

REGULARIZATION OF COULOMB POTENTIAL FOR CALCULATING ELECTRON DENSITY IN QUANTUM MECHANICAL SYSTEMS

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Abstract: In this paper we show a simple and effective method for regularizing the Coulomb potential for numerical calculations of quantum mechanical problems, such as, for example, the solution of the Schrödinger equation, the expansion of charge density and others. The introduction explains why the regularization of the Coulomb potential is important. In the second part, the regularization method itself as well as its advantages and disadvantages will be described in detail. The third part demonstrates some numerical calculations for the Sulfur + Hydrogen system using the proposed method. In the final part, the obtained results are summed up.

Keywords: regularization, Coulomb potential, electron density

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1. Introduction

The numerical methods play an important role in scientific calculations, especially for solving quantum mechanics and quantum chemistry problems. For example, a precise solution of the Schrödinger equation is available only for the case of one particle. Therefore, different methods such as the method of diagonalization, the spectral method, the method of splitting, and many others, are applied for solving quantum-mechanical problems with a large number of degrees of freedom, see [1–3], for example. One of the most promising methods is the Hartree-Fock method [4–6]. In the framework of this method, the problem for many particles with a volume of calculations exponentially increasing with the number of particles is reduced to a simplified problem with a volume of calculations polynomial with respect to the number of particles.

We develop a program that solves the Schrödinger equation for quantum-mechanical systems with a Coulomb interaction potential between nuclei

and electrons. In a number of very simple cases, one has no problems with analytic solution of problems with the Coulomb potential. However, we always have some problems with numerical solution of problems with the Coulomb potential, since the Coulomb potential has the form $\frac{1}{r}$, and this potential has a singularity at $r \rightarrow 0$. $\frac{1}{r}$ tends to infinity when r tends to 0. For example, when one tries to calculate numerically such an integral with a singularity in the integrand applying the usual quadrature formulas and using the integrand values at the points of some mesh, the computational error turns out to be very large. To avoid this, first, we have to understand the integrals of functions with singularities as improper integrals, and secondly, we have to apply special methods of numerical integration, adapted to such dangerous behavior of the integrand functions. Such special methods of special overdetermination of functions with singularities and overdetermination of integrals of functions with singularities and special methods of numerical computation of such dangerous integrals are called the general word "regularization".

In addition to the regularization technique of the Coulomb potential for calculations of integrals for complex quantum-mechanical systems, now the so-called pseudopotential method is applied and it is popular and looks promising [7–9]. Its essence consists in reducing the problem with many electrons and a nucleus to a problem with only valence electrons and a core consisting of a nucleus and all other electrons. Such technique is quite natural, since the main contribution to the behavior of chemical elements in chemical reactions is determined by the valence electrons of these elements. Thus, the fields of such introduced cores are described by pseudopotentials.

We can make the assumption that the correct regularization of singularities, together with the pseudopotential method, may yield a significant gain in the computation of relatively complex quantum-mechanical systems.

Thus, in the first part of the paper we show a simple method for regularizing the Coulomb potential. In the second part, we will test the working capacity of this method on a simple example using the software written by us. In the final part, we sum up the results of the paper.

2. Simple method of Coulomb potential regularization

As has been said, Coulomb potential has a singularity at $r \rightarrow 0$, $\frac{1}{r} \rightarrow \infty$. In the $r = 0$ point the function is undefined and its derivatives do not exist. Therefore, the scalar product $\langle \Psi, \hat{H}\Psi \rangle$ cannot be understood in the usual sense, since the usual integrals do not exist, since $\frac{1}{r}$ is a part of Hamiltonian \hat{H} . Approximation of the integral $\langle \Psi, \hat{H}\Psi \rangle$ with any usual quadratic formulas is incorrect.

In order to describe the essence of this mathematical difficulty more easily, it is convenient to first consider the integral $I = \int_a^b f(x)dx$ of a function of one variable. We "approximate" this integral with the usual quadrature formula

$$\sum_{i=0}^{N-1} f(\xi_i)(x_{i+1} - x_i), \text{ where } \xi_i \in [x_i, x_{i+1}], x_0 = a, x_N = b \quad (1)$$

However, this “approximation” is valid only for smooth functions.

There are functions with integrable singularities among functions with singularities. These are functions for which the integrals can be reasonably redefined in such a way that integrals exist. Obviously, it is possible to propose a numerical method for calculating such integrals. Let us consider, for example, the integral

$$\int_a^b f(x)\psi(x)dx \tag{2}$$

where $f(x)$ is a function with integrable singularity, and $\psi(x)$ is a smooth function. Such an integral can be approximated with the expression

$$\int_a^b f(x)\psi(x)dx \approx \sum_{i=0}^{N-1} \psi(\xi_i) \int_{x_i}^{x_{i+1}} f(x)dx, \quad \xi_i \in [x_i, x_{i+1}] \tag{3}$$

It is assumed that the values of the integrals $\int_{x_i}^{x_{i+1}} f(x)dx$ are known, and we know and apply them.

We shall try to develop this idea and apply it to the calculation of integrals of the form

$$\int_{R^3} \frac{\rho(\acute{x}, \acute{y}, \acute{z})}{\sqrt{(x-\acute{x})^2 + (y-\acute{y})^2 + (z-\acute{z})^2}} d\acute{x}d\acute{y}d\acute{z} \tag{4}$$

of functions with integrable singularity. We change the variables

$$x'' = \acute{x} - x, \quad y'' = \acute{y} - y, \quad z'' = \acute{z} - z \tag{5}$$

and transform the integral to some convenient standard form

$$\int_{R^3} \frac{\rho(x'' + x, y'' + y, z'' + z)}{\sqrt{x''^2 + y''^2 + z''^2}} dx'' dy'' dz'' \tag{6}$$

First of all, we note that it is possible to cut out a small neighborhood Ω_ε of the small radius ε around the singular point $(x'', y'', z'') = (0, 0, 0)$ and approximately replace the integral (6) with a regular integral

$$\int_{R^3/\Omega_\varepsilon} \frac{\rho(x'' + x, y'' + y, z'' + z)}{\sqrt{x''^2 + y''^2 + z''^2}} dx'' dy'' dz'' \tag{7}$$

The integral (7) can be calculated numerically with ordinary means of numerical calculations of integrals. Such a way is possible and justified in [10], but this way is rather crude and leads to an unjustifiably large number of computations.

Suppose we have an Ω grid in the space R^3 with nodes (x''_i, y''_j, z''_k) . We denote a cube with edge h centered in the node (i, j, k) node by ω_{ijk} . Then we can write

$$\int_{R^3} \frac{\rho(x'' + x, y'' + y, z'' + z)}{\sqrt{x''^2 + y''^2 + z''^2}} dx'' dy'' dz'' \approx \sum_{\omega_{ijk}(h)} \rho(x''_i + x, y''_j + y, z''_k + z) \int_{\omega_{ijk}(h)} \frac{1}{\sqrt{x''^2 + y''^2 + z''^2}} dx'' dy'' dz'' \tag{8}$$

Here the calculation of the integral

$$b_{ijk} = \int_{\omega_{ijk}(h)} \frac{1}{\sqrt{x''^2 + y''^2 + z''^2}} dx'' dy'' dz'' \quad (9)$$

is an obvious problem. We shall try to propose a simple and convenient procedure for calculating the integral. It is obvious that far from the center of the coordinate system

$$b_{ijk} \approx \frac{1}{r_{ijk}} h^3 \quad (10)$$

where r_{ijk} is the distance from the center of the coordinate system $(0,0,0)$ to the center of the cube $\omega_{ijk}(h)$. Therefore, it is only the calculation of these integrals near the point $(0,0,0)$ that might pose some difficulty.

We need to find such values a_{ijk} that we can write

$$b_{ijk} = a_{ijk} h^3 \quad (11)$$

This makes it convenient to work with integrals, using formulas for their calculation similar to the usual quadrature formulas. In essence, a_{ijk} is the proportionality coefficient between the value of the integral over the domain $\omega_{ijk}(h)$ and the volume h^3 of the domain $\omega_{ijk}(h)$.

These coefficients of proportionality can be found approximately by calculating the integrals over domains of integration almost coinciding with $\omega_{ijk}(h)$, but these domains of integration are such ones that the integrals can be calculated accurately for them.

Let us begin with consideration of neighborhood of the center of the coordinates system. Let's compute the integral over the ball of ε -radius:

$$\int_0^\varepsilon \frac{1}{r''} 4\pi r''^2 dr'' = 2\pi\varepsilon^2 \quad (12)$$

We divide the result (12) by the volume $\frac{4}{3}\pi\varepsilon^3$ of the ball and obtain the required approximation

$$a_{000} \approx \frac{3}{2\varepsilon} \quad (13)$$

Obviously, the question of a reasonable choice of ε arises. This question will be considered later. Now we only note that $\varepsilon \approx \frac{h}{2}$ should be included.

Now, we calculate an analogous averaging over the layer of a spherical surface of thickness 2ε . The required integral over the layer of a spherical surface of thickness 2ε is equal to

$$\int_{r-\varepsilon}^{r+\varepsilon} \frac{1}{r''} 4\pi r''^2 dr'' = 8\pi r\varepsilon \quad (14)$$

Let us divide the result by the volume $\frac{8}{3}\pi\varepsilon(3r^2 + \varepsilon^2)$ of the spherical layer of width 2ε . We get

$$a_{ijk} \approx \frac{r_{ijk}}{r_{ijk}^2 + \frac{\varepsilon^2}{3}} \quad (15)$$

Here r_{ijk} is the distance from the center to the node (i, j, k) .

Let us choose ε starting from the natural idea that the volume of our ball of radius ε should be equal to the volume h^3 of the cube $\omega_{ijk}(h)$. We obtain the equation

$$\frac{4}{3}\pi\varepsilon^3 = h^3 \quad (16)$$

Consequently,

$$\varepsilon = \left(\frac{3}{4\pi}\right)^{1/3} h \approx 0.6203504908h \quad (17)$$

This relation is satisfactory, since $\varepsilon \approx 0.5h$. And it will be natural in our technique of computing a_{ijk} to replace the cube $\omega_{ijk}(h)$ with a ball of an equal volume.

We note that a high accuracy of computing a_{ijk} is not required, since the main contribution to the integral for sufficiently small h is given by those cubes $\omega_{ijk}(h)$ for which $a_{Ijk} \approx \frac{1}{r_{ijk}}$.

The proposed idea of calculating the integrals of functions with singularities $\frac{1}{r}$ can be transformed to a form convenient for practical use. We combine the formulas (13) and (15) with the help of linear interpolation. As a result, the formula (13) will be a special case for $r = 0$, and the formula (15) will be a special case for $r \geq h$. Thus, we obtain the following convenient combined formula

$$v(r, h) = \begin{cases} \frac{3}{2\varepsilon} - \frac{r}{h} \left(\frac{3}{2\varepsilon} - \frac{h}{h^2 + \frac{\varepsilon^2}{3}} \right) & \text{if } r \leq h \\ \frac{r}{r^2 + \frac{\varepsilon^2}{3}} & \text{if } r > h \end{cases} \quad (18)$$

That is, the potential $\frac{1}{r}$ can be replaced with the potential (18) and can be treated as a normal smooth nonsingular potential. The ‘‘potential’’ $v(r, h)$ is continuous and depends on the grid step h . This dependence of the potential (18) on the step h is a good property because it adjusts the potential to the grid. See (17).

The introduced function is convenient because it is easily and flexibly applied to the grid and allows us to consider conveniently the potential of a charged particle located at any point of space.

3. Practical implementation

We use this method in the program (see the block-scheme in Figure 1) for calculation of the electron density of a quantum system $S^{3+} + H^+$ (for more detail see [11–13]). At this instant, we just take the potential of S^{3+} as the potential of a hydrogen-like atom multiplied by 3. The methods of pseudopotentials are not used in this paper, but we intend to apply them in future.

Thus, the program solves the Schrödinger equation numerically by the successive over-relaxation method – SOR [14]. In this example, the fast convergence of the iterative procedure is achieved at the mesh with 40–55 nodes along each coordinate axis.

As one can see in Figure 2–3, the new potential (18) describes the quantum system at various distances precisely enough.

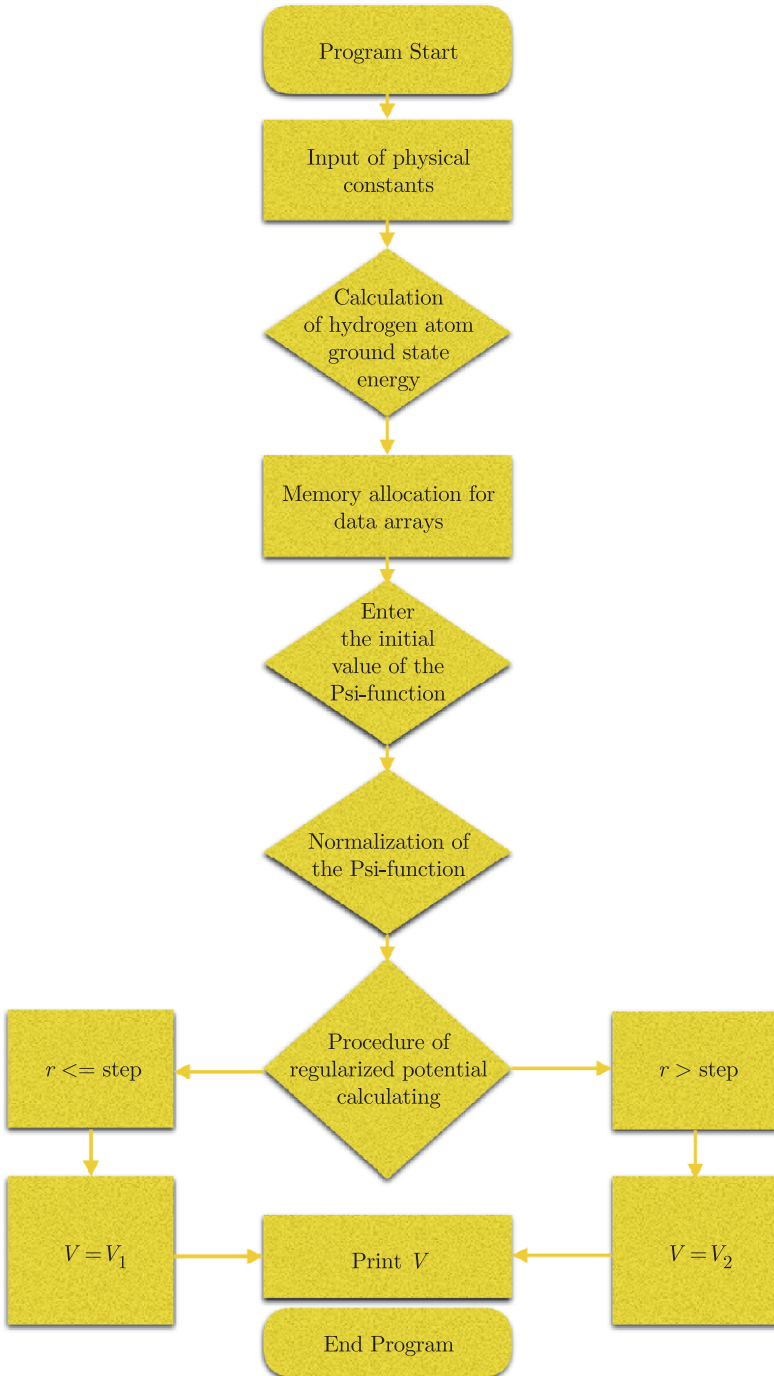


Figure 1. Block-Scheme of a program

$$\text{if } r \leq h \text{ then } V_1 = \frac{3}{2\epsilon} - \frac{r}{h} \left(\frac{3}{2\epsilon} - \frac{h}{h^2 + \frac{\epsilon^2}{3}} \right), \text{ else } V_2 = \frac{r}{r^2 + \frac{\epsilon^2}{3}}$$

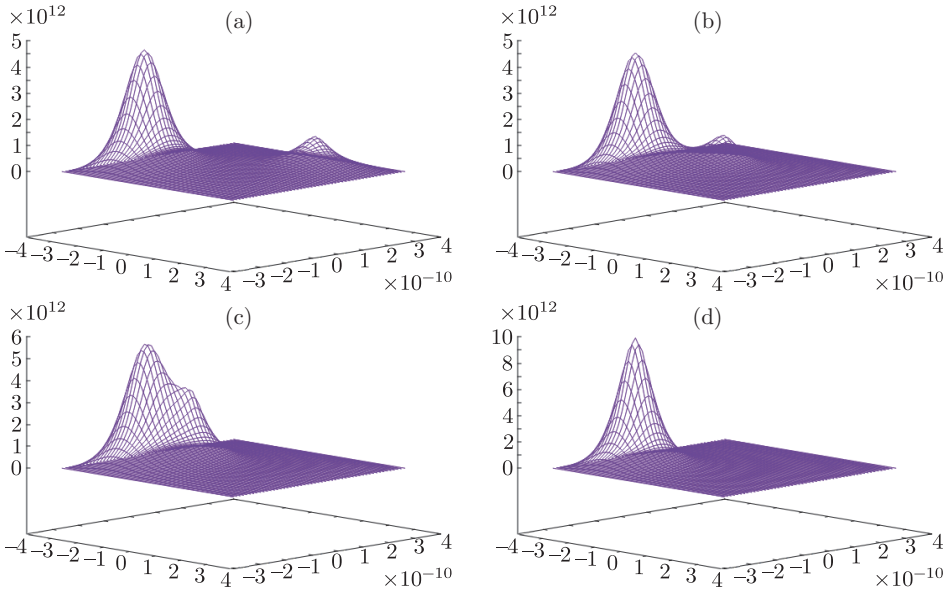


Figure 2. Stationary electron density distribution depending on the distance between potentials centers in 3D

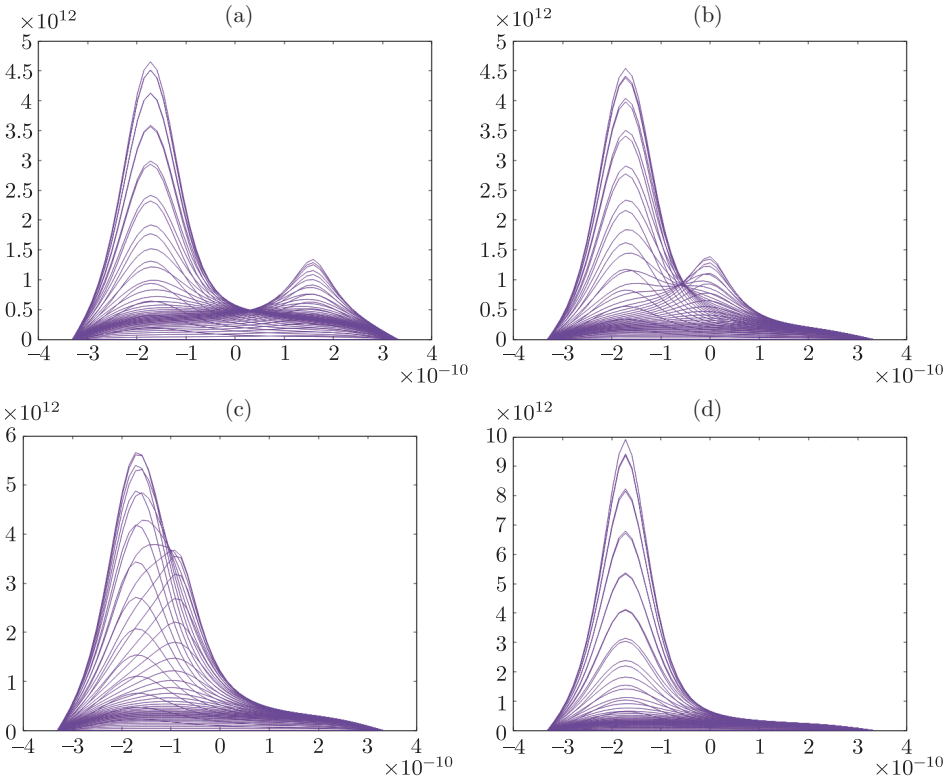


Figure 3. Stationary electron density distribution depending on the distance between potentials centers in 2D

4. Discussion and conclusions

In this paper we have shown that there is a relatively simple and convenient way in numerical calculations of quantum chemical processes performed on a computer to avoid problems due to the singularity of the Coulomb potential. We suppose it is important, since calculations with many standard methods are impossible at the singular point, and lead to significant computational errors near the singularity. The closer we are to the singularity point, the larger the computational error.

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