Max-Planck-Institut
für Mathematik
in den Naturwissenschaften
Leipzig

Chebyshev-Galerkin algorithm for computing 3D Solvation

by

Gennady Chuev

Preprint no.: 86 2011

Chebyshev-Galerkin algorithm for computing 3D Solvation

Gennady N. Chuev[1,2]

[1] *Max Planck Institute for Mathematics in the Sciences,*
Inselstrasse 22, Leipzig, 04103, Germany

[2] *Institute of Theoretical and Experimental Biophysics,*
Russian Academy of Science, Pushchino, Moscow Region, 142290, Russia

(Dated: December 19, 2011)

To solve 3D integral equations of molecular liquids, we have developed a numerical scheme based on the Galerkin method. Using a domain decomposition of the interface region, we reduce the problem to calculations of approximating coefficients and the kernel matrix in spherical shell elements (SSE). Applying the linear transformation of coordinates for each SSE we result in calcualtions of the approximating coefficients in cubic volumes. Using the conventional triple Chebyshev series as a basis set, we derive formulas for calculations of the approximating coefficients and evaluate the computational costs of these operations. We have described the general properties of the Chebyshev-Galerkin matrix and derived analytical expressions for recursion calculations of the matrix elements. We have also outlined an iterative method for the solutions of the nonlinear equations obtained for the approximating coefficients, which is based on the direct inversion in the iterative space. Finally, we have estimated the total computational cost of the proposed scheme and compared it with current algorithms for computing 3D solvation problem. It was found the proposed scheme to be by 2-3 orders effective than the current algorithms based on the uniform FFT.

I. INTRODUCTION

The integral equations theory (IET)[1] is a perspective approach to investigate solvation phenomena. Despite of a recent progress in this field, applications of the theory is still limited in the case of molecular liquids. The reason of that is the absence of fast and effective algorithms for calculating the sought-for correlation functions, which are to be three-dimensional (3D) in the case of molecular solute immersed in a molecular liquid. The current IET algorithms are based on the uniform fast fourier transform (FFT) which implies a uniform cartesian grid in a large region, while the IET approach reduces the problem to evaluations of the sought-for functions at the grid points in this volume. The bottleneck of the current IET algorithms for search of such solution is likely that the extension of the uniform FFT to high dimensions requires to treat enormous large number of grid points. Indeed, high dimensionality of the sought-for functions restricts sufficiently the resolution of the FFT, since evaluations of the functions is problematic when the total number of the sought-for values is greater than 10^8.

Recently we propose a new approach[2] to the 3D solvation problem, which is based on evaluations with the use real-space meshes (RSM). Previously, we have reformulated the IET in terms of the solvent induced potential and reduced the problem to evaluation of the volume integrals in the interface region, which occupies only 1% the uniform FFT grid. We have performed a domain decomposition of the region in terms of spherical shell elements (SSE) built from scaled solvent accessible surfaces. We have found the Chebyshev polynomials to be the most suitable for accurate approximation of the sought-for functions for these finite elements. With the use of the polynomials, our approach is the Galerkin-Chebyshev (GC) method[3] for evaluating the sought-for functions in the 3D domains.

The goal of this paper is to provide details of the GC method for computing the 3D solvation problem. In particularly, we evaluate the cost of computations of the Chebyshev-Galerkin matrix arisen in the solvation problem. We will show that these calculations can be done analytically in the case when the matrix can be approximated by low-order polynomials. We also estimate the cost of computations of the approximating coefficients and indicate that the triple Chebyshev series is to be best for approximating the sought-for functions in the SSEs. We have derived formulas for evaluations of approximating coefficients and the Chebushev-Galerkin matrix. We also give the details of iterative solution of the nonlinear equations for approximating coefficients, namely, the performance of the direct inversion in the iterative space (DIIS) method for the proposed scheme. Finally, we will estimate the total computational costs of the GC algorithm applied for computing 3D solvation problem.

The layout of the paper is the following. We outline briefly the Galerkin scheme in Sec. 2. Then, in Sec.3 we describe how construct the triple Chebyshev basis set for the SSE, using the linear transformation of coordinates for each SSE. We will provide formulas for calculating approximating and evaluate the computational costs of these operations. We investigate in Sec. 4 the general properties of the Chebyshev-Galerkin matrix, and derived analytical formulas for recursion evaluations of the matrix elements in the case of polynomial approximation of the kernel. The summary is given in Sec. 5, while Appendix 1 includes the basic relations of the DIIS method.

II. THE GALERKIN SCHEME

The IET within the framework of the hypernetted chain approximation (HNC) can be written in terms of the solvent induced potential $\mu_i(\mathbf{r})$ as:[2]

$$\beta u_i(\mathbf{r}) = h_i(u_i(\mathbf{r})) + \sum_{j=1}^{N_v} \int_{\mathbf{R}^3} c_{ij}(\mathbf{r}-\mathbf{r}_1) h_j(u_j(\mathbf{r}_1)) d\mathbf{r}_1, \qquad i = 1, ..., N_v, \tag{1}$$

where $h_i(u_i(\mathbf{r}))$ is the solute-solvent total correlation function determined as

$$h_i(u_i(\mathbf{r})) = \exp[-\beta U_i(\mathbf{r}) + u_i(\mathbf{r})] - 1. \tag{2}$$

In the above equations the value β is the inverse temperature, N_v is the number of solvent sites (atoms), c_{ij} is the solvent-solvent direct correlation function defined as a numerical array (input data), and $U_i(\mathbf{r})$ is the solute-solvent potential (input function), which is a sum of the Lennard-Jones and the long-range Coulomb contributions $U_i(\mathbf{r})$:

$$U_{ij}(\mathbf{r}) = \sum_{j}^{N_u} U_{ij}(\mathbf{r}_j - \mathbf{r}_i) = \sum_{j}^{N_u} 4\epsilon_{ij}[\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}] + \frac{q_i q_j}{r_{ij}}, \tag{3}$$

where $r_{ij} = \mathbf{r}_j - \mathbf{r}_i$, while q_i and q_j are the partial charges (input parameters) of the relevant species, and σ_{ij} and ϵ_{ij} are the force field (input) parameters determined the Lennard-Jones contribution, and N_u is the total number of solute sites (atoms).

The above relations can be easily reformulated in terms of the residue correlation function $\Delta h_i = h_i(\mathbf{r}) - h_i^0(\mathbf{r})$, where $h_i^0(\mathbf{r})$ is the zero approximation for the total correlation function defined as

$$h_i^0(\mathbf{r}) = \exp[-\beta U_i(\mathbf{r}) + f_i(\mathbf{r}) + c_{ij} * f_j] - 1, \tag{4}$$

whereas symbol $*$ means a convolution integration, and $f_i(\mathbf{r}) = \exp[-\beta U_i(\mathbf{r})] - 1$ is the Mayer function. The function $h_i^0(\mathbf{r})$ can be easily evaluated before solution of the integral equations. Moreover this approximation reveals all the peculiarities of asymptotical behavior of h, and the difference between $h_i^0(\mathbf{r})$ and $h_i(\mathbf{r})$ is not equal zero only in the narrow interface region. Therefore, using this substitution, we obtain

$$\beta \Delta u_i(\mathbf{r}) = \beta[u_i(\mathbf{r}) - u_i^0(\mathbf{r})] = \Delta h_i(u_i(\mathbf{r})) + \sum_{j=1}^{N_v} \int_{\mathbf{V}_{ir}} c_{ij}(\mathbf{r} - \mathbf{r}_1) \Delta h_j(u_j(\mathbf{r}_1)) d\mathbf{r}_1, \tag{5}$$

while $u_i^0(\mathbf{r})$ is the SIP corresponding to h_i^0, i.e. $\beta u_i^0(\mathbf{r}) = h_i^0(\mathbf{r}) + \sum_{j=1}^{N_v} c_{ij} * h_j^0$.

We decompose the interface region by spliting it into the few scaled surface accessible surfaces (SASs). Thus, the interface region can be presented as a collection of spherical shell elements (SSE) build from the relevant patches of scaled SASs (see, Fig. 1). Each SSE represents a set of scaled SAS elements. There are effective tools[4] which are able to perform fast calculations of the SAS as well as the first and the second derivatives of the SAS with respect to atomic coordinates. Such construction is supposed to decrease significantly the computation of the volume integrals, because the angular dependence of the sought-for functions in each SSE is to be very weak. Therefore, we perform the following division of the interface region:

$$\mathbf{V}_{ir} = \Cup_{s=1}^{N_s} \mathbf{V}_s, \tag{6}$$

where $\mathbf{V}_s$ is the volume of the s-th SSE, and N_s is the total number of the SSE.

Let's us expand the sought-for functions Δu_i and Δh_i in an orthogonal basis set $\mathbf{a_p}(\mathbf{r})$:

$$\beta \Delta u_i(\mathbf{r}) = \sum_{p=1}^{N_\mathbf{p}} \hat{u}_{i\mathbf{p}} a_\mathbf{p}(\mathbf{r}) = \hat{\mathbf{u}} \cdot \mathbf{a}, \qquad \Delta h_i(\mathbf{r}) = \sum_{p=1}^{N_\mathbf{p}} \hat{h}_{i\mathbf{p}} a_\mathbf{p}(\mathbf{r}) = \hat{\mathbf{h}} \cdot \mathbf{a}, \tag{7}$$

where $\mathbf{a}$ is the vector of the basis functions, while $\hat{\mathbf{h}}$ and $\hat{\mathbf{u}}$ are the vectors of the approximating coefficients for the corresponding sought-for functions, while symbol $\cdot$ means the scalar product. Then, the integral equation (5) can be rewritten in the matrix form for the approximating coefficients

$$\hat{\mathbf{u}} = \hat{\mathbf{h}} + \hat{\mathbb{C}} \cdot \hat{\mathbf{h}}, \tag{8}$$

here $\hat{\mathbb{C}}$ is the matrix which elements $C_{ij}(\mathbf{m}, \mathbf{s})$ are obtained by double integration:

$$C_{ij}(\mathbf{m}, \mathbf{s}) = \int_{\mathbf{V}_{ir}} \omega_{\mathbf{r}} \int_{\mathbf{V}_{ir}} \omega_{\mathbf{r}_1} a_{\mathbf{m}}(\mathbf{r}) c_{ij}(\mathbf{r} - \mathbf{r}_1) a_{\mathbf{s}}(\mathbf{r}_1) d\mathbf{r} d\mathbf{r}_1. \tag{9}$$

where $\omega_{\mathbf{r}}$ and $\omega_{\mathbf{r}_1}$ are the relevant weight coefficients. Finally, the problem can be reduced to the iterative solution of the matrix equations

$$\hat{\mathbf{u}}^{(n+1)} = \hat{\mathbf{h}}^{(n)} + \hat{\mathbb{C}} \cdot \hat{\mathbf{h}}^{(n)}, \tag{10}$$

while the n-th iteration of function $\Delta h_i(\mathbf{r})$ is expressed in terms of vectors $\mathbf{a}$ and $\hat{\mathbf{u}}^{(n)}$:

$$h_i^{(n)}(\mathbf{r}) = \exp[-\beta(U_i(\mathbf{r}) + u_i^0(\mathbf{r})) + \hat{\mathbf{u}}^{(n)} \cdot \mathbf{a})] - h_i^0(\mathbf{r}) - 1. \tag{11}$$

Hence, the procedure includes two stages, namely, a) initial stage: fast evaluation of matrix $\hat{\mathbb{C}}$ with the use of a chosen basis set and further storage of the array in the operating memory, b) iterative solution of (10) and (11). Formally, this stage can be written as

$$\hat{\mathbf{u}}^{(n)} \to (11) \to h^{(n)} \to (7) \to \hat{\mathbf{h}}^{(n)} \to (10) \to \hat{\mathbf{u}}^{(n+1)}. \tag{12}$$

This stage requires only evaluation of approximating coefficients $\hat{\mathbf{h}}$ and $\hat{\mathbf{u}}$, then the further iterative solution of nonlinear equations coupled these coefficients.

The proposed scheme is the spectral Galerkin method[5] extended to the case on nonlinear integral equations. It includes three main operations: a) evaluations of matrix $\hat{\mathbb{C}}$; b) calculations of approximating coefficients $\hat{\mathbf{h}}$ and $\hat{\mathbf{u}}$; c) an iterative solution of nonlinear equations. The most time-consuming procedure is the evaluation of $\hat{\mathbb{C}}$. In the general case, it requires calculations of $N_{\mathbf{p}}^2$ matrix elements at the number $N_{\mathbf{p}}^2$ of grid points. However due to recursion relations for orthogonal polynomials, the cost of the computations can be decreased down to $N_{\mathbf{p}}^2$ operations (see, Sec. 4.1). Moreover, we will exploit the smoothness of matrix $\hat{\mathbb{C}}$ like it has been done in Ref.[6]. Due to this effect, the functions $c_{ij}(\mathbf{r})$ can be approximated by low- order polynomials. Then, using a special basis set (Chebyshev polynomials) we can evaluate analytically all the elements of the matrix $\hat{\mathbb{C}}$ (see, Sec. 4.2) that reduces significantly the cost of computations.

In the general case, the evaluations of approximating coefficients require $N_{\mathbf{p}}^2$ operations ($N_{\mathbf{p}}$ coefficients at $N_{\mathbf{p}}$ points). But again, the applications of Chebyshev polynomials can reduce this cost down to $N_{\mathbf{p}} \ln N_{\mathbf{p}}$ due to applicability of the FFT to Chebyshev polynomials. Therefore, the use of Chebyshev polynomials reduces significantly the cost of the main operations, i.e. evaluations of matrix $\hat{\mathbb{C}}$ and calculations of approximating coefficients.

The last task is to provide effective iterative solution of nonlinear equations. For this purpose we will use the DIIS. The method has been introduced in Ref.[7] to accelerate the convergence of solution to nonlinear equations arisen in quantum chemistry. The DIIS method does not guarantee the convergence of solution in the general case, however it provides a superlinear convergence for linear and weakly nonlinear algebraic equations.[8] There is a strong link between the DIIS and Krylov space methods, it can be viewed as a globalization of the well-known GMRES procedure[9] to nonlinear equations.[8] The Appendix 1 includes the basics of the DIIS method. Applications of the DIIS to the IET indicate[10] that the method converges in the most cases with number N_{it} of iterations less than 200. Thus, we need to provide provide efficient evaluations of approximating coefficients and fast evaluation of matrix $\hat{\mathbb{C}}$. Both the procedures depend strongly on the choice of the basis set. Moreover, we will use a special shape-preserving domain decomposition of the interface region. Due to this decomposition, the sought-for functions have weak angular dependencies in each SSE that additionally decreases the number of the approximating coefficients and increases the effectiveness of the scheme. However, to treat this angular dependencies we are to provide a special basis set using the mapping of the SSE to the cube (see Sec. 3).

III. CHOICE OF THE BASIS SET FOR EFFICIENT EVALUATIONS OF APPROXIMATING COEFFICIENTS.

Mapping of shell elements. Therefore, the interface region is decomposed as a set nonoverlapping SSEs, each of them has an annular form which can be characterized by cut-of radii, inclination and azimuth angles, i.e. each SSE represents an annular domain (Fig.1b) limited by boundaries

$$r_s - \sigma_v < r < r_s + \sigma_v, \qquad 0 < \theta < \theta_s, \qquad 0 < \phi < \phi_s(\theta). \tag{13}$$

We should remark that in the general case the dependence $\phi_s(\theta)$ is to be determined by overlapping of solvent induced surfaces, which can be very complicated. Below we consider the simple case then $\phi_s = \mathit{const}$ while the complicated boundaries will be discussed at the end of Sec. 5. The spherical coordinates are to be the natural choice in this case. Then the approximating coefficients are defined by the three-fold integration:

$$\hat{\mathbf{u}} = \int_{r_s-\sigma_v}^{r_s+\sigma_v} \omega_r \int_0^{\theta_s} \omega_\theta \int_0^{\phi_s} \omega_\phi \Delta u_i(\mathbf{r}) a_{\mathbf{s}}(r,\theta,\phi) r^2 dr d(\cos\theta) d\phi \tag{14}$$

where ω_r, ω_θ, and ω_ϕ are the relevant weight factors depending on the choice of the basis set. Thus, our task is to choose a bsis set which provides fast 3D integration in the SSE. We can map each SSE to the unit annulus by the coordinate transformations (Fig.1b):

$$\tilde{r} = (r - r_s)/\sigma_v, \qquad \tilde{\theta} = \pi\theta/\theta_s, \qquad \tilde{\phi} = \pi\phi/\phi_s. \tag{15}$$

Such transformations are often used for spherical-surface limited areas, cups, part of disc, etc (see, for example[11–15]). Then, the basis set expressed in these transformed coordinates becomes to be independent on the index of the shell element and the conventional methods for constructing the basis set may be used.[5]

Radial dependence. Since the radial dependence is limited by the finite interval, the Chebyshev polynomials $T_n(\tilde{r})$ ($\tilde{r} \subset [-1,1]$) seem to be best for the approximation. Of course, there are other possibilities like as Zernike polynomials, radial basis functions, etc (see, Ref.[16]). However we choose the Chebyshev polynomials due to simplicity of the manipulations with them. An advantage of this choice is a possibility of the FFT for fast evaluation of the radial dependence. Another attractive feature of the polynomials is that they provide fast mesh-free evaluation of kernel (see Sec. 4.2). In the case of the discretization of the interval by N_r, the approximating radial coefficients can be computed by $N_r \ln N_r$ operations. The weight factor ω_r is to be determined by the orthogonality of the polynomials at the unit annulus, i.e. $\omega_r = \sigma_v / r(\sigma_v^2 - (r - r_s)^2)^{1/2}$. Using the conventional substitution $\tilde{r} = \cos y$ we transform these polynomials to the suitable form $T_n(\tilde{r}) = c_y \cos(ny)$ where c_y is the normalization constant. Finally, the integration over the radius can be expressed as

$$\int_{r_s-\sigma_v}^{r_s+\sigma_v} \omega_r \Delta u_i(\mathbf{r}) T_n(\tilde{r}) r^2 dr = c_y \int_0^\pi \Delta u_i(\mathbf{r})(r_s - \sigma_v \cos y)\cos(ny) dy. \tag{16}$$

This integration may be discretized with the use the Chebyshev-Gauss-Lobotto points $y_j = \pi j / N_r$ as

$$\approx \frac{2c_{N_r}}{N_r} \sum_{j=0}^{N_r} \Delta u_i(r_s - \sigma_v \cos(\frac{\pi j}{N_r}), \theta, \phi)(r_s - \sigma_v \cos(\frac{\pi j}{N_r})) c_j \cos(\frac{\pi j n}{N_r}), \tag{17}$$

where $c_0 = c_{N_r} = 1/2$, and $c_j = 1, \quad (0 < j < N_r)$.

Angular dependence. The situation with angular dependence is more complicated. There are three possibilities: spherical harmonics, the double Fourier and the double Chebyshev series.[18] In previous paper[2] we propose to use the spherical harmonics. The advantage of this choice is that the harmonics can be effectively used for the Fast Multipole method.[5] The disadvantage of the spherical harmonics is that the direct application of the recursion relations is difficult for higher order polynomials. Another disadvantage of the spherical harmonics is that the FFT can not be applied for inclination angles $\tilde{\theta}$ and the cost to calculate approximating coefficients would be N_θ^2, whereas it would be $N_\phi \ln N_\phi$ for longitudinal direction, where N_θ and N_ϕ are the respective numbers of the grid points in the longitudinal and the latitudinal directions. We expect that $N_\theta < 5$ and hence, the absence of the uniform FFT for the latitude can increase the computational costs by 3-4 times. On the other hand, the integration procedure over latitude may be accelerated by the non-equispaced FFT.[17] Comparative analysis indicates what spherical harmonics provide the best convergence on a sphere for boundary and eigen-value problems.[18] Unfortunately, in the general case we have nonperiodical boundary conditions at each SSE, and hence the Chebyshev polynomials are more suitable in this case since the double Fourier series and the associated Legendre polynomials are useful only in global or hemisphere domains.[18] Therefore, the integration over angles expressed as

$$\int_0^{\theta_s} \omega_\theta \int_0^{\phi_s} \omega_\phi \Delta u_i(\mathbf{r}) a_{\mathbf{s}}(r,\theta,\phi) d(\cos\theta) d\phi = \int_0^{\pi} \int_0^{\pi} \Delta u_i(\mathbf{r}) T_l(\tilde{\theta}) T_m(\tilde{\phi}) d\frac{\theta_s \tilde{\theta}}{\pi} d\frac{\phi_s \tilde{\phi}}{\pi}. \quad (18)$$

Using equispaced discritezation for $\tilde{\phi}_j = \pi j/N_\phi$ and $\tilde{\theta}_p = \pi p/N_\theta$, we transform the above integral into the double sum:

$$\approx \frac{4\phi_s \theta_s c_{N_\theta} c_{N_\phi}}{\pi^2 N_\phi N_\theta} \sum_{p=0}^{N_\theta} \sum_{j=0}^{N_\phi} \Delta u_i(r,\theta,\phi) c_p c_j \cos(\frac{\pi l p}{N_\theta}) \cos(\frac{\pi m j}{N_\phi}), \quad (19)$$

where $c_0 = c_{N_\phi} = c_{N_\theta} = 1/2$, $c_j = 1, \quad (0 < j < N_\phi)$, and $c_p = 1, \quad (0 < p < N_\theta)$.

Then, using the triple Chebyshev series as a basis set, we can apply the FFT in all the directions. Thus, the computational cost of approximating coefficients is to be proportional $N_s * N_r * N_\phi * N_\theta \ln(N_r * N_\phi * N_\theta)$. We should remark that the angular dependence of $\hat{\mathbf{h}}$ and, hence, $\hat{\mathbf{u}}$ are to be very weak, they can be approximated by low-order polynomials.

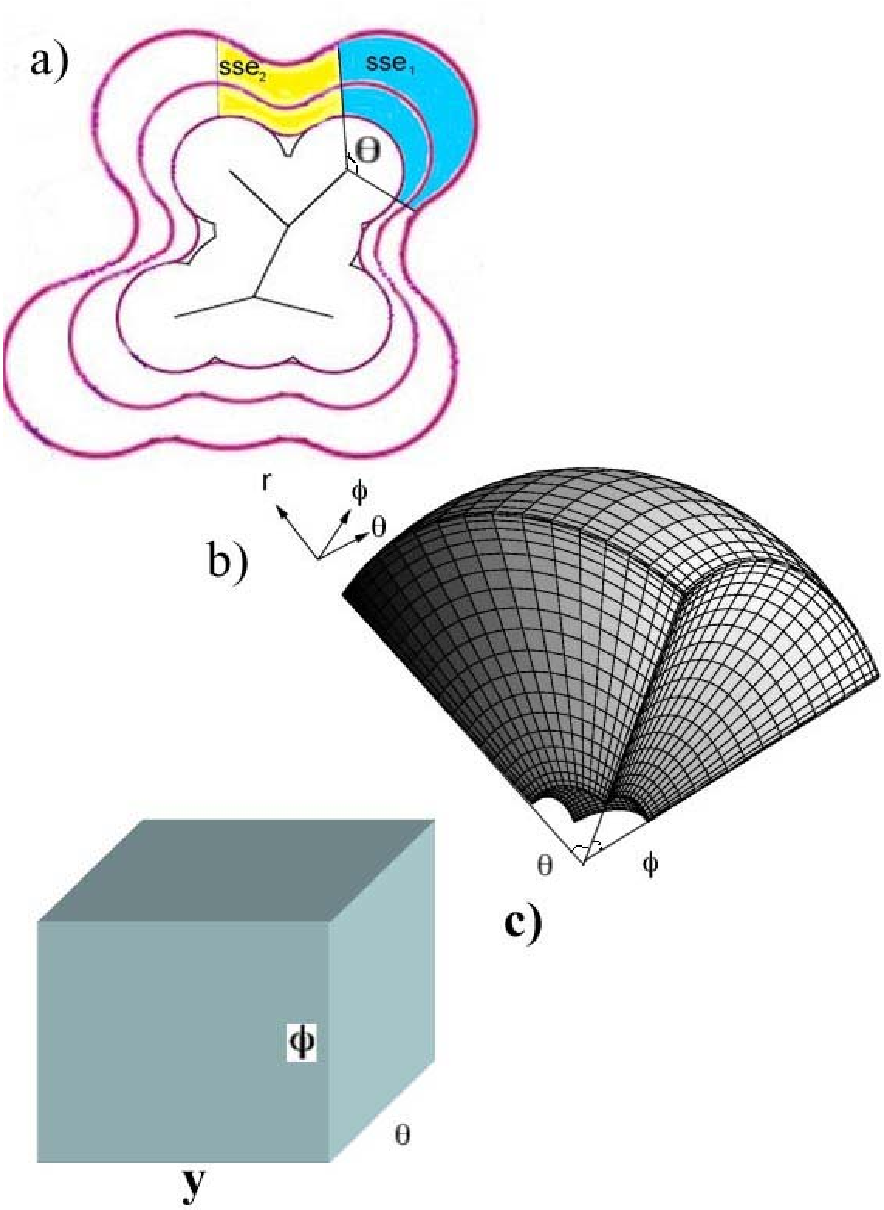

FIG. 1: Sketch of SSEs: a) domain decomposition of the intreface region, b) fine structure of the volume element indicated as SSE$_1$ in (a) , and c) mapping of SSE$_1$ to the cubic element $[0,\pi]^3$ by the transformations of coordinates.

IV. EVALUATIONS OF THE KERNEL

A. General properties of the Chebyshev-Galerkin matrix.

Thus, applying the triple Chebyshev series $T_n(\cos ny)T_l(\cos(l\tilde{\theta}))T_m(\cos(m\tilde{\phi}))$ we need to evaluate the matrix elements $C_{ij}(\mathbf{m},\mathbf{s})$, where $\mathbf{m}$ and $\mathbf{s}$ are to be vectors, i.e. $\mathbf{m}=(n,l,m)$

and $\mathbf{s} = (n_1, l_1, m_1)$. Then, using the Fourier transforms, we express the matrix elements $C_{ij}(\mathbf{m}, \mathbf{s})$ as

$$C_{ij}(\mathbf{m}, \mathbf{s}) = \frac{1}{8\pi^3} \int \tilde{a}_{\mathbf{m}}(\mathbf{k}) c_{ij}(k) \tilde{a}_{\mathbf{s}}(\mathbf{k}) d\mathbf{k} \tag{20}$$

where $\tilde{a}_{\mathbf{s}}(\mathbf{k})$ is the Fourier transform of the basis function, which can be analytically calculated. For example, in the case of spherical solutes we have $a_{\mathbf{s}}(\mathbf{k}) = T_n(\tilde{r})$ and its Fourier transform can be expressed in terms of the Besel functions $J_n(x)$ as:

$$\begin{aligned} \tilde{T}_n(k)_= \int T_n(\tilde{r}) \exp[i\mathbf{kr}] d\mathbf{r}) &= \frac{4\pi}{k} \int_0^\pi \cos(ny) \sin[k(r_s - \sigma_v \cos y)] dy \\ &= \frac{4\pi^2}{k} \sin(kr_s - \frac{\pi n}{2}) J_n(k\sigma_v). \end{aligned} \tag{21}$$

Then integral (20) can be rewritten after discretization by:

$$C_{ij}(m, s) = 8\pi^2 \sum_{p=0}^{N_r} \sin(k_p r_s - \frac{\pi m}{2}) J_m(k_p \sigma_v) c_{ij}(k_p) \sin(k_p r_s - \frac{\pi s}{2}) J_s(k_p \sigma_v), \tag{22}$$

where $k_p = \pi / [r_s - 0.5\sigma_v \cos(\pi p / N_r)]$.

Therefore, we need to evaluate N_r^2 matrix elements at N_r points. The functions $c_{ij}(x)$ are symmetric with respect to change of sign of argument, therefore, we are to evaluate only a half of the matrix elements since $C_{ij}(\mathbf{m}, \mathbf{s}) = C_{ij}(\mathbf{s}, \mathbf{m})$, i.e. the upper triangular part of the matrix. Moreover the sum $m + s$ should be even, hence both the indices are to be even or odd and the entries are calculated independently. The even-even entries can be calculated starting from the top row and the diagonal, while the odd-odd entries starting from the tope row and the first off-diagonal.[19] There is the recursion relation for matrix elements:[19]

$$m[C_{ij}(m, s+1) - C_{ij}(m, s-1)] + s[C_{ij}(m+1, s) - C_{ij}(m-1, s)] = 0. \tag{23}$$

Due to this property, we can generate only $3N_r$ elements and the total cost of the matrix computations decreases down to N_r^2. All the above considerations remain valid in the more complicated case of nonspherical solutes. In the 3D case, the recursion relations are to be given in the vector form by

$$\mathbf{m}(C_{ij}(\mathbf{m}, \mathbf{s} + \mathbf{u}) - C_{ij}(\mathbf{m}, \mathbf{s} - \mathbf{u}) + \mathbf{s}(C_{ij}(\mathbf{m} + \mathbf{u}, \mathbf{s}) - C_{ij}(\mathbf{m} - \mathbf{u}, \mathbf{s})) = 0, \tag{24}$$

where $\mathbf{u}$ is the unit vector, which is $(1,0,0), (0,1,0)$ or $(0,0,1)$, respectively. Hence, we can generate only $27 * N_r * N_\theta * N_\phi$ elements and the total cost of the matrix computations decreases down to $O(N_r^2 * N_\theta^2 * N_\phi^2)$. However, in the case when the functions $c_{ij}(x)$ are smooth, we may avoid the numerical integration at the grid points and reduce the computational costs to $O(M^3)$ where M is the order of the polynomial approximating $c_{ij}(x)$.

B. Polynomial approximation of Chebyshev-Galerkin matrix.

The functions $c_{ij}(x)$ are smooth and have no singularities at $r_s - \sigma_v < x < r_s + \sigma_v$. Therefore they can be approximated by low order polynomial of even powers (the last property due to sign symmetry):

$$c(x) = \sum_{k=0}^{M} c_k x^{2k}. \tag{25}$$

In this equation and below we omit indices ij indicating dependency on the solvent cite. Thus, we have

$$c(|\mathbf{r} - \mathbf{r}_1|) = \sum_{k=0}^{M} c_k((\mathbf{r} - \mathbf{r}_1)^2)^k. \tag{26}$$

Therefore we need to evaluate $(r^2 + r_1^2 - 2\mathbf{r}\cdot\mathbf{r}_1)^k$ at certain k. Using the transformation of coordinates, we obtain

$$(r^2 + r_1^2 - 2\mathbf{r}\cdot\mathbf{r}_1)^k = \sum_{k_1=0}^{k} \binom{k}{k_1} \sigma_v^{k_1} [\Delta r_{ss_1} - \sigma_v(\tilde{r} - \tilde{r}_1)]^{2k-k_1} \cos^{k_1}\gamma \tag{27}$$

where γ is the angle between vectors $\mathbf{r}$ and $\mathbf{r}_1$, while $\Delta r_{ss_1} = r_s - r_{s_1}$. Therefore this factorization allows us to evaluate independently the radial and the angular dependencies. Moreover, since $\cos\gamma = \cos\theta\cos\theta_1 + \sin\theta\sin\theta_1\cos(\phi - \phi_1)$, we may factorize the angular dependencies again

$$\cos^{k_1}\gamma = \sum_{k_2=0}^{k_1} (\cos\theta\cos\theta_1)^{k_1-k_2}(\sin\theta\sin\theta_1)^{k_2}\cos^{k_2}(\phi - \phi_1), \tag{28}$$

and provide a consequent integration over the latitudinal and the longitudinal directions.

Thus, we need to evaluate the integrals of the types:

$$\begin{aligned} I_r(n_a) &= \int_0^{\pi} T_n(\tilde{r})\tilde{r}^{n_a} d\tilde{r}, \\ I_\phi(n_b) &= \int_0^{\phi_s} \cos^{n_b}(\phi - \phi_1) T_m(\tilde{\phi}) d\phi, \\ I_\theta(n_c, n_d) &= \int_0^{\theta_s} \cos^{n_d}(\theta)\sin^{n_c}(\theta) T_l(\tilde{\theta}) d\theta, \end{aligned} \tag{29}$$

where n_a, n_b, n_c and n_d are some integers. The evaluation of the relevant integrals are straightforward and given by the following relations:

$$I_r(n_a) = 2^{1-n_a} \sum_{k=0}^{[n_a/2]} \binom{n_a}{k} \int_0^{\pi} T_n(\tilde{r}) T_{n_a-2k}(\tilde{r}) d\tilde{r} = 2^{1-n_a}\binom{n_a}{n}, \qquad n \leq n_a. \tag{30}$$

At the same time, the angular integrals can be calculated with the use of recursion relations:

$$I_\phi(n_b) = a_{mn_b} \sin(\phi - \phi_1) \cos^{n_b-1}(\phi - phi_1)|_0^{\phi_s} + b_{mn_b} I_\phi(n_b - 2) \tag{31}$$

$$I_\theta(n_c, n_d) = d_{ln_dn_c}(\sin^{n_c-1}\theta \cos\theta^{n_d+1}\theta - \sin^{n_c+1}\theta \cos\theta^{n_d-1}\theta)|_0^{\theta_s}$$
$$+e_{ln_dn_c} I_\theta(n_c - 2, n_d) + g_{ln_dn_c} I_\theta(n_c, n_d - 2), \tag{32}$$

where $a_{mn_b}, b_{mn_b}, d_{ln_dn_c}, e_{ln_dn_c}$, and $g_{ln_dn_c}$ are the recursion coefficients. We should remark that in the general case when $\theta_s \neq \pi$ and $\phi_s \neq \pi$, the free terms in (31) and (32) are also nonzero, and hence the angular recursion relations are to generate infinite chains, corresponding to the infinite number of the relevant matrix elements. This results from a difference in a symmetry of functions $c_{ij}(x)$ and $T_l(\tilde{\theta})$, or $T_m(\tilde{\phi})$. However, as we discussed in ref.[2], we may restrict the angular expansions by some order M_s which corresponds to the symmetry of functions $h_i(\mathbf{r})$ for certain SSE, i.e. $(\mathbf{r} \subset V_s)$.

V. SUMMARY.

We have described the main stages and the details of the Chebyshev-Galerkin scheme for computing 3D solvation problem. The scheme includes three main steps: fast evaluations of the approximating coefficients, calculations of the Chebyshev-Galerkin matrix, and the iterative solution of nonlinear equations for approximating coefficients. Using the linear transformation of coordinates, we reduce the evaluations the approximating coefficients in each SSE to those in a cube of size $N_r * N_\theta * N_\phi$. Further application of the consequent 1D FFTs provides the computational costs of the evaluations to be of the order of $N_r N_\phi N_\theta \ln(N_r N_\phi N_\theta)$. At the same time, the computational cost of kernel calculations are to be sufficiently less this value, since the matrix elements can be calculated analytically due to smoothness of the kernel and the recursion relations for the Chebyshev polynomials. We have derived the main formulas for evaluating the approximating coefficients and the matrix elements in the case of simple SSEs being a part of the sphere. Thus, applying the polynomial approximation of functions $c_{ij}(x)$ and using the above recursion relations, we reduce the problem to $O(N_s^2 M \min^2(M, M_s))$ operations, that it is sufficiently less than $N_{\mathbf{p}}^2$ obtained by the direct method (Sec. 4.1). Moreover, the derived analytical formulas allows us to provide symbolic computations of the matrix elements. We should remark that in the case when a solute atom has more than 2 bonds, the boundary $\phi_s(\theta)$ represents a spherical polygon. Nevertheless, the approach can be applied in this case also, but the recursion relations for latitudinal coefficients are to be modified in the case of complicated geometry of this polygon. The final step of the scheme is to be based on the effective iterative solution of nonlinear equations. For this purpose we use the DIIS method. Therefore, the complete cost of the proposed scheme is to be about of $N_{it}N_sN_rN_\phi N_\theta \ln(N_rN_\phi N_\theta)$. Since, the volume of the interface region is at least by two orders less than the total volume of the cell used in the 3DRISM calculations, the proposed scheme will be by two orders more effective than the 3DRISM calculations. We expect that $N_\phi = N_\theta < 5$. At the same time, the radial dependence will be limited by radial dependence of functions $c_{ij}(r)$. We expect that these functions to be approximated by 3-order polynomials of even powers (see Sec. 4.2). Therefore, $N_r < 5$ and the total number of operations does not exceed $O(600 * N_s)$. If $N_s < 10^3$ then it is by three orders less than cost of computations of small organic solutes provided respectively by current algorithms based on the uniform FFT.[20]

VI. APPENDIX 1. DIIS METHOD.

We need to find solution $\hat{\mathbf{u}*}$ of nonlinear equations:

$$\hat{\mathbf{u}} * - \hat{\mathbf{h}}(\hat{\mathbf{u}}*) - \hat{\mathbb{C}} \cdot \hat{\mathbf{h}}(\hat{\mathbf{u}}*) = F(\hat{\mathbf{u}}*) = 0. \tag{33}$$

Then we compute the $n+1$ iteration in terms of residues $\mathbf{r}_i = \hat{\mathbf{u}}^{(i+1)} - \hat{\mathbf{u}}^{(i)}$ as

$$\hat{\mathbf{u}}^{(n+1)} = \sum_{i=l(n)}^{n} b_i(\hat{\mathbf{u}}^{(i)} + \mathbf{r}_i), \qquad \sum_{i=l(n)}^{n} b_i = 1, \tag{34}$$

by minimazing the least-square functional $J = 0.5|\sum_{i=l(n)}^{n} b_i\mathbf{r}_i)|^2$. That results to the set of linear equations for b_j

$$\sum_{j=l(n)}^{n} [(\mathbf{r}_i \cdot \mathbf{r}_j) - \lambda]b_j = 0, \qquad \sum_{i=l(n)}^{n} b_i = -1. \tag{35}$$

where $(\mathbf{r}_i \cdot \mathbf{r}_j)$ is the norm of the scalar product of the relevant residue vectors. The solution of this set of linear equation is straightforward. The details of convergence of the DIIS scheme have been discussed in Ref.[8].

[1] F. Hirata, Molecular Theory of Solvation (Springer, Berlin, 2003).

[2] G.N. Chuev, Real-Space Mesh Techniques in Molecular Theory of 3D Solvation (Preprint 85/2001, MIS MPG, Leipzig, 2011).

[3] L. M. Delves, J. L. Mohamed, Computational methods for integral equations (Cambridge University Press, Canbridge 1988).

[4] Connolly ML, J. Mol. Graphics 11, 139 (1993); Sridharan S; Nicholls A; Sharp KA, J. Comput. Chem. 16, 1038 (1995); Sanner MF; Olson AJ; Spehner JC, Biopolymers, 38, 305 (1996)); Tsodikov OV; Record MT; Sergeev YV, J. Comput. Chem. 23, 600 (2002).

[5] J.P. Boyd, Chebyshev and Fourier Spectral Methods, (Dover, New York, 2001).

[6] L. Reichel, Numer. Math. 57, 719 (1989).

[7] P. Pulay, Chem. Phys. Lett. 73, 393 (1980).

[8] T. Rohwedder, R. Schneider, J. Math. Chem. 49, 1889 (2011).

[9] Y. Saad, M. H. Schultz, SIAM J. Sci. Statist. Comput. 7 , 856 (1986).

[10] A. Kovalenko, S. Ten-no, and F. Hirata, J. Comput. Chem. 20, 928 (1999).

[11] J.-R. Park, H. B. Cheong, H.-G. Kang, Mon. Wea. Rev., 139, 1256 (2011).

[12] S.A. Orszag, J. Comput. Phys. 37, 70 (1980).

[13] C. S. Tan, J. Comput. Phys. 59, 81. (1985).

[14] I. Christopher, G. Knorr, M. Shoucri, and P. Bertrand, J. Comput. Phys. 131, 323 (1997).

[15] J. Lee, J. Mech. Scie. and Techn. 23 221, (2009).

[16] J. P. Boyd, F. Yu, J. Comput. Phys. 230, 1408 (2011).

[17] A. F. Ware, SIAM Rev. 40, 838 (1998)

[18] J.P. Boyd, Mon. Wea. Rev., 106, 1184 (1978).

[19] D. K. Cope, Adv. Comput. Math. 9, 21 (1998).

[20] Gusarov, S.; Ziegler, T.; Kovalenko, A., J. Phys. Chem. A 110, 6083 (2006).