VARIATIONAL APPROACHES IN MOLECULAR ELECTROSTATICS, SURFACE FORMATION, SHOCK CAPTURING AND NANO-TRANSISTORS

By

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ABSTRACT

VARIATIONAL APPROACHES IN MOLECULAR ELECTROSTATICS, SURFACE FORMATION, SHOCK CAPTURING AND NANO-TRANSISTORS

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This dissertation covers several topics in Applied Mathematics, including nonlinear Poisson equation(NLPE) with application in electrostatics and solvation analysis for biological system, partial differential equation(PDE) transform for hyperbolic conservation laws, high order fractional PDE transform for molecular surface construction and Poisson-Kohn-Sham equation for modeling geometric, thermal and tunneling effects on nano-transistors.

Electrostatic interactions are ubiquitous in nature and fundamental for chemical, biological and material sciences. The Poisson equation is a widely accepted model for electrostatic analysis. However, the Poisson equation is derived based on electric polarizations in a linear, isotropic and homogeneous dielectric medium. We introduce a nonlinear Poisson equation to take into consideration of hyperpolarization effects due to intensive charges and possible nonlinear, anisotropic and heterogeneous media. Variational principle is utilized to derive the nonlinear Poisson model from an electrostatic energy functional. The proposed nonlinear Poisson theory is extensively validated. A good agreement between our results and experimental data as well as theoretical results suggests that the proposed nonlinear Poisson model is a potentially useful model for electrostatic analysis involving hyperpolarization effects.

In our next work, we introduce the use of the PDE transform, paired with the Fourier pseudospectral method (FPM), as a new approach for hyperbolic conservation law problems, which remains an interesting and challenging task due to the diversity of physical origins and complexity of the physical situations. A variety of standard benchmark test problems of hyperbolic conservation laws is employed to systematically validate the performance of the present PDE transform based FPM.

Furthermore, we study the high-order factional PDE transform based on fractional derivative with application in molecular surface generation. Fractional derivative or fractional calculus plays a significant role in theoretical modeling of scientific and engineering problems. However, only relatively low order fractional derivatives are used at present. Our work introduces arbitrarily high-order PDEs to describe fractional hyper-diffusions. The fractional PDEs are constructed via fractional variational principle. The proposed high-order fractional PDE transform are applied to the surface generation of proteins. Computational efficiency of the present surface generation method is compared with the MSMS approach in Cartesian representation. Extensive numerical experiments and comparison with an established surface model indicate that the proposed high-order fractional PDEs are robust, stable and efficient for biomolecular surface generation.

The last part of my work is in the filed of nano-scale electronic transistors. The miniaturization of nano-scale electronic transistors, such as metal oxide semi- conductor field effect transistors (MOSFETs), has given rise to a pressing demand in the new theoretical understanding and practical tactic for dealing with quantum mechanical effects in integrated circuits. We study the effects of geometry of semiconductor-insulator interfaces, phononelectron interactions, and quantum tunneling of nano-transistors. Performances of nanotransistors are explored in terms of current-voltage (I-V) curves and quantized transport energy profiles in a wide range of device parameters. To my wife Chen, our kid Steven, parents, grandparents and extended family.

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Chapter 1

Nonlinear Poisson equation for heterogeneous media

1.1 Introduction

Electrostatic interactions are ubiquitous in nature and fundamental for chemical, biological and material sciences. Among the various components of molecular interactions, electrostatic interactions are of special importance [174, 46, 53, 83, 146, 173, 147, 61, 148, 10, 58, 11] because of their long range and influence on polar or charged molecules – including water, aqueous ions, proteins, nucleic acids, lipid bilayers, sugars, etc. For example, proteins are made up of 20 types of amino acids, 11 of which are charged or polar in neutral solution. Nucleic acids contain long stretches of negative charges from the phosphate groups in nucleotides. In addition, the double-strained DNA chains are found to have an electron charge density as high as one charge per 1.7 Å. Finally, sugars and related glycosaminoglycans can possess some of the highest charge densities of any biomolecules because of the presence of numerous negative functionalities, including carboxylate and sulfate groups. Therefore, electrostatic interactions are some of the most important aspects that determine the physical and chemical properties of biomolecules, such as protein folding, protein-DNA binding, transcription, translation, gene expression, and regulation, etc. As most biological processes occur in aquatic environments, electrostatic solute-solvent interactions are of paramount importance in the exploration of biological mechanism, the analysis of macromolecular behavior, and the modeling of the intramolecular and inter- molecular interactions of biological complexes.

A wide variety of theoretical approaches, ranging from quantum mechanical *ab initio* methods, classic Maxwell's theory of electromagnetism, generalized Born algorithms, to phenomenological modifications of Coulomb's law, has been used for electrostatic analysis. Quantum mechanical methods are generally accurate, but are too expensive to be used for large chemical and biological systems. Generalized Born algorithms are fast, but depend on other methods for calibrations. The Poisson equation, derived by using the Gauss's law and linear polarization, provides a relatively simple and accurate, while much less expensive description of electrostatic interactions for a given charge source density. It works quite well for moderately charged small molecules such as single amino acids [130].

One of most important applications of the Poisson equation is the solvation analysis in the framework of implicit solvent models [175, 92, 139, 37]. Solvation involves interactions between solute molecules and solvent molecules or ions in the aqueous environment. Since 65-90% of cellular mass is water, all important biological processes, such as protein ligand binding, ion transport, signal transduction, gene regulation, transcription, and translation, occur in aqueous environments under physiological conditions. Therefore, one cannot overemphasize the importance of solvation analysis to chemical and biological sciences. The Poisson equation, or the Poisson-Boltzmann equation when the salt is present, is a main workhorse in the electrostatic free energy estimation of solvation because of its balance of model accuracy and computational cost.

However, the Poisson equation is strictly valid for the linear polarization in an isotropic and homogeneous dielectric medium. In contrast, one frequently encounters heavily charged, nonlinear, anisotropic and inhomogeneous materials and strong electric fields in real world problems, for which hyperpolarizations become significant. For example, hyperpolarizability often manifests itself as the Pockels effect and/or the Kerr effect [25, 87, 72, 117, 122]. Nonlinear dielectric response is important for highly charged molecules such as DNA or in protein active sites. It has also been found in composite ferroelectric materials [137, 108, 156]. Nevertheless, for most complex material and devices, such as nanofluidics, fuel and solar cells, electronic transistors, ion channels, molecular motors, etc., the hyperpolarizability is usually neglected in their electrostatic analysis. Therefore, there is a need to consider the nonlinear modification of the Poisson model for practical applications.

In the solvation analysis using the Poisson model or the Poisson-Boltzmann model in the presence of salt, the solute is described in molecular or atomic detail, while the solvent is described by a dielectric continuum, or a mean field approximation. The media in this problem are described by variable coefficients and regarded as heterogeneous. The solventsolute boundary is often prescribed by solvent accessible, solvent excluded or van der Waals surfaces, which gives rise to an unphysical sharp jump in the dielectric profile. Various modifications of the Poisson-Boltzmann model have been considered in the literature, including dipolar solvents [7, 1, 63], multipole effects [145, 102], multiple dielectric constants and multivalent ions [138], solvent-solute interaction [106, 37, 55], and steric effects [24]. Warshel presented a protein-dipole Langevin-dipole (PDLD) model [172], and Freed offered a Langevin-Debye theory [73].

The emphasis in most earlier work is on the solvent, while nonlinear effects in the vicinity of the solute boundary, and their impact to heterogeneous and/or anisotropic media have received relatively less attention. The present work introduces a nonlinear Poisson equation to model nonlinear effects in solvent-solute systems in the absence of salt.

1.2 Models and algorithms

1.2.1 Electrostatic free energy functional

Biomolecules are typically dielectric materials which do not conduct electric current, while their electrons redistributes in response to an applied electric field. The charge redistribution leads to so called dielectric polarization. The polarization density \mathbf{P} is proportional to the electric field \mathbf{E} and can be measured by susceptibility χ_e

$$\mathbf{P} = \varepsilon_0 \chi_e \mathbf{E},\tag{1.1}$$

where ε_0 is the electric permittivity of free space. The susceptibility of a medium is related to its relative permittivity ε by $\chi_e = \varepsilon - 1$, which is set to 0 at vacuum where there is nothing to be polarized. The electric displacement **D** is related to the polarization density **P** by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi_e) \mathbf{E} = \varepsilon_0 \varepsilon \mathbf{E}.$$
 (1.2)

By Gauss's law, one has the Poisson equation

$$\nabla \cdot \mathbf{D} = \nabla \cdot \varepsilon_0 \varepsilon \mathbf{E} = -\nabla \cdot \varepsilon_0 \varepsilon \nabla \phi(\mathbf{r}) = \rho(\mathbf{r}), \qquad (1.3)$$

where $\phi(\mathbf{r})$ is the electrostatic potential and $\rho(\mathbf{r})$ is the charge density. The relation of $\mathbf{E} = -\nabla \phi(\mathbf{r})$ has been used.

An essential assumption in the above derivation of the Poisson equation is that the polarization density is linearly proportional to the electric field \mathbf{E} . However, this is not true for highly charged nonlinear materials under a strong electric field or in an inhomogeneous

medium with a complex interface geometry [87, 72]. Note that according to Coulomb's law, the electric field diverges in the close vicinity of a point charge. In general, the polarization density is of the form

$$\mathbf{P} = \varepsilon_0 \chi^{(1)} \odot^{(1)} \mathbf{E} + \varepsilon_0 \chi^{(2)} \odot^{(2)} \mathbf{E} \mathbf{E}$$
$$+ \varepsilon_0 \chi^{(3)} \odot^{(3)} \mathbf{E} \mathbf{E} \mathbf{E} + \cdots, \qquad (1.4)$$

where $\chi^{(n)}$ is an *n*th order susceptibility and is an (n+1)th order hyperpolarizability tensor and $\odot^{(n)}$ is an *n*th order inner product for appropriate tensorial contraction. The second order susceptibility describes the second order harmonic generation and Pockels effect, while the third order susceptibility represents the Kerr effect [25]. As a vector in \mathbb{R}^3 , the components of **P** are given by

$$\mathbf{P}_{\alpha} = \varepsilon_{0} \chi_{\alpha\beta}^{(1)} \mathbf{E}_{\beta} + \varepsilon_{0} \chi_{\alpha\beta\gamma}^{(2)} \mathbf{E}_{\beta} \mathbf{E}_{\gamma} + \varepsilon_{0} \chi_{\alpha\beta\gamma\delta}^{(3)} \mathbf{E}_{\beta} \mathbf{E}_{\gamma} \mathbf{E}_{\delta} + \cdots, \qquad (1.5)$$

where the Einstein summation convention is used, i.e., repeated indices are summed over all of its possible values. A major difficulty in the application of Eq. (1.5) is that there are too many tensorial components in dealing with high order tensors. Symmetry of the material can be utilized to reduce the number of independent parameters. However, for complex molecules, such as proteins, their symmetry is normally very low and there is little simplification.

The polarization density described in Eq. (1.5) suggests that the linear Poisson equation is a first order approximation. In general, the Poisson equation should be nonlinear in **E** or $\nabla \phi(\mathbf{r})$ so as to partially account for the effect of hyperpolarizations in solvation analysis.

To derive a nonlinear Poisson equation, we consider an energy functional of the form

$$G_{\rm p} = \int \left(\Lambda \left(\nabla \phi(\mathbf{r})\right) + g(\phi(\mathbf{r})) \, d\mathbf{r},\right)$$
(1.6)

where $g(\phi(\mathbf{r}))$ is a source term and $\Lambda(\cdot)$ is an appropriate function to represent nonlinear material properties. Related free energy functionals for electrostatic analysis were discussed in the literature [146, 71, 180]. Energy functionals and variational approaches are now being widely used to derive new and more sophisticated models of solvation [180, 37, 38, 39].

In general, one may set $\Lambda(\cdot)$ as a polynomial of the form

$$\Lambda(\nabla\phi(\mathbf{r})) = a_{j,k} |\nabla^k \phi(\mathbf{r})|^j, \quad j,k = 1, 2, \cdots.$$
(1.7)

In this expression, the high order electric field effects are included. However, similar to Eq. (1.5), to use Eq. (1.7), one faces the difficulty of determining parameters $a_{j,k}$. The lack of detailed information about chemical and physical properties of a molecule in solvent limits the usage of Eq. (1.7).

In the present work, we consider part of the nonlinear polarization effect in the solvation analysis. To avoid the involvement of susceptibility parameters and maintain the simplicity of the implicit solvent model, and to still account for the major hyperpolarizability impact to the solvation, we propose a simple form

$$\Lambda(|\nabla\phi(\mathbf{r})|) = \frac{\varepsilon_m}{2} |\nabla\phi(\mathbf{r})|^2 + \frac{k_B T}{\alpha} (\varepsilon_s - \varepsilon_m) \ln\left(1 + \frac{\alpha}{2k_B T} |\nabla\phi(\mathbf{r})|^2\right), \qquad (1.8)$$

and

$$g(\phi(\mathbf{r})) = -\rho_m(\mathbf{r})\phi(\mathbf{r}) \tag{1.9}$$

where ε_s and ε_m are the permittivities, i.e. dielectric constants, of the solvent and solute respectively, k_B is the Boltzmann constant, T is the temperature, α is a parameter to adjust the strength of the hyperpolarizability, and $\rho_m(\mathbf{r})$ is the molecular charge density

$$\rho_m(\mathbf{r}) = \sum_{i}^{N_m} Q_i \delta(\mathbf{r} - \mathbf{r}_i), \qquad (1.10)$$

with Q_i being the partial charge on an atom located at position \mathbf{r}_i and N_m is the total number of atoms in the molecule. The first term in Eq. (2.11) and the choice of $g(\phi(\mathbf{r}))$ in Eq. (1.9) are standard for the classic electrostatic theory. Whereas, the second term in Eq. (2.11) represents the partial effect of the hyperpolarizability near the solvent-solute boundary.

Certainly, the free energy functional given in Eq. (2.11) is not unique. For example, two alternative forms are given by

$$\Lambda(|\nabla\phi(\mathbf{r})|) = \frac{\varepsilon_m}{2} |\nabla\phi(\mathbf{r})|^2 - \frac{k_B T}{\alpha} (\varepsilon_s - \varepsilon_m) \left[\frac{1}{1 + \frac{\alpha}{2k_B T} |\nabla\phi(\mathbf{r})|^2} - 1 \right], \quad (1.11)$$

and

$$\Lambda(|\nabla\phi(\mathbf{r})|) = \frac{\varepsilon_m}{2} |\nabla\phi(\mathbf{r})|^2 - \frac{k_B T}{\alpha} \left(\varepsilon_s - \varepsilon_m\right) \left(e^{-\alpha \frac{|\nabla\phi(\mathbf{r})|^2}{2k_B T}} - 1\right).$$
(1.12)

These energy functionals describe the α and temperature dependence of the hyperpolarizability. The impact of the hyperpolarization decays as the temperature increases [117, 122].

1.2.2 Nonlinear Poisson equation

Due to the simple form in Eqs. (2.11), (1.11) and (1.12), the energy functional in Eq. (2.11) can be optimized with respect to the electrostatic potential ϕ by using the Euler-Lagrange equation,

$$-\nabla \cdot \frac{\partial \Lambda}{\partial \nabla \phi} + \frac{\partial g}{\partial \phi} = 0. \tag{1.13}$$

Based on the energy functionals in Eqs. (2.11) and (1.11) and Euler-Lagrange equation (1.13), we obtain the nonlinear Poisson equation (NLPE)

$$-\nabla \cdot (\varepsilon(|\nabla \phi(\mathbf{r})|)\nabla \phi(\mathbf{r})) = \rho_m(\mathbf{r}), \qquad (1.14)$$

where the nonlinear dielectric function is given by

$$\varepsilon(|\nabla\phi(\mathbf{r})|) = \varepsilon_m + \frac{\varepsilon_s - \varepsilon_m}{\left(1 + \alpha \frac{|\nabla\phi(\mathbf{r})|^2}{2k_B T}\right)^n}$$
(1.15)

with n = 1 and 2 for energy functionals in Eqs. (2.11) and (1.11), respectively. For Eq. (1.12), the nonlinear dielectric function is given by

$$\varepsilon(|\nabla\phi(\mathbf{r})|) = \varepsilon_m + (\varepsilon_s - \varepsilon_m) e^{-\alpha \frac{|\nabla\phi(\mathbf{r})|^2}{2k_B T}}.$$
(1.16)

It has been shown in the literature [122] that the hyperpolarization decays exponentially as the temperature increases.

The NLPE (1.14) has the same structure as the classic Poisson equation (1.2). However, the dielectric functions in Eqs. (1.15) and (1.16) are no longer discontinuous. To understand the behavior of $\varepsilon(|\nabla \phi|)$, we first analyze two extreme cases,

$$\lim_{|\nabla\phi|\to 0} \varepsilon(|\nabla\phi|) \to \varepsilon_s \tag{1.17}$$

$$\lim_{|\nabla\phi| \to \infty} \varepsilon(|\nabla\phi|) \to \varepsilon_m.$$
(1.18)

Obviously, Eqs. (1.17) and (1.18) give rise to desirable asymptotic dielectric values in the solvent and the solute domains, respectively. It is easy to see that $\varepsilon_m < \varepsilon(|\nabla \phi|) < \varepsilon_s$ for intermediate $|\nabla \phi|$ values. In fact, the dielectric functions $\varepsilon(\phi)$ in Eqs. (1.17) and (1.18) undergo a continuous transition from ε_m to ε_s at the solvent-solute interface when $|\nabla \phi|$ is continuous. An interesting issue is the transition length scale of $\varepsilon(|\nabla \phi|)$. By Coulomb's law, the electrostatic potential ϕ resulting from a point charge, supposed at the origin, decays as $1/\mathbf{r}$. Therefore, the influence of $|\nabla \phi|^2$ decays as $1/\mathbf{r}^4$, which is much faster than the decay of the electrostatic potential and leads to a relatively short transition region of the dielectric function.

Figure 1.1 illustrates the smooth transition of $\varepsilon(|\nabla \phi|)$ from ε_s to ε_m . Here, ε_s and ε_m are set to their conventional values, i.e., 80 and 1, respectively. To understand the impact of the hyperpolarizability, we plot $\varepsilon(|\nabla \phi|)$ with respect to a few α values in Figure 1.1. Larger α values lead to a slower transition of $\varepsilon(|\nabla \phi|)$ to its asymptotic value ε_s . When there is little hyperpolarization, i.e., $\alpha \to 0$, $\varepsilon(|\nabla \phi|)$ undergoes a sharp jump from its molecular value ε_m to its solvent value ε_s . We therefore recover the classic Poisson equation model for



Figure 1.1: The cross section profiles of $\varepsilon(|\nabla \phi|)$ along the *y*-axis at x = 0 and z = 0 at different α values for one-atom system. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.

the solvation analysis. However, the classic Poisson equation is ill-posed unless appropriate interface jump conditions are enforced [67]. Mathematically, the classic Poisson equation is very different from the proposed nonlinear Poisson equation. In fact, physically, it is also very different as demonstarted in the solvation energy calculation. In general, to provide proper prediction of experimental data, the nonlinear Poisson equation, as well as other smooth dielectric Poisson equations, should have its own force field parameters [153, 154, 37]. Note that it is possible to set $\alpha = 1$ so as to arrive at a parameter-free NLPE.

1.2.3 Nonpolar energy

The nonlinear Poisson equation provides a tool for electrostatic analysis. In general, the electrostatic free energy of solvation is complemented by the nonpolar contribution. In the present work, we adopt a popular nonpolar solvation model [114, 165, 37]

$$G_{\rm np} = \gamma {\rm Area} + p {\rm Vol} + \int_{\Omega_s} \rho_s U^{\rm att}(\mathbf{r}) d\mathbf{r}, \qquad (1.19)$$

where γ is the surface tension, Area represents the surface area of the molecule of interest, p is the hydrodynamic pressure, Vol represents the volume occupied by the molecule, ρ_s is the solvent bulk density, Ω_s denotes the solvent accessible region and $U^{\text{att}}(\mathbf{r})$ is the solutesolvent van der Waals interaction potential at point \vec{r} . The first term γ Area is the surface energy, which describes the disruption of intermolecular and/or intramolecular bonds that occurs when the surface of a molecule is created in the solvent. The second term pVol measures the mechanical work of creating the vacuum of a biomolecular size in the solvent. The hydrophobic effect in the first two terms are partially compensated by the third term $\int_{\Omega_s} \rho_s U^{\text{att}}(\mathbf{r}) d\mathbf{r}$, which describes the attractive dispersion effects near the solvent-solute interface.

The nonpolar energy in Eq. (3.44) can be easily computed if the solvent-solute boundary is explicitly given. However, in the present nonlinear Poisson model, there is no sharp interface between the solvent and the solute, which avoids the surface singularity and numerical instability. To obtain a solvent-solute boundary, we define a linear mapping

$$S(\varepsilon) = \frac{1}{\varepsilon_s - \varepsilon_m} \left(\varepsilon_s - \varepsilon(|\nabla \phi(\mathbf{r})|) \right), \qquad (1.20)$$

where $S(\varepsilon)$ is a solute characteristic function such that the solute domain Ω_m is defined by $S(\varepsilon) \ge 0$. Similarly, $1 - S(\varepsilon)$ is a solvent characteristic function such that the solvent domain Ω_s is defined as $1 - S(\varepsilon) \ge 0$. Obviously, in the region $\varepsilon_m < \varepsilon(|\nabla \phi|) < \varepsilon_s$, the solvent domain Ω_s overlaps the solute domain Ω_m . Figure 1.2 illustrates the profile of $S(\varepsilon)$ and $1 - S(\varepsilon)$ computed from Eq. (1.20). The impact of solvent polarity to the solvent cavity or volume was discussed by Papazyan and Warshel [132].



Figure 1.2: The cross line profiles of S and 1 - S along the y-axis at x = 0 and z = 0 for one-atom system.

In order to evaluate the nonpolar energy according to Eq. (3.44), one still needs to compute the surface area and its enclosed volume. Once the surface profile S is provided, it is obvious that the volume of the solute can be expressed as

$$\operatorname{Vol} = \int_{\Omega_m} d\mathbf{r} = \int_{\Omega} S(\varepsilon) d\mathbf{r}, \qquad (1.21)$$

where Ω is the total domain of the solvation problem. Additionally, we rewrite the surface energy term as a function of the surface profile S, which embeds a two-dimensional (2D) surface in the \mathbb{R}^3 . By using the the coarea formula of the geometric measure theory [57, 180], the surface area can also be expressed as a volume integral

Area =
$$\int_{\Omega} |\nabla S(\varepsilon)| d\mathbf{r}.$$
 (1.22)

It is noted that Area only has contribution from $\nabla S \neq 0$, where there is a transition region of the solvent-solute boundary. Finally, the van der Waals dispersion term can be reformulated as

$$\int_{\Omega_s} \rho_s U^{\text{att}}(\mathbf{r}) d\mathbf{r} = \int_{\Omega} \rho_s (1 - S(\varepsilon)) U^{\text{att}}(\mathbf{r}) d\mathbf{r}.$$
(1.23)

We adopted the Weeks-Chandler-Andersen (WCA) decomposition based on the original W-CA theory [176]. Therefore, the nonpolar solvation free energy $G_{\rm np}$ can be defined via the surface profile $S(\varepsilon)$ given in Eq. (1.20),

$$G_{\rm np} = \int_{\Omega} \gamma |\nabla S(\varepsilon)| + pS(\varepsilon) + \rho_s (1 - S(\varepsilon)) U^{\rm att}(\mathbf{r}) d\mathbf{r}.$$
(1.24)

For the attractive dispersion potential U^{att} , which describes the solvent-solute coupling, we have $U^{\text{att}} = \sum_i U_i^{\text{att}}$, where U_i^{att} accounts for the attractive van der Waals interaction due to the *i*th solute atom. The Lennard-Jones (L-J) potential is one way to model the van der Waals interaction. Here we consider the following 6-12 L-J potential at position **r**:

$$U_{i}^{\mathrm{LJ}}(\mathbf{r}) = \varepsilon_{i} \left[\left(\frac{\sigma_{i} + \sigma_{s}}{|\mathbf{r} - \mathbf{r}_{i}|} \right)^{12} - 2 \left(\frac{\sigma_{i} + \sigma_{s}}{|\mathbf{r} - \mathbf{r}_{i}|} \right)^{6} \right], \qquad (1.25)$$

where ε_i characterizes the well-depth, σ_i and σ_s are *i*th solute atomic and solvent radii, respectively, It is seen that $U_i^{\text{LJ}}(\mathbf{r})$ achieves the minimum $-\varepsilon_i$ at the position $r = \sigma_i + \sigma_s$. There are different ways to decompose L-J potential into attractive and repulsive components. One is the "6-12" decomposition, which is :

$$U_i^{\text{att},6/12}(\mathbf{r}) = -2\varepsilon_i \left(\frac{\sigma_i + \sigma_s}{|\mathbf{r} - \mathbf{r}_i|}\right)^6, \qquad (1.26)$$

$$U_i^{\text{rep},6/12}(\mathbf{r}) = \varepsilon_i \left(\frac{\sigma_i + \sigma_s}{|\mathbf{r} - \mathbf{r}_i|}\right)^{12}.$$
 (1.27)

Another popular way is the Weeks-Chandler-Andersen(WCA) decomposition based on the original WCA theory, which has the form of

$$U_{i}^{\text{att,WCA}}(\mathbf{r}) = \begin{cases} -\varepsilon_{i}, & |\mathbf{r} - \mathbf{r}_{i}| < \sigma_{i} + \sigma_{s}; \\ U_{i}^{\text{LJ}}(\mathbf{r}), & |\mathbf{r} - \mathbf{r}_{i}| \ge \sigma_{i} + \sigma_{s}, \end{cases}$$
(1.28)
$$U_{i}^{\text{rep,WCA}}(\mathbf{r}) = \begin{cases} U_{i}^{\text{LJ}}(\mathbf{r}) + \varepsilon_{i}, & |\mathbf{r} - \mathbf{r}_{i}| < \sigma_{i} + \sigma_{s}, \\ 0, & |\mathbf{r} - \mathbf{r}_{i}| \ge \sigma_{i} + \sigma_{s}. \end{cases}$$
(1.29)

In current work, we adopt the WCA decomposition, i.e. we set $U_i^{\text{att}}(\mathbf{r}) = U_i^{\text{att,WCA}}(\mathbf{r})$.

It is worthwhile to point out that the distance in the present 6-12 Lennard Jones potential in Eq. (1.25) are not exactly the same as those in the standard version due to the continuum representation of solvent in our model. As a matter of fact, $|\mathbf{r}-\mathbf{r}_i|$ in Eq. (1.25) is the distance between a specific position \mathbf{r} in the solvent area and the center of a solute atom at \mathbf{r}_i , which is no longer the distance between the center of a solute atom and that of a solvent atom in the standard expression. Consequently, the setting of well depth ε_i differs from those in popular force fields such as from AMBER or OPLS . However the performance of the L-J potential should be based on the same principle, i.e, the value of the L-J potential in the solvent caused by a solute atom only depends on the distance from the center of the atom. This implies that the value of L-J potential caused by a solute atom should be a constant on the van der Waals surface of the atom. In other words, $U_i^{LJ}(\mathbf{r}) = \varepsilon_i \left[\left(\frac{\sigma_i + \sigma_s}{|\mathbf{r} - \mathbf{r}_i|} \right)^{12} - 2 \left(\frac{\sigma_i + \sigma_s}{|\mathbf{r} - \mathbf{r}_i|} \right)^6 \right] = D_i$ if **r** is on the vdW surface of the *i*th atom. Theoretically, the constant D_i should have different values for different types of atoms. For simplicity we use a uniform constant D to determine the value of ε_i given σ_s and σ_i . In the present calculation, we set D = 1.0. Note that WCA expression is chosen as the attractive van der Waals potential.

Thus, the above expression in Eq. (1.24) provides a practical way to compute the nonpolar solvation free energy based on the proposed NLPE (1.14).

1.2.4 Numerical Methods

1.2.4.1 Solution of nonlinear Poisson equation

Because the nonlinear Poisson equation (NLPE) admits a smooth dielectric profile, it is convenient to use the standard second order center difference scheme for the spatial discretization. Denote the position (x_i, y_j, z_k) by the pixel (i, j, k), then the NLPE can be discretized as

$$\varepsilon(x_{i} + \frac{1}{2}h, y_{j}, z_{k})[\phi(i+1, j, k) - \phi(i, j, k)] + \varepsilon(x_{i} - \frac{1}{2}h, y_{j}, z_{k})[\phi(i-1, j, k) - \phi(i, j, k)]$$

$$+ \varepsilon(x_{i}, y_{j} + \frac{1}{2}h, z_{k})[\phi(i, j+1, k) - \phi(i, j, k)] + \varepsilon(x_{i}, y_{j} - \frac{1}{2}h, z_{k})[\phi(i, j-1, k) - \phi(i, j, k)]$$

$$+ \varepsilon(x_{i}, y_{j}, z_{k} + \frac{1}{2}h)[\phi(i, j, k+1) - \phi(i, j, k)] + \varepsilon(x_{i}, y_{j}, z_{k} - \frac{1}{2}h)[\phi(i, j, k-1) - \phi(i, j, k)]$$

$$= -4\rho_{m}(i, j, k)/h,$$

$$(1.30)$$

where h is the grid step size, $\phi(i, j, k)$ and $\rho_m(i, j, k)$ are the discretized electrostatic potential and molecular charge at grid point (x_i, y_j, z_k) respectively. In our work, the second order interpolation (i.e., the trilinear mapping) is used to distribute charge ρ_m to the grid point (i, j, k). The profile of permittivity ε is obtained from the discretization as below

$$\{\varepsilon(|\nabla\phi|)\}_{ijk} = \varepsilon_m + \frac{\varepsilon_s - \varepsilon_m}{\left(1 + \frac{\alpha}{2k_B T} \{|\nabla\phi|^2\}_{ijk}\right)^n}, \quad n = 1, 2,$$
(1.31)

or

$$\{\varepsilon(|\nabla\phi|)\}_{ijk} = \varepsilon_m + (\varepsilon_s - \varepsilon_m)e^{-\alpha \frac{\{|\nabla\phi|^2\}_{ijk}}{2k_BT}},$$
(1.32)

where

$$\{|\nabla\phi|^2\}_{ijk} = \{\phi_x^2\}_{ijk} + \{\phi_y^2\}_{ijk} + \{\phi_z^2\}_{ijk},$$
(1.33)

with

$$\{\phi_x\}_{ijk} = (\phi_{(i+1)jk} - \phi_{(i-1)jk})/2h, \tag{1.34}$$

$$\{\phi_y\}_{ijk} = (\phi_{i(j+1)k} - \phi_{i(j-1)k})/2h, \tag{1.35}$$

and

$$\{\phi_z\}_{ijk} = (\phi_{ij(k+1)} - \phi_{ij(k-1)})/2h.$$
(1.36)

As a result, one attains a system of highly complex and nonlinear equation if $|\nabla \phi|^2$ for ε is directly discretized. To reduce the computational cost, we solve the system by coupling Eq. (1.30) and Eq. (1.31) or Eq. (1.32).

The far field condition similar that used in the Poisson-Boltzmann equation [67] is employed for the nonlinear Poisson equation. As a result, the discretized nonlinear Poisson equation can be cast into a linear algebraic equation system based on Eq. (1.30).

1.2.4.2 Initialization of dielectric profile ε

To compute the dielectric profile ε , we first set up an initial value of ε as

$$\varepsilon(x, y, z) = \begin{cases} \varepsilon_m, & (x, y, z) \in D\\ \varepsilon_s, & \text{otherwise} \end{cases}$$
(1.37)

where the domain D is defined as the region enclosed by the solvent accessible surface, i.e., $D = \bigcup_{i=1}^{N_m} \{\mathbf{r} : |\mathbf{r} - \mathbf{r_i}| < r_i + r_p\}$. Here r_p is the probe radius, r_i is the atomic radius and $\mathbf{r_i} = (x_i, y_i, z_i), i = 1, \dots, N_a$ are the atom centers of the *i*th atom and N_m is the total number of the atoms for a given molecule. In the present work, $\varepsilon(x, y, z)$ is fixed as ε_s outside the solvent accessible surface, and as ε_m within the van der Waals surface, i.e., $(x, y, z) \in \bigcup_{i=1}^{N_a} \{\mathbf{r} : r_i < |\mathbf{r} - \mathbf{r_i}| < (r_i + r_p)\}$, dielectric profile $\varepsilon(x, y, z)$ is determine by Eq. (1.15) or Eq. (1.16). Although the initial value of ε has a sharp jump at the interface of the solvent accessible surface, the iteration procedure of the solution of the nonlinear Poisson equation will generate a smooth ε profile connecting the solvent and the solute regions.

1.2.4.3 Evaluation of solvation free energy

In this subsection, we present the method for the evaluation of solvation free energies. Since the solvation free energy is the energy released or absorbed when the solute molecule is transferred from vacuum to the solvent environment, it is computed by

$$\Delta G = G - G_0, \tag{1.38}$$

where G is the free energy calculated from the solvent environment while G_0 is from the vacuum. Typically, solvation free energy consists of polar and nonpolar contributions. Note that the vacuum environment does not contribute to the nonpolar energy part. Therefore, we have

$$\Delta G = G_{\rm p} + G_{\rm np} - G_0 = \Delta G_{\rm p} + G_{\rm np}, \qquad (1.39)$$

where $\Delta G_{\rm p} = G_{\rm p} - G_0$ and $G_{\rm p}$ and $G_{\rm np}$ denote the polar and nonpolar contribution of G. In the present work, the electrostatic solvation free energy $\Delta G_{\rm p}$ is calculated by

$$\Delta G_{\rm p} = G_{\rm p} - G_0 = \frac{1}{2} \sum_{i=1}^{N_m} Q_i(\phi(\mathbf{r}_i) - \phi_0(\mathbf{r}_i)), \qquad (1.40)$$

where ϕ and ϕ_0 are electrostatic potentials in the solvent and the vacuum environment respectively, and Q_i is the partial charge on *i*th atom located at position \mathbf{r}_i . Finally, the nonpolar solvation free energy is computed by Eq. (1.24).

1.2.4.4 Iteration procedure

The solution of the nonlinear Poisson equation requires appropriate iterations. The procedure of coupling the Poisson equation and dielectric function is follows.

(Step 0): The workflow begins with the initialization of ε .

(Step 1): Then we solve NLPE for the electrostatic potential ϕ .

(Step 2): Next, the gradient $\nabla \phi$ and thus ε is computed.

(Step 3): The electrostatic free energy $\Delta G_{\rm p}$ is calculated.

(Step 4): We check the convergence by comparing $|\Delta\Delta G_p|$, which is the difference between updated electrostatic free energy ΔG_p^{new} and previous value ΔG_p^{old} , with a given tolerance. If convergence is not reached, go back to (Step 1) until convergence. Otherwise, we stop the iteration and compute ΔG , including both polar energy $\Delta G_{\rm p}$ and s non-polar energy $G_{\rm np}$. An overview of the algorithm is showed in the flowchart in Figure 1.3.



Figure 1.3: The flowchart for the solution of the nonlinear Poisson equation.

1.3 Results and Discussion

The Poisson equation has been extensively applied in implicit solvent models to the solvation analysis, which provides a computationally less expensive alternative to the integral equation theory [18, 127], nonlocal dielectric theories [109] and density functional theory models [200]. In our work, we consider solvation applications of our nonlinear Poisson equation.


Figure 1.4: The convergence of electrostatic solvation free energies ΔG_p over number of iteration (N) for one-atom system.

1.3.1 Validation by one atom system

We first consider an atom of unit van der Waals radius and unit charge in the solvent. The atomic center and the charge are both located at the origin. We set $\varepsilon_m = 1$ and $\varepsilon_s = 80$ for dielectric constants in the solute and the solvent, respectively. A fine mesh size of h = 0.25 Å is used in our computation. The convergence of our computational algorithm with respect to the number of iteration is shown in Figure 1.4 while the convergence over the grid size h is validated as in Table 1.1.

Table 1.1: The convergence of $\Delta G_{\rm p}$ with respect to grid size h for one-atom system.

grid size h	0.5	0.25	0.125	0.0625
$\Delta G_{\rm p}$	-183.8562	-183.6532	-183.6531	-183.6531

In general, the dielectric function ε has a smooth profile as shown in Figure 1.1. It is interesting to note that as $\alpha \to 0$, the dielectric profile converges to the discontinuous dielectric constants of the classic linear Poisson model. It is worthwhile to further explore



Figure 1.5: The volume of the nonlinear Poisson model at a wide range of α values for one-atom system with atomic radius 1 Å, $\varepsilon_m = 1$ and $\varepsilon_s = 80$.

the impact of the hyperpolarization by using scaling factor α . To this end, we compute the enclosed volume of the atom by Eq. (1.21) under a wide range of α values. In general, the enclosed volume is larger than that of the linear Poisson model as shown in Figure 1.5. Indeed, the volume converges to that of the linear Poisson model asymptotically $\alpha \to 0$. In fact, the surface area computed with Eq. (1.22) converges to that of the linear Poisson model as $\alpha \to 0$.

Having established the recovery of the linear Poisson model in terms of dielectric function, surface area and enclosed volume, we now investigate polar solvation energy $\Delta G_{\rm p}$ of the nonlinear Poisson model. Figure 1.6 plots the behavior of $\Delta G_{\rm p}$ for various α values. Unlike other quantities, the solvation energy does not recover that of the linear Poisson model,



Figure 1.6: The electrostatic solvation energy of the nonlinear Poisson model at a wide range of α values for one-atom system with atomic radius 1 Å, $\varepsilon_m = 1$ and $\varepsilon_s = 80$.

i.e., the Kirkwood model [105], as $\alpha \to 0$. The plot shows that the Kirkwood model gives $\Delta G_{\rm p} = -163.85$ kcal/mol, while, the present nonlinear Poisson model predicts -183.65 kcal/mol. This behavior reminds us that the present nonlinear Poisson model is inherently a smooth-permittivity model. It is well-known that without appropriate reparameterization, smooth-permittivity or smooth dielectric models lead to an under-estimation of the polar solvation energy [153, 154, 37]. It has been shown that the solvation energy of sharp dielectric models can be recovered by reparameterizing atomic radii with a common factor [154, 37]. This in fact defines their own force field parameters. In the present work, we perform a similar parameter fitting by adjusting the atomic radii so that the $\Delta G_{\rm p}$ of nonlinear Poisson model is the same as that of the Kirkwood model at the limit of $\alpha \to 0$. In this manner,

we can systematically determine the radii of commonly used atoms for our model. Table 1.2 lists the result of our radius set. We present both the enlarged radii as wells as the ratios for the radius enlargement. Here the original radii are from the ZAP-9 force field by Nicholls etc [129]. It should be noted that values of atomic radius from different models may differ significantly. For example, the radius for Hydrogen is 1.20 Å from the Bondi's compilation but is adjusted to 1.10 Å by Nicholls [129]. Furthermore, since the ratios in Table 1.2 vary from 1.06 to 1.12, it is more convenient to apply a common ratio to obtain our parameter set. Figure 1.7 shows that a common ratio of 1.09 fits well with all data. This is consistent with our earlier finding in the differential geometry based solvation model [37] that a common scaling factor of 1.1 gives rise to a good parameterization.

atom-type	radius $[129]$	adjusted-radius	ratio
Н	1.10	1.23	1.12
N	1.40	1.54	1.10
0	1.76	1.88	1.07
Cl	1.82	1.95	1.07
0	1.87	2.00	1.07
S	2.15	2.30	1.07
F	2.40	2.54	1.06

Table 1.2: Comparison of atomic radii and adjusted values (Å).

1.3.2 Application to a set of 17 small molecules

To further validate the proposed nonlinear Poisson model, we apply it to the solvation analysis of a set of 17 small compounds. Various approaches, including quantum mechanics and Poisson-Boltzmann theory, have been applied to this test set by Nicholls *et al* [129]. This test set has also been employed in our earlier work to validate our differential geometry



Figure 1.7: The rescaled atomic radii for the one-atom system with fixed $\varepsilon = \varepsilon_m$ within the solute domain.

based solvation models (DGSMs) [37, 38]. This test set is frequently used because its experimental data of solvation free energies are available. Furthermore, this set was found to be quite challenging to theoretical models because of its hyperpolarization and the existence of polyfunctional or interacting polar groups, which causes strong solvent-solute interactions.

To compare with experimental data of solvation, both polar and nonpolar solvation energies are required. We utilize the nonlinear Poisson equation (1.14) with the anisotropic coefficients given in Eqs. (1.15) and (1.16) for the electrostatic analysis. The nonpolar energy is computed according to Eq. (1.24), which in turn depends on the nonlinear Poisson model for the evaluation of surface function S, volume, and surface area.

The structure and charge parameters of 17 compounds are taken from those of Nicholls et al [129]. In particular, atomic charges are adopted from the OpenEye-AM1-BCC v1 parameters [94]. Atomic coordinates and radii are based on ZAP-9 parameters [129], in which certain types of radii are revised from Bondi radii to improve the agreement with experimental free energy. In our computation, we carry out the smooth-dielectric reparameterization of



Figure 1.8: Correlation of total solvation free energies of 17 compounds between the nonlinear dielectric model and different data. (a) Nonlinear dielectric model and experimental data; (b) Nonlinear dielectric model and DGSM.

atomic radii by using individual radii listed in Table 1.2. Figure 1.8(a) depicts the correlation between the current results and experimental data. The root mean square error (RMSE) of computation results is 1.75 kcal/mol and the average error is 1.40 kcal/mol when the radii in Table 1.2 are used. In comparison, the linear Poisson model offers a RMSE of 1.87 kcal/mol by Nicholls et al [129]. Their explicit solvent approach, which is much more expensive, reduces the RMSE to 1.71 ± 0.05 kcal/mol [129]. Therefore, present nonlinear Poisson model provides a relatively good prediction of solvation energies for this set of molecules.

It is interesting to further compare the performance of the present nonlinear Poisson model with the more complicated DGSM [37], which relies on the Laplace-Beltrami equation to provide the surface function and dielectric profile. The RMSE of the DGSM is 1.76 kcal/mol, which is very close to the present result. Indeed, since both models admit smooth dielectric profiles and employ similar nonpolar energy functionals, there is very good correlation between their solvation predictions as shown in Figure 1.8(b).

Table 1.3 gives a summary of the computation results by the present nonlinear model with a comparison to the experimental data. From Table 1.3, it is seen that the error for this set of 17 molecules varies from -2.41 to 3.86 kcal/mol. However, the major errors are from the calculation of two benzamide molecules. The RMSE will drop from 1.75 kcal/mol to 1.25 kcal/mol without these benzamide compounds. The error with benzamides may be related to the charges of the carbonyl oxygens and tertiary nitrogens in the OpenEye-AM1-BCC v1. This issue will be further explored in our future work.

Similar to the linear Poisson model, the proposed nonlinear Poisson model is also capable of providing surface electrostatic analysis. Figure 1.10 (a) and (b) depict surface electrostatic potentials of four compounds obtained at a given isosurface value S = 0.5. This information can be used in various practical applications.

Compound	$G_{\rm np}$	$\Delta G_{\rm p}$	ΔG	Exptl	Error
glycerol triacetate	2.63	-13.02	-10.40	-8.84	-1.56
benzyl bromide	1.61	-5.01	-3.41	-2.38	-1.03
benzyl chloride	1.57	-5.16	-3.59	-1.93	-1.66
m-bis(trifluoromethyl)benzene	2.44	-3.20	-0.76	1.07	-1.83
n,n-dimethyl-p-methoxybenzamide	2.23	-9.57	-7.34	-11.01	3.67
n,n-4-trimethylbenzamide	2.11	-8.01	-5.90	-9.76	3.86
bis-2-chloroethyl ether	1.66	-4.32	-2.66	-4.23	1.57
1,1-diacetoxyethane	1.89	-8.51	-6.62	-4.97	-1.65
1,1-diethoxyethane	1.74	-4.62	-2.88	-3.28	0.40
1,4-dioxane	1.16	-5.71	-4.55	-5.05	0.50
diethyl propanedioate	2.13	-8.23	-6.10	-6.00	-0.10
dimethoxymethane	1.17	-4.67	-3.49	-2.93	-0.56
ethylene glycol diacetate	1.84	-8.86	-7.02	-6.34	-0.68
1,2-diethoxyethane	1.77	-4.37	-2.60	-3.54	0.94
diethyl sulfide	1.52	-2.44	-0.92	-1.43	0.51
phenyl formate	1.55	-8.03	-6.49	-4.08	-2.41
imidazole	0.96	-11.66	-10.70	-9.81	-0.89

Table 1.3: Comparison of free energies (kcal/mol) for 17 compounds between nonlinear model and experimental data.

Finally, we test the solvation predictions of alternative nonlinear dielectric functions. As shown in Table 1.4, three nonlinear Poisson models based on different dielectric functions provide essentially the same prediction of solvation free energies. Therefore, the proposed nonlinear Poisson models are not sensitive to the functional form of the nonlinear dielectric profile.

Table 1.4: Errors of solvation free energies for a set of 17 small compounds obtained from 3 nonlinear models based on adjusted radius in Table 1.2.

	n = 1	n = 2	exponential
	model	model	model
RMSE (kcal/mol)	1.7505	1.7565	1.7531
Average error (kcal/mol)	1.4011	1.4051	1.4035



Figure 1.9: Correlation between the results obtained by the MIBPB-III [67] and the nonlinear dielectric model for electrostatic solvation free energies of 20 proteins.

1.3.3 Application to a set of 20 proteins

After demonstrating the success in the validation and application in small compounds, we examine our nonlinear Poisson model for the electrostatic solvation of biomolecules. Here we chose 20 proteins which are frequently used in previous studies [67, 37]. The number of atoms for this set of proteins ranges from 519 to 2809.

The initial structure data of all proteins are taken from the Protein Data Bank (PDB) at http://www.pdb.org/. Based on the initial structure data, the hydrogen atoms which are typically missing from the X-ray data are added to the structures and extra water molecules that are attached to proteins are excluded so as to obtain full all-atom models. Partial charges



Figure 1.10: Surface electrostatic potentials of four molecules at their isosurface value S = 0.5. (a) small compound: diethyl propanedioate; (b)small compound: n,n-dimethyl-p-methoxybenzamide; (c)protein: 1vjw; (d) protein: 2pde.

at atomic sites as well as atomic radii in angstroms are assigned from the CHARMM27 force field [120]. Note that a common radius scaling factor of 1.1 is used in this computation. n-polar energy are the same as before.

The results for 20 proteins are summarized in Table 1.5 in the Supporting Information. The magnitude of electrostatic solvation free energies for these proteins are much larger



Figure 1.11: Correlation of solvation free energies predicted by the NLPE model and experimental data for 21 compounds.

than that of the previous set of 17 small compounds due to multiple charges. Since the experimental data for the total solvation free energy for this set of proteins is not available yet, we compare the electrostatic solvation free energies with those from the DGSM [37] and from the MIBPB-III [67]. It is seen that the results are close to each other. An illustration of the correlation between the present nonlinear model and the DGSM is depicted in Figure 1.9. The results of three models are quite close. Figure 1.10 (c) and (d) display the profile of electrostatic potential on the isosurface value S = 0.50 for two proteins, i.e., 1vjw and 2pde, which suggests that the present nonlinear Poisson model is also robust for the visualization of electrostatic surface potentials.

		$\triangle G_{\rm p} \; (\rm kcal/mol)$		
PDB-ID	No. of atoms	MIBPB-III	DGSM	NLPE
1ajj	519	-1137.2	-1178.5	-1109.8
2erl	573	-948.8	-935.8	-930.7
1bbl	576	-986.8	-965.9	-956.8
1vii	596	-901.5	-892.0	-878.3
2pde	667	-820.9	-843.0	-850.9
1 sh1	702	-753.3	-771.8	-797.6
1fca	729	-1200.1	-1200.6	-1223.1
1uxc	809	-1138.7	-1125.7	-1109.4
1fxd	824	-3299.8	-3291.9	-3307.0
1vjw	828	-1237.9	-1226.6	-1233.3
1bor	832	-853.7	-871.4	-872.3
$1 \mathrm{hpt}$	858	-811.6	-808.2	-793.0
$1 \mathrm{mbg}$	903	-1346.1	-1328.2	-1317.9
1r69	997	-1089.5	-1072.7	-1055.1
1neq	1187	-1730.1	-1713.9	-1694.1
451c	1216	-1024.6	-1020.6	-1019.1
1a2s	1272	-1913.5	-1900.3	-1910.7
$1 \mathrm{svr}$	1435	-1711.2	-1704.6	-1682.6
1a63	2065	-2373.5	-2380.5	-2384.5
1a7m	2809	-2155.5	-2179.8	-2201.0

Table 1.5: Electrostatic solvation free energies (kcal/mol) for 20 proteins by different models.

1.3.4 Application to temperature effects

It is well known that solvation free energies are temperature dependent [163]. Although most implicit solvation models are developed for room temperature, temperature effects were considered in the SM6T model [30] and by Elcock and McCammon [56]. In this work, we demonstrate the ability of the NLPE for modeling the temperature effect on solvation free energies. First, one notes that the NLPE explicitly depends on the temperature as shown in Eq. (1.15). Additionally, dielectric constants, ε_m and ε_s , are known to vary with temperature [115]. The dielectric constant of water reduces from 80.10 at 298K to 55.58 at 373K, and its values at other temperatures can be well approximated by a cubic polynomial [115]. In implicit solvation models, ε_m is known to increase as the temperature increases because of atomic fluctuation [164]. In the present model, we set $\varepsilon_m = 1$ at 298K and $\varepsilon_m = 2$ at 373K, with a linear interpolation for other temperatures. It should also be noted that one may need to carefully investigate temperature effects on other parameters, namely, the atomic radius and charge, in the NLPE to fully explore the present model. For simplicity, atomic radius and charge are treated as temperature independent since their change with respect to temperatures is neglectable [30].

To validate the NLPE model for temperature effects, we consider a set of compounds whose free energies of solvation at different temperatures are available from experimental measurement [30]. The structural data of these compounds can be computed by using Pub-Chem (http://pubchem.ncbi.nlm.nih.gov/). However, the corresponding electronic charge densities are obtained from a quantum approach developed by Chen and Wei [39].

Two different temperatures are considered to illustrate temperature effects on solvation free energies of 21 compounds. Due to the availability of experimental data, considered temperatures are not the same for all the compounds, as shown in Table 1.7. As the temperature increases, the average increase in solvation energies is 1.13 kcal/mol in experimental data while that predicted by the NLPE model is 1.05 kcal/mol. The RMSE of solvation free energies predicted by the NLPE model is 1.23 kcal/mol at low temperatures and 1.20 kcal/mol at high temperatures. Figure 1.11 illustrates the correlation between predicted solvation free energies and experimental data at all temperatures. Obviously, the proposed NLPE model does a good job in modeling the temperature effect on the solvation free energy.

Note that by adjusting the dielectric constants, the classical Poisson equation can also be used to model the temperature effect. Table 1.6 shows the RMSE and average $\Delta\Delta G$ of two models at low and high temperatures for 21 compounds. It is seen that the present NLPE

Model	classical Poisson	NLPE $(n=1)$
RMSE (kcal/mol) at low T	1.56	1.23
RMSE (kcal/mol) at high T	1.65	1.20
Average $\Delta\Delta G$ (kcal/mol)	0.86	1.05

Table 1.6: Comparison of RMSE and $\Delta\Delta G$ predicted by the classical Poisson model and the NLPE model for 21 compounds (The average $\Delta\Delta G$ of experimental data is 1.13 kcal/mol).

model performs much better than the classical Poisson equation.

1.4 Chapter conclusion remarks

The classic Poisson theory neglects hyperpolarizations, which are important under a strong electrical field, or involving highly charged nonlinear inhomogeneous media. We propose a new electrostatic solvation free energy functional to partially account for the effect of hyperpolarizations to solvation analysis. A nonlinear Poisson equation is derived from the Euler-Lagrange equation. The present nonlinear Poisson equation gives rise to a smooth dielectric function, which by-passes both conceptual and computational difficulty of employing a sharp solvent-solute boundary. By using geometric measure theory, we also formulate a nonpolar solvation model based on the dielectric profile obtained from the nonlinear Poisson model. The proposed solvation models are extensively validated with the Kirkwood model and experimental measurements of 17 molecules. Our new solvation models out-perform the classic Poisson equation based solvation model. In fact, its performance is very close to the explicit solvation model, which is much more computationally expensive. Application of the proposed nonlinear Poisson model is considered to electrostatic analysis of 20 proteins. Additionly, the test results for the set of 21 compounds at different temperatures further validate our model.

	ΔG at low T		Δ	ΔG at high T			$\Delta\Delta G$	
Compd	Т	Exptl	NLPE	Т	Exptl	NLPE	Exptl	NLPE
anthracene	284	-4.14	-4.75	304	-3.45	-3.23	0.69	1.52
phenanthrene	277	-4.29	-5.67	309	-3.54	-4.85	0.75	0.82
1-methylphenanthrene	277	-4.01	-5.51	304	-3.58	-5.08	0.43	0.43
fluoranthene	283	-5.12	-5.04	328	-3.86	-3.33	1.26	1.71
Acetaldehyde	273	-4.03	-3.51	313	-3.06	-3.37	0.97	0.14
1-Methoxypropane	273	-2.35	-2.15	298	-1.64	-1.58	0.71	0.57
tetrahydrofuran	293	-3.58	-2.31	343	-2.72	-1.43	0.86	0.88
2-Methoxypropane	283	-2.32	-2.16	298	-1.90	-1.61	0.42	0.55
ethyl-formate	278	-2.93	-2.86	349	-2.25	-1.80	0.68	1.06
formic-acid	278	-7.09	-5.68	309	-6.74	-5.06	0.35	0.62
1,2-ethanediol	298	-9.35	-8.19	348	-8.39	-7.42	0.96	0.77
naphthalene	277	-3.01	-1.13	309	-2.13	-0.62	0.88	0.50
1-methylnaphthalene	277	-3.08	-5.06	313	-2.06	-4.45	1.02	0.61
acenaphthylene	277	-3.78	-2.71	304	-2.93	-2.15	0.85	0.56
acetone	274	-4.38	-4.64	333	-3.17	-3.58	1.21	1.07
2-Butanone	283	-4.55	-3.61	373	-2.46	-1.68	2.09	1.93
cyclopentanone	273	-5.83	-7.31	364	-4.31	-5.92	1.52	1.40
benzylal	273	-7.61	-5.04	328	-5.89	-3.70	1.72	1.34
cyclohep	293	-5.77	-5.35	364	-3.59	-3.86	2.18	1.48
2methylc	273	-5.47	-6.73	353	-3.04	-4.46	2.43	2.27
cyclohexylm	303	-4.09	-5.30	363	-2.47	-4.03	1.62	1.27
Mean							1.13	1.05
RMSE			1.23			1.20		

Table 1.7: Temperature effect for 21 compounds between the NLPE model and experimental results.

Chapter 2

PDE transform for hyperbolic conservation laws

2.1 Introduction

Hyperbolic systems of nonlinear conservation laws

$$\mathbf{u}_t + \mathbf{f}(\mathbf{u})_x = 0 \tag{2.1}$$

with an initial condition

$$\mathbf{u}(x,0) = \mathbf{u}_0(x) \tag{2.2}$$

have attracted great attention in the past few decades in mathematical, scientific and engineering communities due to their practical applications in fluid mechanics, aerodynamics, and nano-bio systems, to mention only a few. The solution to this class of problems may not exist in the classical sense because of possible discontinuities in the initial condition, material interface, singularity formation, turbulence, blow-up, etc.

Both global and local methods have been developed for hyperbolic conservation laws. Many up-to-date local methods have been proposed for shock-capturing, turbulence and shock interaction, including weighted essentially non-oscillatory (WENO) scheme [95], central schemes [20, 111, 116, 128], arbitrary-order non-oscillatory advection scheme [158], gas kinetic [187], anisotropic diffusion [131], conjugate filters [86] and image processing based algorithms [79, 179]. An important factor that contributes to the success of the above mentioned local schemes in the shock-capturing is their appropriate amount of intrinsic numerical dissipation, which is introduced either by explicit artificial viscosity, upwinding, relaxation, or by local average strategy in non-oscillatory central schemes [98]. Indeed, the characteristic decomposition based on Roe's mean matrix can also be considered as a local average of the Jacobian matrix. The relation between some approximate Riemann solvers and relaxation schemes was analyzed by LeVeque [113]. Local characteristic decomposition is not necessary in low-order methods because of intrinsic numerical dissipation, while it seems to be indispensable in high-order methods [135]. In general, local and low order methods perform well for problems whose Fourier responses of the solution focus predominantly in the low frequency region. For this class of problems, first order or second order Godunov type of schemes can be very efficient in balancing accuracy and efficiency. When local and low order methods are used for resolving shocks in flows with fine structural details or highly oscillatory patterns, their numerical dissipation is usually too large to offer informative results.

Spectral methods, or global methods, on the contrary, produce little numerical dissipation and dispersion in principle when applied to approximate spatial derivatives. It is well known that spectral methods are some of the most accurate and efficient approaches for solving partial differential equations (PDEs) arising from scientific and engineering applications [28, 62, 159]. Therefore, it is highly desirable to use spectral methods for the solution of hyperbolic conservation laws, because the multiscale features, including Kolmogorov microscales, in the hyperbolic conservation law systems require high resolution methods. Nevertheless, when spectral methods are applied to the approximation of spatial derivatives of a discontinuous function, which often occurs in hyperbolic conservation law problems, one encounters Gibbs' oscillations [77]. Most previous investigations are aimed at improving the rate of convergence away from the discontinuity while recovering smooth solutions from the contamination of Gibbs' oscillations. The suppression of Gibbs' oscillations is necessary in order to avoid unphysical blow-ups in the time integration. Therefore, it has been of tremendous interest in modifying spectral methods for hyperbolic conservation law systems in the past two decades [112, 151]. There are two general types of approaches in spectral based methods for hyperbolic conservation law systems: (1) explicit artificial viscosity, e.g. spectral viscosity method proposed by Tadmor [155], and (2) filtering. It is expected that the appropriate use of spectral methods enables us not merely to capture the shock, but also to resolve the delicate features, immersed interface, and underlying fine structures of the flow.

Filters are designed to apply either in the spectral domain, called spectral filters, or in the physical domain. Typical spectral filters include Lanzos filter, raised cosine filter, sharpened raised cosine filter, Krasny filter [110] and exponential cutoff filter, as listed by Hussaini *et al.* [93]. More sophisticated and effective filters in spectral domain are Vandeven's *p*th order filter [162], and Gottlieb and Tadmor's regularized Dirichlet function [78]. A filter-based Reynolds-averaged Navier-Stokes approach was developed to improve the predictive capability considerably in comparison to the standard $k - \epsilon$ model [101].

Filters in the physical domain are also commonly used alternatives to spectral filters. In the framework of spectral methods, it is generally more difficult to design appropriate filters in the physical domain than in the Fourier domain. A simple procedure is to make use of numerical dissipation contained in some *high-order* shock-capturing schemes [27], such as the ENO scheme, where, actually, numerical dissipation was introduced both in the Fourier domain (via an exponential filter) and in the physical domain (via ENO polynomial filter). Such a strategy was employed by Yee *et al.* [190] to construct characteristic filters in the framework of finite difference methods. Gegenbauer polynomials are used to resolve the oscillatory partial Fourier summation [77]. Promising numerical results were generated by using filter approaches [51, 52, 75].

About a decade ago, we proposed a conjugate filter oscillation reduction (CFOR) scheme [85, 181, 205, 206, 151] for hyperbolic conservation laws. This scheme was constructed within the framework of a local spectral wavelet method, namely, the discrete singular convolution (DSC) algorithm [167, 177, 183]. Here, 'conjugate filters' means that the effective wavenumber range of the low-pass filter is largely overlapped with that of the high-pass filter used for the approximation of spatial derivatives. In fact, the DSC algorithm is used to behave as both low-pass filters and high-pass filters. Extensive validation of the CFOR scheme over a wide range of shock-capturing problems has been carried out [85, 181, 205, 206]. We demonstrated that CFOR scheme provides some of the highest grid resolution, i.e., 5 points per wavelength (PPW), for the interaction of shock and entropy waves, and for many other challenging problems involving natural high frequency oscillations [205, 206, 151].

Despite great effort in the past few decades, the efficient application of filters for hyperbolic conservation law systems remains a challenging problem. To design efficient filter methods, one must control a number of filter properties, such as flatness, ripple, filter length, effective frequency range and length of transition band, to name only a few. Normally, it is desirable to utilize filters that are free of dispersion errors, flat while having very small transition band, short in length while having high resolution. Obviously, some of these properties are conflicting with each other. Adjustable parameters have to be employed to tune filter design properties in the application. In addition to the difficulties in controlling filter properties, there are intrinsic mathematical challenges in developing filtered spectral methods. First, the solutions to different hyperbolic conservation law equations may have different Fourier spectral distributions. Additionally, even for a single conservation law equation, the characteristic of the Fourier spectral distribution may change during the time integration. Finally, the same conservation law equation can exhibit dramatically different Fourier spectral distributions when it is applied to different physical problems, i.e., problems with different initial, interface and boundary conditions. Therefore, an optimal filter has to be fully adaptive to hyperbolic equations, to initial, interface and boundary conditions, and to the variation of spectral characteristic during the time integration. Unfortunately, such a filter approach still does not exist yet. Given the complexity in the hyperbolic conservation law and in filter properties, it is unlikely that there will be a perfect solution to these challenges in the near future. Consequently, these challenging and important problems call for the further study of spectral filter approaches.

To put the matter in perspective, currently, there is no such a method that is perfect for all of the tasks in hyperbolic conservation law systems. The challenges are due to the intrinsic mathematical difficulties of hyperbolic conservation law equations and the inherent limitation in the understanding of the fundamental physics involved in the hyperbolic conservation laws as noticed by Nobel Laureate Richard Feynman. As it is well known, hyperbolic conservation laws can be formally derived from the (quantum) Boltzmann equation, which in turn can be derived from the (quantum) Liouville equation equation via the BBGKY hierarchy [179]. Many physical assumptions are built into these derivations and their validities may not be warranted under certain physical situations. There is a pressing need to revisit basic assumptions and fundamental physics for the hyperbolic conservation laws for complex physical applications.

Most recently, we have introduced PDE transform as a new approach for the analysis of signals, images, surfaces and data [171, 169, 203]. The PDE transform is based on a family of arbitrarily high order nonlinear PDEs first introduced by Wei for edge-preserving image restoration in 1999 [178] and PDE based high-pass filters proposed by Wei and Jia in 2002 [182]. Variational models of PDE transform have also been proposed [169]. With an iterative procedure [170, 171] to incorporate appropriate residues, i.e., initial conditions, the PDE transform is able to extract functional mode functions (FMFs) and allow perfect reconstruction. By FMFs, we mean the mode components which share same band of frequency distribution as well as same category of physical functions, i.e., trend, edge, texture, feature, trait, noise etc. Using the FMFs obtained from the PDE transform, secondary processing, or post-processing, can be performed to achieve desirable tasks, such as edge detection, trend estimation, image enhancement, denoising, texture quantification, segmentation, feature extraction, pattern recognition, etc. The PDE transform can perform as tunable filters. By adjusting the order of the PDE transform, i.e., the highest order of the PDE, one controls time-frequency localization, while by adjusting the diffusion coefficients or propagation time, one obtains desirable frequency precision or multiresolution analysis [203]. The PDE transform can be tuned according to the input data to provide desirable mode information. The full process of the PDE transform is nonlinear even if linear PDEs are employed. Unlike the Fourier transform or the wavelet transform, the PDE transform conserves the data representation. The resulting functional modes are still in the original data form. The PDE transform has been applied to image analysis [171, 169], signal processing [171] and biomolecular surface construction [203]. High order PDE transforms with their order being much higher than 4 are found to play a vital role in signal analysis, image processing and surface generation.

The objective of present work is to explore the utility of the PDE transform for the solution of hyperbolic conservation laws. In fact, such a utility can be realized in a number of ways. For simplicity, we make use of a fast PDE transform, i.e., the PDE transform realized by the fast Fourier transform in a single time stepping. Such a fast algorithm is paired with the Fourier pseudospectral method (FPM) for solving hyperbolic conservation law equations and suppressing Gibbs' oscillations. Therefore, the fast PDE transform implemented in the present work is essentially a spectral filter approach. Nevertheless, the PDE transform can be implemented with geometric structures using mean-curvature flow and/or Willmore flow type of nonlinear PDEs. However, this aspect is beyond the scope of the present work. In fact, the PDE transform has an adjustable effective wavenumber range that makes it viable to capture fine flow structures, which is a desirable objective of spectral methods for hyperbolic conservation law systems. It is this adjustable effective wavenumber range that controls the resolution of the overall scheme. In our design, this adjustable effective wavenumber range can be varied by the highest order of the PDE transform and the duration of time propagation according to the resolution requirement of a hyperbolic conservation equation and the physical problem of interest. Different orders of the PDE transform have different magnitude responses and adjustability in the Fourier domain, which in turn influences the accuracy and resolution of the PDE transform based FPM. It is this flexibility that makes the present method applicable to a wide variety of hyperbolic conservation law systems. The performance of the proposed method is extensively validated and compared with those of other approaches in the literature.

2.2 Theory and algorithm

To establish notation and enhance the basic understanding of the proposed PDE transform strategy for systems of hyperbolic conservation laws, we present a brief introduction of arbitrarily high order nonlinear PDEs and PDE transforms. The detailed numerical algorithm for time integration of evolution equations of hyperbolic conservation laws is described.

2.2.1 Arbitrarily high order nonlinear PDEs

Last two decades have witnessed a dramatical growth in PDE based methods for image analysis. Using the diffusion equation for image denoising was pioneered by Witkin in 1984 [186]. Although, Witkin's algorithm is mathematically simple, it provides the foundation for much later development. Since nonlinear PDEs and variational calculus are attractive research topics, anisotropic diffusion equation introduced by Perona and Malik [134] and total variation models pioneered by Rudin, Osher, and Fatemi [141] have had much impact in the applied mathematical community. These earlier approaches are based on the use of the second order PDEs for image or surface analysis. In 1999, Wei introduced the first family of arbitrarily high order nonlinear PDEs for edge-preserving image restoration [178]

$$\frac{\partial u(\mathbf{r},\tau)}{\partial \tau} = \sum_{q} \nabla \cdot \left[d_q(u(\mathbf{r},\tau), |\nabla u(\mathbf{r},\tau)|, \tau) \nabla \nabla^{2q} u(\mathbf{r},\tau) \right] + e(u(\mathbf{r},\tau), |\nabla u(\mathbf{r},\tau)|, \tau), \quad (2.3)$$

where $\mathbf{r} \in \mathbb{R}^n$, $\nabla = \frac{\partial}{\partial \mathbf{r}}$, $u(\mathbf{r}, \tau)$ is the processed image function, $d_q(u(\mathbf{r}, \tau), |\nabla u(\mathbf{r}, \tau)|, \tau)$ are edge sensitive diffusion coefficients and $e(u(\mathbf{r}, \tau), |\nabla u(\mathbf{r}, \tau)|, \tau)$ is enhancement operator. Equation (2.3) is subject to the initial image data $u(\mathbf{r}, 0) = X(\mathbf{r})$ and appropriate boundary condition. Its construction was motivated by the super flux in the pattern formation in alloys, glasses, polymer, combustion, and biological systems and the Perona-Malik equation [134]. Its essential idea is to accelerate the noise removal by higher order derivatives, which is more efficient in noise dissipation. An interesting feature is that one can recover the Perona-Malik equation by setting q = 0 and $e(u(\mathbf{r}, \tau), |\nabla u(\mathbf{r}, \tau)|, \tau) = 0$. Therefore, Eq. (2.3) is also called generalized Perona-Malik equation. The fourth order version of Eq. (2.3) has been applied to image denoising and restoration by many researchers [178, 119, 70, 69].

As in the original Perona-Malik equation, one can choose the hyperdiffusion coefficients $d_q(u, |\nabla u|, \tau)$ in Eq. (2.3) in many different ways. One of the popular choices is the Gaussian form

$$d_q(u(\mathbf{r},\tau), |\nabla u(\mathbf{r},\tau)|, \tau) = d_{q0} \exp\left[-\frac{|\nabla u|^2}{2\sigma_q^2}\right], \qquad (2.4)$$

where the values of constant d_{q0} depend on the noise level, and σ_0 and σ_1 were chosen as the local statistical variance of u and ∇u

$$\sigma_q^2(\mathbf{r}) = \overline{|\nabla^q u - \overline{\nabla^q u}|^2} \quad (q = 0, 1).$$
(2.5)

The notation $\overline{Y(\mathbf{r})}$ above denotes the local average of $Y(\mathbf{r})$ centered at position \mathbf{r} . In this algorithm, the measure based on the local statistical variance is important for discriminating image features from noise. As such, one can bypass the image preprocessing, i.e., the convolution of the noise image with a test function or smooth mask in the application of the PDE operator.

In the past decade, high order nonlinear PDEs, particularly fourth order nonlinear PDEs, have attracted much attention in image analysis [31, 178, 32, 191, 157, 81, 119, 82, 13]. Unlike

the classical second order PDEs, higher order PDEs are able to suppress high frequency oscillations, including noise, at much faster rates. Mathematical analysis of high order nonlinear PDEs has been a popular research topic in applied mathematics. Bertozzi and Greer proved the existence and uniqueness of the solution of fourth order edge-preserving PDEs in Sobolev space with H^1 initial data and a regularized operator [19, 81, 82]. A similar mathematical analysis was carried out by Xu and Zhou [188] for fourth order nonlinear PDEs. Recently, Jin and Yang have presented an interesting result in which they show that the mathematical structure of Wei's fourth order nonlinear PDE differs from other fourth order PDEs derived from the variational formulation [99]. They have proved the existence of the strong solution of such a PDE [99]. Because high order PDEs are subject to strict stability constraints in their numerical solutions, the development of stable and efficient numerical techniques for higher order PDEs is an important issue, except for digital image processing where the grid size is normally unit. Witelski and Bowen proposed alternating direction implicit (ADI) schemes to solve arbitrarily high order nonlinear PDEs [185]. Similar ADI schemes were also constructed in our work [13].

Recently, another family of arbitrarily high order geometric PDEs was proposed for surface formation and evolution with application to biomolecular systems [13],

$$\frac{\partial S}{\partial \tau} = (-1)^q \sqrt{g(|\nabla \nabla^{2q} S|)} \nabla \cdot \left(\frac{\nabla (\nabla^{2q} S)}{\sqrt{g(|\nabla \nabla^{2q} S|)}}\right) + P(S, |\nabla S|), \tag{2.6}$$

where S is the hypersurface function, $g(|\nabla\nabla^{2q}S|) = 1 + |\nabla\nabla^{2q}S|^2$ is the generalized Gram determinant and P is a generalized potential term, including microscopic potential effect in biomolecular surface construction. Equation (2.6) was designed as a generalization of other important geometric PDEs. For example, when q = 0 and P = 0, it reduces to the mean curvature flow equation used in our earlier construction of minimal molecular surfaces [16], while when q = 1 and P = 0, it is a surface diffusion flow [13]. Certainly, Eq. (2.6) can also be regarded as a variant of Wei's earlier arbitrarily high order PDE (2.3). It is interesting to note that the molecular surface generated by Eq. (2.6) has a morphology distinguished from that generated by using the second order geometric PDEs [13].

Variational approaches provide important theoretical formulations for physical and biological systems [16, 180, 37, 38]. Variational derivation of molecular surfaces are formulated in many of our recent work [180, 37, 38, 34]. Similar approaches are commonly used in image analysis in applied mathematics [140, 16, 14, 49]. Didas *et al.* discussed the variation formulation of high order nonlinear PDEs [49]. Here we provide alternative expressions for the PDE transform by variation. We construct the energy functional as

$$E(u, \nabla u, \nabla^2 u, \cdots, \nabla^m u) = \int \left[\Lambda \left(\sum_{q=1}^m |\nabla^q u|^2 \right) + \epsilon (X-u)^2 \right] d\mathbf{r}, \quad (2.7)$$

where ϵ is a constant, X is the original data, $\epsilon(X - u)^2$ is the fidelity term and $\Lambda(\cdot)$ is an appropriate penalty function. The most commonly used penalty function is the Tikhonov form

$$\Lambda(x^2) = x^2. \tag{2.8}$$

Other useful forms include [49, 119]

$$\Lambda(x^2) = \left(\sigma^2 + x^2\right)^{\frac{1}{2}}$$
(2.9)

$$\Lambda(x^2) = e^{x^2/2\sigma^2}.$$
 (2.10)

Energy functional (2.7) can be minimized by using the Euler-Lagrange equation,

$$\sum_{q=1}^{m} \nabla^{q} \odot^{q} \Lambda_{uq} \left(\sum_{q=1}^{m} |\nabla^{q} u|^{2} \right) \nabla^{q} u + \epsilon (X - u) = 0$$
(2.11)

where \odot^q is a normal product for even q and an inner product for odd q. Here

$$\Lambda_{uq} = (-1)^{q+1} \partial \Lambda / \partial |\nabla^q u|^2.$$
(2.12)

By solving Eq. (2.11), one realizes the energy minimization. A practical way to solve Eq. (2.11) is to introduce an artificial time τ and convert Eq. (2.11) into a time dependent PDE

$$\partial_{\tau} u = \sum_{q=1}^{m} \nabla^{q} \odot^{q} \Lambda_{uq} \left(\sum_{q=1}^{m} |\nabla^{q} u|^{2} \right) \nabla^{q} u + \epsilon (X - u).$$
(2.13)

Equation (2.13) is essentially equivalent to the earlier PDE transform [169].

2.2.2 PDE transform

One of the important properties of the PDE transform is its ability to extract mode functions from a given data X. To illustrate this point, we denote the solution of Eq. (2.3) and/or Eq. (2.13) as $\check{X}(\tau)$ such that

$$\check{X}^{k}(\mathbf{r},\tau) = \mathcal{L}X^{k}(\mathbf{r}) \tag{2.14}$$

where \mathcal{L} is a low-pass PDE transform satisfying $\mathcal{L}u(\mathbf{r}, 0) = u(\mathbf{r}, \tau)$, $\check{X}^k(\mathbf{r}, \tau)$ are mode functions and $X^k(\mathbf{r})$ is the *k*th residue function defined by

$$X^1 = X(\mathbf{r}) \tag{2.15}$$

and

$$X^{k} = X^{1} - \sum_{j=1}^{k-1} \check{X}^{j}, \quad \forall k = 2, 3, \cdots.$$
 (2.16)

Obviously, there is a perfect reconstruction of the original data X in terms of all the mode functions and the last residue

$$X = \sum_{j=1}^{k-1} \check{X}^j + X^k.$$
 (2.17)

Note that the PDE transform given in Eq. (2.14) recursively extracts mode functions based on the input residue function. This procedure is nonlinear even if a linear PDE operator is used because the initial value changes during the repeated operations.

The first mode produced by the PDE transform described above is the trend of the data. The residue of the trend is an edge function, including possible noisy components. By systematically repeating the low-pass PDE transform (2.14), one can extract all the desirable higher order mode functions. In our earlier work, high-pass PDE transforms were also constructed in which the first mode is edge type of information or possible noise; while the final residue is the trend [171].

Solving arbitrarily high order PDEs, such as Eq. (2.3) and/or Eq. (2.13) in the PDE transform can be a very difficult issue for some practical application. A main difficulty is

the stability constraint as the time stepping is normally proportional to the 2mth power of spatial grid spacing, where 2m is the highest order of the PDE transform. An exception is digital image processing, in which the spatial grid spacing is usually unit and thus bypasses the stability constraint. However, spatial grid spacing is normally smaller than one in most other applications.

There is another way that one can entirely bypass the stability constraint and obtain the solution in a single time step. This approach relies on the use of the fast Fourier transform (FFT) for the solution of evolution PDEs [151]. To this end, we linearize Eqs. (2.3) and (2.13), and assume the form

$$\partial_{\tau} v = \sum_{j=1}^{m} (-1)^{j+1} d_j \nabla^{2j} v + \epsilon (X^k - v), \quad \tau \ge 0,$$
(2.18)

where $d_j > 0$, $\epsilon \sim 0$ and $X^k \in \mathbb{R}^n$ is the *k*th residue of the data. When Eq. (2.18) is subject to initial value $v(\mathbf{r}, 0) = X^k$ and periodic boundary conditions, it can be easily solved with the Fourier pseudospectral method. The solution algorithm developed in the above Fourier domain is called a fast PDE transform. In the present work, we explore the use of the fast PDE transform for integrating hyperbolic conservation law systems.

2.2.3 Numerical algorithm

Both linear and nonlinear PDE transforms can be used for systems of hyperbolic conservation laws. For simplicity, we consider only linear PDEs in the present work. The FPM is used for the basic discretization of hyperbolic conservation law equations, while the fast PDE transform is implemented as spectral filters. The numerical scheme can be expressed as the following two-step procedure:

$$\bar{U}^{k+1} = \mathcal{B}U^k \tag{2.19}$$

$$U^{k+1} = \mathcal{L}\bar{U}^{k+1}, \qquad (2.20)$$

where the operator \mathcal{B} in Eq. (2.19) is the basic time integration from time k to time k + 1and the operator \mathcal{L} in Eq. (2.20) is a possible application of the PDE transform. Here, U^k and U^{k+1} is the numerical solution of u in Eq. (2.1) at time step k and k + 1, respectively, while \bar{U}^{k+1} is the intermediate numerical solution of u after implementing operator \mathcal{B} on U^k .

The operator \mathcal{B} in Eq. (2.19) can be defined by a general numerical method for the time evolution. Here, we use the fourth-order Runge-Kutta scheme. The FPM is utilized for the spatial discretization of $f(u)_x$ in the frequency domain.

Specifically, after carrying out the fast Fourier transform on f, we obtain the frequency response \hat{f} , i.e. $\hat{f} = FFT(f)$. Then $i\omega \hat{f}(\omega)$ is the frequency response of f_x , where $i = \sqrt{-1}$ is the imaginary root. By doing the inverse fast Fourier transform on $i\omega \hat{f}(\omega)$, we obtain the spatial discretization of $f(u)_x$ as $IFFT(i\omega \hat{f}(\omega))$.

For simple and continuous problems, scheme (2.19) works well. However, for hyperbolic conservation systems involving discontinuity, the accumulation of Gibbs' oscillations as time evolves may result in spurious solutions or even numerical blow ups. Thus, we make use of PDE transform [151] to eliminate the possible Gibbs' oscillations from basic time integration (2.19). The application of the PDE transform is controlled (i.e., turned on or turned off) by an adaptive sensor. The sensor is characterized by a measure of high frequency denoted by $\parallel \mu \parallel$ and regulated by a threshold value η . Once the increment in high frequency measure,

 $\Delta \mu$, exceeds the threshold η , the PDE transform in Eq. (2.20) is implemented. In our test, we apply a straightforward high frequency measure $\parallel M \parallel$ as the TVD sensor, which is defined by

$$\|\mu(\bar{U}^{k+1})\| = \sum_{i} |\bar{U}_{i+1}^{k+1} - \bar{U}_{i}^{k+1}|, \qquad (2.21)$$

where \bar{U}_i^{k+1} and \bar{U}_{i+1}^{k+1} denote the intermediate numerical solution of u at time k+1 on spatial point i and i+1, respectively, while $\|\mu(\bar{U}^{k+1})\|$ is the total variation measure of \bar{U}^{k+1} . As a result, by checking whether the increment of high frequency $\Delta\mu(\bar{U}^k) = \|\mu(\bar{U}^{k+1})\| - \|\mu(\bar{U}^k)\|$ exceeds η or not, we can decide whether to apply the PDE transform.

Equation (2.20) in the second step is given by the PDE transform to suppress Gibbs' oscillations. We implement the PDE transform in frequency domain, which results in

$$\hat{U}^{k+1} = \hat{\mathcal{L}}\hat{\bar{U}}^{k+1},$$
(2.22)

where \hat{U}^{k+1} and \hat{U}^{k+1} are the frequency responses of U^{k+1} and \bar{U}^{k+1} respectively, while $\hat{\mathcal{L}}$ is the kernel of the fast PDE transform in the Fourier domain. In this work, we adopt the simple implementation of PDE transforms of $d_m = 1$ and $d_i = 0$, $(i = 1, \dots, m-1)$ as well as $\epsilon = 0$, as mentioned before. As a result, the design of the PDE transform depends on the highest order of l = 2m and propagation time τ , whose properties have been analyzed in the last section.

It should be noted that the FPM is normally associated with periodic boundary conditions. However, most conservation law equations admit non-periodic boundary conditions. We handle non-periodic computation domains by symmetrical extension to an auxiliary domain. This approach works well as shown in our previous work [151]. Specifically, the symmetrical extension of the computation domain in 1D is discussed here. Suppose the original domain is discretized by N + 1 grid points indicated by $i = 1, \dots, N + 1$, then the computation domain is doubled with 2N grid points and f(u) and u are extended by

$$\{f(u)\}_i = \{f(u)\}_{2N+2-i}, \qquad i = N+2, \cdots, 2N, \tag{2.23}$$

$$\{u\}_i = \{u\}_{2N+2-i}, \qquad i = N+2, \cdots, 2N, \tag{2.24}$$

where $\{\cdot\}_i$ corresponds to the value at the *i*th pixel. Extensions in 2D and 3D are straightforward as shown Eqs. (2.49)-(2.54) in Section 2.3.3.

After the entire time integration has been completed, we adopt a cosmetic post-processing filter as introduced by Gottlieb *et al.* [76] to make the solution more presentable. In our numerical experiments, we employ the Lagrange-4 as the post processing filter. The reader is referred to our earlier work [152] for its implementation detail.

2.3 Numerical test and validation

The performance of the proposed PDE transform on the solution of hyperbolic conservation law systems is validated through test examples in this section. A number of standard linear and nonlinear benchmark problems are studied in the present work, from scalar conservation law systems including the linear advection equation, Burgers' equation and problem with non-convex flux, to one dimensional (1D) and two dimensional (2D) Euler equations, including shock tube (Sod's and Lax's) problems, 1D and 2D shock-entropy interaction, as well as 2D shock-vortex interaction. The proposed PDE transform can be applied directly on those problem with periodic boundary conditions. However, for non-periodic boundary conditions, the computation domain is symmetrically doubled to convert to a periodic one, as in Example 3 (Inviscid Burgers' equation), Example 4 (Non-convex flux), Example 5 (Sod's and Lax's problems), Example 6 (1D Shock-entropy interaction), Example 7 (Shu-Osher's problem), Example 8 (2D Shock-entropy interaction) and Example 9 (2D Shock-vortex interaction).

In our implementation, the wavenumber w is set by $w_q = (\frac{2\pi q}{N})/\Delta$, $q = -\frac{N}{2}, \dots, 1, \dots, \frac{N}{2} - 1$ where L is the length of computation domain, N is the number of discretized grid points and $\Delta = L/N$ is the grid spacing. This series of wavenumbers ranges over $[-\pi/\Delta, \pi/\Delta)$. The design of PDE transform depends on the order n and propagation time τ . Table 2.1 lists the order l and propagation time τ used in each test problem. To better interpret the frequency response, we rescaled the wavenumber w from $[-\pi/\Delta, \pi/\Delta)$ to $[-\pi, \pi)$. Consequently, the propagation time τ is rescaled to $\tau^* = \tau/(\Delta)^l$ correspondingly.

It is noted that the appropriate selection of order l = 2m and propagation time τ of the PDE transform is quite subtle. On the one hand, the order should not be too high, while the propagation time should not be too small. Otherwise, the PDE transform has little effect in suppressing the Gibbs' oscillation of the solution. On the other hand, the order should not be too low, while the propagation time should not be too large. Otherwise, they result in too much dissipation. Owing to diversity of hyperbolic conservation law systems, the best choices of order and propagation time are problem dependent, which are listed in the table 2.1.

We would like to point out that both the PDE transform and hyperbolic conservation law systems are time dependent. To avoid possible confusion, we denote " τ " as the propagation time of the PDE transform and designate "t" as evolution time of the conservation law

Example No	Case	Order	Propagation time	Rescaled
			when $w \in \left[-\frac{\pi}{\Lambda}, \frac{\pi}{\Lambda}\right)$	propagation time
				when $w \in [-\pi, \pi)$
1	$\kappa = 5, 10$	6	1.0E-13	6.8E-03
1	$\kappa = 20, 25$	12	1.0E-20	4.7E-03
		2	1.0E-05	1.6E-01
9		4	1.0E-12	2.6E-04
2		6	1.0E-16	4.4E-04
		8	1.0E-20	7.2E-04
3	$u_l = 1, u_r = 0$	6	3.0E-15	1.2E-03
0	$u_l = 0, u_r = 1$	6	7.5 E-10	5.3E-02
1		4	5.5E-14	1.0E-03
4		6	6.0E-18	5.9E-05
5	Sod's	6	1.0E-09	4.4E-03
	Lax's	6	1.0E-10	4.4E-04
	$\kappa = 18$	12	3.0E-27	3.4E-06
6	$\kappa = 32$	12	1.5 E- 30	7.0E-06
		6	5.0E-16	1.0E-03
		40	1.0E-95	1.7E-13
	$\kappa = 60$	12	2.0E-34	3.8E-06
7		10	1.0E-23	1.1E-05
		2	5.0E-06	2.0E-02
8		10	3.5E-23	1.2E-05
		6	1.0E-14	3.3E-04
9		10	1.0E-24	1.1E-03

Table 2.1: The order and propagation time of the PDE transform used in test examples.

system in the rest of the paper.

2.3.1 Scalar conservation law systems

We first consider 1D scalar conservation law systems, whose governing equation is expressed in the form of

$$u_t + f(u)_x = 0, (2.25)$$

with f(u) as a function of u. Three types of f(u), including f(u) = u and convex flux $\frac{1}{2}u^2$ as well as non-convex flux $\frac{1}{4}(u^2 - 1)(u^2 - 4)$, are studied in the present work.

2.3.1.1 Example 1 (Linear advection equation with Sine-Gaussian wavepacket)

. The first test example is the linear advection equation given by

$$u_t + cu_x = 0, \qquad -1 < x < 1,$$

 $u(x,0) = u_0(x), \quad \text{periodic},$
(2.26)

where $u_0(x)$ is the initial value. We set $u_0(x)$ as [206]

$$u_0(x) = \sin[2\pi\kappa(x-x_0)]e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$
(2.27)

where the parameter of wavenumber κ can be tuned to produce highly oscillatory wavepacket, x_0 is the initial location of wavepacket center and σ is a constant regularizing the width of the wave packet. We set $x_0 = 0$ and $\sigma = \sqrt{2}/10$ such that the tail of wavepacket is constrained over the computation domain [-1, 1]. It is straightforward to show that the exact solution is given by $u(x, t) = u_0(x - t)$, which is a translation of the initial solution at a unit speed, resulting in the fact that the initial wavepacket repeats itself every two time units over the computation domain [-1, 1]. The mesh size is chosen as N = 128 to implement the PDE transform while the time increment is selected as small as 10^{-4} to ensure that the time discretization error is negligible.

We vary wavenumber κ to explore the accuracy and stability of the PDE transform strategy for the wavepacket propagation. For low frequency waves, a low-order method can work well to obtain accurate solutions. However, as the wavenumber κ increases, the wavepacket



Figure 2.1: Results for $\kappa = 5, 10$ from the PDE transform for the advection equation with the Sine-Gaussian wave packet $(t=100, \Delta t = 10^{-4})$.


(d) $\kappa = 20, N = 128$, after the interpolation

Figure 2.2: Results for $\kappa = 20$ from the PDE transform for the advection equation with the Sine-Gaussian wave packet $(t=100, \Delta t = 10^{-4})$.

Time		10	20	50	80	100
PDE transform	$\kappa = 20$	2.69E-7	5.38E-7	1.34E-6	2.15E-6	2.67E-6
	$\kappa=25$	8.10E-7	1.62E-6	4.06E-6	6.50E-6	8.47E-6
CFOR-Hermite	$\kappa = 20$	2.78E-7	5.56E-7	1.39E-6	2.22E-6	2.78E-6
	$\kappa = 25$	1.51E-6	3.02E-6	7.55E-6	1.21E-5	1.51E-5

Table 2.2: L_{∞} error for long-time integration of the Sine-Gaussian wavepacket.

becomes more and more oscillatory. It is challenging for low resolution schemes to resolve the highly oscillatory advective wavepacket. Therefore, one needs to resort to a high order method. In our test, we apply the 6th-order PDE transform for low frequency wavepackets, i.e., $\kappa = 5$ and 10, and 12th-order PDE transform for high frequency wavepackets, i.e., $\kappa = 20$ and 25.

Figures 2.1(a), (b) and 2.2(a) show the computational results and exact solutions at time t = 100 for three different frequencies $\kappa = 5, 10$ and 20. It is obvious that there is no visual difference between the numerical and exact solutions in Figures 2.1(a) and (b). However, for the case of of $\kappa = 20$, the solution does not show the peaks and valleys of the exact wavepacket. One may regard the solution as being imperfect. In fact, this is not true. The L_{∞} error listed in Table 2.2, is as small as 2.67E-6. Therefore the numerical solution is extremely accurate. The truth is that, because so few grid points are used in our computation, there are not enough grid points to fully represent the wavepacket. Nevertheless, the origin information of the wavepacket is perfectly built in the solution. To illustrate this point, we interpolate the present solution to a denser grid (N = 256) as shown in Figure 2.2(b) by using our DSC algorithm [167, 177, 183]. Indeed, we are able to fully restore all extrema in the wavepacket based on the information presented in Figure 2.2(a). This confirms that our scheme is still able to perform well for high frequency waves under a very small ratio of grid points over wavelength.

It is also meaningful to check the long time integration of the numerical method. Table 2.2 lists the numerical L_{∞} -error from t = 10 to t = 100. One can tell that the numerical errors are under good control during the time integration. As a comparison, we also list in Table 2.2 the results of a CFOR-Hermite method proposed in our earlier work [206]. The CFOR-Hermite method is based on the local spectral wavelet approach for the spatial discretization and the conjugate filter method for oscillation reduction. It has been intensively validated for solving the Navier-Stokes equation and integrating conservation law systems [206].

In the work of [206], the CFOR-Hermite method employs 100 points but takes the same time step $\Delta t = 10^{-4}$. From Table 2.2, one can notice that the errors from the PDE transform is slightly smaller than those from the CFOR-Hermite method. We are quite confident that the results listed in Table 2.2 are some of the best when $\kappa = 25$. It can be concluded that the numerical accuracy and long time stability are well resolved by the proposed PDE transform.

2.3.1.2 Example 2 (Linear advection equation with wave combination)

Another example is also a linear advection equation given by [95]

$$u_t + u_x = 0, \qquad -1 < x < 1,$$

 $u(x, 0) = u_0(x), \quad \text{periodic},$
(2.28)

where $u_0(x)$ is the initial value given by

$$u_{0}(x) = \begin{cases} \frac{1}{6}(G(x,\beta,z-\delta) + G(x,\beta,z+\delta) + 4G(x,\beta,z)), & -0.8 \le x \le -0.6, \\ 1, & -0.4 \le x \le -0.2, \\ 1 - |10(x-0.1)|, & 0 \le x \le 0.2, \\ \frac{1}{6}(H(x,\alpha,a-\delta) + H(x,\alpha,a+\delta) + 4H(x,\alpha,a)), & 0.4 \le x \le 0.6, \\ 0, & \text{otherwise.} \end{cases}$$
(2.29)

The functions G and H are set as

$$G(x, \beta, z) = e^{-\beta(x-z)^2},$$

$$H(x, \alpha, a) = \sqrt{\max(1 - \alpha^2(x-a)^2, 0)},$$
(2.30)

where z = -0.7, $\delta = 0.005$, $\beta = \frac{\log 2}{36\delta^2}$, a = 0.5, and $\alpha = 10$.

The initial value of this problem is a smooth but narrow combination of a Gaussian, a square wave, a sharp triangle wave and a half ellipse. It is easy to show that the exact solution is given by $u(x,t) = u_0(x-t)$, which is a translation of the initial solution at a unit speed. It is well known that due to the contact discontinuity, the propagation by the linear advection equation leads to unphysical Gibbs' oscillations which may be induced by exponentially small numerical errors and their subsequent amplification. In Figure 2.3, the numerical results obtained by using the PDE transform of second, fourth, sixth and eighth orders are demonstrated at t = 8 with 256 grid points. It is interesting to observe that for this simple problem, not only the second order PDE transform works well, but also many higher order PDE transforms produce satisfactory results.



Figure 2.3: Results from the PDE transform of various orders for the advection equation ($t = 8, \Delta t = 0.001, 256$ grid points).



Figure 2.4: Results from the 6th-order PDE transform for the inviscid Burgers' equation at time t = 2. (a) $u_l = 1, u_r = 0$, 257 grid points; (b) $u_l = 0, u_r = 1$, 129 grid points;

2.3.1.3 Example 3 (Inviscid Burgers' equation)

In this example, we test the performance of the present PDE transform for the most classical model, inviscid Burgers' equation with convex flux $f(u) = \frac{1}{2}u^2$ and Riemann type of initial conditions with constant u_l on the left and u_r on the right.

(3a) First we consider the Riemann initial value with $u_l > u_r$ as

$$u(x,0) = \begin{cases} u_l = 1, & x \le 0, \\ u_r = 0, & x > 0. \end{cases}$$
(2.31)

This problem has been studied by numerous researchers because it is a standard benchmark problem in hyperbolic conservation laws. The exact solution is given by a shock wave with a constant velocity σ , i.e.

$$u(x,t) = \begin{cases} u_l, & \frac{x}{t} < \sigma, \\ u_r, & \frac{x}{t} > \sigma, \end{cases}$$
(2.32)

where

$$\sigma = \frac{f(u_l) - f(u_r)}{u_l - u_r} = \frac{1}{2}$$

It is observed that this problem has a non-periodic boundary condition. Consequently, the computational domain needs to be symmetrically doubled in the *x*-direction to obtain periodic boundary condition when applying the Fourier pseudospectral method [151] pairing with the PDE transform. Since the initial condition is piecewise constant and exact solution does not involve large oscillation, a low-order scheme is suitable to render a satisfactory numerical solution. In this case, we apply second, fourth and sixth order PDE transforms to resolve the problem. It is found that all the three schemes work well. The numerical results from the sixth order PDE transform are plotted in Figure 2.4(a) at time t = 2. It is demonstrated that the Gibbs' oscillation is well resolved and the shock front, which moves to x = 1, is well captured. Although this problem prefers low order shock-capturing methods [95], it is concluded that the PDE transform based FPM method works well for this problem too.

(3b) As another example, we check the present method by using the Riemann type initial value with $u_l < u_r$ as

$$u(x,0) = \begin{cases} u_l = 0, & x < 0, \\ u_r = 1, & x \ge 0. \end{cases}$$
(2.33)

The exact solution is given by a rarefaction wave

$$u(x,t) = \begin{cases} 0, & \frac{x}{t} < f'(u_l), \\ G(\frac{x}{t}), & f'(u_l) < \frac{x}{t} < f'(u_r), \\ 1, & f'(u_r) < \frac{x}{t}. \end{cases}$$
(2.34)

with $f'(u_l) = u_l, f'(u_r) = u_r$ and $G(\frac{x}{t}) = (f')^{-1}(\frac{x}{t}) = \frac{x}{t}$.

Similar to Case (3a), the computational domain is symmetrically doubled in the xdirection to obtain periodic boundary condition before applying the PDE transform and FPM. Furthermore, the piecewise constant initial condition and exact solution imply that this problem can be well resolved by a low-order shock-capturing scheme. In our approach, we apply the sixth order PDE transform, paired with the FPM, to solve the equation. The numerical results from the sixth order PDE transform are plotted in Figure 2.4(b) at time t = 2. From the figure, it is seen that the rarefaction fan over [0,2] is free of oscillation. The feature of the solution is well resolved.

2.3.1.4 Example 4 (Non-convex flux)

We next consider a problem with a non-convex flux to test the convergence to the physically correct solution. The non-convex flux is given by

$$f(u) = \frac{1}{4}(u^2 - 1)(u^2 - 4) \tag{2.35}$$

with a Riemann initial condition

$$u(x,0) = \begin{cases} u_l = -3, & x < 0, \\ u_r = 3, & x \ge 0. \end{cases}$$
(2.36)

The exact solution is given by

$$u(x,t) = \begin{cases} u_l, & \frac{x}{t} \le f'(u_l), \\ G(\frac{x}{t}), & f'(u_l) < \frac{x}{t} < 0, \\ -G(-\frac{x}{t}), & 0 < \frac{x}{t} < f'(u_r), \\ u_r, & f'(u_r) \le \frac{x}{t}, \end{cases}$$
(2.37)

with $f'(u_l) = -19.5$, $f'(u_r) = 19.5$ and G(u) is the solution of f'(G(u)) = u in the convex part of f, which is $|u| > \sqrt{5/6}$. It should be noted that the solution is discontinuous at x = 0 and $G(0) = \sqrt{2.5}$.

The exact solution and more detailed information about this problem are given in [90]. This problem is relatively more complicated than the convex flux case. In the literature, commonly reported numerical result is at t = 0.04 [95]. The numerical results of the PDE



Figure 2.5: Comparison between numerical results from the PDE transform and FPM-RSK method for the problem with a non-convex flux (129 grid points, t = 0.04, $\Delta t = 0.0005$).

(b) FPM-RSK (129 grid points)

0

0.5

1

-2

-3• -1

-0.5



(a) The 6th order PDE transform (65 grid points)



Figure 2.6: Comparison between numerical results from the PDE transform and FPM-RSK method for the problem with a non-convex flux (65 grid points, t = 0.04, $\Delta t = 0.0005$).

transform are showed in Figures 2.5(a) and 2.6(a). It is seen that the shock front at x = 0 is almost exactly captured. Particularly, there is no numerical solution point located on the discontinuity.

As a comparison, we consider the Fourier pseudospectral method (FPM) with the regularized Shannon kernel (RSK) approach, which was extensively validated in our earlier work [151]. In Figures 2.5(b) and 2.6(b), this approach is labeled as FPM-RSK. It is obvious that compared with the FPM-RSK, the present PDE transform yields a more satisfactory resolution. We believe that our results from the PDE transform based FPM approach are some of the best ever reported for this classic problem.

2.3.2 1D Euler systems

In this subsection, we carry out numerical experiments by using the proposed PDE transform scheme for the 1D Euler equation of gas dynamics. In one dimension, the Euler equation takes the form [95, 151]

$$U_t + F(U)_x = 0 (2.38)$$

with

$$U = \begin{pmatrix} \rho \\ \rho u \\ E \end{pmatrix}, \quad F(U) = \begin{pmatrix} \rho \\ \rho u \\ E \end{pmatrix} u + \begin{pmatrix} 0 \\ p \\ p u \end{pmatrix}, \quad (2.39)$$

where ρ, u, p and E denote the density, velocity, pressure and total energy per unit mass

$$E = \rho[e + \frac{1}{2}u^2], \qquad (2.40)$$

respectively. Here, e is the specific internal energy. For an ideal gas with the constant specific heat ratio ($\gamma = 1.4$) considered here, one has

$$e = \frac{p}{(\gamma - 1)\rho}.$$
 (2.41)

In the following, we consider two well-known Riemann problems.

2.3.2.1 Example 5 (Sod's and Lax's problems)

Here we apply the PDE transform based FPM on two shock tube problems, i.e., Sod's problem and Lax's problem, which are both standard benchmark tests. In fact, due to their simple profiles, these problems favor low order schemes.

Sod's problem is a special case of shock tube problem with velocities on both sides of the discontinuity being set to zero. It is often used as a test case for validation of numerical shock capturing schemes, because analytical solutions are available. The initial and boundary conditions in the computation domain and boundary for Sod's problem are given by

$$(\rho, u, p)_{t=0} = \begin{cases} (1, & 0, & 1), & -5 \le x < 0, \\ (0.125, & 0, & 0.1), & 0 \le x \le 5; \end{cases}$$
(2.42)



Figure 2.7: Numerical results from the 6th-order PDE transform for Sod's problem (t = 1.5, $\Delta t = 0.02$, 129 grid points). (a) Density; (b) Pressure.

while those for Lax's problem are given by

$$(\rho, u, p)_{t=0} = \begin{cases} (0.445, & 0.698, & 3.528), & -5 \le x < 0, \\ (0.5, & 0, & 0.571), & 0 \le x \le 5. \end{cases}$$
(2.43)

Although there are coupled equations in the system, which make it more complicated than scalar equations, the Sod and Lax problems involve multiple piecewise constant solution without much oscillation. Therefore, these problems favor low-order numerical methods. In our study, we utilize the 6th-order PDE transform method with the FPM to integrate these shock tube equations. Our results of density and pressure for Sod's problem are depicted in Figure 2.7. It is perceived that three characteristics of Sod's problem, including the rarefaction wave, the contact discontinuity and the shock discontinuity are well resolved and captured.

Figures 2.8(a) and (b) illustrate the present numerical results for Lax's problem. Similar



Figure 2.8: Comparison of numerical results from the 6th-order PDE transform and the FPM-RSK for Lax's problem (t = 1.5, $\Delta t = 0.02$, 129 grid points). (a) Density from the PDE transform; (b) Pressure from the PDE transform; (c) Density from the FPM-RSK; (d) Pressure from the FPM-RSK.

to the Sod's case, three characteristics of Lax's problem, including the rarefaction wave, the contact discontinuity and the shock discontinuity are also well captured. It can be seen that the present method gives a good resolution in both cases.

As a comparison, we plot the results obtained by the FPM-RSK approach [151] in Figures 2.8(c) and (d). As discussed earlier, the FPM-RSK scheme is a robust approach for hyperbolic conservation laws. It is seen from Figure 2.8 that the present PDE transform performs at least as good as, if it is not better than, the FPM-RSK approach for shock tube problems.

All of the preceding test examples, except for the high-frequency case in Example 1, favor low order shock capturing schemes. In such a case, although the present method, as well as other high-order shock capturing schemes, works extremely well, it does not have a cutting edge advantage over low order methods. In the next three examples, we consider a class of problems that require high-order shock capturing methods methods for efficient spatial discretizations. Whereas, it will be extremely difficult, if it is not impossible, for low order methods to resolve this class of problems.

2.3.2.2 Example 6 (1D Shock-entropy interaction)

The interaction between a Mach 3 right-moving shock and an entropy wave of small amplitude in a one-dimensional flow, which is a standard test problem [95, 151, 85], is investigated in this example. This problem is important because of its relevance to the interaction of shock and turbulence. We take the computation domain over [0,9] and the initial and boundary



Figure 2.9: The amplitude of entropy waves in the 1D shock-entropy interaction problem for different frequencies resulting from the 12th-order PDE transform.



Figure 2.10: The amplitude of entropy waves in the 1D shock-entropy interaction problem for $\kappa = 32$ resulting from PDE transforms of low and extremely high-order. (a) The 6th-order PDE transform; (b) The 40th-order PDE transform.

conditions in the computation domain and boundary are given by

$$(\rho, u, p)_{t=0} = \begin{cases} (3.85714, & 2.629369, & 10.33333), & 0 \le x < 0.5, \\ (e^{-\epsilon \sin(\kappa x)}, & 0, & 1.0), & 0.5 \le x \le 9. \end{cases}$$
(2.44)

The parameters ϵ and κ are the amplitude and the wave number of the entropy wave before the shock. In this numerical experiment, the small amplitude of the pre-shock entropy is kept the same, i.e. $\epsilon = 0.01$ while the wave number κ is varied. The amplitude of the amplified wave after the shock can be given by linear analysis [123], which is a constant of 0.08690716.

This problem of shock and entropy interaction becomes more and more challenging as the frequency κ increases. The difficulty lies in the fact that it is hard to distinguish the amplified high frequency entropy wave from the spurious oscillations. Low order numerical schemes may dramatically damp the amplitude of the transmitted high frequency wave. Even some high order schemes encounter the same numerical difficulty. A satisfactory numerical scheme should possess the quality of suppressing Gibbs' oscillation while preserving amplitude of the entropy wave as well as capturing the shock [151, 95, 85].

In our numerical test, the shock is set to move from x = 0.5 to x = 8.5. For the convenience of a comparison with previous results, we only display the results at interval [3.0, 9.0]. Furthermore, for the purpose of discharge transient waves due to the non-numerical initial shock profile, we plot the length of the amplified entropy waves in the same manner as that in Ref. [95]. Additionally, we would like to point out two nontrivial details in the illustration. The first one is that the plotted results are obtained by an interpolation of our final numerical results from a coarse grid to a denser grid, which has already been adopted for plotting the high-frequency Sine-Gaussian wavepacket in Example 1. This is

necessary because our computational grid is too coarse to show all the peaks and valleys of our numerical results. The second one is that a post processing filter, which was discussed in Section 2.2.3, is employed to eliminate the oscillations near the shock when we present the final result after the completion of the entire time integration.

First, we test the shock capture for a case with relatively low frequency $\kappa = 18$. We set 513 grid points over the computation domain [0,9] to implement the PDE transform coupled with the Fourier pseudospectral method. It is difficult for a low-resolution method, such as a first order or a second order shock capturing method to preserve the amplitude of high-frequency entropy wave and suppress oscillation [95].

In our numerical test study, we found that the low-order PDE transform does not work well for this problems, although the FPM is employed. Low order PDE transforms either damp the amplitude of the high-frequency entropy wave or cannot suppress Gibbs' oscillations. In contrast, we found that a moderately high order PDE transforms with suitable propagation time perform much better. Figure 2.9(a) shows the amplitude of the shock entropy of $\kappa = 18$ obtained by using the 12th-order PDE transform. It can be seen that the entropy waves almost fully span two strips bounded by two analytical solid lines y = 0.08690716 and y = -0.08690716, which indicates that the amplitude of amplified wave is well preserved. As the amplified entropy wave is monochromic post the shock, it is appropriate to characterize the resolution of the present method by points per wavelength (PPW). A further simple calculation on the amplified entropy wave tells that the resolution is about 5.3 PPW, which is among the best results for this shock entropy problem, to our best knowledge.

Next we increase the frequency to $\kappa = 32$. As there are many more amplified entropy wave post the shock, it is difficult to use 513 grid points to maintain the amplitude of highfrequency wave post shock. Instead, we deploy a mesh of 1025 grid points so as to render a better result. In this case, we still employ a 12th-order PDE transform but with a different propagation time from $\kappa = 18$. One still needs to be careful to design an appropriate PDE transform for this more complicated problem. Figure 2.9(b) shows the amplitude of the shock entropy wave of $\kappa = 32$ by a 12th-order PDE transform. It is perceived that the entropy wave is still able to almost fully span two strips bounded by two solid lines y = 0.08690716and y = -0.08690716. Furthermore, the waves at shock front are free of oscillation.

Finally, we consider a more challenging situation by setting a larger κ . We use 2049 grid points in our spatial discretization of the computation domain [0,9]. Figure 2.9(c) presents the result of the case for $\kappa = 60$. It is clear that the waves post shock are well preserved while the waves at shock front are free of oscillation and well maintained. It also worthwhile to mention that the resolution for this case is about 5.9 PPW, which is still the best record at such a high κ value to our knowledge. Our results indicate that the present PDE transform is able to distinguish the high-frequency entropy waves from spurious oscillation. The above test cases of different frequencies imply that the PDE transform can be a powerful tool for solving hyperbolic conservation law systems involving the interaction of shock and high frequency entropy waves.

As stated earlier, low order shock capturing schemes will encounter difficulties for the above test cases. In fact, not all PDE transforms are suitable for these problems. The inappropriate selections of the PDE transform will either pollute the amplitude of entropy waves or cannot suppress the oscillation. We illustrate this point by using the setting of $\kappa = 32$ and 1025 grid points. Figure 2.10(a) demonstrates the result from a 6th-order PDE transform, which illustrates the effect of a low order PDE transform. Although the waves in the shock front is perfectly kept, the amplitude of the entropy waves post shock is severely damped. We found that second order and fourth order PDE transforms perform even worse



Figure 2.11: Solution to the Shu-Osher problem (t = 0.47, $\Delta t = 0.001$, 129 grid points). (a) Obtained with the 2nd-order PDE transform; (b) Obtained with the 10th-order PDE transform.

for this problem. As another check, we would like to investigate the performance of a very high order PDE transform for this problem. Although a high order PDE transform works well in preserving the high-frequency entropy waves post the shock, it may also pollute the relatively low frequency waves in the shock front. Figure 2.10(b) shows the result from a 40th-order PDE transform. It is clear that the entropy waves in the shock front are polluted by Gibbs' oscillations.

2.3.2.3 Example 7 (Shu-Osher's problem)

We now examine the performance of the PDE transform on the problem of Shu and Osher, which is another typical case to test the capability of a numerical method in predicting shock/entropy interactions. This problem is also initialized by a Mach 3 right-moving shock and an entropy wave, which is in the sine form. Compared with the last problem, Shu and Osher problem involves many different frequencies. We consider the computational domain of [-1, 1] and the initial and boundary conditions in the computation domain and boundary are set as

$$(\rho, u, p)_{t=0} = \begin{cases} (3.85714, & 2.629369, & 10.33333), & -1 \le x < -0.8, \\ (1.0 + \epsilon \sin(\kappa \pi x), & 0, & 1.0), & -0.8 \le x \le 1, \end{cases}$$
(2.45)

where $\epsilon = 0.2$ is the amplitude and $\kappa = 5$ the angular wave number. Although there is no exact solution to this problem, we took the accurate solution as the result given by the highly accurate FPM-RSK method [151], which was calibrated by the 5th order WENO scheme [95] for this problem.

Because of the complicated fluctuation post the shock, it is difficult for low order schemes to capture various frequencies of wave post shock as well as the sharp shock front [95]. High order methods, such as the 5th order WENO scheme [95] and the FPM-RSK method perform extremely well [151].

In the present work, we are interested in the understanding of the performance of the PDE transform of different orders. In fact, through our numerical tests, we found that when one uses the second order PDE transform, one cannot obtain a satisfactory numerical result, no matter what propagation time is chosen. With various choices of the propagation time, the second order PDE transform either damps the amplitude of high frequency waves too much or cannot prevent the solution from blowing up as time evolves. Figure 2.11(a) shows the result of a 2nd-order PDE transform. It is seen that it not only smooths the low frequency waves but also damps the high frequency components.

By contrast, high order PDE transforms work much better. As an illustration, Figure 2.11(b) presents the result from a 10th order PDE transform. Obviously, the 10th-order PDE transform is able to well capture the complicated high-frequency waves post the shock.

Furthermore, the shock front remains sharp in high-order PDE transforms. Although there is some abnormal oscillation at the on-set of low frequency waves, the 10th order PDE transform preserves the majority of the low frequency waves. This difficult case further validates the power of the present PDE transform.

2.3.3 2D Euler systems

In two spatial dimensions, we consider the Euler equation in the conservative form of

$$U_t + F(U)_x + G(U)_y = 0 (2.46)$$

with

$$U = \begin{pmatrix} \rho \\ \rho u \\ \rho v \\ E \end{pmatrix}, \quad F(U) = \begin{pmatrix} \rho \\ \rho u \\ \rho v \\ E \end{pmatrix} u + \begin{pmatrix} 0 \\ p \\ 0 \\ p u \end{pmatrix}, \quad G(U) = \begin{pmatrix} \rho \\ \rho u \\ \rho v \\ E \end{pmatrix} v + \begin{pmatrix} 0 \\ 0 \\ p \\ p v \\ E \end{pmatrix}, \quad (2.47)$$

where (u, v) is the fluid velocity and p is given by

$$p = (\gamma - 1)[E - \frac{1}{2}\rho(u^2 + v^2)].$$
(2.48)

We discretize the conservative quantities $(\rho, \rho u, \rho v, p)$ on the mesh and applied the PDE transform during the time integration.

Like the one dimensional problems, the non-periodic domain in 2D can also be handled by symmetrical extension to the auxiliary domain. Suppose the original domain is discretized by $N_1 \cdot N_2$ grid points indicated by (i, j) with $i = 1, \dots, N_1 + 1$ and $j = 1, \dots, N_2 + 1$. If the 2D domain is non-periodic in only one of the two directions, suppose in x-direction, then the computation domain is doubled with $2N_1 \cdot (N_2 + 1)$ grid points and F(U), G(U) and uare extended by

$$\{F(U)\}_{i,j,k} = \{F(U)\}_{2N_1+2-i,j,k}, \qquad i = N_1 + 2, \cdots, 2N_1, \tag{2.49}$$

$$\{G(U)\}_{i,j,k} = \{G(U)\}_{2N_1+2-i,j,k}, \qquad i = N_1 + 2, \cdots, 2N_1, \qquad (2.50)$$

$$\{U\}_{i,j,k} = \{U\}_{2N_1+2-i,j,k}, \qquad i = N_1 + 2, \cdots, 2N_1.$$
(2.51)

If the 2D domain is non-periodic in both two directions, then the computation domain is doubled with $2N_1 \cdot 2N_2$ grid points and F(U), G(U) and U are extended by

$$\{F(U)\}_{i,j,k} = \begin{cases} \{F(U)\}_{2N_1+2-i,j,k}, & i = N_1+2, \cdots, 2N_1, \\ \{F(U)\}_{i,2N_2+2-j,k}, & j = N_2+2, \cdots, 2N_2, \end{cases}$$

$$\{G(U)\}_{i,j,k} = \begin{cases} \{G(U)\}_{2N_1+2-i,j,k}, & i = N_1+2, \cdots, 2N_1, \\ \{G(U)\}_{i,2N_2+2-j,k}, & j = N_2+2, \cdots, 2N_2, \end{cases}$$

$$\{U\}_{i,j,k} = \begin{cases} \{U\}_{2N_1+2-i,j,k}, & i = N_1+2, \cdots, 2N_1, \\ \{U\}_{i,2N_2+2-j,k}, & j = N_2+2, \cdots, 2N_2. \end{cases}$$

$$(2.52)$$

2.3.3.1 Example 8 (2D Shock-entropy interaction)

Having tested the performance of the PDE transform for 1D shock-entropy interactions, we now consider the case in a 2D setting. The weak entropy wave makes an angle $\theta \in (0, \pi/2)$ against the *x*-axis. If $\theta = 0$, then this 2D problem essentially degenerates into the 1D shock-



Figure 2.12: The amplitude of entropy waves in the 2D shock-entropy interaction problem obtained from PDE transforms of different orders.

entropy problem studied earlier. Since now the entropy waves are oblique to the shock, this 2D problem is more challenging to resolve. Our objective is to further examine the capability of the PDE transform for higher dimensional problems.

Given the right state of the shock as $(\rho_r, u_r, v_r, p_r) = (1, 0, 0, 1)$, a weak entropy is added by changing the density on the right. Here ρ_r is modified by

$$\rho = \rho_r e^{-\epsilon \sin(\kappa z(\theta))/p_r}, \qquad (2.55)$$

where $z(\theta)$ is related to the angle θ by $z(\theta) = x \cos \theta + y \sin \theta$ and ϵ and κ are the amplitude and wave number of the entropy wave, respectively. In this test, we choose parameters $\theta = \pi/6$, $\epsilon = 0.1$ and $\kappa = 15$.

For the computation domain, on the one hand, in order to implement the periodic boundary condition along the y-direction, the computation domain in y is set to be $[0, \frac{2\pi}{\kappa \sin \theta}]$ provided $\theta \neq 0$. On the other hand, the computation domain in x is set as [0,9]. Since the boundary condition in the x-direction is non-periodic, we extend the computation domain in the x-direction symmetrically from [0,9] to [0,18]. We deploy 32 points in $[0, \frac{2\pi}{\kappa \sin \theta}]$ and 1024 points over [0,18], which implies 513 points over [0,9]. In our test, the shock starts at x = 0.5 and moves up to x = 8.5. As we mentioned in the 1D case, a good numerical scheme should be able to preserve the amplitude of the high-frequency entropy waves. It needs to be mentioned that low-order methods do not work well for this problem [95]. Low-order methods would severely damp the amplitude as pointed out in Ref. [95].

For the PDE transform approach, methods of different PDE orders exhibit sharply different behaviors. Figure 2.12 shows the performance of the 6th-order PDE transform by checking the maximum amplitude of the amplified waves along the y-direction for grid points $x \in [7.4, 8.4]$, and furthermore comparing with the amplitude predicted by the linear analysis, i.e., 0.08744786. It is seen that the 6th-order method has an obvious amplitude loss. In fact, to preserve the amplitude of the entropy waves, a high order PDE transform is preferred. We improve the performance by resorting to the 10th-order PDE transform. The result from the 10th-order PDE transform is also illustrated in Figure 2.12. From this result, it is obvious that the amplitude of entropy waves is well maintained in the post-shock region. Although there are small peaks and valleys, such a trivial deficiency appears in other methods as well [95, 151] and is acceptable. This test further validates the capability of the present PDE transform for resolving the shock entropy problem in a higher dimension.

2.3.3.2 Example 9 (2D Shock-vortex interaction)

Finally, we consider the problem of the interaction between a stationary shock and vortex. This problem has attracted much attention from numerous researchers because of its potential applications. This is another problem that poses challenges to low order numerical schemes. High order methods, such as WENO methods [95], spectral methods [151] and CFOR-Hermite scheme [206] work well for this problem. Here we further examine the capability of proposed PDE transforms for shock-vortex interactions.

The set up of the problem is as follows. The original computational domain is set to $[0,1] \times [0,1]$ with a stationary normal shock at x = 0.5 normal to x-axis. A flow with Mach number $M_s = 1.1$ enters at the inlet from the left and the shock is initialized as $(\rho_l, u_l, v_l, p_l) = (1, 1.1\sqrt{\gamma}, 0, 1)$ on the left state. A vortex centered at $(x_c, y_c) = (0.25, 0.5)$ is generated by introducing a perturbation to the original velocity field (u, v), temperature



Figure 2.13: The pressure profile of 2D shock-vortex interaction problem from the 10th-order PDE transform at t = 0.05, 0.2 (20 contours).



Figure 2.14: The pressure profile of 2D shock-vortex interaction problem from the 10th-order PDE transform at t = 0.35, 0.6 (20 contours).

T and entropy S. We denote the perturbation by $(u^\prime,v^\prime,T^\prime,S^\prime)$, which is given as

$$(u',v') = \epsilon \tau e^{\alpha(1-\tau^2)}(\sin \theta, -\cos \theta)$$
(2.56)

$$T' = -\frac{(\gamma - 1)}{4\gamma\alpha} \epsilon^2 e^{2\alpha(1 - \tau^2)}, \qquad (2.57)$$

$$S' = 0,$$
 (2.58)

where, $\tau = \frac{r}{r_c}$, $r = \sqrt{(x - x_c)^2 + (y - y_c)^2}$ and $\theta = \tan^{-1}[(y - y_c)/(x - x_c)]$. By the relation of $T = p/\rho$ and $S = \ln \frac{p}{\rho^{\gamma}}$, the perturbation ρ' and p' to initial ρ and p can be derived from T' and S'. Here ϵ and α are the strength and decay rate of the vortex and r_c is a parameter to regulate the strength of the vortex. In our test, we take $\epsilon = 0.3$, $\alpha = 0.204$ and $r_c = 0.05$.

The computational domain $[0, 1] \times [0, 1]$ is extended to $[0, 2] \times [0, 2]$ and discretized with an even-spacing Cartesian mesh. We use 129 even-spacing grid points in y domain of [0, 1]and 257 grid points in x domain of [0, 1]. The mesh in the x direction is shifted by the Robert transformation [5] to deploy more mesh points towards the stationary shock. The upper and lower boundaries are imposed with the reflective boundary conditions. The time step in our integration is regulated by the CFL condition (CFL=0.5).

This problem prefers moderately high order PDE transforms because of its complicated feature. In fact, we cannot find satisfactory results from low-order PDE transforms yet. As an illustration, Figures 2.13 and 2.14 depicts our results obtained with a 10th-order PDE transform. We plot the pressure profile with 20 contours at t = 0.05, 0.2, 0.35, 0.6.

From Figures 2.13 and 2.14, it is seen that the solution is essentially free of oscillations. It can also be observed that the deformation of the vortex at the shock and the bifurcation after the shock are quite well captured.

2.4 Chapter conclusion remarks

Systems of hyperbolic conservation laws are of fundamental importance in science and engineering. The construction of accurate, efficient and reliable numerical schemes has been an active research topic in applied mathematics over the past half a century. Due to a vast variety of complex problems with extremely diversified physical origins, many hyperbolic conservation law systems remain a challenge to mathematical methods. Typical examples include shock-turbulence interactions which involve a wide range of spatial scales and possible blow ups due to the successive amplification of exponentially small numerical errors during the time integration.

The present work introduces the use of evolution PDEs as a means to efficiently suppress Gibbs' oscillations in the numerical solution of hyperbolic conservation laws. Specifically, during the time integration of a hyperbolic conservation law system, an intermediate numerical solution at a given time step may be used as an initial data for a special evolution PDE. Then the solution of such an evolution PDE is accepted as an updated numerical solution at the given time step. Our approach involves the use of the PDE transform, a technique developed in our recent work [171, 169] for the mode decomposition of signals, image, and data. The PDE transform is based on a family of arbitrarily high order nonlinear PDEs originally introduced by Wei in 1999 [178] and a recursive scheme for reinitializing the input data [170, 169]. Like the wavelet transform, the PDE transform is able to decompose signals, images and data into functional modes, such as edges, trend, texture and feature with controllable frequency ranges and time-frequency localizations, which correspond to appropriate multiresolution analysis in the physical domain. Similarly, the PDE transform also has a prefect reconstruction of original signals, images and data. The PDE transform has found its success in signal processing [171, 169], image analysis [171, 169] and biomolecular surface construction [203].

It may appear computationally inefficient to suppress Gibbs' oscillations at a time step of integrating a hyperbolic conservation law equation by solving another evolution PDE. However, this is not true. Two techniques are proposed to improve the efficiency of the present approach. First, we use an adaptive measure of total variations to automatically determine whether the PDE transform is needed at each time step. Additionally, we utilize a fast PDE transform, which offers the analytical solution of an arbitrarily high order evolution PDE in the Fourier representation. This technique bypasses the stability constraint of solving high order evolution PDEs. Consequently, the present PDE transform algorithm is at least as efficient as our previous windowed Fourier pseudospectral method (FPM) [151] and is slightly more efficient than our earlier conjugate filter oscillation reduction (CFOR) scheme [85, 181, 205, 206].

To be more specific about the efficiency, since the FPM with the fast Fourier transform (FFT) is utilized as the spatial discretization, the complexity of the present PDE transform coupled with the FFT is of $O(N \ln N)$. This feature endows the proposed method with high efficiency, which is desirable for large scale problems in scientific and engineering applications.

A variety of benchmark tests are employed in the present work to validate the proposed approach, ranging from scalar conservation law systems to Euler equations in one and two spatial dimensions. Among these problems, Examples 2-5 typically prefer low-order shock capturing schemes; whereas Examples 1, and 6-9 are well known to require high order numerical methods. For example, low order schemes will severely damp the amplitude of the entropy waves in the shock-entropy interaction described by the Euler equation. The proposed PDE transform based FPM works extremely well for these two types of problems. For instance, it provides some of the best results for solving the Burgers' equation with non-convex flux. Furthermore, only about 5 points per wavelength (PPW) is needed for the present approach to handle the interaction of shock-entropy waves and shock-vortex interactions. To our knowledge, the only other shock-capturing schemes that have demonstrated their ability of operating at 5 PPW are the CFOR scheme [85, 181, 205, 206] and the windowed FPM [151] proposed in our previous work. The performance of the proposed method is compared with those of the CFOR scheme [206] and the windowed FPM [151].

In order to make the present PDE transform based FPM working well for all of the above mentioned problems, we adjust two controlling parameters: the highest order of the PDE transform and the propagation time. In fact, the former is the primary parameter and the latter is less important although indispensable. It is found that the FPM behaves as a low order shock capturing scheme when it is coupled with a relatively low order PDE transform; while it behaves as a high order shock capturing scheme when it is coupled with a moderately high order PDE transform. The preferred orders of the PDE transform for these test examples are in a similar range of orders used in our PDE transform based molecular surface construction [203]. Unlike the signal decomposition, which requires the use of extremely high order PDE transforms [171, 169], the present systems of hyperbolic conservation laws do not need extremely high order PDE transforms. In fact, it is found that the use of extremely high order PDE transforms leads to unphysical oscillations. The selection of PDE transform parameters for all test examples is summarized in the Appendix, where the propagation time is optimized for each given order of the PDE transform.

In the present work, we employ the fast PDE transform essentially as a spectral filter method. However, PDE transform with nonlinear geometric PDEs, such as mean curvature flows, Willmore flows, surface diffusion flows, and potential driven geometric flows [14, 37, 38],

can be similarly used. The advantage of geometry flow equation based nonlinear PDE transform is that it enables the embedding of geometric features. It remains an open question how geometric structures and other mathematical properties, i.e., surface decreasing and volume preserving, will impart the solution of the systems of hyperbolic conservation laws. The investigation of this aspect is beyond the scope of the present work, which serves only as an introduction to the PDE transform approach for systems of hyperbolic conservation laws.

The working principle of the PDE transform is similar to the use of PDE for image analysis, which is an important field. Nonlinear PDEs play a crucial role there. What has been demonstrated in the present work is that when PDEs are used for conservation law problems, appropriate high order PDEs are indispensable. What has not been examined in the present work is the role of nonlinear geometric PDEs for conservation law problems. This aspect is under our consideration. We hope that our work will lead to new exploration in the use of PDEs for systems of hyperbolic conservation laws.

Chapter 3

High order fractional PDE transform for molecular surface construction

3.1 Motivations

Recently, great interests have been witnessed in fractional calculus modeling in many fields of sciences and engineering, from geophysics to biology. Fractional derivatives extend the concept of ordinary derivatives and serves as a good tool for taking into account memory mechanism in the random walk and anomalous diffusion in physical problems [125, 36]. In fact, a fractional derivative occurs as common as an exponent. For example, it is well known that the Kolmogorov scaling exponent that predicts turbulent energy spectrum follows a power law $E(w) \propto w^{-p}$, where w is the wavenumber, p is a real number, and 0 . $Such a power law in the wavenumber corresponds to the fractional derivative of order <math>\alpha$ in the coordinate space, since the inverse Fourier transform of an exponent gives rise to a derivative of the same order. Fractional derivative has found its success in physical and biological modeling [8, 197, 22], financial analysis [74, 136, 142], and image processing [9]. Currently, most attention in the field is paid to the fractional derivatives of order less than 2. high-order fractional derivatives are hardly used, partly due to the limited understanding of their physical meanings.

In our work, we introduce arbitrarily high-order fractional PDEs and the fractional PDE
transform for the analysis of molecular surfaces in molecular biosciences. Since arbitrarily high integer order nonlinear PDEs was originally introduced to account for hyperdiffusion in physical and biological systems [178], it is natural to consider arbitrarily high-order fractional PDEs and the fractional PDE transform, which utilizes arbitrarily high-order fractional derivatives. It is well known that fractional derivatives can be defined in a few different ways. We discuss the finite difference, the Fourier representation and the integral forms of fractional derivatives. A variational derivation of fractional PDEs is presented. To avoid the strict stability constraints of solving high-order fractional PDEs and to achieve the desirable efficiency in the surface generation, we make use of the fast fractional Fourier transform (FFFT) algorithm to realize the fractional PDE transform. The present algorithm is of order $O(N \ln N)$. Extensive numerical test and application validate the proposed fractional PDE transform.

3.2 Theory and algorithm

This section provides theory and algorithm for arbitrarily high-order fractional PDEs and fractional PDE transform. To establish notations, we first briefly discuss a few approaches for fractional derivatives. The fractional PDE transform is constructed via a variational analysis.

3.2.1 Fractional derivatives

There are many different approaches for the definition and understanding of fractional derivatives. Among them, fractional finite difference schemes, fractional Fourier representations and the integral forms of fractional derivatives are the most popular ones.

3.2.2 Fractional finite difference schemes

Finite differences provide a natural representation of fractional derivatives. There are three types of standard finite difference schemes, namely, forward, backward and central finite differences. As a consequence, three fractional finite difference schemes can be defined accordingly. For any integer $\alpha > 0$, the α -th order backward finite difference operator is given by [125]

$$\Delta_{h,b}^{\alpha}u(x) = \sum_{m=0}^{\alpha} (-1)^m \begin{pmatrix} \alpha \\ m \end{pmatrix} u(x-mh), \quad h > 0,$$
(3.1)

where the Binomial coefficients

$$\begin{pmatrix} \alpha \\ m \end{pmatrix} = \frac{\alpha!}{m!(\alpha - m)!}.$$
(3.2)

For example, when $\alpha = 1$ and 2, the first and second order backward finite difference schemes are

$$\frac{\Delta_{h,b}u(x)}{h} = \frac{u(x) - u(x-h)}{h}$$
(3.3)

and

$$\frac{\Delta_{h,b}^2 u(x)}{h^2} = \frac{u(x) - 2u(x-h) + u(x-2h)}{h^2},$$
(3.4)

respectively.

Equation (3.1) can be generalized to the case for any real number $\alpha > 0$, in which the

Binomial coefficients are expressed in terms of Gamma function Γ , i.e.,

$$\begin{pmatrix} \alpha \\ m \end{pmatrix} = \frac{\Gamma(\alpha+1)}{\Gamma(m+1)\Gamma(\alpha-m+1)},$$

and hence

$$\Delta_{h,b}^{\alpha}u(x) = \sum_{m=0}^{\frac{a_2-a_1}{h}} (-1)^m \frac{\Gamma(\alpha+1)}{\Gamma(m+1)\Gamma(\alpha-m+1)} u(x-mh),$$

where a_1 and a_2 are the lower and upper bound of differentiation, respectively. Thus, the factional derivative of order α can be defined as

$$u^{(\alpha)} = \lim_{h \to 0} \frac{\Delta^{\alpha}_{h,b} u}{h^{\alpha}}.$$
(3.5)

One special property of the fractional finite difference operator in Eq. (3.1) is that it utilizes all the node points to the left. Similarly, one can define the fractional derivatives of α -th order by forward and central finite difference operators. Finite difference based fractional derivatives find their applications in anomalous diffusion [126].

3.2.2.1 Fractional Fourier schemes

It is well known that Fourier transform provides a practical approach for computing integer derivatives and solving differential equations. It can be similarly used for fractional derivatives [125]. Consider the Fourier transform

$$\widehat{u}(w) = \int_{-\infty}^{\infty} e^{-iwx} u(x) dx.$$
(3.6)

The Fourier transform of the backward finite difference operator in Eq. (3.1) is given by

$$\widehat{\Delta_{h,b}^{\alpha}u}(w) = \sum_{m=0}^{\infty} (-1)^m \begin{pmatrix} \alpha \\ m \end{pmatrix} e^{-imhw} \widehat{u}(w) = (1 - e^{-ihw})^{\alpha} \widehat{u}(w).$$
(3.7)

where Binomial coefficients vanish when $m > \alpha$. Consequently, the corresponding Fourier transform for (3.5) is

$$\widehat{u^{(\alpha)}}(w) = \lim_{h \to 0} \frac{\widehat{\Delta_{h,b}^{\alpha} u}}{h^{\alpha}} = \lim_{h \to 0} \left(\frac{1 - e^{-ihw}}{h}\right)^{\alpha} \widehat{u}(w) = (iw)^{\alpha} \widehat{u}(w), \tag{3.8}$$

where the last step makes use of the Taylor expansion $e^{-ihw} = 1 - ihw + O(h^2)$ as $h \to 0$.

There are many other ways to derive Eq. (3.8). Consider the central finite difference in the Fourier domain defined as [9]

$$\widehat{D^n u} = (e^{ihw/2} - e^{-ihw/2})\widehat{D^{n-1}u} = \dots = (e^{ihw/2} - e^{-ihw/2})^n\widehat{u},$$
(3.9)

where the *n*th-order finite difference $D^n u$ is defined by

$$D^{n}u(x) = D(D^{n-1}u) = \dots = D^{n-1}(Du) = D^{n-1}\left(u\left(x+\frac{h}{2}\right) - u\left(x-\frac{h}{2}\right)\right).$$
 (3.10)

As an extension of the Fourier transform of the nth-order finite difference, one has

$$\widehat{D^{\alpha}u} = \left(e^{ihw/2} - e^{-ihw/2}\right)^{\alpha}\widehat{u}.$$
(3.11)

Consequently, generalized fractional-order derivative is given by

$$\widehat{u^{(\alpha)}} = \lim_{h \to 0} \frac{\widehat{D^{\alpha}u}}{h} = \lim_{h \to 0} \left(\frac{e^{ihw/2} - e^{-ihw/2}}{h}\right)^{\alpha} \widehat{u} = (iw)^{\alpha} \widehat{u},$$
(3.12)

where the last step uses Taylor expansion $e^{ihw/2} = 1 + ihw/2 + O(h^2)$ and $e^{-ihw/2} = 1 - ihw/2 + O(h^2)$ when $h \to 0$. As a result, Eq. (3.8) is also concluded.

When α is an integer, i.e., $\alpha = n$, Eq. (3.8) becomes

$$\widehat{u^{(n)}} = (iw)^n \widehat{u},\tag{3.13}$$

which is consistent with the classical derivative in the Fourier representation. Moreover, when $\alpha = 2m$ is an even number, we have

$$\widehat{u^{(2m)}} = (-1)^m (w)^{2m} \widehat{u}.$$
(3.14)

Furthermore, using the Euler's formula $i = \exp(i\pi/2)$, Eq. (3.8) can be reformulated as

$$\widehat{u^{(\alpha)}} = e^{i\alpha\pi/2} w^{\alpha} \widehat{u}. \tag{3.15}$$

The expression in Eq. (3.8) can be numerically computed via Eq. (3.15).

3.2.2.2 Integral forms

For any real number $\alpha > 0$, the Caputo fractional derivative of order α is defined as [29]

$$D^{\alpha}u = \frac{1}{\Gamma(n-\alpha)} \int_0^x \frac{u^{(n)}(t)}{(x-t)^{\alpha+1-n}} dt, \quad n-1 < \alpha < n,$$
(3.16)

where it requires the absolute integrability of u up to the *n*-th integer derivatives. Meerschaert has developed a discrete approximation to integral form of fractional derivative in Eq. (3.16) based on the shifted Grünwald approximation [126].

Somewhat less restrictive integral definitions have also been given in the literature by making use of Mittag-Leffler-type functions [121]. For any real number $\beta > 0$, denote by $I^{\beta}f(x)$ the Riemann-Liouville integral

$$I_{t_1,t_2}^{\beta}u(x) = \frac{1}{\Gamma(\beta)} \int_{t_1}^{t_2} u(t)(x-t)^{\beta-1} dt.$$
(3.17)

Then the left and right Riemann-Liouville fractional derivatives of order α for a function u(x) are given by [2]

$$D_l^{\alpha} u = \frac{d^n}{dx^n} I_{a,x}^{n-\alpha} u(x) \tag{3.18}$$

and

$$D_r^{\alpha} u = (-1)^n \frac{d^n}{dx^n} I_{x,b}^{n-\alpha} u(x), \qquad (3.19)$$

respectively. In the integral, a and b are the lower and upper bounds, which are typically taken as $-\infty$ and ∞ , respectively. The right Riemann-Liouville fractional derivative operates on the right (or future) state of the function u(x) and thus is less popular in the literature. However, it is useful in variational formulations.

If α is an integer, these derivatives are defined in the usual sense, namely

$$D_l^{\alpha} u = \frac{d^{\alpha}}{dx^{\alpha}} u(x), \quad \alpha = 1, 2, \cdots,$$
(3.20)

and

$$D_r^{\alpha}u = (-1)^{\alpha} \frac{d^{\alpha}}{dx^{\alpha}} u(x), \quad \alpha = 1, 2, \cdots.$$
(3.21)

The left Riemann-Liouville fractional derivative is one of the most popular definitions. Some interesting properties and history of Riemann-Liouville fractional derivatives have been discussed in Ref [121].

3.2.3 High-order fractional PDEs and fractional PDE transform

3.2.3.1 Variational derivation of high-order fractional PDEs

Motivated by the PDE transform and fractional derivatives, we propose a fractional PDE transform. A key component of the fractional PDE transform is an arbitrarily high-order fractional PDE, which is defined via the fractional variational principle. Many authors have discussed the fractional variational principle [2, 9]. For any $\alpha \in \mathbb{R}$ and $0 < \alpha < \infty$, denote by $\nabla^{\alpha} = \left(\frac{\partial_{l}^{\alpha}}{\partial x^{\alpha}}, \frac{\partial_{l}^{\alpha}}{\partial y^{\alpha}}, \frac{\partial_{l}^{\alpha}}{\partial z^{\alpha}}\right)$ a gradient vector in \mathbb{R}^{3} , where $\frac{\partial_{l}^{\alpha}}{\partial x^{\alpha}}$ is the left Riemann-Liouville fractional derivative of order α in x, according to Eq. (3.18); similar notations are adopted for the fractional derivatives in y and z. The adjoint of ∇^{α} is defined as $\nabla^{\alpha}_{*} = \left(\frac{\partial_{r}^{\alpha}}{\partial x^{\alpha}}, \frac{\partial_{r}^{\alpha}}{\partial y^{\alpha}}, \frac{\partial_{r}^{\alpha}}{\partial z^{\alpha}}\right)$, with the right Riemann-Liouville fractional derivative in (3.19). We now consider the general energy functional

$$E(u, \nabla^{\alpha} u, \nabla^{\alpha}_{*} u) = \int F(u, \nabla^{\alpha} u, \nabla^{\alpha}_{*} u) d\mathbf{r} = \int \left[\Lambda \left(|\nabla^{\alpha} u|^{2}, |\nabla^{\alpha}_{*} u|^{2} \right) + \epsilon (X - u)^{2} \right] d\mathbf{r},$$
(3.22)

where Λ and $\epsilon (X - u)^2$ are similar to the corresponding terms in Eq. (2.7). The Euler-

Lagrange equation of (3.22) is [2]:

$$\frac{\partial F}{\partial u} + \nabla^{\alpha}_{*} \cdot \frac{\partial F}{\partial \nabla^{\alpha} u} + \nabla^{\alpha} \cdot \frac{\partial F}{\partial \nabla^{\alpha}_{*} u} = 0.$$
(3.23)

Applying (3.23) to (3.22), we obtain

$$\frac{1}{2}\nabla^{\alpha}_{*}\cdot\Lambda^{l}_{u\alpha} + \frac{1}{2}\nabla^{\alpha}\cdot\Lambda^{r}_{u\alpha} + \epsilon(X-u) = 0, \qquad (3.24)$$

where

$$\Lambda^{l}_{u\alpha} = -\partial\Lambda/\partial\nabla^{\alpha}u \quad \text{and} \quad \Lambda^{r}_{u\alpha} = -\partial\Lambda/\partial\nabla^{\alpha}_{*}u.$$
(3.25)

Note that Eq. (3.24) is in the similar fashion as Eq. (2.11).

Remarks

1. We can introduce an artificial time t and convert Eq. (3.24) into a time-dependent fractional PDE

$$\frac{\partial u}{\partial t} = \frac{1}{2} \nabla^{\alpha}_* \cdot \Lambda^l_{u\alpha} + \frac{1}{2} \nabla^{\alpha} \cdot \Lambda^r_{u\alpha} + \epsilon (X - u), \qquad (3.26)$$

then the fractional PDE transform is constructed by Eq. (2.14) with the solution operator \mathcal{L} defined via Eq. (3.26).

2. Furthermore, setting $\Lambda = \Lambda(\mu, \nu)$ with $\mu = |\nabla^{\alpha} u|^2, \nu = |\nabla^{\alpha}_* u|^2$, we can apply the chain rule to (3.25), i.e.,

$$\Lambda^{l}_{u\alpha} = -\frac{\partial\Lambda}{\partial\mu}\frac{\partial\mu}{\partial\nabla^{\alpha}u} = -2\frac{\partial\Lambda}{\partial\mu}\nabla^{\alpha}u \doteq -2\Lambda_{\mu}\nabla^{\alpha}u \qquad (3.27)$$

and

$$\Lambda_{u\alpha}^{r} = -\frac{\partial\Lambda}{\partial\nu}\frac{\partial\nu}{\partial\nabla_{*}^{\alpha}u} = -2\frac{\partial\Lambda}{\partial\nu}\nabla_{*}^{\alpha}u \doteq -2\Lambda_{\nu}\nabla_{*}^{\alpha}u.$$
(3.28)

Substituting (3.27)-(3.28) into (3.26), we obtain

$$\frac{\partial u}{\partial t} = -\nabla^{\alpha}_* \cdot \left(\Lambda_{\mu} \nabla^{\alpha} u\right) - \nabla^{\alpha} \cdot \left(\Lambda_{\nu} \nabla^{\alpha}_* u\right) + \epsilon(X - u), \qquad (3.29)$$

where $\Lambda_{\mu}\left(|\nabla^{\alpha}u|^{2}, |\nabla^{\alpha}_{*}u|^{2}\right), \Lambda_{\nu}\left(|\nabla^{\alpha}u|^{2}, |\nabla^{\alpha}_{*}u|^{2}\right)$ can be viewed as anisotropic diffusion coefficients.

3. A special case is that when only $\nabla^{\alpha} u$ (or $\nabla^{\alpha}_{*} u$) appears in (3.22) and Λ takes the simple linear function $\Lambda(\mu) = \mu$, Eq. (3.29) turns into

$$\frac{\partial u}{\partial t} = -\nabla^{\alpha}_* \cdot \nabla^{\alpha} u + \epsilon (X - u)$$

By (3.20) and (3.21), we can recover the simple heat equation $\frac{\partial u}{\partial t} = \nabla^2 u + \epsilon (X - u)$ for $\alpha = 1$.

3.2.3.2 Fractional hyperdiffusions derivation of high-order fractional PDEs

In this section, we derive from Eq. (3.29) an arbitrarily high-order fractional hyperdiffusion equation which has the similar structure of the hyperdiffusion equation (2.3). Actually, letting

$$\Lambda = \Lambda(\mu), \quad \mu = \sum_{q=1}^{m} |\nabla^{\alpha_q} u|^2,$$

where $m \in \mathbb{N}$, $\alpha_q \in \mathbb{R}$, and $0 < \alpha_1 < \alpha_2 < \dots < \alpha_m < \infty$, we have, according to Eq. (3.29),

$$\begin{cases} \frac{\partial u}{\partial t} = -\sum_{q=1}^{m} \nabla_{*}^{\alpha q} \cdot \mathbf{j}^{\alpha q} + e\left(u, \sum_{q=1}^{m} |\nabla^{\alpha q} u|, t\right), \\ \mathbf{j}^{\alpha q} = d_{\alpha q}(u, |\nabla^{\alpha q} u|, t) \nabla^{\alpha q} u, \end{cases}$$
(3.30)

where
$$e\left(u, \sum_{q=1}^{m} |\nabla^{\alpha_{q}} u|, t\right) = \epsilon(X - u)$$
 and $d_{\alpha_{q}}\left(u, \sum_{q=1}^{m} |\nabla^{\alpha_{q}} u|, t\right) = \Lambda_{\mu}\left(\sum_{q=1}^{m} |\nabla^{\alpha_{q}} u|^{2}\right)$.
Setting $m = 1$, $\alpha_{m} = 1$, $e(u(\mathbf{r}, t), |\nabla u(\mathbf{r}, t)|, t) = 0$, and recalling (3.20)-(3.21), one can

reproduce the well-known Perona-Malik equation for anisotropic diffusion [134]:

$$\frac{\partial u}{\partial t} = \nabla \cdot \left[d_{\alpha}(|\nabla u|, t) \nabla u \right].$$

In the current work we study the high-order fractional hyperdiffusion equation with the linear form of Λ , i.e, $\Lambda(\mu) = \mu$, and neglect the term $e(u, |\nabla^{\alpha q} u|, t)$.

3.2.4 Numerical algorithms

In our previous work, high-order nonlinear evolution PDEs have made vital contributions to mode decomposition [171], image analysis [169], and molecular surface generation [204]. However, solving high-order PDE in Eq. (3.26) directly in physical domain can be numerically difficult for some practical applications. A major problem in solving high-order nonlinear evolution PDEs is their stability constraints: in general, in explicit numerical methods, the time increment Δt needs to be proportional to the *n*-th power of the spatial discretization h, i.e., $\Delta t \sim h^n$, for an *n*-th order PDE. Although the constraint has little impact to most image analysis, in which the spacing h is unit, it does lead to some difficulties in other applications. Typically, alternating direction implicit (ADI) methods are implemented to by-pass the stability constraint in solving high-order PDEs [14]. Another approach used in previous PDE transform is the Fourier pseudospectral method via the fast Fourier transform (FFT). These techniques can be analogically applied to the fractional high-order PDE transform. In such an approach, one has to linearize Eq. (3.30) and then solves original nonlinear equation by an iterative procedure as shown in the part of PDE transform.

We consider a linearized fractional PDE of (3.30), i.e. $\Lambda(\mu) = \mu$, $\mu = |\nabla^{\alpha} u|^2$, and m = 1, then

$$\frac{\partial u}{\partial t} = -d_q \nabla^{\alpha}_* \cdot \nabla^{\alpha} u, \quad \alpha \in \mathbb{R}^+,$$
(3.31)

where d_q is a coefficient independent of u. Denote by $\mathcal{F}[u](i\mathbf{w})$ the discrete Fourier transform of $u(\mathbf{r}, t), t \ge 0$.

When Eq. (3.31) is subject to initial value $u(\mathbf{r}, 0) = X^k$ and periodic boundary conditions, it can be easily solved in the Fourier representation. The Fourier transform of Eq. (3.31) is given by

$$\frac{\partial \mathcal{F}[u](\mathbf{w})}{\partial t} = -d_q \mathcal{F}[\nabla^{\alpha}_* \cdot \nabla^{\alpha} u](\mathbf{w}), \qquad (3.32)$$

Because of relations

$$\mathcal{F}[D_l^{\alpha}u] = (i\mathbf{w})^{\alpha} \mathcal{F}[u](\mathbf{w}), \quad \mathcal{F}[D_r^{\alpha}u] = (-i\mathbf{w})^{\alpha} \mathcal{F}[u](\mathbf{w}), \tag{3.33}$$

Eq. (3.32) turns into

$$\frac{\partial \mathcal{F}[u](\mathbf{w})}{\partial t} = (-1)^{\alpha+1} i^{2\alpha} (\mathbf{w})^{2\alpha} d_q \mathcal{F}[u](\mathbf{w}) \quad t \ge 0,$$
(3.34)

where $i^{2\alpha}$ is evaluated as $i^{2\alpha} = e^{i\alpha\pi}$. Therefore, we iteratively solve the linearized high-order fractional PDE until a predesigned accuracy is reached. We can express the solution of the original nonlinear high-order PDE as [169]

$$\widehat{\check{X}}^{k}(\mathbf{w}) = \widehat{\mathcal{L}}\widehat{X}^{k}(\mathbf{w})$$
(3.35)

where \hat{X} and \hat{X}^k are the Fourier transforms of \check{X}^k and X^k , respectively. Here Fourier transform of the evolution operator is $\hat{\mathcal{L}} = \exp\left((-1)^{\alpha+1}i^{2\alpha}(\mathbf{w})^{2\alpha}d_qt\right)$. The solution algorithm developed in the above Fourier domain is called a fast PDE transform.

Given initial value $u(\mathbf{r}, 0) = X^k$, the evolution PDE (3.31) is solved by the fast Fourier transform (FFT) as shown in Eq. (3.35). Specifically, after computing $\hat{u} = \text{FFT}(u)$ by the FFT, we apply the fractional PDE transform in the Fourier space given by Eq. (3.35) so as to obtain $\hat{u} = \hat{\mathcal{L}}\hat{u}$ with corresponding propagation time t. Finally, the inverse FFT (IFFT) is implemented for \hat{u} to produce $\tilde{u} = \text{IFFT}(\hat{u})$. As a result, the new value of u after propagation time t, i.e., $u(\mathbf{r}, t)$, will be given by \tilde{u} . In our experiments, the FFT is implemented by the 'fftw' software package (www.fftw.org).

It is noted that since the fractional PDE transform is implemented in Fourier space, the term $(i\mathbf{w})^{\alpha}$ will involve the complex number when α is not an even integer. Moreover, the complex \hat{u} will result in complex \tilde{u} . However, the information of the biomolecular surface is preferably represented by the real number as the isosurface is from the value of $u(\mathbf{r}, t)$, which

should be real. In the practical implementation, one can either take the real component of Eq. (3.34) (see Ref. [9] for a similar treatment) or the amplitude of the term $(i\mathbf{w})^{\alpha}$. In this work, we explore the performance of both approaches.

3.3 Numerical test and validation

In this section, the proposed fractional PDE transform is tested and validated by molecular surface generation. The initial condition of Eq. (3.31) is set as initial biomolecular surface data and the isosurface obtained from the solution $u(\mathbf{r}, t)$ at time t will be a desired molecular surface after the PDE transform.

3.3.1 Initial data for evolution PDEs

The initial value of Eq. (3.31) is set to be a molecular hypersurface function, which contains atomic coordinates and radius of a molecule. In our computation, three types of initial data are used.

3.3.1.1 Type I: Piecewise-constant initial values

Piecewise-constant initial values are commonly used in our earlier work for molecular surface generation [15, 16, 37]. In this work, we set the piecewise-constant initial value as

$$u(\mathbf{r}, 0) = \begin{cases} 0, & \mathbf{r} \in \bigcup_{i} O(\mathbf{r}_{\mathbf{i}}, r_{i}); \\ 1, & \text{otherwise}, \end{cases}$$
(3.36)

where $\mathbf{r}_{\mathbf{i}}$ and r_i are the atomic coordinate and radius of atom *i*, respectively. The union of all atomic spheres $O(\mathbf{r}_{\mathbf{i}}, r_i)$ is denoted by $\bigcup_i O(\mathbf{r}_{\mathbf{i}}, r_i)$. This type of piecewise-constant initial value is different from the initial value in our geometry flow based solvation model [37], where the two constants 0 and 1 are switched.

3.3.1.2 Type II: Maximum Gaussian initial values

The second type of initial values is defined by the maximum of Gaussian functions [68, 204] as follows

$$u(\mathbf{r},0) = \max_{i} \left(s \, \exp\left(-\frac{\|\mathbf{r} - r_i\|^2 - r_i^2}{r_e^2}\right) \right). \tag{3.37}$$

In this work, we set s = 1 and $r_e = 3$ as recommended in the literature [68].

3.3.1.3 Type III: Summation Gaussian initial values

The third type of initial values is taken from the summation of Gaussian functions [21, 80, 64],

$$u(\mathbf{r}, 0) = \sum_{i} \exp\left(-\kappa(\|\mathbf{r} - r_i\|^2 - r_i^2)\right).$$
(3.38)

In our simulation, we set the decay rate $\kappa = 1$ [198].

The initial molecular surface can be obtained as the isosurface by setting $u(\mathbf{r}, 0) = S$, where S is a pre-designated isovalue of u, for example, $u(\mathbf{r}, 0) = 1$ [198, 204]. Although the two types of Gaussian initial data are able to offer smoother isosurfaces, they may still result in isosurfaces with singularities as demonstrated in the following sections.

3.3.2 Effects of fractional order and propagation time

It is noted from the evolution PDE in Eq. (3.31) that, the performance of the proposed fractional PDE transform depends on the fractional order α , propagation time t, and diffusion coefficient d_q . In the present work, we mainly focus on the role of fractional order and propagation time while set $d_q = 1$.

Figure 3.1 shows the Fourier response of the fractional PDE transform, which is equivalent to the operator $\hat{\mathcal{L}}$ in Eq. (3.35) at different orders. The overall amplitudes of the Fourier responses of fractional PDE transforms with different orders are given in Figure 3.1(a), and 3.1(b)-(c) show the corresponding real and imaginary components, respectively. It can be concluded that the amplitude of Fourier response behaves like classic filters. However, the real component has unfavorable negative values, and the magnitude of the imaginary component is relatively small. These results provide an understanding of the behavior of high-order fractional PDEs.

Figure 3.1(a) also depicts the effects of fractional PDE transform with different orders $(\alpha = 1.5, 5.5, 11.5)$. With a fixed propagation time $t = 10^2$, the fractional PDE transform of order $\alpha = 1.5$ offers a low-pass filter for very low frequency components. Whereas, the fractional PDE transform of order $\alpha = 11.5$ is able to pass a much larger range of frequency components. Based on this feature we choose different fractional orders in mode decompositions and other applications of high-order PDEs.

The effect of propagation time, which is equivalent to the impact of the nonlinear coefficient in the PDE transform, is shown in Figure 3.2, with fixed fractional orders $\alpha \in (11, 12)$ and different propagation time. From Figure 3.2 (a) to Figure 3.2 (c), there display the real components of the Fourier response of the fractional PDE transform with order $\alpha = 11.2$, $\alpha = 11.5$ and $\alpha = 12.0$, respectively. It is concluded that the longer the propagation time is, the faster is the damping of real component. Thus we can conjecture that in order to obtain a smoother molecular surface, a longer propagation time is preferred. We also need to keep in mind that the molecular surface can not be over-smoothed or over-smeared, otherwise it



Figure 3.1: Frequency response of Eq. (3.34) with $t = 10^2$ and different orders. (a) Over all amplitude; (b) Real component; (c) Imaginary component. Red: $\alpha = 1.5$; blue: $\alpha = 5, 5$; and purple: $\alpha = 11.5$.

will become unphysical. It is observed that when the fractional order is closer to an odd number, the real components become more and more oscillatory with all propagation time. Furthermore, Figure 3.3(a) shows the visualization of real component of Fourier response in 2D for $\alpha = 11.5$ and $t = 10^2$; Figure 3.3(b) depicts its contours. Since there are negative oscillations in the Fourier response, there are corresponding oscillations in contours as shown in Figure 3.3(b).

3.3.2.1 Test on a three-atom system

We start the test cases with a simple three-atom system, in which the initial atomic coordinates are given as (0, 0, 1.8), (0, 0, -1.8), (0, 3.12, 0) with a uniform radius of 1.8. Figure 3.4 shows the isosurface of three-atom system from piecewise constant initial value (Figure 3.4 (a)) and after fractional PDE transform by different fractional orders $\alpha = 1.5$ (Figure 3.4 (b)), 5.5 (Figure 3.4(c)) and 11.5 (Figure 3.4(d)); the propagation time is $t = 10^2$ and the isovalue is taken as $u(\mathbf{r}, t) = 1$. We conclude that the piecewise constant initial value does not give an acceptable molecular surface and the low order transform ($\alpha = 1.5$) over-smears the molecular surface. Similar problem of a low order PDE transform at $\alpha = 2$ was also found by Zheng et al [204]. However, both high-orders transforms ($\alpha = 5.5$ and $\alpha = 11.5$) render satisfying molecular surfaces. In the work of integer PDE transform based biomolecular surface generation [204], although $\alpha = 6.0$ works well for small molecular systems, it was found that $\alpha = 6.0$ over-smears large biomolecules such as proteins. In the following test cases, we use the fractional order $\alpha = 11.5$.



Figure 3.2: Real component of frequency response of Eq. (3.34) in 1D, with different values of α and t: (a) $\alpha = 11.2$; (b) $\alpha = 11.5$; (b) $\alpha = 12.0$. Red: $t = 10^6$; blue: $t = 10^4$; and purple: $t = 10^2$.



Figure 3.3: Real component of Fourier response of Eq. (3.34) in 2D for $\alpha = 11.5$ and $t = 10^2$. (a) function value view; (b) contour view.



Figure 3.4: Isosurfaces of a three-atom system after the fractional PDE transform of different fractional orders with the piecewise constant initial value. The isovalue is taken as $u(\mathbf{r}, t) = 1$ and propagation time is $t = 10^2$. (a) Initial value; (b) $\alpha = 1.5$; (c) $\alpha = 5.5$; (d) $\alpha = 11.5$.

3.3.2.2 Test on a four-atom system

We next test the effects of different propagation time and choices of initial data through a four-atom system, in which the initial atomic coordinates are given as (0, 0, 1.8), (0, 0, -1.8),(0, 3.12, 0) and (0, -3.12, 0), with a uniform radius of 1.8. The fractional PDE transforms of different propagation time with three types of initial data discussed in section 3.3.1, are illustrated in Figures 3.5, 3.6 and 3.7, respectively, with the isovalue $u(\mathbf{r}, 0) = 1$ and order $\alpha = 11.5$. For the initial molecular surfaces, the one from Type I is non-smooth (Figure 3.5(a)); isosurface of Type II has singularities (Figure 3.6(a)); and Type III is smooth (Figure 3.7(a)). However, it should be noted that the three types of initial values have different ranges: initial data of Type I is restricted within the range [0, 1], while the values of Types II and III can be greater than one. Although the isosurface of Type III is smooth at $u(\mathbf{r}, 0) = 1$, the surface from other isovalues may not be. For example, the surface obtained by setting $u(\mathbf{r}, 0) = 2$, as showed in Figure 3.7(d), has obvious singularities.

It is noted that Type II initial value depends on the parameter r_e and Type III data relies on the decay rate κ . Figure 3.8 shows the isosurfaces from Type III initial data at two different decay rates, $\kappa = 1$ and $\kappa = 1/9$. It is observed that $\kappa = 1$ gives a much



Figure 3.5: Isosurface of a four-atom system after fractional PDE transform of order $\alpha = 11.5$ and different propagation time, with the piecewise constant initial value. The isovalue is taken as $u(\mathbf{r}, t) = 1$ (a) initial value; (b) t = 1; (c) $t = 10^4$.

better resolution of the molecular surface than $\kappa = 1/9$ does; this fact is consistent with the previous results [198].

The results after fractional PDE transform with order $\alpha = 11.5$ after different propagation time are illustrated in the rest subfigures of Figures 3.5, 3.6 and 3.7. Although the piecewise constant (Type I) initial data is non-smooth, it can offer smooth surfaces by the fractional PDE transform after certain proper propagation time, as noted in Figures 3.6(b) and (c). On the other hand, the singularities resulting from Type II initial data can also be removed at a long propagation time $t = 10^4$ but not after a short time t = 1. Moreover, it is difficult to filter the singularities in the isosurface $u(\mathbf{r}, t) = 2$ with Type III initial value. One may also pay attention to the time cost for generating three types of initial surfaces. Since Types II and III involving searching the maximum or taking the summation, they require more CPU time than Type I does. Indeed, for the four-atom system at h = 1, the computational results show that the CPU cost for surface generation using Type I initial data is about 0.001 seconds, while about 0.2 seconds for using Types II and III initial data.



Figure 3.6: Isosurfaces of a four-atom system after fractional PDE transform of order $\alpha = 11.5$ and different propagation time, with maximum Gaussian initial value. The isovalue is taken as $u(\mathbf{r}, t) = 1$. (a) Initial value; (b) t = 1; (c) $t = 10^4$.



Figure 3.7: Isosurfaces of a four-atom system after fractional PDE transform of oder $\alpha = 11.5$ and different propagation time, with the summation Gaussian initial value. The isovalue is taken as $u(\mathbf{r}, t) = 1$ for (a)-(c) and $u(\mathbf{r}, t) = 2$ for (d)-(f). (a) Initiale value; (b) t = 1; (c) $t = 10^4$; (d) initial value; (e) t = 1; (f) $t = 10^4$.



Figure 3.8: Isosurface of a four-atom system with initial value of Type III (Summation Gaussian initial values) at different κ . The isovalue is taken as $u(\mathbf{r}, 0) = 1$. (a) $\kappa = 1$; (b) $\kappa = 1/9$.

3.3.2.3 Test on two proteins

The fractional PDE transform method is further validated on realistic proteins. In our numerical experiments, the protein data, i.e., atomic coordinates and radii, are obtained from the PDB bank (www.pdb.org) and prepared with the PDB2PQR package [50]. Two proteins, PBD IDs 1R69 and 1FCA, are used in our test. The results are depicted in Figures 3.9 and 3.10, respectively. Initial values of Type I are used for both proteins (Figure 3.9(a) and 3.10(a)). Different orders ($\alpha = 1.5, 11.5$) and the same propagation time ($t = 10^4$) are applied to the protein 1R69, see Figure 3.9(b)-(c), while different propagation time ($t = 1, 10^4$) and the same order ($\alpha = 11.5$) are for the protein 1FCA, see Figure 3.10(b)-(c). It can be concluded that the transform with relatively longer propagation time and higher order produces better molecular surfaces.

Based on the tests on the model three/four-atom systems and the realistic proteins, we summarize that even with the simplest Type I initial surface, satisfactory molecular surfaces can be obtained if the parameters are chosen properly. Specifically, we use order $\alpha = 11.5$, propagation time $t = 10^4$ and isosurface $u(\mathbf{r}, t) = 1$ for later applications unless other values are indicated. The initial values are all of Type one for connivence.



Figure 3.9: Surface of a protein (PDB code: 1R69) after fractional PDE transform of propagation time $t = 10^4$ and different orders. The isovalue is taken as $u(\mathbf{r}, t) = 1$. (a) Initial value (Type I); (b) $\alpha = 1.5$; (c) $\alpha = 11.5$;



Figure 3.10: Surface of a protein (PDB code: 1FCA) after fractional PDE transform of order $\alpha = 11.5$ at different propagation time. The isovalue is taken as $u(\mathbf{r}, t) = 1$. (a) initial value (Type I); (b) $t = 10^{0}$; (c) $t = 10^{4}$;

3.3.3 Computational efficiency

 exit

Computational efficiency is a crucial issue in molecular surface generation. Surface generation time is a bottleneck for many practical applications such as the Poisson-Boltzmann

based molecular dynamics [66] and the solution of coupled nonlinear Poisson-Nernst-Planck equations [202, 201]. Here we examine the computational efficiency of the fractional PDE transform based biomolecular surface generation. Table 3.1 compares the CPU costs (in seconds) for surface generation in Cartesian meshes between the fractional PDE transform (FPDE) with $\alpha = 11.5, t = 10^4$ and the MSMS approach [143] at a typical triangle density 10. In the table, N_a is the total number of atoms in the protein after the PDB2PQR conversion. The total time T_{tot} of the MSMS approach includes the CPU cost from generating surface in the 2D Lagrangian representation T_s and the time cost of converting it to the 3D Eulerian representation T_c , which is required in many applications [204]. Essentially, the CPU time used to create a triangular representation of a protein surface, i.e., T_s , is similar to the total CPU time for the present fractional PDE transform to generate a 3D Eulerian representation of the protein surface. However, the additional CPU used in the Eulerian conversion is quite large, which causes problems in our earlier molecular dynamics simulations [66]. Moreover, the MSMS method encounters problem in generating the triangular surface meshes for three relatively large proteins, 2NCD, 1IWO and 2E2J at the designed density 10. The present fractional PDE transform is very stable and robust for large proteins.

It is interesting to note that the computational cost scales essentially linearly with respected to the number of atoms in proteins for the present fractional PDE transform approach.

3.3.4 Surface areas and surface enclosed volumes

To quantitatively characterize the surface generated by the fractional PDE transform, we examine the surface areas and their enclosed volumes for a number of proteins. These quantities are frequently used in biophysical modeling, such as the solvation free energy estimation.

			h = 1				h = 0.5			
PDB-ID	N_a	T_s	MSMS		FPDE	MS	SMS	FPDE		
		by MSMS	T_c	T_{tot}	T_{tot}	T_c	T_{tot}	T_{tot}		
1R69	596	0.49	2.84	3.33	0.05	2.93	3.42	0.32		
1A2S	667	0.43	3.00	3.43	0.06	3.25	3.68	0.53		
1SH1	702	0.56	3.13	3.69	0.09	3.27	3.83	0.43		
2PDE	729	0.46	2.91	3.37	0.11	3.31	3.77	1.28		
1VII	828	0.54	3.03	3.57	0.06	3.82	4.36	0.60		
1A7M	858	0.64	3.73	4.37	0.05	3.90	4.54	0.57		
1VJW	903	0.65	3.59	4.24	0.08	3.56	4.21	0.67		
1FCA	997	0.62	3.52	4.14	0.08	3.72	4.34	0.55		
1HPT	1272	0.92	5.11	6.03	0.07	5.21	6.13	1.08		
1MBG	1435	0.96	5.15	6.11	0.11	5.34	6.30	1.21		
1A63	2065	1.38	7.92	9.30	0.19	8.09	9.47	1.20		
1SVR	2809	1.58	8.73	10.31	0.19	9.29	10.87	1.82		
2NCD	5665	N/A	N/A	N/A	0.94	N/A	N/A	9.35		
1IWO	30870	N/A	N/A	N/A	3.20	N/A	N/A	23.97		
2E2J	58046	N/A	N/A	N/A	3.48	N/A	N/A	31.36		

Table 3.1: Comparison of CPU costs (in seconds) for surface generation in Cartesian meshes by the fractional PDE transform (FPDE) with $\alpha = 11.5$, $t = 10^4$ and the MSMS approach. N_a : total number of atoms; T_s : CPU time for MSMS to generate surface in 2D Lagrangian representation; T_c : CPU time for converting the Lagrangian representation to 3D Eulerian representation. T_{tot} : Total CPU cost for FPDE and MSMS; h: grid resolution.

The results of fractional PDE transform are in the Eulerian representation, i.e., a 2D surface of a biomolecule embedded in a 3D Cartesian grid. One has to extract the surface area and the enclosed volume by appropriate computational algorithms. A second-order surface integration scheme has been developed in our earlier work [66]

$$\int_{\Gamma} f(x, y, z) dS \approx \sum_{(i, j, k) \in I} \left(f(x_o, y_j, z_k) \frac{\mid n_x \mid}{h} + f(x_i, y_o, z_k) \frac{\mid n_y \mid}{h} + f(x_i, y_j, z_o) \frac{\mid n_z \mid}{h} \right) \mathbb{N}^3.39$$

where h is the grid resolution, (x_o, y_j, z_k) is the intersecting point of the surface Γ and the meshline that passes through the point (x_i, y_j, z_k) , and n_x is the x component of the unit normal vector at (x_o, y_j, z_k) . Similar notations are used for y and z directions. The

	FPDE				MSMS				
PDB-ID	Area	Volume	ΔG_p		Area	Volume	ΔG_p		
1VJW	2847.6	7626.1	-1236.0		2785.8	7693.2	-1237.9		
1FCA	2723.2	6857.1	-1206.0		2546.9	7028.1	-1200.1		
1SH1	2680.7	6418.2	-746.9		2743.8	6400.7	-753.3		
1R69	2978.9	8817.1	-1081.9		3054.5	8777.2	-1089.5		
1MBG	2980.2	7896.8	-1337.9		3070.7	7843.3	-1346.1		
1A2S	4316.1	11629.6	-1902.1		4436.8	11569.7	-1913.5		
1SVR	4582.6	11990.2	-1699.0		4644.0	11961.9	-1711.2		
1VII	2402.0	5091.7	-888.3		2476.2	5050.7	-901.5		
2PDE	2659.2	6080.3	-805.3		2715.9	5994.6	-820.9		
1A7M	7514.9	24125.5	-2129.9		7733.6	24025.1	-2155.5		
1A63	6884.9	18168.8	-2347.0		6973.7	18121.1	-2373.5		
1HPT	3182.9	7706.9	-807.5		3262.9	7660.9	-811.6		

Table 3.2: Comparison of surface areas (unit: $Å^2$), surface enclosed volumes (unit: $Å^3$) and electrostatic free energies of solvation ΔG_p (unit: kcal/mol) with surfaces generated by the fractional PDE transform (FPDE) and the MSMS approach. The grid resolution is 0.5 Å.

summation involves irregular grid points which are the points with at least one neighbor from the other side of the surface Γ in the second-order finite difference discretization. Here I is the set of irregular grid points inside or on the interface [66]. Formula (3.39) is used for surface area calculation by setting f = 1.

The volume integral of a function f is approximated by

$$\int_{\Omega_m} f(x, y, z) d\mathbf{r} \approx \frac{1}{2} \left(\sum_{(i, j, k) \in J_1} f(x_i, y_j, z_k) h^3 + \sum_{(i, j, k) \in J_2} f(x_i, y_j, z_k) h^3 \right)$$
(3.40)

where J_1 is the set of the points inside Ω_m and $J_2 = J_1 \bigcup J_{Irr}$, where J_{Irr} indicates the set of irregular points. The volume is obtained by setting f = 1 in Eq. (3.40).

Table 3.2 lists surface areas and surface enclosed volumes of protein surfaces generated by both the fractional PDE transform and the MSMS approach. In this test, the fractional PDE transform is of order 11.5, propagation time $t = 10^4$, and the grid resolution is 0.5 Å. It can be concluded that the present results are quite consistent with those obtained from the MSMS package, thus the proposed PDE transform is useful in practical applications.

3.4 Applications

Solvent-solute interface plays a critical role in implicit solvent models for applications to electrostatic calculation, solvation analysis and molecular dynamics simulations. It is also important in variational multiscale models for biomolecular systems [180, 184]. In this section, we first apply the fractional PDE transform based biomolecular surfaces to electrostatic calculation of a group of proteins and then analyze the solvation free energies of a set of small compounds, for which have the experimental data are available.

3.4.1 Electrostatic analysis of 15 proteins

3.4.1.1 Electrostatic potential

Once the surface has been generated, the electrostatic potential can be evaluated according to the Poisson equation [194, 67, 33]

$$-\nabla \cdot (\varepsilon \nabla \phi) = \sum_{j} q_j \delta(\mathbf{r} - \mathbf{r}_j), \qquad (3.41)$$

where q_j are the (fractional) charges of atoms at position $\mathbf{r}_j (j = 1, 2, ..., N_a)$. The dielectric function ϵ is defined as a piecewise constant function

$$\varepsilon(\mathbf{r}) = \begin{cases} \varepsilon_m, & \mathbf{r} \in \Omega_m, \\ \varepsilon_s, & \mathbf{r} \in \Omega_s, \end{cases}$$
(3.42)

where $\varepsilon_m = 1$ and $\varepsilon_s = 80$ are the dielectric constants in the molecular and solvent regions, respectively; these two regions are separated by the molecular surface. Equation (3.41) is a typical elliptic interface problem with discontinuous coefficients and singular sources. It is very difficult to construct second-order convergent methods for this equation in the biomolecular context due to the geometric complexity, complex interface, singular charge sources and geometric singularities [194, 67, 33]. In this work, we make use of the secondorder convergent matched interface and boundary (MIB) method [196, 195, 199, 208, 207, 33] to solve Eq. (3.41).

Figure 3.11 displays the electrostatic surface potential of three proteins obtained from solving the Poisson equation (3.41). These potential values are projected on the protein surfaces generated by using the proposed fractional PDE transform. In the figures, red and blue colors represent negative and positive surface electrostatic potentials, respectively. Surface electrostatic potential is highly correlated with ligand binding domains, which are important to drug design.



Figure 3.11: Surface electrostatic potentials of three proteins based on the molecular surface after fractional PDE transform with $\alpha = 11.5$ and $t = 10^4$. (a) PDB code: 1VII; (b) PDB code: 1FCA; (3) PDB code:1R69. Red: negative potential; blue: positive potential.

3.4.1.2 Electrostatic solvation free energy

With the solution of the Poisson equation, one can calculate electrostatic solvation free energies of proteins by

$$\Delta G_p = \frac{1}{2} \sum_j q_j (\phi(\mathbf{r}_j) - \phi_{\text{homo}}(\mathbf{r}_j)), \qquad (3.43)$$

where ϕ and ϕ_{homo} correspond to the electrostatic potentials in the inhomogeneous and homogeneous environments, respectively.

Electrostatic solvation free energies of twelve proteins are listed in Table 3.2. Results are computed by using two types of surface definitions, namely, solvent excluded surface generated by using the MSMS and the fractional PDE transform based surface. A good consistence is obtained between these two methods.

3.4.2 Solvation analysis of 17 small compounds

Total solvation free energies, which include both polar (i.e., electrostatic solvation free energies ΔG_p) and nonpolar solvation free energies G_{np} , are measured in many experiments. The latter component of solvation free energy can be modeled in many ways. One of the most commonly used model can be expressed as [165, 37]

$$G_{\rm np} = \gamma {\rm Area} + p {\rm Vol} + \int_{\Omega_s} \rho_s U^{\rm att} d\mathbf{r},$$
 (3.44)

where γ is the surface tension, p is the hydrodynamic pressure, ρ_s is the solvent bulk density, Ω_s denotes the solvent accessible region, and $U^{\text{att}}(\mathbf{r})$ is the solute-solvent van der Waals interaction potential at point \vec{r} . The first term γ Area is the surface energy, which describes the disruption of intermolecular and/or intramolecular bonds that occurs when the surface of a molecule is created in the solvent. The second term pVol measures the mechanical work of creating the vacuum of a biomolecular size in the solvent. The hydrophobic effect in the first two terms are partially compensated by the third term $\int_{\Omega_s} \rho_s U^{\text{att}} d\mathbf{r}$, which describes the attractive dispersion effects near the solvent-solute interface. The reader is referred to Ref. [37] for detailed description of the van der Waals interaction.

One of the important applications of FPDE transform-based solute-solvent interface is the calculation of total solvation energies. As stated in Section 3.3.4, all the terms in Eq. (3.44) can be calculated from the molecular surfaces generated from FPDE transform of various types of initial data, and according to Section 3.4.1.2, the analysis of electrostatic free energies also requires the definition of solute-solvent interface.

Compound	$G_{\rm np}$	$\Delta G_{\rm p}$	ΔG	Exptl	Error
glycerol triacetate	3.38	-13.54	-10.16	-8.84	-1.32
benzyl bromide	2.00	-5.68	-3.67	-2.38	-1.29
benzyl chloride	1.97	-5.70	-3.73	-1.93	-1.8
m-bis(trifluoromethyl)benzene	4.38	-3.35	1.03	1.07	-0.04
N,N-dimethyl-p-methoxybenzamide	2.85	-10.43	-7.57	-11.01	3.44
N,N-4-trimethylbenzamide	2.71	-8.56	-5.85	-9.76	3.91
bis-2-chloroethyl ether	2.09	-4.57	-2.48	-4.23	1.75
1,1-diacetoxyethane	2.39	-8.77	-6.39	-4.97	-1.42
1,1-diethoxyethane	2.13	-4.52	-2.39	-3.28	0.89
1,4-dioxane	1.38	-6.85	-5.47	-5.05	-0.42
diethyl propanedioate	2.67	-9.04	-6.37	-6.00	-0.37
dimethoxymethane	1.34	-5.23	-3.89	-2.93	-0.96
ethylene glycol diacetate	2.31	-9.88	-7.57	-6.34	-1.23
1,2-diethoxyethane	2.14	-5.30	-3.15	-3.54	0.39
diethyl sulfide	1.74	-2.93	-1.2	-1.43	0.23
phenyl formate	1.98	-8.22	-6.25	-4.08	-2.17
imidazole	1.11	-13.45	-12.34	-9.81	-2.53

Table 3.3: Computation of solvation free energies ΔG (kcal/mol) for the 17 small compounds based on the molecular surface generated by fractional PDE transform with order $\alpha = 11.5$ and propagation time $t = 10^4$. $G_{\rm np}$: nonpolar component; $\Delta G_{\rm p}$: polar component; Exptl: experimental data; Error: $\Delta G_{\rm p}$ - Exptl.

In Table 3.3, there list calculated total solvation free energies of a set of 17 small compounds, compared with corresponding experimental data. The nonpolar free energy G_{np} and electrostatic energy ΔG_p are calculated by Eqs. (3.43) and (3.44), respectively, based on the molecular surface based on the FPDE transform with order $\alpha = 11.5$ and propagation time $t = 10^4$. The reader is referred to Ref. [38] for a detailed description of atomic coordinate and charge parameters. The total solvation free energy $\Delta G = G_{np} + \Delta G_p$. For comparison, the corresponding experimental measurements (Exptl) of these compounds are also listed. We can conclude that the application of FPDE transform-based molecular surface in calculations of free solvation energy is validated, because the agreement between the simulations and experimental data is fairly good. The root mean square error (RMSE) of the computation results is 1.77 kcal/mol and the average error is 1.42 kcal/mol. In comparison, Nicholls et al [129] reported a RMSE of 1.87 kcal/mol for the same set of molecules by the linear Poisson model and further, the RMSE was reduced to 1.71 ± 0.05 kcal/mol [129] by their *explicit* solvent approach, which is much more expensive. Additionally, the RMSE in the current work is only slightly greater than the one (RSME=1.76 kcal/mol) reported in [37], where the biomolecular surface is defined and generated from a nonlinear mean curvature flow equation so extra computational efforts are necessary. Therefore, FPDE transform-based molecular surface provides a relatively good foundation to predict the solvation energies for this set of molecules.

Figure 3.12 depicts the surface morphologies and surface electrostatic potentials of 9 compounds. It is seen that fractional PDE transform offers useful information of molecular morphology, which is crucial to the understanding of molecular physical, chemical and biological properties.

3.5 Chapter conclusion remarks

The emergence of complexity in self-organizing biological systems poses exciting challenges to their quantitative descriptions and predictions. Images, surfaces and visualization of complex biomolecules, such as proteins, DNAs, RNAs, molecular motors and viruses, are crucial to the understanding and conceptualization of biomolecular systems, which in turn can have significant impacts in biomedicine, rational drug design, drug discovery and gene therapy. PDE transform is a new approach for mode decomposition of images, surfaces and data [171, 169]. It makes use of arbitrarily high-order nonlinear PDEs for the control of time-frequency localization and the regulation of spatial resolution. The PDE transform has found its success in the analysis of non-stationary signals and noisy images [171, 169]. Recently, it has also been applied to the molecular generation of biomolecules [204]. However, our previous PDE transform depends on the use of integer order PDEs of arbitrarily highorders. In this work, we extend the PDE transform to fractional PDE transform by using fractional derivatives of arbitrarily high orders.

Fractional derivative or fractional calculus has received much attention in the past decade. Its concept naturally arises in science and engineering, and includes integer derivatives as special cases. However, most work in the field involves only relatively low order fractional derivatives. Fractional derivatives of orders higher than 2 are seldom used. It is not clear that how to use arbitrarily high-order fractional derivatives in theoretical modeling and practical computation.

To demonstrate the utility of fractional derivatives of arbitrarily high-orders, we propose high-order fractional PDEs and the corresponding fractional PDE transform. Using the fractional variational principle, we construct nonlinear fractional PDEs based fractional hyperdiffusion. Introducing an artificial time, the resulting high-order fractional PDEs are converted to time-evolution fractional PDEs. Numerical techniques based on fast fractional Fourier transform (FFFT) is developed to compute the high-order fractional PDEs in three-dimensional setting.

The proposed high-order fractional PDEs are applied to the surface construction of macromolecular surfaces, which are crucial components in the implicit solvent models [67], charge transport models [201] and variational multiscale models [180, 184]. We consider three types of initial values to study the proposed high-order fractional PDEs. Additionally, we examine the effect of the orders of fractional PDEs on the surface morphology. It is found that high-order fractional PDEs are crucial to the quality of molecular surfaces. We also test the impact of the PDE integration time on surface generation. Moreover, we examine the computational efficiency of the present method. Efficiency is one of major motivations for developing new surface generation methods. It is found that the proposed high-order fractional PDEs are of linear scaling with respect to number of atoms in a molecule. We further validate the present method by quantitative analysis of surface areas and surface enclosed volumes of proteins. Finally, the surfaces constructed by the present approach is applied to a couple of biophysical problems, namely, the electrostatic analysis via the Poisson equation and the solvation analysis via a full solvation model. The results from these biophysical problems indicate that the proposed high-order fractional PDEs are a robust and efficient method for macromolecular surface generation.



Figure 3.12: Illustration of surface electrostatic potentials of nine small compounds at their corresponding isosurfaces $u(\mathbf{r}, 10^4) = 0.5$. (a) benzyl bromide; (b) bis-2-chloroethyl ether; (c) 1,1-diacetoxyethane; (d) diethyl propanedioate; (e) diethyl sulfide; (f) dimethoxymethane; (g) m-bis benzene; (h) N,N-4-trimethylbenzamide; (i) phenyl formate.

Chapter 4

Modeling of Impact of geometric, thermal and tunneling effects on nano-transistors

4.1 Introduction

Design, manufacture and operation of electronic devices, such as metal oxide semiconductor field effect transistors (MOSFETs), have been down-scaled to nanometers, due to continuous demand in improving the performance. The ultimate channel length of nano-MOSFETs is expected to be below 10nm [65]. To this end, down-scaling of gate oxide, connecting material, doping size, operating voltages and other physical parameters is required [54, 43, 23]. At such a channel length, characteristics of devices quickly approaches the atomic scale and the associated physical limits. Consequently, quantum mechanical effects, including quantum coherence, correlation and/or entanglement, become significant and will dramatically impact macroscopic quantities of nano-devices, such as current-voltage characteristics and conductance due to channel tunneling and gate leakage. These effects may devastate classical functions of MOSFETs. Recently, many properties of down-scaling associated devices are investigated using quantum mechanical means. Some of these properties include (i) electron
scattering with semiconductor-on-insulator (SOI) interface roughness; (ii) electron scattering under interactions with phonons; (iii) self-heating of devices; (iv) statistical fluctuations due to atomistic dopants; (v) choice of high-k materials for optimal device design and performances. Properties of nano-devices have been extensively studied for MOSFET, FinFET, and various other silicon on insulator (SOI) devices in the literature [3, 84, 104, 189, 192, 193], as well as two dimensional devices based on graphene [161].

Many tools in quantum mechanical theory have been developed in past decades in modeling and simulation of nano-scale devices. First of all, electronic structure in terms of wavefunctions is required in most transport evaluations. However, quantum mechanical first principle description of nano-scale devices is intractable and approximations are indispensable. The coupled system including a Schrödinger equation and a Poisson equation usually serves as one of the lowest levels of approaches [118, 160, 17, 100, 6, 59, 144, 12]. The Schrödinger equation describes a single electron dynamics in a band structure of the solid, whereas the Poisson equation provides the electrical potential of the device. Furthermore, linear combination of bulk band (LCBB) method [97], Hartree-Fock method [149] and the density functional theory (DFT) [91, 107, 133] are theoretical models for many-body electronic interactions at different levels of approximation accuracies and computational costs. The non-equilibrium Green's function (NEGF) method [168, 89, 45, 44] is currently the main workhorse for electron structure and transport modeling of nano-devices. It is a general formalism to utilize the Fermi-Dirac statistics, and to include various interactions of charge carries, such as scattering processes of particles (i.e., electrons and phonons), or correlations due to the surroundings. On the other hand, some classical methods, such as drift-diffusion models, Vlasov-Poisson equation, or Monte Carlo methods, can be modified by "quantum corrections" to study electron transport in the quantum ballistic regime [88, 26, 48, 26, 4, 103]. Additionally, quantum Boltzmann equation, or known as Waldmann-Snider equation [166, 150], can also give derivations of transport equations with quantum corrections. The reader is referred to the literature [40, 60, 124, 84, 96, 35, 42] for many other models and computational methods.

Recently, we have introduced a multiscale variational framework for nano-device modeling [35]. In this framework, the macroscopic description of electrostatic potentials is integrated with the microscopic description of electronic structure. We set up an energy functional for the total energy of the system, which includes the electrostatic energy of the device and the energy of the electron. The latter constitutes kinetic and potential energies. From the variation of the energy functional with respect to electron wavefunction and electrostatic potential, we derive coupled Kohn-Sham equation and Poisson equation for nano electronic devices. When down to nano-scale, the semiconductor-insulator material interface can not be considered to be smooth. We introduced interfaces to model the material separation among different components of device, which has an important impact on the governing equations. For example, in order for the Poisson equation to describe the electrostatic potential involving material interfaces, interface jump conditions are required to ensure the well-posedness of the equation. Additionally, we introduce Dirac delta functions to model random dopings. The resulting problems are elliptic equations with discontinuous coefficients and singular sources. A set of advanced numerical algorithms have been developed to improve computational efficiency and accuracy in nano-device simulations: the matched interface and boundary (MIB) method [207] and Dirichlet-to-Neumann Mapping (DNM) scheme [196] ensure the accuracy of the electric field with abruptly discontinuous dielectric permittivity and individual dopants. We also used a mode-space decomposition method based on the MOSFET geometry to reduce the fully 3D problem into the coupled 2D and 1D ones. A self-consistent iteration method is used to solve the coupled equations.

The objective of the present work is to explore the impact of nano device design parameters on device the performance, including quantum tunneling effects. We show that different configurations of channel geometries have impacts on device performance in terms of currentvoltage curves, or I-V curve, due to the geometry induced changes in electron confinement and electron-interface scattering. Additionally, only electron-potential field scattering is considered in the previous work, while in the formulation of current paper, electron-phonon scattering is accounted as well. Further, temperature dependence and quantum tunneling effects in the channel length are tested for the whole system. In this study, we explore the quantum tunneling effect and macroscopic performances of a four-gate MOSFET model, under different channel geometry, phonon-electron interactions and temperature.

The rest of this paper is organized as follows. In Section 4.2, the theoretical model is briefly reviewed. A total free energy functional is set up and governing equations are derived by the variational principle. Numerical algorithms for each governing equations and the iteration procedure are described in Section 4.3. In Section 4.4, we design a number of interesting channel-crossing section shapes to understand the impact of geometry on a four-gate MOSFET model with silicon/silicon-dioxide (Si/SiO₂) interfaces. Numerical simulations are also carried out to explore quantum tunneling effects and phonon-electron interactions. The paper ends with a conclusion in Section 4.5.

Our model is formulated with a unified free energy functional [35], which consists of the free energy of electrons and electrostatic potential energy of the system. The whole computational domain of the nano-device, denoted by Ω , is partitioned into two subdomains due to the composited semiconductor and insulator materials. The silicon region and the silicon dioxide part are denoted by Ω_{Si} and Ω_{SiO_2} , respectively. The semiconductor-insulator interface separating these two subdomains is Γ_{Si/SiO_2} , i.e., $\Omega = \Omega_{Si} \cup \Omega_{SiO_2}$ and $\Gamma_{Si/SiO_2} = \Omega_{Si} \cap \Omega_{SiO_2}$.

4.2 Theoretical models

Our model is formulated with a unified free energy functional [35], which consists of the free energy of electrons and electrostatic potential energy of the system. The whole computational domain of the nano-device, denoted by Ω , is partitioned into two subdomains due to the composited semiconductor and insulator materials. The silicon region and the silicon dioxide part are denoted by $\Omega_{\rm Si}$ and $\Omega_{\rm SiO_2}$, respectively. The semiconductor-insulator interface separating these two subdomains is $\Gamma_{\rm Si/SiO_2}$, i.e., $\Omega = \Omega_{\rm Si} \cup \Omega_{\rm SiO_2}$ and $\Gamma_{\rm Si/SiO_2} = \Omega_{\rm Si} \cap$ $\Omega_{\rm SiO_2}$.

4.2.1 Free energy of electrons

For simplicity, we consider electrons as the major charge carriers in the device, i.e., density and transport of holes are neglected. Due to the nano-scale of the device, electrons are modeled quantum mechanically. The total Hamiltonian of the electrons includes kinetic energy and potential energy, as described below.

4.2.1.1 Kinetic energy

Let Ψ_j be the Kohn-Sham orbitals of the electrons with energy E_j , then the kinetic energy density of the electrons is

$$\int \sum_{j} \frac{\hbar^2 f(E_j - \mu)}{2m(\mathbf{r})} |\nabla \Psi_j(\mathbf{r})|^2 d\mathbf{r}, \qquad (4.1)$$

where $m(\mathbf{r})$ is the effective mass of electrons, \hbar is the Planck constant, and μ is the Fermi energy related to applied voltages. The general summation \sum_{j} includes the situation when j is continuous, in which we have the identity in \mathbb{R}^s for a function g(j)

$$\sum_{j} g(j) = \frac{2}{(2\pi)^2} \int g(j) (dj)^s.$$
(4.2)

In Eq. (4.1), all energy levels E_j are weighted by the Fermi-Dirac function

$$f(E_j - \mu) = \frac{1}{1 + \exp\left(\frac{E_j - \mu}{k_B T}\right)},\tag{4.3}$$

where k_B is the Boltzmann constant and T is the temperature.

4.2.1.2 Potential energy

The potential energy of electrons is associated with the density of electrons, which can be represented by

$$n(\mathbf{r}) = \sum_{j} |\Psi_j(\mathbf{r})|^2 f(E_j - \mu).$$

$$(4.4)$$

The potential is formulated in terms of the interactions of electrons among themselves and with surroundings. First, electrons interact repulsively among themselves, then the energy is

$$U_{\text{elec/elec}} = \frac{1}{2} \int \frac{q^2 n(\mathbf{r}) n(\mathbf{r'})}{\epsilon |\mathbf{r} - \mathbf{r'}|} d\mathbf{r'}, \qquad (4.5)$$

where ϵ is the dielectric permittivity.

Additionally, electrons interact with nuclei and the energy resulting from this interaction

is described as

$$U_{\text{elec/nuclei}} = -\sum_{i}^{N_a} \frac{q^2 n(\mathbf{r}) Z_i}{\epsilon |\mathbf{r} - \mathbf{r}_i|},\tag{4.6}$$

where $Z_i q$ and \mathbf{r}_i $(i = 1, 2, ..., N_a)$ are the charges and positions of the *i*-th nucleus, respectively.

Furthermore, devices are usually heavily doped, if we consider the specific N-type doping, the interaction of electrons and dopants is

$$U_{\text{elec/dop}} = -\int \frac{q^2 n(\mathbf{r}) n_d(\mathbf{r'})}{\epsilon |\mathbf{r} - \mathbf{r'}|} d\mathbf{r'}, \qquad (4.7)$$

where $n_d(\mathbf{r'})$ is the prescribed doping density. Note that at nano-scale, atomic dopants need to be included. The formulation of interactions between electrons and individual dopants can be accounted by the form of Eq. (4.6).

Since electrons are confined in the channel with the semiconductor-insulator interface Γ_{Si/SiO_2} , we can write the total energy for electrons

$$G_{\Gamma_{\text{Si/SiO}_{2}}}^{\text{electron}}[n] = \int \left\{ \sum_{j} \frac{\hbar^{2} f(E_{j} - \mu)}{2m(\mathbf{r})} |\nabla \Psi_{j}(\mathbf{r})|^{2} + E_{\text{XC}}[n] + E_{\text{phon}}[n] + \frac{1}{2} \int \frac{q^{2} n(\mathbf{r}) n(\mathbf{r}')}{\epsilon(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \sum_{i}^{N_{a}} \frac{q^{2} n(\mathbf{r}) Z_{i}}{\epsilon(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} - \int \frac{q^{2} n(\mathbf{r}) n_{d}(\mathbf{r}')}{\epsilon(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right\} d\mathbf{r}, (4.8)$$

where the exchange correlation $E_{\rm XC}[n]$ and electron-phonon interaction $E_{\rm phon}[n]$ are also included.

4.2.2 Electrostatic free energy of the system

The charge source of the nano-device system includes electrons, nuclei, and dopants, so letting electrostatic potential of the system be $u(\mathbf{r})$, we have the total free energy of electrics as

$$G_{\Gamma_{\text{Si/SiO}_2}}^{\text{elec}}[u] = \int \left\{ \frac{\epsilon(\mathbf{r})}{2} |\nabla u(\mathbf{r})|^2 - u(\mathbf{r}) \left[n(\mathbf{r})(-q) + \sum_i^{N_a} Z_i q \delta(\mathbf{r} - \mathbf{r}'_i) + n_d(\mathbf{r}) q \right] \right\} d\mathbf{r},$$

$$(4.9)$$

where $\epsilon(\mathbf{r})$ is the position-dependent dielectric permittivity since it is different in the semiconductor and the insulator regions. The charge density of nuclei is expressed by $\sum_{i}^{N_a} Z_i q \delta(\mathbf{r} - \mathbf{r'})$. Notice that $u(\mathbf{r})$ can be expressed in a free space as

$$u(\mathbf{r}) = \int \frac{n(\mathbf{r}')(-q)}{\epsilon(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int \frac{n_d(\mathbf{r}')q}{\epsilon(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_i^{N_a} \frac{Z_i q}{\epsilon(\mathbf{r})|\mathbf{r} - \mathbf{r}'_i|},$$
(4.10)

which is the formulation exactly representing the interactions between electrons and nuclei, doping, and themselves in Eq. (4.8).

4.2.3 Total free energy functional

Combining Eqs. (4.8) and (4.9), and with relation (4.10), we obtain the total free energy functional

$$G_{\Gamma_{\rm Si/SiO_2}}[u,n] = \int \left\{ \sum_j \frac{\hbar^2 f(E_j - \mu)}{2m(\mathbf{r})} |\nabla \Psi_j(\mathbf{r})|^2 + U_{\rm elec}[n] + E_{\rm XC}[n] + E_{\rm phon}[n] \right. \\ \left. + u(\mathbf{r})n_d(\mathbf{r})q + u(\mathbf{r})q \sum_i^{N_a} Z_i \delta(\mathbf{r} - \mathbf{r}_i) - \frac{\epsilon(\mathbf{r})}{2} |\nabla u|^2 \right. \\ \left. + \lambda \left[n_0 - \sum_j f(E_j - \mu) |\Psi_j(\mathbf{r})|^2 \right] \right\} d\mathbf{r}.$$

$$(4.11)$$

The last line is the constraint for wavefunction $\Psi_j(\mathbf{r})$, where λ is the Lagrange multiplier and

$$n_0 = \frac{1}{\sqrt{2}} \left(\frac{mk_B T}{\pi\hbar^2}\right)^{3/2}$$

is the intrinsic density-of-state of an electron system.

4.2.4 The Poisson equation

Taking variation of Eq. (4.11) with respect to function $u(\mathbf{r})$, we have the Poisson equation

$$\frac{\delta G_{\Gamma_{\text{Si/SiO}_2}}[u,n]}{\delta u} = 0 \Rightarrow -\nabla \cdot (\epsilon(\mathbf{r})\nabla u(\mathbf{r})) = qn_{\text{total}}, \tag{4.12}$$

where

$$n_{\text{total}} = -n(\mathbf{r}) + n_d(\mathbf{r}) + \sum_i^{N_a} Z_i \delta(\mathbf{r} - \mathbf{r}'_i).$$
(4.13)

Since the permittivity $\epsilon(\mathbf{r})$ takes different values in Si and SiO₂ regions, it is discontinuous across the semiconductor-insulator interface Γ_{Si/SiO_2} . We consider the following jump

conditions along $\Gamma_{\rm Si/SiO_2}$ as

$$[u] = u^{+}(\mathbf{r}) - u^{-}(\mathbf{r}) = 0, \quad \text{at} \quad \Gamma_{\text{Si/SiO}_{2}}$$
(4.14)

$$[\epsilon \nabla u \cdot \vec{n}] = \epsilon^+ \nabla u^+(\mathbf{r}) \cdot \vec{n} - \epsilon^- \nabla u^-(\mathbf{r}) \cdot \vec{n} = 0, \quad \text{at} \quad \Gamma_{\text{Si/SiO}_2}, \quad (4.15)$$

where \vec{n} is the unit outer normal direction of the interface $\Gamma_{\rm Si/SiO_2}$, and the superscripts "+" and "-" represent limiting values of the corresponding functions on $\Omega_{\rm Si}$ and $\Omega_{\rm SiO_2}$, respectively. These conditions make the Poisson equation well-posed [196].

4.2.5 Generalized Kohn-Sham equation

Taking variation of Eq. (4.11) with respect to $\Psi^{\dagger}(\mathbf{r})$, the complex conjugate of $\Psi(\mathbf{r})$, we have the generalized Kohn-Sham equation:

$$\frac{\delta G_{\Gamma}[u,n]}{\delta \Psi^{\dagger}} = 0 \Rightarrow \left(-\nabla \cdot \frac{\hbar^2}{2m} \nabla + u(\mathbf{r})(-q) + U_{\rm XC}[n(\mathbf{r})] + U_{\rm phon}[n(\mathbf{r})] \right) \Psi_j(\mathbf{r}) = E_j \Psi_j(\mathbf{r}),$$
(4.16)

where $U_{\text{XC}}[n(\mathbf{r})] = \frac{\delta E_{\text{XC}}[n(\mathbf{r})]}{\delta n}$ and $U_{\text{phon}} = \frac{\delta E_{\text{phon}}[n(\mathbf{r})]}{\delta n}$ are the exchange-correlation potential and electron-phonon potential, respectively.

The Poisson equation (4.12) and the Kohn-Sham equation (4.16) are to be solved iteratively to obtain the electrostatic potential and the wavefunction. This aspect is described in the next section.

4.3 Computational algorithms

In the present paper, we neglect $U_{\rm XC}[n(\mathbf{r})]$ for simplicity and leave it for future studies. In the following discussion of numerical methods, we first consider the model without phonon effect $U_{\rm phon}$ as in [35] and incorporate the phonon-electron interactions later on. As a result, the equation (4.16) turns into the typical Schrödinger equation.

$$\left(-\nabla \cdot \frac{\hbar^2}{2m} \nabla + u(\mathbf{r})(-q)\right) \Psi_j(\mathbf{r}) = E_j \Psi_j(\mathbf{r}).$$
(4.17)

Note that Eq. (4.17) is coupled back to the Poisson equation (4.12), so it is nonlinear.

4.3.1 The Poisson equation

Individual dopants and their induced fluctuations in device performance have been studied elsewhere [35]. In the present work, we focus on the geometry effects, tunneling behavior and phonon-electron interactions, so only the continuous doping is considered and the Poisson equation is taken as

$$-\nabla \cdot (\epsilon \nabla u) = -q(n + N_{\rm D} - N_{\rm A}), \qquad (4.18)$$

where $N_{\rm D}$ and $N_{\rm A}$ are given continuous doping density functions; the letter D and A denotes donor and acceptor, respectively. For the boundary condition of Eq. (4.18), it takes the Dirichlet boundary condition where external voltages are applied, denoted by $\Gamma_{\rm vol}$, and the Neumann boundary condition for the rest of the device.

Since $N_{\rm D}$ and $N_{\rm A}$ are given fixed functions, it is convenient to decompose the potential

u as $u = u^{\text{fix}} + u^{\text{loop}}$. The potential component u^{fix} solves the equation

$$-\nabla \cdot (\epsilon \nabla u^{\text{fix}}) = -q \left(N_{\text{D}} - N_{\text{A}} \right)$$
(4.19)

$$[u^{\text{fix}}] = 0 \quad \text{at} \quad \Gamma_{\text{Si/SiO}_2} \tag{4.20}$$

$$[\epsilon \nabla u^{\text{fix}} \cdot \vec{n}] = 0 \quad \text{at} \quad \Gamma_{\text{Si/SiO}_2}, \tag{4.21}$$

where the bracket $[\cdot]$ indicates the jump as defined in Eqs. (4.14) and (4.15). We set the boundary conditions

$$u^{\text{fix}} = 0$$
 at Γ_{vol} (4.22)

 $\epsilon \nabla u^{\text{fix}} \cdot \vec{n} = 0$ at other boundaries. (4.23)

And the function u^{loop} solves

$$-\nabla \cdot (\epsilon \nabla u^{\text{loop}}) = -qn(\mathbf{r}) \tag{4.24}$$

$$[u^{\text{loop}}] = 0 \quad \text{in} \quad \Gamma_{\text{Si/SiO}_2} \tag{4.25}$$

$$[\epsilon \nabla u^{\text{loop}} \cdot \vec{n}] = 0 \quad \text{in} \quad \Gamma_{\text{Si/SiO}_2}, \tag{4.26}$$

with boundary conditions

$$u^{\text{loop}} = u^{\text{voltage}}$$
 at Γ_{vol} (4.27)

$$\epsilon \nabla u^{\text{loop}} \cdot \vec{n} = 0$$
 at other boundaries. (4.28)

The elliptic interface problems (4.19)-(4.23) and (4.24)-(4.28) are solved by the matched

interface and boundary (MIB) method [33, 207, 194, 196], which is a high-order numerical scheme that can handle various challenges from material interface and have been successfully applied to many other areas. For more details about the formulation of high-order MIB methods and their applications, the reader is referred to Refs. [33, 207, 194, 196].

4.3.2 Scattering problem

Fully solving Eq.(4.16) in 3D is always a challenge in MOSFET simulations because of the heavy computational cost. However, the computational complexity can be reduced by taking advantage of the geometry and working principles of the devices. Particularly, if we consider the direction connecting source and drain ends of the devices as the transport direction (denoted by x-direction), then electrons are confined within y-z direction due to the insulator. Therefore, the y-z directions are regarded as the confined directions. Based on this consideration, the whole wave function can be written as $\Psi_j(\mathbf{r}) = \Psi_{j,k_x}(\mathbf{r}) = \varphi_j(y,z;x)\varphi_{k_x}^j(x)$, and Eq. (4.16) is thus decomposed as, in the confined y-z directions at each position x_0 :

$$\left[-\frac{\hbar^2}{2m_{y,z}}\left(\frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) - qu(y,z;x_0)\right]\varphi_j(y,z;x_0) = E_{\text{scat}}^j(x_0)\varphi_j(y,z;x_0)$$
(4.29)

and along the *transport* x-direction,

$$\left(-\frac{\hbar^2}{2m_x}\frac{d^2}{dx^2} + E^j_{\text{scat}}(x)\right)\varphi^j_{k_x}(x) = E^j_{k_x}\varphi^j_{k_x}(x),\tag{4.30}$$

where m_x and $m_{y,z}$ are effective electrons mass in the x and y-z directions, respectively.

When the electric filed $u(\mathbf{r})$ is available, we first need to solve eigenvalue problems as Eq. (4.29) at each position x_0 , since the electrons are assumed not to penetrate the Si/SiO₂ interface. The resulting eigenvalues (or confined energies) $E_{\text{scat}}^{j}(x_{0}), j = 1, 2, 3, ...$ are discrete and only the lowest several of them make significant contributions due to the Fermi-Dirac statistics, thus only the first M functions $E_{\text{scat}}^{j}(x), j = 1, 2, ..., M$ and corresponding eigenfunctions $\varphi_{k_{x}}^{j}(x)$ are typically utilized. Here M is usually less than 5 due to the fast increase in energy $E_{\text{scat}}^{j}(x)$ as j increases.

Equation (4.30) is a scattering problem so that the eigenvalue E_{kx}^{j} is continuous; the function $E_{\text{scat}}^{j}(x)$ obtained from Eq. (4.29) is sometimes called subband energy and considered as transport potential energy. The wavefunction $\varphi_{kx}^{j}(x)$ is not directly solved, in stead, the Hamiltonian of electrons in *scattering* direction, \mathbf{H}^{scat} , is given as

$$\mathbf{H}^{\text{scat}} = -\frac{\hbar^2}{2m_x} \frac{d^2}{dx^2} + E^j_{\text{scat}}(x), \qquad (4.31)$$

and the *j*-th scattering electron density in Eq. (4.33) is calculated as [44, 35]:

$$n_{\text{scat}}^{j}(x) = \frac{1}{2\pi} \int_{R} \left(f(\mathbf{H}^{\text{scat}} - \mu_{\text{S}}\mathbf{I}) \mathbf{A}^{\text{S}}(E_{k_{x}}^{j}) + f(\mathbf{H}^{\text{scat}} - \mu_{\text{D}}\mathbf{I}) \mathbf{A}^{\text{D}}(E_{k_{x}}^{j}) \right) dE_{k_{x}}^{j}, \quad (4.32)$$

where **I** is the identity operator, $\mathbf{A}^{\mathrm{S}}(E_{kx}^{j})$ and μ_{S} are the spectral operator and Fermi-level at the source end, respectively. Similar notations, $\mathbf{A}^{\mathrm{D}}(E_{kx}^{j})$ and μ_{D} are used for the drain end.

By this means, the total electron density is given by

$$n(\mathbf{r}) = \sum_{j}^{M} |\psi_{j}(y, z; x)|^{2} |\psi_{kx}^{j}(x)|^{2} f(E_{kx}^{j} - \mu)$$

$$= \sum_{j}^{M} |\psi_{j}(y, z; x)|^{2} n_{\text{scat}}^{j}(x), \qquad (4.33)$$

and total electron current is computed in the formula of

$$I_{\text{tot}} = -\int_{-\infty}^{\infty} \frac{q}{\hbar} \text{Tr} \mathbf{T}_{\text{DS}}(E_{k_x}^j) [f(\mathbf{H}^{\text{tot}} - \mu_{\text{S}}\mathbf{I}) + f(\mathbf{H}^{\text{tot}} - \mu_{\text{D}}\mathbf{I})] dE_{k_x}^j, \qquad (4.34)$$

where $\mathbf{H}^{\text{tot}} = \mathbf{H}^{\text{scat}} + E_{kx}^{j}$ is the total Hamiltonian, $\text{Tr}(\cdot)$ is the trace operator, and \mathbf{T}_{DS} is the transmission operator [44, 35].

4.3.3 Modeling the phonon-electron interaction

Acoustic and optical phonon scattering is an important supplementary component of the interactions of electron with the whole environment. In the Boltzmann transport equation-based classical models [41], the phonon-electron interaction appears in the collision operators of the Boltzmann equation, while in the non-equilibrium Green's function (NEGF) model for nano-devices [44], this interaction is considered as a self-energy function. Equation (4.11) has taken into account the phonon-electron interaction in the total energy framework and our goal here is to develop a direct formulation.

First we assume that, as in [41], all the phonons have a single frequency ω_p and the number density of phonons is homogeneous in the device. Thus we can consider the phononelectron interaction mainly in the transport direction, then the Eq. (4.30) is modified by incorporating U_{phon} :

$$\left(-\frac{\hbar^2}{2m_x}\frac{d^2}{dx^2} + E^j_{\text{scat}}(x) + U_{\text{phon}}\right)\varphi^j_{kx}(x) = E^j_x\varphi^j_{kx}(x).$$
(4.35)

Further, it is assumed that the phonon density depends on its energy $E_p = \hbar \omega_p$ and

follows the Bose-Einstein statistics,

$$N_p = \left[\exp\left(\frac{E_p}{K_B T}\right) - 1 \right]^{-1}.$$
(4.36)

Therefore, we have $U_{\rm phon}$

$$U_{\rm phon} = N_p E_p. \tag{4.37}$$

In the present model, two statistics, the Bose-Einstein statistics for phonons and the Fermi-Dirac statistics for electrons, are involved. Since both statistics depend on temperature, Twill play an important role in the model performance.

4.3.4 Self-consistent iteration

The self-consistence of Eqs. (4.12) and (4.16) are numerically achieved by the Gummel-like iteration [47, 35] and the procedure is outlined as following:

- Step 0 (Solution of u^{fix}) Solving Eq. (4.19-4.23) is out of the whole iteration loop and once u^{fix} is obtained, it remains fixed in every step in the proceeding iterations;
- Step 1 (Solution of u^{loop} by inner iteration): We assume that n_k and u_k^{loop} , k = 0, 1, 2, ... are available from the previous steps, then solve the following non-linear Poisson equation for u_{k+1}^{loop} :

$$-\nabla \cdot (\epsilon \nabla u_{k+1}^{\text{loop}}) = -qn_0 \mathcal{F}_{1/2} \left(\frac{(u^{\text{fix}} + u_{k+1}^{\text{loop}} - \zeta_k)q}{k_B T} \right), \qquad (4.38)$$

where ζ_k is the quasi-Fermi potential in the k-th step calculated through

$$\zeta_k(\mathbf{r}) = u^{\text{fix}} + u_k^{\text{loop}} + \mathcal{F}_{1/2}^{-1}(n_k/n_0), \qquad (4.39)$$

and $\mathcal{F}_{1/2}$ is the Fermi-Dirac integral of order 1/2 defined as

$$\mathcal{F}_{1/2}(x) = \int_0^\infty \frac{y^{1/2} dy}{1 + e^{y - x}}.$$
(4.40)

The non-linear Poisson equation (4.38) is iteratively solved with the corresponding interface and boundary conditions in Eqs. (4.25)-(4.28).

- Step 2 (Eigenvalue problem): We solve Eq. (4.29) in the y-z directions for $\psi_j(y, z; x_i)$ and $E_{\text{scat}}^j(x_i)$ along the x-direction at each grid point x_i .
- Step 3 (Scattering problem and electron density): We solve the scattering problem (4.30)-(4.32); using (4.33), we obtain the electron density $n_{k+1}(\mathbf{r})$ in the k+1-th step.
- Step 4 (Convergence check): The convergence is checked by ||n_{k+1} − n_k|| < δ, where δ is a given criteria. If convergence is achieved, then go to Step 5, otherwise go back to Step 1.
- Step 5 (Electronic current): After we obtained the convergent potential and electron density, we can obtain the electronic current by Eq. (4.34).

Figure 4.1 gives an illustration of the workflow for the current self-consistent iteration scheme.



Figure 4.1: The flowchart of Gummel-like self-consistent iteration.

4.4 Numerical experiments and discussions

4.4.1 A four-gate MOSFET model

To study the channel geometric effects, electron tunneling and electron-phonon interactions by the proposed model, we consider a simple four-gate MOSFET device, i.e., silicon nanowire transistor and present our numerical results for the proposed models. Figure. 4.2(a) illustrates the overall configuration of this type of MOSFET: the semiconductor channel (silicon) in cylinder shape is bounded by the insulator material (silicon dioxide). Functions of the nano-devices are manipulated by two types of voltages: the source-drain denoted by V_{DS} and the voltage applied on the all-around gate denoted by V_{Gate} . Without loss of generality, we set x-direction as the electron transport direction and y-z directions as the confined di-



Figure 4.2: Illustration of a four-gate MOSFET with a cylinder channel: (a) Overall 3D configuration; (b) View of the x-z cross section.

rections. Figure 4.2(b) gives a detailed demonstration of the device in the x-z cross-section, from which it can be seen that N-type doping (denoted by N) is applied to the two ends of the channel. In the current work, we also apply the present model to channels with different shapes of y-z cross-sections other than the disk. As shown in Figure 4.3(a) and (b), the channels with y-z cross-sections of a circle and a flower-like geometry, are also considered. In the sequel, the three types of channels with different cross-sections in y-z directions are called the cube, cylinder and flower-like channels as explained in Figure 4.2. The total length of the device along x-direction is 30nm with 10nm for each doping area and channel.

For computational convenience, the x-z cross-section of the MOSFET shown in Figure 4.2 (b) is simplified as the one in Figure 4.4. The channel (LGHK) is sandwiched by the



Figure 4.3: (a) y-z cross-section of a channel: circle; (b) y-z cross-section of channel: flower-like shape.

insulator layers ABGL and KHCD, and LG and KH are the two Si/SiO₂ interfaces. The boundary segments EF and JI are considered where the gate voltages are applied while LK and GH are regarded as source and drain ends, respectively. Hence, Figure 4.4 also indicates the boundary conditions of the Poisson equation: Dirichlet boundary conditions V_{Gate} are applied on EF and JI. Similarly, Dirichlet boundary conditions V_{DS} are applied on LK and GH. Homogeneous Neumann boundary conditions are imposed on the rest of the boundary.

In solving the Schrödinger equation, electrons are assumed to be confined by LG and KH, along with the boundaries of different shapes in the *y*-*z* cross-section ($n(\mathbf{r}) = 0$ at these boundaries), while scattering boundary conditions are used at LK and GH.



Figure 4.4: Demonstration of the simplified computational domain for the MOSFET. Dark: insulator layer; grey: doped channel region; and white: un-doped channel region. Gate voltages are applied at boundary segments EF and IJ, and source-drain voltages are applied on the boundary segments GH and LK.

In the present model, the parameters for the equations are set as follows. For the Poisson equation, the dielectric constants for silicon layer and silicon dioxide layer are $\epsilon_{\rm Si} = 11.7\epsilon_0$ and $\epsilon_{\rm SiO_2} = 3.9\epsilon_0$, respectively, where ϵ_0 is the dielectric constant for the vacuum. The reference continuous N-doping is taken as $N_{\rm D}(\mathbf{r}) = 2 \times 10^{20}/\text{cm}^3$, $N_{\rm A}(\mathbf{r}) = -1 \times 10^{20}/\text{cm}^3$. For the eigenvalue problem and scattering problem, the first three subbands are adopted since they dominantly contribute to electron density and current over higher ones. The electron effective mass is taken as $m_x = 0.50m_0$ in the transport direction and $m_{yz} = 0.318m_0$ in the confined directions. Room temperature of T = 300K is assumed except when specified.





Figure 4.5: Electrostatic and electron density profiles from the x-z cross-section view at y = 2.5nm in the silicon area of the MOSFET with the cylinder channel (Source-drain voltage $V_{\text{DS}} = 0.4$ V and gate voltage $V_{\text{Gate}} = 0.4$ V). (a) Electrostatic potential energy (eV); (b) Electron density (1e26/m³).

We first present some fundamental profiles of electric field and electron density for the MOSFET with a cylinder channel. In order to give a clear description, 2D data in the x-z cross-section (at y = 2.5nm) of the silicon area of the MOSFET are shown in Figs. 4.5(a) and (b), for electric field and electron density, respectively. In Figure 4.5(a), the electrostatic potential energy of electrons is relatively lower in the source and drain regions due to the dopants while remains as an energy barrier in the middle. Electrons are injected from the source and collected at the drain; they have to overcome the potential barrier in the middle in order to transport along the devices. Correspondingly, as shown by Figure 4.5(b), the resulting electron density is lower in the middle and higher in the source and drain regions. Since we assume that electrons cannot penetrate the semi-conductor-insulator interface, the electron density is zero in the silicon dioxide region, which is not displayed in the figures. In there figures, the source-drain voltage difference is taken as $V_{DS} = 0.4V$ and the gate voltage is taken as $V_{Gate} = 0.4V$. Later on we will see the performance of the device can be controlled by adjusting V_{DS} and V_{Gate} .

The potential barrier in the channel can also be illustrated by the subband energy profiles. Due to the nano scale of the devices, there are strong confinement effects in the *y*-*z* crosssection, thus the total transporting energy can be approximated as discrete subband energies. Because of the Femi-Dirac distribution, only the first or lowest several of them have significant contributions to the total electron current. Figure 4.6 illustrates the first subband energy profiles of the MOSFET at two different gate voltages, with the source-drain voltages fixed at $V_{DS} = 0.4V$. It can be concluded from the figure that increasing the gate voltage will lower down the potential barrier in the device channel and thus lead to a larger electron current, which can be further seen in the I-V_{Gate} curve in Figure 4.7 (b).

Figure 4.7 illustrates the impacts of gate voltage and source-drain voltage differences on



Figure 4.6: Subband energy profile along the transport direction under gate voltages $V_{Gate} = 0.1V$ (Dashed line) and $V_{Gate} = 0.4V$ (Solid line) for the MOSFET with the cylinder channel (source-drain voltages is fixed at $V_{DS} = 0.4V$).



Figure 4.7: Current-voltage (I - V) curves of the MOSFET with the cylinder channel. (a) I-V_{DS} curve (gate voltage fixed at $V_{Gate}=0.4V$); (b) I-V_{Gate} curve (source-drain voltage fixed at $V_{DS}=0.4V$).

the electron current, respectively. It is observed from Figure 4.7(a) that, when the gate voltage is fixed at $V_{Gate}=0.4V$, the electron current increases with the source-drain voltage



Figure 4.8: I-V_{Gate} curves of MOSFETs with different geometries of channel ($V_{DS}=0.4V$). (a) Four types of cross-sections channels; (b) Corresponding I-V_{Gate} curves.

difference and achieves a saturation later on. In contrast, when the source-drain voltage is fixed at $V_{DS}=0.4V$, the electron current grows dramatically when the gate voltage V_{Gate} passes a certain threshold, as shown in Figure 4.7 (b).

4.4.3 Performances of nano-MOSFETs with different channel geometries

Performances of nano-MOSFEs with different channels (cube, cylinder, and flower-like channels) are examined in terms of I-V curves.

In Figure 4.8 we compare the I-V curves of the channels that have different areas of the cross-sections. Four types of channel cross sections, including a small circle, a large circle, a square, and a flower-like shape, are tested in our experiments. These silicon channels are embedded in the insulator materials (SiO₂) of the same dimension (5nm by 5nm). The interfaces enclose different silicon areas and their relations are shown in Figure 4.8(a). In



Figure 4.9: The I-V_{Gate} curves of MOSFETs with different channel cross-sections but with the same cross-section area (source-drain voltage fixed at $V_{DS}=0.4V$).

Figure 4.8(b), the I-V curves of the nano-MOSFETs with the corresponding y-z cross-sections are displayed. It can be easily concluded that given the same gate and source/drain voltage, the smaller of channel cross-section area is, the lower electron current is obtained in the corresponding MOSFET.

It is also interesting to explore the performances of the nano-MOSFETs with different channel geometries but with the same area of the y-z channel cross-section. This set of experiments are designed to test geometry effects of the Si/SiO₂ interfaces. We still consider the nano-MOSFETs with square, circle and flower-like channel cross sections and examine their corresponding I-V curves in Figure 4.9. The areas enclosed by the square, circle and flower-like curve, see Figure 4.9 (a), are the same as the small circle does in Figure 4.8(a). Comparing the three solid I-V curves in Figure 4.8(b) and Figure 4.9(b), respectively, we find that although the areas of the cross-sections are the same, the electron currents at various gate voltages from the cylinder channel are the highest, then followed by the currents from channels with square and flower-like cross sections. Therefore, we conjecture that for the cross-sections of channels in the confined directions, the smaller perimeter of Si/SiO_2 interface will result in larger magnitude of electron current, when the area are the same.

The performances of the three types of channels are further analyzed in terms of their corresponding subband energies along the transport direction. In Figure 4.10, the subband energy profiles of the channels with the same area of cross-sections but with square, circle and flower-like cross section shapes, are plotted along the confined direction. As can be seen in Figure 4.10 (a), the barriers of subband energies (i.e., eigenvalues) of the channels with flower-like and circle cross sections are the highest and lowest, respectively, which are consistent with the corresponding the smallest and largest magnitudes of electron currents. The confinement effects of the three different cross-sections with the same area are shown in Figure 4.10 (b), in which the difference between the first $(u_{\text{scat}}^1(x))$ and the second $(u_{\text{scat}}^2(x))$ subband energies is plotted for each channel. The differences between the first two subband energies from the channels with flower-like and circle cross sections are the strongest and weakest among the three geometries, although their enclosed areas are the same.

4.4.4 Quantum tunneling effects

A significant difference between nano-devices and classical devices is the possible electron tunneling effects. From Figure 4.5(a) or 4.6, we can see that there is an electric energy barrier in the channel. We denote the maximum of subband energy by E_{max} , i.e., $E_{\text{max}} = \sup_{x_0} E_{\text{scat}}^j(x_0)$. In classical models, any electron with energy lower than E_{max} from the source can not overcome the barrier and arrive the drain. However, in a quantum mechanical model,



Figure 4.10: Subband energy profiles along the transport direction for MOSFETs with different geometries of channel cross-sections(source-drain voltages is fixed at $V_{DS} = 0.4V$ and gate voltages $V_{Gate} = 0.4V$). (a) First subband energies of different channels; (b) Difference of first two subband energies of each channel.

electrons with energy less than E_{max} may be able to pass the barrier and result in electron current. This electron tunneling current cannot be neglected in the nano-scale devices.

A method to study the quantum tunneling is to investigate the contribution to the current density by electrons of various energies. The theoretical total current density I_{tot} is computed by the formula in Eq. (4.34). For convenience, we only consider the transport energy E and use the formulation:

$$I_{\text{tot}} = -\int_{-\infty}^{\infty} \frac{q}{\hbar} \text{Tr} \mathbf{T}_{\text{DS}}(E) [f(\mathbf{H}^{\text{tot}} - \mu_{\text{S}}\mathbf{I}) + f(\mathbf{H}^{\text{tot}} - \mu_{\text{D}}\mathbf{I})] dE, \qquad (4.41)$$

define the total current contributed by the tunneling effects, $I_{\rm qt},$ by

$$I_{\rm qt} = -\int_{-\infty}^{E_{\rm max}} \frac{q}{\hbar} \operatorname{Tr} \mathbf{T}_{\rm DS}(E) [f(\mathbf{H}^{\rm tot} - \mu_{\rm S} \mathbf{I}) + f(\mathbf{H}^{\rm tot} - \mu_{\rm D} \mathbf{I})] dE, \qquad (4.42)$$

and denote the ratio of quantum tunneling current by

$$R_{\rm qt} = \frac{I_{\rm qt}}{I_{\rm tot}}.\tag{4.43}$$

Obviously, if $I_{qt} = 0$, the mechanism is entirely classical. By contrast, in the present quantum model, $I_{qt} > 0$ because of the quantum tunneling effect, i.e., there is a nonzero probability for the electron with energy lower than the potential barrier to penetrate through the channel.

In Figure 4.11(a), we demonstrate the electron current (I) as a function of electron energy (E) for a nano-MOSFET with cylinder channel under $V_{\text{Gate}} = 0V$ and $V_{\text{DS}} = 0.4V$. It can be concluded that the electron current increases with higher electron energy (this is quite understandable because the electron with a higher energy can overcome the potential barrier more easily), and saturates fast when the energy is over around E = 0.5V. This is due to the



Figure 4.11: Relation between electron current (μ A) and electron energy E (eV) in the MOS-FET with the cylinder channel. (a)Gate voltage and source-drain voltage are respectively $V_{Gate} = 0.0V$ and $V_{DS} = 0.4V$. The red dot indicates the current when electron energies equal to the maximum energy barrier E_{max} (horizontal coordinate). (b)under various gate voltages V_{Gate} (source-drain voltages fixed at $V_{DS} = 0.4V$). The red dots from right to left correspond to $V_{Gate} = 0, 0.05, 0.1, ..., 0.4V$.

V_{Gate} (V)	tunneling current(μA)	total current(μA)	tunneling ratio
0	1.92×10^{-7}	1.20×10^{-6}	15.94%
0.05	1.36×10^{-6}	8.79×10^{-6}	15.48%
0.10	9.57×10^{-6}	6.42×10^{-5}	14.92%
0.15	6.61×10^{-5}	4.69×10^{-4}	14.11%
0.20	4.44×10^{-4}	3.40×10^{-3}	13.04%
0.25	2.73×10^{-3}	2.43×10^{-2}	11.25%
0.30	1.45×10^{-2}	1.66×10^{-1}	8.78%
0.35	5.70×10^{-2}	9.60×10^{-1}	5.94%
0.40	2.26×10^{-1}	4.07	5.55%

Table 4.1: Tunneling ratio for the cylinder channel at different V_{Gate} ($V_{DS}=0.4V$).

Fermi-Dirac distribution; the probability of electrons with higher energies is lower so they do not contribute significantly. In this simulation, the maximum energy barrier E_{max} of the first subband is $E_{\text{max}} = 0.388 \text{eV}$; the point which has this value as horizontal coordinate on the I-E curve is marked with a red dot. The tunneling current I_{qt} in this circumstance is apparent since the electron current I is non-zero (up to $1.92 \times 10^{-2} \mu \text{A}$) when $E < E_{\text{max}}$. From the total current $I_{\text{tot}} = 1.20 \times 10^{-6} \mu \text{A}$, we compute $R_{\text{qt}} = 15.94\%$.

The tunneling current I_{qt} and ratio of tunneling current R_{qt} depend on the gate voltage of the nano devices. In Figure 4.11(b) there collects the similar current-energy curves as in Figure 4.11(a), but with V_{Gate} takes values from 0.0V to 0.4V. Since the currents are significantly different under values of V_{Gate} , these curves are normalized for better comparison. In this sense the vertical coordinate of the red dots exactly represents the tunneling ratio R_{qt} . We see that as V_{Gate} varies from 0.0V to 0.4V, the I-E curves shift to the left. This is consistent with the fact that the electron with the same energy are easier to overcome the potential barrier with assistance of voltage gate. It is also observed that the tunneling ratio decreases as V_{Gate} increases. The detailed tunneling currents and tunneling ratios under different V_{Gate} are listed in Table 4.1.



Figure 4.12: Relation of electrons tunneling ratio and gate voltages V_{Gate} for nano-MOSFETs with cylinder and flower-like channels (source-drain voltage fixed at $V_{DS} = 0.4V$).

Figure 4.12 illustrates the tunneling ratios for the two different channels, the cylinder channel and the flower-like channel, whose y-z cross-sections are shown in Figure 4.8 (a). For both devices, the tunneling ratio decreases as gate voltages V_{Gate} increases. Furthermore, the tunneling ratio of the device with flower-like channel is higher than the one with cylinder channel. This is the evidence that stronger confinement of channels will result in more significant quantum effects.

4.4.5 Phonon-electron interactions

In this section, we investigate the phonon effects based on the modified scattering equation in Eq. (4.35). As seen from Eqs. (4.35)-(4.36), the potential energy component in Eq. (4.35) will be higher than that in Eq. (4.30). There are essentially a couple of factors to affect the U_{phon} , the phonon energy and phonon number. In the present work, the phonon energy E_p is assumed to take a constant in each simulation.

Figure 4.13(a) gives a comparison of I-V_{Gate} between the models with and without phonon-electron (p-e) interactions. Compared to the model without p-e interactions, the model with p-e interactions gives smaller electron currents. Moreover, the impact in the case of $E_p = 0.03$ eV is greater than that of $E_p = 0.063$ eV. The impact of U_{phon} can be seen as a trade-off between phonon energy and phonon number. In case of higher phonon energy, there are a smaller number of phonons based on Bose-Einstein statistics in Eq. (4.36). Eventually, the magnitude of U_{phon} decreases as E_p increases from $E_p = 0.03$ eV to $E_p = 0.063$ eV, which results in a smaller impact for scattering potential barrier in the scattering problem and furthermore higher current. Figure 4.13(b) gives results for the tunneling ratio. Although the tunneling ratio keeps decreasing as I-V_{Gate} increases, there is no significant difference between models with and without p-e interactions.



Figure 4.13: Effects of phonon-electron interactions in I-V curves and electron tunneling ratio for the cylinder channel. (a) I-V_{Gate} curves with different electron-phonon interactions; (b) Relations of electron tunneling ratios and gate voltages V_{Gate} with different electron-phonon interactions (source-drain volate fixed at $V_{DS}=0.4V$).

Figure 4.14 illustrates the impact of phonon effects at different temperatures. The result in Figure 4.14(a) shows that current density increases with the increase of temperature. It is consistent with the fact that the electronic conductivity of semiconductor enhances as the temperature increases.

Figure 4.13(b) suggests that the tunneling ratio decreases as the temperature increases. This trend is consistent with the quantum mechanical principle that quantum effects play a more important role under lower temperature.



Figure 4.14: Temperature effects on electron currents under different phonon-electron interactions for the cylinder channel ($V_{DS}=0.4V$, $V_{Gate}=0.3V$). (a) Current-temperature curves; (b) Electron tunneling ratios under different temperatures.

4.5 Chapter conclusion remarks

We present mathematical modeling and numerical simulations of semiconductor-insulator geometric effects, quantum tunneling currents and phonon-electron interactions for nanoscale electronic devices, using a four-gate MOSFET model. Transistors in nano-scales will not function in analog with conventional devices by classical physics and will lead to new breakthroughs in devices science and technologies. For example, channel tunneling or gate leakage under various voltage settings of ultimate MOSFETs and other nano-transistors will be of main concerns of the modeling and simulations. Other factors may affect the performances of nano-MOSFETs at such a scale or under quantum mechanics could include channel surface roughness, and phonon scattering effects. However, quantum simulations are intractable for individual particles because of the enormous degrees of freedom. We proposed a two-scale energy functional which describes the electrons and the continuum electrostatic potential of the nano-electronic device [35]. In our framework, the microscopic description of electrons and the macroscopic description of the continuum electrostatic potential are integrated on an equal footing at nano-scale.

The present work, based on our framework of free energy functional, addresses the modeling issues of various types of Si/SiO_2 geometries, tunneling ratios and phonon-electron interface effects. Material interfaces are integrated in the energy formulation and serve as continuity conditions of the Poisson equation and boundary conditions of the Schrödinger equation. Thus, electric field, physical confinement of electrons, and in further macroscopic performances of nano-MOSFETs will depend on these microscopic details. Phonon-electron interactions are modeled as part of transport energy in a fashion of density functional theory, in which density of phonons are assumed to be homogeneous in the channel and follows the Bose-Einstein statistics. Finally, the tunneling effects of devices are measured as tunneling ratios of electron currents.

A four-gate MOSFET with different shapes of channels is considered in the three-dimensional numerical simulation in the present work. In our computations, advanced interface-problem solvers are utilized to solve the Poisson equation for the electrostatic potentials with three semiconductor-insulator geometries. The Schrödinger equation is solved based on the physical properties that electrons have continuous and discrete spectrum along transport and confined direction, respectively. The self-consistence of the coupled system is achieved by the so-called Gummel-like iteration. The performances of the nano-device are examined in terms of current-voltage curves with three types of Si/SiO₂ interfaces, a wide range of source-drain and gate voltages, and different phonon energies.

Chapter 5

Thesis achievements and future work

5.1 Contributions

The main contributions of this thesis are as follows. First, we propose a new electrostatic solvation free energy functional to take into consideration the effect of hyperpolarizations. The nonlinear Poisson equation(NLPE) is derived from electrostatic solvation free energy functional based on the variational principle. Compared to the classic Poisson equation, which is derived based on electric polarizations in a linear, isotropic, and homogeneous dielectric medium, our NLPE partially accounts for the hyperpolarizations, which are important under a strong electrical field, or involving highly charged nonlinear inhomogeneous media. Moreover, our nonlinear Poisson equation gives rise to a smooth dielectric function, which overcomes computational difficulty of employing a sharp solvent-solute boundary. A nonpolar solvation model is further formulated on the basis of the dielectric profile obtained from the nonlinear Poisson model by using geometric measure theory. The proposed solvation models are extensively validated with the Kirkwood model and experimental measurements of 17 molecules. Our new solvation models out-perform the classic Poisson equation based solvation model. In fact, its performance is very close to the explicit solvation model, which is much more computationally expensive. Application of the proposed nonlinear Poisson model is considered to electrostatic analysis of 20 proteins. In addition, the test results for the set of 21 compounds at different temperatures further validate that the proposed NLPE model
does a good job in modeling the temperature effect on the solvation free energy. The good agreement between our results and experimental data as well as theoretical results suggests that the proposed nonlinear Poisson model is a potentially powerful model for electrostatic analysis involving hyperpolarization effects.

Second, we employ the PDE transform to efficiently suppress Gibbs' oscillations in the numerical solution of hyperbolic conservation laws. Specifically, during the time integration of a hyperbolic conservation law system, an intermediate numerical solution at a given time step is used as an initial data for a special evolution PDE. Then the solution of such an evolution PDE is accepted as an updated numerical solution at the given time step. Two techniques are proposed to improve the efficiency of the present approach. First, we use an adaptive measure of total variations to automatically determine whether the PDE transform is needed at each time step. Additionally, we utilize a fast PDE transform, which offers the analytical solution of an arbitrarily high order evolution PDE in the Fourier representation. This technique bypasses the stability constraint of solving high order evolution PDEs. We have employed a variety of benchmark in the present work to validate the proposed approach, ranging from scalar conservation law systems to Euler equations in one and two spatial dimensions. Among these problems, some typically prefer low-order shock capturing schemes; whereas others are well known to require high order numerical methods. For example, low order schemes will severely damp the amplitude of the entropy waves in the shock-entropy interaction described by the Euler equation. The proposed PDE transform provides some of the best results for solving the Burgers' equation with non-convex flux. Furthermore, only about 5 points per wavelength (PPW) is needed for the present approach to handle the interaction of shock-entropy waves and shock-vortex interactions, which is among the fewest number of PPW to out knowledge so far.

Third, we propose high-order fractional PDEs and the corresponding fractional PDE transform. Using the fractional variational principle, we construct nonlinear fractional PDEs based on fractional hyperdiffusion. Introducing an artificial time, the resulting high-order fractional PDEs are converted to time-evolution fractional PDEs. Numerical techniques based on fast fractional Fourier transform (FFFT) is developed to compute the high-order fractional PDEs in three-dimensional setting. The proposed high-order fractional PDEs are applied to the surface construction of macromolecular surfaces, which are crucial components in the implicit solvent models. We consider three types of initial values to study the proposed high-order fractional PDEs. Additionally, we examine the effect of the orders of fractional PDEs on the surface morphology. It is found that high-order fractional PDEs are crucial to the quality of molecular surfaces. We also test the impact of the PDE integration time on surface generation. Moreover, we examine the computational efficiency of the present method. Efficiency is one of major motivations for developing new surface generation methods. It is found that the proposed high-order fractional PDEs are of linear scaling with respect to number of atoms in a molecule. We further validate the present method by quantitative analysis of surface areas and surface enclosed volumes of proteins. Finally, the surfaces constructed by the present approach is applied to a couple of biophysical problems, namely, the electrostatic analysis via the Poisson equation and the solvation analysis via a full solvation model. The results from these biophysical problems indicate that the proposed high-order fractional PDEs are a robust and efficient method for macromolecular surface generation.

Finally, we present mathematical modeling and numerical simulations of semiconductorinsulator geometric effects, quantum tunneling currents and phonon-electron interactions for nano-scale electronic devices, using a four-gate MOSFET model. The present work, based on our framework of free energy functional, addresses the modeling issues of various types of Si/SiO₂ geometries, tunneling ratios and phonon-electron interface effects. Material interfaces are integrated in the energy formulation and serve as continuity conditions of the Poisson equation and boundary conditions of the Schrödinger equation. Thus, electric field, physical confinement of electrons, and in further macroscopic performances of nano-MOSFETs will depend on these microscopic details. Phonon-electron interactions are modeled as part of transport energy in a fashion of density functional theory, in which density of phonons are assumed to be homogeneous in the channel and follows the Bose-Einstein statistics. Finally, the tunneling effects of devices are measured as tunneling ratios of electron currents.

Much of this dissertation has been written based on our papers:

- Langhua Hu and Guo-Wei Wei, Nonlinear Poisson equation for inhomogeneous media.
 Biophysical Journal, 103, 758-766 (2012).
- Langhua Hu, Duan Chen and Guo-Wei Wei, High-order fractional partial differential equations for molecular surface construction, Molecular Based Mathematical Biology, 1-25 (2012).
- Langhua Hu, Duan Chen and Guo-Wei Wei, Geometric and phonon effects on nano transistors, submitted (2013).
- Langhua Hu, Siyang Yang and Guo-Wei Wei, Simulation of inviscid compressible flows using PDE transform, submitted (2013).

5.2 Future work

In our proposed nonlinear Poisson equation (NLPE), we only consider the molecular charge density, which is treated as the point partial charge source as showed in Eq. (1.9). It would be an interesting to consider the salt effect and incorporate the solvent charge distribution in the nonlinear Poisson equation. When the solvent charge in the equilibrium, we can use the Boltzmann distribution to approximate the solvent charge distribution, which is

$$\rho_s(\mathbf{r}) = \sum_{i=1}^{N_c} c_i q_i e^{-\phi(\mathbf{r})q_i/k_B T}$$
(5.1)

where q_i is the charge of ion species i, N_c is the number of ion species, k_B is the Boltzmann constant, T is the temperature, and c_i is the bulk concentration of the *i*th ionic species. When the solvent charge distribution given by Eq. (5.1) appears in the right hand side of the nonlinear Poisson equation in Eq. (1.14), the NLPE will become much more nonlinear. It remain an open question how the proposed nonlinear Poisson equation with salt effect will impact the electrostatic analysis. Furthermore, when the underlying chemical and biological system is far from the equilibrium, the Boltzmann distribution may no longer be valid. Usually, these systems are described by coupled Nernst-Planck equation and Poisson equation, which is replaced by coupled Nernst-Planck equation and nonlinear Poisson equation in the new framework. It's a topic of interest to study how well the conjuncted Nernst-Planck equation and nonlinear Poisson equation will work. Moreover, there are still a huge room to explore in the field of high order PDE transform and fractional PDE transform. For example, the molecular surface generation with the proposed high order fractional PDE transform is much more time efficient than MSMS approach, which makes it possible to greatly facilitate the molecular dynamics. At last, it would be interesting to see how the effect of geometry, thermal and quantum will impact more complicated nano-transistors, such as the nano-scale bio-sensor.

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