

Hartree-Fock Theory *

The HF approximation plays a crucial role in chemistry and constitutes the starting point for more elaborate treatments of electron correlation. Furthermore, many semi-empirical methods are developed by making certain approximations on integrals derived from HF theory.

In the simplest case of a closed-shell system (or an open-shell system with all the unpaired electrons having the same spin) we assume that the N -electron wave function can be written as a single Slater determinant, and we find the best set of spin-orbitals (in a variational sense) by minimizing the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$ upon variations of the spin-orbitals. We will see that in doing so the optimal spin-orbitals satisfy the Hartree-Fock equations:

$$\hat{f}(\mathbf{r})\chi_i(\mathbf{x}) = \epsilon_i\chi_i(\mathbf{x}) \quad (1)$$

where in Eq. (1) $\hat{f}(\mathbf{r}_i)$ is a hermitean operator called the one-particle Fock Hamiltonian of the form:

$$\hat{f}(\mathbf{r}) = -\frac{1}{2}\nabla^2 - \sum_{K=1}^M \frac{Z_A}{|\mathbf{r} - \mathbf{R}_K|} + v^{HF}(\mathbf{r}). \quad (2)$$

In Eq. (2), $v^{HF}(\mathbf{r})$ is an effective single-particle potential, which is built from the *Fock orbitals* $\chi_i(\mathbf{x})$ in a self-consistent manner.

We now proceed to a derivation of the Hartree-Fock equations.

I. DERIVATION OF THE HARTREE-FOCK EQUATIONS

A. The energy of a Slater determinant

We consider a single Slater determinant wave function $|\Phi\rangle = |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle$, where as usual only the diagonal of the determinant is explicitly shown. The electrostatic Hamiltonian can be written as:

$$\hat{H}_e = \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \sum_{i<j=1}^N \hat{g}(\mathbf{r}_i, \mathbf{r}_j) \quad (3)$$

where

$$\hat{h}(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 - \sum_{K=1}^M \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_K|} \quad (4)$$

and

$$\hat{g}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (5)$$

i.e. a sum of one-electron and two electron operators. The expectation value of the Hamiltonian for a single Slater determinant can therefore be readily calculated by using the Slater-Condon rules as follows:

$$\langle \Phi | \hat{H}_e | \Phi \rangle = \sum_{m=1}^N \langle \chi_m(1) | \hat{h}(1) | \chi_m(1) \rangle + \frac{1}{2} \sum_{mn}^N \langle \chi_m(1)\chi_n(2) | | \chi_m(1)\chi_n(2) \rangle \quad (6)$$

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where as a convention the coordinates of electron-one and electron-two have been used. We assume in the following that the set of N spin-orbitals are orthonormal, i.e.

$$\int \chi_m(\mathbf{x})\chi_n(\mathbf{x})d\mathbf{x} = \delta_{mn}. \quad (7)$$

B. Minimization of the energy functional

We want to find the minimum of the expectation value, Eq. (6) upon variation of the spin-orbitals, with the constraint that the spin-orbitals must remain orthogonal. Using the method of the Lagrange undetermined multipliers we need to find the (unconstrained) minimum of the functional:

$$\mathcal{L} = \sum_{m=1}^N \langle \chi_m(1) | \hat{h}(1) | \chi_m(1) \rangle + \frac{1}{2} \sum_{mn}^N \langle \chi_m(1)\chi_n(2) | \chi_m(1)\chi_n(2) \rangle - \sum_{ij} \epsilon_{ij} (\langle \chi_i | \chi_j \rangle - \delta_{ij}). \quad (8)$$

Since the Lagrangian of Eq. (8) has to be real, the Lagrange multipliers are elements of an hermitean matrix, i.e. $\epsilon_{ij} = \epsilon_{ji}^*$. We note that the condition of stationarity of the Lagrangian of Eq. (8) with respect to variation on the Lagrange multiplier, i.e.

$$\frac{\partial \mathcal{L}}{\partial \epsilon_{ij}} = 0. \quad (9)$$

correspond to the orthogonality requirement.

We now proceed by calculating the first order variation of the Lagrangian of Eq. (8). The condition of minimum is obtained by requiring that $\delta \mathcal{L} = 0$. We obtain in a straightforward manner:

$$\begin{aligned} \delta \mathcal{L} = & \sum_{i=1}^N [\langle \delta \chi_i(1) | \hat{h}(1) | \chi_i(1) \rangle + \langle \chi_i(1) | \hat{h}(1) | \delta \chi_i(1) \rangle] \\ & + \frac{1}{2} \sum_{ij}^N [\langle \delta \chi_i(1)\chi_j(2) | \chi_i(1)\chi_j(2) \rangle + \langle \chi_i(1)\delta \chi_j(2) | \chi_i(1)\chi_j(2) \rangle] \\ & + \langle \chi_i(1)\chi_j(2) | \delta \chi_i(1)\chi_j(2) \rangle + \langle \chi_i(1)\chi_j(2) | \chi_i(1)\delta \chi_j(2) \rangle \\ & - \langle \delta \chi_i(1)\chi_j(2) | \chi_j(1)\chi_i(2) \rangle - \langle \chi_i(1)\delta \chi_j(2) | \chi_j(1)\chi_i(2) \rangle \\ & - \langle \chi_i(1)\chi_j(2) | \delta \chi_j(1)\chi_i(2) \rangle - \langle \chi_i(1)\chi_j(2) | \chi_j(1)\delta \chi_i(2) \rangle \\ & - \sum_{ij} \epsilon_{ij} [\langle \delta \chi_i | \chi_j \rangle + \langle \chi_i | \delta \chi_j \rangle] \end{aligned} \quad (10)$$

Note that Eq. (11) can be rewritten in a more concise way by realizing that some terms are just one the complex conjugate of the other. For example:

$$\begin{aligned} \langle \chi_i(1) | \hat{h}(1) | \delta \chi_i(1) \rangle &= \langle \delta \chi_i(1) | \hat{h}(1) | \chi_i(1) \rangle^* \\ \langle \chi_i(1)\chi_j(2) | \delta \chi_i(1)\chi_j(2) \rangle &= \langle \delta \chi_i(1)\chi_j(2) | \chi_i(1)\chi_j(2) \rangle^* \end{aligned} \quad (11)$$

Also the following relation holds generally:

$$\begin{aligned} \langle \chi_i(1)\delta \chi_j(2) | \chi_i(1)\chi_j(2) \rangle &= \langle \delta \chi_j(2)\chi_i(1) | \chi_j(2)\chi_i(1) \rangle \\ &= \langle \delta \chi_j(1)\chi_i(2) | \chi_j(1)\chi_i(2) \rangle \end{aligned} \quad (12)$$

since the integration variables are dummy indexes. The first order variation of the Lagrangian can therefore be re-written as:

$$\begin{aligned} \delta \mathcal{L} = & \sum_{i=1}^N [\langle \delta \chi_i(1) | \hat{h}(1) | \chi_i(1) \rangle + \sum_j^N \{ \langle \delta \chi_i(1) \chi_j(2) | \chi_i(1) \chi_j(2) \rangle - \langle \delta \chi_i(1) \chi_j(2) | \chi_j(1) \chi_i(2) \rangle \\ & - \sum_j \epsilon_{ij} \langle \delta \chi_i | \chi_j \rangle \}] + \text{c.c.} \end{aligned} \quad (13)$$

where c.c. stands for complex conjugate. Introducing the following notation for the operators:

$$\begin{aligned} \hat{J}_i \chi_j(\mathbf{x}_1) &= \left[\int \frac{\chi_i^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \chi_j(\mathbf{x}_1) \\ \hat{K}_i \chi_j(\mathbf{x}_1) &= \left[\int \frac{\chi_i^*(\mathbf{x}_2) \chi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \chi_i(\mathbf{x}_1) \end{aligned} \quad (14)$$

we can re-write Eq. (13) even more concisely:

$$\delta \mathcal{L} = \sum_{i=1}^N \int d\mathbf{x}_1 \delta \chi_i^*(\mathbf{x}_1) [\hat{h}(1) \chi_i(\mathbf{x}_1) + \sum_{j=1}^N \{ \hat{J}_j - \hat{K}_j \} \chi_i(\mathbf{x}_1) - \sum_j \epsilon_{ij} \chi_j] + \text{c.c.} = 0 \quad (15)$$

Since the variations $\delta \chi_i^*$ and $\delta \chi_i$ can be regarded as independent, we obtain the following condition for the extremum of the functional, Eq. (11):

$$[\hat{h}(1) + \sum_{j=1}^N \{ \hat{J}_j - \hat{K}_j \}] \chi_i(\mathbf{x}_1) = \sum_j \epsilon_{ij} \chi_j(\mathbf{x}_1) \quad (16)$$

which are the Hartree-Fock equations. A few words on the operators: the operator \hat{J}_i is called *Coulomb* operator, and one can readily see that the Coulomb integrals are simply expectation values of spin-orbitals with the Coulomb operator:

$$\langle \chi_i | \hat{J}_j | \chi_i \rangle = \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \equiv J_{ij} \quad (17)$$

The Coulomb operators are an example of *local* operators: in order to evaluate their action on a given function at a point in the configurational space, we need to know just the value of the function at the same point. Note that a different meaning for the same terminology is currently in use in Density Functional Theory.

Let's now consider the expectation value for the exchange operator, \hat{K}_j :

$$\langle \chi_i | \hat{K}_j | \chi_i \rangle = \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_2) \chi_j(\mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}_2 \equiv K_{ij}. \quad (18)$$

Analogously the expectation value is the familiar exchange integral. Note that at variance with the Coulomb operators, the exchange operators are *non-local*; we need to know the value of the function χ_i in all the configurational space in order to calculate the result of the action of the exchange operator on the function χ_i , $\hat{K}_j \chi_i$ in a single point in space. The presence of the exchange operator in the Hartree-Fock equations is a consequence of the antisymmetric nature of the Slater determinant. In fact in the closely related Hartree theory, where the *ansatz* is a simple Hartree product, we do not have exchange operators.

The Hartree-Fock equations can therefore be written as:

$$\hat{f}(\mathbf{r}) \chi_i(\mathbf{x}) = \sum_j \epsilon_{ij} \chi_j(\mathbf{x}). \quad (19)$$

where

$$\hat{f}(1) = \hat{h}(1) + \sum_{j=1}^N [\hat{J}_j - \hat{K}_j] \quad (20)$$

and the sum in Eq. (20) is over the N occupied spin-orbitals of lower energy.

C. Canonical Hartree-Fock equations

It is easy to show that a Slater determinant is invariant, up to a constant purely imaginary phase factor, to a unitary transformation of the constituent spin-orbitals.

Suppose that the set of transformed spin-orbitals are derived from the original ones with the transformation:

$$\chi'_i = \sum_j \chi_j U_{ji} \quad (21)$$

such that the matrix U is unitary, i.e. also the set of spin-orbitals χ'_i are orthonormal if the original set is (this is true by assumption). The inverse transformation of Eq. (21) reads:

$$\chi_i = \sum_j \chi'_j (U^\dagger)_{ji}. \quad (22)$$

Now we assume that we have a Slater product built from a set of spin-orbitals:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \dots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \dots & \chi_k(\mathbf{x}_2) \\ \dots & \dots & \dots & \dots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \dots & \chi_k(\mathbf{x}_N) \end{vmatrix}. \quad (23)$$

Consider the matrix A built from the original spin orbitals:

$$A = \begin{pmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \dots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \dots & \chi_k(\mathbf{x}_2) \\ \dots & \dots & \dots & \dots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \dots & \chi_k(\mathbf{x}_N) \end{pmatrix} \quad (24)$$

from which it follows that $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} |A|$.

Consider now the matrix A' built from the set of χ'_i spin-orbitals:

$$A' = \begin{pmatrix} \chi'_i(\mathbf{x}_1) & \chi'_j(\mathbf{x}_1) & \dots & \chi'_k(\mathbf{x}_1) \\ \chi'_i(\mathbf{x}_2) & \chi'_j(\mathbf{x}_2) & \dots & \chi'_k(\mathbf{x}_2) \\ \dots & \dots & \dots & \dots \\ \chi'_i(\mathbf{x}_N) & \chi'_j(\mathbf{x}_N) & \dots & \chi'_k(\mathbf{x}_N) \end{pmatrix} \quad (25)$$

Inserting Eq. (21) we trivially obtain that $A' = AU$ and therefore the Slater determinant built from the set of χ'_i can be written as:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} |AU| = \frac{1}{\sqrt{N!}} |A||U|. \quad (26)$$

Now, since our transformation is unitary, $|U| = e^{i\lambda}$ with $\lambda \in \mathbb{R}$. As a result, the two Slater determinants differ by just a phase factor, which is irrelevant for the computation of most properties (in fact the phase factor cancel when we take the expectation values).

In order to derive the canonical (eigenvalue-type) Hartree-Fock equations, we now consider the effect of a unitary transformation of the spin orbitals on the Fock operator, Eq. (20). Consider now how the Coulomb and exchange operators changes:

$$\begin{aligned} \sum_i \hat{J}'_i(\mathbf{x}_1) &= \sum_i \left[\int \frac{\chi_i'^*(\mathbf{x}_2) \chi_i'(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \\ &= \sum_i \sum_j \sum_k U_{ji}^* U_{ki} \left[\int \frac{\chi_j^*(\mathbf{x}_2) \chi_k(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \\ &= \sum_j \left[\int \frac{\chi_j^*(\mathbf{x}_2) \chi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \end{aligned} \quad (27)$$

due to the fact that U is unitary. For the exchange operator we have similar results, and it follows that the Fock operator is invariant upon a unitary transformation of the spin-orbitals. Let us now consider the Lagrange multipliers. We already saw that they are the elements of an hermitean matrix. Moreover one trivially shows that:

$$\langle \chi_i | \hat{f} | \chi_j \rangle = \sum_k \epsilon_{jk} \langle \chi_i | \chi_k \rangle = \epsilon_{ji}. \quad (28)$$

We can write:

$$\langle \chi'_i | \hat{f} | \chi'_j \rangle = \epsilon'_{ji} \quad (29)$$

with

$$\epsilon'_{ji} = \sum_{kl} U_{kj}^* \epsilon_{kl} U_{li} \quad (30)$$

or, in matrix notation: $\epsilon' = U^\dagger \epsilon U$. It therefore follows that the two matrices are connected by a similarity transformation. Since every hermitean matrix can be diagonalised by a unitary transformation, we can choose to express the Hartree Fock Equations in the set of spin-orbitals obtained by the transformation Eq. (21), where the matrix U diagonalizes the matrix of Lagrange multipliers. In such a set of spin-orbitals, we therefore obtain the canonical Hartree-Fock equations:

$$\hat{f}(\mathbf{r})\chi_i(\mathbf{x}) = \epsilon_i \chi_i(\mathbf{x}). \quad (31)$$

which has the form of an eigenvalue equation. From inspection of Eq. (20) and the form of the Coulomb and Exchange operators, Eq. (14), one realizes that the solutions of the eigenvalue equation enter in the definition of the operator. For this reason the Hartree-Fock equations are often referred to as *pseudo-eigenvalue* equations. A standard solution is to start with a guess for the spin-orbitals, build the Fock operator, solve the eigenvalue equation, and then the procedure must be repeated until the solutions are close enough to the spin-orbitals used for the construction of the operator. This method of solution is often called *self-consistent field*. The spin-orbitals of Eq. (31) are in general *delocalized orbitals*. Clearly we are free to transform this set of canonical Hartree-Fock orbitals to a set of more localized orbitals by applying unitary transformations on the spin-orbitals.

II. SOME GENERAL PROPERTIES OF THE HARTREE-FOCK SOLUTIONS

A. Interpretation of the orbital energies: The Koopmans theorem

The Fock operator is given by:

$$\hat{f} = \hat{h} + \sum_{j=1}^N (\hat{J}_j - \hat{K}_j) \quad (32)$$

where the Coulomb and exchange operators, \hat{J} and \hat{K} are defined by their action on a spin orbital in the following manner:

$$\hat{J}_j \chi_i(\mathbf{x}_1) = \int \frac{\chi_j^*(\mathbf{x}_2) \chi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \chi_i(\mathbf{x}_1) \quad (33)$$

and

$$\hat{K}_j \chi_i(\mathbf{x}_1) = \int \frac{\chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \chi_j(\mathbf{x}_1) \quad (34)$$

Upon resolution of the self-consistent field equations, Eq. (31) we obtain a set of one-particle orbitals, occupied in the ground-state HF wave function. Furthermore one obtains a set of spin-orbitals which are not occupied in the reference HF

wave function. In fact, for a N -electron system, only the N spin-orbitals with lowest orbital energies ϵ_i , $i = 1, 2, \dots, N$ enter in the HF determinant. The set of spin-orbitals which are not occupied in the ground-state are the *virtual* or *particle*-HF spin-orbitals. It is customary to label occupied spin-orbitals with letters a, b, \dots , and virtual orbitals with letters r, s, \dots . The SCF wave function can then be written as $|\Phi\rangle = |\chi_i \chi_j \dots \chi_k\rangle$ and the HF energy is given by:

$$E_{HF} = \langle \Phi | \hat{H} | \Phi \rangle = \sum_{i=1}^N \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \langle \chi_i \chi_j | | \chi_i \chi_j \rangle \quad (35)$$

and can be easily derived by using the Slater-Condon rules. Occupied and virtual spin-orbitals are eigenvectors of the HF operator:

$$\hat{f}(\mathbf{r}) \chi_a(\mathbf{x}) = \epsilon_a \chi_a(\mathbf{x}), \quad (36)$$

and

$$\hat{f}(\mathbf{r}) \chi_r(\mathbf{x}) = \epsilon_r \chi_r(\mathbf{x}). \quad (37)$$

and consequently orbital energies of occupied and virtual spin-orbitals are obtained as expectation values:

$$\langle \chi_a(\mathbf{x}) | \hat{f}(\mathbf{r}) | \chi_a(\mathbf{x}) \rangle = \epsilon_a, \quad (38)$$

and

$$\langle \chi_r(\mathbf{x}) | \hat{f}(\mathbf{r}) | \chi_r(\mathbf{x}) \rangle = \epsilon_r. \quad (39)$$

By using the Slater-Condon rules for matrix-element evaluations, we readily obtain the following expressions for ϵ_a and ϵ_r :

$$\begin{aligned} \epsilon_a &= \langle \chi_a | \hat{f} | \chi_a \rangle = \langle \chi_a | \hat{h} | \chi_a \rangle + \sum_{j=1}^N \langle \chi_a \chi_j | | \chi_a \chi_j \rangle \\ &= \langle \chi_a | \hat{h} | \chi_a \rangle + \sum_{j \neq a}^N \langle \chi_a \chi_j | | \chi_a \chi_j \rangle \end{aligned} \quad (40)$$

since by definition, $\langle \chi_a \chi_a | | \chi_a \chi_a \rangle = 0$, and

$$\epsilon_r = \langle \chi_r | \hat{f} | \chi_r \rangle = \langle \chi_r | \hat{h} | \chi_r \rangle + \sum_{j=1}^N \langle \chi_r \chi_j | | \chi_r \chi_j \rangle. \quad (41)$$

We at once note that the HF energy, Eq. (35) is not simply given as a sum of the orbital energies of the occupied spin-orbitals, i.e. $E_{HF} \neq \sum_{a=1}^N \epsilon_a$.

We want to find an interpretation of the HF orbital energies. Let suppose that we have obtained HF orbitals and energy for a system consisting of N electrons. The N spin-orbitals with lower energy are occupied in the HF determinant. Consider now a system of $N-1$ electrons, obtained by removing an electron from an occupied orbital χ_a of the system of N electrons. If we assume that the SCF orbitals do not change upon ionization, the other $N-1$ electrons still occupying the same orbitals, the total energy of the ionized system, with an electron vacancy in the spin orbital χ_a can be evaluated to be:

$$E_a^{N-1} = \sum_{b \neq a}^N \langle \chi_b | \hat{h} | \chi_b \rangle + \frac{1}{2} \sum_{b \neq a}^N \sum_{c \neq a}^N \langle \chi_b \chi_c | | \chi_b \chi_c \rangle \quad (42)$$

and we readily obtain for the *ionization potential* (IP):

$$\begin{aligned}
E_a^{N-1} - E^N &= -\langle \chi_a | \hat{h} | \chi_a \rangle - \frac{1}{2} \sum_b^N \langle \chi_b \chi_a | | \chi_b \chi_a \rangle - \frac{1}{2} \sum_b^N \langle \chi_a \chi_b | | \chi_a \chi_b \rangle \\
&= -(\langle \chi_a | \hat{h} | \chi_a \rangle + \sum_b^N \langle \chi_a \chi_b | | \chi_a \chi_b \rangle) = -\epsilon_a.
\end{aligned} \tag{43}$$

The result obtained in (43) has a very simple interpretation: in the assumption where the electronic structure of the system is unaffected by the ionization, the ionization potential is simply given as the negative of the HF orbital energy for the ionized level. The *relaxation effects*, i.e. the re-arrangement of the electronic structure of the ion following the ionization, is completely neglected. While this can be a good approximation for the outmost valence levels, it is a bad approximation for core levels and inner valence levels. In fact, from an analysis of the photoionization spectra (line positions and intensities) a break-down (sometimes complete) of the single particle approximation is apparent, with the appearance of satellite lines of intensity sometimes larger than that of the main lines.

In the same spirit also the energies of the virtual orbitals have a simple interpretation. Let consider a system of $N + 1$ electrons where an electron has been added to our system and occupies a virtual orbital (the orbitals and energies of the remaining N electrons being unaffected by the attachment process). We can write for the system of $N + 1$ electron:

$$E_r^{N+1} = \sum_b^N \langle \chi_b | \hat{h} | \chi_b \rangle + \langle \chi_r | \hat{h} | \chi_r \rangle + \frac{1}{2} \sum_b^N \sum_c^N \langle \chi_b \chi_c | | \chi_b \chi_c \rangle + \frac{1}{2} \sum_b^N \langle \chi_r \chi_b | | \chi_r \chi_b \rangle + \frac{1}{2} \sum_b^N \langle \chi_b \chi_r | | \chi_b \chi_r \rangle \tag{44}$$

from which it follows that:

$$E_r^{N+1} - E^N = \langle \chi_r | \hat{h} | \chi_r \rangle + \sum_b^N \langle \chi_r \chi_b | | \chi_r \chi_b \rangle = \epsilon_r. \tag{45}$$

In other words, the energies of the virtual orbitals are approximations to the electron affinities. The HF approximation to the electron affinities are often very poor. In fact usually the HF energies of virtual orbitals are positive, which means that often the anion is predicted to be unstable on the basis of a simple SCF theory. This can be easily understood in terms of electron correlation. When an electron is added to a system, the electron correlation increases simply due to the increase in the number of electron-electron interactions. HF lacks of a complete treatment of electron correlation (it is a mean field approach) and is therefore unable to provide an accurate description of the electron-attachment process.

The relations above, Eq. (43) and (45) are the formal demonstration of the so called Koopman's Theorem: in the frozen-orbital approximation, the orbital energies of occupied levels are the negative of the ionization potentials, IPs, while orbital energies of virtual orbitals equals the electron affinities, AE.

B. The Brillouin theorem

We know that from the self-consistent resolution of the HF equations one obtains a set of hole orbitals, which are occupied in the HF determinant, which will be denoted with $|\Psi_0\rangle$, and a set of particle orbitals, which are unoccupied in the HF reference state. We can construct a set of singly excited determinants, denoted with $|\Psi_a^r\rangle$, by promoting single electron excitations from one occupied HF orbital, χ_a , to a virtual orbital, χ_r . Likewise we can construct doubly excited determinants by promoting a pair of electrons from occupied to virtual levels, and so on for higher excitations. Fixing our notation:

$$|\Psi_0\rangle = |\chi_i \chi_j \dots \chi_a \dots \chi_b \dots \chi_k\rangle, \tag{46}$$

$$|\Psi_a^r\rangle = |\chi_i \chi_j \dots \chi_r \dots \chi_b \dots \chi_k\rangle, \tag{47}$$

$$|\Psi_{ab}^{rs}\rangle = |\chi_i \chi_j \dots \chi_r \dots \chi_s \dots \chi_k\rangle, \tag{48}$$

and so on. Next we evaluate the matrix element, $\langle \Psi_0 | \hat{H} | \Psi_a^r \rangle$ by making use of the Slater-Condon rules:

$$\begin{aligned}
\langle \Psi_0 | \hat{H} | \Psi_a^r \rangle &= \langle \chi_a | \hat{h} | \chi_r \rangle + \sum_b \langle \chi_a \chi_b | | \chi_r \chi_b \rangle \\
&= \langle \chi_a | (\hat{h} + \sum_b [\hat{J}_b - \hat{K}_b]) | \chi_r \rangle \\
&= \langle \chi_a | \hat{f} | \chi_r \rangle \\
&= \delta_{ar} = 0.
\end{aligned} \tag{49}$$

The last result is known as the Brillouin Theorem, and simply states that the optimized HF wave function does not mix with singly excited determinants, or in other words, that the HF wave function is stable with respect to single excitations. This has important consequences in Configuration Interaction (CI) theory; in a CI expansion of the exact non relativistic wave function:

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ar} c_{ra} |\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{rasb} |\Psi_{ab}^{rs}\rangle + \dots \tag{50}$$

the singly excited determinants are expected not to contribute that much to the expansion of the exact wave function and therefore to the ground state energy. This is not completely true since CI matrix elements of the type $\langle \Psi_a^r | \hat{H} | \Psi_{ab}^{rs} \rangle$ are different from zero and the single excitations contribute through coupling with the double excitations.

C. The Hartree-Fock Hamiltonian

The HF determinant, i.e. the determinant constructed from the lowest N spin-orbitals is, in general, not an eigenstate of the true electrostatic Hamiltonian (it would be so if the particles were truly interacting in a mean field sense, i.e. in the absence of two-body interaction terms). Therefore we have:

$$\hat{H}_e |\Psi_0\rangle \neq E |\Psi_0\rangle \tag{51}$$

However, the SCF solution is an eigenstate of a one-particle operator, sometimes called *Fockian*, of the form:

$$\hat{H}_0 = \sum_{i=1}^N \hat{f}(i) \tag{52}$$

as can be easily proven since \hat{H}_0 is invariant over permutation of the electron labels $[\hat{\mathcal{A}}, \hat{H}_0] = 0$ with $\hat{\mathcal{A}}$ the antisymmetrization operator:

$$\begin{aligned}
\hat{H}_0 |\Psi_0\rangle &= \hat{H}_0 \hat{\mathcal{A}} \{ \chi_i \chi_j \dots \chi_a \dots \chi_b \dots \chi_k \} \\
&= \hat{\mathcal{A}} \left(\sum_{i=1}^N \hat{f}(i) \right) \{ \chi_i \chi_j \dots \chi_a \dots \chi_b \dots \chi_k \} \\
&= \left(\sum_{i=1}^N \epsilon_i \right) |\Psi_0\rangle = E_0 |\Psi_0\rangle.
\end{aligned} \tag{53}$$

This result will be used in the perturbation analysis of the correlation energy, later in the course.

III. CLOSED SHELL HARTREE-FOCK EQUATIONS

In this section we specialize to the simpler but important case of closed-shell molecules, which are by far the more common in Chemistry. We first rewrite the Hartree-Fock equations in the special case of a closed-shell system where electrons with α and β spin occupy the same spatial orbitals. These HF equations are some times referred with the term *restricted*. We then invoke the algebraic approximation, we will introduce a finite basis set for the expansion of the spatial function of the spin-orbitals, deriving thus the Roothaan-Hall equations, routinely solved by every quantum chemistry package. We will end the section with some comments on population analysis and the calculation of expectation values.

A. Restricted spin-orbitals

We will consider so called restricted spin-orbitals, for which the radial part of the orbital is the same for α and β spins. Fixing our notation:

$$\begin{aligned}\chi_1 &= \psi_1\alpha \\ \chi_2 &= \psi_1\beta \\ &\dots \\ \chi_{2i-1} &= \psi_i\alpha \\ \chi_{2i} &= \psi_i\beta \\ &\dots \\ \chi_{N-1} &= \psi_{\frac{N}{2}}\alpha \\ \chi_N &= \psi_{\frac{N}{2}}\beta.\end{aligned}$$

In this case, we can derive a set of HF equations involving only the radial part of the spin-orbitals. The HF restricted determinant for a system of N electrons is then obtained by pairing the electrons (with α and β spin) in the $\frac{N}{2}$ lowest energy orbitals. We derive the spatial Hartree Fock equations with reference to α spin spin-orbitals; the same result is obtained if we start with β spin. Therefore we have:

$$\hat{f}\psi_i(\mathbf{r}_1)\alpha(\omega) = \epsilon_i\psi_i(\mathbf{r}_1)\alpha(\omega) \quad (54)$$

and we integrate over the spin, to obtain:

$$\begin{aligned}\int d\omega\alpha^*(\omega)\hat{f}\psi_i(\mathbf{r}_1)\alpha(\omega) &= [\int d\omega\alpha^*(\omega)\hat{f}\alpha(\omega)]\psi_i(\mathbf{r}_1) \\ &= \hat{f}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) \\ &= \epsilon_i\psi_i(\mathbf{r}_1)\end{aligned} \quad (55)$$

with the obvious notation $\hat{f}(\mathbf{r}_1) = \int d\omega\alpha^*(\omega)\hat{f}\alpha(\omega)$.

We now consider the quantity $\hat{f}(\mathbf{r}_1)\psi_i(\mathbf{r}_1)$:

$$\begin{aligned}
\hat{f}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) &= \hat{h}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) + \sum_{j=1}^{\frac{N}{2}} \iint d\omega d\omega' d\mathbf{r}_2 \alpha^*(\omega) [\psi_j^*(\mathbf{r}_2)\beta^*(\omega')] \frac{1}{r_{12}} \psi_j(\mathbf{r}_2)\beta(\omega') \\
&+ \psi_j^*(\mathbf{r}_2)\alpha^*(\omega') \frac{1}{r_{12}} \psi_j(\mathbf{r}_2)\alpha(\omega') \psi_i(\mathbf{r}_1)\alpha(\omega) \\
&- \sum_{j=1}^{\frac{N}{2}} \iint d\omega d\omega' d\mathbf{r}_2 \alpha^*(\omega) [\psi_j^*(\mathbf{r}_2)\beta^*(\omega')] \frac{1}{r_{12}} \psi_i(\mathbf{r}_2)\alpha(\omega') \psi_i(\mathbf{r}_1)\beta(\omega) \\
&+ \psi_j^*(\mathbf{r}_2)\alpha^*(\omega') \frac{1}{r_{12}} \psi_i(\mathbf{r}_2)\alpha(\omega') \psi_j(\mathbf{r}_1)\alpha(\omega) \\
&= [\hat{h} + 2 \sum_{j=1}^{\frac{N}{2}} \int d\mathbf{r}_2 \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_j(\mathbf{r}_2) - \sum_{j=1}^{\frac{N}{2}} \int d\mathbf{r}_2 \psi_j^*(\mathbf{r}_2) \frac{\mathcal{P}_{12}}{r_{12}} \psi_j(\mathbf{r}_2)] \psi_i(\mathbf{r}_1) \\
&= \epsilon_i \psi_i(\mathbf{r}_1),
\end{aligned} \tag{56}$$

due to the orthonormality of the spin eigenfunction, or in other words, as a direct consequence of the absence of exchange interactions between electrons with different spins. \mathcal{P}_{12} in Eq. (56) permutes the electronic coordinates 1 and 2.

We can therefore write the restricted closed-shell Hartree-Fock equations:

$$\hat{f}(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \tag{57}$$

with

$$\hat{f}(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) + \sum_{a=1}^{\frac{N}{2}} \int d\mathbf{r}_2 \psi_a^*(\mathbf{r}_2) \frac{(2 - \mathcal{P}_{12})}{r_{12}} \psi_a(\mathbf{r}_2). \tag{58}$$

B. The Roothaan-Hall Equations

The Hartree-Fock equations can be solved either numerically, as often done for atoms, or by recasting the integro-differential equation to the solution of a pseudo eigenvalue problem, via the introduction of a finite basis set. Quite recently, grid-methods approaches have also been attempted for the resolution of the molecular HF equations, but these methods, although promising, are still not of standard use. In almost every quantum chemistry code the HF equations are solved via the introduction of a finite basis set of either Gaussians or Slater type orbitals, which are used to expand the spatial part of the spin orbitals. Clearly in the limit that the basis set approaches completeness, the HF limit is obtained. For finite basis set, the resulting SCF solution is an approximation to the HF solution. We nonetheless will refer to HF solution also for the solution of the HF equations in a finite basis set.

The spatial part of the HF molecular orbitals is written as a linear combination of known K basis functions:

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^K \phi_{\mu} C_{\mu i} \tag{59}$$

and introducing this linear combination in the restricted HF equations, Eq. (57) one obtains:

$$\hat{f}(\mathbf{r}) \sum_{\mu} \phi_{\mu} C_{\mu i} = \epsilon_i \sum_{\mu} \phi_{\mu} C_{\mu i}. \tag{60}$$

We now multiply the above equation on the left by a generic basis function, ϕ_{ν}^* , and integrate over the configuration space, obtaining:

$$\sum_{\mu} \langle \phi_{\nu} | \hat{f} | \phi_{\mu} \rangle C_{\mu i} = \epsilon_i \sum_{\mu} \langle \phi_{\nu} | \phi_{\mu} \rangle C_{\mu i}. \tag{61}$$

If we now introduce the following notation for the matrix elements of the Fock operator, \hat{f} , and for the overlap between basis functions:

$$\begin{aligned} F_{\nu\mu} &= \langle \phi_\nu | \hat{f} | \phi_\mu \rangle = \int \phi_\nu^*(\mathbf{r}) \hat{f}(\mathbf{r}) \phi_\mu(\mathbf{r}) d\mathbf{r} \\ S_{\nu\mu} &= \langle \phi_\nu | \phi_\mu \rangle = \int \phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (62)$$

then the solution of the HF equations is recast to an algebraic eigenvalue problem:

$$FC = \epsilon SC \quad (63)$$

where ϵ is a diagonal matrix of the eigenvalues, and the expansion coefficients of the molecular orbitals in the finite basis set are arranged into columns:

$$C = \begin{pmatrix} C_{11} & C_{12} & \dots & C_{1K} \\ \dots & \dots & \dots & \dots \\ C_{\nu 1} & C_{\nu 2} & \dots & C_{\nu K} \\ \dots & \dots & \dots & \dots \\ C_{K1} & C_{K2} & \dots & C_{KK} \end{pmatrix}, \quad (64)$$

i.e. the expansion coefficients of the first molecular orbital are arranged in the first column, and so on. It should be clear that the dimension of the basis set determines the dimension of the eigenvalue problem. If we use K basis functions for the expansion of the molecular orbitals, then we obtain, at the end of the SCF procedure, K radial orbitals, and $2K$ spin-orbitals. Of these, the N spin orbitals with the lowest energy will be occupied in the HF reference state, and $N - 2K$ are the set of virtual orbitals. This set of orbitals is important in CI since electron correlation effects will be accounted through virtual excitations to these empty states. Note that the HF eigenvalue equation of Eq. (63) is preferably termed *pseudo-eigenvalue* since the Fock operator is defined through the molecular orbitals, Eq. (58). We will consider this issue in the next subsection.

C. Expressions for the Fock matrix

Let us now evaluate the Fock matrix elements over the basis functions:

$$F_{\mu\nu} = \langle \phi_\mu | \hat{f} | \phi_\nu \rangle = \int \phi_\mu^*(\mathbf{r}) [\hat{h} + \sum_{a=1}^{\frac{N}{2}} (2\hat{J}_a - \hat{K}_a)] \phi_\nu(\mathbf{r}) d\mathbf{r} \quad (65)$$

with

$$\begin{aligned} \hat{J}_a \phi_\nu(\mathbf{r}_1) &= \int \psi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_a(\mathbf{r}_2) d\mathbf{r}_2 \phi_\nu(\mathbf{r}_1) \\ &= \sum_\sigma \sum_\lambda C_{\sigma a}^* C_{\lambda a} \int \phi_\sigma^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\lambda(\mathbf{r}_2) d\mathbf{r}_2 \phi_\nu(\mathbf{r}_1) \end{aligned} \quad (66)$$

and

$$\begin{aligned} \hat{K}_a \phi_\nu(\mathbf{r}_1) &= \int \psi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\nu(\mathbf{r}_2) d\mathbf{r}_2 \psi_a(\mathbf{r}_1) \\ &= \sum_\sigma \sum_\lambda C_{\sigma a}^* C_{\lambda a} \int \phi_\sigma^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\nu(\mathbf{r}_2) d\mathbf{r}_2 \phi_\lambda(\mathbf{r}_1). \end{aligned} \quad (67)$$

Therefore:

$$\begin{aligned}
F_{\mu\nu} = \langle \phi_\mu | \hat{f} | \phi_\nu \rangle &= \langle \phi_\mu | \hat{h} | \phi_\nu \rangle + \sum_{a=1}^{\frac{N}{2}} \sum_{\sigma\lambda} C_{\sigma a}^* C_{\lambda a} [2 \iint \phi_\mu^*(\mathbf{r}_1) \phi_\sigma^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\nu(\mathbf{r}_1) \phi_\lambda(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad - \iint \phi_\mu^*(\mathbf{r}_1) \phi_\sigma^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\lambda(\mathbf{r}_1) \phi_\nu(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2].
\end{aligned} \tag{68}$$

We now define the so-called *density matrix* in the following way:

$$P_{\mu\nu} = 2 \sum_{a=1}^{\frac{N}{2}} C_{\nu a}^* C_{\mu a} \tag{69}$$

which permits us to rewrite the expression for the Fock matrix elements in the following way:

$$\begin{aligned}
F_{\mu\nu} = \langle \phi_\mu | \hat{f} | \phi_\nu \rangle &= \langle \phi_\mu | \hat{h} | \phi_\nu \rangle + \sum_{\sigma\lambda} P_{\lambda\sigma} [\iint \phi_\mu^*(\mathbf{r}_1) \phi_\sigma^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\nu(\mathbf{r}_1) \phi_\lambda(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad - \frac{1}{2} \iint \phi_\mu^*(\mathbf{r}_1) \phi_\sigma^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\lambda(\mathbf{r}_1) \phi_\nu(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2].
\end{aligned} \tag{70}$$

Note that, according to Eq. (70), the Fock matrix is defined once the density matrix is known. Since the knowledge of the density matrix requires a knowledge of the HF molecular orbitals, it is clear that a solution to the HF equations can only be found through an iterative procedure. Hence the terminology SCF (Self-Consistent Field) used for the solution of the HF equations. The SCF cycle must start with a guess to the density matrix. One possible guess would correspond to a null matrix $P = 0$ and the first SCF cycle thus solves the mono-electronic problem. A typical choice would be to use Hückel orbitals. Note also that we need to calculate the matrix elements of the Hamiltonian over the known basis functions. These integrals can be subdivided in *mono-electronic*, i.e. matrix elements over the mono-electronic part of the electrostatic Hamiltonian (kinetic energy and electron-nuclear repulsion):

$$\langle \phi_\mu | \hat{h} | \phi_\nu \rangle = \int \phi_\mu^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 - \sum_K \frac{Z_K}{|\mathbf{r} - \mathbf{R}_K|} \right] \phi_\nu(\mathbf{r}) d\mathbf{r} \tag{71}$$

which are usually computationally inexpensive, and a far larger set of *bi-electronic* integrals:

$$\langle \phi_\mu \phi_\lambda | \phi_\nu \phi_\sigma \rangle = \iint \phi_\mu^*(\mathbf{r}_1) \phi_\lambda^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\nu(\mathbf{r}_1) \phi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{72}$$

which are in number of K^4 for K basis functions. Symmetry properties of the integrals can be used to reduce the scaling to $\frac{K^4}{8}$. Note that in modern quantum chemistry programs, the basis functions (usually GTO or Slater type functions) are centered on the atomic nuclei. Therefore mono-electronic integrals can at most involve two different atomic centers, while bi-electronic integrals can involve up to four different centers. The numerical evaluation of a four-center integral can be very costly, this is the reason for the wide spread use of GTO functions over STOs. Note also that the evaluation of the mono-electronic integrals requires in input to the program a molecular structure, defining the positions of the nuclei (coordinates \mathbf{R}_K). Integrals over basis functions are calculated before the beginning of the SCF cycle and stored on disk or in memory.

D. The Density Matrix

The electron density operator is a one-electron operator, which, in the coordinate representation takes the following form:

$$\hat{\rho} = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \tag{73}$$

The HF electron density is therefore the expectation value of $\hat{\rho}$ with the HF wave function:

$$\begin{aligned}
\rho(\mathbf{r}) &= \langle \Psi_0 | \hat{\rho} | \Psi_0 \rangle \\
&= \langle \Psi_0 | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_0 \rangle \\
&= 2 \sum_{i=1}^{\frac{N}{2}} |\psi_i(\mathbf{r})|^2
\end{aligned} \tag{74}$$

where, in Eq. (74), Ψ_0 is the restricted HF solution, and ψ_i are the set of occupied HF spatial orbitals. The factor 2 in Eq. (74) is due to the spin. The solutions of the restricted HF equations are expressed as a linear combination of the basis elements:

$$\psi_i = \sum_{\mu} \phi_{\mu} C_{\mu i} \tag{75}$$

and after insertion of the linear combination in Eq. (74) one obtains:

$$\begin{aligned}
\rho(\mathbf{r}) &= 2 \sum_{i=1}^{\frac{N}{2}} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \\
&= 2 \sum_{\mu} \sum_{\nu} \phi_{\nu}^* \phi_{\mu} C_{\nu i}^* C_{\mu i} \\
&= \sum_{\mu\nu} P_{\mu\nu} \phi_{\nu}^* \phi_{\mu}.
\end{aligned} \tag{76}$$

from which it is clear that the density matrix is simply the matrix representation of the electron density in the one-electron orbital basis.

The number of electron is given by:

$$\begin{aligned}
\int \rho(\mathbf{r}) d\mathbf{r} &= \sum_{\mu\nu} P_{\mu\nu} \int \phi_{\nu}^* \phi_{\mu} d\mathbf{r} \\
&= \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} \\
&= Tr(PS),
\end{aligned} \tag{77}$$

where $S_{\nu\mu}$ is the overlap matrix.

E. Expectation values and population analysis

In this section we will give a brief outline of the calculation of molecular properties within the HF approach. The first property of interest is certainly the molecular energy. The restricted closed-shell HF energy can be expressed as:

$$\begin{aligned}
E_{HF} &= \sum_{a=1}^N \langle \psi_a | h | \psi_a \rangle + \frac{1}{2} \sum_{ab} \langle \psi_a \psi_b | | \psi_a \psi_b \rangle \\
&= 2 \sum_{i=1}^{\frac{N}{2}} \langle \psi_i | h | \psi_i \rangle + \sum_{ab=1}^{\frac{N}{2}} (2J_{ab} - K_{ab})
\end{aligned} \tag{78}$$

where J_{ij} and K_{ij} are Coulomb and Exchange integrals respectively:

$$J_{ij} = \iint \psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \quad (79)$$

and

$$K_{ij} = \iint \psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \quad (80)$$

The orbital energy of an occupied HF spin orbital can be written as:

$$\begin{aligned} \epsilon_a &= f_{aa} = \langle \psi_a | \hat{f} | \psi_a \rangle \\ &= \langle \psi_a | \hat{h} + \sum_{b=1}^{\frac{N}{2}} (2\hat{J}_b - \hat{K}_b) | \psi_a \rangle \\ &= \langle \psi_a | \hat{h} | \psi_a \rangle + \sum_{b=1}^{\frac{N}{2}} (2J_{ab} - K_{ab}) \end{aligned} \quad (81)$$

and comparing with the expression for the HF energy we get:

$$E_{HF} = \sum_{a=1}^{\frac{N}{2}} (h_{aa} + \langle \psi_a | \hat{f} | \psi_a \rangle) \quad (82)$$

If we express the matrix elements in terms of the elements of the density matrix we readily obtain:

$$E_{HF} = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\nu\mu} (h_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \quad (83)$$

which is a convenient expression for the calculation of the HF energy at each SCF iteration by multiplying the elements of the density matrix with the matrix elements of the Fock operator, $F_{\mu\nu}$, and of the one-electron part of the Hamiltonian, $h_{\mu\nu}^{\text{core}}$. Note that the one electron matrix elements $h_{\mu\nu}^{\text{core}}$ depend only on the molecular geometry and are calculated once and for all at the beginning of the SCF cycle and stored on disk or on memory.

An important one-electron property is the molecular dipole moment. The dipole moment operator is a one-electron operator:

$$\hat{\mu} = - \sum_{i=1}^N \mathbf{r}_i + \sum_{K=1}^M Z_K \mathbf{R}_K \quad (84)$$

where index i runs over the electrons and index K over the nuclei. The quantum mechanical expectation value then becomes:

$$\begin{aligned} \langle \Psi_0 | \hat{\mu} | \Psi_0 \rangle &= \langle \Psi_0 | - \sum_{i=1}^N \mathbf{r}_i + \sum_{K=1}^M Z_K \mathbf{R}_K | \Psi_0 \rangle \\ &= - \sum_{a=1}^{\frac{N}{2}} \langle \psi_a | \mathbf{r} | \psi_a \rangle + \sum_{K=1}^M Z_K \mathbf{R}_K \end{aligned} \quad (85)$$

since the integration is over the electronic coordinates. In terms of the density matrix it becomes:

$$\langle \Psi_0 | \hat{\mu} | \Psi_0 \rangle = - \sum_{a=1}^{\frac{N}{2}} \sum_{\mu} \sum_{\nu} P_{\nu\mu} \langle \phi_{\mu} | \mathbf{r} | \phi_{\nu} \rangle + \sum_{K=1}^M Z_K \mathbf{R}_K \quad (86)$$

and we see that the calculation of the dipole moment is easily accomplished by calculating the dipole matrix elements $\langle \phi_\mu | \mathbf{r} | \phi_\nu \rangle \equiv \int \phi_\mu^*(\mathbf{r}) \mathbf{r} \phi_\nu(\mathbf{r}) d\mathbf{r}$, usually done at the beginning of the SCF procedure, multiplied by the converged density matrix elements.

We finish this section with a discussion on population analysis. In most QM programs basis functions are centered on the atomic nuclei. It is reasonable to calculate the electronic charge on atom A with the following formula:

$$q_A = Z_A - \sum_{\mu \in A} (PS)_{\mu\mu} \quad (87)$$

which is derived from equation Eq. (77). Z_A is the nuclear charge of atoms A , and the sum is only over the basis functions centered on that atom. The above formula is at the basis of the *Mulliken* population analysis. Note that the definition, Eq. (87) is not unique, since we can write:

$$Tr(PS) = Tr(SP) = Tr(S^\alpha PS^{1-\alpha}). \quad (88)$$

If we chose $\alpha = \frac{1}{2}$ we obtain:

$$q_A = Z_A - \sum_{\mu \in A} (S^{\frac{1}{2}} P S^{\frac{1}{2}})_{\mu\mu} \quad (89)$$

which is at the basis of the Lödwin population analysis.

Population analysis are of widespread use and principally for qualitative interpretations. In fact, a mapping of the partial charge on every atom in the molecule could help in predicting the reactivity of the molecule. However, population analysis are basis-set dependent, and not too much meaning should be attached to the predicted partial charges. In fact, if one describe water by using a monocentric expansion (all basis functions are centered on a privileged point, for instance the Oxygen atom) then a population analysis would predict a charge of +1 on both hydrogens, and a charge of -2 on the Oxygen, i.e. an ionic bond situation, which is not realistic. Furthermore usually population analysis lose of significance when the basis set is particularly rich, as it is usually the case for highly correlated electronic structure calculations.

F. Unrestricted Hartree-Fock

In case one wants to describe an open-shell situation, i.e. when the molecular ground-state is not a singlet state, or in situations where chemical bonds are stretched, i.e. in the dissociation process, a restricted closed shell HF determinant is not able to describe, even qualitatively, the electronic distribution. There are two possible ways of applying the HF theory.

In one approach, termed Restricted Open-Shell HF, one uses spin-adapted configuration state functions CSFs, i.e. linear combinations of Slater determinants, but in such a case the HF equations are rather more complicated. In a simpler approach, called Unrestricted Hartree-Fock, UHF, electrons with α and β spins are described by different spatial functions. The UHF equations are very similar to the restricted closed-shell HF equations we described above, but now two set of HF equations must be solved in the SCF procedure, one set for the set of spatial orbitals with α spin, and one set for the set of spatial orbitals with β spin. Upon introduction of a finite basis set we obtain the Pople-Nesbet equations. The UHF wave function is able to qualitatively describe the dissociation of a molecule, although for quantitative agreement one needs to revert to post-HF methods. One drawback of the UHF approach is the spin-contamination of the wave function, since a single open-shell Slater determinant is usually not eigenfunction of the spin operator S^2 .

G. Hartree-Fock solutions of the H_2 molecule in a minimal basis set

In the following we will solve the Hartree-Fock equations for the hydrogen molecule in a minimal basis, i.e. we will use one basis function for each occupied atomic orbital. Since the electron in the hydrogen atom occupies a 1s orbital, we introduce two normalized basis functions, ϕ_1 and ϕ_2 as our minimal basis. These are taken to be the two hydrogen 1s orbitals and are centered on the position of the nuclei. Suppose that the two basis functions have an overlap integral $S = \langle \phi_1 | \phi_2 \rangle$ which depends on the internuclear distance. Orthonormal molecular orbitals of *gerade* (g) and *ungerade* (u) symmetry with respect to the inversion around the mid-bond point can be formed as follows:

$$\psi_1(r) = \frac{1}{\sqrt{2(1+S)}} (\phi_1(r) + \phi_2(r)),$$

and

$$\psi_2(r) = \frac{1}{\sqrt{2(1-S)}}(\phi_1(r) - \phi_2(r)),$$

To derive the above equations we consider two linear combinations of the form:

$$\begin{aligned}\psi_1 &= C_1(\phi_1 + \phi_2) \\ \psi_2 &= C_2(\phi_1 - \phi_2)\end{aligned}$$

The coefficients C_1 and C_2 can be easily found by requiring that ψ_1 and ψ_2 are normalized. For ψ_1 we have:

$$\begin{aligned}\langle \psi_1 | \psi_1 \rangle &= |C_1|^2 \langle \phi_1 + \phi_2 | \phi_1 + \phi_2 \rangle = |C_1|^2 (2 + 2S) \\ &= 1\end{aligned}$$

from which it follows that $C_1 = \frac{1}{\sqrt{2(1+S)}}$. Similarly one obtains that $C_2 = \frac{1}{\sqrt{2(1-S)}}$.

Obviously ψ_1 transforms into itself by application of the inversion operator, i.e. $\hat{i}\psi_1 = +\psi_1$ and ψ_1 is of g symmetry. $\hat{i}\psi_2 = -\psi_2$ and ψ_2 is of u symmetry.

The above molecular orbitals are the eigenfunctions of the Hartree-Fock (HF) equations in a minimal basis. In fact the HF hamiltonian commutes with the symmetry operations of the point group of the hydrogen molecule (which includes the inversion symmetry). Since the two molecular orbitals have different parity, the corresponding matrix element of the Fock matrix, $\langle \psi_1 | \hat{f} | \psi_2 \rangle$ is identically zero. ψ_1 is the bonding orbital and is doubly occupied in the ground state of H_2 .

The HF orbital energies ϵ_1 and ϵ_2 for the two molecular orbitals ψ_1 and ψ_2 respectively, can be expressed in terms of the following quantities:

$$\begin{aligned}h_{11} &= \langle \psi_1 | \hat{h} | \psi_1 \rangle \\ h_{22} &= \langle \psi_2 | \hat{h} | \psi_2 \rangle \\ J_{11} &= \langle \psi_1 \psi_1 | \psi_1 \psi_1 \rangle \\ J_{22} &= \langle \psi_2 \psi_2 | \psi_2 \psi_2 \rangle \\ J_{12} &= \langle \psi_1 \psi_2 | \psi_1 \psi_2 \rangle \\ K_{12} &= \langle \psi_1 \psi_2 | \psi_2 \psi_1 \rangle\end{aligned}\tag{90}$$

Note that the molecular orbitals ψ_1 and ψ_2 are real. In order to derive the expressions for the orbital eigenvalues we note that the restricted Hartree-Fock operator can be written as:

$$\hat{f} = \hat{h} + \sum_{a=1}^{N/2} (2\hat{J}_a - \hat{K}_a)$$

where \hat{h} represent the kinetic energy operator and the electron-nuclei attraction, i.e. the core hamiltonian, while \hat{J}_a and \hat{K}_a are the coulomb and exchange operators. N is the number of electrons and a label the occupied states. For the hydrogen molecule we have $\frac{N}{2} = 1$. Therefore the Fock operator becomes:

$$\hat{f} = \hat{h} + (2\hat{J}_1 - \hat{K}_1)$$

where $\hat{J}_1 = \int \psi_1(\mathbf{r}_2)^* \frac{1}{r_{12}} \psi_1(\mathbf{r}_2) d\mathbf{r}_2$ and $\hat{K}_1 \psi_j(\mathbf{r}_1) = \int \psi_1(\mathbf{r}_2)^* \frac{1}{r_{12}} \psi_j(\mathbf{r}_2) d\mathbf{r}_2 \psi_1(\mathbf{r}_1)$ for the exchange operator. We have:

$$\begin{aligned}\epsilon_1 &= \langle \psi_1 | \hat{f} | \psi_1 \rangle = \langle \psi_1 | \hat{h} | \psi_1 \rangle + 2\langle \psi_1 | \hat{J}_1 | \psi_1 \rangle - \langle \psi_1 | \hat{K}_1 | \psi_1 \rangle \\ &= \int \psi_1(\mathbf{r}_1)^* \hat{h}(\mathbf{r}_1) \psi_1(\mathbf{r}_1) d\mathbf{r}_1 + 2 \int \int \psi_1(\mathbf{r}_1)^* \psi_1(\mathbf{r}_2)^* \frac{1}{r_{12}} \psi_1(\mathbf{r}_2) \psi_1(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad - \int \int \psi_1(\mathbf{r}_1)^* \psi_1(\mathbf{r}_2)^* \frac{1}{r_{12}} \psi_1(\mathbf{r}_2) \psi_1(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= h_{11} + J_{11}\end{aligned}$$

since the wave functions are real. For ϵ_2 we similarly obtain:

$$\epsilon_2 = \langle \psi_2 | \hat{f} | \psi_2 \rangle = \langle \psi_2 | \hat{h} | \psi_2 \rangle + 2 \langle \psi_2 | \hat{J}_1 | \psi_2 \rangle - \langle \psi_2 | \hat{K}_1 | \psi_2 \rangle = h_{11} + 2J_{12} - K_{12}.$$

Let us now consider the ground state Hartree-Fock solution and discuss its spin properties. Since ψ_1 is doubly occupied in the ground state, we have $|HF\rangle = |\psi_1\alpha\psi_1\beta\rangle$. Clearly $\hat{S}_z|HF\rangle = 0|HF\rangle$ and $M_S = 0$. In order to find if $|HF\rangle$ is an eigenstate of the spin operator \hat{S}^2 we make use of the identity $\hat{S}^2 = \hat{S}_+\hat{S}_- - \hat{S}_z + \hat{S}_z^2$ or equivalently $\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z + \hat{S}_z^2$. Recall that $\hat{S}_\pm = \sum_{i=1}^N \hat{s}_\pm(i)$ and that:

$$\begin{aligned}\hat{s}_+|\alpha\rangle &= 0 \\ \hat{s}_-|\alpha\rangle &= |\beta\rangle \\ \hat{s}_+|\beta\rangle &= |\alpha\rangle \\ \hat{s}_-|\beta\rangle &= 0\end{aligned}$$

We therefore have to evaluate the quantity:

$$\hat{S}^2|\psi_1\alpha\psi_1\beta\rangle = (\hat{S}_+\hat{S}_- - \hat{S}_z + \hat{S}_z^2)|\psi_1\alpha\psi_1\beta\rangle$$

and note that $\hat{S}_z|\psi_1\alpha\psi_1\beta\rangle = \hat{S}_z^2|\psi_1\alpha\psi_1\beta\rangle = 0$. By expanding the product $\hat{S}_+\hat{S}_-$ in terms of one-particle operators, $\hat{s}_\pm(i)$ with $i = 1, 2$ we obtain:

$$\begin{aligned}\hat{S}_+\hat{S}_-|\psi_1\alpha\psi_1\beta\rangle &= (\hat{s}_+(1) + \hat{s}_+(2))(\hat{s}_-(1) + \hat{s}_-(2))|\psi_1\alpha\psi_1\beta\rangle \\ &= (\hat{s}_+(1)\hat{s}_-(1) + \hat{s}_+(1)\hat{s}_-(2) + \hat{s}_+(2)\hat{s}_-(1) + \hat{s}_+(2)\hat{s}_-(2))|\psi_1\alpha\psi_1\beta\rangle \\ &= (|\psi_1\alpha\psi_1\beta\rangle + 0 + |\psi_1\beta\psi_1\alpha\rangle + 0) = 0\end{aligned}$$

due to the antisymmetric nature of the wave function. It then follows that $\hat{S}^2|HF\rangle = 0|HF\rangle$ and $S = 0$. This state is therefore a *singlet* state.

Finally, the ground state Hartree-Fock energy can be expressed in terms of the integrals written above. Denoting with $|HF\rangle$ the Hartree-Fock solution we have that $|HF\rangle = |\psi_1\alpha\psi_1\beta\rangle$:

$$\begin{aligned}E_{HF} &= \langle HF | \hat{H}_e | HF \rangle = \langle HF | \hat{h}_1 + \hat{h}_2 | HF \rangle + \langle HF | \frac{1}{r_{12}} | HF \rangle \\ &= h_{11} + h_{11} + \frac{1}{2} [\langle \psi_1\alpha\psi_1\alpha | \psi_1\alpha\psi_1\alpha \rangle \\ &\quad + \langle \psi_1\alpha\psi_1\beta | \psi_1\alpha\psi_1\beta \rangle + \langle \psi_1\beta\psi_1\alpha | \psi_1\beta\psi_1\alpha \rangle \\ &\quad + \langle \psi_1\beta\psi_1\beta | \psi_1\beta\psi_1\beta \rangle] \\ &= 2h_{11} + J_{11}\end{aligned}$$

after the integration over the spin variables and the definition of the $\langle ||| \rangle$ symbols in terms of coulomb and exchange integrals.