УДК 534.2

S. P. Kshevetskii

FINITE-DIFFERENCE-STEEPEST DESCENT PARADIGM: NEW NUMERICAL METHOD OF FOCKIAN SPECTRAL PROBLEM

A new numerical method that unify finite-difference and the method of steepest descent paradigms is suggested. It allows to avoid the wavefuncions space and spin variables division, that leads to superposition in spin projection stacionary states. The approach is verified by comparison with conventional methods.

Предложен новый численный метод, объединяющий конечно-разностный метод и метод парадигм наискорейшего спуска. Это позволяет избежать деления пространства волновых функций и спиновых переменных, что приводит к суперпозиции в стационарных состояниях спиновой проекции. Подход проверен путем сравнения с традиционными методами.

Keywords: Hartree — Fock equation, Fockian, wavefunction, Hamiltonian, electron, exchange.

Ключевые слова: уравнение Хартри — Фока, фокиан, волновая функция, гамильтониан, электрон, обмен.

Introduction

A foundation of quantum chemistry and solid state physics in its modern form is based on ideas of Hartree Fock (HF) method, that presents the best one-electron approximation [1]. The method is formulated as a system of nonlinear equations in which each electrom «lives» in a self-consistent field of other electrons. Namely the self-consistency is a source of nonlinearity, that yields main dificulty of the system solution. It leads to a necessity of computer modelling/simulation of quantum multi-particle systems that is approved in [2]. The abundance of publications related to HF method forces us to very brief review.

A brief history of the development of methods for calculating multi-electron systems

Hartree proposed a method for approximate calculation of multy-electron wave function in 1929. However, he has not taken into account the symmetry of the wave functions of electrons under action of permutations. In 1930, Fock developed Hartree's method taking the Pauli principle into account, it is now named as Hartree — Fock method (HF method). The effective results are obtained on a way of the HF method simplifications, known as density-functional theory (DFT) [3].

Вестник Балтийского федерального университета им. И. Канта.
Сер.: Физико-математические и технические науки. 2020. № 3. С. 90 – 103.

There are also post-Hartree — Fock methods that improve Hartree — Fock calculations. In [4] a concise summary is presented over the existing fully numerical approaches to molecular calculations. The authors own two-dimensional (2D) finite-difference relaxation method for Hartree — Fock, Hartree — Fock — Slater, multiconfiguration Hartree — Fock or Dirac — Slater calculations on diatomic molecules is described in details.

Let us mention popular methods for calculating quantum many-particle systems as an important part of the brief history of the method development. It is matrix and its diagonalization [5] for a Fockian or a Huckel-type models for Hamiltonian matrix of molecule by the non-canonical molecular orbitals (NCMO).

In molecular states calculations of quantum chemistry the so-called molecular orbitals are used. The orbitals are localized in a limited spatial region of a molecule, for example a specific bond or in the case of a lone pair on a specific atom. They can be used to relate molecular orbital calculations to simple bonding theories, and also to speed up post-HartreeвЂ“Fock electronic structure calculations by taking advantage of the local nature of electron correlation. In solid state physics such localized orbitals are build using periodic boundary conditions that are known as Wannier functions, see for example [6].

The main problem of a realization of the mentioned methods is a choice of the basic functions for an eigen wave function of the Fockian [7].

The overview [13] touch early attempts to reduce the many-center problems to a somewhat one-center's concentrating on so-called two-dimensional finite-difference HF method (FDHF) Earlier review of the finite-difference approach to the problem is presented in [4], where authors speak about fully numerical HF methods for molecules.

A continuous spectrum states formation that would be responsible for processes of ionization and recombinations are of extreme difficulty by means of localized or periodic functions, more exactly — the an elegant numerical procedure to find optimally localized set of generalized Wannier functions associated with a set of Bloch bands in a crystalline solid [10].

Basic ideas

To avoid the mentioned difficulties of solution of the Fockian eigenvalue problem by means of variational principle, we suggest a direct application of finite-difference method. To accelerate the solution numerical exploration we use the steepest descent method.

Aims and scope

This paper introduces the novel numerical method that unify finite-difference and the steepest descent paradigms. It unifies two main purposes:

1) the effective numeric code that accelerates calculations especially within an extent atomic systems;

2) it allows to avoid the wavefuncions space and spin variables division, that leads to account of superpositions in spin projection stationary states. The approach is verified by comparison with conventional methods results.

Born — Oppenheimer approximation. Hamiltonian of an electronic system

In the Born — Oppenheimer approximation, the nuclei of a molecule or a solid are assumed to be stationary. The Hamiltonian is written for a system of N electrons, located in the field of a nuclei system:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \Delta_i - \sum_{J,i}\frac{Z_J e^2}{\left|\vec{r}_i - \vec{R}_J\right|} + \sum_{i,j\neq i}\frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|}. \quad (1)$$

In the expression (1), $\sum_i$ is a sum over all electrons, i is the electron number; $\sum_J$ is a sum over all nuclei, J is nucleus number; Z_J is the charge of the nucleus with number J, expressed in charge $|e|$ of an electron; $\vec{R}_J$ is a position of the nucleus J, the vector $\vec{r}_i$ stands for a radius-vector for the electron with number i.

Conventionally, if the energy eigenvalue problem is of interest, the stationary Schrödinger equation writes as :

$$\hat{H}\Phi = E\Phi, \quad (2)$$

where $\Phi = \Phi\left(\vec{R}_1,\cdots,\vec{R}_K,\left(\vec{r}_1,\sigma_1\right),\cdots,\left(\vec{r}_N,\sigma_N\right)\right)$, $\sigma_1,\sigma_2,\ldots\sigma_N$ are spin variables of the electrons. Since the electrons are fermions, the wave function must be antisymmetric in the variables of the electrons, that is, for example, reads

$$\Phi\left(\vec{R}_1,\cdots,\vec{R}_K,\left(\vec{r}_1,\sigma_1\right),\cdots,\left(\vec{r}_N,\sigma_N\right)\right) = -\Phi\left(\vec{R}_1,\cdots,\vec{R}_K,\left(\vec{r}_N,\sigma_N\right),\cdots,\left(\vec{r}_1,\sigma_1\right)\right).$$

It is convenient to mark electrons arguments simply with their numbers, for the case, we introduce the notation $i = \left(\vec{r}_i,\sigma_i\right)$. Then

$$\Phi = \Phi\left(\vec{R}_1,\cdots,\vec{R}_K,1,\cdots,N\right).$$

Notations. The essence of the Hartree — Fock method

Within the framework of the Hartree — Fock method, the wave function $\Phi = \Phi\left(\vec{R}_1,\cdots,\vec{R}_K,1,\cdots,N\right)$ is searched in the form of a Slater determinant composed of single-particle functions

$$\Phi = \begin{vmatrix} \Psi_1(1) & \Psi_2(1) & \cdots & \cdots & \Psi_N(1) \\ \Psi_1(2) & \Psi_2(2) & \cdots & \cdots & \Psi_N(2) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \Psi_1(N) & \Psi_2(N) & \cdots & \cdots & \Psi_N(N) \end{vmatrix}.$$

We skip the nuclei positions parameters $\vec{R}_K$.

From the variational principle $\left(\min\left\langle \Phi, \hat{H}\Phi \right\rangle\right)$ the Fock operator components for the spin-orbitals Ψ_i are derived. as follows:

$$\hat{F}_j \Psi_j(1) = \varepsilon_j \Psi_j(1). \tag{3}$$

Here the functions Ψ_j are spin-orbitals, and the $\hat{F}_j$ are Fockians,

$$\hat{F}_j = \hat{h}_1 + \sum_{i=1}^{N'} \left(\hat{J}'_i - \hat{K}'_i \right), \tag{4}$$

$$\hat{J}'_i \Psi_j = \int \Psi_i^*(2) \frac{1}{r_{12}} \Psi_i(2) d\vec{r}_2 \Psi_j(1), \tag{5}$$

$$\hat{K}'_i \Psi_j = \int \Psi_i^*(2) \frac{1}{r_{12}} \Psi_j(2) d\vec{r}_2 \Psi_i(1), \tag{6}$$

$$\hat{h}_1 = -\frac{\hbar^2}{2m} \Delta_1 - \sum_J \frac{Z_J e^2}{\left| \vec{r}_1 - \vec{R}_J \right|}.$$

A prime by the sum means that a term with $i = j$ is skipped. The integration is carried out over the variables of particle 2, $r_{12} = \left| \vec{r}_1 - \vec{r}_2 \right|$, $\Delta_1 = \frac{\partial^2}{\partial x_1} + \frac{\partial^2}{\partial y_1} + \frac{\partial^2}{\partial z_1}$, $\vec{r}_1 = (x_1, y_1, z_1)$. It is assumed that the functions Ψ_i are orthogonal: $\int \Psi_i^*(1) \Psi_k(1) d\vec{r}_1 = \delta_{ik}$.

Orbitals. Standard method for solving the Hartree — Fock equations

In order to solve the Hartree — Fock equations, the following transformation is usually carried out. The spin variables of the electrons are split off. Namely, it is assumed that a part of electrons have spin up, and the others have spin down. Therefore, the wave functions Ψ_j are taken in the form $\Psi_j(\vec{r}, \sigma) = \varphi_j(\vec{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ and other functions Ψ_i are taken as

$$\Psi_i(\vec{r}, \sigma) = \varphi_j(\vec{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

Substituting these expressions into the Hartree — Fock equations (3), the equations for the orbitals $\varphi_j(\vec{r})$ are derived

$$\hat{F}_j \varphi_j(1) = \varepsilon_j \varphi_j(1). \tag{7}$$

Here φ_j are spin-orbitals, and $\hat{F}_j$ are fokians,

$$\hat{J}_i'\varphi_j = \int \varphi_i^*(2)\frac{1}{r_{12}}\varphi_i(2)\,d\vec{r}_2\Psi_j(1), \tag{8}$$

$$\hat{K}_i'\varphi_j = \int \varphi_i^*(2)\frac{1}{r_{12}}\varphi_j(2)\,d\vec{r}_2\varphi_i(1). \tag{9}$$

These equations (7) are also called Hartree — Fock equations, although the meaning of these equations is essentially different than (3).

The solution of these equations (7) is sought in the form of series with respect to the basis functions $\varphi_j = \sum_k C_{jk}\Theta_k$, where Θ_k are the basis functions.

When we come to equations (7) from equations (3), the ability to calculate magnetic phenomena correctly within the framework of the Hartree — Fock method becomes lost because we have predetermined the spins of the particles. Especially it relates to so-called frustration phenomenon [14].

However, the original Hartree — Fock equations can be solved differently: the electron spin states can be calculated from the Hartree — Fock equations (7) for spin-orbitals, and then the orientations of the particle spins and magnetic phenomena can be calculated, taking into account the spin-orbit interaction.

Two equivalent forms of the Hartree — Fock equations

Equations (3) are a special form of equations of more general kind:

$$\hat{F}_j\Psi_j(1) = \varepsilon_j\Psi_j(1) + \sum_{i\neq j}\lambda_{ji}\Psi_i(1), \tag{10}$$

where obviously

$$\varepsilon_j = \int \Psi_j^*(1)\hat{F}_j\Psi_j(1)\,d\vec{r}_1, \tag{11}$$

$$\lambda_{ji} = \int \Psi_i^*(1)\hat{F}_j\Psi_j(1)\,d\vec{r}_1. \tag{12}$$

It is the equations (10) that are obtained if we derive them from the variational principle neatly.

Both forms of Hartree — Fock equations are equivalent. The operator $\hat{F}_j$ depends on the functions Ψ_j and is invariant under a unitary transformation of the system of functions Ψ_1, Ψ_2, …, Ψ_N. By unitary transformations of the system of functions Ψ_1, Ψ_2, …, Ψ_N, any of these form of equations is transformed to another .

The form (10) of the Hartree — Fock equations is more convenient for calculations. The equivalence of the two forms ((3) and (10) of the Hartree — Fock equations is shown in the literature [11]. However, not all books contain such information.

The resulting equation can be written in the form

$$\hat{S}_j \Psi_j(1) = \varepsilon_j \Psi_j(1), \tag{13}$$

where

$$\hat{S}_j \Psi_j(1) = \hat{F}_j \Psi_j(1) - \sum_{i \neq j} \int \Psi_i^*(2) \hat{F}_j \Psi_j(2) d\vec{r}_2 \Psi_i(1). \tag{14}$$

We multiply the equations (13) by Ψ_k by scalar product, that reads

$$\int \Psi_k^*(1) \hat{S}_j \Psi_j(1) d\vec{r}_1 = \int \Psi_k^*(1) \hat{F}_j \Psi_j(1) d\vec{r}_1 - \sum_{i \neq j} \int \Psi_i^*(2) \hat{F}_j \Psi_j(2) d\vec{r}_2 \int \Psi_k^*(1) \Psi_i(1) d\hat{r}_1 =$$

$$= \int \Psi_k^*(1) \hat{F}_j \Psi_j(1) d\vec{r}_1 - \sum_{i \neq j} \int \Psi_i^*(2) \hat{F}_j \Psi_j(2) d\vec{r}_2 \delta_{i,k} =$$

$$= \int \Psi_k^*(1) \hat{F}_j \Psi_j(1) d\vec{r}_1 - \int \Psi_k^*(2) \hat{F}_j \Psi_j(2) d\vec{r}_2 \delta_{k,j} =$$

$$= \varepsilon_j \int \Psi_k^*(1) \Psi_j(1) d\hat{r}_1 .$$

We see that if $\int \Psi_k^*(1) \Psi_j(1) d\vec{r}_1 = \delta_{j,k}$, then the equality holds.

The new method of solving the Hartree — Fock equations (3) by steepest descent method

To suggest a new solution method, we use some geometric ideas. Let us define a curve $\Psi(t)$ in thh functional space of the HF system solutions.

Suppose the curve ends at some eigenfunction $\Psi_j = \Psi(0)$ and hence mark the function by the index j, having $\Psi_j(t)$. Let's allocate in each point of the curve $\Psi_j(t)$ the components parallel to $\hat{S}_j \Psi_j$, and the component orthogonal to $\hat{S}_j \Psi_j$ and introduce the factor δ so, that:

$$\Psi_j = \left(\Psi_j\right)_{\parallel} + \left(\Psi_j\right)_{\perp} = \delta\left(\hat{S}_j \Psi_j\right) + \left(\Psi_j\right)_{\perp}. \tag{15}$$

Here δ is a certain factor that is easily computed. Multiplying of the equality (15) by scalar product from the left side by $\hat{S}_j \Psi_j$, we get

$$\delta = \int \frac{\left(\hat{S}_j(1) \Psi_j(1)\right)^*}{\left\| \hat{S}_j \Psi_j \right\|^2} \Psi_j(1) d\vec{r}_1 .$$

In this way,

$$\left(\Psi_j\right)_{\parallel} = \int \frac{\left(\hat{S}_j(1) \Psi_j(1)\right)^*}{\left\| \hat{S}_j \Psi_j \right\|^2} \Psi_j(1) d\vec{r}_1 \hat{S}_j \Psi_j ,$$

$$(\Psi\ )_{\perp} = \Psi_j - \int \frac{\left(\hat{S}_j(1)\Psi_j(1)\right)^*}{\left\|\hat{S}_j\Psi_j\right\|^2}\Psi_j(1)\,d\vec{r}_1\hat{S}_j\Psi_j\,.$$

Then it is natural to surmise that $\Psi_j(t)$, is obtained as a result of the following iterative procedure

$$\Psi_j(t+\Delta t) = \Psi_j(t) - \left(\alpha(\Psi\ )_{\perp} + \beta\left(\Psi_j\right)_{\|}\right)\Delta t$$

under the condition of sufficiently small Δt and for $t \to \infty$ converges to the solution of the Hartree — Fock equations (13). Here $\alpha > 0$, $\beta > 0$. The term $\beta\left(\Psi_j\right)_{\|}\Delta t$ is introduced to preserve the normalization and the value of β has to be chosen from the condition of conservation of normalization. For sufficiently small Δt, we can take $\beta = 0$. Therefore, for $\Delta t \to 0$ we arrive at the equation

$$\frac{d\Psi_j}{dt} = -\alpha\left(\Psi_j - \int \frac{\left(\hat{S}_j(1)\Psi_j(1)\right)^*}{\|\hat{S}_j\Psi_j\|^2}\Psi_j(1)\,d\vec{r}_1\mathrm{S}_j\Psi_j\right).$$

We calculate

$$\varepsilon_j^*(t) = \int \frac{\left(\hat{S}_j(1)\Psi_j(1)\right)^*}{\left\|\Psi_j\right\|^2}\Psi_j(1)\,d\vec{r}_1.$$

This equation follows from (13) and corresponds to our equations (13) for eigenvalues. Then we arrive at the equation

$$\frac{d\Psi_j}{dt} = -\alpha\left(\Psi_j - \frac{\varepsilon_j^*(\mathrm{t})\left\|\Psi_j\right\|^2}{\left\|\hat{\mathrm{S}}_j\Psi_j\right\|^2}\mathrm{S}_j\Psi_j\right).$$

This equation is not very convenient for calculations, because in the process it is required to compute $\left\|\hat{S}_j\Psi_j\right\|^2$, and this is laborious. Hoever we can use the approximate relation

$$\left\|\hat{\mathrm{S}}_j\Psi_j\right\|^2 \approx \left|\varepsilon_j(\mathrm{t})\right|^2\left\|\Psi_j\right\|^2,$$

that follows from (13), and to simplify the differential equation. This can also be done because the term $\alpha\psi_j$ affects mainly the normalization change, but normalization can always be corrected. We arrive at a more simple and convenient equation

$$\frac{d\Psi_j}{dt} = -\alpha\left(\Psi_j - \frac{1}{\varepsilon_j(t)}\hat{S}_j\Psi_j\right).$$

It is even more convenient to rewrite this equation in the form

$$\frac{d\Psi_j}{dt} = -\alpha\left(\mathrm{S}_j\Psi_j - \varepsilon_{\mathrm{j}}(\mathrm{t})\Psi_j\right). \tag{16}$$

We have taken into account that the energies are negative for discrete states. The normalization in this equation is retained automatically.

This form of the equation is relatively simple and understandable. We write out this equation in the original operators:

$$\frac{d\Psi_j(1,t)}{dt} = -\alpha\begin{pmatrix}\hat{F}_j(1,t)\Psi_j(1,t) - \sum\limits_{i\neq j}\int\Psi_i^*(2,t)\hat{F}_j\Psi_j(2,t)d\vec{r}_2\,\Psi_i(1,t)\\ -\varepsilon_{\mathrm{j}}(\mathrm{t})\Psi_j(1,t)\end{pmatrix}. \tag{17}$$

Calculation of particle spin states

The solution of the equations (17) for $t\to\infty$ gives the stationary solution of the equations. Equations (17) realize the method of steepest descent. In this case, we do not necessarily fall into the absolute minimum of energy, because there are local energy minima. Consequently, the result of solving the equations (17), in general, depends on the starting spin orbitals $\Psi_j(t=0)$.

Let's consider a concrete example. Suppose we calculate the spin-orbitals for the helium atom. Suppose that for $t=0$ the spins of both electrons are directed upwards. It is not clear from the equations, by what mechanism in the particular case under consideration, the electrons can turn to make spins of electrons oppositely directed at $t\to\infty$. The fact is that the focian $\hat{F}_j$ is an integro-differential operator. By itself, it can not transform the structure $\Psi_j = \begin{pmatrix} u_j \\ 0 \end{pmatrix}$ of Ψ_j function into the structure $\Psi_j = \begin{pmatrix} 0 \\ v_j \end{pmatrix}$ The last term in (17) also can not change the structure of the column $\Psi_j = \begin{pmatrix} u_j \\ 0 \end{pmatrix}$.

Numerical experiments show that in the solution of the equations (17), the correct orientations of electron spins are settled automatically with increasing t, if the orientations of the electron spins for $t=0$ do not differ too much from those corresponding to the energy minimum.

Nevertheless, there exist initial $\Psi_j(0)$ such that the spins of particles with increase of t can not turn around and take a position corresponding to energy minimum. So if in the two-electron system the particle spins are parallel to each other at $t=0$, then in the solution of the equations (17) with increasing t the particle spins can no be transformed although the energy decreases and the local energy minimum is achieved.The energy corresponding to this local extremum is larger, since the exchange term is obtained not equal to zero. The situation corresponds, obviously, to unstable equilibrium.

The structure of the equation (17) does not allow us to get out of this local extremum, and this is apparently related to the structure of the original Hartree — Fock equations. In deriving the Hartree — Fock equations, one searches for a minimum of the energy functional, and calculates variation of the energy functional with respect to spatial variables. The orientations of particle spins are also independent variables, but the corresponding minimization of the energy functional over these variables has not been performed. It should be noted that the contribution of the terms $J_i^{'}$ and $\hat{h}_1$ does not depend on the orientation of the spins, and only the exchange integral determines the contribution of spin-spin interactions of particles into the total energy value.

It is not clear how one can modify the Hartree — Fock equations to exclude local energy extremes corresponding to incorrect spin configurations. But it is relatively easy to propose some modifications of equation (17), which allow minimizing the energy functional over the spin variables.

The simplest way is to introduce into the system of equations the forced oscillations of the spins of particles, which dump with time. This will allow the system to escape from local extremes and help the system to align the spins of the particles so as to find a stable configuration of spins and an absolute minimum of energy. Fortunately, the dead zone in which the spinning of spins to the right directions does not occur, is narrow. We introduce for each spinor $\Psi_j = \begin{pmatrix} u_j \\ v_j \end{pmatrix}$ the orthogonal spinor $\Psi_j^+ = \begin{pmatrix} v_j \\ -u_j \end{pmatrix}$.

We modify the equations (17) as follows

$$\frac{d\Psi_j(1,t)}{dt} = -\alpha \begin{pmatrix} \hat{F}_j(1,t)\Psi_j(1,t) - \sum\limits_{i\neq j}\int \Psi_i^*(2,t)\hat{F}_j(2,t)\Psi_j(2,t)d\vec{r}_2\Psi_i(1,t) \\ -\varepsilon_j(t)\Psi_j(1,t) \end{pmatrix} + \\ + \gamma_j(\mathrm{t})\left(\Psi_j^+(1,t) - \sum_{i\neq j}\int \Psi_i^*(2,t)\Psi_j^+(2,t)d\vec{r}_2\Psi_i(1,t)\right). \qquad (18)$$

Here the conservation of the normalization follows from the fact that the right-hand side is orthogonal to Ψ_j. To preserve the orthogonality of the functions Ψ_i, in the second line (18) a special summand is introduced

$$-\sum_{i\neq j}\int \Psi_i^*(2,t)\Psi_j^+(2,t)d\vec{r}_2\Psi_i(1,t).$$

Here $\gamma_i(t)$ are some small rapidly decreasing functions. It is advisable to relate these functions $\gamma_i(t)$ to the norms of the derivatives $\frac{d\Psi_j(1,t)}{dt}$. For example, for a numerical solution, we can take

$$\gamma_j(\mathrm{t}) = \gamma_0\left|\frac{\partial\Psi_j(t)}{\partial t}\right| * 0.1 * random(-1,1).$$

Here the values from +1 to –1 are chosen randomly. $\gamma_j(t)$ is chosen so that the change $\Psi_j(t)$ due to of the introduced spin oscillations be small in comparison with the change of $\Psi_j(t)$ due to the energy changing to energy minimum. The spin oscillations introduced are small, but they are sufficient for the system to leave the dead zone and adjust the spins to achieve the absolute energy minimum. In addition, $\gamma_i(t)$ becomes negligibly small and tends to zero as the extremum point approaches.

However, the block with the turn of the spins is still underdeveloped. It is possible to accurately calculate the operator turning the spins of particles in such a way as to minimize energy. The idea is fresh and not implemented yet.

Some test ab initio calculations. Calculation of electron clouds and spin orientations in simple electron systems

Below we show some examples of ab initio calculations electronic clouds and spin orientations of simple quantum systems.

In Fig. 1, the right-hand side of the figure shows the electron clouds of the helium atom calculated by the method described above. It should be noted that the electron spins are opposite directed, and the correct orientation of the spins is found by itself, it is the result of calculations. The calculated ground state energy $E_0 = -82.27$ eV (experimental value $E_0 = -78.95$ ev [8]), calculated ionization energy $E_1 = -20.94$ ev (experimental value $E_1 = -24.58$ eV [9]). In this work, we did not have the goal of calculating these energy characteristics with high accuracy but just wished to illustrate the proposed calculation method and show that it works. Obviously, using finer the difference grid, it is possible to increase the calculation accuracy. Although we understand that applying standard methods for solving the Hartry — Fock equations and choosing a very good basis system of functions and the correct spin orientations, one can probably achieve the best accuracy. The advantage of the proposed method is its universality, which is very important, and also in the fact that the correct orientation of the spins is obtained automatically within this method. On the left side of the picture, the initial electron clouds are shown to start the calculations. They were especially initiated to be very different from the actual electron clouds of the helium atom, and even were taken primitive, to demonstrate the work out of the method. The starting cloud of the first electron fills the left half of the square (in reality, of the cube), and the starting cloud of the second electron is in the right half of the square (of the cube). Such a choice of starting clouds is made so that the starting clouds are orthogonal, although this is not important for the computations performed. We see that, as a result of computations, we received not only the correct electron clouds but, and most importantly, the correct orientation of the spins.

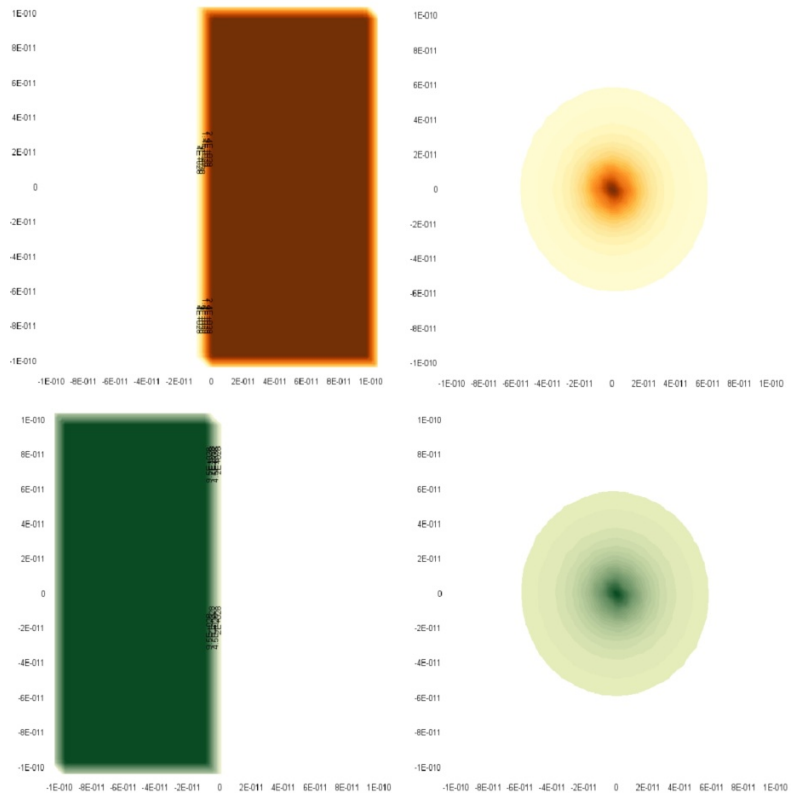

Fig. 1. Helium. On the left side, the initial electron clouds are shown. The computed electron clouds for the helium atom are shown on the right side. The electron spins are directed opposite; this is the result of calculations, and this fact is important

In Fig. 2, the upper row shows the electron clouds of the lithium atom, calculated as described above. It is usually assumed that two electrons in the lithium atom are at the lower level and the spins of these two electrons are directed opposite, while the third electron is at a higher energy level and has one of two possible spin orientations. Simple logic suggests that in reality, the spin of this third electron should rather be in a superposition state because otherwise, the spin-spin interaction is only with one of two lower electrons, which is illogical. The superposition state of the spin of this third electron is shown by calculations. However, if the spin of this third electron is in a superposition state, then the spins of all three electrons must be in a superposition state, and then there must also be a splitting of the lower energy level. This is exactly what we are observing: the lower electrons have slightly different energies. The correct orientations of the spins are found by itself; it is an important result of calculations. The lower part of the figure shows the initial electron clouds to begin the calculations. The initial clouds are taken so that they are orthogonal to each other, and their orthogonality is achieved by the simplest means. We see that we obtained not only the correct electron clouds but also the correct spin orientations.

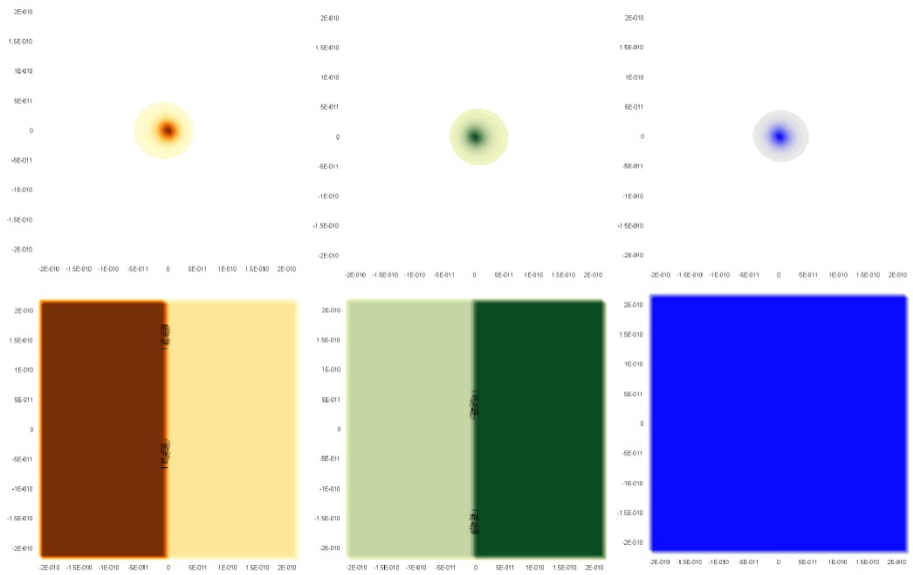

Fig. 2. Lithium. In the upper row, the calculated electron clouds of the lithium atom are shown. Electron spins have been calculated by a computer program. The spins of all three electrons are not pure states, but they are superpositions of states of spin up and spin down. In the bottom row, the initial electron clouds are shown

The electron clouds of a boron atom, calculated in the same way as described above, are shown in Fig. 3 in the top row. Here everything is about the same as in previous cases, but only the number of electrons is more. The lower part of the figure shows the initial electron clouds for starting the calculations, and the initial clouds are orthogonal to each other.

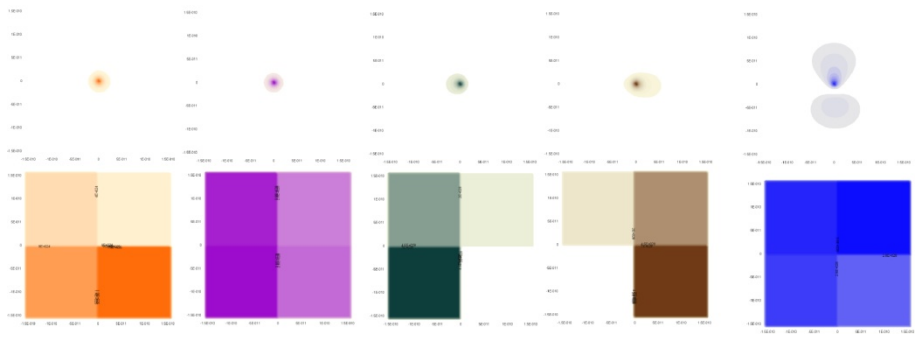

Fig. 3. Boron. In the upper row, calculated electron clouds are shown. Spins of all electrons are calculated by the program. All electron clouds are superpositions of spin-up and spin-down. At the ground energetic level, the two electrons have almost pure spin states. Small displacements of the cloud centers are seen due to the repulsion of electrons at the same level. In the lower row, the initial fields of electron clouds are sown

Discussion

An alternative method for calculating the wave function of electrons is called the DFT method (Density Functional Theory method). It is based on the ideas of Kohn and Sham (1960): the wave function of the ground state is restored with electron density [15]. We do not consider DFT-methods here, but it is quite possible to develop it on base of the ideas, presented here. Some problems However, after all, electrons define how matter is arranged internally, and what happens with it. All that we know about the design of atoms and molecules, we know only from calculations and from our imagination. Therefore, the experimental researches are fundamentally insufficient in modern physics.The significance of the computational part of the work is extremely great in modern physics.

Acknowledgement. Author thanks S. Leble for the essential contribution in literature review and important discussions of statement of problem and its solution.

References

1. *Fock V*. An Approximate Method for Solving the Quantum Many-Body Problem // Zs. Phys. 1930. Bd. 61, №1—2. S. 126—148.

2. *Fock V*. The Fundamental Significance of Approximate Methods in Theoretical Physics // UFN. 1936. Vol. 16, iss. 8. 1070.

3. *Pople J., Gill P., Johnson B*. Kohn-Sham density-functional theory within a finite basis set // Chemical Physics Letters. 1992. Vol. 199, iss. 6. P. 557—560.

4. *Laaksonen L*. Fully numerical Hartree-Fock methods for molecules. Finnish State Computer Center // Computer Physics Reports. 1986. №4. P. 313—344.

5. *Gineityte V*. Block Diagonalization Problem for a Fockian Matrix of Molecule and Its Solution by Means of Noncommutative Rayleigh-Schrödinger Perturbation Theory // International Journal of Quantum Chemistry. 1988. Vol. 68. P. 119—127.

6. *Shukla A., Dolg M., Stoll H*. Wannier-function-based ab initio Hartree-Fock approach extended to polymers: Applications to the LiH chain and trans-polyacetylene // Phys. Rev. B. 1998. №58. 4325.

7. *Evarestov R*. Quantum Chemistry of Solids: The LCAO First Principles Treatment of Crystals. Springer, 2007.

8. *Griffiths D*. Introduction to Quantum Mechanics. Pearson Education, 2005.

9. *NIST* Atomic Spectra Database Ionization Energies Data. Gaithersburg, MD: NIST, 2009.

10. *Marzari N., David D*. Vanderbilt. Maximally localized generalized Wannier functions for composite energy bands // Phys. Rev. B. 1997. №56. 12847.

11. *Dahl J*. Introduction to The Quantum World of Atoms and Molecules. World Scientific Publishing, 2001.

12. *Quantum* Mechanical ab-initio calculations of the properties of crystalline materials. Lecture Notes in Chemistry / ed. by C. Pisam. Springer, 1996.

13. *Kobus J*. Overview of finite difference Hartree-Fock method algorithm, implementation and application //AIP Conference Proceedings. 2012. Vol. 1504, iss. 1. 189. doi: 10.1063/1.4771715.

14. *Zhendong Fu*. Spin Correlations and Excitations in Spin-frustrated Molecular and Molecule-based magnets. Jülich, 2012.

15. *Kohn W*. Nobel Lecture: Electronic structure of matter—wave functions and density functionals // Rev. Mod. Phys. 1991. №71. 1253.

The author

Prof. Sergey P. Kshevetskii, Immanuel Kant Baltic Federal University, Russia.
E-mail: SPKshev@gmail.com

Об авторе

Сергей Петрович Кшевецкий — д-р физ.-мат. наук, проф., Балтийский федеральный университет им. И. Канта, Россия.
E-mail: SPKshev@gmail.com