La boite à outils de l'algèbre extérieure pour le problème à N-corps fermionique

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Introduction:

The common mathematical challenge to Nuclear Physics, Quantum Chemistry and Condensed Matter Physics

Solve to the desired accuracy the eigenvalue equation,

$$H\ \Psi = E\ \Psi$$

for the Hamiltonian H of the nucleons of a nucleus, the electrons of a molecule or those of a condensed phase in the space of n-fermion wave functions, $\Psi \in \wedge^n \mathcal{H}$,

where $\mathcal{H}$ is a Hilbert space of the form:

$$\mathcal{H} := \mathcal{H}_o \otimes \mathcal{H}_s,$$

$\mathcal{H}_s \equiv \mathbb{C}^2$ and $\mathcal{H}_o$ a finite dimensional vector subspace of $L^2(\mathbb{R}^3)$

Scientific lineage

LE JOURNAL DE PHYSIQUE ET LE RADIUM. TOME 12, FÉVRIER 1951, PAGE 131.

SUR LA SECONDE QUANTIFICATION

Par JEAN G. VALATIN.
Institut Henri Poincaré, Paris (1).

Sommaire. — La seconde quantification est exposée pour un système de particules obéissant au principe d'exclusion, en caractérisant les tenseurs antisymétriques représentant l'état du système à l'aide des quantités de l'algèbre extérieure de Grassmann. Cette représentation des états conduit à l'introduction naturelle des opérateurs de création et d'annihilation de la seconde quantification, et fournit une méthode facilitant les calculs portant sur les états du système. L'équivalence des opérateurs correspondants de la méthode de l'espace de configuration et de la seconde quantification se présente d'une façon simple en comparant les expressions (7), (8), (35), (38 *b*) et (40). On peut ainsi éviter l'examen laborieux des changements de signe. Les équations vectorielles correspondantes explicitent cette équivalence et illustrent les règles de calcul des opérateurs et des états.

Outline

- p-internal space
- p-orthogonality
- p-forbidden space

Notation

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

$\rightsquigarrow$ fermionic creation and annihilation operators $a_i^\dagger, a_i$:

$$|\psi_i\rangle = a_i^\dagger|0\rangle,\ \langle\psi_i| = \langle 0|a_i,\ [a_i, a_j^\dagger]_+ = \delta_{i,j}$$

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

any p-particle wave function can be expanded as $\Phi := \sum_{I:=(i_1<\ldots<i_n)} c_I\ \psi_{i_1} \wedge \cdots \wedge \psi_{i_p}$,

$\rightsquigarrow$ extended second quantization notation : $|\Phi\rangle = a^\dagger(\Phi)|0\rangle$

$$a^\dagger(\Phi) = \sum_{I:=(i_1<\ldots<i_p)} c_I\ a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_p}^\dagger\ ,\ a(\Phi) = \sum_{I:=(i_1<\ldots<i_p)} c_I^*\ a_{i_p} \cdots a_{i_2} a_{i_1}$$

$a^\dagger(\psi_i) = a_i^\dagger$, $a^\dagger(\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_p}) = a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_p}^\dagger$, $a(\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_p}) = a_{i_p} \cdots a_{i_2} a_{i_1}$,

p-internal space of a wave function

Definition: $\forall \Psi \in \wedge^n \mathcal{H}$

$$\mathcal{I}^p[\Psi] = \{\Omega \in \wedge^p \mathcal{H}, \exists \Phi \in \wedge^{n-p} \mathcal{H}, a(\Phi)|\Psi\rangle = |\Omega\rangle\}$$

p-external space of a wave function

Definition: $\forall \Psi \in \wedge^n \mathcal{H}$

$$\mathcal{E}^p[\Psi] = \mathcal{I}^p[\Psi]^\perp = \{\Omega \in \wedge^p \mathcal{H}, a(\Omega)|\Psi\rangle = 0\}$$

$$dim\mathcal{H} = m \Rightarrow dim \wedge^p \mathcal{H} = \binom{m}{p} \Rightarrow dim\mathcal{I}^p[\Psi] + dim\mathcal{E}^p[\Psi] = \binom{m}{p}$$

Examples

Example 1:

$$|\Psi\rangle = |\psi_1 \wedge \psi_2 + \psi_4 \wedge \psi_3 + \psi_1 \wedge \psi_3 + \psi_4 \wedge \psi_2\rangle = a_1^\dagger a_2^\dagger|0\rangle + a_4^\dagger a_3^\dagger|0\rangle + a_1^\dagger a_3^\dagger|0\rangle + a_4^\dagger a_2^\dagger|0\rangle$$

$$dim\mathcal{H} = 4,\ dim\mathcal{E}^1[\Psi] = 2,\ dim\mathcal{I}^1[\Psi] = 2,\ \mathcal{I}^1[\Psi] = \mathbb{C}(\psi_1+\psi_4) \oplus \mathbb{C}(\psi_2+\psi_3)$$

$$|\Psi\rangle = |(\psi_1 + \psi_4) \wedge (\psi_2 + \psi_3)\rangle = (a_1^\dagger + a_4^\dagger)(a_2^\dagger + a_3^\dagger)|0\rangle$$

Example 2:

$$|\Psi\rangle = |\psi_1 \wedge \psi_2 \wedge \psi_3 \wedge \psi_4 + \psi_1 \wedge \psi_2 \wedge \psi_5 \wedge \psi_6\rangle = a_1^\dagger a_2^\dagger a_3^\dagger a_4^\dagger|0\rangle + a_1^\dagger a_2^\dagger a_5^\dagger a_6^\dagger|0\rangle$$

$$dim\mathcal{H} = dim\mathcal{I}^1[\Psi] = 6 \quad \Rightarrow \quad dim \wedge^2 \mathcal{I}^1[\Psi] = \binom{6}{2} = 15$$

$$a(\psi_3 \wedge \psi_5), a(\psi_3 \wedge \psi_6), a(\psi_4 \wedge \psi_5), a(\psi_4 \wedge \psi_6), a(\psi_3 \wedge \psi_4 - \psi_5 \wedge \psi_6)|\Psi\rangle = 0$$

$$dim\mathcal{E}^2[\Psi] = 5 \qquad dim\mathcal{I}^2[\Psi] = 10$$

Variational methods

Minimize the energy functionnal $E(\Phi) = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle}$ with $\Phi \in \wedge^n\mathcal{H}$ plus some additional constraints

- Ex.: spin unrestricted - CASSCF(n,p):

Minimize the energy functionnal $E(\Phi) = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle}$ with $dim\mathcal{I}^1[\Phi] \leq p$.

$*$ Case $p = dim\mathcal{H}$: Full Configuration Interaction (FCI) method
additional constraint $= \varnothing$.
$*$ Case $p = n$: Unrestricted Hartree-Fock (UHF) method
additional constraint: Φ of the single Slater determinantal form: $\Phi = a^\dagger(\phi_1)a^\dagger(\phi_2)\cdots a^\dagger(\phi_n)|0\rangle$, $\forall i, \phi_i \in \wedge^1\mathcal{H} \equiv \mathcal{H}$.

- Ex. Geminal Self-Consistent Field (GSCF) method:

Minimize the energy functionnal $E(\Phi) = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle}$ with Φ of the non-orthogonal geminal product form: $\Phi = a^\dagger(\Gamma_1)a^\dagger(\Gamma_2)\cdots a^\dagger(\Gamma_{\frac{n}{2}})|0\rangle$, $\forall i, \Gamma_i \in \wedge^2\mathcal{H}$.

p-orthogonality: Definition

Definition:

Let Ψ_1 be the wave functions of an n_1-particle group and Ψ_2 that of an n_2-particle group. Ψ_1 and Ψ_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 Ψ_1 and Ψ_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" used for one-orthogonality

p-orthogonality: Examples

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

Example 1: For integers, $n \geq p > 0$, the pairs,

$$\Psi_1 := \phi_1 \wedge \cdots \wedge \phi_{n-p} \wedge \phi_{n-p+1} \cdots \wedge \phi_n$$

and

$$\Psi_2 := \phi_1 \wedge \cdots \wedge \phi_{n-p} \wedge \phi_{n+1} \ldots \wedge \phi_{n+p},$$

are $(n-p+1)$-orthogonal but not $(n-p)$-orthogonal since for $\Phi_1 := \phi_{n-p+1} \wedge \ldots \wedge \phi_n$ and $\Phi_2 := \phi_{n+1} \wedge \ldots \wedge \phi_{n+p}$, $\langle a(\Phi_1)\Psi_1 | a(\Phi_2)\Psi_2 \rangle = \langle \phi_1 \wedge \ldots \wedge \phi_{n-p} | \phi_1 \wedge \ldots \wedge \phi_{n-p} \rangle = 1$ is non zero, although $(a(\Phi_i)\Psi_i) \in \mathcal{I}^{n-p}[\Psi_i]$, for $i \in \{1, 2\}$, by definition.

Example 2:

$\Psi_1 := \phi_1 \wedge \phi_2 \wedge \phi_3 + \phi_4 \wedge \phi_5 \wedge \phi_6$ and $\Psi_2 := \phi_1 \wedge \phi_7 + \phi_2 \wedge \phi_8$ are 2-orthogonal (it is impossible to obtain Ψ_2 by annihilating a spinorbital in Ψ_1) but not 1-orthogonal since both ϕ_1 and ϕ_2 belongs to their one-internal space.

p-orthogonality: Fundamental property

Fundamental property (q-particle operator matrix elements):

If two n-particle states represented by the wave functions Ψ_1 and Ψ_2 are p-orthogonal then for any q-particle operator, $O_q, q \leq n-p$, the transition matrix element is zero,

$$\langle \Psi_1 | O_q | \Psi_2 \rangle = 0$$

In the case of strongly orthogonal states, only n-particle operator matrix elements can be non zero.

This property can be exploited to simplify matrix elements:

For a 2-particle operator only at most $n-1$-orthogonal states can possibly have non zero matrix elements. ("generalized Slater rules")

Geminal-SCF and p-orthogonality

Minimize $E(\Phi) = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle}$ with Φ of the geminal product form: $\Phi = a^\dagger(\Gamma_1)a^\dagger(\Gamma_2)\cdots a^\dagger(\Gamma_{\frac{n}{2}})|0\rangle$, $\forall i, \Gamma_i \in \wedge^2\mathcal{H}$.

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

System	LiH	Be	Li_2	BeH_2	BH	Be_2
$d[\Psi]=1$: E^0_{FCI}	-7.882392	-14.403655	-14.667340	-15.594861	-24.809945	-28.804345
$d[\Psi]=n$: E^0_{GSCF}	-7.882372	-14.403655	-14.667114	-15.594715	-24.809938	-28.803212
with 2-orthogonality	-7.882368	-14.403654	-14.667090	-15.594703	-24.809920	-28.803080
with 1-orthogonality	-7.882203	-14.403630	-14.666584	-15.588630	-24.807908	-28.781789
$d[\Psi]=2n$: E^0_{RHF}	-7.862002	-14.351880	-14.638725	-15.559405	-24.752780	-28.698990

Electric dipole moments

System	LiH	BH
D^z_{FCI}	-4.6201	0.6138
D^z_{GSCF}	-4.6197	0.6138
with 2-orthogonality	-4.6189	0.6142
with 1-orthogonality	-4.6269	0.6861
D^z_{RHF}	-4.8578	0.9569

Permutationally invariant 2-orthogonality: Definition

Definition:

Let $\Phi = a^\dagger(\Gamma_1)a^\dagger(\Gamma_2)\cdots a^\dagger(\Gamma_n)|0\rangle$, be a product wave function of n geminals (2-particle functions) $\Gamma_i \in \wedge^2\mathcal{H}$. Its geminals will be said permutationally invariant 2-orthogonal if and only if $\forall i, \Gamma_i$ and $\Phi_{i'} := a^\dagger(\Gamma_1)\cdots a^\dagger(\Gamma_{i-1})a^\dagger(\Gamma_{i+1})\cdots a^\dagger(\Gamma_n)|0\rangle$ are 2-orthogonal.

Theorem:

For n geminals $\Gamma_i \in \wedge^2\mathcal{H}$ to be permutationally invariant 2-orthogonal it is sufficient that:
(I) For all i, j distinct $\langle\Gamma_i|\Gamma_j\rangle = 0$
(II) For all i, j, k distinct $a(\Gamma_k)a^\dagger(\Gamma_i)a^\dagger(\Gamma_j) = 0$

Permutationally invariant 2-orthogonality: matrix version

- Matrix representation for the $(S_z = 0)$-geminals :

$$\Gamma_i = \sum_{a,b} (C_i)_{a,b}\ \psi_a \wedge \bar{\psi}_b$$

* 1-Orthogonality: $\forall i \neq j, \quad C_i^\dagger C_j = 0$

* permutationally invariant 2-Orthogonality:

$$\forall i \neq j, \quad tr[C_i^\dagger C_j] = 0$$

$$and$$

$$\forall i, j, k\ distinct, \quad C_i C_k^\dagger C_j = -C_j C_k^\dagger C_i$$

* 2-Orthogonality:

$$\forall i \neq j, \quad tr[C_i^\dagger C_j] = 0$$

Solving the permutationally invariant 2-Orthogonality relations

- Case 1: (1×1)-matrices C_i

1-orthogonality $\equiv$ 2-orthogonality

Only one C_i is possibly non zero, one generic solution: $C_i \in \{Id_1\}$

- Case 2: (2×2)-matrices C_i

Two generic solutions

a) three C_i are possibly non zero, $C_i \in \{\tau(\alpha), \sigma_x, i\sigma_y\}$

b) four C_i are possibly non zero, $C_i \in \{Id_2, \sigma_x, i\sigma_y, \sigma_z\}$

Id_n identity in n-dimension, σ_i Pauli matrix, and for a given angle α,

$$\tau(\alpha) = \begin{pmatrix} \sqrt{2}Sin\alpha & 0 \\ 0 & \sqrt{2}Cos\alpha \end{pmatrix}$$

Work in progress: "Pauli Block Geminal Model"

$$C_i = \begin{pmatrix}
\lambda^i_1 B^i_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \ddots & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \lambda^i_{n_1} B^i_{n_1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda^i_{n_1+1} B^i_{n_1+1} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \ddots & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \lambda^i_{n_1+n_{2a}} B^i_{n_1+n_{2a}} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \lambda^i_{n_1+n_{2a}+1} B^i_{n_1+n_{2a}+1} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \lambda^i_{n_1+n_{2a}+n_{2b}} B^i_{n_1+n_{2a}+n_{2b}} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots
\end{pmatrix}$$

$$\Downarrow$$

$$\Gamma_i = \lambda^i_1 \phi_1 \wedge \bar{\phi}_1 + \cdots + \lambda^i_{n_1} \phi_{n_1} \wedge \bar{\phi}_{n_1} + \lambda^i_{n_1+1} \begin{cases} \sqrt{2}(Sin\alpha\ \phi_{n_1+1} \wedge \bar{\phi}_{n_1+1} + Cos\alpha\ \phi_{n_1+2} \wedge \bar{\phi}_{n_1+2}) \text{ if } B^i_{n_1+1} = \tau(\alpha) \\ (\phi_{n_1+1} \wedge \bar{\phi}_{n_1+2} + \phi_{n_1+2} \wedge \bar{\phi}_{n_1+1}) \text{ if } B^i_{n_1+1} = \sigma_x \\ (\phi_{n_1+1} \wedge \bar{\phi}_{n_1+2} - \phi_{n_1+2} \wedge \bar{\phi}_{n_1+1}) \text{ if } B^i_{n_1+1} = i\sigma_y \end{cases} + \cdots$$

For each block j at most one, three or four coefficients λ^i_j are non zero depending upon the submatrices B^i_j belong to case 1, 2a or 2b

$\rightsquigarrow$ computational cost is under control

$\rightsquigarrow$ flexibility: includes 1-orth GSCF (HF), GVB, ...

$\rightsquigarrow$ implementation in TONTO

p-forbidden space of a wave function

or "p-annihilator ideal" or "p-excluded space" or "p-Pauli space"

Definition: $\forall \Psi \in \wedge^n \mathcal{H}$

$$\mathcal{F}^p[\Psi] = \{\Omega \in \wedge^p \mathcal{H}, a^\dagger(\Omega)|\Psi\rangle = 0\}$$

Space of states excluded by the Pauli principle

(Recall:) p-external space of a wave function

Definition: $\forall \Psi \in \wedge^n \mathcal{H}$

$$\mathcal{E}^p[\Psi] = \mathcal{I}^p[\Psi]^\perp = \{\Omega \in \wedge^p \mathcal{H}, a(\Omega)|\Psi\rangle = 0\}$$

Examples

Example 1: Slater determinantal function

$$\mathcal{F}^1[\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_n}] = \mathcal{I}^1[\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_n}] = \mathbb{C}\psi_{i_1} \oplus \cdots \oplus \mathbb{C}\psi_{i_n}$$

$$\mathcal{F}^p[\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_n}] = \mathcal{I}^1[\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_n}] \bigwedge \wedge^{p-1}\mathcal{H}$$

Example 2:

$$|\Psi\rangle = |\psi_1 \wedge \cdots \wedge \psi_n + \psi_{n+1} \wedge \cdots \wedge \psi_{2n}\rangle = a_1^\dagger \cdots a_n^\dagger|0\rangle + a_{n+1}^\dagger \cdots a_{2n}^\dagger|0\rangle$$

we define $\psi_i^\pm := \psi_i \pm \psi_{i+n}$
For n even $\psi_{i_1}^+ \wedge \cdots \wedge \psi_{i_r}^+ \wedge \psi_{i_{r+1}}^- \wedge \cdots \wedge \psi_{i_n}^- \in \mathcal{F}^n[\Psi]$ if r is odd
For n odd $\psi_{i_1}^+ \wedge \cdots \wedge \psi_{i_r}^+ \wedge \psi_{i_{r+1}}^- \wedge \cdots \wedge \psi_{i_n}^- \in \mathcal{F}^n[\Psi]$ if r is even

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The geminal self-consistent field (GSCF) method

It consists in constructing successive, approximate, $(2n)$-electron wave functions of the form:

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

where $\Psi_i \in \wedge^2 \mathcal{H}$, by means of a configuration interaction calculation in a basis set of group functions $\{\Psi_1^i \wedge \Psi_2^0 \wedge \cdots \wedge \Psi_n^0\}_i$ 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.

- p-orthogonality constraints can be enforced between the Ψ_i ($p \in \{1, 2\}$).

Open problem - 3

Let $\Psi = \Psi_1 \wedge \Psi_2$, where $\Psi_i \in \wedge^{n_i}\mathcal{H}$,
find all transformations $\mathcal{U}$ such that:
(i) $\mathcal{U}(\Psi_i) = \Phi_i \in \wedge^{n_i}\mathcal{H}$
(ii)$\Psi = \Phi_1 \wedge \Phi_2$

• 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, $g_i = \psi_i \wedge \bar{\psi}_i$ for all i, an HF function can be expressed as:

$$\Psi = g_1 \wedge g_2 \wedge \cdots \wedge g_n. \tag{1}$$

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

$$\Psi = \underbrace{g \wedge g \wedge \cdots \wedge g}_{n factors}, \tag{2}$$

Imposing 2-orthogonality between the two-fermion functions appearing in Eqs.(2) and (1) can discriminate between these two equivalent writings.