Graded Orthogonality for Fermionic States

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Nice, October 2007
Notation-1

- $\mathcal{H}$ : Hilbert space of one-electron functions, spanned by a set of spin-orbitals $(\psi_i)_i$

- $\wedge^n\mathcal{H}$ : Hilbert space of $n$-electron antisymmetric functions, spanned by the Slater determinantal functions $(\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_n})_{(i_1<i_2<\cdots<i_n)}$

- $\wedge\mathcal{H}$ : Fermionic Fock space

$$\wedge\mathcal{H} := \bigoplus_{n\geq 0} \wedge^n\mathcal{H}$$

- $\wedge^{n_1}\mathcal{H} \otimes \cdots \otimes \wedge^{n_k}\mathcal{H}$ : Hilbert space of partially antisymmetric functions for $k$ distinguishable groups of electrons of respectively $n_1, \ldots, n_k$ electrons
For any \( n \)-particle wave function, \( \Phi := \sum_{I := (i_1 < \ldots < i_n)} c_I \psi_{i_1} \land \cdots \land \psi_{i_n} \),

and any ordered sequence of length \( p \), \( K := (k_1 < \ldots < k_p) \in \mathcal{P}_{n,p} \), with \( p \in \{0, \ldots, n\} \), \( 1 \leq k_j \leq n \),

we set,

\[
\cdots (\Phi)_K \cdots (\Phi)_{\bar{K}} \cdots := \rho_{K,\bar{K}} \sum_{I := (i_1 < \ldots < i_n)} c_I \cdots (\psi_{i_{k_1}} \land \cdots \land \psi_{i_{k_p}}) \cdots (\psi_{i_{k_1}} \land \cdots \land \psi_{i_{k_{n-p}}}) \cdots
\]

where \( \bar{K} := (\bar{k}_1 < \ldots < \bar{k}_{n-p}) \), complement of \( K \) in \( (1 < 2 < \cdots < n) \), \( \rho_{K,\bar{K}} \) is the sign of the permutation reordering the concatenated sequence \( K // \bar{K} \) in increasing order; if the length, \( |K| \), of \( K \) is 0 then, by convention, \( (\Phi)_K := (\Phi)_\emptyset = 1 \), and \( \rho_{\emptyset,(1<\ldots<n)} = 1 \); note that, \( (\Phi)_{(1<\ldots<n)} = \Phi \).
Grassmann’s exterior product:

\[ X : \wedge H \otimes \wedge H \mapsto \wedge H \]
\[ \Phi \otimes \Psi \mapsto X(\Phi \otimes \Psi) = \Phi \wedge \Psi \]

The fermionic symmetry is built-in in this exterior algebra because of the following antisymmetry relation between exterior products of 1-particle functions:

\[ X(\phi \otimes \psi) = \phi \wedge \psi = -\psi \wedge \phi = -X(\psi \otimes \phi) \]

which entirely determines the behavior of an \( n \)-fermion wave function under the symmetric group \( S_n \). That is to say, for an \( n \)-fermion single configuration:

\[ \psi_1 \wedge \cdots \wedge \psi_n = (-1)^{|\sigma|}\psi_{\sigma(1)} \wedge \cdots \wedge \psi_{\sigma(n)} \]
Conjugate interior products:

\[ \forall \Theta \in \wedge^{n-p} \mathcal{H}, \forall \Psi \in \wedge^p \mathcal{H}, \forall \Phi \in \wedge^n \mathcal{H}, \]

- “left-interior product” \( \langle \Theta | \Psi \leftrightarrow \Phi \rangle = \langle \Psi \wedge \Theta | \Phi \rangle \)
- “right-interior product” \( \langle \Theta | \Phi \leftrightarrow \Psi \rangle = \langle \Theta \wedge \Psi | \Phi \rangle \)
- “anti-commutativity” \( \Psi \leftrightarrow \Phi = (-1)^{p(n-p)} \Phi \leftrightarrow \Psi \)
- explicit formula

\[ \Psi \leftrightarrow \Phi = \sum_{K \in \mathcal{P}_{n,p}} \langle \Psi | \Phi_K \rangle \cdot \Phi_{\bar{K}} \]

- or for mono-configuration functions (Slater determinants)

\[ (\psi_1 \wedge \cdots \wedge \psi_p) \leftrightarrow (\phi_1 \wedge \cdots \wedge \phi_n) = \sum_{K \in \mathcal{P}_{n,p}} \rho_{K,\bar{K}} \det(\langle \psi_i | \phi_{k_j} \rangle)_{i,j \leq p} \phi_{\bar{k}_1} \wedge \cdots \wedge \phi_{\bar{k}_{n-p}} \]
### 1-internal space of a wave function

**Definition:**

\[
\mathcal{I}^1[\Psi] = \{ \omega \in \mathcal{H}, \exists \Phi \in \wedge^{n-1} \mathcal{H}, \Phi \leftarrow \Psi = \omega \}
\]

**Example:**

\[
\Psi_e = \frac{1}{4} \{ \psi_1^\alpha \wedge \psi_3^\alpha \wedge \psi_5^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \psi_3^\alpha \wedge \psi_6^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
\phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
\phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
\phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
\phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
\phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
\phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
\phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta \}
\]

\[
\mathcal{I}^1[\Psi_e] = \mathbb{C}(\psi_1^\alpha := \frac{1}{\sqrt{2}}(\phi_1^\alpha + \phi_2^\alpha), \psi_1^\beta := \frac{1}{\sqrt{2}}(\phi_1^\beta + \phi_2^\beta), \phi_3^\alpha, \phi_3^\beta, \phi_4^\alpha, \phi_4^\beta, \phi_5^\alpha, \phi_6^\alpha)
\]
Other characterizations

• Smallest one-electron Hilbert-subspace allowing one to express $\Psi$:

$$\forall V \subseteq \mathcal{H}, \Psi \in \wedge^n V, \mathcal{I}^1[\Psi] \subseteq V$$

Application: compact expressions

$$\Psi_e = \frac{1}{2} \psi^\alpha_1 \wedge \psi^\beta_1 \wedge (\phi^\alpha_3 \wedge \phi^\alpha_5 \wedge \phi^\beta_3 + \phi^\alpha_3 \wedge \phi^\alpha_6 \wedge \phi^\beta_4 + \phi^\alpha_4 \wedge \phi^\alpha_6 \wedge \phi^\beta_3 + \phi^\alpha_4 \wedge \phi^\alpha_5 \wedge \phi^\beta_4).$$

• One-electron Hilbert-subspace spanned by the occupied natural spin-orbitals of $\Psi$:

Application: case of open-shell wave function, eigenfunction of $S^2$, but where the natural spin $\frac{1}{2}$ orbitals have are distinct spatial parts from those of the natural spin $-\frac{1}{2}$ orbitals

$\Rightarrow$ There exists a basis set of internal spin-orbitals such that for each spin $\frac{1}{2}$ orbital there is a spin $-\frac{1}{2}$ orbital with same spatial part.
The Complete Active Space Self-Consistent Field Method (CASSCF)

- A UCASSCF calculation with \( m \) active orbitals (and no inactive occupied) consists in finding the stationary points of the energy functional
  \[
  E(\Psi) = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}
  \]
  with the constraint that \( \text{dim} \mathcal{I}_{\Psi} \leq m \) i.e. within
  \[
  \{ \Psi \in \mathcal{F} | \forall \Phi_0, \ldots, \Phi_{m-n} \in \mathcal{F}_{n-1}, (\Phi_0 \leftarrow \Psi) \land \cdots \land (\Phi_{m-n} \leftarrow \Psi) \land \Psi = 0 \}.
  \]
  
  Example: Finite basis set of \( M \) spin-orbitals

  \[
  \forall H_0, \ldots, H_{m-n} \in \mathcal{P}_{M,n-1}, \forall G \in \mathcal{P}_{M,m+1}
  \]

  \[
  \sum_{(k_0<\cdots<k_{m-n}) \subseteq G, \{k_i\} \notin H_i} \rho(k_0,H_0 \cdots \rho(k_{m-n},H_{m-n}) \rho(k_0<\cdots<k_{m-n}),G \setminus (k_0<\cdots<k_{m-n})}
  \]

  \[
  c_{(k_0) \cup H_0 \cdots c_{(k_{m-n})} \cup H_{m-n}} c_{G \setminus (k_0<\cdots<k_{m-n})} = 0
  \]

- The case \( m = n \) with no spin constraint is the UHF method first developed by Prof. Berthier (and not Pople as found in textbooks).
Variational spaces of traditional methods

\[ \Phi = \phi^\alpha \Lambda \phi^\beta + \beta \phi^\alpha_1 \Lambda \phi^\beta_2 + \gamma \phi^\alpha_2 \Lambda \phi^\beta_1 + \delta \phi^\alpha_2 \Lambda \phi^\beta_2 \]

The three, real, parameters \( \beta, \gamma, \delta \) are considered as independent and varying on \( ] - \infty, +\infty[ \) and an axis is associated with each parameter. In the 3-dimensional space obtained, UHF wave functions satisfy:

\[ \beta \gamma = \delta, \]

which is clearly the equation of a set of hyperbolae. Singlet wave functions satisfy:

\[ \beta = \gamma. \]

Fig. 1. 2 electrons, 2 orbitals, \( S_z = 0 \). Each point in the cube corresponds to a multi-configuration, the centre of the cube \( O \) being the configuration \( \phi^\alpha \Lambda \phi^\beta \). The volume of the cube is the full unrestricted CI space, the hyperbolic surface \( (AOB'CD') \) is the UHF space. The plane \( (ADB'C) \) corresponds to the eigenfunctions of \( S^2 \) with \( S = 0 \) (singlet plane). The intersection between the UHF surface and the singlet plane gives the RHF curve \( (AOB') \).
**Strong orthogonality**

Let $\Psi_1$ be the wave functions of an $n_1$ electron group and $\Psi_2$ that of an $n_2$ electron group. $\Psi_1$ and $\Psi_2$ are said strongly orthogonal if and only if:

$$\forall \tau_2, \ldots, \tau_{n_1}, \tau'_2, \ldots, \tau'_{n_2}$$

$$\int d\tau_1 \Psi_1(\tau_1, \tau_2, \ldots, \tau_{n_1}) \Psi_2(\tau_1, \tau'_2, \ldots, \tau'_{n_2}) = \langle \delta_{\tau_2} \land \ldots \land \delta_{\tau_{n_1}} \leftrightarrow \Psi_1 | \delta_{\tau'_2} \land \ldots \land \delta_{\tau'_{n_2}} \leftrightarrow \Psi_2 \rangle = 0.$$  

Or by changing to a basis set representation $\{\phi_i\}_i$,

$$\langle \phi_{i_2} \land \ldots \land \phi_{i_{n_1}} \leftrightarrow \Psi_1 | \phi_{i'_2} \land \ldots \land \phi_{i'_{n_2}} \leftrightarrow \Psi_2 \rangle = 0 \quad \forall i_2, \ldots, i_{n_1}, i'_2, \ldots, i'_{n_2}.$$  

Since, the $(n_1 - 1)$-particle functions, $\phi_{i_2} \land \ldots \land \phi_{i_{n_1}}$, span all of $\wedge^{(n_1-1)}\mathcal{H}$, and the $(n_2 - 1)$-particle functions, $\phi_{i'_2} \land \ldots \land \phi_{i'_{n_2}}$, span all of $\wedge^{(n_2-1)}\mathcal{H}$, the latter equation is equivalent to orthogonality between any pair of 1-internal functions, that is to say:

$$\mathcal{I}^1[\Psi_1] \perp \mathcal{I}^1[\Psi_2]$$
\( p \)-internal space of a wave function

**Definition:**

\[
\mathcal{I}^p[\Psi] = \{ \omega \in \wedge^p \mathcal{H}, \exists \Phi \in \wedge^{n-p} \mathcal{H}, \Phi \leftrightarrow \Psi = \omega \}
\]

**Example:**

\[
\Psi = \psi_1 \wedge \psi_2 \wedge \psi_3 \wedge \psi_4 + \psi_1 \wedge \psi_2 \wedge \psi_5 \wedge \psi_6
\]

\[
\downarrow
\]

\[
dim \mathcal{I}^1[\Psi] = 6 \implies dim \wedge^2 \mathcal{I}^1[\Psi] = 15
\]

**BUT**

\[
\left\{
\begin{array}{l}
\psi_3 \wedge \psi_5, \psi_3 \wedge \psi_6, \psi_4 \wedge \psi_5, \psi_4 \wedge \psi_6 \implies 0 \\
\psi_3 \wedge \psi_4, \psi_5 \wedge \psi_6 \implies \text{linear dependencies}
\end{array}
\right.
\]

\[
\downarrow
\]

\[
dim \mathcal{I}^2[\Psi] = 10
\]
**p-orthogonality**

**Definition:**
Let $\Psi_1$ be the wave functions of an $n_1$ electron group and $\Psi_2$ that of an $n_2$ electron group. $\Psi_1$ and $\Psi_2$ are said *p-orthogonal* if and only if:

$$\mathcal{I}^p[\Psi_1] \perp \mathcal{I}^p[\Psi_2]$$

**Proposition (graded orthogonality):**
If two states represented by the wave functions $\Psi_1$ and $\Psi_2$ are $p$-orthogonal then they are *a fortiori* $q$-orthogonal for all $q$ such that, $\inf(n_1, n_2) \geq q \geq p$.

This justifies the term “strong orthogonality”
\p-orthogonality: Examples

Let \((\phi_i)_i\) be orthonormal spinorbitals.

**Example 1:** For integers, \(n \geq p > 0\), the pairs, \(\Psi_1 := \phi_1 \land \cdots \land \phi_{n-p} \land \phi_{n-p+1} \cdots \land \phi_n\) and \(\Psi_2 := \phi_1 \land \cdots \land \phi_{n-p} \land \phi_{n+1} \cdots \land \phi_{n+p}\), are \((n - p + 1)\)-orthogonal but not \((n - p)\)-orthogonal since for \(\Phi_1 := \phi_{n-p+1} \land \cdots \land \phi_n\) and \(\Phi_2 := \phi_{n+1} \land \cdots \land \phi_{n+p}\),

\[
\langle \Phi_1 \leftarrow \Psi_1 | \Phi_2 \leftarrow \Psi_2 \rangle = \langle \phi_1 \land \cdots \land \phi_{n-p} | \phi_1 \land \cdots \land \phi_{n-p} \rangle = 1
\]

is non zero, although \((\Phi_i \leftarrow \Psi_i) \in \mathcal{I}^{n-p}[\Psi_i]\), for \(i \in \{1, 2\}\), by definition.

**Example 2:**
The functions \(\Psi_1 := \phi_1 \land \phi_2 \land \phi_3 + \phi_4 \land \phi_5 \land \phi_6\) and \(\Psi_2 := \phi_1 \land \phi_7 + \phi_2 \land \phi_8\) are \(2\)-orthogonal (it is impossible to obtain \(\Psi_2\) by annihilating a spinorbital in \(\Psi_1\)) but not \(1\)-orthogonal since both \(\phi_1\) and \(\phi_2\) belongs to their one-internal space.
The Electronic Mean Field Configuration Interaction method

It consists in constructing successive, approximate, $n$-electron wave functions of the form:

$$\Psi = \Psi_1 \wedge \cdots \wedge \Psi_r,$$

where $\Psi_i \in \wedge^{n_i} \mathcal{H}$, with $\sum_i n_i = n$, by means of a configuration interaction calculation in a basis set of group functions $\{\Psi_1^i \wedge \Psi_2^0 \wedge \cdots \wedge \Psi_r^0\}_i$ i.e., the wave functions of the first group functions are optimized in the mean field of the ground states of the other groups.

- The process can be iterated by switching to another group until self-consistence is achieved.

- Or/then a coarser partition of the $n$ electron can be selected.
The Hopf algebra structure of $\wedge \mathcal{H}$

Exterior coproduct:

\[ \mathcal{Y} : \wedge \mathcal{H} \rightarrow \wedge \mathcal{H} \otimes \wedge \mathcal{H} \]
\[ \psi_1 \wedge \cdots \wedge \psi_n \mapsto \mathcal{Y}(\psi_1 \wedge \cdots \wedge \psi_n) = \sum_{I \in \mathcal{P}_n} \rho_{I,\bar{I}} \psi_{i_1} \wedge \cdots \wedge \psi_{i_p} \otimes \psi_{\bar{i}_1} \wedge \cdots \wedge \psi_{\bar{i}_{n-p}} \]

\[ \Psi \mapsto \mathcal{Y}(\Psi) = \sum_{I \in \mathcal{P}_n} \Psi_I \otimes \Psi_{\bar{I}}. \]

The idea behind the coproduct is to split an $n$-fermion single configuration function into a $p$ and an $(n - p)$-fermion single configuration functions in all possible ways, where $p$ ranges from 0 to $n$, the exterior product of the two parts so-obtained giving back the initial function, the sign of the reordering permutation being taken care of.

As an example, let us write down the formula for $\mathcal{Y}$ acting on a 3-fermion configuration,

\[ \mathcal{Y}(\psi_a \wedge \psi_b \wedge \psi_c) = \psi_a \wedge \psi_b \wedge \psi_c \otimes 1 + \psi_a \wedge \psi_b \otimes \psi_c - \psi_a \wedge \psi_c \otimes \psi_b + \psi_b \wedge \psi_c \otimes \psi_a + \psi_a \otimes \psi_b \wedge \psi_c - \psi_b \otimes \psi_a \wedge \psi_c + \psi_c \otimes \psi_a \wedge \psi_b + 1 \otimes \psi_a \wedge \psi_b \wedge \psi_c. \]
Hopf algebra fundamental relation

\[ \mathcal{Y} \circ \mathcal{X} = (\mathcal{X} \otimes \mathcal{X}) \circ (Id \otimes T \otimes Id) \circ (\mathcal{Y} \otimes \mathcal{Y}) \]

where \( T \) is the twisting map:

\[ T(\Psi \otimes \Phi) = (-1)^{pq} \Phi \otimes \Psi. \]

The fundamental Hopf algebra relation expresses the fact that the same decomposition of the product of two single configurations into a tensor product of 2 subconfigurations is obtained by applying the coproduct to the exterior product of the two single configurations, or alternatively, by first splitting each single configuration separately (\( \mathcal{Y} \otimes \mathcal{Y} \)), then grouping the first tensorial components of each decomposition together and the second components together (\( Id \otimes T \otimes Id \)), and finally by taking the exterior product of the first components on the one hand and the exterior product of the second components on the other hand (\( \mathcal{X} \otimes \mathcal{X} \)).
Convolution

\[ A \ast B := \mathcal{X} \circ (A \otimes B) \circ \mathcal{Y}. \]

Ex: the Coulomb repulsion between two electrons, \( V_{ee} = \frac{1}{|\vec{r}_1 - \vec{r}_2|} \), is a 2-electron operator acting on \( \wedge^2 \mathcal{H} \), the convolution with the identity induces an operator on \( \wedge \mathcal{H} \): \( V_{ee} \ast \text{Id} \)

Iterated products and coproducts

- **k**\(^{th}\) iterated product

  \[ \mathcal{X}^{[k]} := \mathcal{X} \circ (\mathcal{X}^{[k-1]} \otimes \text{Id}) , \]

  with \( \mathcal{X}^0 = \text{Id} \).

- **k**\(^{th}\) iterated coproduct

  \[ \mathcal{Y}^{[k]} := (\text{Id} \otimes \cdots \otimes \text{Id} \otimes \mathcal{Y}) \circ \mathcal{Y}^{[k-1]} , \]

  We specify further by \( \mathcal{Y}^{[k]}_{i_0, \ldots, i_k} \) the component of the iterated coproduct corresponding to the decomposition of an \( n \)-Fermion wave function into the tensor product of \( (k+1) \) wave functions of \( i_0, \ldots, i_k \)-particles respectively.
Generalised twist operator

\( T^{(p,q)} \), defined on the tensor product of \( p.q \), \((p \text{ and } q > 1)\), Fermionic Hilbert spaces, \( \wedge^{n_i} \mathcal{H} \), with fixed number of particles, \( n^j_i \), \( i \in 1, \cdots, p \) and \( j \in 1, \cdots, q \).

Let \( \Phi := \phi_1^1 \otimes \cdots \otimes \phi_p^1 \otimes \cdots \otimes \phi_1^q \otimes \cdots \otimes \phi_p^q \) be an element of \( \wedge^{n_1} \mathcal{H} \otimes \cdots \otimes \wedge^{n_q} \mathcal{H} \),

\[
T^{(p,q)}[\Phi] = \rho_{n_1, \ldots, n_p} \phi_1^1 \otimes \cdots \otimes \phi_1^q \otimes \cdots \otimes \phi_p^1 \otimes \cdots \otimes \phi_p^q
\]

where \( \rho_{n_1, \ldots, n_p} \) is the sign of the permutation which would reorder the tensorial components \( \phi_i^j \) in their initial order if we had exterior products in place of tensor products. More explicitly,

\[
\rho_{n_1, \ldots, n_p} = (-1)^{\sum_{i=1}^{p-1} \sum_{j=2}^{q} \sum_{k=i+1}^{p} \sum_{l=1}^{j-1} n_i^i n_k^j}.
\]

In particular, \( Id \otimes T \otimes Id = T^{(2,2)} \).
Generalised Hopf formula

The generalization of the Hopf algebra fundamental relation to the case of iterated product, \( \mathcal{X}^{[p-1]} \), \((p > 1)\), and coproduct, \( \mathcal{Y}^{[q-1]} \), \((q > 1)\), is,

\[
\mathcal{Y}^{[q-1]} \circ \mathcal{X}^{[p-1]} = \left( \mathcal{X}^{[p-1]} \otimes \cdots \otimes \mathcal{X}^{[p-1]} \right) \circ \mathcal{T}^{(q,p)} \circ \left( \mathcal{Y}^{[q-1]} \otimes \cdots \otimes \mathcal{Y}^{[q-1]} \right),
\]

or for a particular coproduct component,

\[
\mathcal{Y}^{[q-1]}_{n_1,\ldots,n_q} \circ \mathcal{X}^{[p-1]} = \sum_{n_i^j, \sum_{j=1}^p n_i^j = n_i} \left( \mathcal{X}^{[p-1]} \otimes \cdots \otimes \mathcal{X}^{[p-1]} \right) \circ \mathcal{T}^{(q,p)} \circ \left( \mathcal{Y}^{[q-1]}_{n_1,\ldots,n_q^1} \otimes \cdots \otimes \mathcal{Y}^{[q-1]}_{n_1^p,\ldots,n_q^p} \right).
\]

Laplace formula

\[
\langle \mathcal{X}(\Theta \otimes \Phi)|\Psi \rangle \equiv \langle \Theta \wedge \Phi|\Psi \rangle = \langle \Theta \otimes \Phi|\mathcal{Y}(\Psi) \rangle
\]
Calculation of matrix elements between group functions

\[ \langle \Phi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_q | (h_2 \ast Id)[\Psi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_q] \rangle \]

We set, \( \Delta_{q-1} := \Phi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_{q-1} \), \( \Psi := \Psi_1 \wedge \cdots \wedge \Gamma_q \), and re-write the matrix element as:

\[ \langle \Delta_{q-1} \wedge \Gamma_q | (h_2 \ast Id)[\Psi] \rangle = \sum'_{n_k} \langle \Delta_{q-1} \otimes \Gamma_q | (X \otimes X) \circ T^{(2,2)} \circ (Y_{n_1^n_2, n_2^n_2} \otimes Y_{n_1^n_1, n_1^n_2}) \circ (h_2 \otimes Id) \circ Y_{2, n-2}[\Psi] \rangle . \]

The constraints on the summation give rise to at most three terms:

- A term where the \( n_q \)-electron integral is an “\( h_2 \)”-type integral and the \( n - n_q \) electron integral is an overlap integral, when \( n_1^1 = 0; n_2^1 = n - n_q; n_2^1 = 2; n_2^2 = n_q - 2 \), provided that \( n_q \geq 2 \).
- A term where the \( n_q \)-electron integral is an overlap integral and the \( n - n_q \) electron integral is a “\( h_2 \)”-type integral, when \( n_1^1 = 2; n_2^1 = n - n_q - 2; n_2^1 = 0; n_2^2 = n_q \), provided that \( n - n_q \geq 2 \).
- A term where the \( h_2 \) integral is splitted accross the \( n_q \)-electron and the \( n - n_q \)-electron integrals, when \( n_1^1 = 1; n_2^1 = n - n_q - 1; n_2^1 = 1; n_2^2 = n_q - 1 \).
Calculation of matrix elements between \( q \)-orthogonal group functions

\[
\langle \Phi_1 \land \Phi_2 | \Psi_1 \land \Psi_2 \rangle = \langle \mathcal{X} [\Phi_1 \otimes \Phi_2] | \mathcal{X} [\Psi_1 \otimes \Psi_2] \rangle \quad \text{(by definition)}
\]

\[
= \langle \Phi_1 \otimes \Phi_2 | \mathcal{Y} \circ \mathcal{X} [\Psi_1 \otimes \Psi_2] \rangle \quad \text{(by Laplace formula)}
\]

\[
= \langle \Phi_1 \otimes \Phi_2 | (\mathcal{X} \otimes \mathcal{X}) \circ (Id \otimes T \otimes Id) \circ (\mathcal{Y} \otimes \mathcal{Y}) [\Psi_1 \otimes \Psi_2] \rangle
\]

\[
= \quad \text{(by Hopf algebra fundamental formula)}
\]

\[
\sum_{\substack{I^1, I^2 \\ |I^1|+|I^2|=n_1 \\ |I^1| \in \{n_1-q+1, \ldots, n_1\}}} (-1)^{|I^2| \cdot (n_1-|I^1|)} \langle \Phi_1 | (\Psi_1)_{I^1} \land (\Psi_2)_{I^2} \rangle \langle \Phi_2 | (\Psi_1)_{\bar{I}^1} \land (\Psi_2)_{\bar{I}^2} \rangle
\]

\( \Phi_1 \) q-orthogonal to \( \Psi_2 \) \( \implies \) \( \sum_{i=n_1-q+1}^{n_1} \binom{n_1}{i} \binom{n-n_1}{n_1-i} \) terms instead of \( \binom{n}{n_1} = \sum_{i=0}^{n_1} \binom{n_1}{i} \binom{n-n_1}{n_1-i} \).
Convergence of the EMFCI method

Ground state energies in Hartree for LiH
(6-31G*, full core calculations at 3.03642 au)

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<th>Step</th>
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<th>2</th>
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<tr>
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</tbody>
</table>

- HF energy: -7.98077 au.
- CCSD(T) energy: -8.00326.
- the antisymmetrized product of strongly orthogonal geminals (APSG) ansatz recovers only 33.5% of the CCSD(T) energy at the scf geometry (i.e. 3.03642 au) for the 6-311G** (5d orbitals) basis (Rosta and Surján, Int. J. Quant. Chem., 80, p.96, 2000).
### Accuracy of the NOG-SCF method

#### Lowest singlet energy levels of Beryllium in Hartree
(6-31G*, 6d calculations)

<table>
<thead>
<tr>
<th>state symmetry</th>
<th>Full CI (frozen core, 105 CSFs)</th>
<th>NOG-SCF (239 Coef.)</th>
<th>Full CI (4200 CSFs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1S</td>
<td>-14.613435</td>
<td>-14.616073</td>
<td>-14.616634</td>
</tr>
<tr>
<td>1P</td>
<td>-14.388909</td>
<td>-14.390291</td>
<td>-14.393112</td>
</tr>
<tr>
<td>1D</td>
<td>-14.311959</td>
<td>-14.312844</td>
<td>-14.316351</td>
</tr>
<tr>
<td>1S</td>
<td>-14.222495</td>
<td>-14.223317</td>
<td>-14.226960</td>
</tr>
<tr>
<td>1P</td>
<td>-14.144298</td>
<td>-14.145614</td>
<td>-14.148581</td>
</tr>
<tr>
<td>1S</td>
<td>-14.106706</td>
<td>-14.108337</td>
<td>-14.109614</td>
</tr>
<tr>
<td>1P</td>
<td>-14.038519</td>
<td>-14.039284</td>
<td>-14.043223</td>
</tr>
</tbody>
</table>

Coef.: Coefficients, CSFs: Configuration state functions.

The Electronic MFCI method dissociates properly
# Geminal-SCF and $p$-orthogonality

**Ground state energies in Hartree at ”experimental” geometry (STO-3G calculations)**

<table>
<thead>
<tr>
<th>System</th>
<th>Be</th>
<th>LiH</th>
<th>Li$_2$</th>
<th>BeH$_2$</th>
<th>BH</th>
</tr>
</thead>
</table>

---

$^a$Upper bound after a large number of iterations; second derivatives are not calculated, the fact that the algorithm reaches a minimum cannot be ascertained. ; Truncation threshold for quasi-linear dependency of geminal products: $10^{-5}$ (Be, LiH) or $10^{-6}$ (Li$_2$, BeH$_2$, BH). Canonical HF initial guess.

$^b$Two-orthogonality between each pair of ground state geminals.

$^c$In fact, best step 0 energy, which can be considered in general as the G-SCF calculation with strong orthogonality constraint (1-orthogonality) within the present algorithm. The best strongly orthogonal G-SCF ground state would require to optimize the partitioning of the orbital Hilbert space between the different groups.

$^d$From NIST website.
\textbf{*-orthogonality: Conclusions - 1}

- Graded measure of indistinguishability in the sense that two sets of identical particles that are \(q\)-orthogonal can be seen as “more indistinguishable” than two sets that are \(p\)-orthogonal if \(q > p\), because a larger subset of particles can possibly share (i.e. occupy) a substate, common (i.e. internal) to the quantum states of both sets.

- \(p\)-orthogonality can be used to remove some arbitrariness in the choice of a representation for a quantum system in the same manner as localization criteria do: By setting, \(g_i = \psi_i \land \bar{\psi}_i\) for all \(i\), an HF function can be expressed as:

\[
\Psi = g_1 \land g_2 \land \cdots \land g_n. \tag{1}
\]

or with \(g = (n!)^{-\frac{1}{n}}(\psi_1 \land \bar{\psi}_1 + \cdots + \psi_n \land \bar{\psi}_n)\), as:

\[
\Psi = g \land g \land \cdots \land g, \quad \text{\(n\) factors} \tag{2}
\]

Imposing 2-orthogonality between the two-fermion functions appearing in Eqs.(2) and (1) can discriminate between these two equivalent writings.
• The graded structure of $p$-orthogonality constraints naturally leads
one to consider a corresponding hierarchy of approximations for methods
based on general antisymmetric product functions.

Acknowledgements

We acknowledge the french ANR for fundings (Project AHBE) and the
SIGAMM Mesocentre for providing computer facilities. We are indebted
to Dr. F. Patras for helpful discussions, which have contributed to the
maturation of this work.