Il metodo di Hartree - Fock

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1 Equazioni di Fock

Il metodo Hartree-Fock ha una impostazione piuttosto chiara:

quale è il migliore SD dal punto di vista dell'energia?

cioè quello che da la minima energia tra tutti i possibili SD all'interno di un definito spazio funzionale.

L'energia di un singolo determinate è un funzionale degli N spin orbitali di cui è composto

$$E\left[\varphi_1...\varphi_N\right] = \sum_{i=1}^{N} \left\langle \varphi_i \left| h \right| \varphi_i \right\rangle + \frac{1}{2} \sum_{ij} \left[\left\langle \varphi_i\varphi_j | \varphi_i\varphi_j \right\rangle - \left\langle \varphi_i\varphi_j | \varphi_j\varphi_i \right\rangle \right] \tag{1}$$

dove h esprime la parte mono -elettronica e

$$\left\langle \varphi_i\varphi_j | \varphi_i\varphi_j \right\rangle = J_{ij} \qquad \left\langle \varphi_i\varphi_j | \varphi_j\varphi_i \right\rangle = \ K_{ij} \tag{2}$$

Avendo a disposizione uno spazio di spin orbitali superiore a N, vogliamo cercare le condizioni a cui devono soddisfare i primi N affinché l'energia sia la minima possibile. Se consideriamo solo la derivata prima possiamo cercare le condizioni per cui E è **stazionaria**, ovvero che la variazione δE sia nulla rispetto alle variazioni degli spin orbitali. Dobbiamo anche imporre che gli spin orbitali siano ortonormali, altrimenti l'espressione sopra dell'energia risulterebbe errata. Usiamo quindi il metodo dei moltiplicatori indeterminati di **Lagrange**, che è utile quando si voglia trovare il minimo di una funzione non nell'intero dominio, ma in un sottodominio che soddisfa a certe condizioni. Consideriamo un funzionale aggiuntivo contenente dei moltiplicatori indeterminati di Lagrange λ, che servono ad imporre il vincolo di ortonormalità su tutte le possibili coppie di spin orbitali

$$\Omega\left[\varphi_1...\varphi_N\right] = E\left[\varphi_1...\varphi_N\right] - \sum_{ij} \Lambda_{ij} \left[\left\langle \varphi_i | \varphi_j \right\rangle - \delta_{ij} \right] \tag{3}$$

Calcoliamo la variazione di E rispetto ad un determinato spin orbitale φ_k. Scriviamo esplicitamente

$$\begin{aligned} \delta E \ &= \ \left\langle \delta\varphi_k \left| h \right| \varphi_k \right\rangle + \frac{1}{2} \sum_j \left[\left\langle \delta\varphi_k\varphi_j | \varphi_k\varphi_j \right\rangle - \left\langle \delta\varphi_k\varphi_j | \varphi_j\varphi_k \right\rangle \right] && (4) \\ &\quad + \frac{1}{2} \sum_i \left[\left\langle \varphi_i\delta\varphi_k | \varphi_i\varphi_k \right\rangle - \left\langle \delta\varphi_i\delta\varphi_k | \varphi_k\varphi_i \right\rangle \right] && (5) \\ &\quad - \sum_j \Lambda_{jk} \left\langle \delta\varphi_k | \varphi_j \right\rangle + c.c. && (6) \end{aligned}$$

dove le variazioni degli orbitali bra sono considerate esplicitamente, mentre che quelle dei ket sono contenute nei termini $c.c$ (complessi coniugati). Dato che $\langle ab|cd\rangle = \langle ba|dc\rangle$, le due sommatorie sugli integrali bi-elettronici sono identiche per cui si ottiene

$$\delta E = \langle \delta\varphi_k |h| \varphi_k \rangle + \sum_j \left[\left\langle \delta\varphi_k\varphi_j | \varphi_k\varphi_j \right\rangle - \left\langle \delta\varphi_k\varphi_j | \varphi_j\varphi_k \right\rangle \right] - \sum_j \Lambda_{jk} \left\langle \delta\varphi_k | \varphi_j \right\rangle + c.c \tag{7}$$

e poiché $\delta\varphi_k$ è arbitrario, affinché $\delta E = 0$, gli orbitali che rendono stazionaria la energia dovranno soddisfare la seguente equazione (equazione di Fock)

$$h\varphi_k(x_1) + \sum_j \int dx_2 \varphi_j^*(x_2)\varphi_j(x_2)\frac{1}{r_{12}}\varphi_k(x_1) - \sum_j \int dx_2 \varphi_j^*(x_2)\varphi_j(x_1)\frac{1}{r_{12}}\varphi_k(x_2) - \sum_j \Lambda_{jk}\varphi_j(x_1) = 0 \tag{8}$$

definiamo poi gli operatori **coulombiano e di scambio**

$$J_m\varphi_k(x_1) = \int dx_2 \varphi_m^*(x_2)\varphi_m(x_2)\frac{1}{r_{12}}\varphi_k(x_1) \tag{9}$$

$$K_m\varphi_k(x_1) = \int dx_2 \varphi_m^*(x_2)\varphi_k(x_2)\frac{1}{r_{12}}\varphi_m(x_1) \tag{10}$$

equazione di Fock in forma compatta

$$\left[h + \sum_m (J_m - K_m) \right] \varphi_k(x) = \sum_m \Lambda_{mk}\varphi_m(x) \tag{11}$$

Operatore di Fock

$$F = h + \sum\nolimits_m (J_m - K_m) \tag{12}$$

Moltiplicatori di Lagrange = elementi di matrice dell'operatore di Fock

$$\Lambda_{lk} = \langle \varphi_l |F| \varphi_k \rangle \tag{13}$$

Equazione di stazionarietà dell'energia (in forma compatta)

$$\boxed{F|\varphi_k\rangle = \sum_m^{occ} \Lambda_{mk}|\varphi_m\rangle} \tag{14}$$

L'operatore di Fock che agisce su uno spin orbitale dà luogo ad una combinazione lineare degli orbitali occupati.

Che significa questa condizione?

In generale l'azione di un operatore su uno spin orbitale è

$$F|\varphi_k\rangle = \sum\nolimits_m \Lambda_{mk}|\varphi_m\rangle + \sum\nolimits_a \Lambda_{ak}|\varphi_a\rangle \tag{15}$$

cioè una comb. lineare di TUTTI gli spin orbitali dello spazio. La condizione consiste nel vincolo che i coefficienti

$$\Lambda_{ak} = \langle \varphi_a |F| \varphi_k \rangle = F_{ak} = 0 \qquad con \;\; k = occupato \qquad a = vuoto \tag{16}$$

Dalle regole di Slater sugli elementi di matrice si ricava che questo è equivalente a

$$\langle \Phi_k^a |H| \Phi \rangle = 0 \tag{17}$$

che esprime il teorema di **Brillouin**.

1.1 Operatore di Fock

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, 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

$$J_m\varphi_k(x_1) = V_m(x_1)\,\varphi_k(x_1) \tag{18}$$

where

$$V_m(x_1) = \int dx_2 \frac{\varphi_m^*(x_2)\,\varphi_m(x_2)}{|r_1 - r_2|} = \int dx_2 \frac{\rho_m(x_2)}{|x_1 - x_2|} \tag{19}$$

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 potential at the point** x_1. We can define the global coulomb operator acting on a spin orbital

$$J\varphi_k(x_1) = \sum_{m=1}^{N} \int dx_2 \frac{\varphi_m^*(x_2)\,\varphi_m(x_2)}{|r_1 - r_2|}\varphi_k(x_1) = V(x_1)\,\varphi_k(x_1) \tag{20}$$

$$V(x_1) = \int dx_2 \frac{\rho(x_2, x_2)}{|r_1 - r_2|} \tag{21}$$

where ρ is the total one-body density function arising from the N electrons in the occupied spin orbitals of the SD. This potential $V(x)$ is repulsive, everywhere positive and it is the analogous of the nuclear 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*.

The term K in eq.s (**??**,**??**) is the **exchange operator**. We can define a full exchange operator acting on a spin orbitals as

$$K\varphi_k(x_1) = \sum_{m=1}^{N} \int dx_2 \frac{\varphi_m^*(x_2)\,\varphi_m(x_1)}{|r_1 - r_2|}\varphi_k(x_2) \tag{22}$$

$$= \int dx_2 \frac{\rho(x_1, x_2)}{|r_1 - r_2|}\varphi_k(x_2) \tag{23}$$

$$= \int dx_2\; K(x_1, x_2)\,\varphi_k(x_2) \tag{24}$$

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, 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 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

$$K\varphi_k(x_1) = \sum_{m=1}^{N} \int dx_2 \frac{1}{r_{12}} \varphi_m^*(x_2) P_{12} \varphi_m(x_2) \varphi_k(x_1) \tag{25}$$

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

$$F(x_1) = h(x_1) + \sum_{m=1}^{N} \int dx_2 \frac{1}{r_{12}} \varphi_m^*(x_2) (1 - P_{12}) \varphi_m(x_2) \tag{26}$$

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

$$F(x_1)\varphi_k(x_1) = h(x_1)\varphi_k(x_1) + \sum_m [J_m(x_1) - K_m(x_1)]\varphi_k(x_1) \tag{27}$$

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

$$[J_k(x_1) - K_k(x_1)]\varphi_k(x_1) = 0 \tag{28}$$

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. The expectation value of the Fock operator for the φ_k spin orbital

$$\langle \varphi_k | F | \varphi_k \rangle = \langle \varphi_k | h | \varphi_k \rangle + \sum_m [\langle \varphi_k \varphi_m | \varphi_k \varphi_m \rangle - \langle \varphi_k \varphi_m | \varphi_m \varphi_k \rangle] \tag{29}$$

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

1.2 The canonical Hartree-Fock spin orbitals

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

$$F|\varphi_1 ... \varphi_N\rangle = |\varphi_1 ... \varphi_N\rangle \mathbf{\Lambda} \tag{30}$$

where $|\varphi_1 ... \varphi_M\rangle$ 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 $N \times N$

$$\mathbf{\Lambda U} = \mathbf{U}\boldsymbol{\varepsilon} \tag{31}$$

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

$$\boldsymbol{\Lambda} = \mathbf{U}\boldsymbol{\varepsilon}\tilde{\mathbf{U}} \tag{32}$$

which may be substituted in eq. (30)

$$F\left|\varphi_1...\varphi_N\right\rangle = \left|\varphi_1...\varphi_N\right\rangle \mathbf{U}\boldsymbol{\varepsilon}\tilde{\mathbf{U}} \tag{33}$$

Multiplying on the right by $\mathbf{U}$

$$F\left|\varphi_1...\varphi_N\right\rangle \mathbf{U} = \left|\varphi_1...\varphi_N\right\rangle \mathbf{U}\boldsymbol{\varepsilon} \tag{34}$$

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

$$\left|\varphi'_1...\varphi'_N\right\rangle = \left|\varphi_1...\varphi_N\right\rangle \mathbf{U} \tag{35}$$

which diagonalize F

$$F\left|\varphi'_1...\varphi'_N\right\rangle = \left|\varphi'_1...\varphi'_N\right\rangle \boldsymbol{\varepsilon} \tag{36}$$

Thus the canonical Hartree-Fock eigenvalue equation are obtained

$$F\varphi'_k = \varepsilon_k\varphi'_k \qquad \forall k = 1...N \tag{37}$$

that is equivalent to the stationary condition (**??**) 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

$$F\varphi_k = \varepsilon_k\varphi_k \qquad \forall k = 1...N \tag{38}$$

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

$$\left\langle i\left|F\right|k\right\rangle = \delta_{ik}\varepsilon_k = \left\langle k\left|h\right|k\right\rangle + \sum_{m=1}^{N}\left[\langle km|km\rangle - \langle km|mk\rangle\right] \tag{39}$$

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

1.3 La matrice densità è invariante per trasformazioni unitarie tra gli spin orbitali occupati

$$\rho(x,x') = \sum_{j=1}^{N} \varphi_j(x)\,\varphi_j^*(x') \tag{40}$$

$$= |\boldsymbol{\varphi}(x)\rangle\,\langle\boldsymbol{\varphi}(x')| \tag{41}$$

e se esprimo i φ attraverso una trasformazione unitaria di un altro set di orbitali χ

$$|\boldsymbol{\varphi}(x)\rangle = |\boldsymbol{\chi}(x)\rangle\,\mathbf{U} \qquad \langle\boldsymbol{\varphi}(x')| = \mathbf{U}^+\,\langle\boldsymbol{\chi}(x')| \qquad \mathbf{U}^+ = \mathbf{U}^{-\mathbf{1}} \tag{42}$$

sostituendo

$$\rho(x,x') = |\boldsymbol{\chi}(x)\rangle\,\mathbf{U}\underset{I}{\mathbf{U}}^+\,\langle\boldsymbol{\chi}(x')| \tag{43}$$

$$= |\boldsymbol{\chi}(x)\rangle\,\langle\boldsymbol{\chi}(x')| \tag{44}$$

$$= \sum_{j=1}^{N} \chi_j(x)\,\chi_j^*(x') \tag{45}$$

Dato che l'operatore di Fock dipende dalla matrice densità si deduce che ogni trasformazione unitaria tra gli spin orbitali occupati, lascia inalterato l'operatore di Fock. Quindi si ha una certa libertà nella scelta degli spin orbitali occupati.

1.4 The Hartree-Fock-Roothaan equation

The stationary conditions for a SD lead to the Hartree-Fock equations 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 Fock equation 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

$$\varphi_k = \sum_{r=1}^{M} C_{rk}\phi_r \qquad \forall k = 1...N \tag{46}$$

In this way the stationariety 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)

$$\varphi_a = \sum_{r=1}^{M} C_{ra}\phi_r \qquad \forall a = N{+}1...M \tag{47}$$

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

$$\underset{\text{row}}{|\varphi_1 ... \varphi_M\rangle} = \underset{\text{row}}{|\phi_1 ... \phi_M\rangle}_{MxM} \underset{matrix}{\mathbf{C}} \tag{48}$$

where $|\varphi_1 ... \varphi_M\rangle$ is a row vector collecting the spin orbitals, $|\phi_1 ... \phi_M\rangle$ collects the basis functions and $\mathbf{C}$ is the MxM 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

$$F \, |\varphi_1 ... \varphi_M\rangle = |\varphi_1 ... \varphi_M\rangle \, \boldsymbol{\varepsilon} \tag{49}$$

and after substitution of projection we obtain

$$F \, |\phi_1 ... \phi_M\rangle \, \mathbf{C} = \quad |\phi_1 ... \phi_M\rangle \, \mathbf{C}\boldsymbol{\varepsilon} \tag{50}$$

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

$$\begin{matrix} \langle \phi_1 | \\ ... \\ \langle \phi_M | \end{matrix} F \, |\phi_1 ... \phi_M\rangle \, \mathbf{C} = \begin{matrix} \langle \phi_1 | \\ ... \\ \langle \phi_M | \end{matrix} |\phi_1 ... \phi_M\rangle \, \mathbf{C}\boldsymbol{\varepsilon} \tag{51}$$

we obtain the matrix equation

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{52}$$

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 symmetric metric matrix $\mathbf{S}$ can be diagonalized with an orthogonal matrix $\mathbf{V}$

$$\mathbf{SV} = \mathbf{VK} \tag{53}$$

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

$$\begin{aligned} \mathbf{S} &= \mathbf{V}\mathbf{K}\tilde{\mathbf{V}} && (54) \\ &= \mathbf{V}\mathbf{K}^{\mathbf{1/2}}\mathbf{K}^{\mathbf{1/2}}\tilde{\mathbf{V}} && (55) \\ &= \mathbf{V}\mathbf{K}^{\mathbf{1/2}}\tilde{\mathbf{V}} \; \mathbf{V}\mathbf{K}^{\mathbf{1/2}}\tilde{\mathbf{V}} && (56) \\ &= \mathbf{S}^{\mathbf{1/2}} \; \mathbf{S}^{\mathbf{1/2}} && (57) \end{aligned}$$

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

$$\mathbf{K} = \mathbf{K}^{1/2}\mathbf{K}^{1/2} \tag{58}$$

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. $\left(K^{1/2}\right)_{ii} = (K_{ii})^{1/2}$. We can also define the inverse of this matrix, $\mathbf{K}^{-1/2}$ which contains as diagonal elements the $(K_{ii})^{-1/2}$ values, and define

$$\mathbf{S}^{-1/2} = \mathbf{V}\mathbf{K}^{\mathbf{-1/2}}\tilde{\mathbf{V}} \tag{59}$$

so that

$$\mathbf{S}^{1/2}\mathbf{S}^{-1/2} = \mathbf{V}\mathbf{K}^{\mathbf{1/2}}\tilde{\mathbf{V}}\ \mathbf{V}\mathbf{K}^{\mathbf{-1/2}}\tilde{\mathbf{V}} = \mathbf{I} \tag{60}$$

In

This is the **Löwdin symmetric orthogonalization**. By substituting the last expression in eq. (52) and applying some algebra we can obtain the desired result

$$\mathbf{F}\mathbf{C} = \mathbf{S}^{1/2}\mathbf{S}^{1/2}\mathbf{C}\boldsymbol{\varepsilon} \tag{61}$$

$$\mathbf{S}^{-1/2}\mathbf{F}\mathbf{C} = \mathbf{S}^{1/2}\mathbf{C}\boldsymbol{\varepsilon} \tag{62}$$

$$\mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{\mathbf{-1/2}}\ \mathbf{S}^{\mathbf{1/2}}\mathbf{C} = \mathbf{S}^{1/2}\mathbf{C}\boldsymbol{\varepsilon} \tag{63}$$

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\varepsilon} \tag{64}$$

where the primed matrices are

$$\mathbf{F}' = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{\mathbf{1/2}} \qquad \text{transformed Fock matrix} \tag{65}$$

$$\mathbf{C}' = \mathbf{S}^{\mathbf{1/2}}\mathbf{C} \qquad \text{transformed eigenvectors} \tag{66}$$

The form (64) allows direct diagonalization of the transformed Fock matrix and the eigenvectors $\mathbf{C}$ can be retrieved by

$$\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{C}' \tag{67}$$

Equation (64) is completely equivalent to eq. (52) (they have the same eigenvalues) and can be solved by standard diagonalization methods.

1.5 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 C matrix in eq. (52) to be used in (48) 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. (64) 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 $\left\{\varphi_1^{(0)}...\varphi_n^{(0)}\right\}$ 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

$$F\left[\rho^{(0)}\right] \tag{68}$$

where $\rho^{(0)}$ is the guess density matrix, built with the guess spin orbitals. By the matrix transformation (65) with the $\mathbf{S}^{-1/2}$ matrix the $\mathbf{F'}\left[\rho^{(0)}\right]$ matrix can be obtained for the first iteration. Once diagonalization of $\mathbf{F'}\left[\rho^{(0)}\right]$ and transformation (66) are accomplished, a new set of M spin orbitals $\left\{\varphi^{(1)}\right\}$ is obtained. These spin orbitals do not satisfy Brillouin theorem (**??**) nor the stationarity conditions (**??**), 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)

$$\left\langle\varphi_r^{(1)}\left|F\left[\rho^{(0)}\right]\right|\varphi_s^{(1)}\right\rangle = \varepsilon_r\delta_{rs} \tag{69}$$

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

$$\left\langle\varphi_r^{(1)}\left|F\left[\rho^{(1)}\right]\right|\varphi_s^{(1)}\right\rangle \neq \varepsilon_r\delta_{rs} \tag{70}$$

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 $F\left[\rho^{(1)}\right]$. This procedure can be repeated forming a new Fock matrix from the density matrix of the previous step: $F\left[\rho^{(n-1)}\right]$. 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

$$\left|\rho^{(n)} - \rho^{(n-1)}\right| < t \tag{71}$$

and, correspondingly, the eigenvalue equation

$$\left\langle\varphi_r^{(n)}\left|F\left[\rho^{(n)}\right]\right|\varphi_s^{(n)}\right\rangle = \varepsilon_r\delta_{rs} \tag{72}$$

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.

1.6 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 (26) is written just for one electron but, as any physical operator, it may be written for N electrons

$$F_N\left(x_1, x_2 ... x_N\right) = \sum_{i=1}^{N} F(x_1) \tag{73}$$

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 (73). 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

$$F_N\left(x_1, x_2 ... x_N\right)\ \Phi_0\left(x_1, x_2 ... x_N\right) = \left(\sum_{i=1}^{N} \varepsilon_i\right)\ \Phi_0\left(x_1, x_2 ... x_N\right) \tag{74}$$

that is a general feature of all one-electron operators. Thus the Fock operator F_N (73) 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 (74) are different from the expectation value of the Hamiltonian

$$\left\langle \Phi \left| F_N \right| \Phi \right\rangle = \sum_{i=1}^{N} \varepsilon_i = \sum_{i=1}^{N} \left(\left\langle i \left| h \right| i \right\rangle + \sum_{m=1}^{N} \left[\langle im|im\rangle - \langle im|mi\rangle \right] \right) \tag{75}$$

$$\left\langle \Phi \left| H_{el} \right| \Phi \right\rangle = \sum_{i=1}^{N} \left(\left\langle i \left| h \right| i \right\rangle + \frac{1}{2} \sum_{m=1}^{N} \left[\langle im|im\rangle - \langle im|mi\rangle \right] \right) \tag{76}$$

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.

1.7 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. (39) for the occupied spin orbitals entering the Hartree-Fock

SD. Such an expression can be specialized for occupied and virtual spin orbitals

$$\varepsilon_k = \langle k\,|h|\,k\rangle + \sum_m \left[\langle km|km\rangle - \langle km|mk\rangle\right] \tag{77}$$

$$\varepsilon_a = \langle a\,|h|\,a\rangle + \sum_m \left[\langle am|am\rangle - \langle am|ma\rangle\right] \tag{78}$$

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

$$\varepsilon_k = \langle k\,|h|\,k\rangle + \sum_{m\neq k} \left[\langle km|km\rangle - \langle km|mk\rangle\right] \tag{79}$$

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.

$$\langle km|km\rangle = \int dr_1 \int ds_1 \int dr_2 \int ds_2\ \varphi_k^*(r_1)\,\sigma_k^*(s_1)\,\varphi_m^*(r_2)\,\sigma_m^*(s_2)\,\frac{1}{r_{12}} \tag{80}$$

$$\varphi_k(r_1)\,\sigma_k^*(s_1)\,\varphi_m(r_2)\,\sigma_m^*(s_2) \tag{81}$$

$$\langle km|mk\rangle = \int dr_1 \int ds_1 \int dr_2 \int ds_2\ \varphi_k^*(r_1)\,\sigma_k^*(s_1)\,\varphi_m^*(r_2)\,\sigma_m^*(s_2)\,\frac{1}{r_{12}} \tag{82}$$

$$\varphi_m(r_1)\,\sigma_m^*(s_1)\,\varphi_k(r_2)\,\sigma_k^*(s_2) \tag{83}$$

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

$$E^N = \left\langle \Phi_0^N \left| H^N \right| \Phi_0^N \right\rangle \tag{84}$$

$$E_k^{N-1} = \left\langle \Phi_k^{N-1} \left| H^{N-1} \right| \Phi_k^{N-1} \right\rangle \tag{85}$$

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 (**??**) by eliminating the k index in all the sums

$$E_k^{N-1} = \sum_{m\neq k}^{N} \langle m \left| h \right| m \rangle + \frac{1}{2} \sum_{m\neq k}^{N} \sum_{j\neq k}^{N} \left[\langle mi | mi \rangle - \langle mi | im \rangle \right] \tag{86}$$

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

$$E^N = \sum_{m\neq k}^{N} \langle m \left| h \right| m \rangle + \langle k \left| h \right| k \rangle + \frac{1}{2} \sum_{m\neq k}^{N} \sum_{i\neq k}^{N} \left[\langle mi | mi \rangle - \langle mi | im \rangle \right] \tag{87}$$

$$+ \frac{1}{2} \sum_{m\neq k}^{N} \left[\langle mk | mk \rangle - \langle mk | km \rangle \right] + \frac{1}{2} \sum_{i\neq k}^{N} \left[\langle ki | ki \rangle - \langle ki | ik \rangle \right] \tag{88}$$

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

$$E_k^{N-1} - E^N = - \langle k \left| h \right| k \rangle - \sum_{m\neq k}^{N} \left[\langle mk | mk \rangle - \langle mk | km \rangle \right] \tag{89}$$

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

$$\mathrm{IP}_k = E_k^{N-1} - E^N = -\varepsilon_k \tag{90}$$

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

$$A \rightarrow A^+ + e^- \tag{91}$$

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

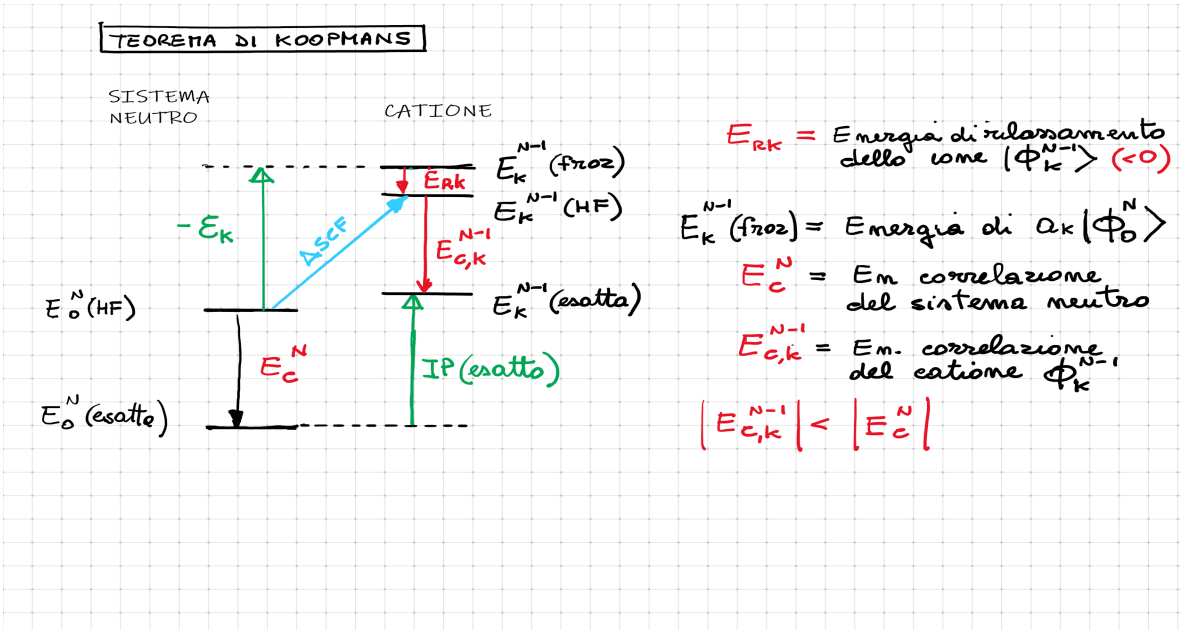


Figure 1: Schematica illustrazione del teorema di Koopmans.

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 orbitals 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].

In the figure also the ΔSCF energy is reported. It corresponds to the IP evaluated as the difference between the HF energies of the cation and the neutral system. In practice it includes the relaxation energy of the cation (at difference with the Koopmans' estimate). As the correlation energy of the cation is less than that of the neutral molecule (in absolute value) the ΔSCF result is an underestimate of the exact IP.

As an example in the the following table the IP's of the H_2O molecule are reported. The compensation already mentioned allows the Koopmans IP to be accurate within about 1 eV. The ΔSCF values are always underestimated sue to the difference between the correlation

energies of the neutral and ionic systems.

	exp (eV)	Koopmans (eV)	ΔSCF (eV)
b_1	12.62	13.8	11.1
a_1	14.74	15.7	13.3
b_2	18.51	19.5	17.6

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

$$\mathrm{EA}_a = E^N - E_a^{N+1} = -\varepsilon_a \tag{92}$$

where

$$E_a^{N+1} = \left\langle \Phi_a^{N+1} \left| H^{N+1} \right| \Phi_a^{N+1} \right\rangle \tag{93}$$

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.

1.8 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 functionβ 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 (**??**), the closed-shell restricted Hartree-Fock SD is

$$|\Phi\rangle = \left|\varphi_{1\alpha}\varphi_{1\beta}\varphi_{2\alpha}\varphi_{2\beta}\cdots\varphi_{N/2\alpha}\varphi_{N/2\beta}\right\rangle \tag{94}$$

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

$$\varphi_{k\alpha}(r) = \varphi_{k\beta}(r) \tag{95}$$

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

$$\left\langle \phi_p\sigma_p \left| F \right| \phi_q\sigma_q \right\rangle = \left\langle \phi_p\sigma_p \left| h + \sum_{m=1}^{N} \left(J_m - K_m \right) \right| \phi_q\sigma_q \right\rangle \tag{96}$$

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

$$\left\langle \phi_p\sigma_p \left| h \right| \phi_q\sigma_q \right\rangle = \int dr\ \phi_p^* h\left(r\right) \phi_q\left(r\right) \int ds\ \sigma_p^*\left(s\right) \sigma_q\left(s\right) \tag{97}$$

$$= \left\langle \phi_p \left| h \right| \phi_q \right\rangle \left\langle \sigma_p | \sigma_q \right\rangle \tag{98}$$

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

$$\mathbf{h}_{p\alpha,q\alpha} = \mathbf{h}_{p\beta,q\beta} = \left\langle \phi_p \left| h \right| \phi_q \right\rangle \qquad\qquad \mathbf{h}_{p\alpha,q\beta} = \mathbf{h}_{p\beta,q\alpha} = 0 \tag{99}$$

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

$$\left\langle \phi_p\sigma_p \left| J_m \right| \phi_q\sigma_q \right\rangle = \left\langle \phi_p\sigma_p\ \varphi_m\sigma_m | \phi_q\sigma_q\ \varphi_m\sigma_m \right\rangle \tag{100}$$

$$= \int dr_1 \int dr_2\ \phi_p^*\left(r_1\right) \varphi_m^*\left(r_2\right) \frac{1}{r_{12}} \phi_q\left(r_1\right) \varphi_m\left(r_2\right) \tag{101}$$

$$\int ds_1\ \sigma_p^*\left(s_1\right) \sigma_q\left(s_1\right) \int ds_2\ \sigma_m^*\left(s_2\right) \sigma_m\left(s_2\right) \tag{102}$$

$$= \left\langle \phi_p\varphi_m | \phi_q\varphi_m \right\rangle \left\langle \sigma_p | \sigma_q \right\rangle \left\langle \sigma_m | \sigma_m \right\rangle \tag{103}$$

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 form 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

$$\left\langle \phi_p\sigma_p \left| K_m \right| \phi_q\sigma_q \right\rangle = \left\langle \phi_p\sigma_p\ \varphi_m\sigma_m | \varphi_m\sigma_m\ \phi_q\sigma_q \right\rangle \tag{104}$$

$$= \int dr_1 \int dr_2\ \phi_p^*\left(r_1\right) \varphi_m^*\left(r_2\right) \frac{1}{r_{12}} \phi_m\left(r_1\right) \varphi_q\left(r_2\right) \tag{105}$$

$$\int ds_1\ \sigma_p^*\left(s_1\right) \sigma_m\left(s_1\right) \int ds_2\ \sigma_m^*\left(s_2\right) \sigma_q\left(s_2\right) \tag{106}$$

$$= \left\langle \phi_p\varphi_m | \varphi_m\phi_q \right\rangle \left\langle \sigma_p | \sigma_m \right\rangle \left\langle \sigma_m | \sigma_q \right\rangle \tag{107}$$

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

$$\langle \phi_p | F | \phi_q \rangle = \left\langle \phi_p \middle| h + \sum_{m=1}^{N/2} (2J_m - K_m) \middle| \phi_q \right\rangle \tag{108}$$

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 (52) 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)

$$E = \sum_{i=1}^{N} \langle i | h | i \rangle + \frac{1}{2} \sum_{ij=1}^{N} (\langle ij|ij\rangle - \langle ij|ji\rangle) \tag{109}$$

$$= 2 \sum_{i=1}^{N/2} \langle i | h | i \rangle + \frac{1}{2} \sum_{i}^{N/2} \sum_{\mu}^{\alpha,\beta} \sum_{j}^{N/2} \sum_{\nu}^{\alpha,\beta} (\langle i\mu, j\nu|i\mu, j\nu\rangle - \langle i\mu, j\nu|j\nu, i\mu\rangle) \tag{110}$$

$$= 2 \sum_{i=1}^{N/2} \langle i | h | i \rangle + \sum_{i}^{N/2} \sum_{j}^{N/2} (2 \langle ij|ij\rangle - \langle ij|ji\rangle) \tag{111}$$

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 μ=ν.

By removing the constraints (95) 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].

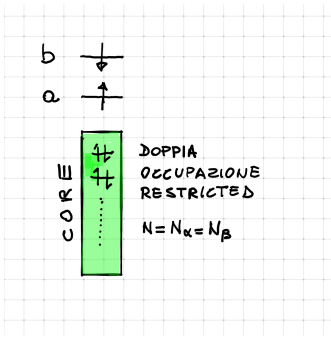
1.9 Energia di singoli determinanti di Slater

Consideriamo un SD come nella figura, costituito da un certo numero di orbitali di doppia occupazione restricted (CORE) e spin orbitali aggiuntivi in cui φ_a e φ_b in cui disponiamo due ulteriori elettroni. Vogliamo scrivere non l'energia totale del sistema ma l'energia in gioco dovuta all'aggiunta di questi due ulteriori elettroni. Vogliamo anche eseguire l'integrazione sulle variabili di spin per cui le quantità che scriveremo saranno relative a integrali nella sola

parte spaziale. Per questo definiamo E_{CORE} come l'energia dovuta agli elettroni che stanno negli orbitali di CORE, che sarà

$$E_{CORE} = 2\sum_{i=1}^{N} h_{ii} + \sum_{ij=1}^{N} (2J_{ij} - K_{ij}) \tag{112}$$

L'energia dello SD completo dovrà includere (oltre a E_{CORE}) diversi altri termini:



1. energia monoelettronica (indipendente dallo spin di φ_a e φ_b): $h_{aa} + h_{bb}$
2. energia di interazione tra l'elettrone in φ_a e gli elettroni negli spin orbitali CORE di spin α. Avendo lo stesso spin ci sono le interazione coulombiana e di scambio: $\sum_{m=1}^{N_\alpha} (J_{ma} - K_{ma})$
3. energia di interazione tra l'elettrone in φ_a e gli elettroni negli spin orbitali CORE di spin β. Avendo diverso spin ci sarà solo l'interazione coulombiana: $\sum_{m=1}^{N_\beta} J_{ma}$
4. Ripetizione dei punti 2,3 per lo spin orbitale φ_b (che ha spin β): $\sum_{m=1}^{N_\alpha} J_{ma} + \sum_{m=1}^{N_\beta} (J_{ma} - K_{ma})$
5. interazione coulombiana tra φ_a e φ_b: J_{ab} (non c'è lo scambio perché hanno diverso spin).

Sommando tutti i contributi si ottiene

$$\begin{aligned} E\left(CORE\varphi_{a\alpha}\varphi_{b\beta}\right) &= E_{CORE} + h_{aa} + h_{bb} && (113)\\ &\quad +(\sum_{m=1}^{N_\alpha} (J_{ma} - K_{ma}) + \sum_{m=1}^{N_\beta} J_{ma} && (114)\\ &\quad + \sum_{m=1}^{N_\alpha} J_{mb} + \sum_{m=1}^{N_\beta} (J_{mb} - K_{mb}) + J_{ab} && (115)\\ &= E_{CORE} + h_{aa} + h_{bb} + \sum_{m=1}^{N} (2J_{ma} - K_{ma}) && (116)\\ &\quad + \sum_{m=1}^{N} (2J_{mb} - K_{mb}) + J_{ab} && (117) \end{aligned}$$

in cui nell'ultimo passaggio abbiamo sfruttato il fatto che gli orbitali CORE sono restricted e di doppia occupazione.

Se adesso considerassimo un SD ottenuto dal precedente cambiando lo spin di φ_b da β a α otterremmo

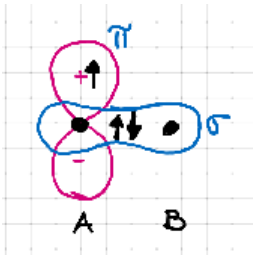
$$\begin{aligned} E\left(CORE\varphi_{a\alpha}\varphi_{b\beta}\right) &= E_{CORE} + h_{aa} + h_{bb} + \sum_{m=1}^{N} (2J_{ma} - K_{ma}) && (118)\\ &\quad + + \sum_{m=1}^{N} (2J_{mb} - K_{mb}) + J_{ab} - K_{ab} && (119) \end{aligned}$$

In pratica abbiamo aggiunto solo un termine di scambio K_{ab}. Quindi questo nuovo SD con spin paralleli in φ_a e φ_b avrà un'energia minore del precedente, dato che i termini di scambio sono attrattivi. Questa considerazione generale costituisce in pratica la regola di Hund (usata spesso per i complessi metallici) che stabilisce che le configurazioni con spin paralleli sono favorite rispetto alle altre.

1.10 Regola di Hund intra-atomica

Consideriamo il sistema della figura (che può essere immaginato anche come un frammento di un sistema più grande) formato da un orbitale Sigma doppiamente occupato che lega gli atomi A e B e da un orbitale semioccupato π in cui

l'elettrone si trova nello spin orbitale α.



Dato che il sistema ha una polarizzazione di spin, vogliamo studiare a livello UHF l'effetto dell'elettrone spaiato sull'orbitale σ, ed in particolare di come gli spin orbitali σ_α e σ_β si polarizzano per effetto dell'elettrone spaiato. Il determinante di riferimanto è

$$|0\rangle = |core, \sigma_\alpha, \sigma_\beta, \pi_\alpha\rangle \tag{120}$$

$$E = \langle 0|H|0\rangle = E_0 + J_{\sigma_\alpha\sigma_\beta} + J_{\sigma_\alpha\pi} + J_{\sigma_\beta\pi} - K_{\sigma_\alpha\pi} \tag{121}$$

dove in generale ci si aspetta che gli spin orbitali σ_α e σ_β abbiano una leggermente diversa parte spaziale. L'elemento decisivo nella espressione deel'energia sopra scritta è l'unico integrale di scambio che è

$$K_{\sigma_\alpha\pi} = \int dr_1 \int dr_2 \; \sigma_\alpha(r_1)\,\pi(r_1)\,\frac{1}{r_{12}}\sigma_\alpha(r_2)\,\pi(r_2) \tag{122}$$

e che sarà tanto più grande quanto più il prodotto $\sigma_\alpha(r)\,\pi(r)$ sarà grande. Quindi ci si aspetta che lo spin orbitale σ_α sarà polarizzato verso l'atomo A e viceversa per σ_β che sarà polarizzato verso B (vedi figura sotto). La conseguenza è che l'eccesso di spin sull'atomo A sarà incrementata rispetto all'eccesso di spin dovuto all'orbitale spaiato π,mentre che sull'atomo B si troverà un eccesso di spin di segno opposto, cioè β. Questo debole eccesso di spin β sull'atomo B potrà avere effetti analoghi a questo su un eventuale atomo C legato a B e così via, dando luogo al fenomeno dell'alternanza di spin. Notare che con calcoli ROHF costringeremmo i due spin orbitali σ ad avere identica parte spaziale, eliminando di fatto ogni possibilità di polarizzazione spaziale indotta dallo spin dell'orbitale π.

Come esempio possiamo considerare il catione della molecola di acqua. L'orbitale semioccupato (il più esterno) è un orbitale pseudo atomico p (di non legame) perpendicolare al piano molecolare. Esso esercita un effetto di polarizzazione di spin sui due orbitali molecolari che

formano i due legami O-H. Se adesso eseguissimo un calcolo ROHF su tale catione troveremmo eccesso di spin 1 sull'atomo di Ossigeno e zero altrove. Eseguendo invece un calcolo UHF troviamo un eccesso di spin 1.11 sull'atomo di Ossigeno e -0.05 sui due atomi di Idrogeno.

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