

#### **§4. Adiabatic approximation**

The general non relativistic Schrödinger equation describing the properties of any substance is as follows:

$$\hat{H} \cdot \Psi = E \cdot \Psi \quad (1)$$

The wavefunction  $\Psi(r, R)$  depend on coordinates of all electrons (r) and nuclei (R).  $\hat{H}$  - the Hamilton operator can be written in the following form:

$$\hat{H} = \hat{T}_e + \hat{T}_N + V_{ee} + V_{eN} + V_{NN} \quad (2)$$

here:

$$\hat{T}_e = -\frac{\hbar^2}{2 \cdot m} \sum_i \Delta_i \quad \text{-kinetic energy operator for all electrons in crystal,} \quad (3)$$

$$\hat{T}_N = -\frac{\hbar^2}{2} \sum_n \frac{\Delta_n}{M_n} \quad (4)\text{-kinetic energy operator for all nuclei,} \quad (4)$$

$$V_{ee} = \frac{e^2}{4 \pi \epsilon_0} \sum_{i,j} \frac{1}{r_{i,j}} \quad (5)\text{- potential energy for interacting electrons,} \quad (5)$$

$$V_{NN} = \frac{e^2}{4 \pi \epsilon_0} \sum_{n,m} \frac{Z_n Z_m}{R_{n,m}} \quad (6)\text{-potential energy for interacting nuclei} \quad (6)$$

$$V_{eN} = \frac{e^2}{4 \pi \epsilon_0} \sum_{i,J} \frac{Z_J}{R_{i,J}} \quad (7)\text{-potential energy describing the interaction of electrons and} \quad (7)$$

nuclei.

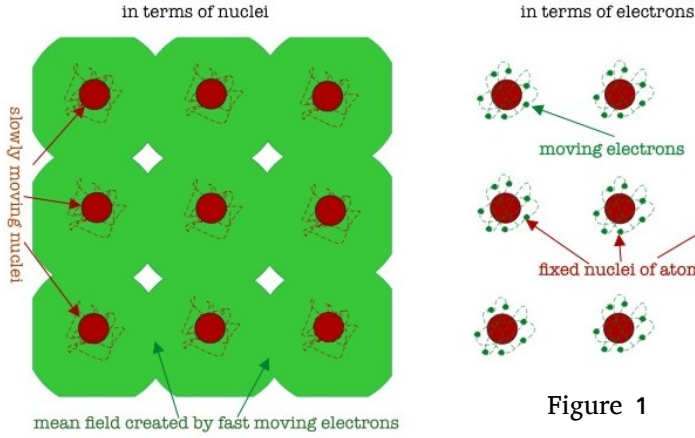
The total number of parameters of total wavefunction is quite large and equal to total number for electrons and nuclei in crystal multiplied to 3 (for 3-dimensional space) and could be represented as follows:

$$\Psi(\vec{r}, \vec{R}) = \Psi(x_1, x_2, \dots, x_{N_e}, y_1, y_2, \dots, y_{N_e}, z_1, z_2, \dots, z_{N_e}, X_1, X_2, \dots, X_{N_n}, Y_1, Y_2, \dots, Y_{N_n}, Z_1, Z_2, \dots, Z_{N_n}) \quad (8)$$

here  $x_i, y_i, z_i$ -coordinates of electrons and  $X_i, Y_i, Z_i$  – coordinates of nuclei. Total number of arguments is proportional to Avogadro number, around  $10^{23}$ . This means that the general Schrödinger equation is impossible not only to solve, but even to write down. We can try to simplify this equation making use of the fact that electrons masses is much less than the mass of nuclear masses. This means that the speed of motion of electrons is much greater than the velocity of nuclei, and we can use the approximation in which electrons move in the field of practically stationary atoms. In this case the motion of electrons and nuclei can be considered separately. By other words, we have two subsystems in a crystal. The mobile electrons and very slow nuclei (see Figure 1).

From the point of view of quantum mechanics the total wave function could be written as follows (separation of motion of electrons and nuclei):

$$\Psi(\vec{r}, \vec{R}) = \psi(\vec{R}) \cdot \varphi(\vec{r}, \vec{R}) \quad (9)$$



$\psi(\vec{R})$  -part of the total wave function describing the properties of practically immobile nuclei. As you can see, this wave function depends only on the coordinates of the nuclei and does not depend on the coordinates of the electrons. This fact can be interpreted as the motion of nuclei in the **mean field** created by all very fast moving electrons.

$\varphi(\vec{r}, \vec{R})$  - The electronic part of the total wave function should depend on the coordinates of electrons and nuclei. For electrons, the nuclei are stationary, but the nature of the motion of the electrons depends on the position (coordinates) of the stationary nuclei.

Now we need to calculate the derivative of total wavefunction with respect to coordinates of nuclei and electrons, see the equations 3 and 4.

$$\Delta_i \Psi(r, R) = \Delta_i (\varphi(r, R) \cdot \psi(R)) = \psi(R) \Delta_i \varphi(r, R) \quad (10)$$

$$\Delta_n \Psi(r, R) = \nabla_n \nabla_n (\varphi(r, R) \psi(R)) = \varphi(r, R) \cdot \Delta_n \psi(R) + 2 \cdot \nabla_n \varphi(r, R) \cdot \nabla_n \psi(R) + \psi(R) \cdot \Delta_n \varphi(r, R) \quad (11)$$

after substitution to (1) we have:

$$\begin{aligned} \psi(R) \cdot \hat{T}_e \cdot \varphi(r, R) - \frac{\hbar^2}{2} \sum_n \frac{1}{M_n} (\varphi(r, R) \cdot \Delta_n \psi(R) + 2 \cdot \nabla_n \varphi(r, R) \cdot \nabla_n \psi(R) + \psi(R) \cdot \Delta_n \varphi(r, R)) + \\ + V_{ee} \cdot \varphi(r, R) \psi(R) + V_{NN} \cdot \varphi(r, R) \psi(R) + V_{eN} \cdot \varphi(r, R) \psi(R) = E \cdot \varphi(r, R) \psi(R) \end{aligned} \quad (12)$$

And after reordering of members in equation (12):

$$\begin{aligned} \psi(R) \cdot \hat{T}_e \cdot \varphi(r, R) + V_{ee} \cdot \varphi(r, R) \psi(R) + V_{eN} \cdot \varphi(r, R) \psi(R) - \frac{\hbar^2}{2} \sum_n \frac{1}{M_n} [ \varphi(r, R) \cdot \Delta_n \psi(R) + \\ + 2 \cdot \nabla_n \varphi(r, R) \cdot \nabla_n \psi(R) + \psi(R) \cdot \Delta_n \varphi(r, R) ] + V_{NN} \cdot \varphi(r, R) \psi(R) = E \cdot \varphi(r, R) \psi(R) \end{aligned} \quad (13)$$

Equation (13) can now be split into two equations. The first of them describes the properties of electrons in the field of stationary nuclei and second- the properties of nuclei in the average field created by all electrons. As you can see, the total energy of electrons plays the role of potential energy for nuclei (together with the pairwise interaction of nuclei with each other  $V_{NN}$ ):

$$\begin{aligned} \psi(R) \cdot \hat{T}_e \cdot \varphi(r, R) + V_{ee} \cdot \varphi(r, R) \psi(R) + V_{eN} \cdot \varphi(r, R) \psi(R) = \epsilon(R) \cdot \varphi(r, R) \psi(R), \\ \text{and} \\ \frac{\hbar^2}{2} \sum_n \frac{1}{M_n} (\varphi(r, R) \cdot \Delta_n \psi(R) + 2 \cdot \nabla_n \varphi(r, R) \cdot \nabla_n \psi(R) + \psi(R) \cdot \Delta_n \varphi(r, R)) + V_{NN} \cdot \varphi(r, R) \psi(R) + \epsilon(R) \cdot \varphi(r, R) \psi(R) = E \cdot \varphi(r, R) \psi(R) \end{aligned} \quad (14)$$

Now we can multiply the second equation in (14) on  $\varphi(\vec{r}, \vec{R})^*$ , followed by integration over the entire crystal with respect to electrons coordinates  $\mathbf{r}$ . Finally we have:

$$-\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \left( \int \varphi(r, R) \varphi(r, R)^* dr^3 \cdot \Delta_I \psi(R) + 2 \cdot \nabla_I \psi(R) \cdot \int \varphi(r, R)^* \cdot \nabla_I \varphi(r, R) dr^3 + \psi(R) \cdot \int \varphi(r, R)^* \Delta_I \varphi(r, R) dr^3 \right) + V_{NN} \cdot \varphi(r, R) \psi(R) = E \cdot \varphi(r, R) \psi(R) \quad (15)$$

We assume that electrons and nuclei wave functions  $\varphi(r, R)$  and  $\psi(R)$  normalized on unit. It means that:

$$\int \varphi(r, R)^* \cdot \varphi(r, R) dr^3 = 1 \quad \text{and} \quad \int \psi(R)^* \cdot \psi(R) dR^3 = 1. \quad (16)$$

By using equation (16) we can show that (15 I) integral is equal to 0:

$$\int \varphi(r, R)^* \cdot \nabla_n \varphi(r, R) dr^3 = 0 \Rightarrow \nabla_n \int \varphi(r, R)^2 dr^3 = 2 \cdot \int \varphi \nabla_n \varphi dr^3 = 0.$$

The integral (15.II)  $\int \varphi(r, R)^* \cdot \Delta_I \varphi(r, R) dr^3$  describes the influence of the motion of nuclei on the states of electrons and has the name integral of nonadiabaticity. This second order effect for example must be taken into the account for multiphonon (creation or destruction of several phonons or, in another interpretation, the exciting or destruction of several harmonic waves of the specific type (acoustic or optical) and with specific wave vectors) transition in crystals. Due to the large difference in the masses of electrons and nuclei (high electron mobility and slow motion of nuclei) this effect is very weak. This means that the corresponding derivative  $\nabla_I \varphi(r, R)$  is almost equal to zero and can be ignored (this is not always possible, but as a first approximation it can be done).

The first equation in (14) can be simplified by the same way by multiplication on followed by integration over the nuclei coordinates R. Finally the system of equations (14) could be represented as follows:

$$\begin{aligned} \hat{T}_e \cdot \varphi(r, R) + V_{ee}(r) \cdot \varphi(r, R) + V_{eN}(r, R) \cdot \varphi(r, R) &= \epsilon(R) \cdot \varphi(r, R) - \text{equation for electrons} \\ \hat{T}_N \psi(R) + V_{NN}(R) \cdot \psi(R) + \epsilon(R) \cdot \psi(R) &= E \cdot \psi(R) - \text{equation for nuclei} \end{aligned} \quad (17)$$

As you see in the adiabatic approximation, the general problem of quantum mechanics for a crystal can be divided into two subtasks, two equations. The first equation describes the properties of the electronic subsystem, and the second describes the motion of nuclei. It is very important to note that each nucleus moves in the field created by all other nuclei and in the mean field created by all electrons. The energy of electrons plays the role of potential energy for nuclei (part of it).

For the equation for nuclei  $\hat{T}_N \psi(R) + U(R) \cdot \psi(R) = E \cdot \psi(R)$ , here  $U(R) = V_{NN}(R) + \epsilon(R)$ , the potential energy can be expanded into a power series in terms of the displacement of nuclei with number **k** from equilibrium positions **u<sub>k</sub>** (see Lecture 3):

$$U = U(0) + \sum_k \frac{dV}{du_k} \Big|_{u=0} \cdot u_k + \frac{1}{2} \cdot \sum_k \frac{d^2V}{du_k du_k} \Big|_{u=0} \cdot u_k \cdot u_k' + \dots \quad (18)$$

The k-index includes the atom number and the x, y, or z offset direction. In harmonic approximation

$$U = \frac{1}{2} \cdot \sum_k \frac{d^2V}{du_k du_k} \Big|_{u=0} \cdot u_k \cdot u_k' = \frac{1}{2} \cdot \sum_k \Phi_{kk'} \cdot u_k \cdot u_k' \quad (19)$$

$\Phi_{kk'}$  - dynamical matrix or matrix of force constants (elastic coefficients for the spring connecting atoms k and k'). This matrix can be diagonalized using normal coordinates:

$$A_q = \sum_k C_k^q u_k \quad \text{in this case} \quad U = \frac{1}{2} \sum_q \omega^2(q) \cdot A_q^2 \quad \text{and Schrodinger equation in normal coordinate representation is}$$

$-\hbar^2 \frac{\partial^2 \psi_q}{\partial A_q^2} + \frac{1}{2} \sum_q \omega^2(q) \cdot A_q^2 \psi_q = 0$  , here q-is a number of harmonic oscillator. The solution for this equations can be

found by using standard methods of quantum mechanics.

Regarding the equation for the electronic subsystem, there are many different methods and approximations for finding the corresponding solution.