## §6. Hartree-Fock method

We more or less know how to describe the motion on nuclei (in the harmonic approximation). But what about the electron subsystem?

The adiabatic approximation make possible to reduce the complicated problem of behavior of an electron-nuclei system to the problem of electron motion in the field of static nuclei and motion of nuclei in average field of all electrons. However in this case the problem of the motion of all electrons remains extremely complicated and require for its solution some or other approximate methods. Unfortunately the all-electrons wave function depends on the position of each electron in crystal (this number is very big and equal around 10<sup>23</sup>). Thus, for electrons we have a very complex many-particle problem which include complicated correlation effects. Methods are needed to simplify the solution of the problem for electrons.

The first simplification in to present the complex multi-electron wave function of all electrons (in this case we consider the electrons as united quantum system) as a combination of wave functions for single electron (one-electron approximation). We consider the electron subsystem as combination of single, independent electrons. But in this case, we need to take into account in the calculations the so-called correlation many-particle effects or simply correlations. The calculation for that correlations is very difficult and nontrivial task.

As always we have to start from Schrodinger equation for electron subsystem:

here:

$$T_e \cdot \varphi + (V_{en} + V_{ee}) \varphi = E \cdot \varphi$$

 $\hat{T}_{e}$ -kinetic energy operator for all electrons  $V_{en}$ -potential energy for electrostatic interaction of electrons and nuclei  $\hat{V}_{ee}$ -potential energy for electrostatic interaction of electrons

or expanded option of (1):

$$-\frac{\hbar^{2}}{2m}\sum_{i}\hat{\Delta}_{i}\cdot\varphi+V_{en}(r_{i})\cdot\varphi+\left(\frac{e^{2}}{2}\sum_{i,j}\frac{1}{r_{i,j}}\right)\cdot\varphi=E\cdot\varphi$$

$$V_{en}=\frac{e^{2}}{2}\sum_{i,n}\frac{Z_{n}}{r_{i,n}}$$
(2)

(1)

here:

In the framework of adiabatic approximation the nuclei are static. It means that in (2) in vector  $r_{i,J} = r_i - r_J$  the term  $r_J$  describing the position of nucleus with number J , must be fixed.

The Hamilton operator for equation (2) we can rewrite by follows:

$$\hat{H} = \sum_{i} \hat{H}_{i} + \frac{e^{2}}{2} \sum_{i,j} \frac{1}{r_{i,j}}$$
(3)

here:

 $\hat{H}_{i} = -\frac{\hbar^{2}}{2m} \hat{\Delta}_{i} + V_{en}(r_{i,n}) \quad \text{this Hamiltonian is depend only on position of electron with}$ number **i** (Individual Hamiltonian for i-th electron). (4)

This Hamiltonian

$$\hat{H} = \sum_{i} \hat{H}_{i} + \frac{e^{2}}{2} \sum_{i,j} \frac{1}{r_{i,j}}$$
(5)

is still describes the many-particle problem, but our goal is to present it as follow:

$$\hat{H} = \sum_{i} \hat{H}'_{i} \tag{6}$$

here:

$$\hat{H}'_{i} = -\frac{\hbar}{2m} \hat{\Delta}_{i} + V_{en}(r_{i}) + U_{eff}(r_{i})$$

We want to replace the many-body electron problem (3,5) into the one-electron problem (6). Each electron here is moving in the **field of fixed nuclei** and **average field of all other electrons**.  $U_{eff}(\mathbf{r}_i)$  describe the averaged action of all electrons on the specified electron with number i. And now we need to find the method to calculate this effective average potential energy.

But there are some problems associated with this transition. Considering a system of many particles as a set of independent particles leads to the loss of some important effects associated with many particles such as multi-particle correlation effects. This means that for real calculations we must add some additional terms to the one-particle Hamiltonian includes correlation effects:

$$\hat{H}'_{i} = -\frac{\hbar}{2m} \hat{\Delta}_{i} + V_{en}(r_{i}) + U_{eff}(r_{i}) + U_{corr}$$
<sup>(7)</sup>

The corresponds method (6) have the name Hartree-Fock method.

Now let's make an additional simplification used in the Hartree-Fock method:

1. we try to calculate electrons properties for ground state. It means that the number of different states is two times less that the number of electrons (Pauli exclusion principle must be applied).

2. it is often difficult or simply impossible to specify or describe the exact wave function for an nelectron system (this function must satisfy the Pauli exclusion principle by default). This problem can be solved by representing the many-electron function as a Slater determinant composed of one-electron wave functions :

$$\Psi(r_{1},r_{2},...,r_{N}) = \frac{1}{\sqrt{N}} \begin{vmatrix} \varphi_{1}(r_{1}) & \varphi_{1}(r_{2}) & \dots & \varphi_{1}(r_{N}) \\ \varphi_{2}(r_{1}) & \varphi_{2}(r_{2}) & \dots & \varphi_{2}(r_{N}) \\ \dots & \dots & \dots & \dots \\ \varphi_{N}(r_{1}) & \varphi_{N}(r_{2}) & \dots & \varphi_{N}(r_{N}) \end{vmatrix}$$

 $\varphi_i(k)$  - wave function for electron with number **k** located at the state with number **i**.

To simplify further consideration, we assume that system have only **two** electrons distributed over two states. At the beginning, we ignore the electron spin. It means that the number of occupied states is equal to number of electrons and equal to 2. As we will see later, these calculations will be extended to any number of electrons.

The wave function of this system (according with the Pauli exclusion principle) is looks like this:

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(r_1) & \varphi_1(r_2) \\ \varphi_2(r_1) & \varphi_2(r_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) \\ \varphi_2(1) & \varphi_2(2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\varphi_1(1) \cdot \varphi_2(2) - \varphi_2(1) \cdot \varphi_1(2))$$
(8)

- first electron
- **O** second electron

ф

1

1

2

1 2 Ψ(1,2)=0

 $\Psi(1,2)=\phi_1(1)\phi_2(2)$ 

 $\begin{array}{l} \mbox{This representation guarantees the antisymmetry of the} \\ \mbox{wave function and the impossibility of simultaneously} \\ \mbox{total wave function } \Psi(r_1,r_2) \mbox{location of two electrons in the same state.} \end{array}$ 

The total energy of ground state of the  $\Psi(1,2)=0$  system of two electrons calculate so:

$$E = \frac{\int \Psi^* \hat{H} \Psi \, dv_1 \, dv_2}{\int \Psi^* \Psi \, dv_1 \, dv_2} \tag{9}$$

If we assume that the one-electron functions are orthonormal:

$$\Psi(1,2) = -\varphi_1(2)\varphi_2(1) \qquad \qquad \int \varphi_i^* \varphi_k \, d\nu = \delta_{ik} \tag{10}$$

For upper expression we have:

$$E = \int \Psi^* \hat{H} \Psi \, dv_1 dv_2 \tag{11}$$

The Hamiltonian for our system of two electrons in ground state is looks like so:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + e^2 \int \Psi^* \frac{1}{r_{1,2}} \Psi \, dv_1 \, dv_2 \tag{12}$$

The individual Hamiltonians  $\hat{H}_1$  and  $\hat{H}_2$  can be written as follows:

$$\hat{H}_{1} = -\frac{\hbar^{2}}{2m} \Delta_{1} + V_{en}(1)$$

$$\hat{H}_{2} = -\frac{\hbar^{2}}{2m} \Delta_{2} + V_{en}(2)$$
(13)

$$E = \int \Psi^* \hat{H} \Psi \, dv_1 dv_2 = \int \Psi^* \hat{H}_1 \Psi \, dv_1 dv_2 + \int \Psi^* \hat{H}_2 \Psi \, dv_1 dv_2 + \int \Psi^* \frac{e^2}{r_{12}} \Psi \, dv_1 dv_2$$
(14)

The total multiparticle wave function we take from (8). The integrals in (14) can be calculated separately. III

$$\int \Psi^{*} \hat{H}_{1} \Psi dv_{1} dv_{2} = \frac{1}{2} \int (\varphi_{1}^{*}(1) \varphi_{2}^{*}(2) - \varphi_{2}^{*}(1) \varphi_{1}^{*}(2)) \hat{H}_{1}(\varphi_{1}(1) \varphi_{2}(2) - \varphi_{2}(1) \varphi_{1}(2)) dv_{1} dv_{2}$$
(15)

After opening brackets we will obtain 4 integrals:

I) 
$$\frac{1}{2}\int \varphi_1^*(1)\varphi_2^*(2)\hat{H}_1\varphi_1(1)\varphi_2(2)dv_1dv_2 = \frac{1}{2}\int \varphi_1^*(1)\hat{H}_1\varphi_1(1)dv_1$$

II) 
$$\frac{1}{2}\int \varphi_2^*(1)\varphi_1^*(2)\hat{H}_1\varphi_2(1)\varphi_1(2)dv_1dv_2 = \frac{1}{2}\int \varphi_2^*(1)\hat{H}_1\varphi_2(1)dv_1dv_2$$

III) 
$$\frac{1}{2}\int \varphi_2^*(1)\varphi_1^*(2)\hat{H}_1\varphi_1(1)\varphi_2(2)dv_1dv_2 = \frac{1}{2}\int \varphi_2^*(1)\hat{H}_1\varphi_1(1)dv_1\int \varphi_1^*(2)\varphi_2(2)dv_2 = 0$$

IV) 
$$\frac{1}{2}\int \varphi_1^*(1)\varphi_2^*(2)\hat{H}_1\varphi_2(1)\varphi_1(2)dv_1dv_2 = \frac{1}{2}\int \varphi_1^*(1)\hat{H}_1\varphi_2(1)dv_1\int \varphi_2^*(2)\varphi_1(2)dv_2 = 0$$

After combination upper integrals the final results is:

$$\int \Psi^* \hat{H}_1 \Psi dv_1 dv_2 = \frac{1}{2} \sum_{i=1}^2 \int \varphi_i^*(1) \hat{H}_1 \varphi_i(1) dv_1$$
(16)

The second integral in (14) can be calculated by same way:

$$\int \Psi^* \hat{H}_2 \Psi \, dv_1 \, dv_2 = \frac{1}{2} \sum_{i=1}^2 \int \varphi_i^*(2) \hat{H}_2 \, \varphi_i(2) \, dv_1 \tag{17}$$

The sum of two first integrals gives:

$$\int \Psi^* \hat{H}_1 \Psi \, dv_1 \, dv_2 + \int \Psi^* \hat{H}_2 \Psi \, dv_1 \, dv_2 = \frac{1}{2} \sum_{i=1}^2 \int \varphi_i^*(1) \hat{H}_1 \varphi_i(1) \, dv_1 + \frac{1}{2} \sum_{i=1}^2 \int \varphi_i^*(2) \hat{H}_2 \varphi_i(2) \, dv_2 \qquad (18)$$

The last two integrals (18) differ only in the integration parameter. In both integrals, one must integrate over the entire volume of the crystal. This means that the integrals are equal, and the final result looks like this:

$$\int \Psi^* \hat{H}_1 \Psi \, dv_1 \, dv_2 + \int \Psi^* \hat{H}_2 \Psi \, dv_1 \, dv_2 = \sum_{i=1}^2 \int \varphi_i^*(1) \, \hat{H}_1 \, \varphi_i(1) \, dv_1 \tag{19}$$

Now we need to calculate the coulomb contribution to the total energy:

$$e^{2}\int\Psi^{*}\frac{1}{r_{12}}\Psi dv_{1}dv_{2} = \frac{e^{2}}{2}\int(\varphi_{1}^{*}(1)\varphi_{2}^{*}(2) - \varphi_{2}^{*}(1)\varphi_{1}^{*}(2))\frac{1}{r_{12}}(\varphi_{1}(1)\varphi_{2}(2) - \varphi_{2}(1)\varphi_{1}(2))dv_{1}dv_{2} \qquad (20)$$

$$IV$$

This integral can be calculated in the same way, separately:

I) 
$$\frac{1}{2}\int \varphi_{1}^{*}(1)\varphi_{2}^{*}(2)\frac{1}{r_{12}}\varphi_{1}(1)\varphi_{2}(2)dv_{1}dv_{2} = \frac{1}{2}\int |\varphi_{1}^{*}(1)|^{2}\frac{1}{r_{12}}|\varphi_{2}(2)|^{2}dv_{1}dv_{2}$$
II) 
$$\frac{1}{2}\int \varphi_{2}^{*}(1)\varphi_{1}^{*}(2)\frac{1}{r_{12}}\varphi_{2}(1)\varphi_{1}(2)dv_{1}dv_{2} = \frac{1}{2}\int |\varphi_{2}^{*}(1)|^{2}\frac{1}{r_{12}}|\varphi_{1}(2)|^{2}dv_{1}dv_{2}$$
III) 
$$-\frac{1}{2}\int \varphi_{2}^{*}(1)\varphi_{1}^{*}(2)\hat{H}_{1}\varphi_{1}(1)\varphi_{2}(2)dv_{1}dv_{2}$$
(21)

IV) 
$$-\frac{1}{2}\int \varphi_1^*(1)\varphi_2^*(2)\hat{H}_1\varphi_2(1)\varphi_1(2)dv_1dv_2$$

Integral (I) gives the potential energy of the Coulomb interaction for the first electron in the first state with the second electron in the second state.

Integral (II) is a Coulomb interaction for the first electron in the second state with the second electron in the first state.

Integrals II and IV have no classical analog, they are purely quantum terms. They describe the interaction of electrons in mixed states. The corresponding interaction is a so called exchange energy. After combination (19) and (21) for total energy of two-electron system in ground state we have :

$$E = \sum_{i=1}^{2} \int \varphi_{i}^{*}(1) \hat{H}_{1} \varphi_{i}(1) dv_{1} + \frac{e^{2}}{2} \sum_{(i \neq j)=1}^{2} \int |\varphi_{i}^{*}(1)|^{2} \frac{1}{r_{12}} |\varphi_{j}(2)|^{2} dv_{1} dv_{2}$$

$$-\frac{e^{2}}{2} \sum_{(i \neq j)=1}^{2} \int \varphi_{i}^{*}(1) \varphi_{j}(1) \frac{1}{r_{12}} \varphi_{i}(2) \varphi_{j}^{*}(2) dv_{1} dv_{2}$$
(22)

The summation is over the occupied states. Important to understand that (22) is not an sum of energies for noninteracting electrons, because wave functions  $\phi_i$  are not an eigenfunctions of one-electron hamiltonian (13) H<sub>i</sub>.

Now we have two questions about calculation of functions  $\phi_i$  and effective potential energy  $U_{eff}$  describing the average field created by all other electrons (exclude the electron with number i). The (22) can be considered as a functional of energy with respect to wave function. A small variation in the wave function  $\phi_i \rightarrow \phi_i + \delta \phi_i$  leads to a small variation in the total energy  $\delta E$ .

Orthonormal property of varied functions  $\phi_i + \delta \phi_i$  (with taken into account (10)) is looks like so:

$$\int \varphi_i^* (\varphi_k + \delta \varphi_k) dv = \delta_{ik}$$

$$\int \varphi_i^* \delta \varphi_k dv = 0, \text{ for any combination of i and k}$$
(23)

Using variational principles and the fact that we are looking for the energy for the ground state (minimum energy) and the corresponding wave function in that state, the final equation for calculating  $\phi_i$  and E is looks like so:

$$\left[\hat{H}_{1} + \sum_{j \neq i} \int \frac{e^{2} |\varphi_{j}(2)|^{2}}{r_{12}} dv_{2} - \sum_{j \neq i} \frac{\varphi_{j}(1)}{\varphi_{i}(1)} \int \frac{e^{2} \varphi_{i}(2) \varphi_{j}^{*}(2)}{r_{12}} dv_{2} \right] \varphi_{i}(1) = E_{i} \varphi_{i}(1)$$
(24)

The mathematical details of calculations you can find in textbook "A. Anselm, "Introduction to the theory of semiconductors".

The comparison (24) with (6) give the expression for calculating the effective potential energy for one-electron task:

$$U_{eff}(1) = \sum_{j \neq i} \int \frac{e^2 |\varphi_j(2)|^2}{r_{12}} dv_2 - \sum_{j \neq i} \frac{\varphi_j(1)}{\varphi_i(1)} \int \frac{e^2 \varphi_i(2) \varphi_j^*(2)}{r_{12}} dv_2$$
(25)

The equations (24) is a Hartree-Fock self-consistent field equations. Since (25) itself depends on wave functions  $\phi_i$ , the equation (24) is a system of integro-differential equations.

The solution of this problem can be presented as follows:

I. Let's start with a zero approximation for wave functions.

II. The next step is to calculate  $U_{eff}$  (25) at the same level of approximation.

III. After that, solution (24) gives the new wave function in the first-level approximation.

IV. Substituting these new functions into (25), we can calculate the effective potential of the next level of approximation, etc.

Now we must go to step III again.

The circle of self-consistent computations can be interrupted if the total energy stops changing (or will be less than some little number). In this case, we assume that we have a wave function and energy for the ground state of the electron system in Hartree-Fock approximation.

It should be noted that although this method is implemented in many so-called abinitio computer programs, the process is not really that simple. The name abinitio means that at the beginning of the calculation we have to determine only the initial positions and types of atoms. This should be enough to calculate any physical property of any material.

This method can be used to search for new stable materials and to calculate their physical properties (without experiment). But we cannot start the calculation from random initial positions of atoms in the crystal lattice. For unstable structures, the self-consistent calculation by the Hartree-Fock method loses stability and diverges, the calculated energy tends to infinity. Of course, a stable initial structure can be determined experimentally if it is known. But to search for completely new stable materials with before unknown physical properties, you need to use the following packages: https://uspex-team.org

Another disadvantage of this method is that it requires large computer resources. Therefore, another approach (DFT, despite its imprecision) is often used for preliminary calculations.

PS! In the Hartree-Fock method, we have non-interacting electrons moving in the field of stationary nuclei and in the meanfield (25) created by all other electrons. The meanfield consist from classical Coulomb potential and non-local exchange potential.