 Conclusions

The well-known TGPT has been generalized by means of the GGPT for the product of an arbitrary number of Cartesian Gaussian functions. The obtained general formula constitutes an algebraic expression dealing with products of an arbitrary number of N GTO. Additionally, it has been shown how its computational implementation is feasible by means of the NSS operators. Such a possibility permits the parallel implementation of the codes within the NSS loops. The mathematical expressions and the schematic programming codes provided here furnish an easy way to compute general GTO product terms, as those appearing within the Molecular Quantum Similarity framework. Multiple GTOs overlap integral measures can be straightforwardly obtained and easily programmed as a result.

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