Chapter 6

Self-consistent Field

A way to solve a system of many electrons is to consider each electron under the electrostatic field generated by all other electrons. The many-body problem is thus reduced to the solution of single-electron Schrödinger equations under an effective potential. The latter is generated by the charge distribution of all other electrons in a self-consistent way. This idea is formalized in a rigorous way in the Hartree-Fock method and in Density-Functional theory. In the following we will see an historical approach of this kind: the Hartree method.

6.1 The Hartree Approximation

The idea of the Hartree method is to try to approximate the wave functions, solution of the Schrödinger equation for \( N \) electrons, as a product of single-electron wave functions, called atomic orbitals. As we have seen, the best possible approximation consists in applying the variational principle, by minimizing the expectation value of the energy \( E = \langle \psi | H | \psi \rangle \) for state \( | \psi \rangle \).

The Hamiltonian of an atom having a nucleus with charge \( Z \) and \( N \) electrons is

\[
H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i Z e_q^2 \frac{1}{r_i} + \sum_{\langle ij \rangle} e_q^2 \frac{1}{r_{ij}} \quad (6.1)
\]

where the sum is over pairs of electrons \( i \) and \( j \), i.e. each pair appears only once. Alternatively:

\[
\sum_{\langle ij \rangle} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \quad (6.2)
\]

It is convenient to introduce one-electron and two-electrons operators:

\[
f_i \equiv -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze_e^2}{r_i} \quad (6.3)
\]

\[
g_{ij} \equiv \frac{q^2}{r_{ij}} \quad (6.4)
\]

With such notation, the Hamiltonian is written as

\[
H = \sum_i f_i + \sum_{\langle ij \rangle} g_{ij} \quad (6.5)
\]
provided that \( g \) act symmetrically on the two electrons (definitely true for the Coulomb interaction).

### 6.2 Hartree Equations

Let us assume that the total wave function can be expressed as a product of single-electron orbitals (assumed to be orthonormal):

\[
\psi(1, 2, \ldots, N) = \phi_1(1)\phi_2(2)\ldots\phi_N(N) \quad (6.6)
\]

\[
\int \phi_i(1)\phi_j(1) \, dv_1 = \delta_{ij}. \quad (6.7)
\]

Variables 1, 2, ..., mean position and spin variables for electrons 1, 2, ...; \( \int \, dv_i \) means integration on coordinates and sum over spin components. Index \( i \) labels instead the quantum numbers used to classify a given single-electron orbital. All orbitals must be different: *Pauli’s exclusion principle* tells us that we cannot build a wave function for many electrons using twice the same single-electron orbital. In practice, orbitals for the case of atoms are classified using the main quantum number \( n \), orbital angular momentum \( \ell \) and its projection \( m \).

The expectation value of the energy is

\[
\langle \psi | H | \psi \rangle = \int \phi_1^*(1)\ldots\phi_N^*(N) \left[ \sum_i f_i + \sum_{(ij)} g_{ij} \right] \phi_1(1)\ldots\phi_N(N) \, dv_1\ldots dv_N
\]

\[
= \sum_i \int \phi_i^*(i) f_i \phi_i(i) \, dv_i + \sum_{(ij)} \int \phi_i^*(i)\phi_j^*(j) g_{ij} \phi_i(i)\phi_j(j) \, dv_i dv_j
\]

\[
= \sum_i \int \phi_i^*(1) f_1 \phi_i(1) \, dv_1 + \sum_{(ij)} \int \phi_i^*(1)\phi_j^*(2) g_{12} \phi_i(1)\phi_j(2) \, dv_1 dv_2
\]

\[
(6.8)
\]

In the first step, we made use of orthonormality \([6.7]\); in the second we just renamed dummy integration variables with the ”standard” choice 1 and 2.

Let us now apply the variational principle to formulation \((4.10)\), with the constraints that all integrals

\[
I_k = \int \phi_k^*(1)\phi_k(1) \, dv_1 \quad (6.9)
\]

are constant, i.e. the normalization of each orbital function is preserved:

\[
\delta \left( \langle \psi | H | \psi \rangle - \sum_k \epsilon_k I_k \right) = 0 \quad (6.10)
\]

where \( \epsilon_k \) are Lagrange multipliers, to be determined. Let us vary only the orbital function \( \phi_k \). We find

\[
\delta I_k = \int \delta \phi_k^*(1)\phi_k(1) \, dv_1 + \text{c.c.} \quad (6.11)
\]
(the variations of all other normalization integers will be zero) and, using the hermiticity of $H$ as in Sec.4.1.1,

$$
\delta \langle \psi | H | \psi \rangle = \int \delta \phi_k^\ast (1) f_1 \phi_k (1) \, dv_1 + c.c. + \sum_{j \neq k} \int \delta \phi_k^\ast (1) \phi_j^\ast (2) g_{12} \phi_k (1) \phi_j (2) \, dv_1 \, dv_2 + c.c. \quad (6.12)
$$

This result is obtained by noticing that the only involved terms of Eq. (6.8) are those with $i = k$ or $j = k$, and that each pair is counted only once. For instance, for 4 electrons the pairs are 12, 13, 14, 23, 24, 34; if I choose $k = 3$ the only contributions come from 13, 23, 34, i.e. $\sum_{j \neq k}$ (since $g$ is a symmetric operator, the order of indices in a pair is irrelevant).

Thus the variational principle takes the form

$$
\int \delta \phi_k^\ast (1) \left[ f_1 \phi_k (1) + \sum_{j \neq k} \int \phi_j^\ast (2) g_{12} \phi_k (1) \phi_j (2) \, dv_2 - \epsilon_k \phi_k (1) \right] \, dv_1 + c.c. = 0
$$

i.e. the term between square brackets (and its complex conjugate) must vanish so that the above equation is satisfied for any variation:

$$
f_1 \phi_k (1) + \sum_{j \neq k} \int \phi_j^\ast (2) g_{12} \phi_k (1) \phi_j (2) \, dv_2 = \epsilon_k \phi_k (1) \quad (6.13)
$$

These are the Hartree equations $(k = 1, \ldots, N)$. It is useful to write down explicitly the operators:

$$
- \frac{\hbar^2}{2m_e} \nabla_1^2 \phi_k (1) - \frac{Z q_e^2}{r_1} \phi_k (1) + \left[ \sum_{j \neq k} \int \phi_j^\ast (2) \frac{q_e^2}{r_{12}} \phi_j (2) \, dv_2 \right] \phi_k (1) = \epsilon_k \phi_k (1)
$$

(6.14)

We remark that each of them looks like a Schrödinger equation in which in addition to the Coulomb potential there is a Hartree potential:

$$
V_H (r_1) = \int \rho_2 (2) \frac{q_e^2}{r_{12}} \, dv_2
$$

(6.15)

where we have used

$$
\rho_2 (2) = \sum_{j \neq k} \phi_j^\ast (2) \phi_j (2)
$$

(6.16)

$\rho_j$ is the charge density due to all electrons differing from the one for which we are writing the equation.

### 6.2.1 Eigenvalues and Hartree energy

Let us multiply Hartree equation, Eq. (6.13), by $\phi_k^\ast (1)$, integrate and sum over orbitals: we obtain

$$
\sum_k \epsilon_k = \sum_k \int \phi_k^\ast (1) f_1 \phi_k (1) \, dv_1 + \sum_k \sum_{j \neq k} \int \phi_k^\ast (1) \phi_k (1) g_{12} \phi_j^\ast (2) \phi_j (2) \, dv_1 \, dv_2.
$$

(6.17)
Let us compare this expression with the energy for the many-electron system, Eq. 6.8. The Coulomb repulsion energy is counted twice, since each $< jk >$ pair is present twice in the sum. The energies thus given by the sum of eigenvalues of the Hartree equation, minus the Coulomb repulsive energy:

$$E = \sum_k \epsilon_k - \sum_{<jk>} \int \phi_k^*(1)\phi_k(1)g_{12}\phi_j^*(2)\phi_j(2)dv_1dv_2.$$

(6.18)

6.3 Self-consistent potential

Eq. 6.15 represents the electrostatic potential at point $\mathbf{r}_1$ generated by a charge distribution $\rho_k$. This fact clarifies the meaning of the Hartree approximation. Assuming that $\psi$ is factorizable into a product, we have formally assumed that the electrons are independent. This is of course not true at all: the electrons are strongly interacting particles. The approximation is however not so bad if the Coulomb repulsion between electrons is accounted for under the form of an average field $V_H$, containing the combined repulsion from all other electrons on the electron that we are considering. Such effect adds to the Coulomb attraction exerted by the nucleus, and partially screens it. The electrons behave as if they were independent, but under a potential $-Zq_e^2/e + V_H(\mathbf{r})$ instead of $-Zq_e^2/e$ of the nucleus alone.

$V_H(\mathbf{r})$ is however not a “true” potential, since its definition depends upon the charge density distributions of the electrons, that depend in turn upon the solutions of our equations. The potential is thus not known a priori, but it is a function of the solution. This type of equations is known as integro-differential equations.

The equations can be solved in an iterative way, after an initial guess of the orbitals is assumed. The procedure is as follows:

1. calculate the charge density (sum of the square modulus of the orbitals)
2. calculate the Hartree potential generated by such charge density (using classical electrostatics)
3. solve the equations to get new orbitals.

The solution of the equations can be found using the methods presented in Ch. 2. The electron density is built by filling the orbitals in order of increasing energy (following Pauli’s principle) until all electrons are “placed”.

In general, the final orbitals will differ from the starting ones. The procedure is then iterated – by using as new starting functions the final functions, or with more sophisticated methods – until the final and starting orbitals are the same (within some suitably defined numerical threshold). The resulting potential $V_H$ is then consistent with the orbitals that generate it, and it is for this reason called self-consistent field.

6.3.1 Self-consistent potential in atoms

For closed-shell atoms, a big simplification can be achieved: $V_H$ is a central field, i.e. it depends only on the distance $r_1$ between the electron and the
nucleus. Even in open-shell atoms, this can be imposed as an approximation, by spherically averaging $\rho_k$. The simplification is considerable, since we know \textit{a priori} that the orbitals will be factorized as in Eq. (2.9). The angular part is given by spherical harmonics, labelled with quantum numbers $\ell$ and $m$, while the radial part is characterized by quantum numbers $n$ and $\ell$. Of course the accidental degeneracy for different $\ell$ is no longer present. It turns out that even in open-shell atoms, this is an excellent approximation.

Let us consider the case of two-electron atoms. The Hartree equations, Eq. (6.14), for orbital $k = 1$ reduces to

$$-\frac{\hbar^2}{2m_e} \nabla^2 \phi_1(1) - \frac{Zq_e^2}{r_1} \phi_1(1) + \left[ \int \phi_2^*(2) \frac{q_e^2}{r_{12}} \phi_2(2) \, dr_2 \right] \phi_1(1) = \epsilon_1 \phi_1(1) \quad (6.19)$$

For the ground state of He, we can assume that $\phi_1$ and $\phi_2$ have the same spherically symmetric coordinate part, $\phi(r)$, and opposite spins: $\phi_1 = \phi(r)v_+(\sigma)$, $\phi_2 = \phi(r)v_-(\sigma)$. Eq. (6.19) further simplifies to:

$$-\frac{\hbar^2}{2m_e} \nabla^2 \phi(r_1) - \frac{Zq_e^2}{r_1} \phi(r_1) + \left[ \int \frac{q_e^2}{r_{12}} |\phi(r_2)|^2 \, dr_2 \right] \phi(r_1) = \epsilon \phi(r_1) \quad (6.20)$$

### 6.4 Code: helium\_hf\_radial

Code helium\_hf\_radial.f90 (or helium\_hf\_radial.c) solves Hartree equations for the ground state of He atom. helium\_hf\_radial is based on code hydrogen\_radial and uses the same integration algorithm based on Numerov’s method. The new part is the implementation of the method of self-consistent field for finding the orbitals.

The calculation consists in solving the radial part of the Hartree equation (6.20). The effective potential $V_{\text{scf}}$ is the sum of the Coulomb potential of the nucleus, plus the (spherically symmetric) Hartree potential

$$V_{\text{scf}}(r) = -\frac{Zq_e^2}{r} + V_H(r), \quad V_H(r_1) = q_e^2 \int \frac{\rho(r_2)}{r_{12}} \, dr_2. \quad (6.21)$$

We start from an initial estimate for $V_H(r)$, calculated in routine init\_pot ( $V_H^{(0)}(r) = 0$, simply). With the ground state $R(r)$ obtained from such potential, we calculate in routine rho\_of\_r the charge density $\rho(r) = |R(r)|^2/4\pi$ (note that $\rho$ is here only the contribution of the other orbital, so half the total charge, and remember the presence of the angular part!). Routine v\_of\_rho re-calculates the new Hartree potential $V_H^{\text{out}}(r)$ by integration, using the Gauss theorem:

$$V_H^{\text{out}}(r) = V_0 + q_e^2 \int_{r_{\text{max}}}^r \frac{Q(s)}{s^2} ds, \quad Q(s) = \int_{r<s} \rho(r) 4\pi r^2 \, dr \quad (6.22)$$

where $Q(s)$ is the charge contained in the sphere of radius $s$; $r_{\text{max}}$ is the outermost grid point, such that the potential has already assumed the asymptotic value $V_0 = q_e^2/r_{\text{max}}$, valid at large $r$. 

1. [http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/F90/helium\_hf\_radial.f90](http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/F90/helium\_hf\_radial.f90)
2. [http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/C/helium\_hf\_radial.c](http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/C/helium\_hf\_radial.c)
The Hartree potential is then re-introduced in the calculation not directly but as a linear combination of the old and the new potential. This is the simplest technique to ensure that the self-consistent procedure converges. It is not needed in this case, but in most cases it is: there is no guarantee that re-inserting the new potential in input will lead to convergence. We can write

\[ V_{H}^{in,new}(r) = \beta V_{H}^{out}(r) + (1 - \beta)V_{H}^{in}(r), \]  

(6.23)

where \(0 < \beta \leq 1\). The procedure is iterated (repeated) until convergence is achieved. The latter is verified on the “variational correction” described below, but other choices are possible (e.g. the norm – the square root of the integral of the square – of \(V_{H}^{out}(r) - V_{H}^{in}(r)\)).

In output the code prints the eigenvalue \(\epsilon_1\) of Eq.6.13 plus various terms of the energy, with rather obvious meaning except the term Variational correction. This is

\[ \delta E = \int (V_{H}^{in}(r) - V_{H}^{out}(r))\rho(r)d^3r \]  

(6.24)

and it is useful to correct the value of the energy obtained by summing the eigenvalues as in Eq.(6.18), so that it is the same as the one obtained using Eq.(6.8), where eigenvalues are not used. The two values of the energy are printed side by side. Also noticeable is the "virial check": for a Coulomb potential, the virial theorem states that \(\langle T \rangle = -\langle V \rangle / 2\), where the two terms are respectively the average values of the kinetic and the potential energy. It can be demonstrated that the Hartree-Fock solution obeys the virial theorem.

6.4.1 Laboratory

- Observe the behavior of self-consistency, verify that the energy (but not the single terms of it!) decreases monotonically.

- Compare the energy obtained with this and with other methods: perturbation theory with hydrogen-like wave functions (\(E = -5.5\) Ry, Sect. C.1), variational theory with effective \(Z\) (\(E = -5.695\) Ry, Sect. C.2), best numerical Hartree(-Fock) result (\(E = -5.72336\) Ry, as found in the literature), experimental result (\(E = -5.8074\) Ry).

- Make a plot of orbitals (file wfc.out) for different \(n\) and \(\ell\). Note that the orbitals and the corresponding eigenvalues become more and more hydrogen-like for higher \(n\). Can you explain why?

- If you do not know how to answer the previous question: make a plot of \(V_{scf}\) (file pot.out) and compare its behavior with that of the \(-Zq^2/r\) term. What do you notice?

- Plot the 1s orbital together with those calculated by hydrogen_radial for Hydrogen (\(Z = 1\)), He\(^+\) (\(Z = 2\)), and for a \(Z = 1.6875\). See Sect. C.2 if you cannot make sense of the results.

\(^3\)Eigenvalues are calculated using the input potential; the other terms are calculated using output potential