Applications of Inward Matrix Products and Matrix Wave Functions to Hückel MO Theory, Slater Extended Wave Functions, Spin Extended Functions, and Hartree Method

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ABSTRACT: The operation of inward matrix product and the concept of extended wave functions are jointly invoked to set up a general theoretical framework to obtain a new look at old quantum chemical procedures like Hückel method, Hartree theory, and some related questions. Among the discussion of several problems, the spin orbitals are presented as a matrix signature option, associated with an extended wave function in matrix form, common to both Hückel and Hartree theories, as well as in the fundamentals of Slater determinants construction. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 91: 607–617, 2003

Key words: extended wave functions; Hückel method; Hartree method; Slater determinants; extended spin functions; Hartree permanents; inward matrix product; matrix signature; fuzzy sign

Introduction

The so-called inward matrix product (IMP) has been described and successfully employed in several previous studies [1–7]. Up to now, IMP utilization has been mainly focused to deal with some problems associated with quantum similarity and has been largely related to the setting up of the quantum quantitative structure–activity relationships (Q²SAR) fundamental equation [8], as well as has been employed in the task of looking for appropriate algorithms to discover its approximate constrained solutions [5]. On the other hand, the development of new ideas about the concepts of extended wave and density functions has been made possible through the above-mentioned IMP structure definition [2]. The application and understanding of IMP potential used to deal with the basic quantum chemical theoretical development has been of capital importance in our research group.
Here, an extensive application of IMP to some quantum mechanical classic problems will be presented, like the search for an alternative establishment of the Hückel and Hartree methods theoretical background. The essential working tool element, which will be employed as the basic mathematical structure, corresponds to a plausible modification of the nature of polyelectronic wave functions, in terms of one-electron orbital functions, which will be described here in an extended form, adopting a matrix configuration. The usual problems, formerly associated with approximate polyelectronic wave functions, expressed as products of monoelectronic wave functions, will be discussed in this context. Finally, the organization of spin orbital arrays will be presented as taking the form of a molecular orbital (MO) matrix signature.

**IMPs**

To ease the reading of this article, a resumed description of IMP and its properties will be given first. Then, suppose an arbitrary dimension matrix space over a field $K$: $M_{(m \times n)}(K)$. By an IMP it is understood a multiplicative internal composition rule over an arbitrary dimension matrix space, which can be simply defined by means of the symbolic formalism:

$$\forall A, B \in M_{(m \times n)}(K) \rightarrow P = A \ast B \in M_{(m \times n)}(K)$$

and can be moreover associated with the following algorithm:

$$\forall i, j: p_{ij} = a_{ij} \ast b_{ij}.$$  

In this way, matrices of arbitrary dimension behave almost as the elements of the field $K$ over which their structures are defined. The main difference with these simpler sets has to be obviously encountered within the structure of the IMP inverses and the mathematical behavior of such matrices. The following algorithm easily defines the IMP inverse:

$$\forall Z \in M_{(m \times n)}(K) \land \forall i, j: z_{ij} \neq 0 \rightarrow \exists Z^{-1} = \{z_{ij}^{-1}\}.$$  

Therefore, the IMP neutral element is the *unity* matrix, defined in turn as

$$1 = \{\forall 1_{ij} = 1\},$$

constituting a special kind of matrix, which can be employed as a natural IMP multiplicative unit, that is,

$$\forall Z \in M_{(m \times n)}(K): 1 \ast Z = Z \ast 1.$$  

Finally, for every nonsingular IMP matrix the following equalities hold:

$$Z \ast Z^{-1} = Z^{-1} \ast Z = 1.$$  

Also, the IMP is associative, commutative, and distributive with respect to the matrix sum; see Ref. [9] for more details. The nonsingular IMP matrices constitute a well-defined subset of the corresponding matrix space, in fact bearing the structure of a multiplicative Abelian group, whose elements, as earlier mentioned, act and behave as the field constituents, which enter at the same time in their own composition. In this context, IMP powers are readily defined as a sequence of repeated IMP applications. The recursion

$$Z^{[a]} = Z \ast Z^{[a-1]} \land Z^{[0]} = 1$$

illustrates such power computation possibility.

The additional usefulness appeal of IMP can be associated with the fact that such an array product is a common operation, included as a native feature in FORTRAN 90 and 95 compilers [4(b. ii)]. Therefore, the development of mathematical theoretical constructs, involving IMP, can be numerically implemented without severe problems, just with the aid of modern FORTRAN compilers.*

In addition, exactly the same IMP definitions and properties as those summarily described above can be extended without difficulties to any arbitrary hypermatrix space [3, 7]. This is easily seen when the above matrix structures employed to describe IMP, instead of scalar elements, are imagined constructed in turn with matrices of arbitrary but homogeneous dimension as building blocks. Thus goes the discussion about IMP algebra.

To extend the applicability of the aforementioned IMP product, simple analysis operations can be also envisaged within the same context. Al-

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*The following subroutine illustrates the FORTRAN ability to perform IMP-like products:

```
Subroutine Inward_Matrix_Product(m,n,A,B,P)
    Dimension A(m,n),B(m,n),P(m,n)
P=A*B
end
```
though almost obvious, IMP derivatives, integrals, and functions can be easily designed. The flexibility of IMP as a matrix operation can be extended to the realm of matrices (or hypermatrices) whose elements are no longer scalars but functions belonging to some functional space. As IMP integration will later be employed; then, this operation will be chosen accordingly as an example of these possibilities.

Suppose a matrix of arbitrary dimension, \( F(x) = \{ f_j(x) \} \), whose elements belong to some space of \( n \)-variable functions, provided with a homogeneous arbitrary number of variables, and whose elements possess convergent integrals over a given domain. Then, an IMP integral is defined as

\[
F(x) = \{ f_j(x) \} \rightarrow Z = \int_D [F(x)]dx = \left\{ z_j = \int_D f_j(x)dx \right\}.
\]

In the same manner, an IMP function can be constructed without much more effort. For example, an IMP sine can be obtained as

\[
\forall Z = \{ z_j \} \in M_{\text{in} \times n}(\mathbb{R}) \rightarrow \sin[Z] = \{ \sin(z_j) \} \in M_{\text{in} \times n}(\mathbb{R}).
\]

These kinds of ideas about functional IMP analysis have been successfully employed to generalize the structure of time-dependent frames [25].

### Hückel Method in the Extended Wave Function Formalism

#### HÜCKEL EXTEDED WAVE FUNCTION

The Hückel MO (HMO) method features [10] are so well known that they will not be repeated here in their classic formalism. Instead, a HMO extended wave function for a system of \( N \) particles will be here defined anew as a kind of \( (N \times N) \) matrix, built up by means of a monoatomic functional array of MO functions: \( \{ \varphi_i(r) = \varphi_i(j) \} \), that is,

\[
\Phi(1, 2, \ldots, N) = \Phi(R) = \begin{pmatrix}
\varphi_1(1) & \varphi_1(2) & \cdots & \varphi_1(N) \\
\varphi_2(1) & \varphi_2(2) & \cdots & \varphi_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_N(1) & \varphi_N(2) & \cdots & \varphi_N(N)
\end{pmatrix},
\]

for the usual HMO settings, where each MO is considered an eigenfunction of an effective monoatomic Hamiltonian. Effective Hamiltonians constitute a set of operators, which once gathered into a sum serve successively to build up the whole HMO Hamilton operator:

\[
H(1, 2, \ldots, N) = \sum_{j=1}^{N} h(j),
\]

while each effective Hamiltonian fulfills a monoatomic secular equation of the type

\[
h(j)\varphi_i(j) = \varepsilon_i\varphi_i(j); \forall i, j.
\]

Thus, by using the wave function as shown in Eq. (1), while constructing a polyatomic Hamiltonian built up as a diagonal matrix

\[
H(1, 2, \ldots, N) = \text{Diag}(h(1), h(2), \ldots, h(N)),
\]

and further employing a diagonal monoatomic MO energy matrix, by ordering in such a way the eigenvalues associated with Eq. (3)

\[
\varepsilon = \text{Diag}(\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N),
\]

a Hückel-Schrödinger extended equation can be easily obtained that can be modeled in the following form:

\[
\begin{pmatrix}
h(1)\varphi_1(1) & h(2)\varphi_1(2) & \cdots & h(N)\varphi_1(N) \\
h(1)\varphi_2(1) & h(2)\varphi_2(2) & \cdots & h(N)\varphi_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
h(1)\varphi_N(1) & h(2)\varphi_N(2) & \cdots & h(N)\varphi_N(N)
\end{pmatrix}
= \begin{pmatrix}
\varepsilon_1\varphi_1(1) & \varepsilon_2\varphi_1(2) & \cdots & \varepsilon_N\varphi_1(N) \\
\varepsilon_1\varphi_2(1) & \varepsilon_2\varphi_2(2) & \cdots & \varepsilon_N\varphi_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
\varepsilon_1\varphi_N(1) & \varepsilon_2\varphi_N(2) & \cdots & \varepsilon_N\varphi_N(N)
\end{pmatrix}
= \Phi\varepsilon.
\]
HÜCKEL SYSTEM TOTAL ENERGY WITHIN EXTENDED WAVE FUNCTIONS

The interesting feature to be studied at this moment, after leaving the previous discussion, consists of the procedure that shall be designed to produce, starting from Eq. (5), the Hückel expectation total energy value of the system by means of the MO energies.

Sum of the Elements of an Arbitrary Matrix

To show how to perform such a task, first one can introduce the definition of a linear operator yielding the sum of the whole elements of an arbitrary matrix (or hypermatrix), which was defined several years ago [9] in another context:

\[
\forall A \in M_{m \times n}(K): \langle A \rangle = \sum_{i=1}^{m} \sum_{j=1}^{n} a_{ij} \tag{6}
\]

Norm of a Hückel Extended Wave Function

Then, employing the simple definition (6), the norm of the extended wave function (1) by using the IMP could be defined as the result of an IMP integral over the IMP extended wave function module:

\[
\langle \Phi | \Phi \rangle = \left( \int_D \Phi^* \Phi dR \right) = \left( \int_D |\Phi|^2 dR \right)
\]

\[
\begin{pmatrix}
\int_D \varphi_1^*(1) \varphi_1(1) d\mathbf{r}_1 \\
\int_D \varphi_1^*(1) \varphi_2(1) d\mathbf{r}_1 \\
\vdots \\
\int_D \varphi_1^*(1) \varphi_N(1) d\mathbf{r}_1 \\
\int_D \varphi_2^*(1) \varphi_1(1) d\mathbf{r}_1 \\
\int_D \varphi_2^*(1) \varphi_2(1) d\mathbf{r}_1 \\
\vdots \\
\int_D \varphi_2^*(1) \varphi_N(1) d\mathbf{r}_1 \\
\vdots \\
\int_D \varphi_N^*(1) \varphi_N(1) d\mathbf{r}_1 \\
\int_D \varphi_2^*(2) \varphi_1(1) d\mathbf{r}_2 \\
\int_D \varphi_2^*(2) \varphi_2(1) d\mathbf{r}_2 \\
\vdots \\
\int_D \varphi_2^*(2) \varphi_N(1) d\mathbf{r}_2 \\
\int_D \varphi_N^*(2) \varphi_1(1) d\mathbf{r}_N \\
\vdots \\
\int_D \varphi_N^*(2) \varphi_N(1) d\mathbf{r}_N \\
\int_D \varphi_N^*(n) \varphi_1(1) d\mathbf{r}_N \\
\int_D \varphi_N^*(n) \varphi_2(1) d\mathbf{r}_N \\
\vdots \\
\int_D \varphi_N^*(n) \varphi_N(1) d\mathbf{r}_N \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
\varphi_1(1) & \varphi_1(2) & \cdots & \varphi_1(N) \\
\varphi_2(1) & \varphi_2(2) & \cdots & \varphi_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_N(1) & \varphi_N(2) & \cdots & \varphi_N(N) \\
\end{pmatrix}
\]

\[
= (1) = N^2.
\]

This result appears immediately in case, as is customary, the involved Hückel orbitals are normalized.

Total Hückel Energy

This result permits us to consider, under the definition of an extended wave function Euclidian norm (7), that the normalization factor of the extended wave function (1) is \(N^{-1}\). The Hückel total expectation energy can be obtained just considering expression (5) and the wave function (1) normalized, according to the result as shown in Eq. (7). In this manner, a simple HMO energy expression arises employing again the IMP and the operator sum (6):

\[
E = \left( \int_D \Phi^* \Phi dR \right) = \left( \int_D |\Phi|^2 dR \right)
\]

\[
= N^{-2}(1E) = N^{-1}(E) = N^{-1} \sum_{i=1}^{N} s_{ii} \tag{8}
\]

where it is taken into account that \(1E = N(E)\). Such a result as in Eq. (8) is nothing else than the average expectation energy over the particle number.

Hückel Density Function and Total Energy

The energy expression (8) can be also associated to the fact that, when employing the extended wave function (1), the associated density function can be connected to the IMP-based definition:
Hückel extended wave function (1), discussed in the previous section, although there appears no need to consider spin functions in the Hückel extended wave function construction. Double occupancy in the Hückel context can be dealt with by repeating the same MO function in the convenient row of the Hückel extended wave function because no determinant of such an extended function has to be involved at the Hückel theoretical level. On the contrary, Slater extended functions shall be written in a phenomenological manner, that is, by multiplying the space part of the orbital by the appropriate spin functions. This is a well-known fact, a compulsive property, which produces the antisymmetrical character of the scalar polyelectronic functions built up as Slater determinants.

The most interesting facet of the present discussion consists of the possibility that, employing again the IMP as the most adequate mathematical device, a Slater extended wave function can be written by simply multiplying a Hückel extended wave function by an extended spin function, that is,

$$\Psi(R; s) = \Phi(R) \ast S(s).$$

where the spatial part can be written exactly in the same manner as it was set in the Hückel extended wave function model (1). The spin extended function part has been simply written using the symbol

$$S(s) = \begin{pmatrix} \sigma_s(1) & \sigma_s(2) & \cdots & \sigma_s(N) \\ \sigma_s(1) & \sigma_s(2) & \cdots & \sigma_s(N) \\ \cdots & \cdots & \cdots & \cdots \\ \sigma_s(1) & \sigma_s(2) & \cdots & \sigma_s(N) \end{pmatrix}.$$ (11)

In the extended spin function, the matrix elements of the spin functions $S = [\sigma_s(j)]$ are just spin functions of type $[\alpha(s); \beta(s)]$, associated with the i-th spin orbital and bearing the spin variable $s_i$ of the j-th particle. To ease the notation, the spin variable symbol has been omitted; thus, $\sigma_s(j) = \sigma(s)_i$. The vector s, acting as a variable in the extended spin function symbol, collects the spin variables of the whole particle set, forming the studied system: $s = (s_1, s_2, \ldots, s_N)$.

### Slater Extended Wave Functions

A Slater extended wave function can be considered defined as the square matrix, associated with any Slater determinant [12], and also constructed in turn by spin orbitals as matrix elements. Such a wave function has a remarkable resemblance to the

$$\rho(R) = (\Phi^* \ast \Phi) = N^{-1} \sum_{i=1}^{N} \Phi^*(i) \varphi(i) = N^{-1} \sum_{i=1}^{N} \rho(i),$$

which necessarily presents an averaging factor over the particle number. Thus, employing the Hadamard product* [4(b. i)] of the sums in the definitions of Hückel Hamiltonian (2) and the Hückel density (9), one obtains for the Hückel expectation energy the same result as before:

$$E = \int_D (H \ast \rho) dR = \sum_{i=1}^{N} \varphi(i) \sum_{i=1}^{N} \rho(i) dR$$

$$= N^{-1} \sum_{i=1}^{N} \sum_{i=1}^{N} \varphi(i) \rho(i) dR = N^{-1} \sum_{i=1}^{N} \psi_i.$$ In the deduction developed above, instead of the quantum mechanical formalism the statistical form has been employed for the expectation value, already described by Landau [11] or McWeeny and Sutcliffe [12], and has been also recently deduced in an extended wave function discussion context [2]. Such an expression has been also recently used to discuss some aspects of the Hohenberg–Kohn theorem [13]. A procedure based on this expectation value statistical form has permitted us to deduce, in the context of extended wave and density functions [2], the so-called fundamental Q^2SAR equation [3, 6, 7]. Such a density function and energy scaling has been also previously analyzed in an SCF context [2]. In the present Hückel formalism, such averages appear because of the chosen theoretical set-up.

### Spin Extended Functions as a Matrix Signature

The possibility to define spin extended functions can be related to a previously published discussion, connected in turn to the so-called matrix signature

$$\Sigma_a b = \sum_{i=1}^{N} a_i b_i,$$

*The Hadamard product of two sums closely corresponds to the IMP in the matrix context. The involved sums must have the same number of elements and the result yields another sum of the same characteristics. The summation terms are multiplied one by one in the same order as they appear in the sum and no cross-terms are involved at all. For example, the following Hadamard product expression holds: $$(\Sigma_a a_i) \ast (\Sigma_b b_i) = \Sigma_a a_i b_i.$$
which constitutes a matrix property further related to IMP properties and structure. Marix signatures permit in one hand, within the \((m \times n)\)-dimensional matrix spaces (or in those of higher-dimension rank), a classification according to the \(2^{(m \times n)}\) possible signatures and, on the other hand, they lead toward the generalization of the concept of sign.

**MATRIX SIGNATURE**

A \((m \times n)\) matrix signature is readily defined in the following terms:

\[
\forall A \in M_{m \times n}(\mathbb{R}) \rightarrow A = \text{Sign}(A) \star |A| \land |A|
\]

\[
= \{a_{ij}\} \in M_{m \times n}(\mathbb{R}^+) \land \text{Sign}(A)
\]

\[
= \{\text{Sign}(a_{ij})\} \in M_{m \times n}([-1; +1]).
\]

Thus, one can conclude that any \((m \times n)\) matrix can be constructed from a matrix semispace* [14–21] of the appropriate dimension, inwardly multiplied by a matrix signature made by means of any of the allowed matrices constructed combining the plus and minus signs. A binary structure can be also alternatively adopted, producing a Boolean matrix signature, which in fact constitutes the used sign device in computer practice, allowing us to electronically construct the signs of the numbers within the machine RAM.

**GENERALIZED SIGN IN THE REAL FIELD AND THE MATHEMATICAL NATURE OF THE SPIN EXTENDED FUNCTIONS**

In this sense, and using the appropriate definitions, one could construct in a general manner the matrix signatures and, thus, even the signature of the positive definite real number set \(\mathbb{R}^+\). This is so because any real number can be structured as a Cartesian product of the sign and the positive definite real part. In this sense, a real number can be considered as an element of a tagged set\(^{†}\) [14, 15] whose objects are the positive definite real numbers and the tags become the signs, that is,

\[
\forall x \in \mathbb{R} \rightarrow x = (\text{Sign}(x); |x|) \land \text{Sign}(x) \in \{-1; +1\}
\]

\[
= S \land |x| \in \mathbb{R}^+ \rightarrow x \in S \times \mathbb{R}^+
\]

\[
= \mathbb{R}.
\]

**Generalized Signs**

A general extension of this way to express real numbers can be described in the following manner. Suppose a tagged set formed by the same positive definite real numbers as objects. The tag signature of such general real numbers can be now considered made by a continuous function of an arbitrary real variable, defined into an arbitrary domain, but with range in the closed interval \([-1; +1]\).

For example, a function such that

\[
\sigma(r): [a; b] \subseteq \mathbb{R} \rightarrow [-1; +1] \quad (12)
\]

could be a suitable candidate for this generalization of the real numbers signature. The signature function produces a fuzzy sign pattern, which precisely coincides with the classic signature when the values of the two limits of the function range are reached. Thus, adopting a function like the one described within Eq. (12), the generalized real number set can be easily defined:

\[
\mathcal{R} = \{x|x = (\sigma(r); r) \land r \in [a; b] \subseteq \mathbb{R} \land \rho \in \mathbb{R}^+\},
\]

which provides a new set of real numbers, possessing an infinite variety of possible signs, attached to each positive definite real element.

Other possibilities are at hand to generalize signs and real numbers. For example, instead of the 1-D Boolean set of classic signs one can adopt a 2-D signature, and then four possible signs will be allowed . . . . Thus, signs become, from this point of view, some kind of classification information that can be attached to positive definite real numbers.

Still, there are possible other alternative interesting outcomes of this idea. One can adopt as generalized signatures some operator eigenfunctions, which like spin functions possess two (or more) well-defined eigenvalues. Then, the sign can be sian product of an arbitrary object set \(\Omega\) and the attached tag set \(T\) forms the basic structure of the tagged set \(Z\), made by an elementary procedure such that that \(Z = T \times \Omega = \{z|\forall \omega \in \Omega \rightarrow \exists r \in T \land z = (r, \omega)\}.

\[^{†}\]Tagged sets are understood as mathematical constructs, defined to allow taking into account a set element and some arbitrary information that can be associated with it. The Cartesian product of an arbitrary object set \(\Omega\) and the attached tag set

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made apparent just acting with the operator over the functional signature. In this sense, electronic spin functions are devices that can be interpreted as providing with a potential Boolean \( \{ -\frac{1}{2}, +\frac{1}{2} \} \), signature the spatial orbitals. The signature in this context is made apparent upon transforming the spin function by the \( s_z \) component of the spin momentum operator.

Then, in this manner it can be seen that it is a trivial matter to adopt any of these definitions as the elementary building blocks of the Slater extended wave functions. Because of all of these previous considerations, the extended spin function defined in Eq. (11) can be considered as a generalized signature of the Hückel extended wave function (1).

**Slater Determinants and Hartree Permanents**

**HADAMARD MULTIPLICATIVE ALGEBRA OF DETERMINANTS AND PERMANENTS**

Before going any further, it seems worthwhile to develop the Hadamard multiplicative algebra involving permanents and determinants, which can be summarized in the following table:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Det</th>
<th>Per</th>
</tr>
</thead>
<tbody>
<tr>
<td>Det</td>
<td>Per</td>
<td>Det</td>
</tr>
<tr>
<td>Per</td>
<td>Det</td>
<td>Per</td>
</tr>
</tbody>
</table>

Thus, the Hadamard product of a permanent and another determinant can formally construct the determinant of a given matrix, expressible at the same time by means of an IMP of two known matrices. In these composite operations involving determinants, it must be kept in mind that they shall not be properly computed before the product of the involved matrices is done. This is so because the Hadamard product of two determinants, whose effective result bears a zero value, can be brought into a nonnull permanent result. Such properties produce a curious algebra, indeed.

**SLATER DETERMINANTS**

It has been said that the Slater extended wave functions, defined according to expression (10), can be transformed at once into scalar **Slater determinants**.

This will be studied just by using the nested summation symbol (NSS)* formalism [9]:

\[
\Delta(R; s) = \text{Det} | \Psi(R; s) | = \sum_{N} (i) \text{P}(i) \text{S}(i) \psi(i), \quad (13)
\]

where the expression of the Slater determinant has been constructed using such a NSS symbol, formally depicted as \( \sum_{N} (i) \). In description (13) also used are the permutation selector \( \text{P}(i) \) and the parity signature \( \text{S}(i) \), both being attached to the index vector: \( i = (i_1, i_2, \ldots, i_N) \). The permutation selector symbol \( \text{P}(i) \) analyzes the entire index set, discards the index sequences with index repetitions, and, in this manner, only selects the set of indices that correspond to permutations. The parity signature symbol \( \text{S}(i) \) produces a minus or plus signature of every product entering the determinant, according to the previously accepted sequence of integers \( i \). These signs correspond to an odd or even permutation of the canonical order of the first \( N \) integers, selected by the permutation selector symbol. Finally, in the Slater expression (13) there appears the product of the spin orbitals, \( \psi(i) \), defined by

\[
\psi(i) = \prod_{k=1}^{N} \psi_k(k),
\]

where one can see involved the \( i_k \)th spin orbital functions and the space and spin coordinates of the \( k \)th particle, symbolized by the index \( k \) enclosed in parentheses.

In this case, the formalism appears to be different from Hückel and Hartree developments because of the forced wave function antisymmetry provided by the determinant structure of the Slater wave functions. There, the unavoidable presence of both the Hückel orbital and the spin function matrices is the most important factor to be taken into account.

Slater determinants can be written in the form (13), developing the signed permutation terms

*The NSS definition deserves some commentary, although for more details the reader should peruse the literature [9]. An NSS is a linear operator that contains a nest of \( N \) sums, whose indices are collected into a \( N \)-dimensional index vector, \( i = (i_1, i_2, \ldots, i_N) \), in the form

\[
\sum_{N} (i) f(i) = \sum_{i_1} \sum_{i_2} \cdots \sum_{i_N} f(i_1, i_2, \ldots, i_N),
\]

where the symbol \( f(i) \) corresponds to an arbitrary expression of the index vector.
among the elements of the spin orbital matrix structure, constructed by the IMP product of the Hückel wave function matrix (1) and the spin function matrix (11), as shown in Eq. (10). However, due to the Hadamard multiplication characteristics, the following sequence of equalities can be easily written:

\[ \Delta(R, s) = \text{Det}[\Psi(R; s)] = \text{Det}[\Phi(R) \ast S(s)] \]
\[ = \text{Det}[\Phi(R)] \ast \text{Per}[S(s)] \]
\[ = \left( \sum_N (i) P(i) S(i) \varphi(i) \right) \ast \left( \sum_N (i) P(i) \sigma(i) \right) \]
\[ = \text{Per}[\Phi(R)] \ast \text{Det}[S(s)]. \quad (14) \]

As previously noted, it must be taken into account the fact that, formally, the determinants entering Hadamard products shall be obtained after the product itself is performed. This could be so because a Hadamard product of a Hartree permanent and a spin function determinant are the two moieties needed to describe the Slater determinant. The exchange part of the Hartree–Fock energy shall be a consequence of the presence of the spin wave function determinant in the function described in Eq. (14). With the Hamiltonian to be employed in this case, bearing the same structure as in the Hartree method, further discussion, as described in Eqs. (20) and (21) shall be performed. No more remains to be said now about these questions. However, the door remains open about additional discussions.

**HARTREE PERMANENTS**

From here, it is elementary to write an alternative scalar polyelectronic function, possessing symmetrical properties when particle coordinates are exchanged. There is an easy way to produce such a function, by using the permanent of the Slater extended function, which is defined as almost the determinant (13), but omitting the parity signature operator \( S(i) \); thus,

\[ \Pi(R, s) = \text{Per}[\Psi(R; s)] = \sum_N (i) P(i) \psi(i). \quad (15) \]

So, all terms have a positive definite signature when this formal structure is used. One can name this definition as a *Hartree permanent* wave function.

**PERMANENT ALGEBRA UNDER HADAMARD PRODUCT**

Employing the Hadamard product as previously defined, the Hartree permanent can be made of two sequences, one involving the Hückel extended wave function and the other used in terms of the spin extended function, as follows:

\[ \Pi(R, s) = \text{Per}[\Psi(R; s)] = \text{Per}[\Phi(R) \ast S(s)] \]
\[ = \text{Per}[\Phi(R)] \ast \text{Per}[S(s)] \]
\[ = \sum_N (i) P(i) \varphi(i) \ast \sum_N (i) P(i) \sigma(i) \]
\[ = \sum_N (i) P(i) \varphi(i) \sigma(i). \quad (16) \]

The Hartree permanent norm can be easily computed, that is,

\[ \langle \Pi | \Pi \rangle = \sum_N (i) \sum_N (j) P(i) P(j) \int_D \varphi^*(i) \varphi(j) d\mathbf{r} \]
\[ \times \int_S \sigma^*(i) \sigma(j) d\mathbf{s} \]
\[ = \sum_N (i) \sum_N (j) P(i) P(j) \delta(i = j) \]
\[ = \sum_N (i) P(i) = N!, \]

where a logical Kronecker delta symbol* has been employed [9].

The logical Kronecker delta symbols were defined long ago, precisely to deal with the building

\*A logical Kronecker delta symbol is in general defined as a device to produce a zero or one factor in the context of any mathematical expression. It can be written as \( \delta(L, L) \), \( L \) being an arbitrary logical expression. Then, one can use the following outcome: \( \delta(T, ) = 1 \wedge \delta(F, ) = 0 \). From the programming point of view, the interesting fact is that a logical Kronecker delta can be translated as a logical if sentence within any high-level programming language.
up of Fock operators in MCSCF [23]. They were brought to operative planes recently with respect to NSS theory [9] and in other contexts [1]. The Slater determinant norm, as is well known, yields the same result.

HARTREE PERMANENT SPINLESS DENSITY

Spinless densities can be computed in both determinant and permanent cases, taking into account the result of the integral of two spin function products. The result is not so obvious when the spin signature permanent is studied. The peculiar structure of the permanent of the spin matrix wave function (11) merits some analysis. To ease such a kind of study, the spin function matrix can be transposed and the resultant columns ordered in a way that the first ones, \( n_{\alpha} \), correspond to the \( \alpha \) functions, say, and the remnant ones to the \( n_{\beta} = N - n_{\alpha} \) spin functions of \( \beta \) type. Then, the index associated to the NSS corresponds to the particle labels, that is,

\[
\text{Per}[\mathbf{S}(s)] = \sum_{N} (i) P(i) \sigma(i) = \sum_{N} \left( i_{\alpha} \oplus i_{\beta} \right) P(i_{\alpha} \oplus i_{\beta}) \alpha(i_{\alpha}) \beta(i_{\beta}),
\]

where the permutations are chosen over the whole index vector \( i = i_{\alpha} \oplus i_{\beta} \) being the first \( n_{\alpha} \) values composed by the possible combinations

\[
N_{C} = \left( \begin{array}{c} N \\ n_{\alpha} \end{array} \right) = \frac{N!}{n_{\alpha}!(N - n_{\alpha})!} = \frac{N!}{n_{\alpha}!n_{\beta}!}.
\]

The number above constitutes the number of possible classes of spin function products that upon integration are not orthogonal, that is,

\[
\langle \sigma(i) | \sigma(j) \rangle = \delta(i \in C \land j \in C), \tag{18}
\]

where \( C \) represents now the collection of all the independent permutations of the \( n_{\alpha} \) indices out of \( N \), together with the respective \( n_{\beta} \) remnant ones. The number of elements of such index collections in every class is \( n_{\alpha}!n_{\beta}! = n_{\alpha}!(N - n_{\alpha})! \). Thus, the norm of the permanent of a spin matrix function can be seen to be expressible as

\[
\int |\text{Per}[\mathbf{S}(s)]|^{2} ds = \sum_{N} (i) \sum_{N} (j) P(i) P(j) \int \sigma(i) \sigma(j) ds = \sum_{N} (i) \sum_{N} (j) P(i) P(j) \times \delta(i \in C \land j \in C) = N!n_{\alpha}!(N - n_{\alpha})! = N!n_{\alpha}!n_{\beta}!,
\]

where property (18) has been employed.

Due to expression (16), the spinless density function in the Hartree permanent context can be constructed as

\[
\int p(\mathbf{R}; s) ds = \int |\mathbf{P}(\mathbf{R}; s)|^{2} ds = |\text{Per}[\Phi(\mathbf{R})]|^{2} + \int |\text{Per}[\mathbf{S}(s)]|^{2} ds.
\]

Then, considering normalized the spin permanent, one arrives at the conclusion that the spinless Hartree permanent density can be obtained in terms of the permanent of the Hückel extended wave function:

\[
\rho(\mathbf{R}) = |\text{Per}[\Phi(\mathbf{R})]|^{2} = |\text{Per}[\Phi^{*}(\mathbf{R}) \ast \Phi(\mathbf{R})]| = \sum_{N} (i) P(i) |\varphi(i)|^{2} = |\varphi(1, 2, \ldots, N)|^{2} = \prod_{i=1}^{N} |\varphi(i)|^{2}. \tag{19}
\]

Thus, a Hartree density function is redefined in this way.

HARTREE ENERGY

Hartree energy [23, 24] can be easily deduced from the result presented in Eq. (19). However, the previous Hückel result and the properties of the Hartree permanent may suggest that a similar reasoning can be used in this case as in the former one. Owing to the fact that the Hartree wave function, from the spin point of view, behaves as a Hückel wave function, there appears the problem to search whether a Hückel extended function, in terms of definition (1), can be used directly in a similar fashion as done before.

The difference between both treatments is in the Hamiltonian partition. In Hartree problems the Hamilton operator can be written as
which suggests a full matrix structure, made by the following elements:

\[
H(1, 2, \ldots, N) = \sum_{j=1}^{N} \left( h(j) + \frac{1}{2} \sum_{k \neq j} |r_j - r_k|^{-1} \right). \tag{20}
\]

In this manner, the following equality can be written using the already defined matrix elements summation symbol:

\[
H(1, 2, \ldots, N) = \langle H(1, 2, \ldots, N) \rangle.
\]

In the context of the present treatment, the next difference between Hückel and Hartree methods appears simply to be the presence in both Hartree Hamiltonian definitions (20) and (21) of two-electron repulsion terms. Thus, a two-electron density shall be obtained from the Hückel extended wave function. The adequate way may be to write it as the IMP:

\[
P^{(2)}(R) = \Phi^+(R) \Phi(R)
= \begin{pmatrix}
|\varphi_1(1)|^2 & \varphi_1(1)\varphi_1(2) & \cdots & \varphi_1(1)\varphi_1(N) \\
\varphi_2(1)\varphi_1(1) & |\varphi_2(1)|^2 & \cdots & \varphi_2(1)\varphi_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_N(1)\varphi_1(1) & \varphi_N(1)\varphi_2(1) & \cdots & |\varphi_N(N)|^2
\end{pmatrix}.
\]

Further, the density matrix can be decomposed into the diagonal part and the out-of-diagonal remnant elements:

\[
P^{(2)} = D^{(2)} + \Omega^{(2)} = \text{Diag}(P^{(2)}) + \text{OutDiag}(P^{(2)}).
\]

The same can be done with the Hamiltonian operator (21):

\[
H(1, 2, \ldots, N) = h + C = \text{Diag}(H) + \text{OutDiag}(H),
\]

the employed symbols bearing obvious meanings. Then, the Hartree energy can be written by means of a sum of two contributions, namely,

\[
E = \left( \int_{D} (h \ast D^{(2)}) \, dr \right) + \left( \int_{D} (C \ast |C^{(2)}|) \, dr \, dr' \right),
\]

which will produce the mono-electronic terms and the Coulomb repulsion of the Hartree energy, respectively. In the present formalism, the orbital occupation shall be considered embedded in the theoretical structure of the matrix wave function, as doubly occupied orbitals will appear twice in the wave function elements.

**Conclusions**

A new point of view based on ideas about the extended wave function structure, previously discussed, can be used to analyze the rearrangement of the Hückel and Hartree methods. The results point out the possible construction of a wave function class made of square matrices, which can be safely employed in the HMO methodology as well as a basic structure from where the Hartree permanent or the Slater determinant functions can be deduced. Hadamard multinomial products, as well as IMP algebra, appear to be complementary useful mathematical tools to operate within the conceptual new structure of these old quantum mechanical methods. It must be finally noted that the concept of generalized or fuzzy signature has been also described here due to the discussion of the mathematical role adopted by the spin functions when used to construct spin orbital functions.

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