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DECOMPOSITION OF MOLECULAR CHARGE SPEEDS UP THE EVALUATION OF COULOMB POTENTIAL

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The method decomposing the molecular electron charge, which facilitates the evaluation of electrostatic potential, is presented. The decomposition is based on the observation, that in a free atom the electron charge distribution in the vicinity of its nucleus does not change, when the atom is incorporated into the molecule. In the decomposed system, the cusp singularity is integrated analytically by the application of the Green's function of Laplace operator for spherically symmetric systems. It is shown, that the residual charge, which is not treated analytically, is a smooth function and is close to zero in the vicinity of the nuclei. In the second part of the paper, the adaptive numerical integration algorithm is applied to obtain the Dirichlet boundary condition, required to any real space solver of Poisson equation.

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1. Introduction

Density Functional Theory (DFT) [13, 16] is a prospective method very popular in the computational quantum chemistry community. The widespread use of the method is mainly due to the low computational cost comparing to the Hartree–Fock method [4]. The Density Functional Theory, developed by Hohenberg, Kohn and Sham [10, 14] states that any property of the ground state molecular system is fully described by its electron charge density, $\varrho(\boldsymbol{r})$. In order to obtain the electron density, $\varrho(\boldsymbol{r})$, the Kohn–Sham eigenvalue problem must be solved:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{eff}}(\boldsymbol{r})\right]\psi_\mu(\boldsymbol{r}) = \varepsilon_\mu \psi_\mu(\boldsymbol{r})\,, \tag{1}$$

where $V_{\mathrm{eff}}(\boldsymbol{r})$ is an effective potential and μ is a multi-index. One of the constituent of the potential $V_{\mathrm{eff}}(\boldsymbol{r})$ is an electrostatic potential generated by the electron charge density $\varrho(\boldsymbol{r})$. Thus, in order to solve the Kohn–Sham equation, the electrostatic potential, $V(\mathbf{r})$, must be evaluated.

There are two common methods [1, 11] of obtaining the electrostatic potential $V(\boldsymbol{r})$ for a given charge distribution $\varrho(\boldsymbol{r})$. First method is based on the direct evaluation of the Coulomb integral:

$$V(\boldsymbol{r}) = \int\limits_{\mathbb{R}^3} \frac{\varrho(\boldsymbol{u})}{|\boldsymbol{u}-\boldsymbol{r}|} d\boldsymbol{u}\,. \tag{2}$$

In second method, the electrostatic potential is a solution of Poisson equation:

$$\nabla^2 V(\boldsymbol{r}) = -4\pi\varrho(\boldsymbol{r})\,. \tag{3}$$

For molecular systems (*i.e.* systems without periodic boundary conditions), the Poisson equation (3) is defined on the whole space $\mathbb{R}^3$ with Dirichlet boundary condition $\lim_{|\boldsymbol{r}|\to\infty} V(\boldsymbol{r}) = 0$.

There exist well developed methods to solve the Poisson equation on the finite domain $\Omega \subset \mathbb{R}^3$. The finite difference method [1], the finite element method [21], the wavelets [12] or the multigrid method [24], each of them transforms the continuous problem to the linear system of algebraic equations. Since the Poisson equation is a second order partial differential equation, in order to obtain the solution, the boundary conditions must be imposed [6] on the boundary of domain Ω. The value of potential $V(\boldsymbol{r})$ on the boundary of domain Ω (*i.e.* Dirichlet boundary condition) are usually obtained by direct integration of Eq. (2).

The accurate solution of the Poisson equation is a difficult task, since the molecular charge distribution has many cusp singularities [1]. Due to the same reason, the evaluation of Dirichelet boundary condition on the border of Ω by direct integration is difficult task, too. In the present paper we describe the method of efficient evaluation of electrostatic potential generated by the molecular charge. The method is based on the decomposition of molecular charge. The decomposition has two advantages:

- removes the cusp singularities,
- allows efficient evaluating of the electrostatic potential.

The structure of the paper is as follows. In Sec. 2 the decomposition of molecular charge is proposed. The equation for electrostatic potential generated by the spherically symmetric atom is derived in Sec. 3. The evaluation of the potential generated by residual charge is described in Sec. 4. The numerical results obtained by adaptive procedure is assessed in Sec. 5.

2. Molecular electrostatic potential

In this section the evaluation method of electrostatic potential $V(\boldsymbol{r})$ for molecular systems is described. Let us denote by $\varrho(\boldsymbol{r})$ the electron charge distribution characterizing the considered finite, molecular system. Let us assume, that the molecule is built from N atoms. Further, let us denote by $\varrho_{\mathrm{a},i}(\boldsymbol{r})$ the electron charge distribution of i-th free atom, which is spherically symmetric:

$$\varrho_{\mathrm{a},i}(\boldsymbol{r}) = \varrho_{\mathrm{a},i}(|\boldsymbol{r}|) = \varrho_{\mathrm{a},i}(r)\,. \tag{4}$$

Let us denote by $\boldsymbol{R}_i$ the center of i-th atom. Then, we define the residual electron charge distribution, $\varrho_{\mathrm{r}}(\boldsymbol{r})$, as a difference between the molecular charge distribution and the sum of atomic charge distributions:

$$\varrho_{\mathrm{r}}(\boldsymbol{r}) = \varrho(\boldsymbol{r}) - \sum_{i=1}^{N} \varrho_{\mathrm{a},i}(\boldsymbol{r} - \boldsymbol{R}_i)\,. \tag{5}$$

Let us assume, that the considered molecule is electrically neutral, and denote by P the total number of protons in the molecule. Then $P = \int \varrho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$. If $\varrho_{\mathrm{a},i}(\boldsymbol{r})$ represents the charge distribution of free, neutral atom, then $P = \sum_{i=1}^{N} \int \varrho_{\mathrm{a},i}(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$. Thus, based on Eq. (5) we have:

$$0 = \int\limits_{\mathbb{R}^3} \varrho_{\mathrm{r}}(\boldsymbol{r}) d\boldsymbol{r}\,. \tag{6}$$

Substituting transformed Eq. (5) into Eq. (2) we obtain:

$$V(\boldsymbol{r}) = \int\limits_{\mathbb{R}^3} \frac{\varrho_{\mathrm{r}}(\boldsymbol{u})}{|\boldsymbol{u} - \boldsymbol{r}|} d\boldsymbol{u} + \sum_{i=1}^{N} \int\limits_{\mathbb{R}^3} \frac{\varrho_{\mathrm{a},i}(\boldsymbol{u} - \boldsymbol{R}_i)}{|\boldsymbol{u} - \boldsymbol{r}|} d\boldsymbol{u}\,. \tag{7}$$

Let us introduce the potential generated by residual charge:

$$V_{\mathrm{r}}(\boldsymbol{r}) = \int\limits_{\mathbb{R}^3} \frac{\varrho_r(\boldsymbol{u})}{|\boldsymbol{u} - \boldsymbol{r}|} d\boldsymbol{u}\,. \tag{8}$$

Further, let us introduce the potential generated by i-th free atom:

$$V_{\mathrm{a},i}(\boldsymbol{r}) = \int\limits_{\mathbb{R}^3} \frac{\varrho_{\mathrm{a},i}(\boldsymbol{u})}{|\boldsymbol{u}-\boldsymbol{r}|} d\boldsymbol{u} \,. \tag{9}$$

Then, the electrostatic potential generated by the molecular electron charge is a sum of potential generated by the residual electron distribution and free atomic electron distribution:

$$V(\boldsymbol{r}) = V_{\mathrm{r}}(\boldsymbol{r}) + \sum_{i=1}^{N} V_{\mathrm{a},i}(\boldsymbol{r}-\boldsymbol{R}_i) \,. \tag{10}$$

The analytic algorithm evaluating the electrostatic potential, $V_{\mathrm{a},i}(\boldsymbol{r})$, generated by the spherical charge distribution, $\varrho_{\mathrm{a},i}(\boldsymbol{r})$, is described in Sec. 3. The adaptive, numerical algorithm evaluating the electrostatic potential $V_{\mathrm{r}}(\boldsymbol{r})$ is described in Sec. 4.

3. Spherical charge distribution

In the previous section, the molecular electron charge, $\varrho(\boldsymbol{r})$, was decomposed into residual charge, $\varrho_{\mathrm{r}}(\boldsymbol{r})$, and free atom charges, $\varrho_{\mathrm{a},i}(\boldsymbol{r})$. In order to obtain $\varrho_{\mathrm{a},i}(\boldsymbol{u})$ in the framework of Density Functional Theory, the Kohn–Sham equation for free atom must be solved. If one assumes, that for free atom the effective potential, $V_{\mathrm{eff}}(\boldsymbol{r})$, in Eq. (1) is spherically symmetric, then the three dimensional Kohn–Sham eigenproblem can be reduced to the one dimensional eigenproblem [15]. One dimensional eigenproblem can be solved efficiently applying the finite element method [21] in B-Spline basis [17] as was demonstrated in Ref. [20] or by the finite difference method as was demonstrated in Ref. [19].

The solution of Kohn–Sham equation, for i-th free atom problem with spherically symmetric potential, $V_{\mathrm{eff}}(r)$, is the spherically symmetric electron charge distribution, $\varrho_{\mathrm{a},i}(r)$. It is known [11], that the electrostatic potential generated by spherically symmetric charge distribution is given by Green's function of Laplace operator:

$$V_{\mathrm{a},i}(r) = 4\pi \left[\frac{1}{r} \int\limits_0^r t^2 \varrho_{\mathrm{a},i}(t) dt + \int\limits_r^\infty t \varrho_{\mathrm{a},i}(t) dt \right] \,. \tag{11}$$

Since the evaluation of electrostatic potential $V_{\mathrm{a},i}(r)$ is mutually independent for free atoms, and in order to simplify the notation, in the following discussion we use: $\rho(r) \equiv \varrho_{\mathrm{a},i}(r)$ and $U(r) \equiv V_{\mathrm{a},i}(r)$.

Let us assume, that $\rho(r)$ has the finite support, *i.e.* vanishes outside the finite interval $[0, r^*]$. Further, let us assume, that $\rho(r)$ is represented as a piecewise cubic spline polynomial [22] on the partition $0 = r_0 < r_1 < \ldots < r_M = r^*$, where M is a number of knots on the interval $[0, r^*]$. Then, the integrand in Eq. (11) is a polynomial of fifth or fourth order, and the potential can be obtained analytically. Let us introduce the set of polynomials $\{h_k(r)\}_{k=1}^{M}$ with real coefficients $a_k, b_k, c_k, d_k \in \mathbb{R}$ determined based on the cubic spline interpolation [18]:

$$h_k(r) = \begin{cases} a_k + b_k r + c_k r^2 + d_k r^3 & \text{for} \quad r \in [r_{k-1}, r_k]\,, \\ 0 & \text{otherwise}\,. \end{cases} \tag{12}$$

Then, the function $\rho(r)$ is represented as a sum:

$$\rho(r) = \sum_{k=1}^{M} h_k(r)\,. \tag{13}$$

Further, let us introduce two auxiliary integrals:

$$I_k(x) \;=\; 4\pi \int x^2 h_k(x) dx = \frac{a_k x^3}{3} + \frac{b_k x^4}{4} + \frac{c_k x^5}{5} + \frac{d_k x^6}{6}\,, \tag{14a}$$

$$J_k(x) \;=\; 4\pi \int x h_k(x) dx = \frac{a_k x^2}{2} + \frac{b_k x^3}{3} + \frac{c_k x^4}{4} + \frac{d_k x^5}{5}\,. \tag{14b}$$

Then, according to Eqs. (11) and (14a), the electrostatic potential generated by $h_k(r)$ is:

$$U_k(r) = \begin{cases} J_k(r_k) - J_k(r_{k-1})\,, & r < r_{k-1}\,, \\ (I_k(r_k) - I_k(r_{k-1}))/r\,, & r > r_k\,, \\ (I_k(r) - I_k(r_{k-1}))/r + J_k(r_{k-1}) - J_k(r)\,, & r_{k-1} < r < r_k\,. \end{cases} \tag{15}$$

Finally, based on Eq. (13) the electrostatic potential generated by $\rho(r)$ is a sum:

$$U(r) = \sum_{k=1}^{M} U_k(r)\,. \tag{16}$$

The solution of the Kohn–Sham equation for free atom is independent on the considered molecular system. Thus, the atomic electron charge distribution, $\rho(r)$, and hence its electrostatic potential, $U(r)$, can be solved once and stored in the database for future use. The evaluation cost of electrostatic potential $U(r)$ scales linearly with M, where M is the number of intervals required to represent the atomic electron distribution, $\rho(r)$.

4. Evaluation of residual potential

The molecular residual charge distribution, $\varrho_{\mathrm{r}}(\boldsymbol{r})$, defined by Eq. (5), is a difference between the molecular charge distribution, $\varrho(\boldsymbol{r})$, and the sum of free atom charge distributions, $\varrho_{\mathrm{a},i}(\boldsymbol{r})$. In the present paper the real molecular systems are considered. Therefore, based on the chemical/physical reasons, we can assume that $\varrho_{\mathrm{r}}(\boldsymbol{r})$ is small in comparison to $\varrho(\boldsymbol{r})$, since $\varrho_{\mathrm{r}}(\boldsymbol{r})$ is a measure of created bonds in the molecule [4, 13, 15]. Moreover, we assume that $\varrho_{\mathrm{r}}(\boldsymbol{r})$ is a smooth function, since bonds are created by the valence electrons, which are diffuse.

It is known that the function $\varrho(\boldsymbol{r})$ has the slope discontinuities (cusps) in the vicinity of nuclei, which are caused by the nuclei attraction. However, it was proved, by the successes of the pseudopotential theory [3, 7, 23], that the charge distribution of free atom in the vicinity of its nucleus does not change, when the atom is incorporated into the molecule. Hence, the cusps in $\varrho(\boldsymbol{r})$ are effectively represented by the cusps of $\varrho_{\mathrm{a},i}(\boldsymbol{r})$. Therefore, $\varrho_{\mathrm{r}}(\boldsymbol{r})$ does not have the cusps and its value in the neighborhood of the nuclei is close to zero.

Since $\varrho_{\mathrm{r}}(\boldsymbol{r})$ is a smooth function with relatively small amplitude in values, it is convenient to apply the adaptive real space method [1, 9] (like the finite element method [21]) to solve the Poisson equation and obtain the electrostatic potential generated by $\varrho_{\mathrm{r}}(\boldsymbol{r})$. However, each real space method is defined on the finite domain. Hence, the boundary condition must be provided.

4.1. Determination of boundary conditions

We are interested in the algorithm evaluating the electrostatic potential for finite, molecular system. The obtained electrostatic potential will be applied to the Kohn–Sham equation, Eq. (1). The Kohn–Sham equation is a second order eigenproblem defined on the whole $\mathbb{R}^3$ space with the boundary conditions $\lim_{|\boldsymbol{r}|\to\infty}\psi_\mu(\boldsymbol{r}) = 0$. Let us assume that, the considered molecular charge distribution, $\varrho_{\mathrm{r}}(\boldsymbol{r})$, has the finite support, and denote its support by Ω_ϱ. It was proved [4, 15], that for these systems the eigenfunction, $\psi_\mu(\boldsymbol{r})$, decays as $\exp(-\alpha||\boldsymbol{r}||)$ with $\alpha > 0$, where $||\boldsymbol{r}||$ is a distance between Ω_ϱ and the point $\boldsymbol{r}$. Because of exponential decay of eigenfunction, the solution domain of the Kohn–Sham equation can be restricted to the finite domain Ω_{ks} and obtain the eigenfunctions close to the one obtained for $\mathbb{R}^3$ space. Moreover, the eigenfunction $\psi_\mu(\boldsymbol{r})$ must fulfill zero Dirichlet boundary condition on the border Ω_{ks}, see Fig. 1.

The electrostatic potential decreases slower than exponentially and cannot be neglected on the border of Ω_{ks}. It means, that to solve the Poisson equation over Ω_{ks}, the electrostatic potential must be determined on the

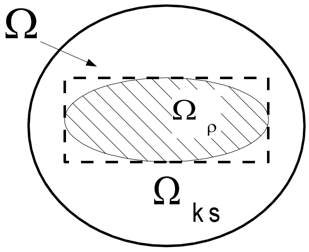

Fig. 1. Mutual relation between $\Omega_\varrho \subset \Omega \subset \Omega_{\mathrm{ks}}$. Ω_{ks} denotes the domain of Kohn–Sham equation. Ω_ϱ, denoted by hatched region, is a molecule. Ω, enclosed by dashed line, is a cuboid. It is assumed that the Kohn–Sham eigenfunction is equal zero on the border of Ω_{ks}. In contrary, the electrostatic potential is usually non-zero on the border of Ω_{ks}.

border of domain Ω_{ks}. The values of the potential on the border of Ω_{ks} can be determined from Coulomb integral, Eq. (8). By construction, Ω_{ks} encloses the charge domain: $\Omega_\varrho \subset \Omega_{\mathrm{ks}}$, see Fig. 1. Hence, for any point $\boldsymbol{q}$ laying on the border of Ω_{ks}, the Coulomb integral, does not possess the singularity and is over the finite domain:

$$V_{\mathrm{r}}(\boldsymbol{q}) = \int\limits_{\Omega_\varrho} \frac{\varrho_{\mathrm{r}}(\boldsymbol{u})}{|\boldsymbol{u}-\boldsymbol{q}|} d\boldsymbol{u}\,. \tag{17}$$

Since $\varrho_{\mathrm{r}}(\boldsymbol{u})$ is a smooth function and term $|\boldsymbol{u}-\boldsymbol{q}|^{-1}$ does not have the singularity over the integration domain, the adaptive, numerical integration algorithm can be applied to evaluate the above integral.

4.2. Adaptive integration algorithm

Let us introduce the Cartesian coordinate system $\mathcal{C}$. Let us denote by Ω the cuboid of the smallest volume with the faces parallel to the planes of $\mathcal{C}$, which encloses the molecule: $\Omega_\varrho \subset \Omega$, see Fig. 1. By construction, the faces of Ω are parallel to planes of system $\mathcal{C}$, hence Ω can be represented as a Cartesian product $\Omega = [x_0, x_1] \times [y_0, y_1] \times [z_0, z_1]$, where $x_0 < x_1$, and $y_0 < y_1$, and $z_0 < z_1$. Since for $\boldsymbol{v} \in \Omega - \Omega_\varrho$ it holds $\varrho_{\mathrm{r}}(\boldsymbol{v}) = 0$, we have:

$$V_{\mathrm{r}}(\boldsymbol{r}) = \int\limits_{\Omega_\varrho} \frac{\varrho_{\mathrm{r}}(\boldsymbol{u})}{|\boldsymbol{u}-\boldsymbol{r}|} d\boldsymbol{u} = \int\limits_{\Omega} \frac{\varrho_{\mathrm{r}}(\boldsymbol{u})}{|\boldsymbol{u}-\boldsymbol{r}|} d\boldsymbol{u}\,. \tag{18}$$

Let us denote the Cartesian coordinates of the point $\boldsymbol{q}$ laying on the border of Ω_{ks} by $\boldsymbol{q} = (a, b, c)$ and the coordinate of the point $\boldsymbol{u} \in \Omega$ by $\boldsymbol{u} = (x, y, z)$. Then, from Eq. (18), we have:

$$
\begin{aligned}
V_{\mathrm{r}}(\boldsymbol{r}) &= \int\limits_{\Omega} \frac{\varrho_{\mathrm{r}}(\boldsymbol{u})}{|\boldsymbol{u}-\boldsymbol{r}|} d\boldsymbol{u} \\
&= \int\limits_{x=x_0}^{x_1} \int\limits_{y=y_0}^{y_1} \int\limits_{z=z_0}^{z_1} \frac{\varrho_{\mathrm{r}}(x,y,z)}{[(x-a)^2+(y-b)^2+(z-c)^2]^{1/2}} dz dy dx \,. \qquad (19)
\end{aligned}
$$

In order to evaluate the above integral, the adaptive numerical algorithm developed by Genz and Malik [2,5,8] can be applied. This algorithm is dedicated to integrate over an N-dimensional cube. It is based on the quadratures, which evaluate exactly the polynomials of fifth and seventh order. In three dimensions, the algorithm requires 33 integrand evaluation to obtain the approximation of the integral and the approximation of the integration error. If the approximated error is two large, the integration domain is divided into two identical parts. The algorithm is adaptive, and stops if the integration error is smaller than the predefined accuracy.

5. Exemplary results

In this section the accuracy and efficiency of the adaptive numerical scheme applied to evaluate the electrostatic potential on the border of domain is assessed. In order to manage this, the analytically solvable problem must be defined.

5.1. Analytically solvable problem

Let us denote the Gaussian function as $g(\boldsymbol{r};\alpha)=\exp(-\alpha|\boldsymbol{r}|^2)$, with coefficient $\alpha>0$. Since $g(\boldsymbol{r};\alpha)$ is spherically symmetric, then the electrostatic potential generated by this charge distribution can by obtained analytically. Substituting $g(\boldsymbol{r};\alpha)$ into Eq. (11) and integrating, we obtain:

$$
V_{\mathrm{g}}(r;\alpha) = \left(\frac{\pi}{\alpha}\right)^{3/2} \frac{\mathrm{Erf}(r\sqrt{\alpha})}{r}\,, \qquad (20)
$$

where $\mathrm{Erf}(x)=2/\sqrt{\pi}\int_0^x \exp(-t^2)dt$ is the error function.

We consider the residual charge distribution, $\varrho_{\mathrm{r}}(\boldsymbol{r})$, represented as a sum of four Gaussian functions with equal coefficients α, centered at four points:

$$
\varrho_{\mathrm{r}}(\boldsymbol{r}) = \sum_{k=1}^{4} g(\boldsymbol{r}-\boldsymbol{Q}_k;\alpha) \quad \Rightarrow \quad V_{\mathrm{r}}(\boldsymbol{r}) = \sum_{k=1}^{4} V_g(|\boldsymbol{r}-\boldsymbol{Q}_k|;\alpha)\,, \qquad (21)
$$

where $\boldsymbol{Q}_1=(q_{1,x},q_{1,y},q_{1,z})=(0,0,0)$, $\boldsymbol{Q}_2=(q_{2,x},q_{2,y},q_{2,z})=(1,0,0)$, $\boldsymbol{Q}_3=(q_{3,x},q_{3,y},q_{3,z})=(0,1,0)$ and $\boldsymbol{Q}_4=(q_{4,x},q_{4,y},q_{4,z})=(-1,-1/2,1)$.

The coefficient $\alpha = 2$ is so chosen that the Gaussian functions overlap. Since the present algorithm is defined for the system with the finite support, the Gaussian function is truncated. The value of Gaussian function is set to zero, if its value drops below $\epsilon = 10^{-13}$. Hence $g(\boldsymbol{r};\alpha)$ vanishes for $|\boldsymbol{r}| > \gamma = \sqrt{-\ln(\epsilon)/\alpha}$. Based on this value, the cuboid Ω enclosing four truncated Gaussian functions has the coordinates:

$$\begin{aligned} x_0 &= \min_k\{q_{k,x}\} - \gamma \approx -4.9\,, & x_1 &= \max_k\{q_{k,x}\} + \gamma \approx 4.9\,,\\ y_0 &= \min_k\{q_{k,y}\} - \gamma \approx -4.4\,, & y_1 &= \max_k\{q_{k,y}\} + \gamma \approx 4.9\,,\\ z_0 &= \min_k\{q_{k,z}\} - \gamma \approx -3.9\,, & z_1 &= \max_k\{q_{k,z}\} + \gamma \approx 4.9\,. \end{aligned}$$

The mutual relation $\Omega_\varrho \subset \Omega \subset \Omega_{\text{ks}}$ is depicted in Fig. 1.

5.2. Numerical results

In order to obtain the numerical values for the system defined in Sec. 5.1, the cube of edge length 20 and centered at the origin of coordinate system was chosen as Ω_{ks}. The values of the electrostatic potential evaluated for the selected points located on the border of Ω_{ks} are listed in Table I.

In Table I the analytic values, $V_{\text{r}}^{(a)}(\boldsymbol{r})$ obtained from Eq. (21) are listed in the column Analytic. Let us denote by $V_{\text{r}}^{(n)}$ the numeric value obtained by the adaptive algorithm from Sec. 5.1. Then, in column titled Diff, the difference $|V_{\text{r}}^{(a)} - V_{\text{r}}^{(n)}|$ is listed. The measure of the efficiency of the adaptive algorithm is the number of divisions required to achieve the accuracy set to $\delta = 10^{-4}$. For the studied example, the number of divisions is presented in column DivNo.

The values of the electrostatic potential were evaluated in 8 cube vertices and 6 middle points of cube faces. For each studied case, the difference $|V_{\text{r}}^{(a)} - V_{\text{r}}^{(n)}|$ is smaller than the set accuracy $\delta = 10^{-4}$. Moreover, the number of divisions is small (less than 700), hence the algorithm is fast.

6. Summary

The key point in the solution of Kohn–Sham equation for the molecular system is the evaluation of electrostatic potential required to determine the effective interaction potential. It is known that the molecular charge distribution has the cusps in the vicinity of the nuclei. In the present paper we show how to decompose the molecular charge distribution into atomic charges and residual charge. The decomposition is based on the physical/chemical reasons. It was shown how to analytically evaluate the electrostatic potential generated by the atomic parts, which posses the cusp

TABLE I

Analytic values of electrostatic potential generated by four Gaussian function, see Eq. (21). In the column Diff the absolute difference between analytic and numeric values is listed. The column DivNo contains the number of divisions generated by Genz-Malik adaptive algorithm. The potential were calculated for a characteristic point of cube. Numbers in square brackets represent powers of 10.

a	b	c	Analytic	Diff	DivNo
Cube vertices					
10	10	10	0.459960	1.7[−8]	454
−10	10	10	0.460303	2.0[−6]	442
−10	−10	10	0.457382	2.5[−6]	444
10	−10	10	0.456148	3.9[−7]	459
10	10	−10	0.453444	3.1[−6]	462
−10	10	−10	0.452399	2.2[−6]	452
−10	−10	−10	0.448588	2.6[−6]	448
10	−10	−10	0.448994	2.3[−6]	456
Middle of cube faces					
0	0	10	0.805732	6.3[−6]	612
0	0	−10	0.766712	3.2[−6]	569
0	10	0	0.797325	2.0[−6]	596
0	−10	0	0.776709	1.4[−6]	613
10	0	0	0.789563	2.3[−6]	562
−10	0	0	0.788812	2.7[−6]	559

singularity. We also proved the smoothness of the residual charge, therefore it is expected that the adaptive real space Poisson solvers will run efficiently for the residual charge. Moreover, it was shown, that the adaptive numerical integration scheme applied to the Coulomb integral with the residual charge, is an efficient evaluation method of Dirichled boundary conditions, which are required to start up any real space Poisson solver.

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