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Geometrical constraints to reduce complexity in quantum molecular systems

Thomas Perez[1], Patrick Cassam-Chenaï[1]

[1] Laboratoire J. A. Dieudonné, UMR 7351 UCA-CNRS, Nice (tperez@unice.fr, cassam@unice.fr)

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 $\Psi_e = g_1 \wedge \cdots \wedge g_n$ can also be described by a set of matrices $C_k = \left(c^k_{i,j}\right)_{1\le i,j\le m}$, one for each geminal $g_k = \sum_{1\le i,j\le m} c^k_{i,j}\, \varphi_i \wedge \overline{\varphi_j}$, where $(\varphi_i)_{1\le i\le m}$ (resp. $(\overline{\varphi_j})_{1\le j\le m}$) 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.

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 $\Psi_e = g_1 \wedge \cdots \wedge g_n$ and $\Psi'_e = g'_1 \wedge \cdots \wedge g'_n$ is given by the formula :*

$$\langle \Psi_e | \Psi'_e \rangle = \langle g_1 \wedge \cdots \wedge g_n | g'_1 \wedge \cdots \wedge g'_n \rangle = \sum_{\substack{0\le N_{n,0},\dots,N_{n,n}\le n \\ \sum_{i=0}^{n} N_{n,i} = \sum_{i=0}^{n} i N_{n,i} = n}} (-1)^{N_{n,0}} \sum_{\sigma,\sigma'\in\mathfrak{S}_n} \prod_{i=1}^{n} \frac{\prod_{j=1}^{N_{n,i}} T^{N_{n,i}}_{N_{n,0},\dots,N_{n,i-1}}(\sigma,\sigma')}{i^{N_{n,i}}\, N_{n,i}!}$$

with :

$$T^{N_{n,i}}_{N_{n,0},\dots,N_{n,i-1}}(\sigma,\sigma') = \mathrm{tr}\Big[C^{\dagger}_{\sigma\left(\sum_{p=0}^{i-1} pN_{n,p}+(j-1)i+1\right)} C'_{\sigma'\left(\sum_{p=0}^{i-1} pN_{n,p}+(j-1)i+1\right)} \cdots C^{\dagger}_{\sigma\left(\sum_{p=0}^{i-1} pN_{n,p}+ji\right)} C'_{\sigma'\left(\sum_{p=0}^{i-1} pN_{n,p}+ji\right)}\Big] .$$

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 :

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

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.

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* :

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

- The "maximal" linearly independent family of 2×2 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 σ_x, σ_y and σ_z are the *Pauli matrices*.

Expression of the overlap for a simplified model

Model : By considering integers $h_0 = 0 < h_1 < \cdots < h_n$, 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 $\lambda^j_k\, B^j_k$ of size 2×2 each proportionnal to $I_2, \sigma_x, i\sigma_y$ or σ_z :

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

The number of 2×2 blocks is $m' = \frac{m-h_n}{2} \in \mathbb{N}$.
For all j, there is no more than one nonzero λ^j_k 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 :*

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

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.