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A Convergence Analysis of a Structure-Preserving Gradient Flow Method for the All-Electron Kohn-Sham Model

Yedan Shen[1], Ting Wang[2], Jie Zhou[3,4] and Guanghui Hu[2,5,6,*]

[1] *School of Mathematics and Information Science, Guangzhou University, Guangzhou, China*
[2] *Faculty of Science and Technology, University of Macau, Macao SAR, China*
[3] *Hunan Key Laboratory for Computation and Simulation in Science and Engineering, Xiangtan University, Xiangtan, China*
[4] *School of Mathematical Computational Sciences, Xiangtan University, Xiangtan, China*
[5] *Zhuhai UM Science & Technology Research Institute, Zhuhai, China*
[6] *Guangdong-Hong Kong-Macao Joint Laboratory for Data-Driven Fluid Mechanics and Engineering Applications, University of Macau, Macao SAR, China*

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Abstract. In [Dai *et al.*, Multi. Model. Simul. 18(4) (2020)], a structure-preserving gradient flow method was proposed for the ground state calculation in Kohn-Sham density functional theory, based on which a linearized method was developed in [Hu *et al.*, EAJAM. 13(2) (2023)] for further improving the numerical efficiency. In this paper, a complete convergence analysis is delivered for such a linearized method for the all-electron Kohn-Sham model. Temporally, the convergence, the asymptotic stability, as well as the structure-preserving property of the linearized numerical scheme in the method is discussed following previous works, while spatially, the convergence of the h-adaptive mesh method is demonstrated following [Chen *et al.*, Multi. Model. Simul. 12 (2014)], with a key study on the boundedness of the Kohn-Sham potential for the all-electron Kohn-Sham model. Numerical examples confirm the theoretical results very well.

AMS subject classifications: 35Q41, 81Q05, 65M60, 65M12, 65M50

Key words: Kohn-Sham density functional theory, gradient flow model, structure-preserving, linear scheme, convergence analysis.

*Corresponding author. *Email address:* garyhu@um.edu.mo (G. Hu)

1. Introduction

The Kohn-Sham density functional theory (KSDFT) proposed in 1965 is one of the most successful approximation models towards the computational quantum chemistry, condensed matter physics, etc., for many-body electronic structure calculations [15, 36]. Due to the nonlinearity of the governing equation and the complexity of the given electronic structure system, obtaining a high-quality numerical solution has been becoming an important issue in the simulation.

For the ground state calculation, concerned with the nonlinearity of the Kohn-Sham equation caused by the Hamiltonian operator, the self consistent field (SCF) iteration is a classical choice [22, 24]. Several types of numerical methods are employed in the simulation of Kohn-Sham equation, such as finite element methods [2, 4, 12, 20], finite difference methods [30], spectral methods [18, 25, 35], discontinuous Galerkin methods [23], finite volume methods [9], plane-wave methods [17], etc. Besides directly solving the Kohn-Sham equation, minimizing the total energy is also a popular way to obtain the ground state of the quantum system. The ground state of the system can be obtained by solving the following minimization model with orthogonality constraints [26]:

$$\begin{aligned} &\min_{U} E_{KS}(U), \\ &\langle U, U\rangle = I_p. \end{aligned} \tag{1.1}$$

There are several types of optimization methods for the Kohn-Sham energy minimization model such as the quasi-Newton methods [28], the constrained minimization methods [11, 33], the conjugate gradient methods [10, 26]. A main advantage of this approach is that the solution of nonlinear eigenvalue problems can be avoided, based on which the main cost becomes the assembling of the total energy functional and operations on the manifold. It should be pointed out that the orthonormalization has to be invoked explicitly or implicitly by using most of the existing optimization methods. However, implementing such orthogonality-preserving strategies would occupied a large part of the CPU time, which makes it a tough task for the ground state calculation of a large scale quantum system. Thus, concerned with the efficiency and the parallel scalability, an orthogonalization-free model is needed towards the simulation of large scale system. It is worth mentioning that in [16], an infeasible approach has been proposed based on the finite element method for calculating the ground state, which successfully removed the orthogonalization operation in the simulation.

Towards the same purpose, another approximation to avoid the orthogonalization is the gradient flow method [12, 19, 32]. Recently, Dai *et al.* [12] have introduced and analyzed a Kohn-Sham gradient flow based model for electronic structure calculations, in which an extended gradient flow has been proposed. It has shown that the orthonormalization relation among those wavefunctions can be automatically preserved during the simulation on a Stiefel manifold. Concerned with the numerical scheme in [12], an implicit midpoint scheme has been employed for temporal discretization, based on which the effectiveness of the algorithm has been demonstrated successfully. Motivated