

# Geometric Approach in the Calculation of Ground State Electronic Structures

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**ABSTRACT** For many-electron systems in the ground state the wave function and the Hamiltonian are to be expressed in terms of the configuration space (CS), a replica of real space for each electron. Here we present a geometric formulation of the CS, of the wave function, and of the Hamiltonian to compute the electronic structure of the system. Then, using the new geometric notation and the indistinguishability and equivalence of the electrons, we obtain an alternative computational method for the ground state of the system.

## 1 Introduction

There is a large amount of research based on the calculation of the ground state electronic structures of atoms, molecules and solids. The basic approach [1, 2] considers the steady state Born-Oppenheimer approximation: a fixed given configuration of charged point-like nuclei, the so called ‘structure’ of the molecule, cluster or crystal. The computational procedure involves the simultaneous calculation of: the ground state electronic wave function  $\Psi_N$ , the (ground state) electronic density  $\rho_N(x)$ , the total electronic energy  $E_N$  for the  $N$  electrons, a set of  $M \geq N$  auxiliary spin-orbitals (SO), and the SO-energy eigenvalues  $\varepsilon_a$ . A minimum set of  $N$  functions is required by Pauli’s principle. The SO and the  $\varepsilon_a$  are important as far as they are related to the response function of the electronic system and as such to its spectroscopic properties. The electronic density, wave function, SO, and  $\varepsilon_a$  are not observable in themselves but, through several spectroscopy’s, they can be studied as indirect observables. Point-Contact Spectroscopy and other recent techniques (see Itatani J. et al. 2004 [3] and references therein) are good examples of such tools. The computational techniques can also be extended to time dependent [4, 5] and to beyond Born-Oppenheimer [6] cases. In these approaches the electron is

defined as a physical entity which obeys the Dirac Equation for the electron's experimental mass and charge, the non-relativistic limit of the Dirac equation is given by the Schrödinger equation if the spin of the electron is considered for magnetic interactions and for statistics.

Several features made the, now known as Hartree-Fock method (HF), the reference: it is a formally correct variational procedure based in the use of a determinant of auxiliary functions for which a differential equation is deduced within the method. It includes (through the basic properties of the Slater determinant) the Pauli Exclusion Principle as well as the indistinguishability of equivalent fermions. HF is also a suitable starting calculation for establishing the procedure known as Configuration Interaction (CI), introducing a set of variational constants, when the spin-orbitals resulting from the HF calculation are used to construct a formally complete wave function as a sum of mutually orthogonal Slater determinants. The standard definition of 'exchange energy' and of 'correlation energy' is given in relation to the HF+CI procedures. In the determinants no two-electron-relative-coordinates functions are used, neither in these approaches nor in the one described below.

Another widely used methodology, based on the Density Functional Theory (DFT) a correct formal procedure itself [7, 8], can be considered as related to HF+CI as the standard calculations include local density functionals for the exchange and correlation energies and potentials.

Recently we have shown that there is a new, geometrical, starting point for formulating a mathematical theory for the density and for the related wave function [9]-[13], we call KKW. A resulting methodology, developed here, shares both all the favorable features of the HF+CI method and the advantages of the DFT procedure. This suggests that there should be a relation between all three procedures HF+CI, DFT and KKW.

In the calculation of the stationary ground state of the many electron (many equivalent fermions in general) wave function and densities a variational approach optimizes the solutions with respect to desirability criteria, in our case, the lowest ground state energy  $E$ . The variational procedure provides a suitable set of constants and/or a set of auxiliary functions. For computational method  $\mathcal{M}$  of lowest ground state energy  $E = \int \bar{\Psi} \hat{H}_{\mathcal{M}} \Psi dV$  we should consider the variation of a functional  $\delta \left( \left[ \int \bar{\Psi} \hat{H}_{\mathcal{M}} \Psi dV - E \right] - \mu \left( \int \bar{\Psi} \Psi dV - N \right) \right) = 0$ , where the second parenthesis imposes the condition that this is an  $N$  electron system.

The basic formulation can be summarized as follows: to the  $N$  equivalent electron system in volume  $V$ , obeying the Pauli's exclusion principle, corresponds an *analytical finite non-negative* total density function  $\rho_N(x)$  such that the total electronic energy  $E = \int \varepsilon \rho_N(x) dV$  is well defined and proportional to its integral in the system's volume. To fulfil this condition there should exist a many electron *analytical square integrable* wave function  $\Psi_N(\{x_n\}; n = 1, \dots, N)$  such that  $\rho_N(x) = |\Psi_N|^2 = \sum_{c=1}^N \rho_c(x)$

$$= \sum_{u=1}^{M \geq N} \rho_u(x).$$

Notice that two different expansions of the density are used simultaneously: one (  $\sum_{c=1}^N \rho_c(x)$  ) is the description of the equivalent electrons in the system, the second (  $\sum_{u=1}^{M \geq N} \rho_u(x)$  ) describes the shell structure (atomic or molecular orbitals). In the Hartree-Fock method, with  $M = N$ , one description corresponds to the columns and the other to the rows of the determinant.

We have also indicated that this Hermitian square should be describable as either a sum of non negative, finite analytical functions  $\rho_c(x) = |\psi_c|^2$ , one equivalent  $\psi_c$  for each electron in the system, or (to be able to agree with the Pauli's principle) as a sum of  $M \geq N$ , weighted by  $w_u = |b_u|^2$ , spin-orbital  $\phi_u$  contributions  $\rho_u(x) = |b_u \phi_u|^2$ . This ensures that the physical conditions, which must be obeyed by the wave function itself and by the density, are fulfilled. In the case of the many electron (fermion) system *all N electrons (fermions) are equivalent*. The 'system' to be studied is such that no electron can be distinguished by position. This equivalence requires that the density itself should be describable as a sum of  $N$  equal densities  $\rho_{one\ electron}(x)$  which should be generated by equivalent contributions. That is  $\rho_{one\ electron}(x) = 1/N \sum_u \rho_u(x)$ . The many-electron wave function  $\Psi_N(\{x_n\}; n = 1, \dots, N)$  should be used to compute the total energy and other properties of this ground state of the system. Historically the Hartree-Fock method (and its complement Configuration Interaction) fulfilled the conditions above.

What is needed is to find the analytical, possible complex, function  $\Psi(\{x_n\})$  of a set  $\{x_n; n = 1, \dots, N\}$  of  $N$  coordinates which allows the factorization of a *finite non-negative* function

$$\rho(x) = \Psi^\dagger(\{x_n\}) \widehat{N}(x, \{x_n\}, \{x'_n\}) \Psi(\{x'_n\}) \subset \mathbb{R}^+$$

(the real numbers  $\mathbb{R} = \{\mathbb{R}^-, 0, \mathbb{R}^+\}$  are either negative, zero or positive). Here  $\widehat{N}(x, \{x_n\}, \{x'_n\}) = \sum_{nn'} \delta x_n x'_n \delta x x_n$  is a projector from configuration space  $X$  into the real space coordinates  $x$ .

In the KKW theory (all relevant points are presented below) the basic idea is that the density appears as a sum of densities and then the wave function  $\Psi_N$  should both be the square root of the total density function  $\rho(x) = \sum_u \rho_u(x)$  and also provide the square root  $\phi_u$  of each one of the contributions  $\rho_u(x)$  to the total density. For this we require the use of geometric (multivector analysis) techniques. In fact the problem is similar to that of finding the linear form (geometric square root)  $\mathbf{d} = a\mathbf{e}_1 + b\mathbf{e}_2 + c\mathbf{e}_3 + \dots$  which corresponds to the quadratic form  $d^2 = a^2 + b^2 + c^2 + \dots \subset \mathbb{R}^+$ . Here  $\mathbf{d}$  is the *geometric square root* of the scalar quantity  $d^2$ .

For a positive definite function  $\rho(x) = \mathbf{d}^\dagger(x) \mathbf{d}(x) \subset \mathbb{R}^+$  an ordinary (scalar) square root  $d(x) = \sqrt{\mathbf{d}^\dagger(x) \mathbf{d}(x)} = \sqrt{a^2(x) + b^2(x) + c^2(x) + \dots}$  is not necessarily *analytical*, whereas the geometric square root function  $\mathbf{d}(x) = a(x)\mathbf{e}_1 + b(x)\mathbf{e}_2 + c(x)\mathbf{e}_3 + \dots$ , through the use of an *analytical* set

$\phi$  of auxiliary complex functions  $\phi = \{a(x), b(x), c(x), \dots\} \subset \mathbb{C}$ , can be demanded to be *analytical*. The Hermitian squares  $\{a^2(x), b^2(x), c^2(x), \dots\} \subset \mathbb{R}^+$ . The analyticity property allows that a set of differential equations  $\widehat{D}a(x) = \epsilon_a a(x)$ ,  $\widehat{D}b(x) = \epsilon_b b(x), \dots$  which incorporates physical and mathematical boundary conditions can be found.

### 1.1 The Geometric Square Root

There is a freedom to choose, for the description (shell structure in our particular case), the most convenient anticommuting normalized basis set  $\{\mathbf{e}_u; \mathbf{e}_u \mathbf{e}_v = -\mathbf{e}_v \mathbf{e}_u, u \neq v; u = 1, \dots, M \geq N\}$ .

Otherwise, as the electrons are equivalent, we will also need a symmetrized form of  $\mathbf{d}$ . For this purpose we will simultaneously introduce a second (one basis element per electron) anticommuting normalized basis set  $\{\omega^S_i; \omega^S_i \omega^S_j = -\omega^S_j \omega^S_i, j \neq i; i = 1, \dots, N\}$  and a normalized vector  $\underline{\mathbf{S}} = \sqrt{1/N} (\omega^S_1 + \omega^S_2 + \omega^S_3 + \dots + \omega^S_N)$  and our definitions imply that  $(\sqrt{1/N} (\omega^S_1 + \omega^S_2 + \omega^S_3 + \dots + \omega^S_N))^2 = \underline{\mathbf{S}}^2 = 1$ . The  $\omega^S_i$ , therefore  $\underline{\mathbf{S}}$ , commute with the  $\mathbf{e}_u$ . Define  $\mathbf{d} = (a\mathbf{e}_1 + b\mathbf{e}_2 + c\mathbf{e}_3 + \dots + M\mathbf{e}_M) \underline{\mathbf{S}}$ , then  $d^2 = (d/N)^2 + (d/N)^2 + (d/N)^2 + \dots + (d/N)^2$ . There is a double summation: over the basis set  $\{\mathbf{e}_u\}$  and over the per electron in the system set  $\{\omega^S_i\}$ . The summations can be interchanged. This is the geometric procedure used below. The algebra of the  $\{\mathbf{e}_u\}$  or of the  $\{\omega^S_i\}$  is a Grassmann-Clifford algebra (see [11]-[13]). Notice that there is no need to define a vector scalar product.

## 2 Geometric Formulation of the calculation of the Stationary Ground State of a Many-Electron System

Here we present the formalism for the calculation of the stationary ground state of the many electron (many equivalent fermions in general) wave function and densities and the corresponding variational approach.

### 2.1 Configuration Space and Real Space.

A basic concept in the study of a many-electron system ( $N$  interacting fermions) is, from the considerations above, the simultaneous, repeated, use of real space (the space of the observer) for each one of the fermions of the system: configuration space. Then, if  $\mathbf{x}$  represents a point in real space, it is customary to represent by  $\mathbf{X} = \{\mathbf{x}_a; a = 1, \dots, N\}$  the set of points in the configuration space  $\mathbf{X}$  for  $N$  fermions.

The volume integral  $\int d\Omega$  when referred to the coordinates of fermion  $a$  is denoted by  $\int d\Omega_a$ . Also  $\int d\Omega_N$  indicates the integration over all  $N$  space replicas  $\int d\Omega_a$ . In the formal notation below we introduce an integration operator  $\widehat{\int d\Omega_N}$  to denote that repeated space integration for all  $N$  electrons is to be performed. The absolute value of the distance between two fermion points  $x_{ab} = |\mathbf{x}_b - \mathbf{x}_a|$ .

Here and in the rest of our presentation we use a geometric notation

$$\mathbf{X} = \sum_a \omega_a \mathbf{x}_a; \{a = 1, \dots, N; \omega_a \omega_b = -\omega_b \omega_a, b \neq a\}, \quad (2.1)$$

introducing the per electron operator  $\omega_a$  and, also, the projection operators  $\bar{\omega}_a$  such that  $\bar{\omega}_a \omega_b = \delta_{ab}$  selecting the part of the configuration space which corresponds to electron  $a$ ; this is  $\bar{\omega}_a \mathbf{X} = \mathbf{x}_a$ .

This construction allows a clear formal definition of the electrons involved in each part of the calculation. Our geometric procedure introduces one feature of the statistics of the fermion system from the beginning because the interchange  $\omega_a \leftrightarrow \omega_b$  in the products  $\omega_a \omega_b$  for two electrons, in any given expression, will change the sign of the corresponding terms.

When the argument of a function is position we will also use the fermion's numeral, say  $\phi(\mathbf{x}_1) \doteq \phi(1)$ , as equivalent argument.

## 2.2 Basic Principles

The Principles implied without further discussion in this paper are the same as those of the Hartree-Fock approach:

- The total energy is a functional of the wave function.
- The possibility of using the Schrödinger equation for the  $N$  electron system. The kinetic energy is the sum of independent electron-like kinetic energies for each electron.
- The ground state of the many electron system corresponds to the lowest total energy.
- The Pauli exclusion principle requires that the description for  $N$  electrons, included in the wave function, contains the occupancy of at least  $M \geq N$  pseudo-electron orthonormal spin-orbitals  $\phi_u$ .
- The equivalency and indistinguishability of the electrons require that all electrons are equivalently described.
- A variational approach can be used.

The electronic structure calculation of a many electron system in the ground state requires then the simultaneous calculation of: the ground state electronic wave function  $\Psi_N$ , the (ground state) electronic density  $\rho_N(x)$ ,

the total electronic energy  $E_N$  for the  $N$  electrons, a set of  $M \geq N$  auxiliary spin-orbitals (SO), and the SO-energy eigenvalues  $\varepsilon_a$ . A minimum set of  $N$  functions is required by Pauli's principle.

Both quantities, wave function  $\Psi(\mathbf{X})$  and density  $\rho(\mathbf{x}) = \bar{\Psi}\Psi$ , can be considered as the fundamental variable. In our theory the density appears as a sum of densities and then the wave function  $\Psi$  should both:

- 1) be a factorization of the total density  $\rho(x) = \sum_{n=1}^N \rho_{one\ electron}(x) = \sum_{i=1}^M \rho_i(x) = |\Psi|^2$  and
- 2) provide the square root of each one of the  $M$  shell structure contributions  $\rho_i(x) = |b_i \phi_i|^2$  to the total density.

### 2.3 The Energy Calculation.

We rewrite the usual expression for the total non-relativistic electronic energy operator or Hamiltonian  $\hat{H}_0$  in correspondence with our formal definition of configuration space (an atom electron structure is used to simplify the notation). We use the above defined per electron geometric notation  $\{\omega_b, \bar{\omega}_b\}$  to select, from the wave function  $\Psi_N^{KKW}$  and its conjugate  $\bar{\Psi}_N^{KKW}$ , the corresponding contributions. A *per electron* operator is an *effective one-body* operator.

We consider first the per electron 'a' kinetic energy operator

$$-\omega_a (\hbar^2 \nabla^2 / 2m_e) \bar{\omega}_a$$

and the electron nucleus potential energy operator  $-\omega_a (Ze^2/|x_n|) \bar{\omega}_a$ . Second the pair-wise Coulomb interaction  $V_{e-e, Coul}$  between the electrons: for electron 'a' in the pair  $a, b$  we have

$$(V_{e-e, Coul})_a = +\frac{1}{2} \sum_{a=1}^N \omega_a \int \widehat{d\Omega}_N \sum_{b \neq a} \left( \omega_b \frac{e^2}{|x_{ab}|} \bar{\omega}_b \right) \bar{\omega}_a$$

(notice that after performing the indicated  $\int \widehat{d\Omega}_N$  integration for all  $b \neq a$  this is reduced to a per electron operator).

Then

$$\begin{aligned} \hat{H}_0 = & \int \widehat{d\Omega}_N \sum_{a=1}^N \omega_a \left[ -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{|x_a|} \right. \\ & \left. + \frac{1}{2} \int \widehat{d\Omega}_N \sum_{b \neq a} \left( \omega_b \frac{e^2}{|x_{ab}|} \bar{\omega}_b \right) \right] \bar{\omega}_a . \end{aligned} \quad (2.2)$$

Correspondingly, the wave function  $\Psi_N^{KKW}$  is (first in a per electron  $n$  basis and second in a per orbital  $i$  description; using the geometric operators  $\alpha_i$  per auxiliary basis function  $\phi_i$  (SO) with weight  $b_i$ ,  $\alpha_i \alpha_j = -\alpha_j \alpha_i$ ,  $j \neq i$ , and the projection operators  $\bar{\alpha}_i \alpha_j = \delta_{ij}$ ):

$$\Psi_N^{KKW} = \sum_{n=1}^N (\omega\psi)_n, \quad (2.3)$$

$$\text{where } (\omega\psi)_n = \omega_n \left[ \sum_{i=1}^{M \geq N} b_i \alpha_i \phi_i(x_n) \right], \quad (2.4)$$

$$\text{and } \overline{\Psi_N^{KKW}} = \sum_{n=1}^N (\overline{\psi\varpi})_n, \quad (2.5)$$

$$\text{where } (\overline{\psi\varpi})_n = \left[ \sum_{i=1}^{M \geq N} b_i^* \bar{\alpha}_i \phi_i^*(x_n) \right] \varpi_n, \quad (2.6)$$

with normalization

$$\begin{aligned} N &= \int \overline{\Psi_N^{KKW}} \Psi_N^{KKW} d\Omega_N \\ &= \sum_{c=1}^N \int \left\{ \overline{\Psi_N^{KKW}} \omega_c \bar{\omega}_c \Psi_N^{KKW} d\Omega_c \right\}, \end{aligned} \quad (2.7)$$

and, when written in terms of the auxiliary spin-orbitals  $\phi_i$

$$\begin{aligned} N &= N \int \overline{\psi\psi} d\Omega = N \sum_{i=1}^{M \geq N} \int \overline{b_i \alpha_i \phi_i} b_i \alpha_i \phi_i d\Omega \\ &= N \sum_{i=1}^{M \geq N} |b_i|^2 \int |\phi_i|^2 d\Omega = N \sum_{i=1}^{M \geq N} |b_i|^2 \langle i | i \rangle. \end{aligned} \quad (2.8)$$

In this paper we assume equal number of spin up and spin down electrons, the spin restricted case. The second line in (2.7), from the definition of  $\int d\Omega_N$  in the Configuration Space section above, is an identity. In (2.8) we use the orthonormality of the  $\alpha_i$ .

Note that a double set of Grassmann (anticommuting) numbers  $\{\omega_a; \alpha_i\}$  has been introduced, this has an analytical analogue in the HF method determinant where either the exchange of columns or of rows change the sign of the determinant. Formally the wave function  $\Psi$  could be represented by a rectangular  $M \times N$  matrix with entries  $\alpha_i \omega_a$ . The second line in (2.3) would correspond to the (real positive number) trace of  $\overline{\Psi\Psi}$ . Exchange terms will arise from (2.3) when used in (2.2). The  $\phi_i$ 's form an orthonormal set of spin-orbitals  $\langle i | j \rangle \equiv \int \phi_i^* \phi_j d\Omega = \delta_{ij}$  and we introduced the normalization  $\sum_i |b_i|^2 = 1$ . Then the one electron density  $\rho_1(\mathbf{x}) = \overline{\psi}(\mathbf{x})\psi(\mathbf{x}) = \sum_i |b_i|^2 \phi_i^*(\mathbf{x})\phi_i(\mathbf{x})$ .

In (2.2) the Hamiltonian  $\hat{H}_0$  for electron  $n$ :  $H^{core}(x) + H^{interaction}(x)$  where the second term is a local one-electron operator, even if the electron repulsion, being dependent on the inter-electron distance, is a two-electron ( $i$  for  $n$ ,  $j$  for  $m$ ) operator. The resulting potential is the same for all components of  $\psi$ .

## 2.4 Core Energy

Denote the first two terms in (2.2) as  $\sum_{c=1}^N \omega_c \hat{H}^{core}(c) \bar{\omega}_c$ , then

$$\begin{aligned} E_{core} &= \int \bar{\Psi} \left\{ \sum_{c=1}^N \omega_c \hat{H}^{core}(c) \bar{\omega}_c \right\} \Psi d\Omega_c \\ &= \int \sum_{d'} \bar{\omega}_{d'} \bar{\psi}_{d'}(\mathbf{x}_{d'}) \left\{ \sum_{c=1}^N \omega_c \hat{H}^{core}(c) \bar{\omega}_c \right\} \times \\ &\quad \sum_d \omega_d \psi_d(\mathbf{x}_d) d\Omega_c, \end{aligned} \quad (2.9)$$

and from (2.4) and (2.6), orthonormality and equivalence:

$$\begin{aligned} E_{core} &= N \int \bar{\psi}_1(\mathbf{x}_1) \hat{H}^{core}(1) \psi_1(\mathbf{x}_1) d\Omega_1 \\ &= N \int \sum_i |b_i|^2 \phi_i^* \hat{H}^{core} \phi_i d\Omega. \end{aligned} \quad (2.10)$$

The  $\{\omega_c, \bar{\omega}_c\}$  and the  $\{\alpha_i, \bar{\alpha}_i\}$  above have selected the sum of the diagonal elements in (2.9). Note that the shell structure can not be avoided [9, 10].

## 2.5 Electron-Electron Interaction Energy

For the electron-electron interaction (e-e)

$$\begin{aligned} E^{e-e} &= \int \bar{\Psi}_N^{KKW} \sum_a \omega_a \\ &\quad \left[ \frac{1}{2} \sum_{b \neq a}^N \int \left( \omega_b \frac{e^2}{|x_{ab}|} \bar{\omega}_b \right) d\Omega_b \right] \bar{\omega}_a \Psi_N^{KKW} d\Omega_a. \end{aligned} \quad (2.11)$$

here, from the equivalence of the  $N$  electrons, we have  $N$  equal pair-wise  $1 \Leftrightarrow 2$  contributions which consider all spin-orbitals. Using the expansion of the  $\psi$ , we obtain

$$\begin{aligned} E^{e-e} &= \frac{N}{2} \int \int \sum_i \phi_i^*(1) b_i^* \bar{\alpha}_i \sum_j \phi_j^*(2) \bar{\alpha}_j \frac{e^2}{|x_{12}|} \\ &\quad \sum_k \phi_k(2) \alpha_k \sum_l \phi_l(1) \alpha_l d\Omega_1 d\Omega_2. \end{aligned} \quad (2.12)$$

Considering the property  $\bar{\alpha}_i \alpha_j = \delta_{ij}$  there are 3 types of e-e terms:

I)  $j = k$  and  $i = l$  which gives

$$\begin{aligned} & \frac{N}{2} \int \left\{ \sum_i \int \left[ \sum_{j \neq i} |b_j|^2 |\phi_j(2)|^2 \frac{e^2}{|x_{12}|} \right] \mathbf{1}(x_2) d\Omega_2 \times \right. \\ & \left. |b_i|^2 |\phi_i(1)|^2 \right\} \mathbf{1}(x_1) d\Omega_1 \\ & = \frac{N}{2} \sum_i \sum_{j \neq i} |b_j|^2 |b_i|^2 (ij, ij) = \frac{N}{2} E_I, \end{aligned} \quad (2.13)$$

where we have introduced the notation  $(ij, ij)$  for the integrals, as they are ‘‘Coulomb integrals’’ in the accepted electronic structure calculation language. Also the formal local unit factor  $\mathbf{1}(x) = \bar{\psi}(x) \psi(x) / \rho_1(x)$  will be fundamental to perform the variational procedure below to find the effective equations for the  $\psi(x)$ . Note that the  $\mathbf{1}(x)$  appear twice in this term resulting in a factor 2 in the variational wave equation.

II)  $j = l \neq i$  and  $i = k$  (the  $\delta_{s_i}^{s_j}$  from spin orthonormality, and one change of sign from the interchange  $\alpha_i \alpha_j = -\alpha_j \alpha_i$  is needed!)

$$\begin{aligned} & -\frac{N}{2} \sum_{i, j \neq i} \delta_{s_i}^{s_j} |b_j|^2 |b_i|^2 \\ & \int \int \left[ \phi_j^*(1) \phi_i^*(2) \frac{e^2}{|x_{12}|} \phi_i(1) \phi_j(2) \right] d\Omega_2 \mathbf{1}(x_1) d\Omega_1 \\ & = -\frac{N}{2} \sum_{i, j \neq i} \delta_{s_i}^{s_j} |b_j|^2 |b_i|^2 (ji, ij) = \frac{N}{2} E_{II}, \end{aligned} \quad (2.14)$$

where we have used the notation  $\delta_{s_i}^{s_j} (ji, ij)$  for the integrals, as they are ‘‘exchange integrals’’ corresponding to the  $[i, j]$  pair of spin-orbitals in the accepted electronic structure calculation language; the  $\delta_{s_i}^{s_j}$  requires  $s_i = s_j$  and ensures that the product  $\phi_j^*(1) \phi_i(1)$  of the SO, with spin  $s_i$  and  $s_j$  respectively, is not null. We use again the formal local unit factor  $\mathbf{1}(x)$ .

III) Null terms, where  $(i \neq l$  and  $i \neq k)$  or  $(j \neq l$  and  $j \neq k)$ .

$E_I$  and  $E_{II}$  also contribute to the formal interpretation of the Pauli Exclusion Principle: a given electron is not interacting with itself and there is an ‘exchange’ term for fermions, where from  $\alpha_i \alpha_j = -\alpha_j \alpha_i$  a negative sign appears.

## 2.6 Variation of the Total Energy with respect to the $\psi$

Here we consider the total energy in terms of the  $\psi$  as above. From the normalization (2.8) the per electron density is  $\rho_{one-electron}(x) = \bar{\psi}(x) \psi(x)$  and the total density  $N \rho_{one-electron}(x)$ .

We write the total energy

$$E_{total} = E_{core} + \frac{N}{2} (E_I^{e-e} + E_{II}^{e-e}). \quad (2.15)$$

For the *core* term

$$E_{core}/N = \int \bar{\psi}_1(\mathbf{x}_1) \hat{H}^{core}(1) \psi_1(\mathbf{x}_1) d\Omega_1, \quad (2.16)$$

the variation with respect to  $\bar{\psi}_1(\mathbf{x}_1)$  gives

$$\hat{H}^{core}(1) \psi_1(\mathbf{x}_1) = \left\{ -\frac{\hbar^2 \nabla_{(1)}^2}{2m_e} - \frac{Ze^2}{|\mathbf{x}_1|} \right\} \psi_1(\mathbf{x}_1). \quad (2.17)$$

For the variation of  $E_I^{e-e}/2$  with respect to  $\bar{\psi}_1(\mathbf{x}_1)$  we obtain, defining

$$V_I(\mathbf{x}_1) = \sum_i \left\{ \frac{|b_i|^2 |\phi_i(\mathbf{x}_1)|^2}{\rho_1(\mathbf{x}_1)} \right. \quad (2.18)$$

$$\left. \int \left[ \sum_{j \neq i} |b_j|^2 |\phi_j(2)|^2 \frac{e^2}{|x_{12}|} \right] d\Omega_2, \right\}$$

and, considering that the factor  $\mathbf{1}(\mathbf{x}_k)$  appears twice in (2.13), the repulsive electron-electron term

$$2 \frac{1}{2} V_I(\mathbf{x}_1) \bar{\psi}_1(\mathbf{x}_1) = V_I(\mathbf{x}_1) \bar{\psi}_1(\mathbf{x}_1). \quad (2.19)$$

Finally for the variation of  $E_{II}^{e-e}/2$  with respect to  $\bar{\psi}_1(\mathbf{x}_1)$  we obtain, assuming equal number of spins ‘up’ and ‘down’, defining

$$V_{II}(\mathbf{x}_1) = - \sum_{i,j \neq i} \frac{\delta_{s_i}^{s_j} |b_j|^2 |b_i|^2}{2\rho_1(\mathbf{x}_1)} \quad (2.20)$$

$$\int \left[ \phi_j^*(1) \phi_i^*(2) \frac{e^2}{|x_{12}|} \phi_i(1) \phi_j(2) \right] d\Omega_2,$$

the attractive ‘functions interchange’ electron–electron term

$$V_I(\mathbf{x}_1) \bar{\psi}_1(\mathbf{x}_1). \quad (2.21)$$

## 2.7 The KKW auxiliary equations

The variational procedure must be carried with respect to the  $\psi$ ’s

$$\delta \left[ \int \Psi_N^\dagger \hat{H}_0 \Psi_N d\Omega_N - \mu \left( \int |\Psi_N^{KKW}|^2 d\Omega_N - N \right) \right] = 0, \quad (2.22)$$

to obtain the formal equation which describes any electron  $n$  in the system (reminder  $\psi$  is a vectorial sum of functions  $\phi_i$ ). We collect the different terms of  $\int \Psi_N^\dagger \hat{H}_0 \Psi_N d\Omega_N$  from (2.10)-(2.14) as in (2.15)

$$\int \Psi_N^\dagger \hat{H}_0 \Psi_N d\Omega_N = E [\psi, \bar{\psi}],$$

$$\text{also } \int |\Psi_N^{KKW}|^2 d\Omega_N = N \int |\psi|^2 d\Omega,$$

and perform the variation with respect to  $\bar{\psi}(x)$ , as shown in the previous section, to obtain

$$\widehat{H^{KKW}} \psi(x) = \mu \psi(x) \quad (2.23)$$

$$\widehat{H^{KKW}} \equiv \left\{ -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{|\mathbf{x}|} + V_I(\mathbf{x}) + V_{II}(\mathbf{x}) \right\}.$$

The expansion of the  $\psi$  in terms of the  $\phi$  allows a further reduction, write (2.23) as

$$\widehat{H^{KKW}} \sum_{i=1}^{M \geq N} b_i \alpha_i \phi_i(x_n) = \mu \sum_{i=1}^{M \geq N} b_i \alpha_i \phi_i(x_n), \quad (2.24)$$

apply on both sides the projector  $\bar{\alpha}_i$  to obtain the practical equations for the set of auxiliary orthonormal functions  $\phi_i$  (from  $\bar{\alpha}_i \psi = b_i \phi_i$ )

$$\widehat{H^{KKW}} \phi_i = \varepsilon_i \phi_i. \quad (2.25)$$

We obtain, by left multiplication with  $\bar{\psi}$  of (2.23), integration and the normalization  $\langle \psi | \psi \rangle = 1$ ,  $\langle \phi_i | \phi_i \rangle = 1$ , a relation between the  $\mu$  and the  $\varepsilon_i$ 's given by  $\mu = \sum_i \varepsilon_i |b_i|^2 = \bar{\varepsilon}$ , that is:  $\mu$  is the weighted average eigenvalue.

## 2.8 A more familiar form of the auxiliary wave equations

We can rewrite the electron-electron interaction energy in a form which started with the Hartree-Fock methodology. Consider

$$E^{e-e} = \frac{N}{2} \{E_I + E_{II}\},$$

and rewrite as

$$\Rightarrow \frac{N}{2} \int \{E_{Coul}(\mathbf{x}_1) + E_{XC}(\mathbf{x}_1)\} \bar{\psi}(x_1) \psi(x_1) d\Omega_1,$$

obtained if, in the definitions above, the 'self-coulomb' integrals  $|b_i|^2(ii, ii)$  are added to remove the condition  $j \neq i$ , to  $E_I$ . The 'self-exchange' integrals  $-|b_i|^2(ii, ii)$  are added to remove the condition  $j \neq i$ , to  $E_{II}$ . (The

$E_{II}$  is now as in the formally equivalent Slater(1951) idea [14], which here is no longer an approximation). Then

$$\begin{aligned}\widehat{H^{KKW}} &\equiv \left\{ -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{|\mathbf{x}|} + V_{Coul}(\mathbf{x}) + V_{xc}(\mathbf{x}) \right\}, \\ V_{Coul}(\mathbf{x}_1) &= N \int \left[ \rho(2) \frac{e^2}{|x_{12}|} \right] d\Omega_2, \\ V_{xc}(\mathbf{x}_1) &= -\frac{N}{\rho(\mathbf{x})} \sum_{i,j} \delta_{s_i^s}^{s_j} |b_j|^2 |b_i|^2 \times, \\ &\int \left[ \phi_j^*(1) \phi_i^*(2) \frac{e^2}{|x_{12}|} \phi_i(1) \phi_j(2) \right] d\Omega_2.\end{aligned}\quad (2.26)$$

By substitution of (2.26) in (2.25)

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{|\mathbf{x}|} + V_{Coul}(\mathbf{x}) + V_{xc}(\mathbf{x}) \right\} \phi_i(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x}) \quad (2.27)$$

Reminder  $\widehat{H^{KKW}}$  is the same for all  $\phi_i$ 's.

The total energy given in a form related to HF is obtained by direct integration of the set of equations (2.27) multiplied on the left by  $\sum_i |b_i|^2 \phi_i^*$  and comparing with (2.15):

$$E[\Psi] = \sum_i |b_i|^2 \varepsilon_i - \frac{E_{coul}}{2} - \int V_{XC}(\mathbf{x}) \rho(\mathbf{x}) d\Omega + E_{XC} \quad (2.28)$$

(customary form  $E_{coul}$  and  $E_{XC}$  include the self-coulomb and the self-exchange respectively).

With variational constants  $b_i = \sqrt{(1 - \sum_{j>N} b_{ij})/N}$  for  $i \leq N$  and  $b_j = \sqrt{\sum_{i \leq N} b_{ij}/N}$ , the variational procedure to obtain the set  $\{b_{ij}\}$  is similar to CI. A secular determinant can be constructed and solved. If the basis  $\{\phi_i\}$  is large enough a time dependent formulation with  $\Delta V(t)$  can be constructed where  $b_i \Rightarrow b_i(t)$  and the  $b_{ij} \Rightarrow b_{ij}(t)$  describe induced transitions.

Finally the basic definition for the total energy  $E = E[\bar{\psi}(x)\psi(x)]$  of  $N$  **equivalent** carriers (electrons), in terms of the density  $N\bar{\psi}(x)\psi(x)$  defining

$$\begin{aligned}E_{core} &= N \int \left[ \sum_i \frac{|b_i|^2 \phi_i^*(\mathbf{x}_1) \hat{H}^{core} \phi_i(\mathbf{x}_1)}{\rho_1(\mathbf{x}_1)} \right] \times \\ &\bar{\psi}(\mathbf{x}_1) \psi(\mathbf{x}_1) d\Omega_1 \\ &= N \int \varepsilon^{core}(\mathbf{x}_1) \bar{\psi}(\mathbf{x}_1) \psi(\mathbf{x}_1) d\Omega_1.\end{aligned}\quad (2.29)$$

$$E = N \int \{ \varepsilon^{core}(\mathbf{x}_1) + \varepsilon^{inter}(\mathbf{x}_1) \} \bar{\psi}(x) \psi(x) d\Omega_1, \quad (2.30)$$

here, considering  $E = N \int \varepsilon \bar{\psi}(x) \psi(x) d\Omega_1$

$$\varepsilon^{core}(\mathbf{x}_1) + \varepsilon^{inter}(\mathbf{x}_1) = \varepsilon.$$

### 3 The Properties of the Wave Function. Conclusions.

The KKW wave function describes a system of  $N$  electrons with an expansion based on  $M \geq N$  auxiliary, mutually orthogonal functions, solutions of the same ‘‘KKW’’ Hamiltonian. The complete wave function, then the one density, is directly optimized and not each auxiliary function at a time.

From the many possibilities to construct the  $\psi$  it is useful to choose the one presented here because the eigenvalues  $\varepsilon_i$ , by construction the rate of change of the total energy with respect to occupation of the ‘ $i$ ’ spin-orbital, are an approximation to the removal energy of one electron, from that SO, in the system. Also because the SO functions, being related to the response function of the system, have become observables (Itatani J. et al. 2004 [3]). Below we quote standard use of the so called *ab-initio* and DFT methods, see for example [15, 16].

- The KKW method offers a complete variational solution to the problem of finding the wave function and simultaneously the energy of the ground state of the  $N$  electron system.
- The KKW method ( $M = N$ ) requires the self-consistent solution of  $N$  differential equations, as in DFT, unlike the HF which is a  $N \times N$  formulation.
- If, as in the HF method, each auxiliary function were to be optimized separately one at a time in a self-consistent set, from the equivalent expressions for the total energy, we go back to the HF procedure and results. Our method has the advantage that the complete set is optimized simultaneously to search for the lowest total energy.
- The KKW method in the minimum auxiliary functions procedure is equivalent to the Slater (1951) average exchange proposal (with the so called ‘exact’ exchange) and in fact transforms this Slater ‘approximation’ into a non approximate procedure where all auxiliary functions are optimized simultaneously.
- To find the limit for the ground state energy of the system the number of auxiliary functions to be considered is  $M > N$ . The practical

approach to this calculation will be twice variational, first in the sense that the auxiliary functions are found from the variation of a functional, and second because the weight of the contributions of the remaining  $M - N$  functions will require a set of variational parameters to be found. This being not the only possibility even if it appears as the simplest one.

- The formal structure of the new method enriches the methodology of the DFT by showing that the Slater exchange and the Kohn-Sham procedures are formally integrated to the general scheme and also because an  $N$ -electron wave function  $\Psi$ , which is required in the theorems of the formal DFT theory, is constructed and used within the formalism.
- The new method systematically includes the kinetic and the potential energy for the additional  $M - N$  auxiliary functions. It has otherwise the advantage, as in multiconfiguration calculations, that all spin-orbitals are self-consistently optimized.
- The use in the Hamiltonian of selective pair-wise interaction terms

$$(\Delta V_{e-e})_{ab} = \omega_a \omega_b (\Delta V_{mn}) \bar{\omega}_b \bar{\omega}_a,$$

allows the description of pairing of any origin, magnetic or electron-phonon or from any other indirect type. Also specific one spin-orbital cases  $(\Delta V)_a = \omega_a (\Delta V_a) \bar{\omega}_a$ . This being a further advantage of the geometric notation.

The KKW approach also shows, from the different analysis presented here, DFT both as an ab-initio and as a first principles method. This is an important formal contribution of our study.

Computationally there is no need to consider a self-coulomb energy. As all electrons have equivalent descriptions, with the same density per electron, there is an exact resultant factor  $((N - 1)/N)$  in the electron-electron Coulomb interaction. It is basic for the calculation of the hydrogen atom. It is dominant in the calculation of the Helium atom where each of the two electrons interact with the other but not with itself, and progressively less important for larger systems where the interchange part of the interaction grows. Standard DFT programs [17, 18] for atomic electronic structure calculations are easily modified, a  $(N - 1)/N$  factor in the Coulomb potential, replacement of the exchange-correlation and total energy subroutines, to solve the KKW equations (2.27). As a numerical test the relativistic program “David” [18] was adapted, the H atom calculation used as a first check of the numerical procedures, the He atom with  $M = N$ , the Hartree-Fock limit for the Coulomb interaction and the He atom with (1s,2s,2p) for the  $M > N$  case, Beryllium and Krypton in the  $M = N$  as further tests.

All results are acceptable in the limit of the corresponding approximations (Hartree atomic units):

<i>Atom</i>	$E_{total}$	$E_{HF}$	$E_{DFT}$	$E_{exp.}$
<i>H</i>	-0.5	-0.5	-	-0.5
<i>He</i>	-2.886	-2.864	-2.867	-2.90
<i>Be</i>	-14.603	-14.573	-14.592	-14.673
<i>Ne</i>	-128.87	-128.55	-128.62	-128.94
<i>Kr</i>	-2799.49	-2796.72	-2787.80	-

In our analysis we have gone beyond complex algebra and calculus, in fact we have gone to the more general domain of the Grassmann-Clifford algebra and analysis.

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