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FINITE ELEMENT APPROXIMATIONS FOR SCHRÖDINGER EQUATIONS WITH APPLICATIONS TO ELECTRONIC STRUCTURE COMPUTATIONS*

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Dedicated to Professor Junzhi Cui on the occasion of his 70th birthday

Abstract

In this paper, both the standard finite element discretization and a two-scale finite element discretization for Schrödinger equations are studied. The numerical analysis is based on the regularity that is also obtained in this paper for the Schrödinger equations. Very satisfying applications to electronic structure computations are provided, too.

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Key words: Error analysis, Finite element, Eigenvalue, Quantum chemistry, Schrödinger equation, Two-scale.

1. Introduction

This paper is concerned with the finite element approximations to the following Schrödinger problem: Find $(\lambda, u) \in \mathbb{R} \times H_0^1(\Omega)$ such that

$$\begin{cases} -\Delta u + Vu = \lambda u & \text{in } \Omega, \\ \|u\|_{0,\Omega} = 1, \end{cases} \tag{1.1}$$

where Ω is a bounded domain in $\mathbb{R}^3$, $V = V_{ne} + V_0$ is the so-called effective potential. Here, $V_0 \in L^\infty(\Omega)$ and

$$V_{ne}(x) = -\sum_{j=1}^{N_{atom}} \frac{Z_j}{|x - r_j|} \tag{1.2}$$

with $r_j \in \Omega$, Z_j some positive constant $(j = 1, \cdots, N_{atom})$, where N_{atom} is the total number of the atoms in the system.

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It is known that modern electronic structure computations require solving the following Kohn-Sham equations (see, e.g., [6, 16, 23, 24])

$$\left(-\frac{1}{2}\Delta - \sum_{j=1}^{N_{atom}} \frac{Z_j}{|x-r_j|} + \int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|}dy + V_{xc}(\rho)\right) u_i = \lambda_i u_i \ \text{ in } \mathbb{R}^3, \tag{1.3}$$

where Z_j is the valance charge of this ion (nucleus plus core electrons), r_j is the position of the j-th atom ($j = 1, \cdots, N_{atom}$),

$$\rho = \sum_{i=1}^{N_{occ}} c_i |u_i|^2 \tag{1.4}$$

with u_i the i-th smallest eigenfunction, c_i the number of electrons on the i-th orbit, and N_{occ} the total number of the occupied orbits. It is known that such nonlinear Schrödinger equation (1.3) is a key model in modern physics, materials science and quantum chemistry [6, 23, 24, 32]. The central computation in solving the Kohn-Sham equation is the repeated solution of (1.1) with some effective potential V that has a singular part as (1.2). Indeed, the original (high dimensional) Schrödinger equation modeling the behavior of a quantum molecular system is also of (1.1) and the Kohn-Sham equation is nothing but one of the simplified models of the original linear high dimensional Schrödinger equation only.

In most applications, a number of eigenpairs are desired and the worst thing is that the self-consistent iteration is not so easy to converge and it often takes several tens of steps. Consequently, it is very important to improve the accuracy and reduce the computational cost in solving (1.1) at each iteration step. More precisely, highly efficient computation of (1.1) is essential when the simulated system becomes large. Although the finite element method has been successful in quantum chemistry (see, e.g., [6, 25, 29, 34, 35, 36, 41, 42] and references therein), to our knowledge, there is no any rigorous finite element analysis for solving (1.1) in literature. Also, the computation scale in electronic structure computations is still limited by the large number of basis functions required to adequately describe all-electron solutions near nuclei, where the solutions can have cusps and oscillate rapidly [6, 25, 35, 36]. Hence it is significant to design and analyze an efficient finite element scheme for (1.1) when V is singular. It is noted that a finite element analysis is presented in [41] for the Schrödinger equation of the $S-$state of helium atoms based on some variational form in a weighted Sobolev space.

To study a finite element approximation to (1.1) when V has a singular part as (1.2), we need to investigate the regularity of solution of (1.1). After analyzing the one-scale finite element discretization (more precisely, the standard finite element discretization), we then consider to reduce the computational cost and propose a two-scale finite element discretization scheme. For applications, we will apply the two-scale discretization approach to electronic structure computation. Different from that of [41], our analysis of the one-scale finite element discretization is set in the standard Sobolev space. It should be mentioned that the two-scale discretization scheme for elliptic eigenvalue problems is first proposed in [19] and later developed in [8, 9, 10, 20, 21, 37, 38], where only problems with smooth coefficients are studied. Our two-scale discretization work may be viewed as a generalization of that in the literature to the case of that the coefficient is not smooth. The two-scale approach is an iterative method, which is, in a way, related to that in [18, 31].

The rest of the paper is organized as follows. In Section 2, some basic notations and the regularity properties of (1.1) are provided. In Section 3, the standard finite element discretization scheme and the two-scale discretization scheme are presented and analyzed. In Section 4,