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ANTICOMMUTING SPACE: AN ALTERNATIVE FORMULATION OF THE WAVEFUNCTION ANTISYMMETRY DESCRIPTION

by

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ABSTRACT

We introduce the Multilinear Alternating Space (MAS-G) as a N-linear map Λ: $H \times H \times \ldots \times H \longrightarrow G$ of the Hilbert Space H. We use the properties of the MAS-G in order to obtain the antisymmetry of the wave function and the Pauli principle. We also discuss an alternative interpretation to the description of creation and annihilation operators.

Key words: Anticommuting Space ; Antisymmetry

1. INTRODUCTION

As is well known, the antisymmetry of the wavefunction ψ and the Pauli principle were formulated by defining the functions ψ as linear combinations of Slater determinants [1]. The second quantization formalism [2] describes them in an elegant way through the anticommuting operators. A different formulation would be to use the properties of an anticommuting variable space. The Grassmann anticommuting algebra - which has been known for a long time by mathematicians - was used by Berezin and Marinov [3-4] to develop and to explore an application of the functional generators method in the second quantization theory. Schwinger [5], Matheus and Salam [6] used the anticommuting c-Numbers in studies of fermionic systems. Since then, due to the operational adequacy of Grassmann algebra to describe systems of Fermions and supersymmetry, many authors have been working on this subject [3-10].

We shall present an alternative formulation to the description of antisymmetric properties of wavefunction and the Pauli principle, and we show that the antisymmetry of Slater determinants becomes a particular case of this formulation. We define the state vectors starting from the generators of multilinear alternating space G, which is introduced as a N-linear alternating application of the Hilbert space H, $\Lambda : H \times \ldots \times H \longrightarrow G$.

We interpret differently the conventional creation and annihilation operators $a_k^\dagger$ and a_k [2] and we show that the elements $\epsilon_k^\dagger$ and ϵ_k (which are equivalent to a_k and $a_k^\dagger$) can be understood as products of generators elements of the alternating space G.

2. MULTILINEAR ALTERNATING APPLICATION

In this section we present some properties of a linear alternating space in order to make clear the next steps definitions [11].

Since $E_1, \ldots, E_r$, U are vectorial spaces, an application;

$$f : E_1 \times E_2 \times \ldots \times E_r \longrightarrow U \qquad (1)$$

is named r-linear if it is linear in each variable separately, $\epsilon_1 \in E_1, \ldots, \epsilon_i$ and $\eta \in E_i, \ldots, \epsilon_r \in E_r$ and $\alpha \in R$, so that

$$f(\epsilon_1, \ldots, \epsilon_i+\eta, \ldots, \epsilon_r) = f(\epsilon_1, \ldots, \epsilon_i, \ldots, \epsilon_r) + f(\epsilon_1, \ldots, \eta, \ldots, \epsilon_r) \qquad (2)$$

and

$$f(\epsilon_1, \ldots, \alpha\epsilon_k, \ldots, \epsilon_r) = \alpha\, f(\epsilon_1, \ldots \epsilon_k, \ldots, \epsilon_r) \qquad (3)$$

We denote as $\mathcal{L}(E_1, \ldots, E_r; U)$ the group of r-linear f applications.

A r-linear application $f : E \times \ldots \times E \longrightarrow U$ is called alternating when

$$f(\epsilon_1, \ldots, \epsilon_r) = 0 \qquad (4)$$

i.e. whenever the sequence $(\epsilon_1, \ldots, \epsilon_r)$ has repetitions. In other words

$$f(\epsilon_1, \ldots, \epsilon_{j-1}, \epsilon, \epsilon_{j+1}, \ldots, \epsilon_{k-1}, \epsilon, \epsilon_{k+1}, \ldots, \epsilon_r) = 0 \qquad (5)$$

where $\epsilon_1, \ldots, \epsilon_r, \epsilon \in E$.

In order that $f \in \mathcal{L}_r(E, U)$ be alternating, it is necessary and sufficient that f is antisymmetric, that is :

$$f(\epsilon_1, \ldots, \epsilon_j, \ldots, \epsilon_k, \ldots, \epsilon_r) = - f(\epsilon_1, \ldots, \epsilon_k, \ldots, \epsilon_j, \ldots, \epsilon_r) \qquad (6)$$

We observe that the r-multilinear alternating maps fulfil conditions completely analogous to those of determinants. Thus, the multilinear alternating maps can be understood as a generalization of determinants.

Proposition :

$f : E \times \ldots \times E \longrightarrow U$ is a r-linear alternating application. Since we have an ordered basis $(y_1, \ldots, y_r)$ at E, for each subgoup $J = \{ j_1 < \ldots < j_n \} \subset I_m = \{1, 2, \ldots, m\}$, and

$$f(y_{j_1}, \ldots, y_{j_n}) = u_r \in U \qquad (7)$$

If $\epsilon_1 = \sum_I \alpha_1{}^I y_1, \ldots, \epsilon_r = \sum_I \alpha_r{}^I y_1$ are vectors of E, we have

$$f(\epsilon_1, \ldots, \epsilon_r) = \sum_J \det(\alpha^J)\, u_J \qquad (8)$$

where $\alpha = (\alpha_j{}^i)$ is a submatrix of the m x r matrix from coefficients of the vectors ϵ_j .

3. SPINORBITAL IN THE HILBERT-GRASSMANN SPACE

In this section we define the spinorbitals as products among generator elements of the G - space and we show that this definition is a generalization of the spinorbitals definition as linear combination of Slater determinants.

For this purpose we shall define the vectorial space E which we have mentioned in section 2.1, equivalent to Hilbert space H . So, a N-linear alternating map in space H will be :

$$A : H \times H \times \ldots \times H \longrightarrow G \qquad (9)$$

and we call the space G a Hilbert-Grassmann space.

Now, supposing that a group of one-electron spinorbitals $\epsilon_1, \epsilon_2, \ldots, \epsilon_r$ belong to $H \sim E$; and some are occupied and others are vacant, then:

I) Vacuum's state: when all orbitals are vacant. It is represented by $|\ >$

$$|\ > = O = O_1 \wedge O_2 \wedge \ldots \wedge O_N \tag{10}$$

O_k is the null element belong to H or a spinorbital with zero electron.

II) One-electron: when the spinorbital $|k >$ is occupied and all others are vacant

$$|k > = \epsilon_k(1) \tag{11}$$

III) Two-electrons: when two spinorbitals ϵ_j, ϵ_k have one electron each and the others are vacant

$$|\ jk > \ = \epsilon_j \wedge \epsilon_k \ = \ - \epsilon_k \wedge \epsilon_j \ = \ -|\ kj > \tag{12}$$

These cases suffice to explain the meaning of a spinorbital in the Hilbert-Grassmann space. So, we can easily generalize the state vectors to an N-electron system.

$$|1 \ldots N > = \epsilon_1 \wedge \epsilon_2 \wedge \ldots \wedge \epsilon_N \tag{13}$$

Using multilinear alternating maps properties (section 2.1) we can easily show that the vector in eq. (1) obeys the Pauli principle, that is

$$|1\ldots i\ldots j\ldots N\rangle = \epsilon_1\wedge\ldots\wedge\epsilon_i\wedge\ldots\wedge\epsilon_j\wedge\ldots\wedge\epsilon_N$$

$$= -\epsilon_1\wedge\ldots\wedge\epsilon_j\wedge\ldots\wedge\epsilon_i\wedge\ldots\wedge\epsilon_N$$

$$= -|1,\ldots,j,\ldots,i,\ldots,N\rangle \quad \text{to } i \neq j \qquad (14)$$

and

$$|1\ldots i\ldots j\ldots N\rangle = \epsilon_1\wedge\ldots\wedge\epsilon_i\wedge\ldots\wedge\epsilon_j\wedge\ldots\wedge\epsilon_N = 0 \qquad (15)$$

if $\epsilon_i = \epsilon_j$; $i \neq j$

where $\epsilon_i\wedge\epsilon_j$ is a tensor product.

As is known, the N-multilinear alternating maps can be understood as generalization of determinants. So, when we use an appropriate basis, $y_1, y_2, \ldots, y_N$, we can show that our N-linear map on the Hilbert space H gives the following equation:

$$|1\ldots N\rangle = b\sum_J \det(\alpha^J)\ |J\rangle \qquad (16)$$

where matrices α^J are the matrices N x N defined by the vector components in Hilbert space.

As an example, let us give the state vector of a two-electron system

$$|12> = \frac{1}{\sqrt{2!}} e_1 \wedge e_2 \tag{17}$$

where

$$e_k = \sum_i \psi_k{}^i \gamma_i \tag{18}$$

thus

$$|12> = \frac{1}{\sqrt{2}} \sum_i \psi_1{}^i \gamma_i \wedge \sum_i \psi_1{}^i \gamma_i \tag{19}$$

$$= \frac{1}{\sqrt{2}} (\psi_1{}^1 \gamma_1 + \psi_1{}^2 \gamma_2) \wedge (\psi_2{}^1 \gamma_1 + \psi_2{}^2 \gamma_2)$$

$$= \frac{1}{\sqrt{2}} (\psi_1{}^1 \psi_2{}^1 \gamma_1 \wedge \gamma_1 + \psi_1{}^1 \psi_2{}^1 \gamma_1 \wedge \gamma_2 + \psi_1{}^2 \psi_2{}^1 \gamma_2 \wedge \gamma_1 + \psi_1{}^2 \psi_2{}^2 \gamma_2 \wedge \gamma_2)$$

Since $\gamma_k \wedge \gamma_k = 0$, the first and last terms are zero; the second and third terms are related by $\gamma_j \wedge \gamma_k = - \gamma_k \wedge \gamma_j$, $k \neq j$. Thus

$$|12> = \frac{1}{\sqrt{2}} (\psi_1{}^1 . \psi_2{}^2 - \psi_1{}^2 . \psi_2) \gamma_1 \wedge \gamma_2 \tag{20}$$

where the term inside parenthesis is the Slater determinant of a system with two electrons.

4. ANNIHILATION AND CREATION ELEMENTS

In this section we define the annihilation and creation elements $\epsilon_k^\dagger$ and ϵ_k in a space of anticommuting variables, and we show that these elements fulfil the same properties of conventional annihilation and creation operators a_k and $a_k^\dagger$

I) Annihilation Element - $\epsilon_k^\dagger$

As in a conventioanl case, an annihilation element $\epsilon_k^\dagger$ removes or annihilates an electron in the k-th orbital

$$a_k \cdot \psi_{kjm} = \psi_{jm} \tag{21}$$

and

$$\epsilon_k^\dagger | kjm > = \epsilon_k^\dagger \wedge \epsilon_k \wedge \epsilon_j \wedge \epsilon_m \tag{22}$$

then we have the equivalence

$$a_k \longrightarrow \epsilon_k^\dagger \qquad \text{and} \qquad a_k^\dagger \longrightarrow \epsilon_k \tag{23}$$

The annihilation element is thus defined in the conjugated $G^\dagger$ space.

a) Annihilation Elements Properties

Due to the definition of a multilinear alternating space generator

$$\epsilon_j^\dagger |kjm\rangle = \epsilon_j^\dagger \wedge \epsilon_k \wedge \epsilon_j \wedge \epsilon_m$$

$$= -\epsilon_j^\dagger \wedge \epsilon_j \wedge \epsilon_k \wedge \epsilon_m = -\epsilon_k \wedge \epsilon_m = -|km\rangle \tag{24}$$

We define as zero, the annihilation of a vacant spinorbital

$$\epsilon_i^\dagger |jkm\rangle = |\rangle \tag{25}$$

From this definition we have

$$\epsilon_1^\dagger \mid > = \epsilon_1^\dagger \wedge \epsilon_1 \mid klm > = 0 \qquad (26)$$

This is easily generalized for more than two annihilation elements. Thus,

$$\epsilon_k^\dagger \wedge \epsilon_1^\dagger \mid ikm > = \epsilon_k^\dagger \wedge \epsilon_1^\dagger \wedge \epsilon_1 \wedge \epsilon_k \wedge \epsilon_m = \epsilon_m = \mid m > \qquad (27)$$

$$\epsilon_1^\dagger \wedge \epsilon_k^\dagger \mid ikm > = -\mid m > \qquad (28)$$

As we stated, the annihilation elements $\epsilon_k^\dagger$ and the annihilation operators a_k share the same anticommutation properties. From equations (28) and (29), we have

$$\epsilon_1^\dagger \wedge \epsilon_k^\dagger + \epsilon_k^\dagger \wedge \epsilon_1^\dagger = \{\epsilon_i^\dagger, \epsilon_k^\dagger\} = 0 \qquad (29)$$

which has the immediate consequence that

$$\epsilon_k^\dagger \wedge \epsilon_k^\dagger = \epsilon_k^{\dagger 2} = 0 \qquad (30)$$

It means that one electron in the k-th orbital can be anni-

hilation element ϵ_k find a vacancy. It is precisely the Pauli principle.

b) Creation Element - ϵ_k

After having defined an annihilation element, it should be possible to introduce a creation element ϵ_k too, which creates a particle in the vacant k-th spinorbital.

We introduce the creation element ϵ_k as the adjoint of the annihilation element ϵ_k. In analogy with equation (25), we define ϵ_k as

$$\epsilon_k \, |ijm\rangle = |kijm\rangle \tag{31}$$

with the properties

$$\epsilon_k|\,\rangle = \epsilon_k = |k\rangle \quad ; \quad \epsilon_k|m\rangle = \epsilon_k \wedge \epsilon_m = |km\rangle \tag{32}$$

however, by the Pauli principle equation (5)

$$\epsilon_k|km\rangle = \epsilon_k \wedge \epsilon_k \wedge \epsilon_m = 0 \tag{33}$$

We can also define a mixed product of ϵ_k an $\epsilon_k^\dagger$ too. For example.

$$\epsilon_m \wedge \epsilon_k^\dagger \, |k\rangle = \epsilon_m = |m\rangle \tag{34}$$

$$\epsilon_k^\dagger \wedge \epsilon_m |k) = \epsilon_k^\dagger \wedge \epsilon_m \wedge \epsilon_k = -\epsilon_k^\dagger \wedge \epsilon_k \wedge \epsilon_m = -|m\rangle \tag{35}$$

Therefore

$$\epsilon_k \wedge \epsilon_m^\dagger + \epsilon_m^\dagger \wedge \epsilon_k = \{\epsilon_k, \epsilon_m^\dagger\} = 0 \qquad \text{if } m \neq k \tag{36}$$

When $m = k$ we have

$$\epsilon_m \wedge \epsilon_m^\dagger | \rangle = 0 \quad ; \quad \epsilon_m^\dagger \wedge \epsilon_m | \rangle = \epsilon_m^\dagger |m\rangle = | \rangle \tag{37}$$

and

$$\epsilon_m^\dagger \wedge \epsilon_m \, |m\rangle = 0 \quad ; \quad \epsilon_m \wedge \epsilon_m^\dagger \, |m\rangle = |m\rangle \tag{38}$$

Hence

$$\epsilon_k^\dagger \wedge \epsilon_m + \epsilon_m \wedge \epsilon_k^\dagger = \{\epsilon_k^\dagger, \epsilon_m\} = \delta_{km} \tag{39}$$

The adjoint of equation (32) is defined by

$$< klm| \ \epsilon_i^\dagger = < iklm| \tag{40}$$

5. HARTREE-FOCK ELECTRONIC GROUND STATE ENERGY

We shall apply what precedes to estimate the energy Hartree-Fock ground state energy of a N-electron

$$|i...N > = \epsilon_1 \wedge ... \wedge \epsilon_N \tag{41}$$

We define one-electron operators through the creation and annihilation elements:

$$h = \sum_{ik} h_{ik} \ \epsilon_i \wedge \epsilon_k^\dagger \tag{42}$$

$$h_{ik} = \int \psi_i^* \left(-\frac{1}{2}\nabla^2 - \sum_s (Z_s/r_s)\right) \psi_k \, d\tau \tag{43}$$

For the one-electron operator we have

$$\langle 1\ldots N|\ h\ |1\ldots N\rangle = \sum_{ij} h_{ij}\ \langle 1\ldots N|\ \epsilon_i \wedge \epsilon_j^{\dagger} |1\ldots N\rangle$$

$$= \sum_{ij} h_{ij}\ \langle 1\ldots N|\delta_{ij} - \epsilon_j^{\dagger}\wedge\epsilon_i|1\ldots N\rangle \qquad (44)$$

where we used equation (39) in order to move ϵ_i to the right side,

$$\langle 1\ldots N|h|1\ldots N\rangle = \sum_{ij} h_{ij}(\delta_{ij}\ \langle 1\ldots N|1\ldots N\rangle - \langle 1\ldots N|\epsilon_j^{\dagger}\wedge\epsilon_i|1\ldots N\rangle) \qquad (45)$$

Let us remark that $\langle 1\ldots N|1\ldots N\rangle = 1$ and the second term is zero, because

$$\epsilon_k\ |1\ldots N\rangle = \epsilon_k\wedge\epsilon_1\wedge\ldots\wedge\epsilon_k\wedge\ldots\wedge\epsilon_N = 0 \qquad (46)$$

Thus

$$\langle 1\ldots N|\ h\ |1\ldots N\rangle\ = \sum_{ij} h_{ij}\ \delta_{ij}\ = \sum_i h_i \qquad (47)$$

Where h_i is the expectation value of the one-electron core hamiltonian corresponding to the molecular orbtital in Eq.(43). For the two-electron interation term we define the following operator,

$$g = \frac{1}{2} \sum_{ijkm} g_{ijkm}\, \epsilon_i \wedge \epsilon_j \wedge \epsilon_k^{\dagger} \wedge \epsilon_m^{\dagger} \tag{48}$$

$$g_{ijkm} = \int \psi_i^{*} \psi_j^{*} \frac{1}{r_{12}} \psi_k \psi_m \, d\tau_1 \, d\tau_2 \tag{49}$$

The contribution to the total energy due to the repulsion between electron is hence written as

$$\langle 1\ldots N|\, g\,|1\ldots N\rangle = \sum_{ijkm} g_{ijkm} \langle 1\ldots N|\epsilon_i \wedge \epsilon_j \wedge \epsilon_k^{\dagger} \wedge \epsilon_m^{\dagger}|\, 1\ldots N\rangle \tag{50}$$

Using the same arguments as for the one-electron case, we have

$$\langle 1\ldots N|\, \epsilon_i \wedge \epsilon_j \wedge \epsilon_k^{\dagger} \wedge \epsilon_m^{\dagger}|1\ldots N\rangle = \delta_{jk} \langle 1\ldots N|\, \epsilon_i \wedge \epsilon_m^{\dagger}|1\ldots N\rangle$$

$$- \langle 1\ldots N|\epsilon_i \wedge \epsilon_k^{\dagger} \wedge \epsilon_j \wedge \epsilon_m^{\dagger}|1\ldots N\rangle$$

$$= \delta_{jk} \cdot \delta_{im} \langle 1\ldots N|1\ldots N\rangle - \delta_{jk}\, 1\ldots N\, |\epsilon_m^{\dagger} \wedge \epsilon_i|\, 1\ldots N\rangle$$

$$- \delta_{jm} \langle 1\ldots N|\, \epsilon_i \wedge \epsilon_k^{\dagger}|\, 1\ldots N\rangle + \langle 1\ldots N\, |\epsilon_i \wedge \epsilon_k^{\dagger} \wedge \epsilon_j|\, 1\ldots N\rangle$$

$$= \delta_{jk} \cdot \delta_{im} - \delta_{jm} \cdot \delta_{ik} \tag{51}$$

As in the first term j = k, i = m and in the second term j = m, i = k

$$\langle 1...N|\ g\ |1...N\rangle = \frac{1}{2}\sum_{ij}(g_{ij} - g_{ji}) \tag{52}$$

Integrating over spin variables in the terms h_k, g_{ij} and g_{ji} we have the terms H_k, J_{ij}, K_{ij}

$$\langle 1...N|\ h|1...N\rangle = 2\sum_{k} H_k \tag{53}$$

and

$$\langle 1...N|\ g\ |1...N\rangle = \sum_{ij}\ (2J_{ij} - K_{ij}) \tag{54}$$

where J_{ij} and K_{ij} are the Coulomb integrals and exchange integrals, respectively.

The total electronic energy is then

$$\langle 1...N|\ h + g|1...N\rangle = 2\sum_{i} H_i + \sum_{ij}(2J_{ij} - K_{ij}) \tag{55}$$

which is the well known expression of the Hartree-Fock total electronic energy for a closed shell ground state.

In short, we see that the antisymmetry of the wavefunction built from Slater determinant is contained within a more general mathematical structure.Elsewhere we shall show other applications concerning quantum chemistry.

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