Chapter 7

The Hartree-Fock approximation

The Hartree method is useful as an introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent-field, but its importance is confined to the history of physics. In fact the Hartree method is not just approximate: it is wrong, by construction, since its wave function is not antisymmetric! A better approach, that correctly takes into account the antisymmetric character of the the wave functions is the Hartree-Fock approach. The price to pay is the presence in the equations of a non local, and thus more complex, exchange potential.

7.1 Hartree-Fock method

Let us re-consider the Hartree wave function. The simple product:

$$\psi(1, 2, \ldots, N) = \phi_1(1)\phi_2(2)\ldots\phi_N(N)$$  \hspace{1cm} (7.1)

does not satisfy the principle of indistinguishability, because it is not an eigenstate of permutation operators. It is however possible to build an antisymmetric solution by introducing the following Slater determinant:

$$\psi(1, \ldots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \ldots & \phi_1(N) \\ \vdots & \ddots & \vdots \\ \phi_N(1) & \ldots & \phi_N(N) \end{vmatrix}$$  \hspace{1cm} (7.2)

The exchange of two particles is equivalent to the exchange of two columns, which produces, due to a known property of determinants, a change of sign. Note that if two rows are equal, the determinant is zero: all $\phi_i$’s must be different. This demonstrates Pauli’s exclusion principle: two (or more) identical fermions cannot occupy the same state.

Note that the single-electron orbitals $\phi_i$ are assumed to be orthonormal:

$$\int \phi_i^*(1)\phi_j(1)dv_1 = \delta_{ij}$$  \hspace{1cm} (7.3)
where the “integral” on $dv_1$ means as usual “integration on coordinates, sum over spin components”. We follow the same path of Sec. (6.2) used to derive Hartree equations, Eq.(6.13). Since a determinant for $N$ electrons has $N!$ terms, we need a way to write matrix elements between determinants on a finite paper surface. The following property, valid for any (symmetric) operator $F$ and determinantal functions $\psi$ and $\psi'$, is very useful:

$$
\langle \psi | F | \psi' \rangle = \frac{1}{N!} \int \begin{vmatrix} \phi_1^*(1) & \phi_1^*(N) \\ \phi_N^*(1) & \phi_N^*(N) \end{vmatrix} \begin{vmatrix} \phi_1'(1) & \phi_1'(N) \\ \phi_N'(1) & \phi_N'(N) \end{vmatrix} dv_1 \ldots dv_N
$$

(by expanding the first determinant, one gets $N!$ terms that, once integrated, are identical). From the above property it is immediate (and boring) to obtain the matrix elements for one- and two-electron operators:

$$
\langle \psi | \sum_i f_i | \psi \rangle = \sum_i \int \phi_i^*(1) f_1 \phi_i(1) dv_1
$$

(as in the Hartree approximation), and

$$
\langle \psi | \sum_{ij} g_{ij} | \psi \rangle = \sum_{ij} \int \phi_i^*(1) \phi_j^*(2) g_{12} [\phi_i(1) \phi_j(2) - \phi_j(1) \phi_i(2)] dv_1 dv_2
$$

The integrals implicitly include summation over spin components. If we assume that $g_{12}$ depends only upon coordinates (as in Coulomb interaction) and not upon spins, the second term:

$$
\int \phi_i^*(1) \phi_j^*(2) g_{12} \phi_i(1) \phi_j(2) dv_1 dv_2
$$

is zero if $i$ and $j$ states are different (the spin parts are not affected by $g_{12}$ and they are orthogonal if relative to different spins).

The spin variable is hidden in the orbital index. It is convenient to make spin variables explicit. Eq.(7.6) can then be written as

$$
\langle \psi | \sum_{ij} g_{ij} | \psi \rangle = \sum_{ij} \int \phi_i^*(1) \phi_j^*(2) g_{12} [\phi_i(1) \phi_j(2) - \delta(\sigma_i, \sigma_j) \phi_i(1) \phi_j(2)] dv_1 dv_2
$$

where $\sigma_i$ is the spin of electron $i$, and:

$$
\delta(\sigma_i, \sigma_j) = \begin{cases} 
0 & \text{if } \sigma_i \neq \sigma_j \\
1 & \text{if } \sigma_i = \sigma_j
\end{cases}
$$

In summary:

$$
\langle \psi | H | \psi \rangle = \sum_i \int \phi_i^*(1) f_1 \phi_i(1) dv_1
$$

$$
+ \sum_{ij} \int \phi_i^*(1) \phi_j^*(2) g_{12} [\phi_i(1) \phi_j(2) - \delta(\sigma_i, \sigma_j) \phi_i(1) \phi_j(2)] dv_1 dv_2
$$
Now that we have the expectation value of the energy, we can apply the variational principle. In principle we must impose normalization constraints such that not only all $\phi_i$ stay normalized (as we did in the derivation of Hartree’s equation) but also all pairs $\phi_i, \phi_j$ with same spin are orthogonal, i.e., a (triangular) matrix $\epsilon_{ij}$ of Lagrange multipliers would be needed. It can be shown however (details e.g. on Slater’s book, *Quantum theory of matter*) that it is always possible to find a transformation to a solution in which the matrix of Lagrange multipliers is diagonal. We assume that we are dealing with such a case.

Let us omit the details of the derivation (similar to those of Sec. (6.2). We finally obtain the Hartree-Fock equations:

$$f_1 \phi_k(1) + \sum_j \int \phi_j^*(2) g_{12} [\phi_k(1) \phi_j(2) - \delta(\sigma_k, \sigma_j) \phi_j(1) \phi_k(2)] \, dv_2 = \epsilon_k \phi_k(1)$$  \hspace{1cm} (7.10)

or, in more explicit form,

$$- \frac{\hbar^2}{2m_e} \nabla^2 \phi_k(1) - \frac{Zq_e^2}{r_1} \phi_k(1) + \sum_j \int \phi_j^*(2) \frac{q^2}{r_{12}} [\phi_j(2) \phi_k(1)$$

$$- \delta(\sigma_k, \sigma_j) \phi_k(2) \phi_j(1)] \, dv_2 = \epsilon_k \phi_k(1)$$  \hspace{1cm} (7.11)

The energy of the system, Eq. 7.9, can be expressed, analogously to the Hartree case, via the sum of eigenvectors of Eq. (7.11), minus a term compensating the double counting of Coulomb repulsion and of the exchange energy:

$$E = \sum_k \epsilon_k - \sum_{<jk>} \int \phi_k^*(1) \phi_j^*(2) g_{12} [\phi_k(1) \phi_j(2) - \delta(\sigma_j, \sigma_k) \phi_j(1) \phi_k(2)] \, dv_1 dv_2.$$  \hspace{1cm} (7.12)

Eq. (7.11) has normally an infinite number of solutions, of which only the lowest-energy $N$ will be occupied by electrons, the rest playing the role of excited states. The sum over index $j$ runs only on occupied states.

Let us carefully observe the differences with respect to Hartree equations, Eqs. [6.13]:

1. for electrons in orbital $j$ having the same spin of orbital $k$, there is an additional exchange term;
2. $\sum_j$ also includes the case $j = k$.

### 7.1.1 Coulomb and exchange potentials

Let us analyze the physical meaning of the Hartree-Fock equations. We re-write them under the form

$$- \frac{\hbar^2}{2m_e} \nabla^2 \phi_k(1) - \frac{Zq_e^2}{r_1} \phi_k(1) + V_H(1) \phi_k(1) + (\hat{V}_x \phi_k)(1) = \epsilon_k \phi_k(1),$$  \hspace{1cm} (7.13)

where we have introduced a "Hartree potential" $V_H$ (it is not the same as in the Hartree equations!) and an "exchange potential" $V_x$. The Hartree potential is
the same for all orbitals:

\[ V_H(1) = \sum \int \phi_j^*(2) \frac{q_2^2}{r_{12}} \phi_j(2) dv_2 \equiv \int \rho(2) \frac{q_2^2}{r_{12}} dv_2, \quad (7.14) \]

where we have introduced the charge density

\[ \rho(2) = \sum \phi_j^*(2) \phi_j(2). \quad (7.15) \]

We can verify that \( \rho(1) \) is equal to the probability to find an electron in \( (1) \), that is,

\[ \rho(1) = N \int |\Psi(1, 2, \ldots, N)|^2 dv_2 \ldots dv_N. \quad (7.16) \]

The exchange term:

\[ (\hat{V}_x \phi_k)(1) = -\sum \delta(\sigma_k, \sigma_j) \int \phi_j(1) \phi_j^*(2) \frac{q_2^2}{r_{12}} \phi_k(2) dv_2 \quad (7.17) \]

does not have the simple form of the Hartree potential: \( V_H(1)\phi_k(1) \), where \( V_H(1) \) comes from an integration over variable 2. It has instead a form like

\[ (\hat{V}_x \phi_k)(1) \equiv \int V_x(1, 2) \phi_k(2)dv_2 \quad (7.18) \]

typical of a non local interaction.

Note that the “self-interaction” of an electron with itself, present in the Hartree potential, cancels out because it is present also in the exchange potential.

### 7.1.2 Correlation energy

The Hartree-Fock solution is not exact: it would be if the system under study were described by a wave function having the form of a Slater determinant. This is in general not true. The energy difference between the exact and Hartree-Fock solution is known as correlation energy. The origin of the name comes from the fact that the Hartree-Fock approximation misses part of the "electron correlation": the effects of an electron on all others. This is present in Hartree-Fock via the exchange and electrostatic interactions; more subtle effects are not accounted for, because they require a more general form of the wave function. For instance, the probability \( P(r_1, r_2) \) to find an electron at distance \( r_1 \) and one at distance \( r_2 \) from the origin is not simply equal to \( p(r_1)p(r_2) \), because electrons try to "avoid" each other. The correlation energy in the case of He atom is about 0.084 Ry: a small quantity relative to the energy (\( \sim 1.5\% \)), but not negligible.

An obvious way to improve upon the Hartree-Fock results consists in allowing contributions from other Slater determinants to the wave function. This is

\footnote{Feynman called it \textit{stupidity energy}, because the only physical quantity that it measures is our inability to find the exact solution!}
the essence of the “configuration interaction” (CI) method. Its practical application requires a sophisticated "technology" to choose among the enormous number of possible Slater determinants a subset of most significant ones. Such technique, computationally very heavy, is used in quantum chemistry to get high-precision results in small molecules. Other, less heavy methods (the so-called Møller-Plesset, MP, approaches) rely on perturbation theory to yield a rather good estimate of correlation energy. A completely different approach, which produces equations that are reminiscent of Hartree-Fock equations, is Density-Functional Theory (DFT), much used in condensed-matter physics.

7.1.3 The Helium atom

The solution of Hartree-Fock equations in atoms also commonly uses the central field approximation. This allows to factorize Eqs.\ref{eq:7.11} into a radial and an angular part, and to classify the solution with the ”traditional” quantum numbers \( n, \ell, m \).

For He, the Hartree-Fock equations, Eq.\ref{eq:7.11}, reduce to

\[
-\frac{\hbar^2}{2m_e} \nabla^2 \phi_1(1) - \frac{Zq_e^2}{r_1} \phi_1(1) + \int \phi_1^*(2) \frac{q_e^2}{r_{12}} [\phi_2(2)\phi_1(1) - \phi_1(2)\phi_1(1)] \, dv_2 \\
+ \int \phi_2^*(2) \frac{q_e^2}{r_{12}} [\phi_2(2)\phi_1(1) - \delta(\sigma_1, \sigma_2)\phi_1(2)\phi_2(1)] \, dv_2 = \epsilon_1 \phi_1(1) \tag{7.19}
\]

Since the integrand in the first integral is zero,

\[
-\frac{\hbar^2}{2m_e} \nabla^2 \phi_1(1) - \frac{Zq_e^2}{r_1} \phi_1(1) + \int \phi_2^*(2) \frac{q_e^2}{r_{12}} [\phi_2(2)\phi_1(1) - \delta(\sigma_1, \sigma_2)\phi_1(2)\phi_2(1)] \, dv_2 = \epsilon_1 \phi_1(1). \tag{7.20}
\]

In the ground state, the two electrons have opposite spin \( \delta(\sigma_1, \sigma_2) = 0 \) and occupy the same spherically symmetric orbital (that is: \( \phi_1 \) and \( \phi_2 \) are the same function, \( \phi \)). This means that the Hartree-Fock equation, Eq.\ref{eq:7.20}, for the ground state is the same as the Hartree equation, Eq.\ref{eq:6.19}. In fact, the two electrons have opposite spin and there is thus no exchange.

In general, one speaks of Restricted Hartree-Fock (RHF) for the frequent case in which all orbitals are present in pairs, formed by a same function of \( r \), multiplied by spin functions of opposite spin. In the following, this will always be the case.

7.2 Code: helium_hf_gauss

The radial solution of Hartree-Fock equations is possible only for atoms or in some model systems. In most cases the solution is found by expanding on a suitable basis set, in analogy with the variational method.

Let us re-write the Hartree-Fock equation – for the restricted case, i.e. no total spin – in the following form:

\[
\mathcal{F}\phi_k = \epsilon_k \phi_k, \quad k = 1, \ldots, N/2 \tag{7.21}
\]
The index $k$ labels the coordinate parts of the orbitals; for each $k$ there is a spin-up and a spin-down orbital. $\mathcal{F}$ is called the Fock operator. It is of course a non-local operator which depends upon the orbitals $\phi_k$. Let us look now for a solution under the form of an expansion on a basis of functions: $\phi_k(r) = \sum_{i=1}^{M} c_i^{(k)} b_i(r)$. We find the Rothaan-Hartree-Fock equations:

$$ Fc^{(k)} = \epsilon_k S c^{(k)} $$

(7.22)

where $c^{(k)} = (c_1^{(k)}, c_2^{(k)}, \ldots, c_M^{(k)})$ is the vector of the expansion coefficients, $S$ is the superposition matrix, $F$ is the matrix of the Fock operator on the basis set functions:

$$ F_{ij} = \langle b_i | \mathcal{F} | b_j \rangle, \quad S_{ij} = \langle b_i | b_j \rangle. $$

(7.23)

that after some algebra can be written as

$$ F_{ij} = f_{ij} + \sum_l \sum_m \left( 2 \sum_{k=1}^{N/2} c_{i}^{(k)*} c_{m}^{(k)} \right) \left( g_{ljm} - \frac{1}{2} g_{ijm} \right), $$

(7.24)

where, with the notations introduced in this chapter:

$$ f_{ij} = \int b_i^*(r_1) f_{1} b_j(r_1) d^3r_1, $$

(7.25)

$$ g_{ljm} = \int b_i^*(r_1) b_j(r_1) g_{12} b_l^*(r_2) b_m(r_2) d^3r_1 d^3r_2. $$

(7.26)

The sum over states between parentheses in Eq. (7.24) is called density matrix. The two terms in the second parentheses come respectively from the Hartree and the exchange potentials.

The problem of Eq. (7.22) is more complex than a normal secular problem solvable by diagonalization, since the Fock matrix, Eq. (7.24), depends upon its own eigenvectors. It is however possible to reconduct the solution to a self-consistent procedure, in which at each step a fixed matrix is diagonalized (or, for a non-orthonormal basis, a generalized diagonalization is performed at each step).

Code helium_hf_gauss.f90\(^2\) (or helium_hf_gauss.c\(^3\)) solves Hartree-Fock equations for the ground state of He atom, using a basis set of S Gaussians. The basic ingredients are the same as in code hydrogen_gauss (for the calculation of single-electron matrix elements and for matrix diagonalization). Moreover we need an expression for the $g_{ljm}$ matrix elements introduced in Eq. (7.26). Using the properties of products of Gaussians, Eq. (5.16), these can be written in terms of the integral

$$ I = \int e^{-ar_1^2} e^{-\beta r_2^2} \frac{1}{r_{12}} d^3r_1 d^3r_2. $$

(7.27)

Let us look for a variable change that makes $(r_1 - r_2)^2$ to appear in the exponent of the Gaussians:

$$ a r_1^2 + \beta r_2^2 = \gamma [(r_1 - r_2)^2 + (ar_1 + br_2)^2] $$

(7.28)

http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/F90/helium_hf_gauss.f90
http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/C/helium_hf_gauss.c
Let us now introduce a further variable change from \((r_1, r_2)\) to \((r, s)\), where

\[
\begin{align*}
    r &= r_1 - r_2, \\
    s &= \sqrt{\frac{\alpha}{\beta}} r_1 + \sqrt{\frac{\beta}{\alpha}} r_2;
\end{align*}
\]

(7.30)

The integral becomes

\[
I = \int e^{-\frac{\alpha \beta}{\alpha + \beta} \frac{1}{r} \left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2} \left(\frac{\alpha \beta}{\alpha + \beta}\right)^{3} |\frac{\partial (r_1, r_2)}{\partial (r, s)}| d^3r d^3s,
\]

where the Jacobian is easily calculated as the determinant of the transformation matrix, Eq.(7.30):

\[
|\frac{\partial (r_1, r_2)}{\partial (r, s)}| = \left(\frac{\sqrt{\alpha \beta}}{\alpha + \beta}\right)^{3}.
\]

(7.32)

The calculation of the integral is trivial and provides the required result:

\[
g_{iljm} = \frac{2\pi^{5/2} q_e^2}{\alpha \beta (\alpha + \beta)^{1/2}}
\]

(7.33)

where \(\alpha = \alpha_i + \alpha_j, \beta = \alpha_l + \alpha_m\).

The self-consistent procedure is even simpler than in code helium_hf_radial: at each step, the Fock matrix is re-calculated using the density matrix at the preceding step, with no special tricks or algorithms, until energy converges within a given numerical threshold.

### 7.2.1 Laboratory

- Observe how the ground-state energy changes as a function of the number of Gaussians and of their coefficients. You may take the energy given by helium_hf_radial as the reference. Start with the 3 or 4 Gaussian basis set used for Hydrogen, then the same set of Gaussians with rescaled coefficients, i.e. such that they fit a Slater 1s orbital for He\(^+\) \((Z = 2)\) and for a Hydrogen-like atom with \(Z = 1.6875\) (see Sect. C.2).

- Write to file the 1s orbital (borrow the relative code from hydrogen_gauss), plot it. Compare it with

  - the 1s Slater orbital for \(Z = 1, Z = 1.6875, Z = 2\), and
  - the 1s orbital from code helium_hf_radial.

Beware: there is a factor between the orbitals calculated with radial integration and with a Gaussian basis set: which factor and why?

- Try the following optimized basis set with four Gaussians, with coefficients:

  \[
  \alpha_1 = 0.297104, \alpha_2 = 1.236745, \alpha_3 = 5.749982, \alpha_4 = 38.216677 \text{ a.u.}
  \]