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Convergent and Orthogonality Preserving Schemes for Approximating the Kohn-Sham Orbitals

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Abstract. To obtain convergent numerical approximations without using any orthogonalization operations is of great importance in electronic structure calculations. In this paper, we propose and analyze a class of iteration schemes for the discretized Kohn-Sham Density Functional Theory model, with which the iterative approximations are guaranteed to converge to the Kohn-Sham orbitals without any orthogonalization as long as the initial orbitals are orthogonal and the time step sizes are given properly. In addition, we present a feasible and efficient approach to get suitable time step sizes and report some numerical experiments to validate our theory.

AMS subject classifications: 37M15, 37M21, 65M12, 65N25, 81Q05

Key words: Gradient flow based model, density functional theory, orthogonality preserving scheme, convergence, temporal discretization.

1. Introduction

Electronic structure calculations play an important role in numerous fields such as quantum chemistry, materials science and drug design. Due to the good balance of accuracy and computational cost, the Kohn-Sham Density Function Theory (DFT) model [20,22,29,31,32] has become one of the most widely used models in electronic structure calculations which is usually treated as either a nonlinear eigenvalue problem (Kohn-Sham equation) or an orthogonality constraint minimization problem (Kohn-Sham total energy direct minimization problem).

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In the literature, there are a number of works on the design and analysis of numerical methods for solving the Kohn-Sham equation (see, e.g., [5, 7, 8, 14, 24, 37, 44] and references cited therein). To obtain the solution of this nonlinear eigenvalue problem, we observe that some self consistent field (SCF) iterations are usually used [29] (see also [2, 4, 21, 25, 33, 34, 47]). Unfortunately, the convergence of SCF iterations is uncertain. We understand that its convergence has indeed been investigated when there is a sufficiently large gap between the occupied and unoccupied states and the second-order derivatives of the exchange correlation functional are uniformly bounded from above [3, 26, 27, 41], which is important in the theoretical point of view. It becomes significant to investigate the convergence of SCF iterations when the gap is not large in application.

We see that an alternative approach to obtain the ground states is to solve the Kohn-Sham total energy minimization problem, which is an orthogonality constrained minimization problem [32]. The direct minimization approach attracts the attention of many researchers in recent years [6, 17, 30], and many different kinds of optimization methods are applied to electronic structure calculations and investigated (see, e.g., [10, 11, 18, 19, 38, 42, 45, 46]).

For solving either the nonlinear eigenvalue problem or the orthogonality constrained minimization problem, except for few works such as [19], the orthogonalization procedure is usually required, which is very expensive and limits the parallel scalability in numerical implementation.

Recently, Dai *et al.* proposed a gradient flow based Kohn-Sham DFT model [12] that is a time evolution problem and is completely different from either the nonlinear eigenvalue problem or the orthogonality constrained minimization problem. It is proved in [12] that the flow of the new model is orthogonality preserving, and the solution can evolve to the ground state. Consequently, the gradient flow based model provides a novel and attractive approach for solving Kohn-Sham DFT apart from the eigenvalue problem model and the energy minimization model. In other words, the gradient flow based model is quite promising in ground state electronic structure calculations and deserves further investigation. For the sake of clarity, we would like to mention that the gradient flow based Kohn-Sham DFT model is different from the time dependent Kohn-Sham equation in [28, 36, 43].

In this paper, we propose a general framework of orthogonality preserving schemes that produce efficient approximations of the Kohn-Sham orbitals with the help of the gradient flow based model. In addition, we prove the global convergence and local convergence rate of the new schemes under some mild assumptions. We also provide some typical choices for the auxiliary mapping appeared in the framework, and a feasible and efficient approach to obtain the desired time step sizes that satisfy the assumptions required in the analysis, which result in several typical orthogonality preserving schemes that can produce convergent approximations of the Kohn-Sham orbitals.

The rest of the paper is organized as follows. In Section 2, we briefly review the gradient flow based Kohn-Sham DFT model and some notation frequently used throughout this paper. We then propose a framework for orthogonality preserving schemes for solv-