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# Geometrical constraints to reduce complexity in quantum molecular systems

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## PRESENTATION OF THE PROBLEM

The **energy of a molecule** is not the sum of the energies of its atomic components. Our aim is to compute an accurate approximation of this quantity based on an **electron pair model**, that is to say by using an **antisymmetric product of two-electron wave functions**, called "geminals". In this model, the total wave function  $\Psi_e = g_1 \wedge \dots \wedge g_n$  can also be described by a set of matrices  $C_k = (c_{i,j}^k)_{1 \leq i,j \leq m}$ , one for each geminal  $g_k = \sum_{1 \leq i,j \leq m} c_{i,j}^k \varphi_i \wedge \bar{\varphi}_j$ , where  $(\varphi_i)_{1 \leq i \leq m}$  (resp.  $(\bar{\varphi}_j)_{1 \leq j \leq m}$ ) is a basis orbital of spin  $+\frac{1}{2}$  (resp.  $-\frac{1}{2}$ ).

However, without further restrictions, such a model has a factorial computational complexity with the number of electrons determined by the calculation of geminal product overlaps and its applicability is therefore limited to small systems. We will introduce **generalized orthogonality constraints** between geminals to reduce the computational effort, without sacrificing the indistinguishability of the electrons.

## INTRODUCTION OF CONSTRAINTS FOR A SIMPLER ANSATZ

We will consider wave functions which are products of  $n$  singlet or triplet geminals (i.e. with symmetric or antisymmetric associated matrices) and we will impose to our geminals  $g_k$ 's the so-called **permutationally invariant 2-orthogonality constraints** :

$$\forall i, j, k \in \{1, \dots, n\} \text{ distinct, } \begin{cases} \langle g_i | g_j \rangle = 0 \\ g_k \perp (g_i \wedge g_j) = 0 \end{cases} \text{ i.e. in terms of matrices : } \begin{cases} \text{tr}(C_i^\dagger C_j) = 0 \\ C_i C_k^\dagger C_j + C_j C_k^\dagger C_i = 0 \end{cases}$$

► The "maximal" linearly independent family of  $2 \times 2$  matrices verifying these conditions is :

$$I_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad i\sigma_y = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix},$$

where  $\sigma_x, \sigma_y$  and  $\sigma_z$  are the *Pauli matrices*.

## GENERAL GEMINAL PRODUCT OVERLAP FORMULA

**Theorem 1 :** For  $k \in \{1, \dots, n\}$ , let  $g_k$  and  $g'_k$  be geminals whose associated matrices are denoted respectively  $C_k$  and  $C'_k$ . The overlap between the wave functions  $\Psi_e = g_1 \wedge \dots \wedge g_n$  and  $\Psi'_e = g'_1 \wedge \dots \wedge g'_n$  is given by the formula :

$$\langle \Psi_e | \Psi'_e \rangle = \langle g_1 \wedge \dots \wedge g_n | g'_1 \wedge \dots \wedge g'_n \rangle = \sum_{\substack{0 \leq N_{n,0}, \dots, N_{n,n} \leq n \\ \sum_{i=0}^n N_{n,i} = \sum_{i=0}^n i N_{n,i} = n}} (-1)^{N_{n,0}} \sum_{\sigma, \sigma' \in \mathfrak{S}_n} \prod_{i=1}^n \frac{T_{N_{n,0}, \dots, N_{n,i-1}}^{N_{n,i}}(\sigma, \sigma')}{i^{N_{n,i}} N_{n,i}!}$$

with :

$$T_{N_{n,0}, \dots, N_{n,i-1}}^{N_{n,i}}(\sigma, \sigma') = \text{tr} \left[ C_{\sigma(\sum_{p=0}^{i-1} p N_{n,p+(j-1)i+1})}^\dagger C'_{\sigma'(\sum_{p=0}^{i-1} p N_{n,p+(j-1)i+1})} \dots C_{\sigma(\sum_{p=0}^{i-1} p N_{n,p+ji})}^\dagger C'_{\sigma'(\sum_{p=0}^{i-1} p N_{n,p+ji})} \right]$$

**Example ( $n = 3$ ) :** We compute  $\langle g_1 \wedge g_2 \wedge g_3 | g'_1 \wedge g'_2 \wedge g'_3 \rangle = A_1 + A_2 + A_3$ , as follow :

$$\begin{aligned} \blacktriangleright 3=0+0+3 : N_{3,0} = 2, N_{3,1} = 0, N_{3,2} = 0, N_{3,3} = 1 \rightsquigarrow A_1 &= \sum_{\sigma, \sigma' \in \mathfrak{S}_3} \frac{\text{tr} \left[ C_{\sigma(1)}^\dagger C'_{\sigma'(1)} C_{\sigma(2)}^\dagger C'_{\sigma'(2)} C_{\sigma(3)}^\dagger C'_{\sigma'(3)} \right]}{3} \\ \blacktriangleright 3=0+1+2 : N_{3,0} = 1, N_{3,1} = 1, N_{3,2} = 1, N_{3,3} = 0 \rightsquigarrow A_2 &= - \sum_{\sigma, \sigma' \in \mathfrak{S}_3} \frac{\text{tr} \left[ C_{\sigma(1)}^\dagger C'_{\sigma'(1)} \right] \text{tr} \left[ C_{\sigma(2)}^\dagger C'_{\sigma'(2)} C_{\sigma(3)}^\dagger C'_{\sigma'(3)} \right]}{2} \\ \blacktriangleright 3=1+1+1 : N_{3,0} = 0, N_{3,1} = 3, N_{3,2} = 0, N_{3,3} = 0 \rightsquigarrow A_3 &= \sum_{\sigma, \sigma' \in \mathfrak{S}_3} \frac{\text{tr} \left[ C_{\sigma(1)}^\dagger C'_{\sigma'(1)} \right] \text{tr} \left[ C_{\sigma(2)}^\dagger C'_{\sigma'(2)} \right] \text{tr} \left[ C_{\sigma(3)}^\dagger C'_{\sigma'(3)} \right]}{6} \end{aligned}$$

## EXPRESSION OF THE OVERLAP FOR A SIMPLIFIED MODEL

**Model :** By considering integers  $h_0 = 0 < h_1 < \dots < h_n$ , each matrix  $C_k$  (associated to  $g_k$ ) consists of a 1-orthogonal diagonal part of size  $h_n \times h_n$  where only the coefficients of lines and columns  $h_{k-1} + 1, \dots, h_k$  are nonzero, and of blocks  $\lambda_k^j B_k^j$  of size  $2 \times 2$  each proportionnal to  $I_2, \sigma_x, i\sigma_y$  or  $\sigma_z$  :

$$C_k = \begin{pmatrix} D_k & & & \\ & \lambda_k^1 B_k^1 & & \\ & & \ddots & \\ & & & \lambda_k^{m'} B_k^{m'} \end{pmatrix} \quad \text{with} \quad D_k = \begin{pmatrix} 0_{h_{k-1}} & & & \\ & \lambda_k^{-(h_{k-1}+1)} & & \\ & & \ddots & \\ & & & \lambda_k^{-h_k} \\ & & & & 0_{h_n-h_k} \end{pmatrix}$$

The number of  $2 \times 2$  blocks is  $m' = \frac{m-h_n}{2} \in \mathbb{N}$ .

For all  $j$ , there is no more than one nonzero  $\lambda_k^j$  for each type of block ( $I_2, \sigma_x, i\sigma_y, \sigma_z$ ). Moreover, each  $C'_k$  has the same matrix form as  $C_k$  (same types of blocks and zeros at the same places).

**Theorem 2 :** Let  $g_1, \dots, g_n$  and  $g'_1, \dots, g'_n$  be geminals verifying our constrained model conditions. We have :

$$\langle g_1 \wedge \dots \wedge g_n | g'_1 \wedge \dots \wedge g'_n \rangle = \sum_{\substack{0 \leq j_1, \dots, j_n \leq m' \\ \text{distinct if nonzero}}} \zeta_{g_1, g'_1}^{j_1} \dots \zeta_{g_n, g'_n}^{j_n}, \quad \text{with} \quad \zeta_{g_u, g'_u}^j = \begin{cases} \sum_{t=h_{u-1}+1}^{h_u} \bar{\lambda}_u^{-t} \lambda_u^{-t} & \text{if } j = 0 \\ 2 \bar{\lambda}_u^j \lambda_u^j & \text{otherwise} \end{cases}$$

## SCALING OF THE OVERLAP FORMULA FOR $H_m$ LINEAR CHAINS

$H_m$ molecules	$H_6$	$H_8$	$H_{10}$	$H_{12}$	$H_{14}$	$H_{16}$
( $n$ , number of partitions of $n$ )	(3, 3)	(4, 5)	(5, 7)	(6, 11)	(7, 15)	(8, 22)
Number of terms in the sum ( $= (n!)^2$ )	36	576	14 400	518 400	25 401 600	1 625 702 400

The computational cost rises too fast and makes the general model unpractical.

## SCALING OF THE CONSTRAINED MODEL FOR $H_m$ LINEAR CHAINS

$H_m$ molecules	$H_6$	$H_8$	$H_{10}$	$H_{12}$	$H_{14}$	$H_{16}$
( $n, h_n, m'$ )	(3, 4, 1)	(4, 4, 2)	(5, 6, 2)	(6, 6, 3)	(7, 8, 3)	(8, 8, 4)
Number of terms in the sum	4	21	22	95	100	441

The cost is reduced, but we need to check that the constrained model physical accuracy is still acceptable.