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

Xingao Gong
Department of Physics, Fudan University, Shanghai 200433, China
Email: ??

Lihua Shen
Department of Mathematics, Capital Normal University, Beijing 100037, China
Email: ??

Dier Zhang
Department of Physics, Fudan University, Shanghai 200433, China
Email: ??

Aihui Zhou
LSEC, ICMSEC, Academy of Mathematics and Systems Science, Chinese Academy of Sciences,
Beijing 100080, China
Email: azhou@lsec.cc.ac.cn

Dedicated to the 70th birthday of Professor Junzhi Cui

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.

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

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

(1.1)

where \(\Omega\) 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

\[
V_{ne}(x) = -\sum_{j=1}^{N_{\text{atom}}} \frac{Z_j}{|x - r_j|}
\]

(1.2)

with \(r_j \in \Omega\), \(Z_j\) some positive constant \((j = 1, \cdots, N_{\text{atom}})\), where \(N_{\text{atom}}\) is the total number of the atoms in the system.
It is known that modern electronic structure computations require solving the following Kohn-Sham equations (see, e.g., [6, 16, 23, 24])

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

where $Z_j$ is the valance charge of this ion (nucleus plus core electrons), $r_j$ is the position of the $j$-th atom ($j = 1, \ldots, N_{\text{atom}}$), and $\rho = \sum_{i=1}^{N_{\text{occ}}} c_i |u_i|^2$.

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 become 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 solving (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].
several applications to ground state computations of atoms in quantum chemistry are reported.

Finally, some concluding remarks are given.

2. Preliminaries

Let $\Omega$ 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 $H^1_0(\Omega) = \{ v \in H^1(\Omega) : v|_{\partial \Omega} = 0 \}$, where $v|_{\partial \Omega} = 0$ 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 $a(w, v) = \int_\Omega \nabla w \nabla v + V w v, \ w, v \in H^1_0(\Omega)$, where $V$ is that stated in Section 1.

A number $\lambda$ is called an eigenvalue of the form $(\cdot, \cdot)$ relative to the form $(\cdot, \cdot)$ if there is a nonzero vector $u \in H^1_0(\Omega)$, called an associated eigenfunction, satisfying

$$a(u, v) = \lambda (u, v) \ \forall \ v \in H^1_0(\Omega). \tag{2.1}$$

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

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

$$\|w\|_{1,\Omega}^2 - C^{-1} \|w\|_{0,\Omega}^2 \leq 2a(w, w) \ \forall \ w \in H^1_0(\Omega). \tag{2.2}$$

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

$$\int_{\mathbb{R}^3} \frac{w^2(x)}{|x|^2} \leq 4 \int_{\mathbb{R}^3} |\nabla w|^2 \ \forall \ w \in C^\infty_0(\mathbb{R}^3), \tag{2.3}$$

we obtain

$$\int_\Omega \frac{w(x)v(x)}{|x|} \leq 4\|\nabla w\|_{0,\Omega}\|v\|_{0,\Omega} \ \forall \ w, v \in H^1_0(\Omega),$$

which together with the Young’s inequality produces

$$\sum_{j=1}^{N_{\text{atom}}} Z_j \int_\Omega \frac{w^2(x)}{|x - r_j|} \leq \|\nabla w\|_{0,\Omega}^2/2 + \left(8N_{\text{atom}} \sum_{j=1}^{N_{\text{atom}}} Z_j^2\right) \|w\|_{0,\Omega}^2 \ \forall \ w \in H^1_0(\Omega). \tag{2.4}$$

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

$$C^{-1} \|w\|_{1,\Omega}^2 \leq a_\mu(w, w) \ \forall \ w \in H^1_0(\Omega) \tag{2.5}$$

for some constant $C > 0$, where

$$a_\mu(w, v) = a(w, v) + \mu(w, v), \ w, v \in H^1_0(\Omega).$$
Note that (2.1) is equivalent to
\[ a(\mu(u, v) = E(u, v) \quad \forall v \in H^1_0(\Omega) \] (2.6)
with \( E = \lambda + \mu \). Hence (2.1) has a countable sequence of real eigenvalues, \( \lambda_1 < \lambda_2 \leq \lambda_3 \leq \cdots \), and the corresponding eigenfunctions in \( H^1_0(\Omega) \), \( u_1, u_2, u_3, \cdots \), which can be assumed to satisfy
\[ (u_i, u_j) = \delta_{ij}, \quad i, j = 1, 2, \cdots . \]
In the sequence \( \{\lambda_j\} \), the \( \lambda_j \)'s are repeated according to geometric multiplicity.

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

**Theorem 2.1.** If \((\lambda, u) \in \mathbb{R} \times H^1_0(\Omega)\) is an eigenpair of (2.1), then \( u \in H^1_0(\Omega) \cap W^{2, p}(\Omega) \) (\( 2 \leq p < q_0 \)) for some \( q_0 \in (2, 3) \).

**Proof.** Thanks to (2.3), we have that \( V u \in L^2(\Omega) \). Thus, we get from the regularity of the Poisson equation [14, 15] that
\[ u = (-\Delta)^{-1} (-V u + \lambda u) \in H^2(\Omega), \]
which together with Sobolev imbedding theorem leads to that \( u \in C(\Omega) \).

Noting that if \( R_0 \) is the diameter of \( \Omega \), then from
\[
\int_{\Omega} \frac{w^p(x)}{|x - r_j|^p} \, dx \leq \|u\|^{p}_{0, \infty, \Omega} \int_{\Omega} \frac{dx}{|x - r_j|^p} \\
\leq C\|u\|^p_{0, \infty, \Omega} \int_0^{r_j + R_0} \frac{dt}{t^{p-2}},
\]
we obtain that \( V u \in L^p(\Omega) \) (\( 2 \leq p < 3 \)). Therefore, there exists \( q_0 \in (2, 3) \) such that (see, e.g., [14, 15])
\[ u = (-\Delta)^{-1} (-V u + \lambda u) \in W^{2, p}(\Omega) \quad \forall p \in [2, q_0), \]
due to \(-V u + \lambda u \in L^p(\Omega)(2 \leq p < 3)\). This completes the proof. \( \square \)

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 \((\lambda, u)\) be an eigenpair of (2.1). For any \( w \in H^1_0(\Omega) \setminus \{0\} \),
\[
\frac{a(w, w) - \lambda}{a(w, w)} = \frac{a(w - u, w - u)}{a(w, w)} - \lambda \frac{a(w - u, w - u)}{a(w, w)}, \quad (2.7)
\]

### 3. Finite Element Discretization

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

**A.0.** There exists \( \nu \geq 1 \) such that
\[
h^\nu \leq C h(x), \quad x \in \Omega, \quad (3.1)
\]
where \( h \) 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 \( \Omega \) such that for \( v \in S^h(\Omega) \), \( v \) restricted to each \( \tau \) is a linear, namely

\[
S^h(\Omega) = \{ v \in C(\bar{\Omega}) : v|_\tau \text{ is linear} \ \forall \ \tau \in T^h(\Omega) \}.
\]  

Set \( S^h_0(\Omega) = S^h(\Omega) \cap H^1_0(\Omega) \). These are Lagrange finite element spaces and we refer to [11, 12] for their basic properties. For instance, there holds

\[
\inf_{v \in S^h_0(\Omega)} (\| h^{-1}(w-v) \|_{0,\Omega} + \| w-v \|_{1,\Omega}) \leq C \| h^s w \|_{1+s,\Omega}, \ 0 \leq s \leq 1,
\]

which will be used in our analysis. If \( P_h : H^1_0(\Omega) \rightarrow S^h_0(\Omega) \) satisfies

\[
a_\mu(w - P_h w, v) = 0 \ \forall \ v \in S^h_0(\Omega) \ \forall \ w \in H^1_0(\Omega),
\]

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

\[
\| w - P_h w \|_{0,\Omega} + h \| w - P_h w \|_{1,\Omega} \leq C h^{1+s} \| w \|_{1+s,\Omega}, \ 0 \leq s \leq 1.
\]

### 3.1. One-scale discretization scheme

A standard finite element scheme for (2.1) is a one-scale discretization: Find a pair of \( (\lambda_h, u_h) \), where \( \lambda_h \) is a number and \( 0 \neq u_h \in S^h_0(\Omega) \), satisfying

\[
a(u_h, v) = \lambda_h(u_h, v) \ \forall \ v \in S^h_0(\Omega)
\]

or equivalently

\[
a_\mu(u_h, v) = E_h(u_h, v) \ \forall \ v \in S^h_0(\Omega)
\]

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

\[
\lambda_{1,h} < \lambda_{2,h} \leq \cdots \leq \lambda_{n_h,h}, \ n_h = \dim S^h_0(\Omega),
\]

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

\[
\lambda_i \leq \lambda_{i,h}, \ i = 1,2,\cdots,n_h.
\]

Set

\[
\rho(h) = \sup_{f \in L^2(\Omega), \| f \|_{0,\Omega} = 1} \inf_{v \in S^h_0(\Omega)} \| (-\Delta + V)^{-1} f - v \|_{1,\Omega},
\]

\[
\delta_h(\lambda_i) = \sup_{w \in M(\lambda_i), \| w \|_{0,\Omega} = 1} \inf_{v \in S^h_0(\Omega)} \| w - v \|_{1,\Omega},
\]

\[
M(\lambda_i) = \{ w \in H^1_0(\Omega) : w \text{ is an eigenfunction of (2.1) corresponding to } \lambda_i \}.
\]

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) $(i = 1, 2, \cdots, nh)$, there is an eigenfunction $u^i$ of (2.1) corresponding to $\lambda_i$ satisfying $\|u^i\|_{0, \Omega} = 1$ and

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

Moreover,

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

(3.8)

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

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

(3.9)

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 $(\lambda, u)$ be the solution of (2.1) and $(\lambda_h, u_h)$ be the associated solution of (3.6). Then there hold

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

(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 grid and a solution of linear algebraic system associated with the Poisson equation on the fine grid.

Let $H \gg h$ and assume that $S^H_0(\Omega) \subset S^h_0(\Omega)$. We consider the approximation of any eigenvalue $\lambda$ of (2.1). Here and hereafter we let $\lambda_H$ be the finite element eigenvalue of (3.6) corresponding to $S^H_0(\Omega)$, which satisfies

$$|\lambda_H - \lambda| \leq CH^2.$$  

(3.12)

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

<table>
<thead>
<tr>
<th>Two-scale discretization scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1. Find $(\lambda_H, u_H) \in \mathbb{R} \times S^H_0(\Omega)$ such that $|u_H|_{0, \Omega} = 1$ and $a(u_H, v) = \lambda_H(u_H, v) \ \forall \ v \in S^H_0(\Omega)$.</td>
</tr>
<tr>
<td>Step 2. Find $u_h \in S^h_0(\Omega)$ satisfying $\int_{\Omega} \nabla u^h \nabla v = \lambda_H(u_H, v) - (V u_H, v) \ \forall \ v \in S^h_0(\Omega)$.</td>
</tr>
<tr>
<td>Step 3. Compute the Rayleigh quotient: $\lambda^h = \frac{a(u^h, u^h)}{(u^h, u^h)}$.</td>
</tr>
</tbody>
</table>
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 \((\lambda^h, u^h)\) 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

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

while the Sobolev imbedding theorem and the Hölder inequality imply

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

Hence we have

\[
|\langle V(u_H - P_h u), v \rangle| \leq C_q \|u_H - P_h u\|_{0,q,\Omega} \|v\|_{1,\Omega}, \quad \forall \ v \in H^1_0(\Omega). \tag{3.15}
\]

From the construction of \( u^h \), we immediately obtain

\[
\int_{\Omega} \nabla(u^h - P_h u) \nabla v = (\lambda H - \lambda)(u,v) + \lambda_H(u_H - u,v) + \langle V(P_h u - u_H), v \rangle \quad \forall v \in S^h_0(\Omega),
\]

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

\[
\|\nabla(u^h - P_h u)\|_{0,\Omega} \leq CH^2 + C_q h_m^{5/2(1/2)} \|u_H - P_h u\|_{0,\Omega},
\]

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

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

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. \( \square \)
**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 \(u_h \in S_h(\Omega)\) satisfying
\[
a(u_h, v) = \lambda_H(u_h, v) \quad \forall \ v \in S_h(\Omega).
\]

**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
\[
(\lambda_i, u_i) \in \mathbb{R} \times H^1_0(\mathbb{R}^3), \quad i = 1, \cdots, N_{occ},
\]

such that
\[
- (\Delta + V_{ne} + V_0(\rho)) u_i = \lambda_i u_i \text{ in } \mathbb{R}^3, \quad i = 1, \cdots, N_{occ},
\]
\[
\int_{\mathbb{R}^3} u_i u_j = \delta_{ij}, \quad i, j = 1, \cdots, N_{occ},
\]
where \(N_{occ}\) the total number of the occupied orbits, \(V_{ne}\) and \(\rho\) 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 $\rho_{in}$ by superposing atomic charge densities and obtain $V_0(\rho_{in})$.

2. Find $u_i$ satisfies (4.1b) and
   \[
   \left(-\frac{1}{2}\Delta + V_{ne} + V_0(\rho_{in})\right) u_i = \lambda_i u_i \quad \text{in } \mathbb{R}^3. \tag{4.2}
   \]

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 $\rho_{in}$, we may construct the following two-scale discretization scheme:

Step 1. Find $(\lambda_i, u_i, H) \in \mathbb{R} \times S^H_0(\Omega)$ such that $u_i$ satisfies (4.1b) and
   \[
   (\nabla u_i, \nabla v) + (V_{ne} u_i + V_0(\rho_{in}) u_i, v) = \lambda_i (u_i, v) \quad \forall v \in S^H_0(\Omega). \tag{4.3}
   \]

Step 2. Find $u_i^h \in S^H_0(\Omega)$ ($i = 1, \cdots, N_{occ}$) satisfying
   \[
   (\nabla u_i, \nabla v) = \lambda_i (u_i, v) - (V_{ne} u_i + V_0(\rho_{in}) u_i, v) \quad \forall v \in S^H_0(\Omega). \tag{4.4}
   \]

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
   \[
   \rho^h = \sum_{i=1}^{N_{occ}} c_i |u_i|^2. \tag{4.6}
   \]

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
   \[
   \eta_r = \eta_{r,G} = \|A^{-1/2}(G_h u_h - A \nabla u_h)\|_{0,\tau}^2, \quad \tau \in T^h(\Omega),
   \]
   where $A = \text{diag}(1/2, 1/2, 1/2)$ and the locally averaging operator $G_h : S^H_0(\Omega) \to S^h(\Omega) \times S^h(\Omega)$
is defined by (see, e.g., [22, 29, 39, 43])

\[ G_h v = \sum_{z \in \partial^2 T^h} (A \nabla v)_z \phi_z, \quad (A \nabla v)_z = \sum_{j=1}^{J_z} \alpha_z^j (A(z) \nabla v)_{\tau_z^j} \quad \forall \ v \in S^0_h(\Omega). \]

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

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

(for instance, \( \alpha_z^j = 1/J_z \alpha_z^1 = |\tau_z^j|/|\omega_z| \), 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

\[ E_{\text{total}} = \sum_{i=1}^{N_{\text{occ}}} c_i \lambda_i - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)dxdy}{|x-y|} + E_{\text{xc}}(\rho) \]

\[ + \frac{1}{2} \sum_{p,q=1,p\neq q}^{N_{\text{atom}}} \frac{Z_p Z_q}{|r_p - r_q|}, \]

where \( E_{\text{xc}}(\rho) \) is the exchange-correlation energy, \( \lambda_i \ (i = 1, \ldots, N_{\text{occ}}) \) are the eigenvalues of (4.1), \( N_{\text{atom}} \) 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 \( \Omega \) 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

\[ E_{\text{total}}^h = \sum_{i=1}^{N_{\text{occ}}} c_i \lambda_i^h - \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{\rho^h(x)\rho^h(y)dxdy}{|x-y|} + E_{\text{xc}}(\rho^h) \]

\[ + \frac{1}{2} \sum_{p,q=1,p\neq q}^{N_{\text{atom}}} \frac{Z_p Z_q}{|r_p - r_q|}, \]

where \( \lambda_i \) and \( \rho^h \) 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.
Finite Element Approximations for Schrödinger Equations

Table 4.1: Numerical solutions of Example 4.1.

<table>
<thead>
<tr>
<th>$N_H$</th>
<th>$N_h$</th>
<th>$\lambda_H$</th>
<th>$\lambda_h$</th>
<th>$\lambda_H - \lambda$</th>
<th>$\lambda_h - \lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>567</td>
<td>49313</td>
<td>1.595172e+00</td>
<td>1.512358e+00</td>
<td>9.517151e-02</td>
<td>1.235783e-02</td>
</tr>
<tr>
<td>1635</td>
<td>108305</td>
<td>1.536066e+00</td>
<td>1.504803e+00</td>
<td>3.606443e-02</td>
<td>4.803290e-03</td>
</tr>
<tr>
<td>4873</td>
<td>316377</td>
<td>1.515997e+00</td>
<td>1.502279e+00</td>
<td>1.599673e-02</td>
<td>2.279329e-03</td>
</tr>
<tr>
<td>14673</td>
<td>355473</td>
<td>1.506393e+00</td>
<td>1.500774e+00</td>
<td>6.393485e-03</td>
<td>7.74004e-04</td>
</tr>
</tbody>
</table>

Table 4.2: Numerical solutions of Example 4.2.

<table>
<thead>
<tr>
<th>$N_H$</th>
<th>$N_h$</th>
<th>$\lambda_H$</th>
<th>$\lambda_h$</th>
<th>$\lambda_H - \lambda$</th>
<th>$\lambda_h - \lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3423</td>
<td>217697</td>
<td>-4.846029e-01</td>
<td>-4.976628e-01</td>
<td>1.539713e-02</td>
<td>2.337195e-03</td>
</tr>
<tr>
<td>6493</td>
<td>347020</td>
<td>-4.902730e-01</td>
<td>-4.986565e-01</td>
<td>9.727038e-03</td>
<td>1.343541e-03</td>
</tr>
<tr>
<td>14457</td>
<td>869513</td>
<td>-4.944337e-01</td>
<td>-4.992690e-01</td>
<td>5.566281e-03</td>
<td>7.310055e-04</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Equation</th>
<th>method</th>
<th>reference</th>
<th>unknowns</th>
<th>energy</th>
<th>$\Delta E(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schrödinger</td>
<td>FEM</td>
<td>[27]</td>
<td>6,720</td>
<td>-2.90289</td>
<td></td>
</tr>
<tr>
<td>Hatree-Fock</td>
<td>FEM Hatree</td>
<td>[36]</td>
<td>500,000</td>
<td>-2.8522</td>
<td>0.33</td>
</tr>
<tr>
<td>Hatree-Fock</td>
<td>Hatree</td>
<td>[35]</td>
<td>unknown</td>
<td>-2.861678</td>
<td></td>
</tr>
<tr>
<td>Kohn-Sham</td>
<td>$X_\alpha$</td>
<td>[33]</td>
<td>unknown</td>
<td>-2.72</td>
<td></td>
</tr>
</tbody>
</table>

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

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

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 $X_\alpha$ 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

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

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

$$\left( -\frac{1}{2} \Delta - \frac{Z}{|x|} + \int \frac{\rho(y)}{|x-y|} dy + V_{xc}(\rho) \right) u = \lambda u, \quad (4.10)$$
Table 4.4: Example 4.3: the two-scale scheme.

<table>
<thead>
<tr>
<th>$N_h$</th>
<th>$N_{eh}$</th>
<th>$E_H$</th>
<th>$E_n$</th>
<th>CPU time (secs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>497</td>
<td>45193</td>
<td>-1.960392e+00</td>
<td>-2.724644e+00</td>
<td>1.506124e+02</td>
</tr>
<tr>
<td>515</td>
<td>46225</td>
<td>-2.262290e+00</td>
<td>-2.897167e+00</td>
<td>1.692926e+02</td>
</tr>
<tr>
<td>679</td>
<td>55041</td>
<td>-2.484488e+00</td>
<td>-2.919425e+00</td>
<td>2.212407e+02</td>
</tr>
<tr>
<td>1029</td>
<td>76601</td>
<td>-2.570763e+00</td>
<td>-2.913713e+00</td>
<td>3.179586e+02</td>
</tr>
<tr>
<td>1191</td>
<td>85409</td>
<td>-2.637899e+00</td>
<td>-2.918088e+00</td>
<td>3.754206e+02</td>
</tr>
<tr>
<td>2023</td>
<td>136257</td>
<td>-2.749499e+00</td>
<td>-2.913211e+00</td>
<td>6.212172e+02</td>
</tr>
<tr>
<td>3771</td>
<td>239249</td>
<td>-2.795651e+00</td>
<td>-2.903013e+00</td>
<td>1.102675e+03</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$N_h$</th>
<th>$E_h$</th>
<th>$N_{eh}$</th>
<th>$E_{eh}$</th>
<th>CPU time (secs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>679</td>
<td>-2.484488e+00</td>
<td>2593</td>
<td>-2.777429e+00</td>
<td>31121</td>
</tr>
<tr>
<td>1125</td>
<td>-2.570763e+00</td>
<td>3771</td>
<td>-2.795651e+00</td>
<td>45949</td>
</tr>
<tr>
<td>1191</td>
<td>-2.637899e+00</td>
<td>5067</td>
<td>-2.816476e+00</td>
<td>102467</td>
</tr>
<tr>
<td>1581</td>
<td>-2.707981e+00</td>
<td>6353</td>
<td>-2.826997e+00</td>
<td></td>
</tr>
<tr>
<td>2023</td>
<td>-2.749499e+00</td>
<td>9817</td>
<td>-2.835543e+00</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$N_h$</th>
<th>$N_{eh}$</th>
<th>$E_H$</th>
<th>$E_n$</th>
<th>CPU time (secs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>661</td>
<td>7277</td>
<td>-6.198066e+00</td>
<td>-7.174421e+00</td>
<td>1.429924e+02</td>
</tr>
<tr>
<td>1089</td>
<td>10437</td>
<td>-6.579749e+00</td>
<td>-7.319871e+00</td>
<td>2.083374e+02</td>
</tr>
<tr>
<td>1265</td>
<td>11845</td>
<td>-6.781116e+00</td>
<td>-7.387384e+00</td>
<td>2.869570e+02</td>
</tr>
<tr>
<td>1799</td>
<td>15985</td>
<td>-7.029342e+00</td>
<td>-7.413942e+00</td>
<td>4.173074e+02</td>
</tr>
<tr>
<td>3093</td>
<td>25629</td>
<td>-7.175916e+00</td>
<td>-7.40785e+00</td>
<td>6.309228e+02</td>
</tr>
<tr>
<td>10247</td>
<td>78769</td>
<td>-7.359014e+00</td>
<td>-7.475724e+00</td>
<td>1.941627e+03</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$N_h$</th>
<th>$E_h$</th>
<th>$N_{eh}$</th>
<th>$E_{eh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1119</td>
<td>-6.612568e+00</td>
<td>3093</td>
<td>-7.175916e+00</td>
</tr>
<tr>
<td>1265</td>
<td>-6.781116e+00</td>
<td>3773</td>
<td>-7.221930e+00</td>
</tr>
<tr>
<td>1565</td>
<td>-6.949232e+00</td>
<td>5641</td>
<td>-7.281180e+00</td>
</tr>
<tr>
<td>1799</td>
<td>-7.029342e+00</td>
<td>7653</td>
<td>-7.335161e+00</td>
</tr>
<tr>
<td>2197</td>
<td>-7.124327e+00</td>
<td>10247</td>
<td>-7.359014e+00</td>
</tr>
</tbody>
</table>

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.

Acknowledgments. This work was partially supported by the National Science Foundation of China under grant 10425105 and the National Basic Research Program under grant 2005CB321704.

References


