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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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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,

several applications to ground state computations of atoms in quantum chemistry are reported. Finally, some concluding remarks are given.

2. Preliminaries

Let Ω be a convex polyhedral domain in $\mathbb{R}^3$. We shall use the standard notation for Sobolev spaces $W^{s,p}(\Omega)$ and their associated norms and seminorms, see, e.g., [1, 12]. For $p = 2$, we denote $H^s(\Omega) = W^{s,2}(\Omega)$ and $H_0^1(\Omega) = \{v \in H^1(\Omega) : v\mid_{\partial\Omega} = 0\}$, where $v\mid_{\partial\Omega} = 0$ is in the sense of trace, $\|\cdot\|_{s,\Omega} = \|\cdot\|_{s,2,\Omega}$ and $\|\cdot\|_{\Omega} = \|\cdot\|_{0,2,\Omega}$. We let $(\cdot,\cdot)$ to be the standard inner-product of $L^2(\Omega)$. For $x = (x_1, x_2, x_3) \in \mathbb{R}^3$, we set $|x| = \sqrt{x_1^2 + x_2^2 + x_3^2}$. Throughout this paper, we shall use the letter C (with or without subscripts) to denote a generic positive constant which may stand for different values at its different occurrences.

Define

$$a(w, v) = \int_\Omega \nabla w \nabla v + V w v, \quad w, v \in H_0^1(\Omega),$$

where V is that stated in Section 1.

A number λ is called an eigenvalue of the form $a(\cdot,\cdot)$ relative to the form $(\cdot,\cdot)$ if there is a nonzero vector $u \in H_0^1(\Omega)$, called an associated eigenfunction, satisfying

$$a(u, v) = \lambda(u, v) \quad \forall\ v \in H_0^1(\Omega). \tag{2.1}$$

To study the eigenpair of (2.1), we need the following result.

Lemma 2.1. *There is a constant $C > 0$ such that*

$$\|w\|_{1,\Omega}^2 - C^{-1}\|w\|_{0,\Omega}^2 \le 2a(w, w) \quad \forall\ w \in H_0^1(\Omega). \tag{2.2}$$

Proof. Using the uncertainty principle lemma (see, p. 169 of [26])

$$\int_{\mathbb{R}^3} \frac{w^2(x)}{|x|^2} \le 4 \int_{\mathbb{R}^3} |\nabla w|^2 \quad \forall\ w \in C_0^\infty(\mathbb{R}^3), \tag{2.3}$$

we obtain

$$\int_\Omega \frac{w(x)v(x)}{|x|} \le 4\|\nabla w\|_{0,\Omega}\|v\|_{0,\Omega} \quad \forall\ w, v \in H_0^1(\Omega),$$

which together with the Young's inequality produces

$$\sum_{j=1}^{N_{atom}} Z_j \int_\Omega \frac{w^2(x)}{|x - r_j|} \le \|\nabla w\|_{0,\Omega}^2/2 + \Big(8N_{atom} \sum_{j=1}^{N_{atom}} Z_j^2\Big)\|w\|_{0,\Omega}^2 \ \ \forall\ w \in H_0^1(\Omega). \tag{2.4}$$

Thus we obtain (2.2) from the definition of $a(\cdot,\cdot)$ and the assumption $V_0 \in L^\infty(\Omega)$. This completes the proof. □

It is seen from Lemma 2.1 that there exists a $\mu > 0$ such that

$$C^{-1}\|w\|_{1,\Omega}^2 \le a_\mu(w, w) \quad \forall\ w \in H_0^1(\Omega) \tag{2.5}$$

for some constant $C > 0$, where

$$a_\mu(w, v) = a(w, v) + \mu(w, v), \quad w, v \in H_0^1(\Omega).$$

Note that (2.1) is equivalent to

$$a_\mu(u,v) = E(u,v) \quad \forall\ v \in H_0^1(\Omega) \tag{2.6}$$

with $E = \lambda + \mu$. Hence (2.1) has a countable sequence of real eigenvalues, $\lambda_1 < \lambda_2 \le \lambda_3 \le \cdots$, and the corresponding eigenfunctions in $H_0^1(\Omega)$, $u_1, u_2, u_3, \cdots$, which can be assumed to satisfy

$$(u_i, u_j) = \delta_{ij},\ i,j = 1,2,\cdots .$$

In the sequence $\{\lambda_j\}$, the λ_j's are repeated according to geometric multiplicity.

Although the coefficient V of (1.1) is singular, we have

Theorem 2.1. *If $(\lambda, u) \in \mathbb{R} \times H_0^1(\Omega)$ is an eigenpair of (2.1), then $u \in H_0^1(\Omega) \cap W^{2,p}(\Omega)$ $(2 \le p < q_0)$ for some $q_0 \in (2,3)$.*

Proof. Thanks to (2.3), we have that $Vu \in L^2(\Omega)$. Thus, we get from the regularity of the Poisson equation [14, 15] that

$$u = (-\triangle)^{-1}(-Vu + \lambda u) \in H^2(\Omega),$$

which together with Sobolev imbedding theorem leads to that $u \in C(\Omega)$.

Noting that if R_0 is the diameter of Ω, then from

$$\begin{aligned}\int_\Omega \frac{u^p(x)}{|x - r_j|^p} dx &\le \|u\|_{0,\infty,\Omega}^p \int_\Omega \frac{dx}{|x - r_j|^p} \\ &\le C\|u\|_{0,\infty,\Omega}^p \int_0^{r_j + R_0} \frac{dt}{t^{p-2}},\end{aligned}$$

we obtain that $Vu \in L^p(\Omega)$ $(2 \le p < 3)$. Therefore, there exists $q_0 \in (2,3)$ such that (see, e.g., [14, 15])

$$u = (-\triangle)^{-1}(-Vu + \lambda u) \in W^{2,p}(\Omega)\ \ \forall\ p \in [2, q_0),$$

due to $-Vu + \lambda u \in L^p(\Omega)(2 \le p < 3)$. This completes the proof. □

It is seen that some useful regularity of the general electronic Schrödinger equation in the mixed Sobolev space is presented in [40]. In our error analysis, however, we need the regularity in the standard Sobolev space as stated in Theorem 2.1.

Our analysis for the two-scale finite element eigenvalue approximation is based on the following crucial (but straightforward) property of eigenvalue and eigenfunction approximations (see, e.g., [4, 5] or [37]).

Proposition 2.1. *Let (λ, u) be an eigenpair of (2.1). For any $w \in H_0^1(\Omega) \setminus \{0\}$,*

$$\frac{a(w,w)}{(w,w)} - \lambda = \frac{a(w-u, w-u)}{(w,w)} - \lambda \frac{(w-u, w-u)}{(w,w)}. \tag{2.7}$$

3. Finite Element Discretization

Assume that $T^h(\Omega) = \{\tau\}$ is a mesh of Ω with mesh-size function $h(x)$ whose value is the diameter h_τ of the element τ containing x. One basic assumption on the mesh is that

A.0. There exists $\nu \ge 1$ such that

$$h^\nu \le Ch(x), \quad x \in\ \Omega, \tag{3.1}$$

where $h = \max_{x\in\Omega} h(x)$ is the (largest) mesh size of $T^h(\Omega)$.

This is apparently a very mild assumption and most practical meshes satisfy this assumption. For simplicity, let $T^h(\Omega)$ consist of shape-regular simplices and define $S^h(\Omega)$ to be a space of continuous functions on Ω such that for $v \in S^h(\Omega), v$ restricted to each τ is a linear, namely

$$S^h(\Omega) = \{v \in C(\bar{\Omega}) : v\mid_\tau \quad \text{is linear} \ \ \forall\ \tau \in T^h(\Omega)\}. \tag{3.2}$$

Set $S_0^h(\Omega) = S^h(\Omega) \cap H_0^1(\Omega)$. These are Lagrange finite element spaces and we refer to [11, 12] for their basic properties. For instance, there holds

$$\inf_{v\in S_0^h(\Omega)} (\|h^{-1}(w-v)\|_{0,\Omega} + \|w-v\|_{1,\Omega}) \le C\|h^s w\|_{1+s,\Omega}, \quad 0 \le s \le 1, \tag{3.3}$$

which will be used in our analysis. If $P_h : H_0^1(\Omega) \longrightarrow S_0^h(\Omega)$ satisfies

$$a_\mu(w - P_h w, v) = 0 \ \ \forall\ v \in S_0^h(\Omega)\ \forall\ w \in H_0^1(\Omega), \tag{3.4}$$

then (see, e.g., [11, 12])

$$\|w - P_h w\|_{0,\Omega} + h\|w - P_h w\|_{1,\Omega} \le Ch^{1+s}\|w\|_{1+s,\Omega}, \quad 0 \le s \le 1. \tag{3.5}$$

3.1. One-scale discretization scheme

A standard finite element scheme for (2.1) is a one-scale discretization: Find a pair of (λ_h, u_h), where λ_h is a number and $0 \ne u_h \in S_0^h(\Omega)$, satisfying

$$a(u_h, v) = \lambda_h(u_h, v) \quad \forall\ v \in S_0^h(\Omega) \tag{3.6}$$

or equivalently

$$a_\mu(u_h, v) = E_h(u_h, v) \quad \forall\ v \in S_0^h(\Omega) \tag{3.7}$$

with $E_h = \lambda_h + \mu$. One sees from (2.5) that (3.6) has a finite sequence of eigenvalues

$$\lambda_{1,h} < \lambda_{2,h} \le \cdots \le \lambda_{n_h,h}, \quad n_h = \dim\ S_0^h(\Omega),$$

whose corresponding eigenfunctions, $u_{1,h}, u_{2,h}, \cdots, u_{n_h,h}$, satisfy

$$(u_{i,h}, u_{j,h}) = \delta_{ij},\ i, j = 1, 2, \cdots.$$

It follows directly from the minimum-maximum principle (see [5] or [9]) that

$$\lambda_i \le \lambda_{i,h}, \quad i = 1, 2, \cdots, n_h.$$

Set

$$\begin{aligned}
\rho(h) &= \sup_{f\in L^2(\Omega), \|f\|_{0,\Omega}=1} \inf_{v\in S_0^h(\Omega)} \|(-\triangle + V)^{-1} f - v\|_{1,\Omega},\\
\delta_h(\lambda_i) &= \sup_{w\in M(\lambda_i), \|w\|_{0,\Omega}=1} \inf_{v\in S_0^h(\Omega)} \|w - v\|_{1,\Omega},\\
M(\lambda_i) &= \{w \in H_0^1(\Omega) : w \text{ is an eigenfunction of (2.1) corresponding to } \lambda_i\}.
\end{aligned}$$

Applying the classical theory (see, e.g., [4, 5, 9] or [37]) to (2.6) and (3.7), we then have

Proposition 3.1. (*i*) *For any* $u_{i,h}$ *of* (3.6) ($i = 1, 2, \cdots, n_h$), *there is an eigenfunction* u^i *of* (2.1) *corresponding to* λ_i *satisfying* $\|u^i\|_{0,\Omega} = 1$ *and*

$$\|u^i - u_{i,h}\|_{1,\Omega} \leq C_i \delta_h(\lambda_i). \tag{3.8}$$

Moreover,

$$\|u^i - u_{i,h}\|_{0,\Omega} \leq C_i \rho(h) \|u^i - u_{i,h}\|_{1,\Omega}. \tag{3.9}$$

(*ii*) *For the eigenvalues* λ_i *and* $\lambda_{i,h}$,

$$\lambda_i \leq \lambda_{i,h} \leq \lambda_i + C_i \delta_h^2(\lambda_i), \tag{3.10}$$

where C_i *is some constant depending on* i *but not on the mesh parameter* h.

Combining Theorem 2.1 and Proposition 3.1, we have the following error estimates for the one-scale discretization.

Theorem 3.1. *Let* (λ, u) *be the solution of* (2.1) *and* (λ_h, u_h) *be the associated solution of* (3.6). *Then there hold*

$$\lambda_h - \lambda + \|u - u_h\|_{0,\Omega} + h\|u - u_h\|_{1,\Omega} \leq Ch^2. \tag{3.11}$$

3.2. Two-scale discretization scheme

To reduce the computational cost, we shall now introduce a two-scale discretization scheme. The two-scale finite element discretization approach for eigenvalue problems may be dated back to [19] (see also a general formwork in [37] when $a(\cdot, \cdot)$ is a positive symmetric definite bilinear form). In this subsection, we will modify and generalize this approach to solve (2.1). With our two-scale scheme, the solution of an eigenvalue problem with singular coefficient on a fine grid is reduced to the solution of an eigenvalue problem with singular coefficient on a much coarser gird and a solution of linear algebraic system associated with the Poisson equation on the fine grid.

Let $H \gg h$ and assume that $S_0^H(\Omega) \subset S_0^h(\Omega)$. We consider the approximation of any eigenvalue λ of (2.1). Here and hereafter we let λ_H be the finite element eigenvalue of (3.6) corresponding to $S_0^H(\Omega)$, which satisfies

$$|\lambda_H - \lambda| \leq CH^2. \tag{3.12}$$

Our two-scale discretization scheme for (2.1) is constructed as follows:

Two-scale discretization scheme

Step 1. Find $(\lambda_H, u_H) \in \mathbb{R} \times S_0^H(\Omega)$ such that $\|u_H\|_{0,\Omega} = 1$ and

$$a(u_H, v) = \lambda_H(u_H, v) \quad \forall\ v \in S_0^H(\Omega).$$

Step 2. Find $u^h \in S_0^h(\Omega)$ satisfying

$$\int_\Omega \nabla u^h \nabla v = \lambda_H(u_H, v) - (Vu_H, v) \quad \forall\ v \in S_0^h(\Omega).$$

Step 3. Compute the Rayleigh quotient:

$$\lambda^h = \frac{a(u^h, u^h)}{(u^h, u^h)}.$$

It is seen from Proposition 3.1 that associated with the eigenfunction u_H obtained by Step 1 in the two-scale scheme, there exists an exact eigenfunction u of (2.1) satisfying $\|u\|_{0,\Omega} = 1$ and

$$\|u - u_H\|_{0,\Omega} + H\|u - u_H\|_{1,\Omega} \leq CH^2. \tag{3.13}$$

For this two-scale scheme, the resulting approximation still maintains an optimal accuracy. Indeed, we have

Theorem 3.2. *Let (λ^h, u^h) be obtained from the two-scale discretization scheme. If $H = \mathcal{O}(h^{1/2+\varepsilon})$ for some $\varepsilon \in (0, 1/2)$, then*

$$|\lambda - \lambda^h| + h\|u - u^h\|_{1,\Omega} \leq C_\varepsilon h^2. \tag{3.14}$$

Proof. Note that for $q \in (2, \infty)$, there holds

$$\int_\Omega \frac{1}{|x - r_j|^{6q/(5q-6)}} < \infty, \quad j = 1, 2, \cdots, N_{atom},$$

while the Sobolev imbedding theorem and the Hörder inequality imply

$$\int_\Omega \frac{wv}{|x - r_j|} \leq \left(\int_\Omega \frac{1}{|x - r_j|^{6q/(5q-6)}} \right)^{(5q-6)/(6q)} \|w\|_{0,q,\Omega}\|v\|_{0,6,\Omega} \quad \forall\ w \in L^q(\Omega)\ \forall\ v \in L^6(\Omega).$$

Hence we have

$$|(V(u_H - P_h u), v)| \leq C_q\|u_H - P_h u\|_{0,q,\Omega}\|v\|_{1,\Omega} \quad \forall v \in H_0^1(\Omega). \tag{3.15}$$

From the construction of u^h, we immediately obtain

$$\int_\Omega \nabla(u^h - P_h u)\nabla v = (\lambda_H - \lambda)(u, v) + \lambda_H(u_H - u, v) + (V(P_h u - u_H), v) \quad \forall v \in S_0^h(\Omega),$$

which together with (3.15) leads to

$$\|\nabla(u^h - P_h u)\|_{0,\Omega} \leq C(|\lambda_H - \lambda| + \lambda_H\|u_H - u\|_{0,\Omega} + \|u_H - P_h u\|_{0,q,\Omega}) \tag{3.16}$$

is true for any $q \in (2, \infty)$.

Using (3.12), (3.13) and the inverse inequality, we then get

$$\|\nabla(u^h - P_h u)\|_{0,\Omega} \leq CH^2 + C_q h_m^{3(1/q-1/2)}\|u_H - P_h u\|_{0,\Omega},$$

where $h_m = \min_{x\in\Omega} h(x)$. Thus, combining (3.5), (3.13) and (3.1), we arrive at

$$\|\nabla(u^h - P_h u)\|_{0,\Omega} \leq C_q H^2 h^{3\nu(1/q-1/2)}.$$

Choosing $q = 6\nu/(3\nu - 4\varepsilon)$, we conclude that

$$\|\nabla(u^h - u)\|_{0,\Omega} \leq C_\varepsilon h, \tag{3.17}$$

which together with Proposition 2.1 completes the proof. □

Remark 3.1. We may also obtain similar results for the following scheme (cf. [37]):

Step 1. Find $(\lambda_H, u_H) \in \mathbb{R} \times S_0^H(\Omega)$ such that $\|u_H\|_{0,\Omega} = 1$ and

$$a(u_H, v) = \lambda_H(u_H, v) \quad \forall\ v \in S_0^H(\Omega).$$

Step 2. Find $u^h \in S_0^h(\Omega)$ satisfying

$$a(u^h, v) = \lambda_H(u_h, v) \quad \forall\ v \in S_0^h(\Omega).$$

Step 3. Compute the Rayleigh quotient:

$$\lambda^h = \frac{a(u^h, u^h)}{(u^h, u^h)}.$$

Similar to [38], we may design some local and parallel version of the two-scale finite element scheme.

4. Applications to Electronic Structure Computation

In this section, we shall construct some two-scale finite element discretization scheme for electronic structure computations and apply the scheme to obtain the ground state energies for several typical atoms. Physically, the ground state energy of a system is associated with some linear or nonlinear eigenvalue problem which is set in the whole space $\mathbb{R}^3$. Computationally, we can only carry out in some bounded domain. As a result, it is expected that the exact conclusion from the numerical results may not agree well with the theory. Anyway, it is shown by our numerical experiments that the two-scale discretization scheme is very efficient and recommended for quantum eigenvalue computations.

4.1. Two-scale discretizations for nonlinear Schrödinger equations

The two-scale approach may also be applied to the nonlinear eigenvalue problems. For instance, it can be used for the following Kohn-Sham equation: Find

$$(\lambda_i, u_i) \in \mathbb{R} \times H_0^1(\mathbb{R}^3), \quad i = 1, \cdots, N_{occ},$$

such that

$$(-\Delta + V_{ne} + V_0(\rho))\, u_i = \lambda_i u_i \text{ in } \mathbb{R}^3, \tag{4.1a}$$

$$\int_{\mathbb{R}^3} u_i u_j = \delta_{ij}, \quad i, j, = 1, \cdots, N_{occ}, \tag{4.1b}$$

where N_{occ} the total number of the occupied orbits, V_{ne} and ρ are defined by (1.2) and (1.4), respectively.

Since the Kohn-Sham equations (4.1) are nonlinear eigenvalue system, we need to linearize and solve them iteratively, which is called the self-consistent approach, see, e.g., [6, 16, 23, 33]. The self-consistent iteration is described as follows:

Self Consistent Iteration

1. Given an initial ρ_{in} by superposing atomic charge densities and obtain $V_0(\rho_{in})$.
2. Find u_i satisfies (4.1b) and
$$\left(-\frac{1}{2}\Delta + V_{ne} + V_0(\rho_{in})\right) u_i = \lambda_i u_i \ \text{ in } \mathbb{R}^3. \tag{4.2}$$
3. Set $\rho_{out} = \sum_{i=1}^{N_{occ}} c_i |u_i|^2$.
4. If self-consistent, stop, else repeat from Step 2.

Consequently, the main computation in solving the Kohn-Sham equations is the repeated solution of the linear eigenvalue problems (4.2) when $\mathbb{R}^3$ is replaced by some bounded domain $\Omega \subset \mathbb{R}^3$. And we can apply the two-scale finite element discretization scheme designed in Section 3 to solve the linear eigenvalue problems (4.2). Given an initial density ρ_{in}, we may construct the following two-scale discretization scheme:

Step 1. Find $(\lambda_{i,H}, u_{i,H}) \in \mathbb{R} \times S_0^H(\Omega)$ such that $u_{i,H}$ satisfies (4.1b) and
$$(\nabla u_{i,H}, \nabla v) + (V_{ne} u_{i,H} + V_0(\rho_{in}) u_{i,H}, v) = \lambda_{i,H}(u_{i,H}, v) \quad \forall\ v \in S_0^H(\Omega). \tag{4.3}$$
Step 2. Find $u_i^h \in S_0^h(\Omega)$ $(i = 1, \cdots, N_{occ})$ satisfying
$$(\nabla u_i^h, \nabla v) = \lambda_{i,H}(u_{i,H}, v) - (V_{ne} u_{i,H} + V_0(\rho_{in}) u_{i,H}, v) \quad \forall\ v \in S_0^h(\Omega). \tag{4.4}$$
Step 3. Compute the Rayleigh quotient:
$$\lambda_i^h = \frac{(\nabla u_i^h, \nabla u_i^h) + (V_{ne} u_i^h + V_0(\rho^h) u_i^h, u_i^h)}{(u_i^h, u_i^h)}, \quad i = 1, \cdots, N_{occ}, \tag{4.5}$$
where
$$\rho^h = \sum_{i=1}^{N_{occ}} c_i |u_i^h|^2. \tag{4.6}$$

In the above discretization scheme, it is noted that the singular eigenvalue problem is solved only on a relatively coarse grid and hence it would be significant in electronic structure computations.

We consider to apply piecewise linear finite elements to solve (4.2). As we see, it is expensive to solve 3-dimensional singular problems by using uniform grids when accurate approximate solutions are required. Thus, in our computations, we will employ adaptive grids instead of uniform grids. The globally coarse grids that we will use are some adaptive finite element grids, which are constructed from the bisection approaches [3] and the error indicators
$$\eta_\tau = \eta_{\tau,G} = \|A^{-1/2}(G_h u_h - A\nabla u_h)\|_{0,\tau}^2, \quad \tau \in T^h(\Omega),$$
where $A = \mathrm{diag}(1/2, 1/2, 1/2)$ and the locally averaging operator $G_h : S_0^h(\Omega) \to S^h(\Omega) \times S^h(\Omega)$

is defined by (see, e.g., [22, 29, 39, 43])

$$G_h v = \sum_{z\in\partial^2 T^h} (A\nabla v)_z \phi_z, \quad (A\nabla v)_z = \sum_{j=1}^{J_z} \alpha_z^j (A(z)\nabla v)_{\tau_z^j} \ \ \forall\ v \in S_0^h(\Omega).$$

Here $\partial^2 T^h$ is the set of all vertices of $T^h(\Omega)$, ϕ_z is the nodal basis function of $S^h(\Omega)$ corresponding to $z \in \partial^2 T^h$,

$$\omega_z = \bigcup_{j=1}^{J_z} \{\tau_z^j : \tau_z^j \in T^h(\Omega), z \in \tau_z^j\}, \quad \sum_{j=1}^{J_z} \alpha_z^j = 1 \ \text{ with } \alpha_z^j \geq 0$$

(for instance, $\alpha_z^j = 1/J_z$ $\alpha_z^j = |\tau_z^j|/|\omega_z|$), and $J_z = \#\{\tau_z : \tau_z \in T^h(\Omega), z \in \tau_z\}$ is the number of elements containing z (see, e.g., [22, 29]). While the fine grids are obtained from the globally coarse grids directly by using some tetrahedral bisection strategy.

4.2. Computation of total energy

The most important one for the molecular system, is the total energy of the ground state

$$E_{total} = \sum_{i=1}^{N_{occ}} c_i\lambda_i - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)dxdy}{|x-y|} + E_{xc}(\rho) - \int_{\mathbb{R}^3} \rho(x)V_{xc}(\rho)dx + \frac{1}{2}\sum_{p,q=1,p\neq q}^{N_{atom}} \frac{Z_pZ_q}{|r_p - r_q|},$$

where $E_{xc}(\rho)$ is the exchange-correlation energy, λ_i $(i = 1, \cdots, N_{occ})$ are the eigenvalues of (4.1), N_{atom} is the total number of the atoms, Z_p is the electron number of the p-th atom, and r_p is the position of the p-th atom.

Now we present several numerical examples in quantum chemistry. These examples are physically set in $\mathbb{R}^3$. But in our computations, we have to pose them in some bounded domain Ω in $\mathbb{R}^3$, which is reasonable since the wave functions u exponentially decay to zero (see, e.g., [2, 13, 30]). In the first example, we use $\Omega = (-5.0, 5.0)^3$ while in other three examples, we set $\Omega = (-10.0, 10.0)^3$. We apply the self-consistent approach to linearize (4.1) and use the two-scale finite element discretization scheme to solve (4.2) on each iteration. The numerical total energy of the ground state is defined by

$$E_{total}^h = \sum_{i=1}^{N_{occ}} c_i\lambda_i^h - \frac{1}{2}\int_\Omega\int_\Omega \frac{\rho^h(x)\rho^h(y)dxdy}{|x-y|} + E_{xc}(\rho^h) - \int_\Omega \rho^h(x)V_{xc}(\rho^h)dx + \frac{1}{2}\sum_{p,q=1,p\neq q}^{N_{atom}} \frac{Z_pZ_q}{|r_p - r_q|},$$

where λ^h and ρ^h are computed by (4.5) and (4.6), respectively.

Example 4.1. *Consider the oscillator equation*

$$-\frac{1}{2}\Delta u + \frac{1}{2}|x|^2 u = \lambda u. \tag{4.7}$$

The first eigenvalue of (4.7) *is* 1.5.

Table 4.1: Numerical solutions of Example 4.1.

N_H	N_h	λ_H	λ^h	$\lambda_H - \lambda$	$\lambda^h - \lambda$
567	49313	1.595172e+00	1.512358e+00	9.517151e-02	1.235783e-02
1635	108305	1.536066e+00	1.504803e+00	3.606643e-02	4.803290e-03
4873	316377	1.515997e+00	1.502279e+00	1.599673e-02	2.279329e-03
14673	335473	1.506393e+00	1.500774e+00	6.393485e-03	7.744004e-04

Table 4.2: Numerical solutions of Example 4.2.

N_H	N_h	λ_H	λ^h	$\lambda_H - \lambda$	$\lambda^h - \lambda$
3423	217697	-4.846029e-01	-4.976628e-01	1.539713e-02	2.337195e-03
6493	347020	-4.902730e-01	-4.986565e-01	9.727038e-03	1.343541e-03
14457	869513	-4.944337e-01	-4.992690e-01	5.566281e-03	7.310055e-04

Table 4.3: The results of helium atoms in the references.

Equation	method	reference	unknowns	energy	ΔE(%)
Schrödinger	FEM	[27]	6,720	-2.90289	
Hatree-Fock	FEM Hatree	[36]	500,000	-2.8522	0.33
Hatree-Fock	Hatree	[35]	unknown	-2.861678	
Kohn-Sham	X_α	[33]	unknown	-2.72	

The coefficient in (4.7) is smooth. It is seen from Tables 4.1 that the numerical solutions obtained by the two-scale scheme are much cheaper than that solved by the one-scale scheme.

Example 4.2. *Consider the Schrödinger equation for hydrogen atoms*

$$-\frac{1}{2}\Delta u - \frac{1}{|x|}u = \lambda u. \tag{4.8}$$

The first eigenvalue of (4.8) *is* -0.5.

This is a typical example of Schrödinger equation (1.1). The numerical results are shown in Table 4.2, which support that our two-scale scheme is efficient.

In the last two examples, we apply the X_α method to approximate V_{xc} (see, e.g., [23, 24]), namely, we choose $V_{xc} = -3\alpha(3\rho/(4\pi))^{1/3}$ with $\alpha = 0.77298$ in Example 4.3 and 0.781 in Example 4.4 respectively.

Example 4.3. *Consider the Kohn-Sham equation for helium atoms*

$$\left(-\frac{1}{2}\Delta - \frac{Z}{|x|} + \int \frac{\rho(y)}{|x-y|}dy + V_{xc}(\rho)\right)u = \lambda u, \tag{4.9}$$

where $Z = 2$ *and* $\rho = 2|u|^2$.

The value of the total energy is about -2.90, which is referred to Table 4.3 for relevant references. Our numerical results of Example 4.3 are presented in Tables 4.4 and 4.5. It is seen from Tables 4.4 and 4.5 that the two-scale finite element discretization is very efficient.

Example 4.4. *We compute the numerical solution to the Kohn-Sham equation for lithium atoms*

$$\left(-\frac{1}{2}\Delta - \frac{Z}{|x|} + \int \frac{\rho(y)}{|x-y|}dy + V_{xc}(\rho)\right)u = \lambda u, \tag{4.10}$$

Table 4.4: Example 4.3: the two-scale scheme.

N_H	N_h	E_H	E^h	CPU time(secs.)
497	45193	-1.960392e+00	-2.724644e+00	1.506124e+02
515	46225	-2.262290e+00	-2.897167e+00	1.692926e+02
679	55041	-2.484488e+00	-2.919425e+00	2.212407e+02
1029	76601	-2.570763e+00	-2.913713e+00	3.179586e+02
1191	85409	-2.637899e+00	-2.918088e+00	3.754206e+02
2023	136257	-2.749499e+00	-2.913211e+00	6.212172e+02
3771	239249	-2.795651e+00	-2.903013e+00	1.102675e+03

Table 4.5: Example 4.3: the one-scale scheme; CPU time over the finest grid is 8.181e+03(secs.).

N_h	E_h	N_h	E_h	N_h	E_h
679	-2.484488e+00	2593	-2.777429e+00	31121	-2.843077e+00
1125	-2.570763e+00	3771	-2.795651e+00	45949	-2.845915e+00
1191	-2.637899e+00	5067	-2.816476e+00	102467	-2.846857e+00
1581	-2.707981e+00	6353	-2.826997e+00		
2023	-2.749499e+00	9817	-2.835543e+00		

Table 4.6: Example 4.4: the two-scale scheme.

N_H	N_h	E_H	E^h	CPU time(secs.)
661	7277	-6.198066e+00	-7.174421e+00	1.429924e+02
1089	10437	-6.579749e+00	-7.319871e+00	2.083374e+02
1265	11845	-6.781116e+00	-7.387384e+00	2.869570e+02
1799	15985	-7.029342e+00	-7.413942e+00	4.173074e+02
3093	25629	-7.175916e+00	-7.440785e+00	6.309228e+02
10247	78769	-7.359014e+00	-7.475724e+00	1.941627e+03

Table 4.7: Example 4.4: the one-scale scheme; CPU time over the finest grid is 2.8020e+04(secs.).

N_h	E_h	N_h	E_h	N_h	E_h
1119	-6.612568e+00	3093	-7.175916e+00	15761	-7.382195e+00
1265	-6.781116e+00	3773	-7.221930e+00	23229	-7.400717e+00
1565	-6.949223e+00	5641	-7.281180e+00	31521	-7.410653e+00
1799	-7.029342e+00	7653	-7.335161e+00	74715	-7.422772e+00
2197	-7.124327e+00	10247	-7.359014e+00	102859	-7.427083e+00

where $Z = 3$, $\rho = 2|u_1|^2 + |u_2|^2$, and u_1 and u_2 are eigenfunctions associated with the first two minimum eigenvalues.

The value of the total energy is about -7.47807 [42]. Our numerical results of Example 4.4 are provided in Tables 4.6 and 4.7, which again indicate that our two-scale scheme is efficient.

5. Concluding Remarks

In this paper, we have studied some finite element approximations for Schrödinger (type) equations. In particular, we have proposed and analyzed a two-scale finite element discretization scheme and applied the scheme to several typical electronic structure computations very

successfully. With the numerical analysis in Section 3, we are also able to design local and parallel finite element algorithms for solving the Schrödinger equations based on the two-scale discretizations (cf. [21, 28, 38]). We believe that the two-scale computational approach is a powerful technique in obtaining accurate and efficient approximations for large scale quantum eigenvalue problems. Indeed, to apply the approach to complex quantum chemistry computations is our on-going project. In this case, however, many practical issues, including the local and parallel computations for the kinetic energy term, the implementation details for local density approximations and pseudopotentials, need to be addressed. We will report our progresses in our forthcoming papers.

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