

Simulation of Spherical Metal Nanoclusters Containing Monovacancy

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The goal of this work was to increase the stability of the simulation based on the Numerov method during the calculation of the electron wave functions in a metal cluster and to ensure the stability of self-consistent calculations of the energy characteristics of metal clusters by limitation of the electrostatic potential changes. The object of the study is the method for calculation of the electron wave functions and energy eigenvalues by the Numerov and Shooting methods. At the modeling stage, in order to increase the efficiency of the model, the density functional theory (DFT) was used in conjunction with the Kohn-Shem formalism, which allowed us to simplify the complex problem of the electron interaction in the field of charged ions and to obtain the model of independent electrons moving in some effective potential. We used the stabilized jellium model (SJM) and local density approximation (LDA) for the exchange and correlation energies. The change of the electrostatic potential profile limitation is used by adding coefficients that determine the contributions of the previous and current electrostatic potential profile to the resultant one. Models of a metal cluster with a centered monovacancy and approaches for calculating its parameters were developed. To ensure the convergence and stability of the Numerov method, methods of two-side calculation with "cross-linking" of the wave function at the empirically selected point were proposed. The method of simulation with the optimal step is developed and implemented in the program code for calculating the energy characteristics of metal nanoclusters containing the monovacancy. Simulation allowed to obtain the electron density and effective potential profiles for charged and neutral clusters. The results of the calculations were compared with experimental data, as well as with *ab initio* computations. Developed approaches and simulation techniques can be recommended for the analysis of low-dimensional metal systems, including systems with a layered structure.

Keywords: Metal clusters, Energy characteristics, DFT, Wave function, Numerov method, "Cross-linking" of functions, Stability of the simulation.

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1. INTRODUCTION

In modern technologies where nanomaterials, atomic clusters, or island films are used, we need diagnostics, defect control and determination of their energy characteristics. On the one hand, the calculations of such characteristics as the ionization potential and electron affinity, the cohesive energy, the dissociation energy and the energy vacancy formation can be used to control the defects and melting temperature of small metal clusters. On the other hand, it is very useful for modeling the composite instrumental materials during the design of metallized and glue coatings, etc.

Today, *ab initio* methods are commonly used which give the greatest reliability and can describe systems of any geometry [1-4]. However, if high-precision calculations are not required, more economical methods such as the Kohn-Sham method [5-8] can be used. Despite the quantitative difference between *ab initio* and Kohn-Sham version we can estimate qualitative tendencies of the energy characteristics of metal clusters.

Thus, the sufficient accuracy of the selected model, together with its universality and efficiency, determines its choice for this study.

When vacancies appear, the problem of simulation for energy characteristics of metal clusters becomes more complicated. Thus, in order to reduce the simulation time, it is necessary not only to simplify the model, but also to choose the most economical approach for solving the obtained differential equations.

Simulation is based on the Kohn-Sham method and

stabilized jellium model (SJM).

The subject of study is the optimal method for calculating the electron density profile and potential one of defect-free metal clusters and clusters with the centered monovacancy based on the Numerov method.

The purpose of the work is to develop the procedure for calculating the electron wave functions, energy characteristics of a metal cluster, and to increase the stability of the simulation based on the Numerov method.

2. MODEL

When constructing the model (at the modeling stage), we assume that a simplest low-dimensional metal system is the spherical cluster of radius R_N . Then the problem of analyzing the energy characteristics of such system is reduced to the solution of the boundary value problem with the initial assumption about a rectangular finite depth potential well.

To calculate the characteristics, the formalism of DFT on the basis of the self-consistent Kohn-Sham method was used. The SJM is used as the model of the metal, in which the electron-electron, ion-ion and electron-ion interactions are averaged over the Wigner-Seitz cell volume, and therefore the energy characteristics of the metal are described "on average".

The solution of this problem is an iterative process of refining the effective one-electron potential, or the shape of a potential well, using the space distribution of electron density (profiles) as the variable. The numerical integration of the Schrödinger equation for the

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search of wave functions was carried out by the Numerov method. The initial approximation for the distribution of electron density has the form:

$$n(r) = \begin{cases} \bar{n}, & r \leq R_N, \\ 0, & r > R_N \end{cases} \quad (1)$$

The problem of the interaction of electrons with the ions can be greatly simplified under the condition of using the DFT in conjunction with the Kohn-Sham formalism. As a result, we have the simple conceptual cluster model, in which independent electrons move in some effective potential. Further simplifications of the model are possible if assumptions [9, 10] for the SJM [11] using LDA for the exchange and correlation energies [12].

The superconducting state of small nanoclusters is directly related to the phenomenon of pair correlation. Coupling of electrons leads to a strong modification of the energy spectrum. There is a hypothesis that transitions to the superconducting state occur in clusters whose electronic shells are completely filled [13, 14]. In filled spherical shells, the upper filled electron energy levels are strongly degenerate ("magic numbers" of atoms). The presence of even one vacancy in the cluster, as shown in [9, 10], may lead to changes in the magic numbers of atoms.

Thus, the problem of studying the energy characteristics of the cluster with the monovacancy appears. The models and simulation methods should provide the optimal combination of sufficient accuracy of the results amid reasonable simulation time (efficiency).

Mathematical emulation of physical objects consists of two stages: modeling and simulation. The main criterion for modeling quality is precision and algorithmic reliability (lack of algorithmic failures). The assumptions and simplifications, adopted at the modeling stage, are most affected to accuracy. However, even we have a sufficiently precise model, the results of the simulation may be totally inadequate due to the loss of stability. Thus, the chosen method of solving the equations obtained at the stage of modeling is important.

During the cluster model design, an assumption of its sphericity was made. To determine the effect of vacancy to the characteristics of the cluster, the characteristics of the spheres with the same number of atoms N at zero temperature were compared. In this case, the radii of defect-free spheres R_N and spheres with a monovacancy $R_{N,v}$ differ from each other:

$$\begin{aligned} R_N &= N^{1/3} r_0, \\ R_{N,v} &= (N+1)^{1/3} r_0, \end{aligned} \quad (2)$$

It is assumed here that the radius of an elementary Wigner-Seitz cell r_0 is equivalent to the radius of the single atom.

In the SJM, the vacancy is represented as a spherical cavity of radius r_0 in a homogeneous positively charged background, which is created by the ions of the cluster. The distribution of the positive charge of a cluster with a vacancy is described by the Heaviside step function:

$$\rho_v(r) = \bar{n} \theta(r - r_0) \theta(R_{N,v} - r). \quad (3)$$

Here we use the Hartree atomic units.

The total energy of the metal sphere is represented in the form of electron density functional $E_{N,v}[n(r)]$. The electrostatic potential profile $\phi_i(r)$ is determined by the Poisson equation [15] taking into account (3). Spherical symmetry allows us to divide the variables in the wave equation:

$$-\frac{1}{2} \nabla^2 \psi_i(r) + v_{\text{eff}}(r) \psi_i(r) = \varepsilon_i \psi_i(r).$$

In this case, the one-electron wave functions and energies are characterized by radial n_r and orbital l quantum numbers. The radii of clusters differ in accordance with definition (2) (see Fig. 1).

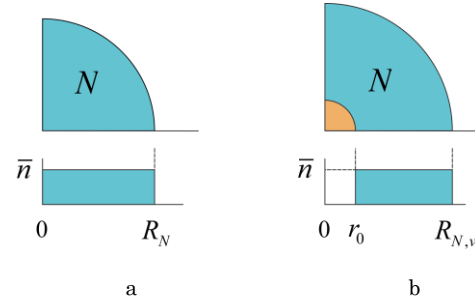


Fig. 1 – The spherical cluster model: without vacancies (a); with a vacancy (b)

The numerical integration of the wave equation was carried out by the Numerov method using the straightforward shooting method (ShM). Numerov method (also called as Cowell method) is a numerical method to solve ordinary differential equations of second order, in which the first-order term does not appear. It is a fourth-order linear multistep method [16].

The method is implicit, but can be made explicit if the differential equation is linear. For an implicit method, in its cycles, an algorithm for solving the resulting nonlinear algebraic equation is established, for example, by Newton method, half-division, etc. The concept of this method's application is to consistently approximate the solution by selecting the electron energy in a given interval, focusing on the boundary conditions for the solution of the wave equation.

By using the ShM method it is possible to transform the boundary value problem into a sequence of Cauchy problems, which are further solved by the Numerov method [17]. The ShM is one of the simplest numerical algorithms and its key idea is to replace a boundary condition problem with multiple trial runs of a simple initial condition task. This is also the most useful for solution of the time-independent Schrödinger equation if energy is the varied trial parameter. This method is simple, but may produce the sufficiently accurate results for the adopted spherical model of the cluster.

The Numerov method, in combination with the ShM, is the optimal choice for simulation, given the economy of machine time (time saving is the main criterion). However, the Numerov method has problems with stability [18], which is due to the complex exponential nature of wave functions.

Consequently, the task is to develop additional facili-

ties to ensure the stability of the computational algorithm, and therefore to obtain a reliable result.

3. METHOD

To conduct model experiment, the simulation technique was developed that consists of a sequence of tasks described as subroutines.

3.1 The Main Sequence of Calculation

Fig. 2 shows the general sequence of the DFT calculation, which consists of the following blocks.

Start – the program starts, with the startup parameters given through the command line.

Initialization – routine initialization of the system, setting it in the initial state/condition, the first approximation, suitable for further calculation.

Main loop – is the main loop, which is the iterative process of finding the stable state of the system.

The loop has 2 exit conditions:

1) number of iterations exceeds 1200;

2) when cumulative profile's change approaches to the adopted computational errors (provides the maximum accuracy).

Finding eigenvalues – the routine for finding all possible electron energy terms in the current form of a potential well and the wave functions corresponding to these states.

Finding electron density – the subroutine that distributes electrons to energy levels based on the principle of minimum energy of the system and the Pauli one. Then, by this distribution and by the form of the wave function, which corresponds to these electrons, the electron density profile is calculated as

$$n_e(r) = \sum_{i=1}^{N_e} |\Psi_i(r)|^2. \quad (4)$$

Finding potential is the subroutine for finding an effective one-electron potential consisting of the electrostatic and the exchange-correlation potentials. It uses the current electron density profile and the previously obtained electrostatic one.

Incrementing iteration counter (n) – increases by 1 the current value of the cycle counter.

Calculate the difference between old and new δV_{eff} – calculates the difference between the previous and current values of the effective potential as the sum of the modulus of their differences at each point.

Modification coefficients – conditional modification of coefficients that determine the contribution of the previous and current electrostatic potentials to the resulting one. This technique is implemented to ensure the stability of the simulation.

Data output – calculation of full energies and saving of calculation results. In more detail, the most meaningful routines are discussed below.

When iteration process is over, the exchange-correlation energy

$$E_{xc}[n] = -\frac{0.1423}{1 + \frac{c_1}{\sqrt[6]{n(r)}} + \frac{c_2}{\sqrt[3]{n(r)}}} - \frac{3}{4\pi} \sqrt[3]{3\pi^2 n(r)}, \quad (5)$$

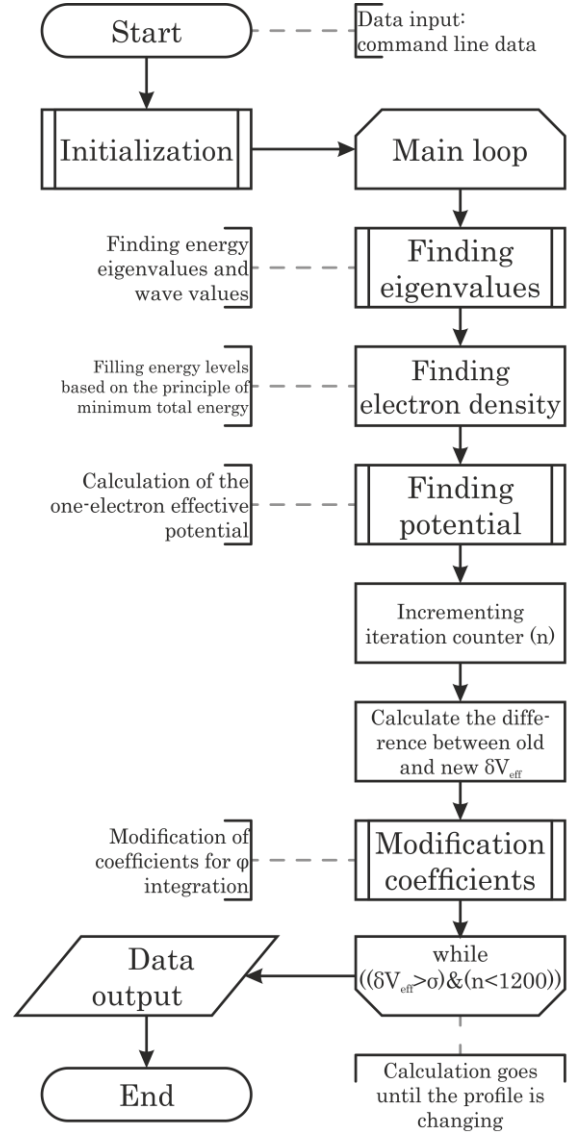


Fig. 2 – The calculation scheme of the parameters of the spherical metal cluster by DFT

and the total energy of the cluster

$$E_N = T_s + \frac{1}{2} \int d^3r \phi(r)[n(r) - \rho(r)] + \int d^3r n(r) \varepsilon_{xc}(r) - \Delta \bar{\varepsilon} \int d^3r \rho(r) + \langle \delta v \rangle_{WS} \int d^3r \theta(R_N - r) n(r) \quad (6)$$

is calculated. Here, c_1 and c_2 are parameters; the kinetic energy of non-interacting electrons T_s was taken into account in the form

$$T_s = \sum_{i=1}^{N_e} \varepsilon_i - \int d^3r n(r) v_{eff}(r),$$

and the last two terms in (6) take into account the structure of the ion subsystem, as well as the electron-ion interaction in the form of the Ashcroft pseudopotential. Here, the stabilization correction $\langle \delta v \rangle_{WS}$ is calculated by the formula:

$$\langle \delta v \rangle_{\text{WS}} = \frac{\left(\frac{9\pi}{4}\right)^{\frac{2}{3}}}{5r_s^2} - \frac{\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}}{4r_s} - \frac{0.1423r_s}{3} \frac{\left(\frac{1.0529}{2\sqrt{r_s}} + 0.3334\right)}{\left(1 + 1.0529\sqrt{r_s} + 0.3334r_s\right)^2}.$$

To save the results, two text files were used, the first one – to save the distributions, profiles and wave functions that correspond to the final state of the system, and the second – to save the energy characteristics of the system, the energy eigenvalues and their quantum numbers, including.

End – the completion of the main program cycle.

3.2 Headers and Footers

The main loop is based on the previous system state, which is defined by initialization.

The sequence of initialization consists of blocks:

Initialization Start is the beginning of the procedure. Initial filling datasets are the code area responsible for initial filling of data arrays and initial initialization of variables.

Task first approximation V_{eff} – to obtain the initial state of the system; one iteration of finding the effective potential by the formula (7) with the initial parameters (1) is executed. Finding eigenvalues – for finding eigenvalues (see Fig. 3); Finding electron density – finding the electron density profile; Finding potential – finding a potential profile (see Fig. 5).

At first, the one-electron effective potential is calculated by the formula:

$$v_{\text{eff}}(r) = \begin{cases} \langle \delta v \rangle_{\text{WS}} + \bar{v}_{\text{xc}} - A, & r \leq R_N \\ 0, & r > R_N \end{cases}, \quad (7)$$

where $A = 4$ and 16 eV for Na and Al, respectively.

Here, an exchange-correlation potential contribution

$$v_{\text{xc}} = -\sqrt[3]{\frac{3\bar{n}}{\pi}} - \frac{0.1423}{u} \left(1 + \frac{1}{u} \left(\frac{c_1}{6\sqrt[6]{\bar{n}}} + \frac{c_2}{3\sqrt[3]{\bar{n}}} \right) \right),$$

where the SJM parameters

$$u = 1 + \frac{c_1}{\sqrt[6]{\bar{n}}} + \frac{c_2}{\sqrt[3]{\bar{n}}}, c_1 = 1.0529\sqrt[6]{\frac{3}{4\pi}}, c_2 = 0.3334\sqrt[3]{\frac{3}{4\pi}}.$$

Setting to zero iteration counter is responsible for resetting the main loop variable. Initialization End – completion of the initialization procedure.

3.3 Finding Eigenvalues

This subroutine, by solving the wave equation by the Numerov method, finds in the potential well of the cluster all possible energy levels (eigenvalues) and wave functions which correspond to them, and then stores these data together with the corresponding quantum numbers. It is depicted in Fig. 3.

Blocks of subroutine are:

Initialization energy interval – this block determines the energy interval and generates the table of energy values in interval with the given step.

Loop for l – on each iteration of the cycle, the energy eigenvalues are performed for orbital quantum number l . The cycle finished when no eigenvalue was found for the last value l .

Finding intervals – the calculation of wave functions is carried out by the obtained grid of energies and in another array the found values at the last point can be saved. After viewing this array, the intervals at which zero crossing occurs, were obtained.

Loop for n – the real energy eigenvalue and the wave function on each iteration of the cycle are calculated in the corresponding interval, marked in the Finding intervals block. The cycle finished when all the eigenvalues in a potential well are considered for a given orbital quantum number. The serial number of eigenvalues for a given orbital quantum number is the main quantum number.

Finding eigenvalues – finding by the ShM [19] the specific eigenvalue of the energy level and the left part of the wave function (Fig. 4).

Due to the fact of an accumulated error the full wave function cannot be straightforwardly obtained, as the result, the computational process loses stability.

When solving the equation in the direction of increasing distance from the center of the cluster we have $\lim_{r \rightarrow \infty} \psi(r) \rightarrow \pm\infty$ (function Ψ_1 in Fig. 4, upper graph).

Similarly, when moving to the center of the cluster we have $\lim_{r \rightarrow 0} \psi(r) \rightarrow \pm\infty$ (dotted line of dependence Ψ_2 in Fig. 4, upper graph).

Since the second boundary condition for the solution of the wave equation is $\lim_{r \rightarrow \infty} \psi(r) \rightarrow 0$, then when we search for the eigenvalue by the ShM, we can focus not on the value of the wave function, but only on its sign. Thus, the calculation of the eigenvalue and part of the wave function, which is localized in the cluster and around it, is carried out with maximum accuracy.

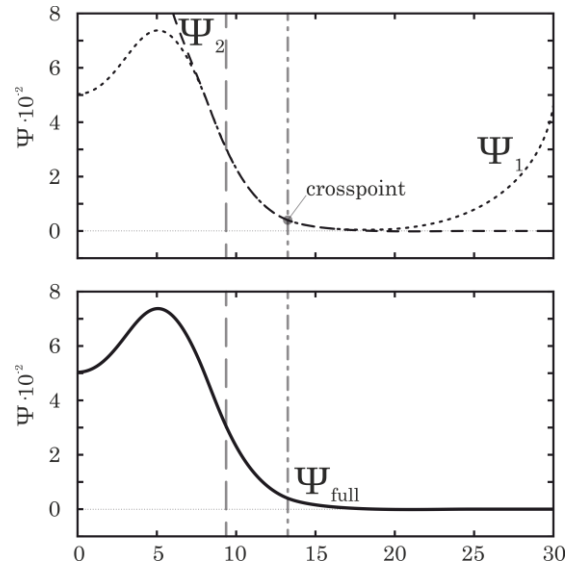


Fig. 4 – Loss of simulation stability and functions linking

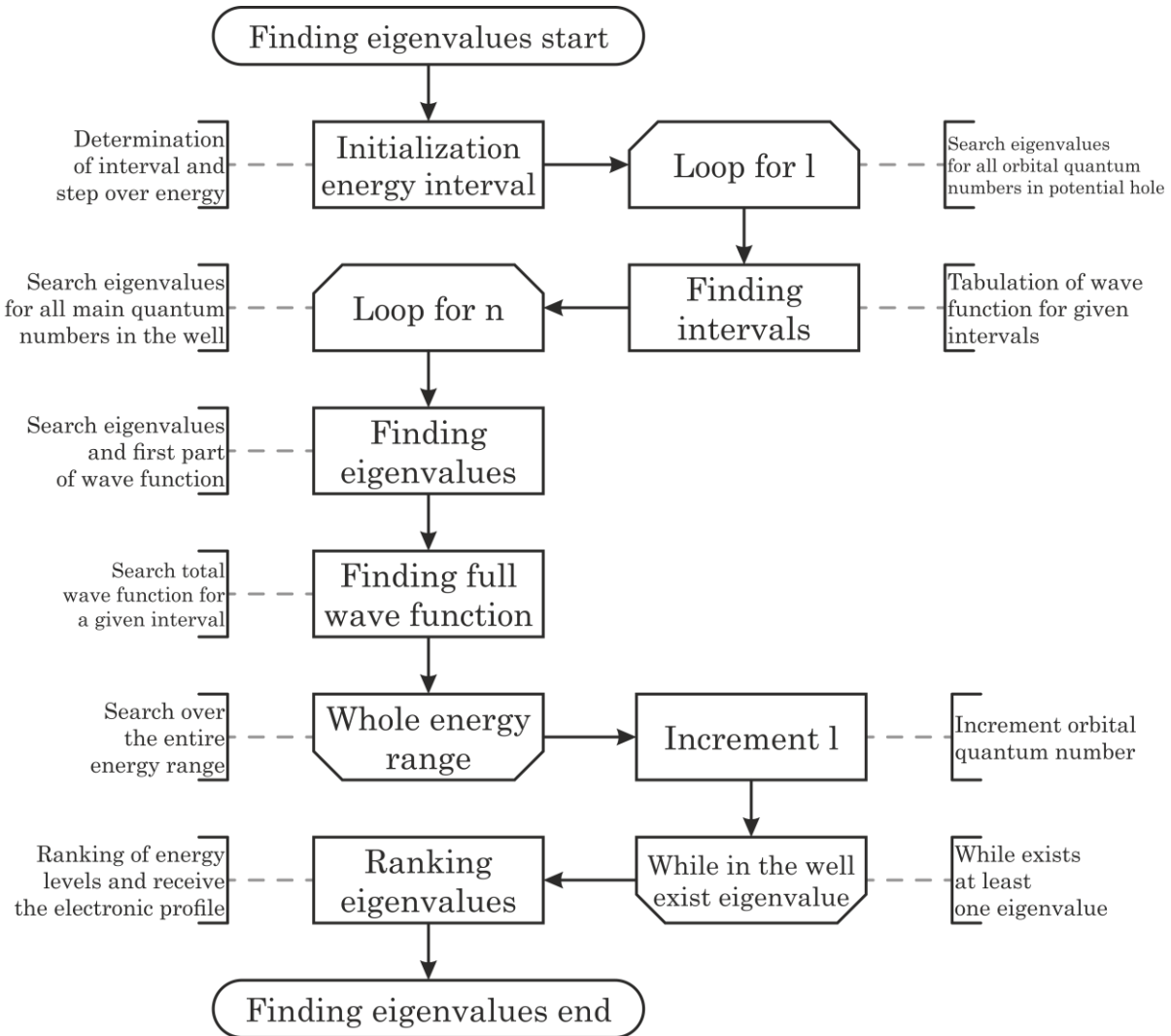


Fig. 3 – The subroutine to find the energy levels in a potential well

Finding full wave function – to find the full wave function, the real eigenvalue and part of the wave function found in the previous Finding eigenvalues block are used. Then, the calculation of the wave function from the last point to $r = R + 0.5r_0$ is continued. Near the point where the derivatives of both parts of the functions are equal to each other (Fig. 4, "Cross-point" on the upper graph), the linking of the left and right parts of functions is performed.

So, the total wave function consists of two parts, the first is calculated from the center of cluster, the second is calculated from the point "vacuum", with the same values of the orbital quantum number and energy. The results are loaded into separate arrays. At an empirically determined point, the results are linked.

Since the values of functions at the point of cross-linking may differ, due to the absence of normalization, it is necessary to bring them to one level, by multiplying one of the parts on the corresponding coefficient. The result is recorded in the new array, and then the normalization of the entire function is performed in accordance with the condition $\int |\Psi|^2 dr^3 = 1$. Calculations were made in the atomic system of the Hartree units ($e = m = \hbar = 1$).

Step Δr in the cluster bulk equals $0.002a_0$ approximately. However, using this step across the entire r -axis $r = R_N + 900a_0$, leads to a significant increase of computer memory and calculation time. Outside the cluster, the wave function varies quite slowly, so it is advisable to increase the sampling step there. Immediately outside the cluster it doubles and then, at $r = 250$, it is doubled again and at $r = 550$ it increases by 8 times. Using this technique we can to increase significantly the speed of computing while maintaining accuracy.

Increment l – repetition of the cycle for the next l .

Ranking eigenvalues – ranking of eigenvalues and corresponding wave functions with increasing energy.

3.4 Finding Potentials

The one-electron potential is determined by the sum of the electrostatic, exchange-correlation and stabilized components:

$$v_{\text{eff}}(r) = \phi(r) + v_{\text{xc}}(r) + \langle \delta v \rangle_{\text{WS}} \theta(R_{N,\sigma} - r),$$

where the first and second terms depend on the electron density profile.

Due to the fluctuations of the calculated profile, the

stability of the simulation may be very low. To ensure the stability of the simulation, several techniques have been proposed, as described in Fig. 5. Subroutine for potential profiles finding is the following:

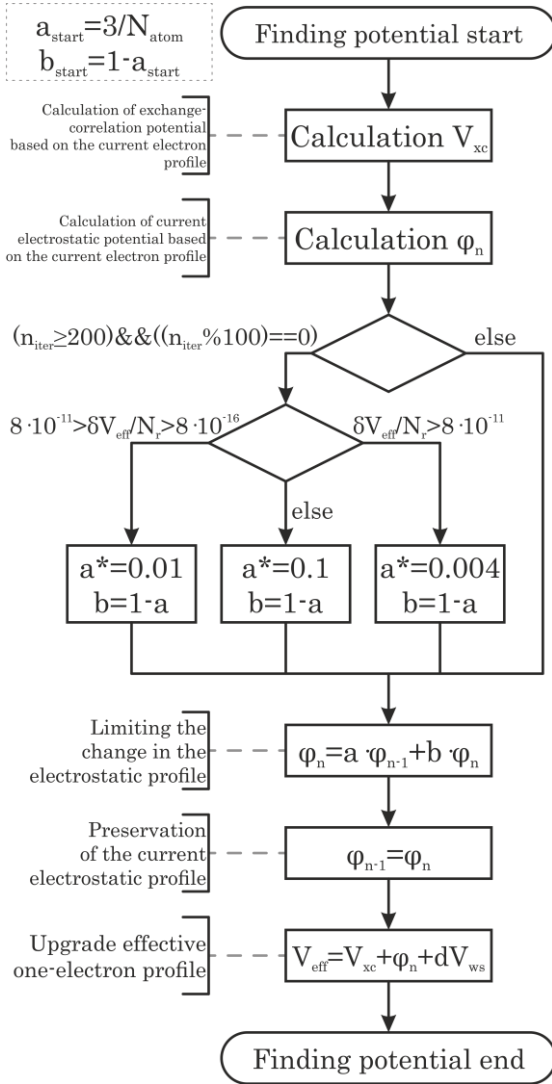


Fig. 5 – Subroutine for potential profiles finding

Calculation of exchange-correlation potential $v_{xc}(r)$ is based on the known electron density profile. An electrostatic potential was obtained from the Poisson equation under boundary [10]:

$$\phi(r) = 4\pi \left\{ \frac{1}{r} \int_0^r dr' r'^2 [n(r') - \rho(r')] + \int_r^\infty dr' r' [n(r') - \rho(r')] \right\}.$$

In order to ensure the convergence of the iterative process, the artificial limitation of electrostatic potential change has been proposed. It is done by the expression:

$$\phi_n(r) = a\phi_{n-1}(r) + b\phi(r), \quad (9)$$

where a and b are the weight coefficients, $a + b = 1$.

For small clusters ($N < 10$), the initial values of a and b are empirically chosen equal to 0.7 and 0.3, respectively. In other cases, $b = 3/N$ is used. However, as the number of iterations increases, and if it exceeds 200, the selection of b requires a modification, which is

shown in the corresponding part of the subroutine of finding the potential profiles shown in Fig. 5.

The limit value $\eta \equiv \Delta v_{eff} / \Delta r$ for change of the total profile $v_{eff}(r)$ becomes comparable to the numerical error of the calculation. The critical value $\eta_{cr} \approx 8 \cdot 10^{-19}$ a.u. was empirically determined. Thus, η_{cr} describes the maximum accuracy of the profile calculation for the selected data type (80-bit, *longdouble*, accuracy 19-20 characters after the floating point).

Finally, the method of determining the coefficient b for expression (9) on each 100-th iteration is:

$$\begin{cases} b = b / 250, \eta > 8 \cdot 10^{-11}, \\ b = b / 100, 8 \cdot 10^{-11} \geq \eta > 8 \cdot 10^{-16} \\ b = b / 10, \eta \leq 8 \cdot 10^{-16} \end{cases}$$

The block diagram of this technology is also shown in Fig. 5.

4. RESULTS AND DISCUSSION

Part of the results, namely the calculated electron density $n(r)$ and effective potential $v_{eff}(r)$ profiles for charged and neutral free-defect clusters (solid lines) and clusters with the vacancy (dashed lines) for the purpose of illustration is shown in Fig. 6, where: 1 – negatively charged, 2 – neutral, 3 – positively charged cluster. Cluster of Na contains $N = 12$ atoms.

Despite the fact that electronic distributions are rapidly decreasing (it can be seen from Fig. 6), the tail potentials reach far enough (the calculation was made approximately to $r = R_N + 900a_0$). Using the calculated profiles, the total energy of the cluster and then its characteristics can be obtained [10].

In [1], the results of ab initio calculations for neutral clusters $Na_N = 55, 147, 309$, the optimal form of which is the icosahedron, were reported about. The numbers $N = 55, 147$, and 309 correspond to 2-, 3-, and 4-atom layers of defect-free clusters. It was also shown that the monovacancy formation energy in a cluster essentially depends on the place of the vacancy creation and on the final position of the displaced atom.

The values are in good agreement. In order to demonstrate the dependence of vacancy position for $N = 147$, two values are given: 0.43/0.63 eV, which correspond to the displacement of an atom from the center/from the first atomic shell of the icosahedron to a flat section of its surface.

Table 1 presents the vacancy formation energies $\epsilon_{N,v}^{vac,Sh}$ for comparison. Although the comparison of the values of $\epsilon_{N,v}^{vac,Sh}$ shows a difference of about 0.4-0.5 eV, the size dependence of ab initio calculations of [1] is reproduced in our simple model.

Table 1 – Comparison of energy vacancy formation

No	$\epsilon_{N,v}^{vac,Sh}$, eV		$\epsilon_{N,v}^{vac,blow}$, eV	
	Present	[1]	Present	[1]
55	1.80	1.35	0.49	0.49
147	1.58	1.18	0.66	0.63

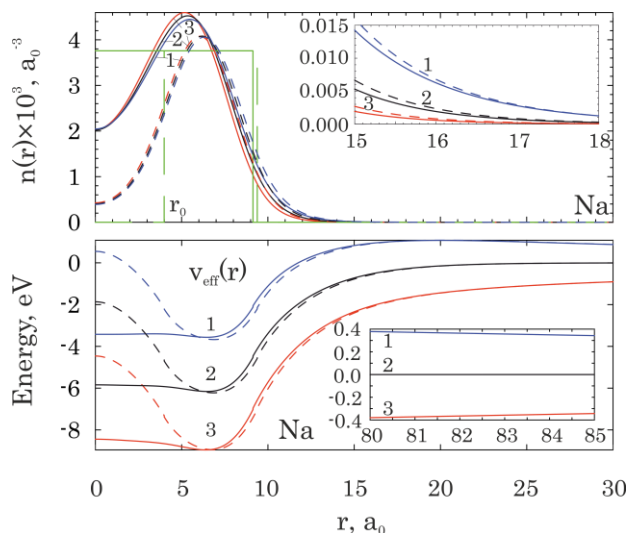


Fig. 6 – Profiles of electron distribution and effective potential for charged and neutral clusters of Na_{12}

Depending on the number of atoms in the cluster, the calculation of its characteristics can last from 3 to 28 hours on the Intel Xeon 5345 2.2 GHz processor. So, in order to calculate the energy characteristics of neutral, positively and negatively charged clusters with and without the vacancy, consisting of different numbers of atoms, it was decided to use a supercomputer SCIC-3 of the Institute of Cybernetics National Academy of Sciences of Ukraine ($R_{\text{peak}} = 7.4$ Tflops).

As the research in SCIC-3 has shown, parallel simulation is hard to organize, but it can be distributed according the calculation flows for clusters with different parameters (charge, availability of vacancies). Therefore, the program was supplemented with MPI [20] procedures, but their functions were limited by the

distribution of calculations flows for clusters with different parameters (for one metal).

The problem of obtaining the energy characteristics of metallic nanoclusters with the vacancy by mathematical modeling is solved in this work.

The scientific novelty. The simulation method on the basis of "two-sided" solution of the boundary value problem by ShM and Numerov method is proposed, taking into account limitation of the electrostatic potential change, which ensures the absence of algorithmic failures and allows to increase the efficiency of simulation. This allowed for the first time to obtain the total energy of neutral and charged defective clusters, on the basis of which direct calculations of dissociation, cohesion, vacancy formation energies, electron affinity, ionization potential, and electric capacitance were made. The simulation results are in good agreement with similar calculations and experiments for defect-free clusters.

The practical significance of obtained results is the automation of calculations of low-dimensional metal system energy characteristics, both charged and neutral. Prospects for further research: calculation of the parameters of low-dimensional metal systems of arbitrary geometry and topology of clusters.

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Моделювання сферичних металевих нанокластерів, що містять моновакансію

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Метою даної роботи було підвищення стійкості симуляції на основі методу Нумерова при розрахунку хвильових функцій електронів в металевому кластері та забезпечення стабільності самоузгоджених розрахунків енергетичних характеристик металевих кластерів, шляхом обмеження зміни електростатичного потенціалу. Об'єктом дослідження є методика розрахунку хвильових функцій електронів методом Нумерова та знаходження власних значень енергетичних рівнів методом пристрілки. На етапі моделювання, з метою підвищення ефективності моделі було використано метод функціоналу густини (DFT) у поєднанні з формалізмом Кона-Шема, що дозволило спростити складну задачу про взаємодію електронів в полі заряджених іонів та отримати модель, в якій незалежні електрони рухаються в деякому ефективному потенціалі. Для розрахунку обмінних і кореляційних енергій ми використовували модель стабільного желе (SJM) та наближення локальної густини (LDA). Зміна обмеження профілю електростатичного потенціалу здійснювалася шляхом введення коефіцієнтів, що визначають внески попереднього та поточного профілів електростатичного потенціалу до результуючого. Розроблено модель металевого кластера із центрованою моновакансією та методику для розрахунку його параметрів. Для забезпечення збіжності та стійкості методу Нумерова запропоновано методику двостороннього обчислення з "зшиванням" хвильової функції в емпірично обраній точці. Розроблено методику симуляції з оптимальним кроком, яку реалізовано в програмному коді для розрахунку енергетичних характеристик металевих нанокластерів, що містять моновакансії. Моделювання дозволило отримати профілі електронної густини та ефективного потенціалу для заряджених та нейтральних кластерів. Результати розрахунків порівнювалися з даними експерименту, а також із *ab initio* обчисленнями. Розроблені підходи та методики моделювання можуть бути рекомендовані для аналізу низькорозмірних металевих систем, систем із шаруватою структурою в тому числі.

Ключові слова: Металеві кластери, Енергетичні характеристики, Метод функціоналу густини, Хвильова функція, Метод Нумерова, "Зшивання" функцій, Стійкість моделювання.