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NUMERICAL SOLUTION OF KOHN–SHAM EQUATION FOR ATOM

Zbigniew Romanowski

Interdisciplinary Centre for Materials Modelling
Pawinskiego 5a, 02-106 Warsaw, Poland

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The numerical algorithm solving Kohn–Sham (KS) equation for the free or confined atom on uniform mesh is presented. Using the spherical symmetry of system, the three-dimensional KS equation is reduced to the one-dimensional functional eigenproblem. The functional eigenproblem is transformed to the algebraic eigenproblem with symmetric, tridiagonal matrix where the smallest eigenvalues are searched by the bisection. The Poisson equation is solved using Numerov algorithm. The atom electron density is calculated by the self-consistent-field procedure. The final solution is obtained by the Richardson extrapolation. The `RAtom` program is presented, where all described algorithms are implemented. The `RAtom` is used to analyze N, Al, Ga and In atom applying Slater and VWN approximation for the correlation and exchange energy. For these atoms the eigenvalues, the components of total energy and the electron distribution are calculated. The obtained eigenvalues agree with the results reported for the shooting method on the logarithmic mesh within 10^{-5} Ha.

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1. Introduction

The Density Functional Theory (DFT) was originated by two seminal papers [12,16] written by Hohenberg, Kohn and Sham. Since then the method has been developed and applied to huge number of problems [4,5,14]. The last decade gave the examples of successful applications of this theory in the computational quantum chemistry and physics. The success of DFT is caused by: (a) the simple and precise approximations of exchange and correlation energy, (b) the existence of the effective algorithms for solution of equation for many-electron systems.

The simplest system considered in DFT is the atom in the spherical symmetric potential. The application of the symmetry reduces the Kohn–Sham (KS) equation to the one-dimensional functional eigenproblem for the second order differential operator with the Dirichlet boundary conditions. Usually this eigenproblem is solved using shooting method with Numerov algorithm for the initial-value problem [7, 10, 18, 21]. To start the shooting method the good estimation of the eigenvalue is required. It is a drawback of the shooting method, since is not easy to give a good estimation of the eigenvalue especially for unusual boundary conditions.

In this paper we present easy to implement algorithm for solving KS equation for an atom. This algorithm uses uniform mesh and does not need any estimation of the eigenvalues. The eigenvectors and the electron density is calculated in the mesh nodes, there is no interpolation between nodes. The second order differential operator is represented as the symmetric three point finite difference. Based on this representation the functional eigenproblem is transformed to the symmetric algebraic eigenproblem with the tridiagonal matrix. For this problem a few lowest eigenvalues are calculated using the bisection method. For completeness, the theorems used by the bisection are given. The effective implementation of this algorithm can calculate 5 lowest eigenvalues for matrix of dimension 5×10^4 in less then one second on PC machine. The bisection method in conjunction with the Richardson extrapolation facilitate eigenvalues calculations for atoms with the accuracy of 10^{-5} Ha.

In addition to the algorithm solving the eigenproblem, we present the short review of DFT and the expressions required to perform the numerical computations. The equations for the electron density and the energy are listed. Also the details of the solution of the Poisson equation and the occupation factors are given. The theorems used in the self-consistent-field (SCF) procedure are cited. The short resume of the Richardson extrapolation is written. For completeness, the equations for approximation of exchange (Slater) and correlation (VWN) terms are reproduced.

In the last part of the paper the short description of the `RAtom` program is given. In the program the algorithms described in the second part have been implemented. Using the `RAtom` eigenvalues and electron distribution for the III group metals and the nitrogen atom were calculated. Finally we show that this method can be used to calculate the eigenvalues of Ga atom located in infinite quantum well of finite radius.

2. Physical motivation

Solving the Kohn–Sham equation in DFT framework is complicated and difficult task [15]. Currently available algorithms can be grouped into two categories:

- algorithms in reciprocal space,
- algorithms in real space.

Most algorithms in the reciprocal space are based on the plane wave expansion. The most common algorithms in the real space are founded on the Linear Combination of Atomic Orbital (LCAO). If we denote by $\chi_i(\boldsymbol{r})$ the i-th atomic orbital (basis function) then the eigenfunction $\psi(\boldsymbol{r})$ of the investigated system is expressed as $\psi(\boldsymbol{r}) = \sum_i a_i \chi_i(\boldsymbol{r}),\ a_i \in \mathbb{R}$. In the real space method the approximate solution of the Kohn–Sham equation is searched by variational method in the space spanned by the set of the basis functions $\{\chi_i(\boldsymbol{r})\}$. The accuracy of the approximate solution strongly depends on the choice of the basis functions. Thus the great care must be undertaken to choose the proper basis set. In principle, the infinite basis set $\{\chi_i(\boldsymbol{r})\}_{i=1}^{\infty}$ would be sufficient. But this is not tractable numerically, since the variational method leads to the algebraic eigenvalue problem with the size of the matrix equal to the number of the basis functions.

There are not strict rules how to build the suitable basis set. But it is possible to give some recommendations that must be fulfilled. Below we mention three of them. The first and second have the numerical background. The third one has the physical explanation.

- Basis set has to be finite.
  Since the number of basis functions N determinate the size of the matrix, keeping N as small as possible is highly recommended.

- Basis function has to have the finite support.
  Basis functions with finite support lead to sparse Hamiltonian and overlap matrix. For sparse matrices there exists more efficient algorithm of solving the eigenvalue problem then for full matrices. Additionally, the memory usage for sparse matrices is proportional to N compared to N^2 for full matrices. The general rule is: the shorter the support the sparser the matrices.

- Basis set has to describe the free atom and molecule.
  One of the crucial physical property characterizing the molecule is the binding energy $E_{\mathrm{b}} = E_{\mathrm{t}}^{\mathrm{m}} - \sum_i E_{\mathrm{t},i}^{\mathrm{a}}$, where $E_{\mathrm{t}}^{\mathrm{m}}, E_{\mathrm{t},i}^{\mathrm{a}}$ is the total energy of molecule and i-th atom, respectively. Thus to determine accurately E_{b} the free atom and molecule must be well described within the same basis set.

For example in `DMol` program [6] the basis functions are the eigenfunctions of free atom with spherical symmetry. To extend the basis the unoccupied states are included. Additionally the eigenfunction for cations can be incorporated into the basis set. In `SIESTA` program [24] the basis functions are constructed similar to the `DMol` program plus the eigenfunctions of the confined atom are included.

Recently the attention is focused on the research the nanostructures. One-dimensional nanostructures, such as nanowires and nanotubes have numerous potential applications in science and technology [4,13]. The unique electrical, optical and magnetic properties have been studied both experimentally and theoretically. Among these materials III–V semiconductors (in particular group-III nitrides) have attracted much attention, showing peculiar properties suitable for promising application. Some preliminary theoretical investigations within density functional theory have been also performed [19,23,30].

Our motivation is to give the complete, easy to implement algorithm facilitating the generation of the basis function suitable for density functional study of group-III nitrides nanostructures. The algorithm described in the present paper fulfills above listed recommendations. It allows generate the basis similar to basis generated by DMol and SIESTA but is more general and powerful.

Moreover, this work can be useful for anyone interested in the details of the applied algorithms and implementation. All needed details required for the efficient and stable implementation are presented. Up to the authors knowledge the complete description of the whole algorithm is not available in the public literature.

3. Kohn–Sham equation

3.1. *Basics of density functional theory DFT*

The most important result of DFT is the theorem stating that any property of the system is the unique functional of the electron density. It means that in order to calculate any physical/chemical properties of molecule, the wave function is not needed, the electron density $\rho(\boldsymbol{r})$ is sufficient. The example property of this kind can be the correlation and exchange energy. When the exchange and correlation depend only on the values of $\rho(\boldsymbol{r})$ then the approximation is called LDA (local density approximation). If the exchange and correlation terms depend also on gradient of $\rho(\boldsymbol{r})$ then the approximation is called GGA (general gradient approximation). However, DFT does not define the procedures for calculation the exchange and correlation (XC). There were published many papers considering XC approximation. The review is given in Ref. [14,15]. In this paper we use VWN for correlation [26,27] and Slater approximation for exchange [15]. DFT uses density of the XC energy and its potentials. All needed expressions are reproduced in Sec. 3.9.

3.2. Interaction potential

As was stated in previous section in DFT approach all properties of the molecular system can be expressed as the functional of $\rho(\boldsymbol{r})$. It can be shown [12, 16] using the variational analysis that the equivalent of Schroedinger equation in DFT is Kohn–Sham equation[1]

$$\Big[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r})\Big]\psi_\mu(\boldsymbol{r}) = E_\mu\psi_\mu(\boldsymbol{r})\,. \tag{1}$$

Eq. (1) is the functional eigenproblem. In this equation the potential $V(\boldsymbol{r})$ is defined by the sum

$$V(\boldsymbol{r}) = V_\mathrm{n}(\boldsymbol{r}) + V_\mathrm{e}(\rho(\boldsymbol{r})) + V_\mathrm{x}(\rho(\boldsymbol{r})) + V_\mathrm{c}(\rho(\boldsymbol{r}))\,, \tag{2}$$

where: V_n the nuclear electrostatic potential, V_e the electrostatic potentials of the electrons (Hartree potential), V_x the exchange potential, V_c the correlation potential. The potentials $V_\mathrm{e}, V_\mathrm{x}, V_\mathrm{c}$ depend on density $\rho(\boldsymbol{r})$. V_n is the sum of the nucleus Coulomb potentials. For single atom it reduces to

$$V_\mathrm{n}(\boldsymbol{r}) = V_\mathrm{n}(|\boldsymbol{r}|) = V_\mathrm{n}(r) = -\frac{Z}{r}\,, \tag{3}$$

where Z is the nuclear charge. Potential $V_\mathrm{x}, V_\mathrm{c}$ are calculated according to the selected approximation, for example Slater and VWN. The Hartree potential, V_e, is the solution of the Poisson equation

$$\nabla^2 V_e(\boldsymbol{r}) = -4\pi\rho(\boldsymbol{r})\,. \tag{4}$$

The method of solution the Poisson equation for spherical symmetric systems is described in Sec. 3.6.

3.3. Spherical symmetric potential

In general, the solution of the functional eigenproblem (1) is the sequence of pairs $\{E_\mu, \psi_\mu(\boldsymbol{r})\}_{\mu=0}^{\infty}$, where E_μ is the eigenvalue and $\psi_\mu(\boldsymbol{r})$ is the eigenfunction. The potential $V(\boldsymbol{r})$ defines all interactions in the system. For closed shell system $V(\boldsymbol{r})$ is spherically symmetric

$$V(\boldsymbol{r}) = V(|\boldsymbol{r}|) = V(r)\,. \tag{5}$$

For the system with spherical symmetry, it is easier to solve Eq. (1) in the spherical coordinates, where Laplace operator, ∇^2, has the form

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hat{L}^2}{r^2}\,, \tag{6}$$

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[1] The atomic units are used: $m = 1, \hbar = 1, e = 1$. The length unit is bohr (1 bohr = 0.529117 Å), the energy unit is hartree (1 Ha = 27.21165 eV).

where $\hat{L}^2$ is a square of angular momentum [20]. Substituting (6) into (1) and using (5) we get

$$\Big[-\frac{1}{2r}\frac{\partial^2}{\partial r^2}r+\frac{\hat{L}^2}{2r^2}+V(r)\Big]\,\psi_\mu(\boldsymbol{r})=E_\mu\psi_\mu(\boldsymbol{r})\,. \tag{7}$$

It is possible to simplify this equation when $\psi_\mu(\boldsymbol{r})$ is represented as a product of radial function and spherical harmonic

$$\psi_\mu(\boldsymbol{r})=\psi_{n,l,m}(\boldsymbol{r})=\frac{1}{r}R_{n,l}(r)Y_{l,m}(\theta,\phi)\,. \tag{8}$$

The eigenfunction $\psi_{n,l,m}(\boldsymbol{r})$ has three indices (n,l,m) substituting the single one μ used so far. The radial function $R_{n,l}(r)$ has two indices (n,l). Substituting Eq. (8) into Eq. (7), using the relation $\hat{L}^2Y(\theta,\phi)=l(l+1)Y(\theta,\phi)$ and comparing the radial part we get

$$\Big[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V(r)\Big]R_{n,l}(r)=E_{n,l}R_{n,l}(r)\,. \tag{9}$$

The index m was omitted in the eigenvalue since it does not depends on it. Eq. (9) is the functional eigenproblem for second order differential operator on $r\in[0,\infty]$ domain. Since Eq. (9) is second order two boundary conditions are required, for example the values at the ends of the interval $[0,\infty]$. The boundary conditions come from the physical conditions. Since $\psi_{n,l,m}(\boldsymbol{r})$ must be finite then, based on Eq. (8), we have

$$\lim_{r\to 0}R_{n,l}(r)=0\,. \tag{10}$$

This is first boundary condition. From quantum mechanics [20] we know that radial function must decay faster than r^{-1}, so based on Eq. (8) we get second boundary condition

$$\lim_{r\to\infty}R_{n,l}(r)=0\,. \tag{11}$$

Condition (11) is equivalent to $\forall_\epsilon\exists_\chi\forall_{r>\chi}R_{n,l}(r)<\epsilon$. It means that we can assume $R_{n,l}(\chi)=0$ for some large enough χ. Thus the infinite interval $[0,\infty]$ reduces to the finite interval $[0,\chi]$. Let denote by

$$\alpha=-\frac{1}{2}\,,\qquad g_l(r)=\frac{l(l+1)}{2r^2}+V(r)\,. \tag{12}$$

Then Eq. (9) has the form:

$$\alpha R''_{n,l}(r)+g_l(r)R_{n,l}(r)=E_{n,l}R_{n,l}(r)\,, \tag{13}$$

where $r\in[0,\chi]$ and $R_{n,l}(0)=R_{n,l}(\chi)=0$. The solution algorithm of problem (13) based on the reduction to the algebraic eigenproblem with tridiagonal, symmetric matrix is presented in Sec. 3.10.

3.4. Electron density

The eigenfunction $\psi_\mu(r)$ of Eq. (1) can be used [12, 16] to calculate the electron density

$$\rho(\boldsymbol{r}) = \sum_\mu f_\mu |\psi_\mu(\boldsymbol{r})|^2 = \sum_{\mu\in\mathrm{occ}} f_\mu |\psi_\mu(\boldsymbol{r})|^2\,, \tag{14}$$

where symbol $\sum_\mu$ denotes summation over all states. The coefficient $0 \le f_\mu \le 1$ means occupation fraction of eigenfunction μ. By definition $f_\mu = 0$ for empty state and $f_\mu = 1$ for occupied state. Therefore the summation in Eq. (14) my be reduced to occupied states, as is marked by symbol $\sum_{\mu\in\mathrm{occ}}$. The sum of all coefficients is equal to the number of the electrons in the system

$$N = \sum_\mu f_\mu\,. \tag{15}$$

Eq. (14) defines the electron density, $\rho(\boldsymbol{r})$, at any point in $\mathbb{R}^3$ for any system. The eigenfunction of Kohn–Sham equation for atom has special form given by Eq. (8). Since we are interested in the spherically symmetric systems then we must average $\rho(\boldsymbol{r})$ over the sphere of radius r

$$\rho(r) = \rho(|\boldsymbol{r}|) = \frac{1}{4\pi}\int\limits_{\Omega} \rho(\boldsymbol{r})d\Omega\,. \tag{16}$$

Let substitute Eq. (8) into Eq. (14) and use Eq. (16). Let change the index μ to 3-tuplet (n, l, m). Using the variable separation and the orthonormality of the spherical harmonics, we get

$$\begin{aligned}\rho(r) &= \frac{1}{4\pi}\int \Big[\sum_{n,l,m} f_{n,l}\frac{R^2_{n,l}(r)}{r^2}\,Y^2_{l,m}(\theta,\phi)\Big]d\Omega \\ &= \frac{1}{4\pi}\sum_{n,l,m}\Big[f_{n,l}\frac{R^2_{n,l}(r)}{r^2}\int Y^2_{l,m}(\theta,\phi)d\Omega\Big] = \frac{1}{4\pi}\sum_{n,l,m} f_{n,l}\frac{R^2_{n,l}(r)}{r^2}\,,\end{aligned} \tag{17}$$

The index m in $f_{n,l}$ was omitted to emphasize, that the occupation factor does not depend on the index m. Let us use the fact that $R_{n,l}$ does not depend on m. Using the fact that $-l \le m \le l$ we can sum up on index m explicitly (using expression $\sum_{m=-l}^{l} 1 = 2l + 1$)

$$\begin{aligned}\rho(r) &= \frac{1}{4\pi}\sum_{n,l,m} f_{n,l}\,\frac{R^2_{n,l}(r)}{r^2} = \frac{1}{4\pi}\sum_{n,l}\sum_{m=-l}^{l} f_{n,l}\,\frac{R^2_{n,l}(r)}{r^2} \\ &= \frac{1}{4\pi}\sum_{n,l}(2l+1)f_{n,l}\,\frac{R^2_{n,l}(r)}{r^2}\,.\end{aligned} \tag{18}$$

But the spines up and down are treated equally so the coefficients $f_{n,l}$ have to be multiplied by 2 giving the final equation for the electron distribution in the atom

$$\rho(r) = \frac{1}{2\pi} \sum_{n,l} (2l+1) f_{n,l} \, \frac{R_{n,l}^2(r)}{r^2} \,. \tag{19}$$

3.5. Energy of the system

In the Ref. [12, 16] it was shown how to calculate the total energy of system, E_{t}. In this section we list all required equations to calculate E_{t} with the emphasis on the efficient implementation. Assume that the solution of Eq. (1) is known and the electron density $\rho(\boldsymbol{r})$ is calculated by Eq. (14). Then we have

$$E_{\mathrm{t}}[\rho] = E_{\mathrm{k}}[\rho] + E_{\mathrm{n}}[\rho] + E_{\mathrm{e}}[\rho] + E_{\mathrm{x}}[\rho] + E_{\mathrm{c}}[\rho] \,, \tag{20}$$

$E_{\mathrm{k}}[\rho]$ is the kinetic energy

$$E_{\mathrm{k}}[\rho] = \sum_{\mu} f_{\mu} \int \psi_{\mu}^{*}(\boldsymbol{r}) \Big(-\frac{1}{2}\nabla^2 \Big) \psi_{\mu}(\boldsymbol{r}) \, d\boldsymbol{r} \,, \tag{21}$$

$E_{\mathrm{n}}[\rho]$ is the energy of the interaction of electrons with nucleus

$$E_{\mathrm{n}}[\rho] = \int V_{\mathrm{n}}(\boldsymbol{r}) \rho(\boldsymbol{r}) \, d\boldsymbol{r} \,, \tag{22}$$

$E_{\mathrm{e}}[\rho]$ is the electrostatic self-interaction energy of the electrons (Hartree energy)

$$E_{\mathrm{e}}[\rho] = \frac{1}{2} \int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \, d\boldsymbol{r} d\boldsymbol{r}' = \frac{1}{2} \int V_{\mathrm{e}}(\boldsymbol{r}) \rho(\boldsymbol{r}) \, d\boldsymbol{r} \,, \tag{23}$$

$E_{\mathrm{x}}[\rho]$ is the exchange energy

$$E_{\mathrm{x}}[\rho] = \int \varepsilon_{\mathrm{x}}[\rho(\boldsymbol{r})] \rho(\boldsymbol{r}) \, d\boldsymbol{r} \,, \tag{24}$$

$E_{\mathrm{c}}[\rho]$ is the correlation energy

$$E_{\mathrm{c}}[\rho] = \int \varepsilon_{\mathrm{c}}[\rho(\boldsymbol{r})] \rho(\boldsymbol{r}) \, d\boldsymbol{r} \,. \tag{25}$$

Quantities $\varepsilon_{\mathrm{c}}[\rho(\boldsymbol{r})]$, $\varepsilon_{\mathrm{x}}[\rho(\boldsymbol{r})]$ define the density of correlation and exchange energy and are calculated using the approximations, for example VWN [26, 27] or Slater [15]. All terms of the sum (20) (except the kinetic energy) are calculated by the three dimensional integration. Eq. (21), for the kinetic energy, can be simplified using Eq. (1). Let multiply both sides of Eq. (1) by $f_\mu \psi^*(\boldsymbol{r})$ and integrate on $\mathbb{R}^3$, giving

$$\begin{aligned}\int f_\mu \psi_\mu^*(\boldsymbol{r})\Big(-\tfrac{1}{2}\nabla^2\Big)\psi_\mu(\boldsymbol{r})\,d\boldsymbol{r} \;&=\; f_\mu E_\mu \int \psi_\mu^*(\boldsymbol{r})\psi_\mu(\boldsymbol{r})d\boldsymbol{r} \\ &\quad - f_\mu \int V(\boldsymbol{r})\psi_\mu^*(\boldsymbol{r})\psi_\mu(\boldsymbol{r})\,d\boldsymbol{r} \qquad (26)\end{aligned}$$

and assume that the eigenfunctions $\psi_\mu(\boldsymbol{r})$ are normalized

$$\int \psi_\mu^*(\boldsymbol{r})\psi_\mu(\boldsymbol{r})\,d\boldsymbol{r} = \int |\psi_\mu(\boldsymbol{r})|^2 d\boldsymbol{r} = 1\,. \qquad (27)$$

Substituting (27) into (26) and summing up all states we get

$$\begin{aligned}E_{\mathrm{k}} \;&=\; \sum_\mu \int f_\mu \psi_\mu^*(\boldsymbol{r})\Big(-\tfrac{1}{2}\nabla^2\Big)\psi_\mu(\boldsymbol{r})d\boldsymbol{r} \\ &=\; \sum_\mu f_\mu E_\mu - \sum_\mu \int f_\mu V(\boldsymbol{r})|\psi_\mu(\boldsymbol{r})|^2 d\boldsymbol{r}\,. \qquad (28)\end{aligned}$$

The left side of Eq. (28) is the kinetic energy, E_k. Let change the order of summation and integration in Eq. (28) and use Eq. (14):

$$E_{\mathrm{k}} = \sum_\mu f_\mu E_\mu - \int V(\boldsymbol{r})\Big[\sum_\mu f_\mu |\psi_\mu(\boldsymbol{r})|^2\Big]d\boldsymbol{r} = \sum_\mu f_\mu E_\mu - \int V(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r}\,. \qquad (29)$$

Substituting (29), (22), (23), (24), (25) into (20) we get

$$E_{\mathrm{t}}[\rho] = \sum_\mu f_\mu E_\mu + \int (V_{\mathrm{n}} + \tfrac{1}{2}V_{\mathrm{e}} + \varepsilon_{\mathrm{x}} + \varepsilon_{\mathrm{c}} - V)\rho(\boldsymbol{r})\,d\boldsymbol{r}\,. \qquad (30)$$

The sum under the integral can be simplified using explicit form of potential, Eq. (2)

$$\tilde{V} = V_{\mathrm{n}} + \tfrac{1}{2}V_{\mathrm{e}} + \varepsilon_{\mathrm{x}} + \varepsilon_{\mathrm{c}} - V = (\varepsilon_{\mathrm{x}} - V_{\mathrm{x}}) + (\varepsilon_{\mathrm{c}} - V_{\mathrm{c}}) - \tfrac{1}{2}V_{\mathrm{e}}\,. \qquad (31)$$

Finally, substituting (31) into (30), we get the equation for the total energy of the system as the functional of electron density

$$E_{\mathrm{t}}[\rho] = \sum_\mu f_\mu E_\mu + \int \tilde{V}(\boldsymbol{r})\rho(\boldsymbol{r})\,d\boldsymbol{r}\,. \qquad (32)$$

The above results indicate that to calculate the potential energy $\tilde{V}(\boldsymbol{r})$ the following quantities must be known: (a) the difference between the density of correlation energy and correlation potential ($\varepsilon_{\mathrm{c}} - V_{\mathrm{c}}$); (b) the difference between the density of exchange energy and exchange potential ($\varepsilon_{\mathrm{x}} - V_{\mathrm{x}}$); (c) the Hartree potential, V_{e}. When potential $\tilde{V}(\boldsymbol{r})$ is known, the total energy is calculated by one summation and one integration in $\mathbb{R}^3$.

The above presented equations are valid for any system. For atom with spherical symmetry both $\tilde{V}(\boldsymbol{r})$ and $\rho(\boldsymbol{r})$ have spherical symmetry: $\tilde{V}(\boldsymbol{r}) = \tilde{V}(r)$, $\rho(\boldsymbol{r}) = \rho(r)$. Thus also product of two has spherical symmetry: $g(r) = \tilde{V}(r)\rho(r)$. Hence to calculate E_{t} from Eq. (32) we must calculate integral $I = \int g(r) d\boldsymbol{r}$. This integral can be calculated using spherical coordinates, where integration over the sphere can be done explicitly

$$I = \int g(r) d\boldsymbol{r} = \int\int r^2 g(r) dr d\Omega = 4\pi \int\limits_{r=0}^{\infty} r^2 g(r)\, dr\,. \tag{33}$$

Since $V(r)$ and $\rho(r)$ are defined in the mesh nodes, then to calculate the one dimensional integral (33) one can use Newton–Cotes quadrature [25]. In program `RAtom`, the extended Newton–Cotes quadrature of order 9 are implemented. Using this approximation, the integral on interval $[a, b]$ can be expressed as

$$I = \int\limits_a^b g(x) dx \approx \sum_{i=1}^{6} B_i\, g(x_i)\,, \tag{34}$$

where $x_i = a + ih$ for $h = (b - a)/6$ and the coefficients B_i are the rational numbers: $B_0 = 41/840, B_1 = 216/840, B_2 = 27/840, B_3 = 272/840$, $B_4 = B_2, B_5 = B_1, B_6 = B_0$.

3.6. Poisson equation

In this section we present the algorithm of solution the Poisson equation in $\mathbb{R}^3$ for the charge distribution $\rho(r)$ with the spherical symmetry

$$\nabla^2 V_e(r) = -4\pi\, \rho(r)\,. \tag{35}$$

The solution of Eq. (35) is the electrostatic potential, $V_e(r)$, of self-interaction (Hartree potential) of the charge $\rho(r)$. The Laplace operator, ∇^2, in the spherical coordinates is given by Eq. (6). For systems with the spherical symmetry, the operator ∇^2 reduces to

$$\nabla^2 = \frac{1}{r} \frac{d^2}{dr^2}\, r\,. \tag{36}$$

Let use the trial solution of Eq. (35) as

$$V_e(r) = \frac{U_e(r)}{r}\,. \tag{37}$$

Substituting (36) and (37) into (35) we get

$$\frac{d^2U_{\mathrm{e}}(r)}{dr^2} = U''_{\mathrm{e}}(r) = -4\pi r\rho(r)\,. \tag{38}$$

This is ordinary differential equation of order two, defined on interval $[0,\infty]$. In order to solve this equation two boundary conditions are needed. We know that the V_e must be finite: $\exists_{M\in\mathbb{R}}\,\forall_{r\geq 0}\,V_{\mathrm{e}}(r) < M$. Using the Eq. (37) and last condition we get

$$U_{\mathrm{e}}(0) = 0\,. \tag{39}$$

This is first boundary condition. Assume that charge is confined (what is physically reasonable): $\exists_\gamma\,\forall_{r>\gamma}\rho(r) = 0$. The total charge of system, Ω, is given by the integral

$$\Omega = \int \rho(\boldsymbol{u})d\boldsymbol{u} = 4\pi\int\limits_0^\gamma u^2\rho(u)\,du\,. \tag{40}$$

For $R \gg \gamma$ the continuous, confined charge can be treated as the pointwise charge. Then the electrostatic potential can be calculated from Coulomb law

$$V_{\mathrm{e}}(r) = \frac{\Omega}{r}\,, \qquad \text{for} \quad r \geq R\,. \tag{41}$$

Comparing Eq. (41) with Eq. (37), we get

$$U_{\mathrm{e}}(R) = \Omega\,. \tag{42}$$

This is second boundary condition. Let $\tilde{U}(r)$ be any solution of Eq. (38) neither fulfilling the boundary conditions (39) nor (42). Since the second derivative of linear function is zero then the function $U(r) = \tilde{U}(r) + \alpha r + \beta$ for $\alpha, \beta \in \boldsymbol{R}$ is also the solution of Eq. (38). Since (39) and (42) are Dirichlet boundary conditions, then for any $\tilde{U}(0), \tilde{U}(R)$ there exist α, β that $U(r)$ fulfills (39) and (42). The coefficients α, β are calculated from equations

$$\left.\begin{array}{ll} 0 & = U(0) = \tilde{U}(0) + \alpha 0 + \beta \\ \Omega & = U(R) = \tilde{U}(R) + \alpha R + \beta \end{array}\right\} \Rightarrow \left\{\begin{array}{ll} \beta & = -\tilde{U}(0)\,, \\ \alpha & = \dfrac{[\Omega - \tilde{U}(R) + \tilde{U}(0)]}{R}\,. \end{array}\right. \tag{43}$$

If we assume $\tilde{U}(0) = 0$ then we have

$$\beta = 0\,, \qquad \alpha = \frac{\Omega - \tilde{U}(R)}{R}\,. \tag{44}$$

Finally, the solution of Eq. (38) that fulfills the boundary conditions (42) and (39) is given by

$$U_e(r) = \tilde{U}(r) + \frac{r}{R}\left(\Omega - \tilde{U}(R)\right) . \qquad (45)$$

The solution $\tilde{U}(r)$ can be found using Numerov algorithm [3] treating Eq. (38) as an initial value problem with boundary condition $\tilde{U}(0) = 0$, $\tilde{U}'(0) = 1$. Numerov algorithm runs on uniform mesh and calculates the values in the mesh nodes. Above presented algorithm is very efficient since one call of Numerov procedure calculates values of potential $V_e(r)$ in any mesh node.

3.7. Self-consistent-field SCF

To calculate $\rho(\boldsymbol{r})$ from Eq. (14) the eigenfunctions $\psi_\mu(\boldsymbol{r})$ must be known. The eigenfunctions $\psi_\mu(\boldsymbol{r})$ are the solutions of Kohn–Sham Eq. (1), where the potential $V(\boldsymbol{r})$ given by Eq. (2), is used. It is assumed in DFT method that $V(\boldsymbol{r})$ depends on $\rho(\boldsymbol{r})$. From the above it follows that charge distribution $\rho(\boldsymbol{r})$ is recursively defined. This kind of problems can be solved iteratively. The initial value of the charge must be set and updated according to the appropriate scheme. The initial value $\rho_0(\boldsymbol{r})$ must be chosen so that the total charge is equal to the total numbers of the electrons. Additionally $\rho_0(\boldsymbol{r})$ must lie inside the convergence radius of the applied scheme. It is evident that the number of iterations depends on initial guess $\rho_0(\boldsymbol{r})$. For example for atom one can use

$$\rho_0(r) = \frac{p^4}{64\pi}\, e^{-pr/2} , \qquad (46)$$

where p is the number of the electrons. It is easy to verify that $p = 4\pi \times \int_0^\infty r^2 \rho_0(r) dr$, as required.

The update schema for the electron density is based on fixed point theorems [9]. There are two theorems about fixed point: Banach and Schauder listed below without proof. Let $\mathcal{X}$ denote Banach space.

Theorem 1 (Banach) *Let $\mathcal{A} : \mathcal{X} \to \mathcal{X}$ be a nonlinear mapping satisfying:*

$$||\mathcal{A}[u] - \mathcal{A}[\tilde{u}]|| < \gamma ||u - \tilde{u}|| \quad \forall u, \tilde{u} \in \mathcal{X}$$

for constant $\gamma < 1$. Then $\mathcal{A}$ has exactly one fixed point.

Theorem 2 (Schauder) *Assume $\mathcal{K} \subset \mathcal{X}$ is compact, convex set. If $\mathcal{A} : \mathcal{K} \to \mathcal{K}$ is continuous mapping then $\mathcal{A}$ has a fixed point in $\mathcal{K}$.*

Based on these theorems the following electron density updating scheme was proposed [15]

1. Calculate V_e, solving Poisson equation for charge ρ, Sec. 3.6.
2. Calculate interaction potential $V(\boldsymbol{r})$, Eq. (2).
3. Solve Eq. (9), with potential $V(\boldsymbol{r})$, Sec. 3.10.
4. Calculate occupation coefficient f_μ and charge ρ_{new}, Sec. 3.4.
5. Calculate total energy E_{new} for ρ_{new}, Sec. 3.5.
6. If $|E_{\mathrm{new}} - E| < \varepsilon_e$ and $||\rho_{\mathrm{new}} - \rho|| < \varepsilon_\rho$ then END. Else $E = E_{\mathrm{new}}$, $\rho = \rho_{\mathrm{new}}$ and go to point 1.

This is the self-consistent-field (SCF) procedure. The convergence radius of this procedure is finite. To increase the convergence radius the coefficient κ is introduced mixing old and new charge density

$$\rho = (1 - \kappa)\rho + \kappa\rho_{\mathrm{new}} \,. \tag{47}$$

If $\kappa = 1$ then $\rho = \rho_{\mathrm{new}}$ and there is no mixing. Applying $\kappa < 0.1$ facilitates SCF procedure to converge even for "difficult" systems. Usually the convergence is achieved for less then 100 iterations with the convergence criteria $\varepsilon_e = \varepsilon_\rho = 10^{-7}$.

3.8. Extrapolation of approximated solution

Assume that Eq. (1) was solved by SCF procedure using the uniform mesh $\mathcal{M}_h$ having the distance h between nodes. Denote by $\mathcal{S}_h$ the obtained solution. Let introduce the sequence of meshes $\{\mathcal{M}_{h_i}\}_{i=0}^m$ and solutions $\{\mathcal{S}_{h_i}\}_{i=0}^m$ that $h_0 > h_1 > \ldots > h_m$. Each solution $\mathcal{S}_{h_i}$ is the approximation of exact solution $\mathcal{S}$ which can be obtained as the limit

$$\mathcal{S} = \lim_{h \to 0} \mathcal{S}_h \,. \tag{48}$$

This limit cannot be achieved numerically due to the finite computer capacity. Despite that, the limit (48) can be estimated by extrapolation for $h = 0$ using Neville algorithm [25]. This procedure is called the Richardson extrapolation and it is valuable tool in the solution of differential equations on the discrete meshes. Since the finite difference approximation of second derivative given by Eq. (53) is of order $\mathcal{O}(h^2)$, the Richardson extrapolation must be done for h^2 variable.

When starting SCF procedure for mesh $\mathcal{M}_{h_{i+1}}$, the electron density $\rho(r)$ calculated in SCF procedure for mesh $\mathcal{M}_{h_i}$ is used. Since $h_{i+1} < h_i$ interpolation of $\rho(r)$ on mesh points is needed. The interpolation is the easiest when $h_{i+1} = h_i/2$. The application of interpolated electron density in consecutive SCF procedures decreases the number of iterations. The convergence criteria of SCF for mesh $\mathcal{M}_{h_i}$ can be larger then for mesh $\mathcal{M}_{h_{i+1}}$. This feature also decreases the number of iterations needed to achieve the convergence.

3.9. VWN and Slater approximation for exchange and correlation

In the description we use the quantity $r_s = (3/(4\pi\rho))^{1/3} \Leftrightarrow \frac{4}{3}\pi r_s^3 = 1/\rho$. In Slater approximation the exchange energy density, ε_x, and potential, V_x, are given by [15]

$$\varepsilon_x(r_s) = \frac{3}{4}\frac{c}{r_s}\,, \qquad V_x(r_s) = \frac{c}{r_s}\,, \qquad c = -\left(\frac{3}{2\pi}\right)^{2/3}. \tag{49}$$

In the Ref. [26, 27] the following equation for VWN density of correlation energy was given

$$\varepsilon_c(r_s) = \frac{a}{2}\left\{\ln\left(\frac{x^2}{P(x)}\right) + \frac{2b}{q}Y(x) - \frac{bx_0}{P(x_0)}\left[\ln\left(\frac{(x-x_0)^2}{P(x)}\right) + \frac{2(b+2x_0)}{q}Y(x)\right]\right\}. \tag{50}$$

For the clarity of the implementation this can be presented in equivalent form

$$\varepsilon_c(r_s) = \frac{a}{2}\Big[\ln(D(x)) + f_1 Y(x) + f_2 \ln(W(x)) + f_3 Y(x)\Big]. \tag{51}$$

According to VWN the potential is given by

$$V_c(r_s) = \varepsilon_c(r_s) - \frac{a}{6}\frac{c(x-x_0) - bxx_0}{(x-x_0)P(x)}\,. \tag{52}$$

In the above equations the following coefficients and functions were used:

$a = 0.0621814\,,$ $\quad x = \sqrt{r_s}\,,$ $\quad P(x) = x^2 + bx + c = r_s + bx + c\,,$
$b = 3.72744\,,$ $\quad q = \sqrt{4c - b^2}\,,$ $\quad D(x) = x^2/P(x) = r_s/P(x)\,,$
$c = 12.9352\,,$ $\quad f_1 = 2b/q\,,$ $\quad Y(x) = \arctan(q/(2x+b))\,,$
$x_0 = -0.10498\,,$ $\quad f_2 = -bx_0/P(x_0)\,,$ $\quad W(x) = (x-x_0)^2/P(x)\,,$
$f_3 = 2(b+2x_0)f_2/q\,,$

3.10. Eigenproblem $\alpha y''(x) + g(x)y(x) = \lambda y(x)$

Let consider the algorithm of numerical solution of the following eigenproblem

$$\alpha y''(x) + g(x)y(x) = \lambda y(x)\,, \tag{53}$$

where the function $g(x)$ is given and $\alpha \in \mathbb{R}, \alpha \neq 0$. We look for pairs $(\lambda, y(x))$ being the solution of Eq. (53). Additionally, assume that $y(x)$ is defined on the interval $[a, b]$ and that $y(x)$ has to satisfy Dirichlet boundary conditions

$$y(a) = y(b) = 0\,. \tag{54}$$

We are interested in finding a few (usually less then 10) lowest eigenvalues and eigenfunctions. In this section we present the algorithm reducing Eq. (53) to the algebraic eigenvalue problem. We present also the theorems used by the bisection method.

Let define the sequence of nodes $\{x_i\}_{i=0}^{N+1}$ on the interval $[a, b]$ that $a = x_0 < x_1 \ldots < x_N < x_{N+1} = b$. Let the distance between nodes be $h = (b-a)/(N+1)$ then $x_i = a + ih$ for $i = 0, 1, \ldots, N+1$. The algorithm below calculates the values of the function $y(x)$ in the nodes x_i. To simplify the notation we put $y_i = y(x_i)$, $f_i = f(x_i)$, $g_i = g(x_i)$. Then the function $y(x)$ is represented by the vector $\boldsymbol{y} = [y_0, y_1, \ldots, y_{N+1}]^T$. In this notation the Dirichlet boundary conditions (54) are

$$y_0 = y_{N+1} = 0\,. \tag{55}$$

3.10.1. Finite difference

The finite difference algorithm approximates the second derivative as the linear combination of the values in three consecutive nodes

$$y''_{i+1} = \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2}\,, \tag{56}$$

what can be derived using Taylor expansion [25]. Substituting Eq. (56) into Eq. (53) we get

$$w\alpha y_{i-1} + (g_i - 2w\alpha)y_i + w\alpha y_{i+1} = \lambda y_i\,, \tag{57}$$

where $w = 1/h^2$. Eq. (57) is valid for $i = 1, \ldots, N$. Substituting Dirichlet boundary conditions (55) into Eq. (57) we get the algebraic eigenproblem

$$\boldsymbol{A}\boldsymbol{y} = \lambda \boldsymbol{y}\,. \tag{58}$$

The matrix $\boldsymbol{A}$ of dimension $N \times N$ is real, symmetric and tridiagonal. The elements of the matrix $\boldsymbol{A}$ are defined by

$$a_{ij} = \begin{cases} g_i - 2w\alpha & \text{for} \quad i = j\,, \\ w\alpha & \text{for} \quad |i-j| = 1\,. \end{cases} \tag{59}$$

In this way we reduced the functional eigenproblem (53) to the algebraic eigenproblem with symmetric, tridiagonal matrix. The effective algorithm calculating the selected eigenvalues and eigenfunctions is given in the next section.

3.10.2. Eigenproblem $\boldsymbol{T}\boldsymbol{y} = \lambda \boldsymbol{y}$ for tridiagonal matrix

In this section we give the effective algorithm (based on the bisection) of finding the selected eigenvalues and eigenvectors of the real, symmetric, tridiagonal matrix $\boldsymbol{T}$. The justification of this algorithm can be found in Ref. [1, 2, 8, 25]. The bisection method is based on the following theorem:

Theorem 3 *Let symmetric tridiagonal matrix* $\boldsymbol{T}$ *has diagonal elements* $c_1, \ldots, c_N$ *and nonzero off-diagonal* $b_1, \ldots, b_{N-1}$, $b_i \neq 0$. *For given* $\lambda \in \mathbb{R}$ *define sequence* $\{q_i\}_{i=1}^{N}$:

$$\begin{aligned} q_1(\lambda) &= c_1 - \lambda\,, \\ &\text{if} \qquad q_{i-1}(\lambda) \neq 0\,, \qquad q_i(\lambda) = (c_i - \lambda) - \frac{b_{i-1}^2}{q_{i-1}(\lambda)}\,, \\ &\text{if} \qquad q_{i-1}(\lambda) = 0\,, \qquad \left\{ \begin{array}{ll} q_i(\lambda) & = -1\,, \\ q_{i+1}(\lambda) & = c_{i+1} - \lambda\,. \end{array} \right. \end{aligned}$$

Then the number, $\eta(\lambda)$*, of negative elements of sequence* $\{q_i(\lambda)\}$ *is equal to the number of the eigenvalues less then* λ.

It is easy to note the following properties of the function $\eta(\lambda)$:

- It is piecewise constant and non-decreasing.
- It is greater or equal to zero: $\forall_\lambda\ \eta(\lambda) \geq 0$.
- It has the discontinuity for any eigenvalue of the matrix $\boldsymbol{T}$.
- The jump at the discontinuity point z is 1:

$$\lim_{\lambda \to z^-} \eta(\lambda) = \lim_{\lambda \to z^+} \eta(\lambda) - 1\,. \tag{60}$$

It means that searching j-th eigenvalue of $\boldsymbol{T}$ is equivalent to searching j-th discontinuous point of function $\eta(\lambda)$. The bisection is the best choice to find the discontinuity of the piecewise constant function [22]. To start up the bisection algorithm we must know the bounds for the eigenvalue z_j. The estimation of the bounds can be calculated from Gershgorin theorem [25] valid for any square matrix:

Theorem 4 (Gershgorin) *Let $\mathbb{C}$ be set of complex numbers and a_{ij} denote elements of square matrix $\boldsymbol{A}$ of dimension N. Then the sum of all circles*

$$\mathcal{K}_i = \left\{ \mu \in \mathbb{C} : |\mu - a_{ii}| \leq \sum_{k=1, k\neq i}^{N} |a_{ik}| \right\} \tag{61}$$

contains all eigenvalues of matrix $\boldsymbol{A}$.

The real, symmetric matrix has the real eigenvalues [25]. Thus the circles in Gershgorin theorem reduces to the intervals of the real numbers. Additionally, for the tridiagonal matrix $\boldsymbol{T}$, the sum in (61) reduces to two elements. Using the notation from Theorem 3 we get:

$$\mathcal{K}_i = \{ \mu \in \mathbb{R} : |\mu - c_i| \leq |b_i| + |b_{i-1}| \} \,. \tag{62}$$

Now it is easy to give lower, $\lambda_{\min}$, and upper, $\lambda_{\max}$, bound of the eigenvalue for the tridiagonal matrix $\boldsymbol{T}$. The lower (upper) bound is the smallest (greatest) element from all intervals $\mathcal{K}_i$

$$\begin{aligned} \lambda_{\min} &= \min_i (c_i - |b_i| - |b_{i-1}|) \,, \\ \lambda_{\max} &= \max_i (c_i + |b_i| + |b_{i-1}|) \,. \end{aligned}$$

The above mentioned arguments are sufficient to calculate jth eigenvalue. In order to calculate w the smallest eigenvalues it is sufficient to call w-times this algorithm, for $j = 1, \ldots, w$.

The j-th eigenvector, $\boldsymbol{y}^{(j)}$, for the eigenvalue λ_j is calculated by the inverse iteration (also called Wielandt iteration). The description of this method can be found in Ref. [22,25]. The procedure in `Algol` for tridiagonal matrix is given in Ref. [29]. The algorithm assume that the eigenvalue λ_j is close enough to exact eigenvalue of matrix $\boldsymbol{T}$. This assumption is satisfied for λ_j calculated by the bisection method described above. The eigenvector $\boldsymbol{y}^{(j)}$ is calculated iteratively using the fact that the matrix $\boldsymbol{T} - \lambda_i \mathbf{1}$ is almost singular.

4. `RAtom` program

4.1. The structure and implementation

The algorithm of the solution Kohn–Sham equation for the atom in the spherical symmetric potential is implemented in the program `RAtom`. The implemented algorithms are identical to described in the present work. `RAtom` is the command line program. It needs one argument — the name of the file with the parameters. `RAtom` was implemented in `C++` language according to the best style of the object programming. The classes was designed to represent the algorithms and the concepts described in this paper. The simple interfaces enable easy communication between the objects.

The Kohn–Sham equation is solved on the radial uniform mesh. The properties of the mesh are implemented in the class `Mesh`. The quantities such as potential or the electron density are calculated at the mesh nodes. Only values in the mesh nodes are used. The interpolation is not needed. Therefore, often used class is `Vec`, representing vector of the real numbers. The algorithm of solving the Poisson equation is implemented in the class `Poisson`. This class calculates the electrostatic potential using the Numerov algorithm for the given charge distribution. The bisection algorithm of finding the selected eigenvalues and eigenvectors is implemented in the class `EigenProb`. The information about considered atom and its states are located in the class `Atom`. This class keeps information about the eigenvectors and it calculates the electron distribution used to evaluate the total energy. The exchange and correlation potential are defined in the class `Dft`. Information about results of SCF procedure are written in `ScfInfo`. The class `KohnSham` coordinates data flow between used objects. The input-output operations are realized by the class `InOut`. The errors are signaled by throwing the exceptions of the class `Except`.

4.2. The solutions for N, Al, Ga and In

`RAtom` was used to calculate the eigenvalues of N, Al, Ga and In atom. For each atom maximum number of the nodes in the mesh was 32 000 (in case of In it was 64 000). The radius of the mesh applied to solve Kohn–Sham equation was 30 bohr, but the radius used to solve the Poisson equation was twice larger. For calculation of the exchange and correlation energies the VWN and Slater approximations were chosen. The convergence conditions in SCF procedure for the energy and electron density was 10^{-7}. The convergence was achieved in less then 100 iterations. The Richardson extrapolation was done using meshes having $4, 8, 16, 32, (64)$ thousands of nodes. The extrapolated eigenvalues are listed in Table I. In Table II the extrapolated components of total energy are given. Both quantities are expressed using atomic energy units: hartree [Ha].

`RAtom` calculates also the radial electron distribution. However, the more intuitive quantity is the charge distribution integrated over the sphere:

$$W(r) = \int_{\Omega} \rho(r) d\Omega = 4\pi r^2 \rho(r) \,. \tag{63}$$

TABLE I

Energy eigenvalues for atom N, Al, Ga and In in [Ha]. VWN and Slater approximations were used for the correlation and exchange. The Richardson extrapolation was done using meshes with $4, 8, 16, 32$ thousand of nodes. The radius of the mesh is 30 bohrs. The convergence level for the total energy and the electron density was set to 10^{-7}.

	RAtom	NIST		RAtom	NIST
N, 1s	−14.011502	−14.011501	Al, 1s	−55.156045	−55.156044
N, 2s	−0.676151	−0.676151	Al, 2s	−3.934827	−3.934827
N, 2p	−0.266297	−0.266297	Al, 2p	−2.564018	−2.564018
			Al, 3s	−0.286883	−0.286883
In, 1s	−983.647451	−983.647445	Al, 3p	−0.102545	−0.102545
In, 2s	−144.078363	−144.078357			
In, 2p	−134.628851	−134.628845	Ga, 1s	−370.170639	−370.170639
In, 3s	−27.220606	−27.220600	Ga, 2s	−45.200869	−45.200869
In, 3p	−23.345783	−23.345778	Ga, 2p	−40.093340	−40.093339
In, 3d	−16.139829	−16.139823	Ga, 3s	−5.241645	−5.241645
In, 4s	−4.062645	−4.062639	Ga, 3p	−3.584667	−3.584666
In, 4p	−2.795838	−2.795832	Ga, 3d	−0.736205	−0.736204
In, 4d	−0.730487	−0.730481	Ga, 4s	−0.328019	−0.328019
In, 5s	−0.290503	−0.290497	Ga, 4p	−0.101634	−0.101634
In, 5p	−0.101788	−0.101782			

TABLE II

Total energy and its constituents for N, Al, Ga and In in [Ha]. Rows marked by $\ast$ denote data from `NIST`, Ref. [17]. Rows marked by $\diamond$ denote data obtained by program `RAtom`. See description for Table I.

	E_t	E_k	E_{xc}	E_e
$\diamond$ N	−54.025018	53.731727	−6.140359	25.799841
$\ast$ N	−54.025016	53.731727	−6.140359	25.799845
$\diamond$ Al	−241.315578	240.663490	−17.444038	112.670728
$\ast$ Al	−241.315573	240.663489	−17.444038	112.670733
$\diamond$ Ga	−1921.846447	1919.894801	−71.919391	833.754972
$\ast$ Ga	−1921.846456	1919.894783	−71.919393	833.754978
$\diamond$ In	−5737.309210	5733.944125	−150.814984	2334.432301
$\ast$ In	−5737.309064	5733.944120	−150.814984	2334.432447

In Fig. 1, the density $W(r)$ for N, Al, Ga and In is presented. The logarithmic scale is used on the vertical axis. For all atoms the maxima are easily visible, which is related to the atomic shell structure. The In atom has four maxima, the Ga has three, the Al and N atom have two. For example the maxima for Ga are located at the following distances: $r_1 = 0.035$, $r_2 = 0.16$, $r_3 = 0.55$ bohr.

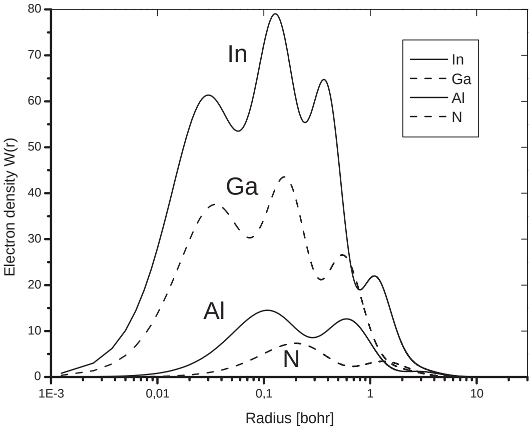

Fig. 1. Distribution of the electron density integrated over the sphere for atom N, Al, Ga and In, Eq. (63). On the horizontal axis the logarithmic scale is used. The shell structure of the atom is easily seen.

If we draw $\ln(W(r))$ in the figure with linear scale, then we note that for $r > 3$ the function is approximately linear. Using the least square method, it is easy to calculate the coefficients of line $\ln(W(r)) = A + Br$ for N, Al, Ga and In

$$\begin{array}{rll} \text{N:} & A = 1.36\,, & B = -0.64\,, \\ \text{Al:} & A = 1.23\,, & B = -0.40\,, \\ \text{Ga:} & A = 1.27\,, & B = -0.40\,, \\ \text{In:} & A = 1.46\,, & B = -0.41\,. \end{array}$$

It it clear that all group III metal atoms (Al, Ga, In) have similar asymptotic behavior of $W(r)$. The quantity $W(r)$ decays as $W(r) \propto e^{-0.4r}$.

4.3. Comparison with shooting method

In Ref. [17, 18] the eigenvalues for all free atoms from periodic table are given. The calculations were performed using VWN and Slater approximation. Eq. (9) was solved using shooting method [7] on the logarithmic meshes and then extrapolated. The eigenvalues obtained by method described in

Ref. [17, 18] are listed in Table I in the column `NIST`. The eigenvalues calculated by algorithm described in this paper are given in Table II in the column `RAtom`. The component of total energy are written in Table II. The differences between the eigenvalues calculated by `RAtom` and the values from `NIST` are less then 10^{-5} Ha $\approx 3 \times 10^{-4}$ eV. The difference between the components of the total energy is less then 2×10^{-4} Ha $\approx 6 \times 10^{-3}$ eV. The difference increases with increasing the number of the electrons in the atom.

The following conclusions can be drawn: the finite difference approximation on the uniform mesh and the Richardson extrapolation is the sufficient tool to calculate the eigenvalues with the accuracy of 10^{-5}Ha. This precision is sufficient in the majority of the practical calculations.

To start the shooting method the estimation of the eigenvalues is needed. This is the drawback of the shooting method. This shortcoming does not exist in the algorithm described in this paper. The calculations of the eigenvalues are based on the bisection. The bisection follows from the theorems that guarantee the existence of the solution. Additionally ours method is very efficient. For example, the calculation for In atom takes less than 5 minutes on Pentium IV, 1.7 GHz PC. The features of `RAtom` are used to calculated eigenvalues of atoms confined in the infinite quantum well.

4.4. Atom in quantum well

In section 4.2 we presented the eigenvalues of Eq. (9) defined on interval $r \in [0, \chi]$ (where $\chi = 30$ bohr) with the Dirichlet boundary conditions: $R_{n,l}(0) = R_{n,l}(\chi) = 0$. Zeroing of each atom eigenfunction, $R_{n,l}(r)$, for $r \geq \chi$ is equivalent to putting the atom inside the infinite quantum well [20] of the radius χ. By decreasing χ, the atom is squeezed by the external potential. The total charge of the atom during squeezing is preserved, thus the charge distribution must be changed. For the free atom the electron distribution gives the lowest possible energetic states. Thus the electron distribution changed by squeezing will give the higher eigenvalues.

In this section we present results obtained for atom Ga located in infinite quantum well of radius $\chi \leq 30$ bohr. The four highest eigenvalues of Ga $(4p, 4s, 3d, 3s)$ as a function the radius χ is shown in Fig. 2. The decrease of the radius χ of the quantum well leads to increase of the energy eigenvalues. For example for $\chi = 5$ bohr we get the eigenvalue for $4p$ greater then zero: $E_{4p} = 0.017$ Ha. When the radius of quantum well is less then 5 bohr the eigenvalues increase rapidly. On the other side, the eigenvalues for $\chi = 20$ and $\chi = 30$ are essentially the same. This is the computational proof that the calculation for $\chi = 30$ represents the free atom. In the Ref. [11] the similar results for the sodium atom were obtained. In Fig. 3, the eigenvectors $4p$ for Ga atom, located in the quantum well of the radius 30 and 5 bohr,

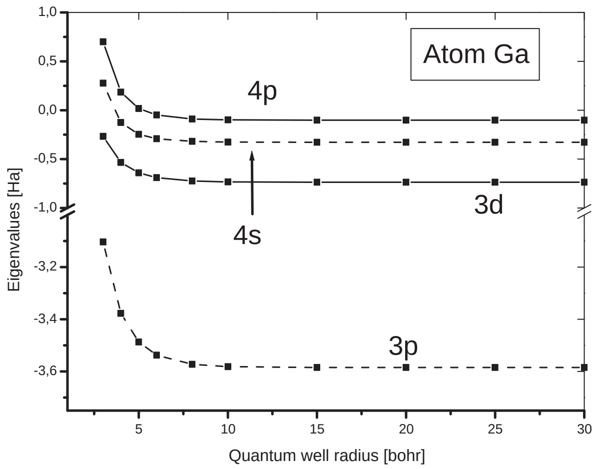

Fig. 2. Energy of four highest states for Ga atom $(4p, 4s, 3d, 3s)$ as the function of the quantum well radius. The energy rises when atom is squeezed by the infinite quantum well.

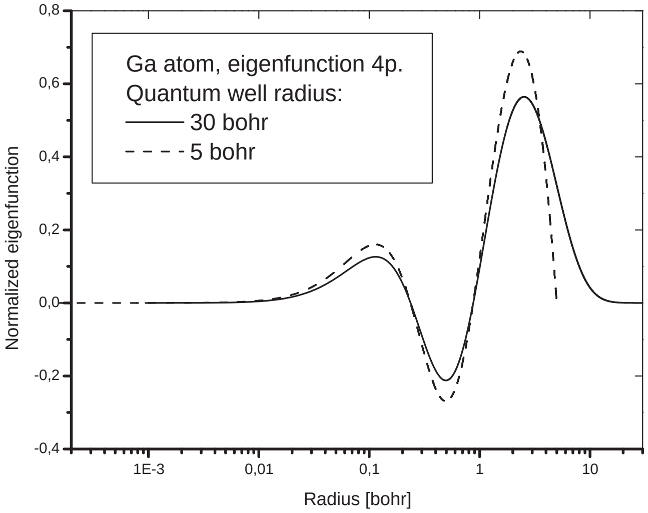

Fig. 3. Eigenvector of $4p$ for Ga atom. The Ga atom is located in the infinite quantum well. The diameter of well is 30 and 5 bohrs. The squeezing of Ga atom in 5 bohr quantum well causes the increase in the gradients of the eigenfunction $4p$. On the vertical axis the logarithmic scale.

are presented. Locating Ga atom in the quantum well of the radius 5 bohr causes the changes of $4p$ eigenvector even for distances of 0.1 bohr. Squeezing the Ga atom causes the increase in the gradient of the electron density distribution.

All above results were obtained by `RAtom`. We noted that the implemented algorithms were stable for all studied cases. The eigenvalues did not need be estimated. It is valuable advantage, especially during the squeezing of the atoms where the estimation of the eigenvalues is not straightforward.

5. Summary

The efficient and easy to implement algorithm of solution the Kohn–Sham equation for atom on uniform mesh was presented. The program written in `C++` is efficient and stable. Application to the III–V group atoms gives eigenvalues with accuracy higher then 10^{-5} Ha. The reported results were obtained with VWN and Slater approximations. It is equally easy to implement in `RAtom` any LDA approximation. The program was applied to study the influence of the infinite quantum well on the eigenvalues of Ga atom. The eigenfunctions calculated for the atom located in the infinite quantum well can serve as a basis functions applied in DFT LCAO calculations for the molecules and clusters. The application of this basis will be reported in the separate article.

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