

The Hartree-Fock method

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Abstract

Starting from the general context of the time-independent Schrödinger equation, the Hartree-Fock method is presented in a didactic way in order non experts readers can understand some subtle problems arising along the development of the theory. Emphasis is given to the accordance of Slater determinants with the first principles of quantum mechanics and to rationalize in a intuitive way some properties of the Hartree-Fock wave function. The projected equations and the Koopmans' theorem are discussed in some detail and the restricted and unrestricted treatments are briefly presented.

0.1 Introduction

The exact solution of the Schrödinger equation for an atom or molecule with more than two electrons is a rather formidable problem. Within the Born-Oppenheimer approximation, the difficulty is mainly due to the two electron terms of the Hamiltonian which introduce a correlation between the motion of the electrons, in the fields of the attractive potential of the nuclei. For this reason one has to look for approximate solutions, whose accuracy is determined by the observable one wants to evaluate as well as by the computer resources at disposal. One of the most popular approximation is the Hartree-Fock method in which the wave function is as simple as possible, provided in accordance with the principles of quantum mechanics and in particular with the indistinguishability principle of identical particles. This principle imposes that the electronic wave function must be antisymmetric with respect to the exchange of any two electrons i.e. it must change its sign when the position of two electrons is interchanged. The most simple function that satisfies this requirement is the Slater determinant built on a set of one-electron functions called spin orbitals. A spin orbital is a function of the three spatial variables and one spin coordinate, which describes the spatial-spin distribution of just one

electron. A spin orbital is the wave function of the one-electron systems as for instance, the hydrogen-like atoms. In the case of many-electron systems the motion of each electron can no more be described by a single particle function which does not depend explicitly on the motion of the other electrons and the attempt to describe such systems through spin orbitals leads to approximate wave functions. However, from a number of spin orbitals a Slater determinant can be formed that represents a wave function which, hopefully, is able to capture the main physics of the system. The Hartree-Fock problem is just the search of the ‘best’ set of spin orbitals, or, by invoking the variational theorem, the set of spin orbitals which minimizes the energy of the corresponding Slater determinant.

Now let’s consider the general context of the Hartree-Fock theory. The molecular electronic Hamiltonian in atomic units has the following expression

$$H_{el} = \sum_i -\frac{1}{2}\nabla_i^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} \quad (1)$$

where the three terms are the kinetic energy, nuclear attraction and electron-electron repulsion operators, respectively. The indices i, j run over the N electrons of the system and the index A over the nuclei. The electrostatic potential depends on the electron-nucleus distances r_{iA} and the electron-electron distances r_{ij} . By collecting the one-electron terms, the Hamiltonian can be written in a more compact form

$$H_{el} = \sum_i h(r_i) + \sum_{i<j} 1/r_{ij}$$

where it is evident that h includes kinetic energy, nuclear attraction operators. The electronic Hamiltonian arises from the separation of the nuclear and electronic motion within the Born-Oppenheimer approximation. In fact in the electronic Hamiltonian (1) the nuclear positions are not dynamical variables, rather they are fixed parameters which affect the electron-nucleus attractive potential. Thus the eigenvalue of the time-independent Schrödinger equation

$$H_{el}(x, R) \Phi(x, R) = E(R) \Phi(x, R) \quad (2)$$

is just a point in the multi-dimensional potential energy at a given nuclear arrangement. In the above equation x collects all the spatial-spin electronic coordinates whereas the parameter R indicates a given nuclear conformation and affects the nuclear attractive potential in the Hamiltonian.

0.2 The Slater determinant

For one-electron systems the solution of the time-independent Schrödinger equation is just a function of the three spatial coordinates x, y, z and the spin coordinate s , $\varphi(x, y, z, s)$. As the electrons are fermions with spin $1/2$, the possible spin functions are well defined: $\alpha(s)$ and $\beta(s)$ which correspond respectively to eigenvalues $1/2$ and $-1/2$ of the spin operator projected onto the z axis. The spin variable s is a formal coordinate which allows to write the integrals involving the spin functions in the same manner as the spatial integrals. The physically relevant quantities are the α and β functions which correspond to different intrinsic angular momentum of the electron along the quantization axis. This type of function $\varphi(x, y, z, s)$ suitable to describe the motion of a single electron is called ‘spin orbital’.

In the case of two-electron systems, a reasonable approximation to the exact antisymmetric wave function, could be an antisymmetrized product of two spin orbitals φ_a and φ_b

$$\Phi(x_1, x_2) = \frac{1}{\sqrt{2}} [\varphi_a(x_1)\varphi_b(x_2) - \varphi_b(x_1)\varphi_a(x_2)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(x_1) & \varphi_b(x_1) \\ \varphi_a(x_2) & \varphi_b(x_2) \end{vmatrix} \quad (3)$$

where the symbol $|\dots|$ stands for the determinant of the enclosed matrix and the argument x_1 and x_2 indicates the spatial-spin coordinate of the two electrons. The above formula expresses the wave function in terms of a Slater determinant (SD) in which each column includes a different spin orbital as a function of the coordinates of electron 1 in the first row and of electron 2 in the second row. So, it is never possible to say that φ_a describes the first electron and φ_b the second electron. The terms 'first electron' and 'second electron' have no meaning as the electrons are indistinguishable and it is never possible to put a label on one specific electron. In fact the spin orbital φ_a appears two times in the expression: in the first term with x_1 as argument and the second time with x_2 as argument. Moreover the function (3) obeys to the antisymmetry principle as the exchange of the position of the two electrons (i.e. x_1 exchanged with x_2) originates a change of sign of the entire wave function [1].

In the case $\varphi_a = \varphi_b$ the two electrons would be in the same spin orbitals and the matrix in (3) has two identical columns, so that its determinant is null for all possible values of the spatial-spin coordinates. Therefore the wave function is everywhere null. *This is the famous Pauli principle which descends from the antisymmetry principle and says that two electrons can never occupy the same spin orbital in a Slater determinant.* In addition, when $x_1=x_2$ the two rows of the matrix (3) are identical and again the SD vanishes in accordance with the antisymmetry principle of fermions which establishes that two identical particles can never be found in the same point of the spatial-spin coordinates [2,3].

A generic Slater determinant for N electrons is

$$\Phi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \dots & \varphi_N(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \dots & \varphi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(x_N) & \varphi_2(x_N) & \dots & \varphi_N(x_N) \end{vmatrix} \quad (4)$$

which again is consistent with the principle of indistinguishability of identical particles. The normalization factor accounts for the $N!$ permutations terms arising from the determinant. As in the previous case, each electron is associated with every spin orbital and therefore there is no one-to-one mapping between electrons and spin orbitals, rather the correspondence is all-to-all. A Slater determinant can be specified by the indices of its spin orbitals, without indicating explicitly the electronic coordinates. In the above formula the spin orbitals entering the SD go from 1 to N so that the short notation

$$|\Phi\rangle = |\varphi_1\varphi_2\varphi_3\dots\varphi_N\rangle \quad (5)$$

indicates the (ket) SD (4). In the case we have at disposal a number of spin orbitals greater than N , many SDs can be built and each of them can be specified by a sequence of the N indices of the involved spin orbitals. The properties of the SD for two electrons deduced above, are still true for a generic SD: the SD is null when two spin orbitals are identical and when two electrons are put in the same spatial-spin coordinate. Thus for instance

$$|\varphi_1\varphi_2\varphi_2\varphi_3\dots\varphi_N\rangle = 0 \quad \Phi(x_1, x_2, x_3, x_4, x_3, \dots, x_N) = 0 \quad (6)$$

Because of the two electron terms in the Hamiltonian, it is clear that a Slater determinant can never be the exact solution of the Schrödinger equation for $N > 1$. Only in the case of one electron Hamiltonian's (typical of independent particle systems) the exact solutions can be written as a product (or an antisymmetrized product) of spin orbitals, but this is not the case for real systems like atoms and molecules.

The general energy formula for any normalized wave functions Ψ is

$$E = \langle \Psi | H_{el} | \Psi \rangle \quad (7)$$

which in the case Ψ is a SD assumes the expression [4]

$$E [\varphi_1 \dots \varphi_N] = \langle \Phi | H_{el} | \Phi \rangle = \sum_{i=1}^N \langle \varphi_i | h | \varphi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N [\langle \varphi_i \varphi_j | \varphi_i \varphi_j \rangle - \langle \varphi_i \varphi_j | \varphi_j \varphi_i \rangle] \quad (8)$$

or in compact notation

$$E = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} [\langle ij | ij \rangle - \langle ij | ji \rangle] \quad (9)$$

where the one-electron integrals are

$$\langle i | h | j \rangle = \int dx \varphi_i^*(x) h(x) \varphi_j(x) \quad (10)$$

and the two-electron integrals in Dirac notation are defined as

$$\langle ij | kl \rangle = \int dx_1 \int dx_2 \varphi_i^*(x_1) \varphi_j^*(x_2) \frac{1}{r_{12}} \varphi_k(x_1) \varphi_l(x_2) \quad (11)$$

The two-electron contribution to the energy in the expression (9) includes two distinct types of integrals: the coulomb $\langle ij | ij \rangle$ and the exchange $\langle ij | ji \rangle$ terms. To better rationalize these energy contributions we introduce the one-body density matrix arising from a generic wave function Ψ

$$\rho(x_1, x'_1) = N \int dx_2 \dots \int dx_N \Psi(x_1, x_2, \dots, x_N) \Psi^*(x'_1, x_2, \dots, x_N) \quad (12)$$

which depends on two spatial-spin variables, and for this reason can be thought as a matrix with continuum indices [5]. The density function $\rho(x_1) \equiv \rho(x_1, x_1)$ corresponding to the diagonal elements $x_1 = x_2$ has an important physical meaning, namely $\rho(x_1) dx_1$ is the probability of finding any of the N electrons in the infinitesimal spatial-spin volume dx_1 around x_1 . Thus, whereas the spin orbitals and the density matrix (for $x_1 \neq x_2$) are mathematical objects, the density function is a physical object. When the wave function is a SD formed by N spin orbitals, the density matrix assumes the expression

$$\rho(x_1, x_2) = \sum_{i=1}^N \varphi_i(x_1) \varphi_i^*(x_2) \quad (13)$$

which may be used to rationalize the coulomb and exchange elements in the energy expression (9). Indeed the coulomb terms in (13) can be written in terms of the density function

$$E_{coul} = \frac{1}{2} \sum_{ij} \langle ij|ij \rangle = \frac{1}{2} \int dx_1 \int dx_2 \frac{\rho(x_1) \rho(x_2)}{r_{12}} \quad (14)$$

and represents the electrostatic interaction between the density charge with itself. As it includes electrostatic interaction between charge of the same sign, it is a repulsive term and its contribution to the total energy is always positive. This expression is the same of classical physics and there is no apparent signature we are dealing with a quantum system. The second term is the exchange contribution that can be expressed in terms of the density matrix (not by the density function)

$$E_{exch} = -\frac{1}{2} \sum_{ij} \langle ij|ji \rangle = -\frac{1}{2} \int dx_1 \int dx_2 \frac{|\rho(x_1, x_2)|^2}{r_{12}} \quad (15)$$

Its origin is in the antisymmetrized property of the SD and for this reasons it has no counterpart in classical physics. Notice that since the integral is always positive, the results is always negative and therefore the exchange energy is attractive. Although it is not easy to rationalize this result by simple physical intuition, is the indistinguishability principle that originates the exchange terms which are attractive for fermions and repulsive for bosons, because of their different statistics. One key feature of the coulomb and exchange terms is that in the case $i = j$ in (9) the coulomb and exchange terms cancel to each other, with the remarkable consequence of avoiding the non physical electrostatic interaction of an electron with itself. This is not an accidental cancellation but results from the accordance of SDs with the principles of quantum mechanics, although they are a form of simplified wave function.

A further consideration about SDs concerns with the electron correlation. The two-body density function whose general definition is

$$\rho_2(x_1, x_2) = N(N-1) \int dx_3 \dots \int dx_N |\Psi(x_1, x_2, x_3, \dots x_N)|^2 \quad (16)$$

represent the simultaneous density probability of finding any two electrons at points x_1 and x_2 . Thus the probability of any one electron being found in the infinitesimal spatial-spin volume dx_1 around x_1 and one other electron in the infinitesimal volume dx_2 around x_2 is

$$\rho_2(x_1, x_2) dx_1 dx_2 \quad (17)$$

In the case the Φ appearing in the expression (16) is a SD, the two-body density function assumes the simpler expression

$$\rho_2(x_1, x_2) = \rho(x_1) \rho(x_2) - \rho(x_1, x_2) \rho(x_2, x_1) \quad (18)$$

which shows that the simultaneous probability concerning two electrons, is written as a product of two probabilities both referred to one electron, with the addition of a second corrective term. The latter accounts for the antisymmetrized nature of the SD, as in the case $x_1 = x_2$ the function $\rho_2(x_1, x_2)$ is null, meaning that there is no chance two electrons occupy the same spin-space point, in agreement with the indistinguishability principle of identical fermions. This

feature is generally known as the Fermi correlation; so we may say that the SD includes Fermi correlation, which concerns pair of electrons with the same spin. However from (18), neglecting for a moment the corrective term, the probability of the simultaneous event of finding two any electrons at x_1 and x_2 is the product of the probability of two single events, which means that the occurrence of one event does not affect the probability of the other. In other word the two events are independent to each other, which translated in quantum mechanics means that the probability of finding any two electrons at x_1 and x_2 is the product of probability of finding one electron at x_1 times the probability of finding one electron at x_2 . For this reason the SD does not contain the electron correlation and the methods concerning SDs are said independent particle methods or even mean field methods. However the second term in (18) make this consideration not true, because, owing to the non-classical antisymmetrized nature of the wave function, classical probability theory is not completely adequate to treat quantum systems. What is certainly true is that for a SD the two-body density matrix can be expressed by quantities concerning the one electron density matrix and that, due to (6), two identical fermions can never be completely independent.

0.3 The Hartree-Fock equations and the Brillouin theorem

For a Slater determinant the energy is expressed by integrals involving all the spin orbitals which form the SD. At this point it is evident that the energy depends on the form of the spin orbitals. But what spin orbitals? How can we find a criterion to choose the 'best' spin orbitals? Fortunately, the variational theorem comes in handy. It states that the mean value of the energy of any physically acceptable wave function, as just the expression (7), is surely higher than the exact energy of the system. Therefore the 'best' spin orbitals will be those that minimize the energy. Thus if we think the energy as a functional of the spin orbitals, we require that the energy is stationary with respect to arbitrary variation of the spin orbitals and that it increases for simultaneous arbitrary variation of any pair of spin orbitals. As the second condition is rather cumbersome, the Hartree-Fock equations will be determined by the condition of stationarity of the energy, although this does not guarantee that the energy is at a minimum.

Thus we want to find N spin orbitals to form the ground state SD Φ_0 which should have the property that the energy is stationary with respect to arbitrary changes in the orbitals $\varphi_i \rightarrow \varphi_i + \delta\varphi_i$. Such a stationary condition must be looked for by imposing that the spin orbitals remain orthonormal, i.e.

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \tag{19}$$

A stationary condition with some constraints can be conveniently treated with the method of the undetermined Lagrange multipliers, by forming an additional functional Ω defined as

$$\Omega[\varphi_1 \dots \varphi_N] = E[\varphi_1 \dots \varphi_N] - \sum_{ij} \Lambda_{ji} [\langle \varphi_i | \varphi_j \rangle - \delta_{ij}] \tag{20}$$

where the Λ_{ij} are indeterminate Lagrange multipliers. It is evident that we have added to E a function always null, in the case the spin orbitals are orthonormal. The change of the functional Ω^1 with respect to arbitrary variations of the spin orbital φ_k , which we suppose to be a real

¹A functional F of a function $g(x)$ is a recipe to get a number from an integral which include $g(x)$. For instance in the expression $F[g] = \int dx x^2 \sqrt{g(x)}$ we say that F is a functional of the function $g(x)$.

function, is

$$\delta\Omega = \langle \delta\varphi_k | h | \varphi_k \rangle + \frac{1}{2} \sum_j [\langle \delta\varphi_k \varphi_j | \varphi_k \varphi_j \rangle - \langle \delta\varphi_k \varphi_j | \varphi_j \varphi_k \rangle] \quad (21)$$

$$+ \frac{1}{2} \sum_i [\langle \varphi_i \delta\varphi_k | \varphi_i \varphi_k \rangle - \langle \varphi_i \delta\varphi_k | \varphi_k \varphi_i \rangle] + \sum_j \Lambda_{jk} \langle \delta\varphi_k | \varphi_j \rangle + c.c. \quad (22)$$

where the variations of the bra spin orbitals are considered explicitly whereas those of the ket spin orbitals are contained in the *c.c.*(complex conjugate) term which can be neglected since it does not include additional information. The two sums arise from the case $k=i$ and $k=j$. As $\langle ab|cd \rangle = \langle ba|dc \rangle$, the two sums over two-electron integrals are identical and can be collected by eliminating the 1/2factor

$$\delta\Omega = \langle \delta\varphi_k | h | \varphi_k \rangle + \sum_j [\langle \delta\varphi_k \varphi_j | \varphi_k \varphi_j \rangle - \langle \delta\varphi_k \varphi_j | \varphi_j \varphi_k \rangle] - \sum_j \Lambda_{jk} \langle \delta\varphi_k | \varphi_j \rangle \quad (23)$$

For $\delta\varphi_k$ completely arbitrary, the condition $\delta\Omega = 0$ is satisfied by the spin orbital φ_k which obeys to the following equation

$$h(x_1) \varphi_k(x_1) + \sum_j \int dx_2 [\varphi_j^*(x_2) \varphi_j(x_2) \varphi_k(x_1) / r_{12} - \varphi_j^*(x_2) \varphi_j(x_1) \varphi_k(x_2) / r_{12}] \quad (24)$$

$$= \sum_j \Lambda_{jk} \varphi_j(x_1) \quad (25)$$

By defining the coulomb J_m and exchange K_m operators

$$J_m \varphi_k(x_1) = \int dx_2 \varphi_m^*(x_2) \varphi_m(x_2) \varphi_k(x_1) / r_{12} \quad (26)$$

$$K_m \varphi_k(x_1) = \int dx_2 \varphi_m^*(x_2) \varphi_k(x_2) \varphi_m(x_1) / r_{12} \quad (27)$$

this equation can be rewritten in a more compact form

$$\left[h + \sum_m (J_m - K_m) \right] \varphi_k(x) = \sum_j \Lambda_{jk} \varphi_j(x) \quad (28)$$

We notice that the left hand side of the above equation is just an operator which act on a spin orbital, This operator is called the Fock operator

$$F = h + \sum_m (J_m - K_m) \quad (29)$$

and has the very advantageous feature that it does not depend on the spin orbital on which it acts. It is just an one-electron operator that includes kinetic energy, nuclear attraction and electron repulsion. A very important feature of the Fock operator is that it is an hermitian operator, then its eigenfunctions form an orthogonal set and its eigenvalues are real. We will discuss later of this operator in more details. Now we want to complete the derivation of the

Hartree-Fock equations. In order the functional Ω is stationary for arbitrary variations, this equation must hold for every spin orbital

$$F \varphi_k = \sum_{j=1}^N \Lambda_{jk} \varphi_j \quad \forall k, j \leq N \quad (30)$$

where the Lagrange multipliers are deduced to be the matrix elements of the Fock operator

$$\Lambda_{jk} = \langle \varphi_j | F | \varphi_k \rangle \quad (31)$$

which is hermitian [4]. This equation has to be read as: the stationary conditions are satisfied if the action of the Fock operator on each spin orbital yields a linear combination of the same spin orbitals forming the Slater determinant. At first sight this does not seem a very remarkable condition, but it is not so. Let's assume to work in a functional space formed by M orthonormal spin orbitals (with $M > N$) and the first N form the optimal SD. For sake of clarity in the following we use the indices i, j, k, l, m (going from 1 to N) for the spin orbitals that enter the Slater determinant and with a, b, c, d (going from $N+1$ to M) the remaining spin orbitals. The former may also be denoted as occupied spin orbitals whereas the latter as empty or virtual spin orbitals. The indices p, q, r, s run over the full space and therefore go from 1 to M . In this whole space the action of a generic one-electron hermitian operator T on a generic spin orbital (included or not in the SD) yields a linear combination of the spin orbitals of the whole space

$$T \varphi_k = \sum_{r=1}^M T_{rk} \varphi_r = \sum_{i=1}^N T_{ik} \varphi_i + \sum_{a=N+1}^M T_{ak} \varphi_a \quad (32)$$

where $T_{rk} = \langle \varphi_r | T | \varphi_k \rangle$ is a matrix element of the T operator. By comparing (30) with (32) it is apparent that (30) expresses a clear condition on the occupied spin orbitals: the action of the Fock operator on any occupied spin orbitals gives rise to a linear combination of spin orbitals which must not include virtual spin orbitals. Therefore the stationarity condition implies that the Lagrange multipliers between an occupied and a virtual spin orbital must vanish. Then the condition to be satisfied is

$$\langle \varphi_a | F | \varphi_k \rangle = 0 \quad \forall k \leq N \quad \forall a \mid N < a \leq M \quad (33)$$

This is the first form to express the Brillouin theorem. The spin orbitals entering the best SD obtained with the Hartree-Fock method have to satisfy the Brillouin theorem. Notice that condition (33) says nothing of definite about each virtual spin orbital, rather it states that the action of the Fock operator on any element of the space spanned by the occupied spin orbitals must remain within itself. The second form of the Brillouin theorem can be obtained by noticing that in the full spin orbital space it is possible to build a large number of Slater determinants other than Φ_0 , simply by choosing a sequence of N spin orbitals out of the M included in the space. The set of SDs obtained by substituting one occupied spin orbital φ_k with a virtual spin orbital φ_a forms the class of single excited determinants and are denoted by Φ_k^a . It turns out that the Hamiltonian matrix element between Φ_0 and Φ_k^a

$$\langle \Phi_0 | H_{el} | \Phi_k^a \rangle = \langle \varphi_k | F | \varphi_a \rangle = 0 \quad (34)$$

is just the Fock matrix element between an occupied and a virtual spin orbital, which is null in the case the φ_k are the Hartree-Fock spin orbitals. Therefore the second way to express the Brillouin theorem is: the Hamiltonian matrix element between the Fock Slater determinant and any single excited determinant is null.

0.4 The Fock operator

The Fock operator is the key object in the Hartree-Fock method and it is worthwhile to analyze it in some details. A very important feature is that it is an hermitian one-electron operator. Besides the kinetic energy operator and the nuclear attraction potential (29), it includes a sort of electron-electron potential with a sum over the spin orbitals entering the SD. The coulomb term J does not depend on the antisymmetrized form of the wave function and has a rather simple physical interpretation. Eq. (26) may be rewritten as

$$J_m \varphi_k(x_1) = v_m(x_1) \varphi_k(x_1) \quad (35)$$

where

$$v_m(x_1) = \int dx_2 \frac{\varphi_m^*(x_2) \varphi_m(x_2)}{|r_1 - r_2|} = \int dx_2 \frac{\rho_m(x_2)}{|x_1 - x_2|} \quad (36)$$

is the electrostatic potential in the point r_1 arising from the electronic density connected with the spin orbital φ_m . By summing over all φ_m we obtain the total *averaged* electron-electron potential in the point x_1 . We can define the global coulomb operator acting on a spin orbital

$$J \varphi_k(x_1) = \sum_{m=1}^N \int dx_2 \frac{\varphi_m^*(x_2) \varphi_m(x_2)}{|r_1 - r_2|} \varphi_k(x_1) = v(x_1) \varphi_k(x_1) \quad (37)$$

$$v(x_1) = \int dx_2 \frac{\rho(x_2, x_2)}{|r_1 - r_2|} \quad (38)$$

where now ρ is the total one-body density function (13) arising from the N electrons in the occupied spin orbitals of the SD. This potential $v(x)$ is repulsive as it is everywhere positive and it is the analogous of the nuclei-electron potential, which, on the contrary, is attractive. As the J operator is defined in every point of the coordinate space, J is a *local operator*. Few rows above we have used the adjective *averaged* in referring to $v(x)$. Why? There is a subtle consideration about this. The term *averaged* arises from the fact that this potential does not account for the specificity of the spin orbital to which F operates. The potential at the point r_1 is fixed and is independent from the density charge in that point. In other words the charge distribution is fixed and a direct correlation between pairs of electrons is absent. In the exact wave function such a fixed potential can not exist, although we may imagine a sort of potential in the point r_1 but its value should depend on the electron density in r_1 . This aspect is typical of the uncorrelated wave functions like SDs, as we discussed in the first section about the two-body density function of a SD.

The term K in eq.s (27,29) is the exchange operator. We can define a full exchange operator

acting on a spin orbitals as

$$K\varphi_k(x_1) = \sum_{m=1}^N \int dx_2 \frac{\varphi_m^*(x_2)\varphi_m(x_1)}{|r_1 - r_2|} \varphi_k(x_2) \quad (39)$$

$$= \int dx_2 \frac{\rho(x_1, x_2)}{|r_1 - r_2|} \varphi_k(x_2) \quad (40)$$

$$= \int dx_2 K(x_1, x_2) \varphi_k(x_2) \quad (41)$$

where now is the density matrix that appears within the integral. In the last formula the $K(x_1, x_2)$ function is the analogous of the kernel function in integral equations. This operator arises from the antisymmetrized nature of the SD and, unlike the coulomb operator (37), it is a *non-local operator* since it does not generate a simple potential at each value of the coordinate. When it operates on φ_k the integral in (39) involves all the occupied spin orbitals (including φ_k), so that the result depends on the value of φ_k at every point of the space weighted with the kernel two-variable function. The exchange operator can be also written using the P_{12} operator which interchanges electron 1 and electron 2

$$K\varphi_k(x_1) = \sum_{m=1}^N \int dx_2 \frac{1}{r_{12}} \varphi_m^*(x_2) P_{12} \varphi_m(x_2) \varphi_k(x_1) \quad (42)$$

In such a way, the Fock operator can be written with a definite argument x_1 irrespectively of the function on which it acts

$$F(x_1) = h(x_1) + \sum_{m=1}^N \int dx_2 \frac{1}{r_{12}} \varphi_m^*(x_2) (1 - P_{12}) \varphi_m(x_2) \quad (43)$$

A further very important feature of the Fock operator concerns the combined action of the coulomb and exchange operators. Let's consider the action on the spin orbital φ_k and write the Fock operator in the form (29)

$$F(x_1) \varphi_k(x_1) = h(x_1) \varphi_k(x_1) + \sum_m [J_m(x_1) - K_m(x_1)] \varphi_k(x_1) \quad (44)$$

In the case the summation index m is equal to k , the J and K terms cancel to each other

$$[J_k(x_1) - K_k(x_1)] \varphi_k(x_1) = 0 \quad (45)$$

This conclusion is quite important, as these two terms would represent the interaction of the electron in $\varphi_k(x_1)$ with itself. These non physical terms are called self interaction terms and are not present neither in the Fock operator nor in the expectation value of the energy, according to the fact that the Hartree-Fock method does not violate the first principles of quantum mechanics. According to (45) the expectation value of the Fock operator for the φ_k spin orbital

$$\langle \varphi_k | F | \varphi_k \rangle = \langle \varphi_k | h | \varphi_k \rangle + \sum_m [\langle \varphi_k \varphi_m | \varphi_k \varphi_m \rangle - \langle \varphi_k \varphi_m | \varphi_m \varphi_k \rangle] \quad (46)$$

includes both the coulomb and exchange two-electron integrals, which cancel to each other when $m=k$.

0.5 The canonical Hartree-Fock spin orbitals

Now we want to explore the possibility of transforming eq. (29) in a eigenvalue equation, without altering the stationary conditions. Let's suppose we have found a solution of eq. (29) which we rewrite in compact form

$$F |\varphi_1 \dots \varphi_N\rangle = |\varphi_1 \dots \varphi_N\rangle \mathbf{\Lambda} \quad (47)$$

where $|\varphi_1 \dots \varphi_N\rangle$ is a row ket vector collecting the N occupied spin orbitals and $\mathbf{\Lambda}$ is a $N \times N$ matrix. As $\mathbf{\Lambda}$ is a symmetric matrix (for real spin orbitals), it can be diagonalized through an orthogonal transformation matrix \mathbf{U} of dimension $N \times N$

$$\mathbf{\Lambda} \mathbf{U} = \mathbf{U} \varepsilon \quad (48)$$

where ε is the diagonal matrix containing the eigenvalues. The $\mathbf{\Lambda}$ matrix can then be written as

$$\mathbf{\Lambda} = \mathbf{U} \varepsilon \tilde{\mathbf{U}} \quad (49)$$

which may be substituted in eq. (47)

$$F |\varphi_1 \dots \varphi_N\rangle = |\varphi_1 \dots \varphi_N\rangle \mathbf{U} \varepsilon \tilde{\mathbf{U}} \quad (50)$$

Multiplying on the right by \mathbf{U}

$$F |\varphi_1 \dots \varphi_N\rangle \mathbf{U} = |\varphi_1 \dots \varphi_N\rangle \mathbf{U} \varepsilon \quad (51)$$

an eigenvalue equation is obtained. A new set of spin orbitals connected to the φ 's by a unitary transformation can be defined

$$|\varphi'_1 \dots \varphi'_N\rangle = |\varphi_1 \dots \varphi_N\rangle \mathbf{U} \quad (52)$$

which diagonalize F

$$F |\varphi'_1 \dots \varphi'_N\rangle = |\varphi'_1 \dots \varphi'_N\rangle \varepsilon \quad (53)$$

Thus the canonical Hartree-Fock eigenvalue equation are obtained

$$F \varphi'_k = \varepsilon_k \varphi'_k \quad \forall k = 1 \dots N \quad (54)$$

that is equivalent to the stationary condition (30) because the Brillouin theorem is satisfied both by the $\{\varphi\}$ and the $\{\varphi'\}$ sets. As demonstrated before, the Fock operator does not change in passing from the set $\{\varphi\}$ to the set $\{\varphi'\}$ so that with a little change of notation we may write the canonical Hartree-Fock equation as

$$F \varphi_k = \varepsilon_k \varphi_k \quad \forall k = 1 \dots N \quad (55)$$

where the superscript has been omitted and the set $\{\varphi\}$ are the canonical Hartree-Fock orbitals i.e. those orbitals which are eigenfunctions of the Fock operator. The canonical Hartree-Fock orbitals are unique in contrast to the infinite number of orbital sets connected to them by a unitary transformation and that describe the same SD, although they do not diagonalize the Fock operator. The eigenvalues ε_k are the diagonal elements of the Fock operator and are called orbital energies

$$\langle i | F | k \rangle = \delta_{ik} \varepsilon_k = \langle k | h | k \rangle + \sum_{m=1}^N [\langle km | km \rangle - \langle km | mk \rangle] \quad (56)$$

as they represent the kinetic, nuclear attraction and electron repulsion energy of one electron in the spin orbital φ_k . The orbital energies will be discussed in more details later on.

0.6 The Hartree-Fock-Roothaan equation

The stationary conditions for a SD lead to the Hartree-Fock equations (28,55) which must be satisfied by the N optimal spin orbitals. The exact solution of this integro-differential equation will give the "exact" Hartree-Fock spin orbitals. In practical cases we are forced to project the spin orbitals in a finite set of basis functions [4,5] and the integro-differential equations translate into a set of matrix equations. In the case the basis set is complete the solutions are identical, otherwise, for finite basis sets, the φ 's are a more or less good approximation of the "exact" Hartree-Fock spin orbitals. We start with a set of M (with $M > N$) spin orbitals ϕ_r which do not satisfy eq. (28) and form a basis for the projection of the Hartree-Fock spin orbitals. The basis may or may not be orthogonal. Therefore the goal is to find a linear combination of the M spin orbitals, such that the first resulting N spin orbitals do satisfy the Hartree-Fock equations

$$\varphi_k = \sum_{r=1}^M C_{rk} \phi_r \quad \forall k = 1 \dots N \quad (57)$$

In this way the stationarity condition is transferred to the C coefficients. The above equation may be extended to the remaining spin orbitals φ_a (with a from $N+1$ to M)

$$\varphi_a = \sum_{r=1}^M C_{ra} \phi_r \quad \forall a = N+1 \dots M \quad (58)$$

It is clear that such spin orbitals have no relevance in the stationarity condition, but they have to be always considered as it will become clear in the following, when the iterative solution of the Hartree-Fock equations will be discussed. In order to preserve orthonormality the C coefficients have to form a unitary matrix i.e. we are dealing with a linear unitary transformation in the space spanned by the basis of spin orbitals ϕ_r . The above equations can be rewritten in a more compact form using the Dirac bra-ket notation as

$$|\varphi_1 \dots \varphi_M\rangle = |\phi_1 \dots \phi_M\rangle \mathbf{C} \quad (59)$$

where $|\varphi_1 \dots \varphi_M\rangle$ is a row vector collecting the spin orbitals, $|\phi_1 \dots \phi_M\rangle$ collects the basis functions and \mathbf{C} is the matrix of the coefficients. The k -th column of the \mathbf{C} matrix contains the coefficients C_{rk} which give the spin orbital φ_k from the basis function ϕ_r , $C_{rk} = \langle \phi_r | \varphi_k \rangle$. Therefore the goal of the Hartree-Fock method is to find the first N columns of the \mathbf{C} matrix for such a transformation.

The matrix form of the Hartree-Fock equations is obtained by projecting the eigenvalue problem onto the $\{\phi\}$ basis. The starting equation is

$$F |\varphi_1 \dots \varphi_M\rangle = |\varphi_1 \dots \varphi_M\rangle \varepsilon \quad (60)$$

and after substitution of projection (59) we obtain

$$F |\phi_1 \dots \phi_M\rangle \mathbf{C} = |\phi_1 \dots \phi_M\rangle \mathbf{C} \varepsilon \quad (61)$$

By taking the scalar product with the bra column vector formed by the $\{\phi\}$ basis

$$\begin{pmatrix} \langle \phi_1 | \\ \dots \\ \langle \phi_M | \end{pmatrix} F |\phi_1 \dots \phi_M\rangle \mathbf{C} = \begin{pmatrix} \langle \phi_1 | \\ \dots \\ \langle \phi_M | \end{pmatrix} |\phi_1 \dots \phi_M\rangle \mathbf{C} \varepsilon \quad (62)$$

we obtain the matrix equation

$$\mathbf{FC} = \mathbf{SC}_\varepsilon \quad (63)$$

where $F_{rs} = \langle \phi_r | F | \phi_s \rangle$ is the projected $M \times M$ Fock matrix. The metric matrix \mathbf{S} whose elements are $S_{rs} = \langle \phi_r | \phi_s \rangle$ is the overlap matrix between the basis functions. The projected form of the equation is called Hartree-Fock-Roothaan equation.

In the case of non orthonormal basis sets the \mathbf{S} matrix is different from the identity matrix and complicates the eigenvalue equation. The pseudoeigenvalue problem (29) can be efficiently faced by orthogonalizing the basis set through a non unitary matrix \mathbf{X} which transforms the non orthogonal basis $\{\phi\}$ into an orthonormal basis $\{\phi'\}$

$$|\phi'\rangle = |\phi\rangle \mathbf{X}$$

where the bold face $|\phi\rangle$ and $|\phi'\rangle$ collect the row of ϕ and ϕ' functions, respectively. Each column of the \mathbf{X} matrix represents a new functions ϕ' as linear combination of the original functions ϕ . The orthonormality condition on the new basis set is

$$\langle \phi' | \phi' \rangle = \tilde{\mathbf{X}} \langle \phi | \phi \rangle \mathbf{X} = \tilde{\mathbf{X}} \mathbf{S} \mathbf{X} = \mathbf{I} \quad (64)$$

A solution for the transformation matrix \mathbf{X} can be found by working on the metric matrix \mathbf{S} , which is symmetric and can be diagonalized with an orthogonal matrix \mathbf{V}

$$\mathbf{SV} = \mathbf{VK} \quad (65)$$

where \mathbf{K} is a diagonal matrix. Using the spectral decomposition theorem, the matrix \mathbf{S} can be expressed through its eigensolutions

$$\mathbf{S} = \mathbf{VK}\tilde{\mathbf{V}} \quad (66)$$

Since for any reasonable basis set, \mathbf{S} is positive definite [4], its eigenvalues are positive and the matrix \mathbf{K} can be expressed by

$$\mathbf{K} = \mathbf{K}^{1/2} \mathbf{K}^{1/2} \quad (67)$$

where the elements of the $\mathbf{K}^{1/2}$ matrix are just the square root of the corresponding elements of the \mathbf{K} matrix i.e. $(K^{1/2})_{ii} = (K_{ii})^{1/2}$. We can also define the inverse of this matrix, $\mathbf{K}^{-1/2}$ which contains as diagonal elements the $(K_{ii})^{-1/2}$ values. The two currently employed choices for the \mathbf{X} matrix are the following. In the Löwdin symmetric orthogonalization $\mathbf{X} = \mathbf{VK}^{-1/2}\tilde{\mathbf{V}}$, whereas in the canonical orthogonalization $\mathbf{X} = \mathbf{VK}^{-1/2}$. In both cases the relation (64) is satisfied and, most important, the overlap matrix can be factorized as the product of two matrices $\mathbf{X}^{-1}\tilde{\mathbf{X}}^{-1}=\mathbf{S}$, as can easily be verified. By substituting the last expression in eq. (63) and applying some simple algebra we can obtain the desired result

$$\mathbf{FC} = \mathbf{X}^{-1}\tilde{\mathbf{X}}^{-1}\mathbf{C}_\varepsilon \quad (68)$$

$$\mathbf{XFC} = \tilde{\mathbf{X}}^{-1}\mathbf{C}_\varepsilon \quad (69)$$

$$\mathbf{XF}\tilde{\mathbf{X}} \tilde{\mathbf{X}}^{-1}\mathbf{C} = \tilde{\mathbf{X}}^{-1}\mathbf{C}_\varepsilon \quad (70)$$

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'_\varepsilon \quad (71)$$

where the primed matrices refers to the orthonormal basis $\{\phi'\}$ and are defined as

$$\mathbf{F}' = \mathbf{X}\mathbf{F}\tilde{\mathbf{X}} \quad \text{transformed Fock matrix} \quad (72)$$

$$\mathbf{C}' = \tilde{\mathbf{X}}^{-1}\mathbf{C} \quad \text{transformed eigenvectors} \quad (73)$$

The form (71) allows direct diagonalization of the transformed Fock matrix and the eigenvectors \mathbf{C} can be retrieved by

$$\mathbf{C} = \tilde{\mathbf{X}}\mathbf{C}' \quad (74)$$

Equation (71) is completely equivalent to eq. (63) (they have the same eigenvalues) and can be solved by standard diagonalization methods.

0.7 Solution of the Hartree-Fock equations

Once a method to face the possible non orthogonality of the basis set has been found, we can pass to the problem of solving the Hartree-Fock equations. The solution of the Hartree-Fock equations require to determinate the \mathbf{C} matrix in eq. (63) to be used in (59) to obtain the Hartree-Fock orbitals projected in the basis $\{\phi\}$. To be precise only the N vectors corresponding to the occupied spin orbitals are necessary, but there is no real advantage in exploiting this change and the whole set of eigensolutions of eq. (71) can be determined. The main difficulty arises from the dependence of the coulomb and exchange terms from the density matrix, which in turn is formed by the occupied spin orbitals. Thus the Fock operator depends on its solutions $\{\varphi\}$ and the resulting non linear equation must be solved by iterative procedures.

Let's suppose we are able to find a reasonable set of guess spin orbitals $\{\varphi_1^{(0)} \dots \varphi_n^{(0)}\}$ using our chemical intuition or performing a calculation with a certain semiempirical method, or even only using the one-electron terms of the Hamiltonian instead of the Fock operator. The corresponding density matrix allows to determine the coulomb and exchange matrix elements, so the first Fock matrix can be built

$$F[\rho^{(0)}] \quad (75)$$

where $\rho^{(0)}$ is the guess density matrix, built with the guess spin orbitals. By the matrix transformation (72) with the $\mathbf{S}^{-1/2}$ matrix the $\mathbf{F}'[\rho^{(0)}]$ matrix can be obtained for the first iteration. Once diagonalization of $\mathbf{F}'[\rho^{(0)}]$ and transformation (73) are accomplished, a new set of M spin orbitals $\{\varphi^{(1)}\}$ is obtained. These spin orbitals do not satisfy Brillouin theorem (34) nor the stationarity conditions (30), so they are not yet the Hartree-Fock spin orbitals. The reason is that they are eigenvectors of a Fock matrix built with different spin orbitals (the guess spin orbitals)

$$\langle \varphi_r^{(1)} | F[\rho^{(0)}] | \varphi_s^{(1)} \rangle = \varepsilon_r \delta_{rs} \quad (76)$$

but do not satisfy the same equation with the Fock operator they originate

$$\langle \varphi_r^{(1)} | F[\rho^{(1)}] | \varphi_s^{(1)} \rangle \neq \varepsilon_r \delta_{rs} \quad (77)$$

Nevertheless the spin orbitals $\varphi^{(1)}$ corresponding to the lowest N eigenvalues ε can be used to form a new density matrix $\rho^{(1)}$, which in turn allows to set up a new Fock operator $F[\rho^{(1)}]$.

This procedure can be repeated forming a new Fock matrix from the density matrix of the previous step: $F[\rho^{(n-1)}]$. At each step n the first N spin orbitals $\varphi^{(n)}$ will be a mixing of occupied and virtual spin orbitals $\varphi^{(n-1)}$ of the previous step. The procedure will continue until convergence is reached i.e. when the density matrices at two consecutive steps differs by less than a given small threshold t

$$|\rho^{(n)} - \rho^{(n-1)}| < t \quad (78)$$

and, correspondingly, the eigenvalue equation

$$\langle \varphi_r^{(n)} | F[\rho^{(n)}] | \varphi_s^{(n)} \rangle = \varepsilon_r \delta_{rs} \quad (79)$$

is satisfied within the same threshold t . When this occurs the Brillouin theorem is also satisfied, the current spin orbitals are the Hartree-Fock orbitals and the SD is the Hartree-Fock wave function. The corresponding energy will be the lowest possible for a SD, within the given basis set.

0.8 The Fock operator as the molecular Hamiltonian

The SD is the most crude approximation to the exact wave function which retains consistency with the principles of quantum mechanics. We have seen that the spin orbitals to be used to build the best SD are the lowest eigenstates of the Fock operator. The Hartree-Fock method belongs to the class of the so called independent particle methods, which are characterized by the fact that the spin orbitals are eigensolution of an effective one-electron Hamiltonian. The term 'effective' means that each electron feels the nuclear attraction and a kind of effective field due to the remaining electrons of the molecule. In the Hartree-Fock method this one-electron operator is the Fock operator, which has the rewarding property of being the same for all spin orbitals. Its 'effective' form includes all the electrostatic Hamiltonian terms, adapted to the case where the wave function is a SD. The Fock operator (43) is written just for one electron but, as any physical operator, it may be written for N electrons

$$F_N(x_1, x_2 \dots x_N) = \sum_{i=1}^N F(x_i) \quad (80)$$

and it is sometimes called the Fock Hamiltonian. Just as for all one-electron operators, it may be demonstrated that each SD built with spin orbitals which are eigenfunctions of $F(x_1)$, is an exact eigenstate of the operator (80). Indeed, if the orbital energies are arranged in increasing order $\varepsilon_i \leq \varepsilon_{i+1}$, the eigenvalue of the Hartree-Fock SD is the sum of the orbital energies of the first N spin orbitals

$$F_N(x_1, x_2 \dots x_N) \Phi_0(x_1, x_2 \dots x_N) = \left(\sum_{i=1}^N \varepsilon_i \right) \Phi_0(x_1, x_2 \dots x_N) \quad (81)$$

that is a general feature of all one-electron operators. Thus the Fock operator F_N (80) can be considered as *the molecular Hamiltonian which is the best one-electron approximation of the true Hamiltonian, for a system of N electrons in the ground state* [6]. Moreover it shares with the Hamiltonian the feature of possessing an infinite number of eigenfunctions, that is a key

characteristic to be physically consistent. It should be noted that the energy of the system is not simply the expectation value of F_N since the eigenvalue of eq (81) are different from the expectation value of the Hamiltonian

$$\langle \Phi | F_N | \Phi \rangle = \sum_{i=1}^N \varepsilon_i = \sum_{i=1}^N \left(\langle i | h | i \rangle + \sum_{m=1}^N [\langle im | im \rangle - \langle im | mi \rangle] \right) \quad (82)$$

$$\langle \Phi | H_{el} | \Phi \rangle = \sum_{i=1}^N \left(\langle i | h | i \rangle + \frac{1}{2} \sum_{m=1}^N [\langle im | im \rangle - \langle im | mi \rangle] \right) \quad (83)$$

The difference is in the 1/2 factor, which appears in the correct energy mean value and avoids the double counting of the electron-electron interaction, since the double sum of the orbital energies includes the interaction between different spin orbitals twice. As the two-electron repulsion term is always positive, the expectation value of the Hamiltonian is always lower than the expectation value of the Fock operator. We conclude that the eigenvalue of the N -electron SD has no relevant meaning being the energy the only relevant observable. Nevertheless the molecular Fock operator is the best approximation of the true Hamiltonian.

0.9 Orbital energies and Koopmans' theorem

The eigenvalues of the Fock operator for the one-electron case are the orbital energies whose expression has been given in eq. (56) for the occupied spin orbitals entering the Hartree-Fock SD. Such an expression can be specialized for occupied and virtual spin orbitals

$$\varepsilon_k = \langle k | h | k \rangle + \sum_m [\langle km | km \rangle - \langle km | mk \rangle] \quad (84)$$

$$\varepsilon_a = \langle a | h | a \rangle + \sum_m [\langle am | am \rangle - \langle am | ma \rangle] \quad (85)$$

In the case of the occupied spin orbital φ_k the term of the sum with $m=k$ is null as the coulomb and exchange integrals cancel to each other. This is relevant from a physical point of view since it would represent the self interaction of one electron in a given spin orbital. Thus the orbital energies of the occupied spin orbitals can be rewritten in a more physically consistent way

$$\varepsilon_k = \langle k | h | k \rangle + \sum_{m \neq k} [\langle km | km \rangle - \langle km | mk \rangle] \quad (86)$$

where the self interaction term is omitted. The energy of one electron in an occupied spin orbitals accounts for the one electron terms plus the coulomb and exchange interaction with the $N-1$ electrons occupying the remaining spin orbitals. Conversely, no cancellation occurs for the orbital energies of the virtual spin orbitals. They are determined in the field of all the N electrons of the SD and feel a less attractive potential with respect to the corresponding occupied spin orbitals.

Further insight in the orbital energies may be obtained by writing the coulomb and exchange

terms with explicit factorization of the spatial and spin parts.

$$\langle km|km\rangle = \int dr_1 \int ds_1 \int dr_2 \int ds_2 \varphi_k^*(r_1) \sigma_k^*(s_1) \varphi_m^*(r_2) \sigma_m^*(s_2) \frac{1}{r_{12}} \quad (87)$$

$$\varphi_k(r_1) \sigma_k^*(s_1) \varphi_m(r_2) \sigma_m^*(s_2) \quad (88)$$

$$\langle km|mk\rangle = \int dr_1 \int ds_1 \int dr_2 \int ds_2 \varphi_k^*(r_1) \sigma_k^*(s_1) \varphi_m^*(r_2) \sigma_m^*(s_2) \frac{1}{r_{12}} \quad (89)$$

$$\varphi_m(r_1) \sigma_m^*(s_1) \varphi_k(r_2) \sigma_k^*(s_2) \quad (90)$$

The σ functions can be α or β and due to their orthonormality, the integrals on the formal spin variables are 0 or 1. The spin integration is irrelevant for the coulomb integral, whereas the exchange vanishes in the case $\sigma_k \neq \sigma_m$. Thus we deduce a very general rule: *the exchange interaction only occurs between electrons with parallel spin i.e. with the same spin function.* Conversely the coulomb interaction is irrespective of the spin of the involved electrons. Thus we may modify the comment about the orbital energy of an occupied spin orbital as follows: the energy of one electron in an occupied spin orbitals accounts for the one electron terms plus the coulomb interaction with the $N-1$ electrons occupying the remaining spin orbitals and minus the exchange interaction with all the remaining occupied spin orbitals with the same spin.

As the Fock operator is an effective operator whose relevance stands in its capability of find the spin orbitals entering the best SD, it is not clear what is the physical meaning of its eigenvalues i.e. the orbital energies. Moreover the possibility of performing unitary transformations among the occupied spin orbitals without affecting the SD (except for a phase factor) could make these quantities just as mathematical objects, as they are defined for canonical spin orbitals. Nevertheless the Koopmans' theorem give a rather interesting physical meaning to the orbital energies.

Let's consider a SD of $N-1$ electrons obtained from the Hartree-Fock SD by removing one electron from the canonical spin orbital φ_k without altering the spatial function of the spin orbitals. The energy of these two SDs are

$$E^N = \langle \Phi_0^N | H^N | \Phi_0^N \rangle \quad (91)$$

$$E_k^{N-1} = \langle \Phi_k^{N-1} | H^{N-1} | \Phi_k^{N-1} \rangle \quad (92)$$

where we have added a superscript N or $N-1$ to indicate the number of electrons of the system. Depending on the choice of the spin orbital φ_k , the SD Φ_k^{N-1} may or may not represent the ground state of the ionized system. In any case the energy of the ionized system can be obtained by the general formula (8) by eliminating the k index in all the sums

$$E_k^{N-1} = \sum_{m \neq k}^N \langle m | h | m \rangle + \frac{1}{2} \sum_{m \neq k}^N \sum_{j \neq k}^N [\langle mi | mi \rangle - \langle mi | im \rangle] \quad (93)$$

whereas the energy of the N electron SD can be written by expliciting the terms involving the k -th spin orbital

$$E^N = \sum_{m \neq k}^N \langle m | h | m \rangle + \langle k | h | k \rangle + \frac{1}{2} \sum_{m \neq k}^N \sum_{i \neq k}^N [\langle mi | mi \rangle - \langle mi | im \rangle] \quad (94)$$

$$+ \frac{1}{2} \sum_{m \neq k}^N [\langle mk | mk \rangle - \langle mk | km \rangle] + \frac{1}{2} \sum_{i \neq k}^N [\langle ki | ki \rangle - \langle ki | ik \rangle] \quad (95)$$

where the two-electron term with $m=j=k$ has been omitted since it is null. The last two sums are identical for real spin orbitals and can be collected in a single sum by eliminating the 1/2 factor. Taking the difference between these two energies

$$E_k^{N-1} - E^N = -\langle k|h|k\rangle - \sum_{m \neq k}^N [\langle mk|mk\rangle - \langle mk|km\rangle] \quad (96)$$

it is apparent that the right expression is just the orbital energy of the system with N electrons and the left expression is an ionization potential of the N electron system

$$\text{IP}_k = E_k^{N-1} - E^N = -\varepsilon_k \quad (97)$$

This is the Koopmans' theorem which establishes that *the ionization potential of the system obtained by removing one electron from the spin orbital φ_k is the orbital energy of the same spin orbital with the opposite sign*. The orbital energies of the occupied spin orbitals are generally negative so that the corresponding ionization potential is positive, in agreement with what we expect at least for neutral molecules, where in the ionization process



requires some energy to bring one electron to an infinite distance from the molecular ion.

It is clear that the Koopmans' theorem is an approximation to the exact ionization potential since it includes several approximations. Let's consider the usual case in which the N electron system corresponds to a neutral molecule and the $N-1$ system corresponds to the cation. The first approximation is that the spin orbitals used to build the ionized SD are the same used for the neutral molecule (frozen orbital approximation) i.e they are not the optimal spin orbital for the positive ion. Since the Hartree-Fock spin orbitals of the ion feel the repulsive field of $N-2$ electrons and the attractive field of N protons, they are in general less diffuse than the corresponding HF spin orbitals of the neutral species. In other words the Koopmans' theorem neglects the relaxation effects of the spin orbitals in the positive ion, so that $-\varepsilon_k$ is higher than the difference between the best SD of the ion and the best SD of the neutral system. Hence the inclusion of relaxation would lead to a decrease of the ionization potentials. On the other hand Hartree-Fock theory neglects correlation effects other than Fermi correlation and, since the correlation energy is larger for the neutral system, such correction would lead to an increase of the ionization potentials. Therefore the corrections due to relaxation and correlation effects tend to cancel to each other and the Koopmans' estimate is reasonable, at least for the outer shell spin orbitals. For inner shell spin orbitals the relaxation effects are much higher and the above cancellation does not yet occur. In these cases a reasonable estimate of the ionization potential can be obtained by performing separate Hartree-Fock calculations of the ionized and neutral species [4].

Finally we mention that by a similar procedure, a number of $N+1$ SDs can be formed by putting one electron in a spin orbital which is empty in the N electron SD. In the case the N electron SD represents a neutral system, these $N+1$ electron states represent the possible anions. The corresponding electron affinity of the system is the orbital energy of the involved virtual orbital φ_a with opposite sign

$$\text{EA}_a = E^N - E_a^{N+1} = -\varepsilon_a \quad (99)$$

where

$$E_a^{N+1} = \langle \Phi_a^{N+1} | H^{N+1} | \Phi_a^{N+1} \rangle \quad (100)$$

In this case the frozen approximation and the neglecting of correlation effects make the Koopmans' results rather inaccurate and the above formula is of little use.

0.10 Restricted and Unrestricted Hartree-Fock

In the above discussion we have defined the spin orbitals as functions able to describe the motion of one electron, and consequently, they have as argument both the spatial and spin coordinates of one electron. Since the spin functions are simple mathematical objects and the nonrelativistic electronic Hamiltonian does not include spin operators, it is rather convenient both from physical and computational points of views, to perform the integrals involving the spin functions and write the equations in terms of spatial orbitals. Let's consider the restricted case characterized by the assumption that for each spin orbital with spin function α there is a corresponding spin orbital with spin function β and with the same spatial function. Then the spin orbitals can be grouped into pairs: each pair is formed by a spatial orbital times the α and the β spin function. Such an approximation is suitable for closed-shell molecules characterized by an even number of electrons distributed in pairs in the orbitals, so that each spatial orbital contains zero or two electrons. Therefore if the spin orbital $\varphi_k(r)\alpha(s)$ is occupied by one electron then it is also $\varphi_k(r)\beta(s)$ and the same holds for unoccupied pairs. According to the definition (5), the closed-shell restricted Hartree-Fock SD is

$$|\Phi\rangle = |\varphi_{1\alpha}\varphi_{1\beta}\varphi_{2\alpha}\varphi_{2\beta}\dots\varphi_{N/2\alpha}\varphi_{N/2\beta}\rangle \quad (101)$$

where now the spin orbitals are written with explicit reference to their spin function and the first $N/2$ spatial orbitals are doubly occupied. The restricted constraints are expressed by

$$\varphi_{k\alpha}(r) = \varphi_{k\beta}(r) \quad (102)$$

It can be demonstrated that such a SD is eigenstate of the spin operators with null eigenvalue i.e. it is a singlet state. This method is called restricted Hartree-Fock (RHF).

The general spin orbital Hartree-Fock equation can be converted to a spatial orbital equation by performing integration on the spin coordinates. Let's start with the Fock matrix elements between two generic spin orbitals which are now written by explicit reference to the spatial and spin functions

$$\langle \phi_p \sigma_p | F | \phi_q \sigma_q \rangle = \left\langle \phi_p \sigma_p \left| h + \sum_{m=1}^N (J_m - K_m) \right| \phi_q \sigma_q \right\rangle \quad (103)$$

It is evident that since h has no reference with the spin, the first term can be factorized in two distinct integrals over the spatial and spin coordinates

$$\langle \phi_p \sigma_p | h | \phi_q \sigma_q \rangle = \int dr \phi_p^*(r) h(r) \phi_q(r) \int ds \sigma_p^*(s) \sigma_q(s) \quad (104)$$

$$= \langle \phi_p | h | \phi_q \rangle \langle \sigma_p | \sigma_q \rangle \quad (105)$$

where it is understood that the first two brackets have spatial and spin coordinate, respectively, as integration variable. Owing to the orthonormality of the spin functions we obtain

$$\mathbf{h}_{p\alpha,q\alpha} = \mathbf{h}_{p\beta,q\beta} = \langle \phi_p | h | \phi_q \rangle \quad \mathbf{h}_{p\alpha,q\beta} = \mathbf{h}_{p\beta,q\alpha} = 0 \quad (106)$$

Each two electron integral can be factorized in three distinct integrals over the spatial and spin coordinates and in particular for the coulomb integrals

$$\langle \phi_p \sigma_p | J_m | \phi_q \sigma_q \rangle = \langle \phi_p \sigma_p \varphi_m \sigma_m | \phi_q \sigma_q \varphi_m \sigma_m \rangle \quad (107)$$

$$= \int dr_1 \int dr_2 \phi_p^*(r_1) \varphi_m^*(r_2) \frac{1}{r_{12}} \phi_q(r_1) \varphi_m(r_2) \quad (108)$$

$$\int ds_1 \sigma_p^*(s_1) \sigma_q(s_1) \int ds_2 \sigma_m^*(s_2) \sigma_m(s_2) \quad (109)$$

$$= \langle \phi_p \varphi_m | \phi_q \varphi_m \rangle \langle \sigma_p | \sigma_q \rangle \langle \sigma_m | \sigma_m \rangle \quad (110)$$

It is apparent that the integral is null for $\sigma_p^* \neq \sigma_q$ and that the spin of the occupied spin orbitals φ_m is irrelevant i.e. the result is identical for $\varphi_{m\alpha}$ and for $\varphi_{m\beta}$. Therefore the total coulomb potential is twice the coulomb potential arising from the α (or β) occupied spin orbitals. This confirms that the coulomb interaction is not affected by the spin and occurs for all pairs of electrons. For the exchange terms the two-electron integral can be manipulated as before

$$\langle \phi_p \sigma_p | K_m | \phi_q \sigma_q \rangle = \langle \phi_p \sigma_p \varphi_m \sigma_m | \varphi_m \sigma_m \phi_q \sigma_q \rangle \quad (111)$$

$$= \int dr_1 \int dr_2 \phi_p^*(r_1) \varphi_m^*(r_2) \frac{1}{r_{12}} \phi_m(r_1) \varphi_q(r_2) \quad (112)$$

$$\int ds_1 \sigma_p^*(s_1) \sigma_m(s_1) \int ds_2 \sigma_m^*(s_2) \sigma_q(s_2) \quad (113)$$

$$= \langle \phi_p \varphi_m | \varphi_m \phi_q \rangle \langle \sigma_p | \sigma_m \rangle \langle \sigma_m | \sigma_q \rangle \quad (114)$$

and the results shows that the product between the two overlap integrals over the spin coordinates is different from zero only in the case $\sigma_p = \sigma_q = \sigma_m$. So we found again that the exchange interaction occurs between electrons with parallel spin and that the exchange matrix elements are null for $\sigma_p \neq \sigma_q$. Therefore in the case of restricted spin orbitals and closed shell systems, the Fock matrix between two spatial orbitals is

$$\langle \phi_p | F | \phi_q \rangle = \left\langle \phi_p \left| h + \sum_{m=1}^{N/2} (2J_m - K_m) \right| \phi_q \right\rangle \quad (115)$$

where it is understood that the integrals are on the spatial coordinates. There is no need to specify the spin function of the orbitals ϕ_p and ϕ_q as the results in the same for both α and both β . Thus the matrices involved in Hartree Fock eigenvalue problem (63) are formed by two identical diagonal blocks; one of them is to be diagonalized and the eigenvectors are the coefficients of the spin orbitals irrespectively of their spin.

The energy expression can also be expressed in terms of spatial orbitals by performing spin

integration (we use here a more compact notation)

$$E = \sum_{i=1}^N \langle i | h | i \rangle + \frac{1}{2} \sum_{ij=1}^N (\langle ij | ij \rangle - \langle ij | ji \rangle) \quad (116)$$

$$= 2 \sum_{i=1}^{N/2} \langle i | h | i \rangle + \frac{1}{2} \sum_i^{N/2} \sum_{\mu}^{\alpha, \beta} \sum_j^{N/2} \sum_{\nu}^{\alpha, \beta} (\langle i\mu, j\nu | i\mu, j\nu \rangle - \langle i\mu, j\nu | j\nu, i\mu \rangle) \quad (117)$$

$$= 2 \sum_{i=1}^{N/2} \langle i | h | i \rangle + \sum_i^{N/2} \sum_j^{N/2} (2 \langle ij | ij \rangle - \langle ij | ji \rangle) \quad (118)$$

The last expression has been obtained by noticing that the coulomb terms are never null whereas the exchange terms are different from zero only in the case $\mu=\nu$.

By removing the constraints (102) that each α spin orbital has a partner β with identical spatial function, we obtain the unrestricted Hartree Fock (UHF) equations which are useful for radicals, where the number of spin up and spin down electrons is different, or when the molecule is placed in a magnetic field, which discriminates between spin up and spin down electrons. In UHF the Fock matrix is always made by two diagonal blocks but, since they are different, both of them have to be diagonalized. Therefore, from a computational point of view, UHF method is more expensive than RHF. In the usual case where the Hartree-Fock iterative procedure leads to the absolute energy minimum, the UHF energy is always lower or equal than the RHF energy, since the former is subject to no constraint. An unpleasant feature of the UHF wave function is that it is not an eigenfunction of the spin operators, since the UHF SD contains some spin contaminants. However UHF is more flexible than RHF and it is capable of describing in a qualitative way the dissociation of bonded atoms [4].

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