Commun. Comput. Phys.
doi: 10.4208/cicp.OA-2024-0053

Vol. **37**, No. 4, pp. 921-941
April 2025

An Unconditionally Energy-Stable and Orthonormality-Preserving Scheme for the Kohn-Sham Gradient Flow Based Model Based on a Tetrahedral Spectral Element Method

Hongfei Zhan[1], Ting Wang[2] and Guanghui Hu[3,4,*]

[1] *School of Mathematical Sciences, Peking University, Beijing, China.*
[2] *School of Sciences, Southwest Petroleum University, Chengdu, Sichuan Province, China.*
[3] *State Key Laboratory of Internet of Things for Smart City and Department of Mathematics, University of Macau, Macao SAR, China.*
[4] *Zhuhai UM Science & Technology Research Institute, Zhuhai, Guangdong Province, China.*

Received 10 March 2024; Accepted (in revised version) 20 September 2024

Abstract. In this paper, the unconditionally energy-stable and orthonormality-preserving iterative scheme proposed in [X. Wang et al. (2024), J. Comput. Phys., 498:112670] is extended both theoretically and numerically, including (i) the exchange-correlation energy is introduced into the model for a more comprehensive description of the quantum system, utilizing the local density approximation used by the National Institution of Science and Technology Standard Reference Database; (ii) both the unconditional energy-stability and orthonormality-preservation are attained in the newly derived scheme; (iii) a C^0 tetrahedral spectral element method is adopted for the quality spatial discretization, of which a quality initial condition can be designed using low order one for effectively accelerating the simulation. A series of numerical experiments validate the effectiveness of our method, encompassing various atoms and molecules. All the computations successfully reveal the anticipated spectral accuracy and the exponential error dependence to the cubic root of the degree of freedom number. Moreover, the efficiency of the extended framework is discussed in detail on updating schemes.

AMS subject classifications: 37M05, 37N40, 65N25, 65N35, 70G60

Key words: Kohn-Sham density functional theory, gradient flow model, structure-preserving scheme, energy stability, tetrahedral spectral element method.

*Corresponding author. *Email addresses:* garyhu@um.edu.mo (G. Hu), hfzhan20@gmail.com (H. Zhan), tinawang92@126.com (T. Wang)

1 Introduction

The Kohn-Sham density functional theory (KSDFT) [14,28] stands as a widely acclaimed and successful approximation model for electronic structure calculations. The ground state solution is determined by solving the Kohn-Sham equations [4–6,9,16,17] derived from variation principle of the total energy. A common approach for solving the Kohn-Sham equation is the self-consistent field iteration [23,27]. However, there is no guarantee for the convergence to the ground state, especially in large-scale systems with small band gaps [19,25]. This has sparked a growing interest in energy minimization methods to overcome this challenge. Various optimization approaches have been proposed for the Kohn-Sham energy minimization model [7,25,31,34,38,40,41,43]. To handle the orthogonal constraint that should be either explicit or implicit preserved during simulations, an infeasible method was proposed in [12,13], requiring only a single orthogonalization for finalization. Furthermore, an extended gradient flow based model for electronic structure calculations was proposed in [8], automatically preserving orthogonality among all wave functions when the initial guess is orthogonal. This approach has been further advanced by Hu et al. in [15], where the extensions in both linearization and adaptivity are introduced.

Unconditionally energy stable schemes have been actively studied in recent two decades [1, 10], it is worth mentioning that an unconditionally energy-stable and orthonormality-preserving scheme was proposed by Wang et al. in [37] based on the work of Dai et al. [8]. This work represents the first instance of achieving both unconditional energy stability and orthonormalization preservation for the Kohn-Sham gradient flow-based model in electronic structure calculations. Additionally, from a numerical perspective, the scheme allows for the utilization of large time step sizes in simulations, resulting in significant computational cost savings compared to other algorithms. However, despite these advancements, there remains room for further improvement of the scheme. Theoretically, the absence of exchange-correlation energy in the model limits the applications of this scheme. Numerically, the numerical accuracy of the method is not entirely satisfactory, suggesting that high-order discretizations may deliver improved results.

In contrast to extensively efforts toward low-order methods such like the finite difference methods [32,36], finite element methods [2,22,29,33,39], enriched finite element methods [21, 26], and finite volume methods [6], there is a burgeoning interest in the realm of high-order discretization techniques. On the one hand, the ground state wave function exhibits satisfactory smoothness except known nucleus positions. On the other hand, high-order methods become imperative for accurately capturing complex physical phenomena such as high-harmonic generation. Furthermore, a well-designed high-order method has the potential to significantly enhance the efficiency, particularly for large-scale systems. Consequently, the spectral element method emerges as a compelling choice, integrating the flexibility of the finite element method and the high accuracy of the spectral method.