

Variational spaces of electronic calculations in quantum chemistry

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The exterior algebra formalism is presented, then used to obtain, in a very simple way, Brillouin's theorem, and to derive the general algebraic equations of the various variational spaces explored by RHF, ROHF, UHF, CASSCF, UCASSCF, CI methods. When a given basis set of one-electron orbitals (not necessarily orthogonal) is fixed, these equations lead to analytical equations for the CI coefficients only. The important algebraic concepts (i.e. concepts that do not refer to any particular basis set) of internal space, length and factorization of a multi-configuration are also introduced.

1. Introduction

The main objective of this paper is to provide a new algebraic insight into the traditional variational methods of quantum chemistry. In this respect, the exterior algebra formalism has been found to be a more convenient alternative to describe a set of fermions than the traditional Slater determinant formalism. The exterior algebra [1] is a Clifford algebra [2] similar to the multi-vector algebra [3] used by Hestenes in many fields of physics, but the exterior algebra has been preferred in this paper, because it affords a more specific approach to a fermionic system, in the same way as the symmetric algebra [4] would do, for a bosonic system. The Grassman algebra, also well known in physics [5], is the coalgebra of the exterior algebra, and this pair constitutes a Hopf algebra [6]. However, in finite dimension, the Grassman algebra and the exterior algebra are usually considered as identical [7].

In this paper we assume that the basic notions of quantum chemistry (natural orbitals, self-consistent field (SCF) methods, etc.) are known, though we recall that the variational method in quantum physics solves the problem of the stationary points $stat_{\Psi \in V} \langle O \rangle_{\Psi}$ of the expectation value of an operator O , when the n -particle wave function Ψ runs over a chosen variational space V (and when the derivatives do exist). However, for the whole class of SCF methods, extensively used in quantum chemistry, the variational space V was not known, and the actual variational

problem was solved indirectly. We present here the first explicit equations which characterize the variational spaces explored by the main SCF methods in use in quantum chemistry.

The paper is organized so that the mathematical tools offered by the exterior algebra are first introduced, followed by a simple proof of Brillouin's theorem [8] for unrestricted methods and, finally, we show how powerful the exterior algebra formalism can be by working out the algebraic equations of the variational spaces explored by quantum chemistry calculations. These equations give analytical equations when an arbitrary basis set of configurations is chosen, and this leads to interesting possibilities for the theoretical investigation of variational methods.

2. The exterior algebra ΛE

2.1. THE ELEMENTS OF THE ALGEBRA ΛE

The algebra first contains a field K (real or complex numbers), and the K -vector space E of the one-fermion, say the one-electron, spin-orbitals, whose basis set is $(\psi_i)_{i \leq m}$. It also contains the exterior products of p spin-orbitals of E , $\phi_1 \wedge \dots \wedge \phi_p$, which are the p -electron configurations (in this definition a configuration is not necessarily an eigenfunction of \mathbf{S}^2), it finally contains the linear combinations of all the elements already described.

2.2. STRUCTURE OF THE ALGEBRA ΛE

The vector space of p -electron multi-configurations, denoted $\Lambda^p E$ (that is the set of linear combinations of p -electron configurations) is a vector subspace of ΛE whose dimension is

$$C_m^p = \frac{m!}{(m-p)!p!} \quad 0 \leq p \leq m.$$

The set of p -electron configurations

$$(\Psi_I)_{I \in P_{m,p}} = (\psi_{i_1} \wedge \dots \wedge \psi_{i_p})_{1 \leq i_1 < \dots < i_p \leq m}$$

built by using the basis set of E , is a basis set of $\Lambda^p E$. ($P_{m,p}$ denotes the set of the p -element subsets of $\{1, \dots, m\}$, by convention $\Psi_\emptyset = 1$.)

The algebra ΛE has a graded structure, that is to say:

$$(a) \quad \Lambda E = \bigoplus_{p=0}^m \Lambda^p E \quad \text{with} \quad \Lambda^0 E \equiv K, \quad \Lambda^1 E \equiv E,$$

$$(b) \quad (\Lambda^p E) \wedge (\Lambda^q E) \subseteq \Lambda^{p+q} E.$$

Attention is drawn to the fact that the Fock space of second quantization has the same structure.

2.3. PRODUCTS OF THE ALGEBRA

2.3.1. The exterior product Λ

This product, first used in quantum chemistry by Coleman [9] and followers, allows us, as do creation operators of second quantization, to add a spin-orbital ϕ to a p -electron multi-configuration,

$$\Phi = \sum_{K \in P_{m,p}} \lambda_K \Psi_K,$$

to give a $(p + 1)$ -electron multi-configuration,

$$\phi \Lambda \Phi = \sum_K \lambda_K \phi \Lambda \psi_{k_1} \Lambda \dots \Lambda \psi_{k_p}.$$

The main properties of this product are the following:

$$(a) \phi_1 \Lambda \dots \Lambda \phi_p = 0$$

if and only if ϕ_1, \dots, ϕ_p are not linearly independent.

$$(b) \phi_{\sigma(1)} \Lambda \dots \Lambda \phi_{\sigma(p)} = \epsilon_\sigma \phi_1 \Lambda \dots \Lambda \phi_p, \tag{2.1}$$

where σ is a permutation of $\{1, \dots, p\}$ and ϵ_σ is +1 if σ is even, -1 if σ is odd.

$$(c) \phi_1 \Lambda \dots \Lambda (\lambda \phi_i + \mu \phi'_i) \Lambda \dots \Lambda \phi_p \\ = \lambda \phi_1 \Lambda \dots \Lambda \phi_i \Lambda \dots \Lambda \phi_p + \mu \phi_1 \Lambda \dots \Lambda \phi'_i \Lambda \dots \Lambda \phi_p. \tag{2.2}$$

2.3.2. The interior product \lrcorner

Denote $\langle \phi | \psi \rangle$ as the inner product on the one-electron space E (this can be $\int dr$ or $\int dp$ for the spatial part). An induced inner product is defined on $\Lambda^p E$ for $\Phi = \phi_1 \Lambda \dots \Lambda \phi_p, \Psi = \psi_1 \Lambda \dots \Lambda \psi_p$, by setting

$$\langle \Phi | \Psi \rangle = \det(\langle \phi_i | \psi_j \rangle)_{i,j \leq p},$$

where the right-hand side (r.h.s.) is the determinant of the matrix $(\langle \phi_i | \psi_j \rangle)_{i,j \leq p}$. The interior product is a generalization of the induced inner product, to the case where the two multi-configurations do not have the same number of electrons.

In order to define the interior product, we set, for all H, K subsets of $\{1, \dots, m\}$,

$$\rho_{H,K} = 0 \quad \text{if } H \cap K \neq \emptyset$$

and

$$\rho_{H,K} = (-1)^\nu \quad \text{if } H \cap K = \emptyset,$$

where ν is the number of couples $(i, j) \in H \times K$ such that $i > j$, so that

$$\Psi_H \wedge \Psi_K = \rho_{H,K} \Psi_{H \cup K};$$

for all $K \in P_{p,q}$, we denote K' the element of $P_{p,p-q}$ such that

$$K' \cup K = \{1, \dots, p\}.$$

Let $\Phi = \phi_1 \wedge \dots \wedge \phi_q$ and $\Psi = \psi_1 \wedge \dots \wedge \psi_p$ be two configurations, then the interior product is defined by a formula analogous to the one used by Greub [10]:

if $q > p$

$$\Phi \lrcorner \Psi = 0,$$

if $q \leq p$

$$\Phi \lrcorner \Psi = \sum_{K \in P_{p,q}} \det(\langle \phi_i | \psi_{k_j} \rangle)_{i,j \leq q} \rho_{K,K'} \Psi_{K'}. \quad (2.3)$$

This definition is extended linearly to multi-configurations.

Remark 2.1

If Φ is a scalar λ ,

$$\lambda \lrcorner \Psi = \lambda \wedge \Psi = \lambda \Psi.$$

The interior product allows us, as do annihilation operators of second quantization, to kill a spin-orbital ϕ in a p -electron multi-configuration Φ , $\phi \lrcorner \Phi \in \Lambda^{p-1} E$. We must draw attention to the fact that when we mix the interior product with the exterior product, the order of parentheses is very important: $(\Phi \lrcorner \Psi) \wedge X$ is usually different from $\Phi \lrcorner (\Psi \wedge X)$. Indeed, an interesting relation given by Bourbaki [11] is

$$\Phi \lrcorner (\Psi \lrcorner X) = (\Phi \wedge \Psi) \lrcorner X.$$

2.4. RELATION WITH THE TRADITIONAL FORMALISM

The traditional way of building antisymmetrical functions is as follows [5]. First a 1-particle Hilbert space E is given and the Fock space F , i.e., the tensorial algebra of E is built,

$$F = E^0 \oplus \dots \oplus E^n \oplus \dots$$

where \oplus is the direct sum and E^n the n -particle space (tensorial product of n times E)

$$E^n = E \otimes \dots \otimes E.$$

Then, fermionic n -electron functions are obtained by applying the projection operator,

$$A^{(n)} = \frac{1}{n!} \sum_P (-1)^P P,$$

(where P is a permutation of the tensorial components), and by renormalizing, since a projector does not preserve the norm.

So $\phi_1 \otimes \dots \otimes \phi_n$ gives

$$\sqrt{n!} A^{(n)} \phi_1 \otimes \dots \otimes \phi_n = \frac{1}{\sqrt{n!}} \sum_P (-1)^P \phi_{P(1)} \otimes \dots \otimes \phi_{P(n)}, \tag{2.4}$$

which is in the r -representation the usual Slater determinant

$$\frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(r_1) & \phi_1(r_2) & \dots & \phi_1(r_n) \\ \phi_2(r_1) & \phi_2(r_2) & \dots & \phi_2(r_n) \\ \dots & \dots & \dots & \dots \\ \phi_n(r_1) & \phi_n(r_2) & \dots & \phi_n(r_n) \end{vmatrix}.$$

The exterior algebra used in this paper, though isomorphic to the traditional formalism, is of a more convenient use. For instance, the l.h.s. of eq. (2.4) is written simply $\phi_1 \wedge \dots \wedge \phi_n$. The product being intrinsically antisymmetrical, there is no need for renormalization.

In the traditional approach, second quantization creation operators can be written formally as

$$a_i^+ \equiv \phi_i \otimes .$$

Then, in order to obtain fermion creation operators, use of the antisymmetrical operator

$$A = \sum_n A^{(n)}$$

has to be made

$${}^F a_i^+ = A a_i^+ A.$$

In the exterior algebra formalism, second quantization fermionic operators are obtained readily by writing formally

$${}^F a_i^+ \equiv \phi_i \wedge, \quad {}^F a_i \equiv \phi_i \lrcorner$$

As a result, density operators are neatly expressed without need for normalization factors. The p -particle density matrix elements and kernel of the density operator of a pure n -particle state Φ are written, respectively, as

$$\gamma_{i_1 \dots i_p, j_1 \dots j_p} = \langle (\phi_{i_1} \wedge \dots \wedge \phi_{i_p}) \lrcorner \Phi | (\phi_{j_1} \wedge \dots \wedge \phi_{j_p}) \lrcorner \Phi \rangle, \tag{2.5}$$

and

$$\gamma(r_1\mu_1 \dots r_p\mu_p | r'_1\mu'_1 \dots r'_p\mu'_p) = \langle (\delta_{r_1\mu_1} \Lambda \dots \Lambda \delta_{r_p\mu_p}) \lrcorner \Phi | (\delta_{r'_1\mu'_1} \Lambda \dots \Lambda \delta_{r'_p\mu'_p}) \lrcorner \Phi \rangle,$$

where r_i and μ_i , are respectively, space and spin variables, and $\delta_{r\mu}$ the Dirac distribution centered on the point (r, μ) .

Finally, the exterior algebra happens to be, even when it is used at the level of wave functions, i.e. in the Schrödinger representation of quantum mechanics, as convenient as fermionic second quantization is in the Heisenberg representation.

2.5. GEOMETRICAL INTERPRETATION OF A MULTI-CONFIGURATION

One can associate to any n -electron multi-configuration Φ of $\Lambda^n E$ one and only one vector subspace of the one-electron vector space E , that we call the “internal space of Φ ”. This subspace is defined to be the smallest, with regards to its dimension, vector subspace $N \subseteq E$ such that $\Phi \in \Lambda^n N$ (identifying $\Lambda^n N$ as a vector subspace of $\Lambda^n E$), and is denoted by $[\Phi]$. The dimension of $[\Phi]$ is called the “rank of Φ ” and is denoted by $\rho(\Phi)$,

$$\rho(\Phi) = \dim[\Phi] \geq n.$$

When $\rho(\Phi) = n$, Φ is said to be “decomposable” and can be condensed into only one configuration.

This provides us with a geometrical picture of a multi-configuration Φ in the vector space E . The interior product plays a part, similar to that usually played by scalar products, in obtaining the orthogonal complement of $[\Phi]$,

$$[\Phi]^\perp = \{\phi \in E, \phi \lrcorner \Phi = 0\}. \quad (2.6)$$

Let's notice that a diagonal matrix element γ_{ii} (see eq. (2.5)) is equal to 0 if and only if $\phi_i \lrcorner \Phi = 0$ i.e. $\phi_i \in [\Phi]^\perp$, so that the internal space $[\Phi]$ is the vector space spanned by the occupied natural spin-orbitals (the natural spin-orbitals are defined to be those which diagonalize the one-electron density matrix). As an example take the two electrons of the hydrogen molecule, and the four spin-orbitals $1_{S_A}^\alpha, 1_{S_B}^\alpha, 1_{S_A}^\beta, 1_{S_B}^\beta$

(a) Consider the non-normalized covalent function,

$$\Phi_c = 1_{S_A}^\alpha \Lambda 1_{S_B}^\beta + 1_{S_B}^\alpha \Lambda 1_{S_A}^\beta,$$

we have, by using eq. (2.6) and denoting by $1_{S_A}^{\alpha*}, 1_{S_B}^{\alpha*}, 1_{S_A}^{\beta*}, 1_{S_B}^{\beta*}$ the dual basis set,

$$[\Phi_c]^\perp = \{\psi = x1_{S_A}^{\alpha*} + y1_{S_B}^{\alpha*} + z1_{S_A}^{\beta*} + t1_{S_B}^{\beta*}, \psi \lrcorner \Phi_c = 0\}.$$

For ψ expressed as above we obtain by using eq. (2.3)

$$\psi \lrcorner \Phi_c = x1_{S_B}^\beta + y1_{S_A}^\beta - z1_{S_B}^\alpha - t1_{S_A}^\alpha$$

so that

$$[\Phi_c]^\perp = \{0\},$$

and thus

$$[\Phi] = E,$$

$$\rho(\Phi) = 4,$$

and Φ_c is not decomposable.

(b) Now consider the case of the non-normalized, half-ionic, half-covalent function,

$$\Phi = 1_{S_A}^\alpha \Lambda 1_{S_B}^\beta + 1_{S_B}^\alpha \Lambda 1_{S_A}^\beta + 1_{S_A}^\alpha \Lambda 1_{S_A}^\beta + 1_{S_B}^\alpha \Lambda 1_{S_B}^\beta. \quad (2.7)$$

This time we find for

$$\psi = x 1_{S_A}^{\alpha*} + y 1_{S_B}^{\alpha*} + z 1_{S_A}^{\beta*} + t 1_{S_B}^{\beta*},$$

$$\psi \lrcorner \Phi = (x + y)(1_{S_A}^\beta + 1_{S_B}^\beta) - (z + t)(1_{S_A}^\alpha + 1_{S_B}^\alpha).$$

Since $1_{S_A}^\alpha + 1_{S_B}^\alpha$ and $1_{S_A}^\beta + 1_{S_B}^\beta$ are linearly independent,

$$\psi \lrcorner \Phi = 0$$

gives

$$\begin{cases} x = -y, \\ z = -t. \end{cases}$$

so that

$$[\Phi]^\perp = K(1_{S_A}^{\alpha*} - 1_{S_B}^{\alpha*}) \oplus K(1_{S_A}^{\beta*} - 1_{S_B}^{\beta*})$$

and thus

$$[\Phi] = K(1_{S_A}^\alpha + 1_{S_B}^\alpha) \oplus K(1_{S_A}^\beta + 1_{S_B}^\beta),$$

$$\rho(\Phi) = 2,$$

and Φ is decomposable. Indeed it is well known, that Φ can be constructed from only two spin-orbitals

$$\Phi = (1_{S_A}^\alpha + 1_{S_B}^\alpha) \Lambda (1_{S_A}^\beta + 1_{S_B}^\beta), \quad (2.8)$$

where the two electrons are in the bonding orbital. This example is interesting because it can be checked by hand; however the procedure works for arbitrary numbers of electrons and orbitals and could be used to analyze the wave function given by a large configuration interaction calculation. It is mathematically simpler than the extraction of the natural spin-orbitals.

2.6. LENGTH OF A MULTI-CONFIGURATION

Another concept to be introduced is called the length of a multi-configuration Φ [12], and denoted by $l(\Phi)$. It is defined to be the least integer k such that we may write Φ as a sum of k decomposable elements:

$$\Phi = \sum_{i \leq k} D_i \quad (D_i \text{ decomposable}).$$

The D_i are generally not unique. For instance, in the case $l = 2$,

$$\phi_1^\alpha \Lambda \phi_1^\beta + \phi_2^\alpha \Lambda \phi_2^\beta = \left(\frac{\phi_1^\alpha + \phi_2^\alpha}{\sqrt{2}} \right) \Lambda \left(\frac{\phi_1^\beta + \phi_2^\beta}{\sqrt{2}} \right) + \left(\frac{\phi_1^\alpha - \phi_2^\alpha}{\sqrt{2}} \right) \Lambda \left(\frac{\phi_1^\beta - \phi_2^\beta}{\sqrt{2}} \right).$$

Obviously $l(\Phi) = 1$ if and only if Φ is decomposable.

The problem of the determination of the length of a multi-configuration has not been solved. Its solution nonetheless could help us to understand why the non-orthogonal orbitals of Valence-Bond functions reduce the number of configurations needed to expand the wave function.

2.7. FACTORIZATION OF A MULTI-CONFIGURATION

The partitioning of the one-electron orbitals in use in quantum chemistry is summarized in the diagram below:

$$\text{one-electron orbitals} \left\{ \begin{array}{l} \text{internal orbitals} \left\{ \begin{array}{l} \text{core orbitals} \\ \text{valence orbitals (occupied in the reference)} \end{array} \right. \\ \text{external orbitals} \left\{ \begin{array}{l} \text{valence orbitals (not occupied in the reference)} \\ \text{virtual orbitals} \end{array} \right. \end{array} \right.$$

This terminology is usually employed with respect to a given calculation; however, some of these terms can be defined for an arbitrary multi-configuration without any reference to any calculation. For instance, an internal orbital of a multi-configuration Φ can be defined to be any orbital of the internal space $[\Phi]$. Then, for a given calculation, a set of internal orbitals is defined rigorously as a set of orbitals that spans the sum of the internal space of the reference multi-configurations. The sets of internal orbitals defined this way are the most compact sets that can be used to excite a multi-configuration (compare eqs. (2.7) and (2.8)).

The core orbitals of a multi-configuration can also be given a proper definition, since the core spin-orbitals are those that factorize the multi-configurations. So, an orbital ϕ is said to belong to the core of an n -electron multi-configuration Φ , if and only if, Φ can be written as

$$\Phi = \phi^\alpha \Lambda \phi^\beta \Lambda \Phi',$$

where Φ' is an $(n - 2)$ -electron multi-configuration. The problem of the factorization of a multi-configuration has been addressed, and a solution has been found [13] which states that one can factorize Φ by a spin-orbital ϕ , if and only if, adding an electron in ϕ to Φ gives zero, $\phi\Lambda\Phi = 0$. This theorem can be used to obtain the core orbitals of a multi-configuration. For a given calculation the core orbitals are then defined to be the orbitals belonging to the intersection of the core spaces of the reference multi-configurations.

The occupied valence space is the orthogonal complement of the core space in the internal space.

Finally, we define the active space of a multi-configuration involved in a multi-configuration self-consistent field (MCSCF) process to be the orthogonal complement of the frozen space (space spanned by the non variationally optimized orbitals) in the internal space. In the following, we only consider the case where no orbital is frozen, so that the active space and internal space are identical.

3. Brillouin's theorems

3.1. THE UHF CASE

Take a configuration optimized at the unrestricted Hartree-Fock (UHF) level for the ground state of a Hamiltonian H ,

$$\Phi = \phi_1\Lambda\phi_2\Lambda\dots\Lambda\phi_n.$$

Now consider a mono-excited configuration,

$$\Phi' = \psi\Lambda\phi_2\Lambda\dots\Lambda\phi_n$$

with

$$\psi \in [\Phi]^\perp \tag{3.0}$$

Denote by Ψ a general multi-configuration built with Φ and Φ' ,

$$\Psi = \lambda\phi_1\Lambda\phi_2\Lambda\dots\Lambda\phi_n + \mu\psi\Lambda\phi_2\Lambda\dots\Lambda\phi_n.$$

Ψ is decomposable

$$\Psi = (\lambda\phi_1 + \mu\psi)\Lambda\phi_2\Lambda\dots\Lambda\phi_n.$$

Since the UHF process has selected the best decomposable function with respect to energy (within a constant factor), the energy of Ψ can only be higher than the energy of Φ , so that Φ' cannot improve the energy obtained with Φ , and as a result the matrix element of the Hamiltonian between Φ and Φ' must be zero.

3.2. THE UMCSCF CASE

Consider a multi-configuration optimized at the unrestricted multi-configuration self-consistent field (UMCSCF) level,

$$\Phi = \lambda_1 \phi_1^1 \Lambda \phi_2^1 \Lambda \dots \Lambda \phi_n^1 + \dots + \lambda_p \phi_1^p \Lambda \phi_2^p \Lambda \dots \Lambda \phi_n^p$$

with

$$\sum_{i=1}^p |\lambda_i|^2 = 1.$$

Assuming, without loss of generality, $\phi_j^k = \phi_1^1$ if and only if $j = 1$ and $k \leq l$, we consider the multi-configuration Φ' (with relation (3.0) satisfied),

$$\Phi' = \lambda_1 \psi \Lambda \phi_2^1 \Lambda \dots \Lambda \phi_n^1 + \dots + \lambda_l \psi \Lambda \phi_2^l \Lambda \dots \Lambda \phi_n^l.$$

We set

$$\Psi = \mu \Phi + \nu \Phi'$$

with μ, ν such that Ψ is normalized. Then Ψ can be written as

$$\begin{aligned} \Psi = & \lambda'_1 \frac{(\mu \phi_1^1 + \nu \psi)}{\sqrt{|\mu|^2 + |\nu|^2}} \Lambda \dots \Lambda \phi_n^1 + \dots + \lambda'_l \frac{(\mu \phi_1^l + \nu \psi)}{\sqrt{|\mu|^2 + |\nu|^2}} \Lambda \dots \Lambda \phi_n^l \\ & + \dots + \lambda'_p \phi_1^p \Lambda \dots \Lambda \phi_n^p, \end{aligned}$$

where

$$\lambda'_i = \lambda_i \mu \quad \text{for } i > l,$$

$$\lambda'_i = \lambda_i \sqrt{|\mu|^2 + |\nu|^2} \quad \text{for } i \leq l.$$

$$\sum_i |\lambda'_i|^2 = \langle \Psi | \Psi \rangle = 1$$

so that Ψ belongs to the variational space explored by the UMCSCF calculation. The same argument as previously gives us that

$$\langle \Phi | H | \Phi' \rangle = 0. \tag{3.1}$$

More generally, a Brillouin theorem is obtained by considering the set of multi-configurations which, when linearly combined with the variational solution, give a multi-configuration that belongs to the variational space explored by the calculation performed. Lemma 5 of Wei-Liang Chow [14] claims that a linear combination of two n -electron configurations is an n -electron configuration only if the intersection of the internal spaces of the two configurations is of dimension $n - 1$, which implies that our proof of Brillouin's theorem cannot be extended to a multi-excita-

tion in the UHF case; however, in the UMCSCF case, one can find a more general theorem. For instance, if

$$\Phi = \frac{1}{\sqrt{2}}(\phi_1\Lambda\phi_2 + \phi_3\Lambda\phi_4)$$

then for doubly excited functions like

$$\Phi' = \frac{1}{\sqrt{2}}(\psi_1\Lambda\phi_2 + \psi_3\Lambda\phi_4)$$

our argument can be applied to prove directly that eq. (3.1) is satisfied. As a general rule, when different spin-orbitals are such that we never have two of them in the same configuration of Φ , the multi-excitations from these spin-orbitals give multi-configurations Φ' such that again we get eq. (3.1). This section points out the importance of a knowledge of variational spaces and leads us to study the spaces explored by various, well-known, variational methods of quantum chemistry.

4. Variational spaces of quantum chemistry

We have already given a geometrical interpretation of a multi-configuration in the vector space E , and are now going to visualize variational spaces in $\Lambda^n E$. We begin by defining the unrestricted complete active space self-consistent field (UCASSCF) process, and giving the equation of the associated variational space, then we explain how to get the CASSCF variational spaces, we next illustrate the equations previously derived in the case of two electrons and two orbitals, and finally we make some remarks about the CI process.

4.1. THE UCASSCF SPACE

We will assume henceforth that the exact solution of the problem we are considering is an eigenfunction of \mathbf{S}^2 , \mathbf{S}_z , and the point group symmetry operators. Consequently, we deal here with eigenfunctions of \mathbf{S}_z , and a variational process will be “unrestricted” when it does not constrain its solution to be an eigenfunction of \mathbf{S}^2 or of the point group symmetry operators.

Assume there are n electrons, and m independent fixed orbitals. Define the UCASSCF process of dimension p to be the variational calculation that explores all the n -electron, normalized, eigenfunctions of \mathbf{S}_z with rank less than or equal to p (i.e. whose active space’s dimension is less than or equal to p). This can be a process searching for a minimum or a stationary point. Such a calculation provides the best multi-configuration built with the best p linear combinations of the $2m$ spin-orbitals, with respect to the variational observable. That is precisely the idea of a calculation that optimizes both the “CI vectors” and p spin-orbitals.

It has been shown [15] that the multi-configurations explored by such a process have an active space that can be written as a direct sum of an α -spin part and a β -spin part. That means that the active spin-orbitals can be chosen to be a linear combination of spin-orbitals of the same spin, as expected.

The equation of the variational space of a UCASSCF of dimension p is given by the following theorem [15], provided that one adds the normalization restriction

$$\langle \Phi | \Phi \rangle = 1, \quad (4.1)$$

and the “ S_z restriction”

$$S_z \Phi = S_z \Phi. \quad (4.2)$$

(The spin operators defined on the tensorial algebra induce well-defined spin operators on the exterior algebra.)

THEOREM 4.1

The active space of an n -electron multi-configuration Φ has a dimension less than or equal to p ($p \geq n$) if and only if for all $\Phi_0, \Phi_1, \dots, \Phi_{p-n} \in \Lambda^{n-1} E$ we have

$$(\Phi_0 \lrcorner \Phi) \wedge (\Phi_1 \lrcorner \Phi) \wedge \dots \wedge (\Phi_{p-n} \lrcorner \Phi) \wedge \Phi = 0. \quad (4.3)$$

Practically, the $(n-1)$ -electron multi-configurations Φ_i run over a basis set and lead to a finite system of equations. We remark that for $p = n$ we obtain the UHF equation, that is the equation of the space of decomposable multi-configurations.

Remark 4.1

A well-known result for the exterior algebra claims that the rank of an n -electron multi-configuration cannot be $(n+1)$. So that the case $p = n+1$ is not relevant.

4.2. THE CASSCF SPACE

The CASSCF case is “spin-restricted” because of the spin-equivalence restriction [16], i.e. the spatial part of the spin-orbitals must be equal for pairs of α - and β -spin-orbitals. For instance in the restricted open-shell Hartree–Fock (ROHF) case, the restriction means that the occupation number of the occupied (natural) orbitals can only be 1 or 2. This restriction turns out to be equivalent to the “ S^2 restriction” [17], i.e. the multi-configuration is an eigenfunction of S^2 . Therefore, in order to obtain the CASSCF space, it is only necessary to add the following restriction to eqs. (4.1), (4.2) and (4.3):

$$S^2 \Phi = S(S+1) \Phi. \quad (4.4)$$

Remark 4.2

Strictly speaking, restrictions due to the symmetry of the molecule must also be added.

Remark 4.3

The case $n = p$ gives the ROHF space. We consider through this paper the restricted Hartree–Fock (RHF) space as a particular case of ROHF space.

Remark 4.4

The dimension of a CASSCF, in this paper, is defined to be the dimension of the active space, which is twice the dimension of the “spatial active space” [17] if $S = 0$. Usually the dimension of a CASSCF is defined to be the dimension of the spatial active space.

Remark 4.5

The extended Hartree–Fock space is the projection of the UHF space on a given eigenspace of \mathbf{S}^2 , E_S . It contains the ROHF space which is the intersection of the UHF space and E_S .

4.3. EXAMPLE

Consider the problem of two electrons and two orbitals. Denoting by $\phi_1^\alpha, \phi_2^\alpha, \phi_1^\beta$ and ϕ_2^β the four fixed spin-orbitals (assumed to be orthonormal for simplicity), the most general 2-electron multi-configuration is written as

$$\Phi = a \phi_1^\alpha \Lambda \phi_1^\beta + b \phi_1^\alpha \Lambda \phi_2^\beta + c \phi_2^\alpha \Lambda \phi_1^\beta + d \phi_2^\alpha \Lambda \phi_2^\beta + e \phi_1^\alpha \Lambda \phi_2^\alpha + f \phi_1^\beta \Lambda \phi_2^\beta.$$

(a) Derivation of eq. (4.3) for $p = 2$:

$$\phi_1^\alpha \lrcorner \Phi = a \phi_1^\beta + b \phi_2^\beta + e \phi_2^\alpha,$$

$$\begin{aligned} (\phi_1^\alpha \lrcorner \Phi) \Lambda \Phi &= ab \phi_1^\beta \Lambda \phi_1^\alpha \Lambda \phi_2^\beta + ad \phi_1^\beta \Lambda \phi_2^\alpha \Lambda \phi_2^\beta + ae \phi_1^\beta \Lambda \phi_1^\alpha \Lambda \phi_2^\alpha \\ &\quad + ab \phi_2^\beta \Lambda \phi_1^\alpha \Lambda \phi_1^\beta + bc \phi_2^\beta \Lambda \phi_2^\alpha \Lambda \phi_1^\beta + be \phi_2^\beta \Lambda \phi_1^\alpha \Lambda \phi_2^\alpha \\ &\quad + ae \phi_2^\alpha \Lambda \phi_1^\alpha \Lambda \phi_1^\beta + be \phi_2^\alpha \Lambda \phi_1^\alpha \Lambda \phi_2^\beta + ef \phi_2^\alpha \Lambda \phi_1^\beta \Lambda \phi_2^\beta, \end{aligned}$$

then making use of eq. (2.1) and eq. (2.2),

$$(\phi_1^\alpha \lrcorner \Phi) \Lambda \Phi = (bc - ad + ef) \phi_2^\alpha \Lambda \phi_1^\beta \Lambda \phi_2^\beta,$$

so eq. (4.3) leads to

$$bc - ad + ef = 0. \tag{4.5}$$

$(\phi_2^\alpha \lrcorner \Phi) \wedge \Phi$, $(\phi_1^\beta \lrcorner \Phi) \wedge \Phi$, $(\phi_2^\beta \lrcorner \Phi) \wedge \Phi$ should be evaluated as well, nevertheless, because of the invariance under exchange of the part played by $\phi_1^\alpha, \phi_2^\alpha, \phi_1^\beta, \phi_2^\beta$, they would yield the same equation. The final equation, for $p = 2$, is thus eq. (4.5).

Remark 4.6

Eq. (4.5) is not the equation of a vector subspace, actually UCASSCF spaces are cones but not vector spaces in general, so that the optimized wave function is not an eigenfunction of the variational observable.

Remark 4.7

Eq. (4.5) is easy to compute since only very simple algebraic rules are required to derive it; however the elimination of redundant equations produced by eq. (4.3) may need a more subtle algorithm.

Remark 4.8

The case $p = 3$ is equivalent to the case $p = 2$ (remark 4.1), and for $p \geq 4$ we find that the UCASSCF is the full (unrestricted) configuration interaction (CI) case.

(b) The normalization restriction is very simple in the case of an orthonormal basis set:

$$|a|^2 + |b|^2 + |c|^2 + |d|^2 + |e|^2 + |f|^2 = 1. \quad (4.6)$$

(c) Derivation of the S_z restriction:

$$S_z \Phi = -\Phi \Leftrightarrow a = b = c = d = e = 0, \quad (4.7)$$

$$S_z \Phi = +\Phi \Leftrightarrow a = b = c = d = f = 0, \quad (4.8)$$

$$S_z \Phi = 0 \Leftrightarrow e = f = 0. \quad (4.9)$$

(d) Derivation of the S^2 restriction: We easily find using

$$S^2 = \frac{1}{2}(S_+ S_- + S_- S_+) + S_z^2$$

that

$$S = 0 \Leftrightarrow S^2 \Phi = 0 \Leftrightarrow \begin{cases} b = c \\ e = f = 0, \end{cases} \quad (4.10)$$

$$S = 1 \Leftrightarrow S^2 \Phi = 2\Phi \Leftrightarrow \begin{cases} b = -c \\ a = d = 0. \end{cases} \quad (4.11)$$

Among the eqs. (4.5) to (4.11), eq. (4.6) is the only one that would change if ϕ_1, ϕ_2 were not orthonormal, so we can check eq. (4.5) using the non-orthonormal

wave function (2.6) where $a = b = c = d = 1, e = f = 0$. In this case eqs. (4.5), (4.9) and (4.10) are found to be satisfied.

(e) The relevant case $S_z = 0$ has been represented in fig. 1. Assuming $a \neq 0$ and real coefficients we have rewritten Φ as

$$\Phi = a(\phi_1^\alpha \Lambda \phi_1^\beta + \beta \phi_1^\alpha \Lambda \phi_2^\beta + \gamma \phi_2^\alpha \Lambda \phi_1^\beta + \delta \phi_2^\alpha \Lambda \phi_2^\beta)$$

by setting

$$a\beta = b, \quad a\gamma = c, \quad a\delta = d.$$

The four parameters are linked by the normalization condition

$$\beta^2 + \gamma^2 + \delta^2 = \frac{1}{a^2} - 1.$$

The three, real, parameters β, γ, δ are considered as independent and varying on $] -\infty, +\infty[$ and an axis is associated with each parameter. In the 3-dimensional space obtained, eq. (4.5) becomes

$$\beta\gamma = \delta, \tag{4.12}$$

which is clearly the equation of a set of hyperbolae. Equation (4.10) gives

$$\beta = \gamma. \tag{4.13}$$

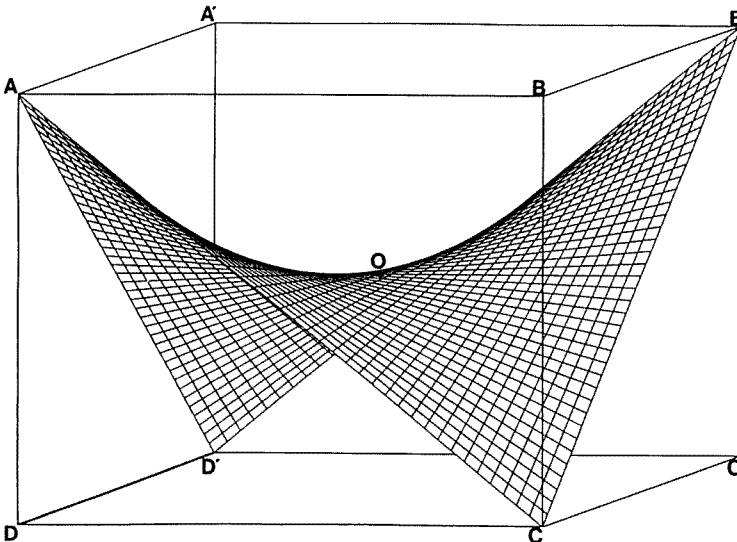


Fig. 1. 2 electrons, 2 orbitals, $S_z = 0$. Each point in the cube corresponds to a multi-configuration, the centre of the cube O being the configuration $\phi_1^\alpha \Lambda \phi_1^\beta$. The volume of the cube is the full unrestricted CI space, the hyperbolic surface $(AOB'CD')$ is the UHF space. 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') .

Since eqs. (4.12) and (4.13) are invariant under the transformation

$$\beta \rightarrow \alpha\beta, \quad \gamma \rightarrow \alpha\gamma, \quad \delta \rightarrow \alpha^2\delta,$$

it is only necessary to picture these equations in a cube, the figure remaining the same when the scale is changed according to the above transformation.

The cube of fig. 1 has the following summits:

$$A = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta - \phi_1^\alpha \Lambda \phi_2^\beta - \phi_2^\alpha \Lambda \phi_1^\beta + \phi_2^\alpha \Lambda \phi_2^\beta),$$

$$B = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta + \phi_1^\alpha \Lambda \phi_2^\beta - \phi_2^\alpha \Lambda \phi_1^\beta + \phi_2^\alpha \Lambda \phi_2^\beta),$$

$$C = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta + \phi_1^\alpha \Lambda \phi_2^\beta - \phi_2^\alpha \Lambda \phi_1^\beta - \phi_2^\alpha \Lambda \phi_2^\beta),$$

$$D = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta - \phi_1^\alpha \Lambda \phi_2^\beta - \phi_2^\alpha \Lambda \phi_1^\beta - \phi_2^\alpha \Lambda \phi_2^\beta),$$

$$A' = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta - \phi_1^\alpha \Lambda \phi_2^\beta + \phi_2^\alpha \Lambda \phi_1^\beta + \phi_2^\alpha \Lambda \phi_2^\beta),$$

$$B' = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta + \phi_1^\alpha \Lambda \phi_2^\beta + \phi_2^\alpha \Lambda \phi_1^\beta + \phi_2^\alpha \Lambda \phi_2^\beta),$$

$$C' = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta + \phi_1^\alpha \Lambda \phi_2^\beta + \phi_2^\alpha \Lambda \phi_1^\beta - \phi_2^\alpha \Lambda \phi_2^\beta),$$

$$D' = \frac{1}{2}(\phi_1^\alpha \Lambda \phi_1^\beta - \phi_1^\alpha \Lambda \phi_2^\beta + \phi_2^\alpha \Lambda \phi_1^\beta - \phi_2^\alpha \Lambda \phi_2^\beta).$$

The centre of the cube is

$$O = \phi_1^\alpha \Lambda \phi_1^\beta.$$

The figure provides an interesting comparison of the different variational methods. The volume of the cube ($ABCD A' B' C' D'$) corresponds to all the wavefunctions that a full unrestricted CI would consider (though its solution would be an eigenfunction of S^2). The plane ($ADB' C'$), whose equation is eq. (4.13), corresponds to the surface a full CI with $S = 0$ would explore. The Hyperbolic surface ($AOB' CD'$) is the set of wavefunctions considered by a UHF process. Finally the one-dimensional line (AOB'), which is the intersection between the plane $S = 0$ and the UHF surface, represents RHF wavefunctions.

In the case $a = 0$, another 3-dimensional representation would be relevant, the three axis being associated with the parameters b, c, d . Equations (4.5) and (4.9) would give

$$bc = 0,$$

so that the UHF space would be the reunion of the two circles

$$b^2 + d^2 = 1,$$

$$c^2 + d^2 = 1.$$

The ROHF space reduces to only two points, $\pm\phi_2^\alpha\Lambda\phi_2^\beta$ if $S = 0$, and to \emptyset if $S = 1$.

(f) Generalization. The previous example provides a simple 3-dimensional figure that more complicated cases would not provide. However, the general equation exhibits the same hyperbolic structure. Equation (4.3) does not imply a particular choice of basis, nevertheless if a fixed induced basis set, $(\Psi_I)_{I \in P_{2m,n}}$, is chosen eq. (4.5) can be generalized.

Writing

$$\Phi = \sum_I a_I \Psi_I$$

it has been shown [15] that eq. (4.3) yields the following system of equations: for all $H_0, \dots, H_{p-n} \in P_{2m,n-1}$ and $G \in P_{2m,p+1}$

$$\sum_{\substack{k_0, \dots, k_{p-n} \in G \\ k_i \notin H_i, k_i \neq k_j \text{ if } i \neq j}} \rho_{H_0, \{k_0\}} \cdots \rho_{H_{p-n}, \{k_{p-n}\}} \rho_{\{k_0, \dots, k_{p-n}\}, G \setminus \{k_0, \dots, k_{p-n}\}}$$

$$\times a_{H_0 \cup \{k_0\}} \cdots a_{H_{p-n} \cup \{k_{p-n}\}} a_{G \setminus \{k_0, \dots, k_{p-n}\}} = 0,$$

which holds whether the one-electron orbitals are orthogonal or not.

Remark 4.9

In practice, when the variational observable commutes with S^2 and S_z , we may deal with a basis of eigenfunctions of S^2 and S_z , so that the number of parameters required is given by the Weyl’s dimension formula [18]. The dimension of the problem can also be reduced by making use of the symmetry of the molecule, and the formula above simplifies accordingly. In the example, in the case $S_z = 0, S = 0$, we need only 3 parameters $a, b = c, d$, and eq. (4.5) reduces to the RHF equation

$$b^2 = ad,$$

or, making use of the normalization condition,

$$(a + d)^2 = 1.$$

4.4. CONFIGURATION INTERACTION

A natural question that arises is: How is a result obtained in the basis $(\Psi_I)_I$ transformed on changing to another induced basis $(X_I)_I = (\chi_{i_1} \Lambda \dots \Lambda \chi_{i_n})_{i_1 < \dots < i_n}$?

If we call u the linear mapping of E defined by

$$\psi = u(\chi_i), \quad \text{for all } i,$$

and $\Lambda^n u$ the induced mapping on $\Lambda^n E$ defined by

$$\Lambda^n u(X_I) = u(\chi_{i_1}) \Lambda \dots \Lambda u(\chi_{i_n}), \quad \text{for all } I,$$

then $\Lambda^n u$ is such that

$$\Lambda^n u(X_I) = \Psi_I,$$

and can be used to transfer results from one basis set to the other. The numerous properties of $\Lambda^n u$ will be extensively used in a forthcoming paper [19].

The relevant set of spin-orbitals ψ_i being chosen, the variational space explored by a CI calculation is the vector space spanned by the multi-configurations of the CI.

Remark 4.10

The space of the multi-configurations that belongs to any possible reference space of, at most, p configurations (these p configurations being any elements of the vector space V spanned by say h given configurations) is the space denoted L_V^p of elements of V whose length is less than or equal to p ,

$$L_V^p = \{\Phi \in V, l(\Phi) \leq p\}.$$

A variational process in L_V^p could be used to give a good reference space of p configurations, and would be useful to test a code like CIPSI [20] which selects reference spaces in a perturbational way.

5. Conclusion

Any profound result of quantum physics is expected to be expressible in terms of basis set independent (i.e. algebraic) concepts. In this regard, the new algebraic concepts of internal space, core space, length of a multiconfiguration have been introduced.

In the study presented here, the variational observable does not appear explicitly, it can be the Hamiltonian or any other operator for which there is a variational theorem, it may include relativistic terms or not.

The proof of Brillouin theorem presented here is different from the usual one because it only relies on a simple property of Hermitian matrices, and is interesting because it gives directly more general functions satisfying Brillouin theorem.

Equations (4.1)–(4.4) are algebraic, i.e. they do not imply any specific basis set, thus it is obvious that a CASSCF procedure is invariant under a unitary transformation of the basis set orbitals.

One of the main features of our approach is that, when we choose a basis set, we deal with only one kind of coefficients, instead of two kinds of redundant coefficients in the usual MCSCF theory. This affords comparison of the various variational methods in the same framework, which is not the case in the traditional approach where the one-electron basis set is ever changing in the optimization process. Moreover, this approach suggests a new way to construct a CASSCF program (for small-size problems at least), since, actually, eq. (4.3) gives the constraint

that an optimization with constraint algorithm needs to explore the relevant energy surface.

But the main interest of the equations of this paper lies in the new insight in quantum chemistry methods they provide. So far CASSCF equations had been investigated from the numerical analysis point of view. We have given here algebraic and purely analytical equations. These three levels should not be seen in a hierarchical manner but as forming a trinity in quantum chemistry.

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