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About One Method of Numerical Solution of Schrodinger's Equation

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Abstract—The paper considers the method of the numerical solution of the Schrodinger equation, which can partly be attributed to the class of Monte Carlo methods. The method is presented and simultaneously illustrated by the examples of solving the one-dimensional and multidimensional Schrodinger equation in the problems of a linear one-dimensional oscillator, hydrogen atom, and benzene atom.

Keywords: Schrodinger equation, numerical methods, Monte Carlo method

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1. INTRODUCTION

In [1], attention was drawn to the fact that the solution of the Schrödinger equation, which describes the dynamics of most of the interesting quantum systems, cannot be obtained constructively due to the large dimension of the wave function. Indeed, if the quantum system includes n particles (hereinafter, the particle spin is not taken into account), then the wave function ψ will depend on $(1 + 3n)$ arguments, i.e., $\psi = \psi(t, \mathbf{r}_1, \ldots, \mathbf{r}_N)$, where t is time $\mathbf{r}_1$, ..., $\mathbf{r}_N$ of the radius vector of the position of the particles in three-dimensional space. In quantum chemistry [2], in the quantum Monte Carlo method [3], this problem is solved in different ways. We note a group of variational methods and approaches, starting with the classical Hartree-Fock method [4] and subsequent variations and modernizations of the density functional method type [5].

In this paper, we consider a method for solving the Schrödinger equation, which will overcome the indicated non-constructivity. The method is based on the idea of representing the set of quantum particles of an arbitrary molecule in the form of a finite set of subparticles (subunits). In terms of positioning a set of subparticles in a space of dimension $3n$ a specially prepared random procedure is applied, the repeated application of which allows reconstructing the distribution of the average positions of the quantum particles of a molecule in ordinary three-dimensional space. The proposed numerical method is efficient and economical in terms of calculations and can be assigned to the class of Monte Carlo methods.

2. ONE QUANTUM PARTICLE

We write the Schrödinger equation for one quantum particle in the one-dimensional case, i.e.,

$$i\hbar\psi_t = -\frac{\hbar^2}{2m}\psi_{xx} + U\psi, \tag{1}$$

where $\hbar$ is the Planck constant, $\psi_t = \partial\psi/\partial t, \psi_{xx} = \partial^2\psi/\partial x^2$, x is a spatial variable, $U = U(t, x)$ is the potential, m is the mass of a quantum particle, and $i^2 = -1$.

We substitute in (1) the wave function in the form of a decomposition into real and imaginary components, i.e., $\psi(t, x) = u(t, x) + iv(t, x)$; then

$$\begin{cases} \hbar u_t = -\dfrac{\hbar^2}{2m} v_{xx} + Uv \\ -\hbar v_t = -\dfrac{\hbar^2}{2m} u_{xx} + Uu. \end{cases} \tag{2}$$

We represent the initial quantum particle as the set of N subparticles. Let each of the subparticles have a corresponding positioning in space, $x_i, i = 1,\ldots,N$. One of the important aspects of the considered numerical method is the method of replacing the second spatial derivatives in system (2) with the following expressions:

$$u_{xx} \to -\sum_{j=1, j\neq i}^{N} g_{i,j} u_{i,j}, \quad v_{xx} \to -\sum_{j=1, j\neq i}^{N} g_{i,j} v_{i,j}, \tag{3}$$

where $u_{i,j} = u_i - u_j$, $v_{i,j} = v_i - v_j$, and $g_{i,j}$, $i, j = 1,\ldots,N$ is a matrix.

We rewrite the system of equations (2), taking into account substitutions (3); then

$$\begin{cases} \dot{u}_i = \dfrac{\hbar}{2m} \displaystyle\sum_{j=1, j\neq i}^{N} g_{i,j} v_{i,j} + \dfrac{1}{\hbar} U_i v_i \\ \dot{v}_i = -\dfrac{\hbar}{2m} \displaystyle\sum_{j=1, j\neq i}^{N} g_{i,j} u_{i,j} - \dfrac{1}{\hbar} U_i u_i, \end{cases} \tag{4}$$

where the dot denotes the time derivative and $U_i = U(t, x_i)$, $i = 1,\ldots,N$. It is easy to see that to save the probability in the format $\sum_{i=1}^{N} (u_i^2 + v_i^2) = \text{const} = 1$ in the system of equations (4), it suffices to assume the symmetry of the matrix g, i.e., require the condition $g_{i,j} = g_{j,i}$, $i, j = 1, \ldots, N$ to exist. To select the type of matrix g, we compare the solution of the Schrödinger equation in format (4) with the finite-difference representation of Eq. (1).

Let some scale of length L_0 that allows us to enter a characteristic time equal to $mL_0^2/\hbar$ and carry out the non-dimensionalization of Eq. (1) be defined. We consider further that the spatial variable x varies in the range $[-L, L]$, and the value L is expressed in units of L_0.

We introduce a uniform grid $x_i = -L + h(i-1)$, $i = 1,\ldots,N$, where $h = 2L/(N-1)$ is the grid step. Using the finite-difference three-point approximation pattern of the second derivative with respect to space, in dimensionless form, Eq. (1) without potential can be rewritten in the form

$$i\dot{\psi}_i = -\frac{1}{2} \frac{\psi_{i+1} - 2\psi_i + \psi_{i-1}}{h^2}, \quad i = 2,\ldots,N-1. \tag{5}$$

From the system of equations (5), it follows that as the matrix g we should choose a symmetric matrix with non-negative elements of the form

$$g_{i,j} = \begin{cases} h^{-2}, & |i-j| = 1 \\ 0, & |i-j| \neq 1. \end{cases} \tag{6}$$

The finite-difference version of the solution of the Schrödinger equation (5) does not suit us for two reasons: (1) it is necessary to determine the boundary conditions, which is not very important when solving the Schrödinger equation in the context of quantum-mechanical problems; and (2) the finite-difference method of type (5) has no obvious prospect of generalization to the multidimensional case. Matrix (6) describing the finite-difference scheme (5) has a special form, from which it follows that the elements of the matrix far from the main diagonal are zero. Taking into account the last remark, we consider the generalized representation for the matrix g of the type

$$g_{i,j} = \begin{cases} \rho_1 h^{-2} \exp(-\rho_2 |i-j|), & i \neq j \\ 0, & i = j, \end{cases} \tag{7}$$

where ρ_1 and ρ_2 are nonnegative parameters. In (7), in comparison with (6), it is considered that the elements of the matrix decay exponentially with distance from the main diagonal. Moreover, representation (7) does not have a direct link to the finite-difference scheme (5).

We rewrite the system of equations (4) in dimensionless form and in the absence of potential; then,

$$\begin{cases} \dot{u}_i = \frac{1}{2}\sum_j g_{i,j}v_{i,j} \\ \dot{v}_i = -\frac{1}{2}\sum_j g_{i,j}u_{i,j}. \end{cases} \tag{8}$$

We introduce a column vector $y = (u_1,\ldots,u_N,v_1,\ldots,v_N)^T$ and the block matrix $G = \begin{vmatrix} 0(N\times N) & \frac{1}{2}(g_2 - g) \\ -\frac{1}{2}(g_2 - g) & 0(N\times N) \end{vmatrix}$, where g is matrix (7), and matrix g_2 is diagonal, with the sum on the diagonal $g_{2,i,i} = \sum_{j,j\neq i} g_{i,j}$, $i = 1,\ldots,N$. Note that the vector of unknowns y has dimension $2N$, and the matrix G has a size of $2N \times 2N$. Taking the vector y and matrices G into account, the system of equations (8) can be rewritten in the following compact form:

$$\dot{y} = Gy. \tag{9}$$

Let us compare the solutions of Eqs. (5) and (9). To do this, substitute in (5) a solution in the form $\psi_i = \frac{1}{\sqrt{2L}}\exp(i(-\omega t - kx_i))$. We impose periodic boundary conditions $\psi_1 = \frac{1}{\sqrt{2L}}\exp(i(-\omega t - kL)) = \psi_N = \frac{1}{\sqrt{2L}}\exp(i(-\omega t + kL))$. Then we find $k = \pi l/L$, $l = 0,\pm1,\pm2,\ldots$, and after substituting in (5), we obtain the expression for the energy

$$\omega_l = \frac{1}{h^2}\left[1 - \cos\left(\frac{\pi h}{L}l\right)\right],\quad l = 0,\pm1,\pm2,\ldots\,. \tag{10}$$

Similarly, we consider the solution of the system of equations (9) with matrix (7). To do this, we present the solution of Eq. (9) in the form $y = \exp(i\Omega t)$, where z is some constant column vector of dimension $(2N \times 1)$. In this case, the value $i\Omega$ acts as an eigenvalue of matrix G. In general, there are 2 such eigenvalues N. It is easy to see that the search for the eigenvalues of matrix G comes down to solving the equation

$$\det\left\|\frac{1}{2}(g_2 - g) \pm \Omega e_N\right\| = 0, \tag{11}$$

where e_N is the identity matrix of size $N \times N$. We write the solutions of Eq. (11) as the set $\pm\Omega_1,\ldots,\pm\Omega_N$. Choose the top plus sign. In this case, we obtain the set of frequencies $\Omega_1,\ldots,\Omega_N$, which can be compared with set (10), when $l = 0, \ldots, N-1$.

Let us verify that the energy spectra of the finite-difference problem (5), (10) and the studied scheme (9), (11) in the form of a pair of sets $\omega_0,\ldots,\omega_{N-1}$ and $\Omega_1,\ldots,\Omega_N$ can be made close to each other. To ensure proximity, we select the appropriate parameter values h and L entering into Eq. (10). We call these values approximating and denote h_{app} and L_{app}. From these values, we can also find the number of nodes N_{app} of a finite-difference scheme of format (5), which is equivalent to our numerical scheme in terms of the maximum proximity of the spectra. We find options h_{app} and L_{app} by comparing the spectra, i.e., by minimizing the final error of the comparison of the form

$$S = S(a,b) = \sum_{i=1}^{N}\{a - a\cos[b(i-1)] - \Omega_i\}^2. \tag{12}$$

Let function (12) reach the minimum when $a = a_{\text{opt}}$ and $b = b_{\text{opt}}$, then, taking into account (10), we find $h_{\text{app}} = \frac{1}{\sqrt{a_{\text{opt}}}}$, $L_{\text{app}} = \frac{\pi}{b_{\text{opt}}\sqrt{a_{\text{opt}}}}$, and $N_{\text{app}} = 1 + \frac{2L_{\text{app}}}{h_{\text{app}}}$. Figure 1 shows two graphs of the spectral decompositions of a pair of schemes studied and finite-difference, obtained for $N = 10$ (Fig. 1a) and $N = 100$ (Fig. 1b), respectively. The spectra of the finite-difference and studied schemes are indicated by the solid line and the discrete set of markers in the form of stars, respectively. Note that the proximity of the spectra strongly depends on coefficients ρ_1 and ρ_2. In the calculations, the results of which are shown in Fig. 1, the optimal values of the coefficients were found: $\rho_{1,\text{opt}} = 25, \rho_{2,\text{opt}} = 5$.

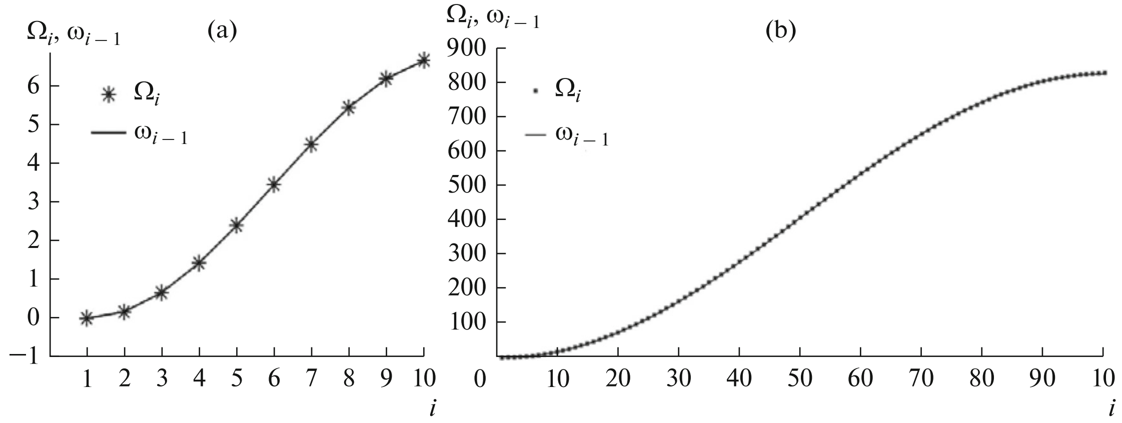

Fig. 1. (a) Comparison of the spectra of the studied and finite-difference schemes for $N = 10$. (b) Comparison of the spectra of the studied and finite-difference schemes for $N = 10^2$.

Note that similar constructions can be carried out for one quantum particle in space, and the corresponding Laplacian $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is replaced by amounts analogous to (3).

3. LINEAR OSCILLATOR IN THE ONE-DIMENSIONAL CASE

We write the potential function of the one-dimensional oscillator in the form $U(x) = \frac{1}{2}m\omega^2 x^2$, where ω is the oscillation frequency of the oscillator. Introducing characteristic values of time and length ω^{-1} and $(\hbar/m\omega)^{1/2}$, we rewrite the corresponding Schrödinger equation in dimensionless form:

$$\begin{cases} u_t = -\frac{1}{2}v_{xx} + \frac{1}{2}x^2 v \\ v_t = \frac{1}{2}u_{xx} - \frac{1}{2}x^2 u. \end{cases} \tag{13}$$

We choose some interval $[-L, L]$ of integration over the space of the system of equations (13). Define on this interval in general an uneven grid with nodes: $-L = x_1 < x_2 < \ldots < x_{N-1} < x_N = L$. We rewrite Eqs. (13) in the form

$$\begin{cases} \dot{u}_i = \frac{1}{2}\sum\limits_{j=1, j\neq i}^{N} g_{i,j}v_{i,j} + \frac{1}{2}x_i^2 v_i \\ \dot{v}_i = -\frac{1}{2}\sum\limits_{j=1, j\neq i}^{N} g_{i,j}u_{i,j} - \frac{1}{2}x_i^2 u_i, \end{cases} \tag{14}$$

where $i = 1, \ldots, N$. We take the expression for the matrix $g_{i,j}, i, j = 1, \ldots, N$ from (7).

If we enter the column vector $y = (u_1, \ldots, u_N, v_1, \ldots, v_N)^T$, then the system of equations (14) can be rewritten in a form similar to (9), where $G = \begin{vmatrix} 0 & Q \\ -Q & 0 \end{vmatrix}$, $Q = Q(N \times N) = \frac{1}{2}(g_2 - g)$, and $g_2 = \operatorname{diag}(\sum_{j=1, j\neq i}^{N} g_{i,j} + x_i^2)$ is a diagonal matrix of size $N \times N$.

We find solutions to the linear system of equations (9). To do this, we will seek a solution in the form $y = \exp(\delta t)z$, where z is some constant column vector of size $2N \times 1$. Let vector z consist of two subvectors $a = (a_1, \ldots, a_N)^T$ and $b = (b_1, \ldots, b_N)^T$, i.e., $z = \begin{vmatrix} a \\ b \end{vmatrix}$. We substitute the selected solution into Eq. (9); then we

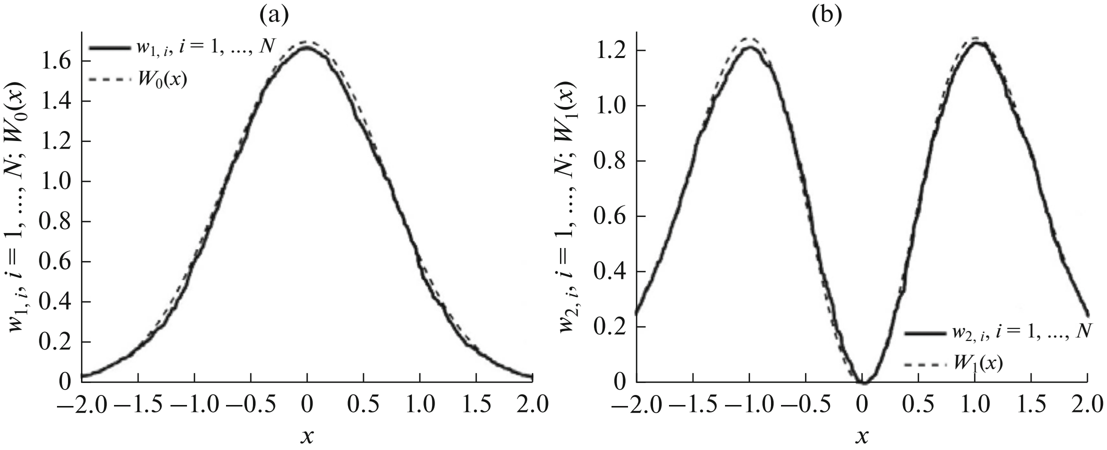

Fig. 2. (a) Comparison of the approximate distribution $w_{1,i}$, $i = 1, ..., N$, and exact distribution $W_0(x)$. (b) Comparison of the approximate distribution $w_{2,i}$, $i = 1, ..., N$, and exact distribution $W_1(x)$.

obtain the following problem for searching for eigenvalues (δ) and vectors (z) of matrix G: $\begin{vmatrix} 0 & Q \\ -Q & 0 \end{vmatrix} \times \begin{vmatrix} a \\ b \end{vmatrix} = \delta \begin{vmatrix} a \\ b \end{vmatrix}$. The last task is reduced to a simpler problem of finding eigenvalues (Ω) and vectors ($c(N \times 1)$) of matrix Q, i.e., $Qc = \Omega c$; at the same time,

$$\delta = \pm i\Omega, \quad \begin{vmatrix} a \\ b \end{vmatrix} = \begin{vmatrix} c \\ \pm ic \end{vmatrix}. \tag{15}$$

Choose some eigenvalue Ω and the corresponding eigenvector c and write down a valid partial solution $y_\Omega(t)$ of Eq. (9), i.e.,

$$y_\Omega = \begin{vmatrix} (C_1 \cos \Omega t + C_2 \sin \Omega t)c \\ (-C_1 \sin \Omega t + C_2 \cos \Omega t)c \end{vmatrix}, \tag{16}$$

where C_1 and C_2 are arbitrary real constants. Let us compare some approximate solutions (16) of the considered scheme with exact solutions for a quantum oscillator.

As is known [6], the energy of a quantum oscillator (in dimensionless form) is found by the formula $E_n = \frac{1}{2} + n,\ n = 0, 1, \ldots$. We write out the known first two exact wave functions:

$$\psi_0 = \frac{1}{\pi^{1/4}} \exp\left(-\frac{1}{2}it - \frac{1}{2}x^2\right), \quad \psi_1 = \frac{\sqrt{2}}{\pi^{1/4}} x \exp\left(-\frac{3}{2}it - \frac{1}{2}x^2\right). \tag{17}$$

Given (17), we find the probability densities $W_0 = \psi_0^* \psi_0$ and $W_1 = \psi_1^* \psi_1$ and compare them with the probability densities of the solutions of (16) for the first two eigenvalues Ω_1 and Ω_2. We denote the corresponding probability distributions constructed using solutions (16) in the form $w_{1,i},\ i = 1, \ldots, N$, and $w_{2,i},\ i = 1, \ldots, N$, for eigenvalues Ω_1 and Ω_2, respectively.

Figure 2 shows a comparison of the approximate (solid line) and exact solution (dashed line). Figure 2a compares the distribution densities $w_{1,i}, i = 1, \ldots, N$, and $W_0(x)$; and in Fig. 2b, $w_{2,i}, i = 1, \ldots, N$, and $W_1(x)$. In the calculations of approximate solutions, the following parameter values were used: $L = 2, N = 2 \times 10^3, h = 6/1999, \rho_1 = 25$, and $\rho_2 = 3.35$. Approximate solutions are constructed according to (16), the values of t, C_1, and C_2 were chosen randomly.

4. HYDROGEN ATOM

We construct an algorithm for calculating the dynamics of a pair of quantum particles, a proton, and an electron interacting according to the Coulomb law.

Let m_1 and m_2 be the masse of the proton and electron. We write the Schrödinger equation describing the dynamics of a hydrogen atom in the form

$$i\hbar\psi_t = -\frac{\hbar^2}{2m_1}\Delta_1\psi - \frac{\hbar^2}{2m_2}\Delta_2\psi - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi, \tag{18}$$

where $\psi = \psi(t, \mathbf{r}_1, \mathbf{r}_2)$ is the wave function of the hydrogen atom, $\mathbf{r}_1$ and $\mathbf{r}_2$ are the spatial positions of the proton and electron, respectively, and e is the magnitude of the charge. The Laplace operators for each of the quantum particles have the form

$$\Delta_1 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}, \quad \Delta_2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}.$$

We rewrite Eq. (18) in dimensionless form. To do this, we introduce the characteristic length, mass, and time: $r_\mathrm{B} = \hbar^2/(m_2e^2) \cong 5.2918 \times 10^{-9}$ cm (r_B is the Boron radius), $m_2 = 9.1093 \times 10^{-28}$ g, and $\hbar^3/(m_2e^4) = 2.4189 \times 10^{-17}$ sec; then,

$$i\psi_t = -\frac{\mu}{2}\Delta_1\psi - \frac{1}{2}\Delta_2\psi - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi, \tag{19}$$

where $\mu = m_2/m_1 = 5.4462 \times 10^{-4}$ is the ratio of the mass of the electron to the mass of the proton.

We change the variables in (19) $\mathbf{r}_1 \to \sqrt{\mu}\mathbf{r}_1$ and we pass to the real and imaginary parts of the wave function by representing $\psi = u + iv$; then Eq. (19) can be rewritten in the form

$$\begin{cases} u_t = -\dfrac{1}{2}\Delta v - \dfrac{1}{|\sqrt{\mu}\mathbf{r}_1 - \mathbf{r}_2|}v \\ v_t = \dfrac{1}{2}\Delta u + \dfrac{1}{|\sqrt{\mu}\mathbf{r}_1 - \mathbf{r}_2|}u, \end{cases} \tag{20}$$

where $\Delta = \Delta_1 + \Delta_2$ is the single Laplace operator for a pair of quantum particles.

Define N points with coordinates $\mathbf{r}_i = (\mathbf{r}_{1,i}, \mathbf{r}_{2,i})$, $i = 1, \ldots, N$. The selected points have six coordinates, the first three of which characterize the first quantum particle, and the second three characterize the second quantum particle. Following the previous sections in the development of the numerical algorithm, we replace the Laplace operators in the system of equations (20) with the expressions

$$\Delta u \to -\sum_{j=1, j\neq i}^{N} g_{i,j}u_{i,j}, \quad u_{i,j} = u_i - u_j, \quad \Delta v \to -\sum_{j=1, j\neq i}^{N} g_{i,j}v_{i,j}, \quad v_{i,j} = v_i - v_j.$$

After these substitutions, the system of equations (20) is rewritten in the form of a system of linear ordinary differential equations of the form

$$\begin{cases} \dot{u}_i = \dfrac{1}{2}\displaystyle\sum_{j=1, j\neq i}^{N} g_{i,j}v_{i,j} - \dfrac{v_i}{|\sqrt{\mu}\mathbf{r}_{1,i} - \mathbf{r}_{2,i}|} \\ \dot{v}_i = -\dfrac{1}{2}\displaystyle\sum_{j=1, j\neq i}^{N} g_{i,j}u_{i,j} + \dfrac{u_i}{|\sqrt{\mu}\mathbf{r}_{1,i} - \mathbf{r}_{2,i}|}. \end{cases} \tag{21}$$

To complete the algorithm for calculating the hydrogen atom according to scheme (21), it is necessary to construct the matrix $g_{i,j}, i, j = 1, \ldots, N$. Given the example of constructing this matrix in (7), we choose the following matrix form:

$$g_{i,j} = \begin{cases} \rho_1 h^{-2}\exp(-\rho_2|r_i - r_j|/h), & i \neq j \\ 0, & i = j, \end{cases} \tag{22}$$

where $i, j = 1, \ldots, N$ and h is the step of the equivalent uniform grid.

Given the definition $\mathbf{r}_i = (\mathbf{r}_{1,i}, \mathbf{r}_{2,i})$, $i = 1,\dots,N$, we write the module in (22) and return to the original $\mathbf{r}_1$ by reverse replacement $\mathbf{r}_1 \to (1/\sqrt{\mu})\mathbf{r}_1$, then

$$g_{i,j} = \begin{cases} \rho_1 h^{-2} \exp\left(-\dfrac{\rho_2}{h}\sqrt{\dfrac{1}{\mu}(\mathbf{r}_{1,i} - \mathbf{r}_{1,j})^2 + (\mathbf{r}_{2,i} - \mathbf{r}_{2,j})^2}\right), & i \neq j \\ 0, & i = j. \end{cases} \tag{23}$$

In order for both terms of the radical expression in (23) to be identical in order of magnitude, we require the following representations for the positions of the first and second quantum particles:

$$\mathbf{r}_{1,i} = \mathbf{a}_1 + \sqrt{\mu}(-L + 2L\boldsymbol{\xi}_{1,i}), \quad \mathbf{r}_{2,i} = \mathbf{a}_2 - L + 2L\boldsymbol{\xi}_{2,i}, \tag{24}$$

where $i = 1, \dots, N$; $\mathbf{a}_1$ and $\mathbf{a}_2$ are constant vectors, which will be interpreted in the future as the centers of the scattering of the possible positions of the proton and electron. We consider that the vectors $\boldsymbol{\xi}_{1,i}$ and $\boldsymbol{\xi}_{2,i}$ in (24) have independent uniformly random values of coordinates from the interval [0,1]. As a choice of the step of the equivalent uniform grid, we assume that the cube $(2L)^3$ is broken into N subcubes of volume h^3; then, $h = 2L/N^{1/3}$.

Representation (24), in which independent uniformly random variables $\boldsymbol{\xi}_{1,i}$ and $\boldsymbol{\xi}_{2,i}$, $i = 1,\dots,N$ appear, means that the method under consideration for the numerical solution of the Schrödinger equation becomes stochastic and can be assigned to the class of Monte Carlo methods.

Taking into account the considerations set forth in (20)–(24), after the reverse replacement $\mathbf{r}_1 \to (1/\sqrt{\mu})\mathbf{r}_1$, we rewrite the system of equations (21) in the form

$$\begin{cases} \dot{u}_t = \dfrac{1}{2}\displaystyle\sum_{j=1, j\neq i}^{N} g_{i,j} v_{i,j} - \dfrac{v_i}{|\mathbf{r}_{1,i} - \mathbf{r}_{2,i}|} \\ \dot{v}_t = -\dfrac{1}{2}\displaystyle\sum_{j=1, j\neq i}^{N} g_{i,j} u_{i,j} + \dfrac{u_i}{|\mathbf{r}_{1,i} - \mathbf{r}_{2,i}|}, \end{cases} \tag{25}$$

where $i = 1, \dots, N$.

The transition from Eqs. (21) to Eqs. (25) made it possible to naturally take into account the different masses of the quantum particles and determine their scattering centers. In this case, as will be made clear below, the described procedure is universal and applicable to systems with many particles.

Consider the solutions of the system of equations (25), the expressions for which are given in (16), where Ω and c are the eigenvalue and eigenvector of the matrix $Q = \frac{1}{2}(g_2 - g) + \mathrm{diag}(U_i)$, $g_2 = \mathrm{diag}(\sum_{j=1, j\neq i}^{N} g_{i,j})$, and $U_i = -\dfrac{1}{|\mathbf{r}_{1,i} - \mathbf{r}_{2,i}|}$. Since matrix Q has dimensions $N \times N$ as in the general case we have N eigenvalues $\Omega_1,\dots,\Omega_N$ and vectors $c_1,\dots,c_N$.

Assuming that the eigenvectors are normalized to unity, we can find the probability of localization $w_i, i = 1,\dots,N$, of the hydrogen atom at one of the points $\mathbf{r}_i = (\mathbf{r}_{1,i}, \mathbf{r}_{2,i})$, $i = 1,\dots,N$. For this, it is necessary to normalize the length of vector (16) per unit, which is ensured by an elementary transformation: $y_\Omega \to y_\Omega/\sqrt{C_1^2 + C_2^2}$. As a result, we have $\|y_\Omega\|^2 = \|c\|^2 = 1$, where $\|\dots\|$ is the norm of the vector. Thus, for any of the eigensolutions (16) y_{Ω_i}, the probability w_j of the localization of a hydrogen atom at the point r_j coincides with the square of the coordinate of the eigenvector c_i, i.e., $w_j = c_{i,j}^2$, $i, j = 1,\dots,N$.

We will carry out a series of calculations in volume M, in each of which new positions of proton and electron subparticles are randomly selected according to formulas (24) and an own solution with the given energy E is found. In total, in this way, we will find M own solutions $y_{\Omega_\alpha}^{(\alpha)}$, $\alpha = 1,\dots,M$ whose eigenvalues selected from the set $\Omega_1,\dots,\Omega_N$ are close to the value of energy E, i.e., $\Omega_\alpha \cong E$, $\alpha = 1,\dots,M$.

Figure 3 shows the typical examples of the localization sites of the subparticles of a hydrogen atom, the probability of remaining in which was divided into three categories. The first category includes places with the probabilities of remaining in which exceed the threshold p_{th}; they are indicated by markers in the form of black dots and stars. The second and third categories include places with the probabilities of remaining in the ranges $[(1/3)p_{\text{th}}, p_{\text{th}}]$ and $[(1/9)p_{\text{th}}, (1/3)p_{\text{th}}]$, respectively; these positions are indicated by markers in the form of circles and rhombuses. The markers in the form of stars indicate the positions of the proton,

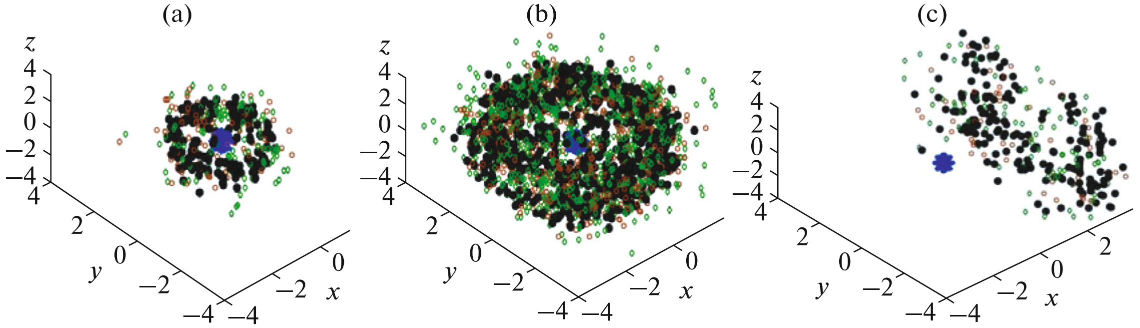

Fig. 3. (a) Multiple places localization of the hydrogen atom when $E \cong -0.5$. (b) Multiple localization of the hydrogen atom when $E \cong -0.25$. (c) Multiple localization of the hydrogen atom when $E \cong -0.05$.

and those in the form of dots, circles, and rhombuses indicate the positions of the electron. The other parameters were selected as follows: $L = 4$, $M = 50$, $N = 10^3$, $\rho_1 = 0.1$, $\rho_2 = 1$, $p_{\text{th}} = 5/N = 0.005$, $\mathbf{a}_1 = (-0.5;0;0), \mathbf{a}_2 = (0.5;0;0)$.

Figure 3a shows that the hydrogen atom itself is quite compact when $E \cong -0.5$. The locations of the electron (markers in the form of points, circles, and rhombuses) surround the proton, which is positioned in the center (the marker in the form of a star) of the electron accumulation sites. After increasing the energy of the hydrogen atom to the value $E \cong -0.25$ the region of electron accumulation sites significantly increases (Fig. 3b). Finally, when the energy approaches zero, $E \cong -0.05$, and hydrogen turns into a pair of particles—a proton and an electron—and the cloud of electron accumulation sites noticeably moves away from the positions of the proton, which is clearly seen in Fig. 3c.

5. BENZENE MOLECULE

Let us consider the application of the investigated algorithm for the numerical solution of the Schrödinger equation to a benzene molecule. In a benzene molecule, whose chemical formula is C_6H_6, there are 54 quantum particles: 6 carbon atoms, 6 protons, and 42 electrons. Given (24), we write the algorithm for generating the set of vectors $\mathbf{r}_i = (\mathbf{r}_{1,i},\dots,\mathbf{r}_{54,i})$, $i = 1,\dots,N$, namely,

$$\mathbf{r}_{k,i} = \mathbf{a}_k + \sigma 2L\sqrt{\mu_k}\boldsymbol{\eta}_{k,i}, \tag{26}$$

where σ is a constant; k is the mass to electron ratio of the kth particle of the molecule; and $\mathbf{a}_k$ is the scattering center of the $k$the quantum particle of the benzene molecule, $k = 1, \dots, 54$. It is believed that the coordinates of the vectors $\boldsymbol{\eta}_{k,i}$, $k = 1, \dots, 54$, $i = 1, \dots, N$, in (26) have independent random values with zero mathematical expectation and finite dispersion.

Using the example of a benzene molecule, we study the feature of the considered algorithm; it is related to matrix g, the typical form of which is given in (23). Given (26), we generalize (23); then,

$$g_{i,j} = \begin{cases} \rho_1 h^{-2} e^{-\frac{\sigma 2L\rho_2}{h}\sqrt{\sum_{k=1}^{54}[(\eta_{x,k,i}-\eta_{x,k,j})^2+(\eta_{y,k,i}-\eta_{y,k,j})^2+(\eta_{z,k,i}-\eta_{z,k,j})^2]}}, & i \neq j \\ 0, & i = j, \end{cases} \tag{27}$$

where the subindices x, y, and z denote the projections of vectors $\boldsymbol{\eta}_{k,i}$, $k = 1, \dots, 54$, $i = 1, \dots, N$, to the corresponding coordinate axes. Note that in (27), under the sum sign, 54 × 3 = 162 terms are contained, each of which is a realization of the same random variable $\Phi = (\eta_{*,*,*}-\eta_{*,*,*})^2$, where the stars indicate the coordinates x, y, and z and indices k, i, and j. Since the number of terms in the sum of random numbers is quite large, we can use the central limit theorem of probability theory.

Find the mathematical expectation $M\Phi$ and variance $D\Phi$ of the random variable Φ, assuming that all quantities $\eta_{*,*,*}$ are independent and subject to the standard normal distribution $N(0,1)$. In this case it is easy to find $M\Phi = 2$ and $D\Phi = 12$. Define a sample mean $\bar{\Phi}_n = \frac{1}{n}\sum_{k=1}^{n}\Phi_k$, then, according to the central limit theorem, we can write $\sqrt{n}\frac{\bar{\Phi}_n - M\Phi}{\sqrt{D\Phi}} = \sqrt{n}\frac{\bar{\Phi}_n - 2}{12} \to N(0,1)$ by distribution when $n \to \infty$. In other

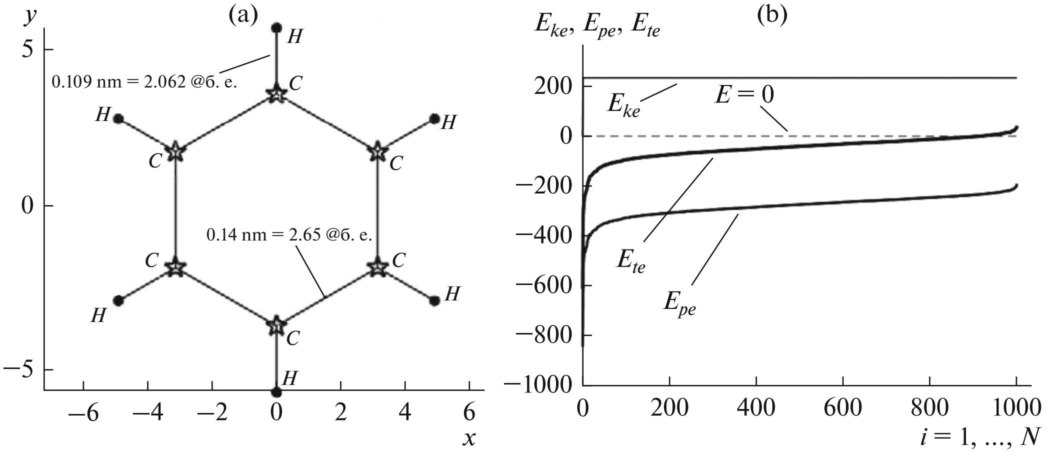

Fig. 4. (a) The external form of the benzene ring. (b) Kinetic, potential, and total energy of a benzene molecule.

words, $\overline{\Phi}_n = 2 + \frac{12}{\sqrt{n}}\eta \to 2,\ n \to \infty$. The last passage to the limit allows, in expression (27), the amount to be approximately replaced by the constant 162 × 2; in this case it is considered that $n = 162$. It is in this that the new feature of the considered algorithm lies, and the substitution mentioned will be more accurate the greater the number of quantum particles in the molecule.

Rewrite the expression for matrix g given this feature; then, $g_{i,j} = \begin{cases} \varepsilon, & i \neq j, \\ 0, & i = j, \end{cases}$ where $\varepsilon = \rho_1 h^{-2}\exp\left(-36L\sigma\rho_2/h\right)$. Taking into account the last remark, the eigenvalue problem for the matrix $Q = \frac{1}{2}(g_2 - g)$, $g_2 = \mathrm{diag}(\sum_{j=1, j\neq i}^{N} g_{i,j})$ can be solved analytically. In this case, the spectrum of kinetic energy contains two non-negative values Ω_1 and Ω_2, one of which is zero. The corresponding characteristic equation has the form $\Omega(\Omega - \varepsilon N/2)^{N-1} = 0$, from which it follows that $\Omega_1 = 0$ and $\Omega_2 = \varepsilon N/2$ and the second eigenvalue has degeneration of order $N - 1$.

Note that the matrix feature discussed above g remains in the case when random variables of the type $\Phi = (\eta_{*,*,*} - \eta_{*,*,*})^2$ are subject to different distributions. Due to the well-known generalized Chebyshev theorem, only require their independence, the existence of averages, and the boundedness of variances on aggregate are required.

Figure 4a shows a structural diagram of a benzene molecule known in chemistry in the form of a ring. Figure 4a shows the characteristic ring sizes in nanometers (nm) and in dimensionless units (d.u.).

We calculate the energy of the complete dissociation of the benzene ring, $E_{C_6H_6}$. The ionization energy of the carbon atom (MJ/mol) [7] is 1.09, 2.35, 4.62, 6.22, 37.83, and 47.28. Summarizing, we find $E_C = -99.39$ MJ/mol $= -37.8669$ d.u. The ionization energy of the hydrogen atom will be $E_{\mathrm{H}} = -0.5$ d.u. Finally, according to [8], the energy of the benzene ring is $E_{\text{⬢}} = -1323$ kcal/mol $= -2.1089$ d.u. As a result, we find the total dissociation energy of the benzene ring: $E_{C_6H_6} = 6E_{\mathrm{C}} + 6E_{\mathrm{H}} + E_{\text{⬢}} = -232.3103$ d.u.

We define the kinetic spectra E_{ke} of the potential E_{pe} and complete E_{te} energies by the formulas

$$\begin{gathered} E_{ke} = \mathrm{eig}\left[\frac{1}{2}\mathrm{diag}\left(\sum_{j=1, j\neq i}^{N} g_{i,j}\right) - \frac{1}{2}g\right], \\ E_{pe} = \underset{1\leq i\leq N}{\mathrm{sort}}\, U_i, \\ E_{te} = \mathrm{eig}\left[\frac{1}{2}\mathrm{diag}\left(\sum_{j=1, j\neq i}^{N} g_{i,j}\right) - \frac{1}{2}g + \mathrm{diag}(U_i)\right], \end{gathered} \tag{28}$$

where U_i is the potential energy, eig (...) is a procedure that returns the set of eigenvalues of a matrix ranked in ascending order and sort is the operation of sorting ther set of values in ascending order.

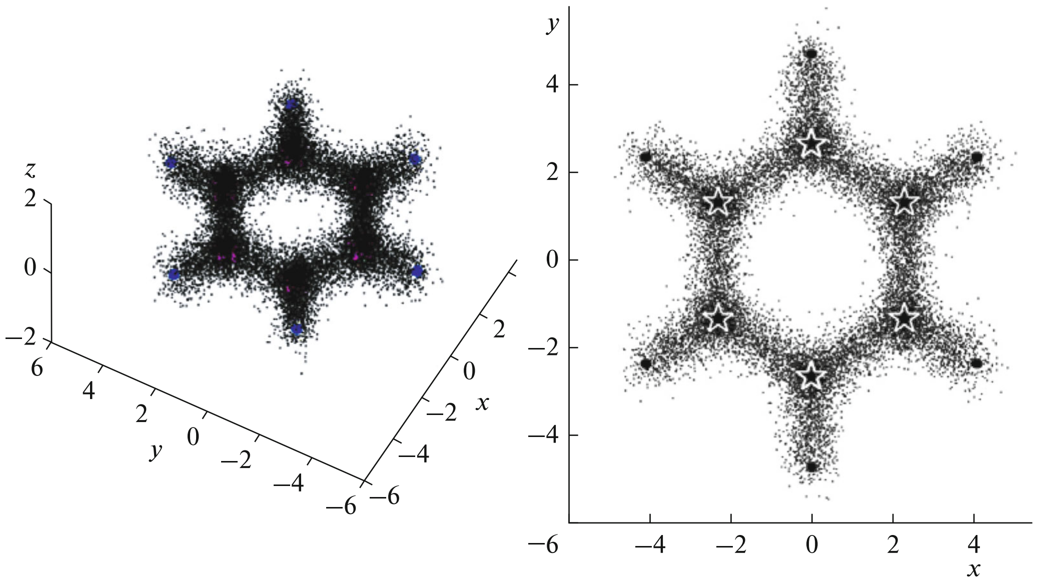

Fig. 5. Localization places of the average positions of quantum particles of a benzene molecule in space (graph on the left) and in projection onto a plane (graph on the right).

We can use the virial theorem to determine the unknown constant ε. In this case, just put $E_{ke} = \varepsilon N/2 = -E_{te} = -E_{C_6H_6} = 232.3103$ d.u. It follows that $\varepsilon = -2E_{C_6H_6}/N$. Figure 4b shows the typical distributions of the kinetic, potential, and total energies of a benzene molecule obtained by a computational experiment.

Taking into account (26), we can consider several schemes for choosing the electron scattering centers of the benzene molecule. This circumstance is caused by the fact that several schemes of the delocalization of double bond electrons in a benzene molecule are considered in chemistry.

We assume that the electrons are of hydrogen and four electrons from each of the carbon atoms are uniformly randomly distributed over the benzene ring. When positioning 30 valence electrons, we believe that in each statistical experiment, the electron scattering centers are uniformly randomly positioned over a length of $6 \times 2.6465 + 6 \times 2.0605$ d.u. of the total benzene ring (Fig. 4a), where 2.6465 d.u. is the distance between a pair of carbon atoms and 2.0605 d.u. is the distance between carbon and hydrogen.

Figure 5 shows the typical result of calculating the average localization sites of quantum benzene particles in space (x, y, z) and in the projection onto a plane (x, y) The calculation parameters were selected as follows: $L = 7$, $N = 10^3$, $M = 500$, and $\varepsilon = -2E_{C_6H_6}/N = 0.4646$, $\sigma = 0.025$. Carbon atoms, protons, and electrons are indicated by markers in the form of pentagrams, large points, and small points, respectively.

Let us present in a generalized form the considered numerical algorithm for solving the Schrödinger equation in terms of constructing pure states of a molecule with the number of quantum particles greater than several tens.

Let the molecule consist of n quantum particles and energy E_Σ. We believe that the quantum particles of a molecule are characterized by the ratios of the mass of an electron to the mass of atoms, including electrons $\mu_1, \ldots, \mu_n$ and charges $q_1, \ldots, q_n$, respectively.

1. We introduce N radius vectors $\mathbf{r}_i = (\mathbf{r}_{1,i}, \ldots, \mathbf{r}_{n,i})$, $i = 1, \ldots, N$ in a space of dimension $3n$ according to point (4) of this algorithm.

2. Make a matrix $Q = \frac{1}{2}\varepsilon N e_N - \frac{1}{2}\varepsilon o_N + \mathrm{diag}(U_i)$, where $\varepsilon = -2E_\Sigma/N$ is a non-negative parameter ensuring the fulfillment of the conditions of the virial theorem as applied to the molecule under consideration; e_N is the identity matrix of size $N \times N$; o_N is a special matrix of size $N \times N$, all elements of which are units; and $\mathrm{diag}(U_i)$ is the diagonal matrix on the diagonal of which the values of the potential energy of the molecule at the points $\mathbf{r}_i, i = 1, \ldots, N$ are found. Potential energy is calculated by the formula

$$U_i = \sum_{j,k=1, j<k}^{n} \frac{q_j q_k}{|\mathbf{r}_{j,i} - \mathbf{r}_{k,i}|}, \quad i = 1, \ldots, N.$$

3. Find the eigenvalues $\Omega_1, \ldots, \Omega_N$ and eigenvectors $c_1, \ldots, c_N$ of matrix Q. Among the set of eigenvalues, we choose the $\Omega_\alpha \cong E_\Sigma$ which is closest to the total energy of the molecule. Assuming that the eigenvectors are normalized to unity, we find the localization $k = 1,\ldots,n$ of the average positions of the quantum particles in a molecule by the formula $\mathbf{R}_{k,\alpha} = \sum_{i=1}^{N} \mathbf{r}_{k,i} c_{\alpha,i}^2$.

4. We repeat the procedure in paragraphs (1)–(3) M times, considering that the radius vectors $\mathbf{r}_i = (\mathbf{r}_{1,i},\ldots,\mathbf{r}_{n,i})$, $i = 1,\ldots,N$ are each time selected according to the scheme of the type $\mathbf{r}_{k,i} = \mathbf{a}_k + \sigma 2L\sqrt{\mu_k}\boldsymbol{\eta}_{k,i}$, $k = 1,\ldots,n$, $i = 1,\ldots,N$, where a_k, $k = 1, \ldots, n$, are the so-called scattering centers of quantum particles, which in the general case can vary from one statistical test to another; σ is some nonnegative fitting factor; L is the characteristic size of the problem or, otherwise, a three-dimensional box, $[-L, L]^3$ in which the molecule is placed; $\boldsymbol{\eta}_{k,i}, k = 1,\ldots,n$, $i = 1,\ldots,N$, are vectors of random variables whose coordinates are independent, and have zero mathematical expectation and dispersion on the order of unity.

5. We construct the final graphs of the average positions $\mathbf{R}_{k,\alpha}$, $k = 1, \ldots, n$, $\alpha = 1, \ldots, M$, of the molecule's quantum particles in three-dimensional physical space.

6. CONCLUSIONS

The article proposes a numerical method for solving the multidimensional Schrödinger equation. The method combines the finite difference and Monte Carlo approaches; it turns out to be efficient and economical in computational terms. The finite-difference approach appears in the form of a special approximation procedure for the sum of Laplace operators, each of which takes into account the contribution of the quantum particle of the molecule. The exponential format of the dependence on the distance between points in the finite-difference approximation of the sum of Laplacians was tested on a number of examples, taking into account the traditional finite-difference method for solving the Schrödinger equation. The nodes of the computational grid are generated in the configuration space of the molecular system of the specially formulated Monte Carlo procedure, and the corresponding variability ranges are determined by the mass ratio of the particles of the molecule. The method is illustrated by examples of calculating a linear oscillator, a hydrogen atom, and benzene. In this approach, it was found that with an increase in the number of particles in the molecular system, the calculation algorithm is noticeably simplified due to the central limit theorem of probability theory, which is illustrated by the example of a benzene molecule. The method may be useful in quantum physics and chemistry as a heuristic tool for constructing complex molecular systems. In the presented method, it was possible to preserve the basic property of the Schrödinger equation: its linearity. Thus, for example, in the quantum mechanics of D. Bohm [9], due to the well-known nonlinear substitution, this feature disappears, and, as is well known, nontrivial hydrodynamic analogies appear, which in turn redirect the bridge to statistical physics, to the Vlasov equation and the corresponding self-consistent field [10].

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