Numerical analysis of finite dimensional approximations of Kohn–Sham models

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Abstract In this paper, we study finite dimensional approximations of Kohn–Sham models, which are widely used in electronic structure calculations. We prove the convergence of the finite dimensional approximations and derive the a priori error estimates for ground state energies and solutions. We also provide numerical simulations for several molecular systems that support our theory.

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1 Introduction

Density functional theory (DFT) is a theory of many-body systems and has become a primary tool for electronic structure calculations in atoms, molecules, and condensed matter [17, 19, 22, 24, 26, 28]. The most widely used is the Kohn–Sham model, in which a many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The purpose of this paper is to analyze the finite dimensional approximations of Kohn–Sham models so as to provide a mathematical justification for both the directly numerical minimizing energy functional method [25, 29] and the numerical Euler–Lagrange method (namely, solving the Kohn–Sham equation self-consistently) [24] and some understanding of several existing approximate methods in modern electronic structure calculations.

Throughout this paper, we restrict our mathematical analysis and numerical simulations to non-relativistic, spin-unpolarized models. In the pseudopotential setting, the ground state solutions of the Kohn–Sham model for a molecular system can be obtained by minimizing the Kohn–Sham energy functional

$$E(\{\phi_i\}) = \frac{1}{2} \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \phi_i(x)|^2 dx + \int_{\mathbb{R}^3} V_{\text{loc}}(x) \rho(x) dx + \sum_{i=1}^{N} \int_{\mathbb{R}^3} \phi_i(x) V_{\text{nl}} \phi_i(x) dx$$

$$+ \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho(y)}{|x-y|} dxdy + \int_{\mathbb{R}^3} E(\rho(x)) dx$$

(1.1)

with respect to wavefunctions $\{\phi_i\}_{i=1}^{N}$ under the orthogonality constraints

$$\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad 1 \leq i, j \leq N,$$

where $N$ is the number of valence electrons in the system, $\rho = \sum_{i=1}^{N} |\phi_i(x)|^2$ is the electron density, $V_{\text{loc}}$ and $V_{\text{nl}}$ are the local and nonlocal pseudopotential operators respectively, that treat the core electrons and the nuclei as a unit and represent the interactions on the valence electrons [24], and $E(\rho)$ denotes the exchange-correlation energy per unit volume in an electron gas with density $\rho$. The Euler–Lagrange equation corresponding to this minimization problem is
Finite dimensional approximations of Kohn-Sham models

the so-called Kohn–Sham equation: find \( \lambda_i \in \mathbb{R}, \phi_i \in H^1(\mathbb{R}^3) \) \((i = 1, 2, \cdots, N)\) such that

\[
\begin{cases}
\left( -\frac{1}{2} \Delta + V_{\text{eff}}(\{\phi_i\}) \right) \phi_i = \lambda_i \phi_i & \text{in } \mathbb{R}^3, \quad i = 1, 2, \cdots, N, \\
\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad & i = 1, 2, \cdots, N,
\end{cases}
\]

where \( V_{\text{eff}}(\{\phi_i\}) \) is the effective potential. This is a nonlinear integro-differential eigenvalue problem, and (1.2) is often called self-consistent field (SCF) equation as to emphasize the nonlinear feature encoded in \( V_{\text{eff}}(\{\phi_i\}) \). It is assumed in most of the simulations that the ground state solutions can be found by occupying the lowest eigenstates of Kohn–Sham equation (1.2) \([6, 13]\).

The main difficulties of numerical analysis for Kohn–Sham models lie in that we have to either handle the global minimization problems whose energy functionals may be nonconvex or deal with the nonlinear eigenvalue problems whose eigenvalues may not be nondegenerate. To our best knowledge, except for the very recent works of Cancès et al. \([6]\) and Suryanarayana et al. \([31]\), there is no any other numerical analysis for Kohn–Sham models in the literature. We see that the numerical analysis of Kohn–Sham models is crucial to understand the efficiency of the numerical methods widely used in electronic structure calculations. Under a coercivity assumption of the so-called second order optimality condition, \([6]\) provided numerical analysis of plane wave approximations and showed that every ground state solution can be approximated by plane wave solutions with convergence rate, and \([31]\) gave the convergence of ground state energy approximations based on finite element discretizations only. In this paper, we shall present a systematic analysis for a general finite dimensional discretization and prove that all the limit points of finite dimensional approximations are ground state solutions of the system, and every solution can be approximated by finite dimensional solutions if the associated local isomorphism condition is satisfied. We provide not only convergence of ground state energy approximations but also convergence rates of both eigenvalue and eigenfunction approximations. We point out that the local isomorphism condition should be very mild and is indeed satisfied if the second order optimality condition is provided.

Besides the Kohn–Sham models, there is another approach in DFT that is not so popular and is called of orbital-free DFT \([10, 33]\), in which approximate functionals in terms of electron density alone are used for the kinetic energy of the non-interacting system and only the lowest eigenvalue needs to be computed. There are several related works on its convergence analysis \([8, 20, 35, 36]\) and a priori error estimates \([5, 6, 9]\).

This paper is organized as follows. In the coming section, we give a brief overview of the Kohn–Sham models and some preparations. In Section 3, we derive the existence of a unique local discrete solution under some reasonable assumptions. In Section 4, we prove the convergence of finite dimensional approximations of the ground state solutions with quite weak assumptions.
and derive the error estimates of ground state energy, eigenfunctions and eigenvalues. In Section 5, we present some numerical results that support our theory. Finally, we give some concluding remarks.

2 Preliminaries

Physically, the Kohn–Sham model is set over \( \mathbb{R}^3 \). But in a lot of computations, \( \mathbb{R}^3 \) may be replaced by some polyhedral bounded domain \( \Omega \subset \mathbb{R}^3 \), for example, a supercell for crystal or a large enough cuboid for finite system, which is reasonable since the solution of (1.2) for a confined system decays exponentially [1, 16, 30]. Thus we study numerical analysis of finite dimensional approximations of Kohn–Sham equation as follows:

\[
\begin{align*}
\left\{ \left( -\frac{1}{2} \Delta + V_{\text{eff}}(\{\phi_i\}) \right) \phi_i = \lambda_i \phi_i \quad &\text{in } \Omega, \quad i = 1, 2, \cdots, N, \\
\int_{\Omega} \phi_i \phi_j = \delta_{ij}, \quad &i, j = 1, 2, \cdots, N
\end{align*}
\]

(2.1)

with the Dirichlet boundary condition \( \phi_i = 0 \) on \( \partial \Omega \) for finite systems and periodic boundary conditions for crystals, where \( \Omega \subset \mathbb{R}^3 \) is a polyhedral bounded domain.

We shall use the standard notation for Sobolev spaces \( W^{s,p}(\Omega) \) and their associated norms and seminorms, see, e.g., [11]. 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 understood in the sense of trace, \( \| \cdot \|_{s,\Omega} = \| \cdot \|_{s,2,\Omega} \), and \((\cdot, \cdot)\) is the standard \( L^2 \) inner product. The space \( Y^* \), the dual of the Banach space \( Y \), will also be used. For convenience, the symbol \( \lesssim \) will be used in this paper. The notation \( A \lesssim B \) means that \( A \leq CB \) for some constant \( C \) that is independent of the mesh parameters.

Given \( c_1 \in \mathbb{R} \) and \( p, c_2 \in [0, \infty) \), we define

\[
\mathcal{P}(p,(c_1,c_2)) = \{ f : \exists a_1, a_2 \in \mathbb{R} \text{ such that } c_1 t^p + a_1 \leq f(t) \leq c_2 t^p + a_2 \quad \forall \ t \geq 0 \}.
\]

For \( \kappa \in \mathbb{R}^{N \times N} \), we denote its Frobenius norm by \( \| \kappa \| \). We consider the functional space\(^1\)

\[
\mathcal{H} = \left( H^1_0(\Omega) \right)^N = \left\{ (\phi_1, \phi_2, \cdots, \phi_N) : \phi_i \in H^1_0(\Omega) \ (i = 1, 2, \cdots, N) \right\},
\]

which is a Hilbert space associated with norm \( \| \Phi \|_{1,\Omega} = \left( \sum_{i=1}^N (\| \phi_i \|_{0,\Omega}^2 + \| \nabla \phi_i \|_{0,\Omega}^2) \right)^{1/2} \) and inner product \((\nabla \Phi, \nabla \Psi) = \sum_{i=1}^N (\nabla \phi_i, \nabla \psi_i)\) for \( \Phi = (\phi_1, \phi_2, \cdots, \phi_N), \Psi = (\psi_1, \psi_2, \cdots, \psi_N) \in \mathcal{H} \).

\(^1\)In fact, our theory also applies to space \( \mathcal{H} = (H^1_0(\Omega))^N \), where \( \Omega \) is the unit cell of a periodic lattice \( \mathcal{R} \) of \( \mathbb{R}^d \) and \( H^1_0(\Omega) = \{ v|_{\Omega} : v \in H^1_0(\mathbb{R}^d) \text{ and } v \text{ is } \mathcal{R}-\text{periodic} \} \).
Finite dimensional approximations of Kohn-Sham models

For simplicity of notation, we will sometimes abuse the notation by
\[ \|\Phi\|_{m,\omega} = \left( \sum_{i=1}^{N} \|\phi_i\|_{m,\omega}^2 \right)^{1/2}, \quad \|\Phi\|_{0,p,\omega} = \left( \sum_{i=1}^{N} \|\phi_i\|_{0,p,\omega}^p \right)^{1/p} \]
for subdomain \(\omega \subset \Omega\) and \(\Phi = (\phi_1, \phi_2, \cdots, \phi_N) \in \mathcal{H}\). For any \(\Phi = (\phi_1, \phi_2, \cdots, \phi_N)\), \(\Psi = (\psi_1, \psi_2, \cdots, \psi_N) \in \mathcal{H}\), we define \(\rho_{\Phi} = \sum_{i=1}^{N} |\phi_i|^2\) and
\[ \Phi^T \Psi = \left( \int_{\Omega} \phi_i \psi_j \right)_{i,j=1}^{N} \in \mathbb{R}^{N \times N}. \]

In our discussion, we shall also use the following three sets:
\[ S^{N \times N} = \{ M \in \mathbb{R}^{N \times N} : M^T = M \}, \quad A^{N \times N} = \{ M \in \mathbb{R}^{N \times N} : M^T = -M \}, \quad \mathcal{Q} = \{ \Phi \in \mathcal{H} : \Phi^T \Phi = I^{N \times N} \}. \]

We may decompose \(\mathcal{H}\) as a direct sum of three subspaces (see, e.g., [14, 23]):
\[ \mathcal{H} = S_\Phi \oplus A_\Phi \oplus T_\Phi \]
for any \(\Phi \in \mathcal{Q}\), where \(S_\Phi = \Phi S^{N \times N}, \quad A_\Phi = \Phi A^{N \times N}\), and \(T_\Phi = \{ \Psi \in \mathcal{H} : \Psi^T \Phi = 0 \in \mathbb{R}^{N \times N} \}\).

2.1 Kohn–Sham models

In the most commonly setting of local density approximation (LDA) [24], the associated Kohn–Sham energy functional of (2.1) is expressed as
\[ E(\Phi) = \int_{\Omega} \left( \sum_{i=1}^{N} \frac{1}{2} |\nabla \phi_i|^2 + V_{\text{loc}}(x) \rho_{\Phi} + \sum_{i=1}^{N} \phi_i V_{\text{nl}} \phi_i + \mathcal{E}(\rho_{\Phi}) \right) + \frac{1}{2} D(\rho_{\Phi}, \rho_{\Phi}) \]
(2.2)
for \(\Phi = (\phi_1, \phi_2, \cdots, \phi_N) \in \mathcal{H}\), where \(V_{\text{loc}}\) is a smooth local pseudopotential, \(V_{\text{nl}}\) is the nonlocal pseudopotential operator (see, e.g., [24]) given by
\[ V_{\text{nl}} \phi = \sum_{j=1}^{M} (\phi, \zeta_j) \zeta_j \]
with \(\zeta_j \in L^2(\Omega)(j = 1, 2, \cdots, M)\), \(D(\rho_{\Phi}, \rho_{\Phi})\) denotes electron–electron coulomb energy with
\[ D(f, g) = \int_{\Omega} f(g * r^{-1}) = \int_{\Omega} \int_{\Omega} f(x)g(y) \frac{1}{|x-y|} dxdy, \]
and \(\mathcal{E}(t)\) is some real function over \([0, \infty)\). We may assume that \(V_{\text{loc}} \in L^2(\Omega)\). We see that the function \(\mathcal{E} : [0, \infty) \to \mathbb{R}\) does not have a simple analytical
expression. In applications, we shall use some approximations to \( \mathcal{E} \), for which we shall make the assumption that \( \mathcal{E}(t) \in \mathcal{P}(3, (c_1, c_2)) \) with \( c_1 \geq 0 \) or \( \mathcal{E}(t) \in \mathcal{P}(4/3, (c_1, c_2)) \) that is satisfied by most of the approximations.

First of all, we have

**Proposition 2.1** 
Functional (2.2) is invariant with respect to unitary transformations, i.e.,

\[
E(\Phi) = E(\Phi U) \quad \forall \Phi \in \mathcal{Q}
\]

for any matrix \( U = (u_{ij})_{i,j=1}^{N} \in \mathcal{O}^{N \times N} \), where \( \mathcal{O}^{N \times N} \) is the set of orthogonal matrices.

Using similar arguments in [8], we obtain that \( E(\Psi) \) is bounded below over \( \mathcal{Q} \). More precisely, we have

**Proposition 2.2** 
There exist constants \( C > 0 \) and \( b > 0 \) such that

\[
E(\Psi) \geq C^{-1} \|\Psi\|_{1,\Omega}^2 - b \quad \forall \Psi \in \mathcal{Q}.
\]

To prove the convergence of the numerical approximations, we need the lower semi-continuity of the energy functional in the weak topology of \( \mathcal{H} \), whose proof can be referred to [8].

**Proposition 2.3** 
If \( \Psi_k \) converge weakly to \( \Psi \) in \( \mathcal{H} \), then

\[
E(\Psi) \leq \liminf_{k \to \infty} E(\Psi_k).
\]

The ground state energy of the system is the global minimum of \( E(\Psi) \) in the admissible class \( \mathcal{Q} \) and we shall study the following minimization problem

\[
\inf \{ E(\Phi) : \Phi \in \mathcal{Q} \}.
\]  

The existence of a minimizer of (2.4) can be found in [2, 21, 31] or by similar arguments to that in the proof of Theorem 4.1. We see from Proposition 2.1 that if \( \Phi \) is a minimizer of (2.4), then \( \Phi U \in \mathcal{Q} \) is also a minimizer for any \( U \in \mathcal{O}^{N \times N} \). Note that the uniqueness of a minimizer of (2.4) is open even up to an orthogonal transform since the energy functional may not be convex for almost all systems of practical interest. Therefore, we need to define the set of ground state solutions as follows

\[
\mathcal{G} = \left\{ \Phi \in \mathcal{Q} : E(\Phi) = \min_{\Psi \in \mathcal{Q}} E(\Psi) \right\}.
\]
We see that a minimizer \( \Phi = (\phi_1, \phi_2, \ldots, \phi_N) \) of (2.4) satisfies the associated Euler–Lagrange equation:

\[
\begin{aligned}
(A_\Phi \phi_i, v) &= \left( \sum_{j=1}^{N} \lambda_{ij} \phi_j, v \right) \quad \forall \ v \in H^1_0(\Omega), \ i = 1, 2, \ldots, N, \\
\int_{\Omega} \phi_i \phi_j &= \delta_{ij},
\end{aligned}
\]

(2.5)

where \( A_\Phi \) is the Kohn–Sham Hamiltonian operator given by

\[
A_\Phi = -\frac{1}{2} \Delta + V_{\text{loc}} + V_{nl} + \int_{\Omega} \frac{\rho_{\Phi}(y)}{|\cdot - y|} dy + \mathcal{E}'(\rho_{\Phi})
\]

(2.6)

with the Lagrange multiplier

\[
\Lambda = (\lambda_{ij})_{i,j=1}^{N} = \left( \int_{\Omega} \phi_j A_\Phi \phi_i \right)_{i,j=1}^{N}.
\]

(2.7)

We define the set of ground state eigenpairs by

\[
\Theta = \{(\Lambda, \Phi) \in \mathbb{R}^{N \times N} \times \mathbb{H} : \Phi \in \mathcal{G} \text{ and } (\Lambda, \Phi) \text{ solves (2.5)}\}.
\]

To obtain the a priori error estimates of the finite dimensional approximations, we shall represent Kohn–Sham equation in another setting. Define

\[
Y = \mathbb{R}^{N \times N} \times \mathcal{H}
\]

with the associated norm \( \|(\Lambda, \Phi)\|_Y = |\Lambda| + \|\Phi\|_{1,\Omega} \) for each \( (\Lambda, \Phi) \in Y \). We may rewrite (2.5) as a nonlinear problem as follows:

\[
F((\Lambda, \Phi)) = 0 \in Y^*,
\]

(2.8)

where \( F : Y \rightarrow Y^* \) is given by

\[
\langle F((\Lambda, \Phi)), (\varphi, \Gamma) \rangle = \sum_{i=1}^{N} \left( A_\Phi \phi_i - \sum_{j=1}^{N} \lambda_{ij} \phi_j, \gamma_i \right) + \sum_{i,j=1}^{N} \chi_{ij} \left( \int_{\Omega} \phi_i \phi_j - \delta_{ij} \right)
\]

(2.9)

with \( \Gamma = (\gamma_1, \gamma_2, \ldots, \gamma_N) \in \mathcal{H} \) and \( \varphi = (\chi_{ij})_{i,j=1}^{N} \in \mathbb{R}^{N \times N} \).

The Fréchet derivative \( F'_((\Lambda, \Phi)) \) of \( F \) at \( (\Lambda, \Phi) : Y \rightarrow Y^* \) is defined as

\[
\langle F'_((\Lambda, \Phi))(\varphi, \Psi), (\varphi, \Gamma) \rangle = \langle \mathcal{L}'_{\Phi} (\Lambda, \Phi) \Psi, \Gamma \rangle - \sum_{i,j=1}^{N} (\mu_{ij} \phi_j, \gamma_i)
\]

\[
+ \sum_{i,j=1}^{N} \chi_{ij} \int_{\Omega} (\psi_i \phi_j + \phi_i \psi_j)
\]

\[
\times \forall (\varphi, \Psi), (\varphi, \Gamma) \in Y,
\]

(2.10)
where

\[
\langle \mathcal{L}_\Phi'(\Lambda, \Phi) \Psi, \Gamma \rangle = \frac{1}{2} E''(\Phi)(\Psi, \Gamma) - \sum_{i,j=1}^{N} (\lambda_{ij} \psi_i, \gamma_i)
\]

\[
= \sum_{i=1}^{N} \left( \frac{1}{2} (\nabla \psi_i, \nabla \gamma_i) + (V_{\text{loc}} \psi_i, \gamma_i) + \sum_{j=1}^{M} (\zeta_j, \psi_i) (\zeta_j, \gamma_i) \right.
\]

\[
+ \left( E'(\rho_\Phi) \psi_i, \gamma_i \right) + D (\rho_\Phi, \psi_i \gamma_i)
\]

\[
- \left( \sum_{j=1}^{N} \lambda_{ij} \psi_j, \gamma_i \right)
\]

\[
+ \left( 2\phi_i E''(\rho_\Phi) \sum_{j=1}^{N} \phi_j \psi_j, \gamma_i \right) + \sum_{j=1}^{N} 2D(\phi_j \psi_j, \phi_i \gamma_i) \right) \quad (2.11)
\]

for \( \Psi = (\psi_1, \psi_2, \cdots, \psi_N) \in \mathcal{H} \) and \( \mu = (\mu_{ij})_{i,j=1}^{N} \in \mathbb{R}^{N \times N} \).

2.2 Basic assumptions

The a priori error estimate of finite dimensional approximations will be carried out under certain assumptions, which are stated as follows

**A1** \( |E'(t)| + |tE''(t)| \in \mathcal{P}(p_1, (c_1, c_2)) \) for some \( p_1 \in [0, 2] \).

**A2** There exists a constant \( \alpha \in (0, 1] \) such that \( |E''(t)| + |tE'''(t)| \lesssim 1 + t^{\alpha-1} \quad \forall \ t > 0 \).

**A3** \( (\Lambda_0, \Phi_0) \in Y \) is a solution of (2.5) and \( \mathcal{L}'_{\Phi_0}(\Lambda_0, \Phi_0) \) is an isomorphism from \( \mathcal{T}_{\Phi_0} \) to \( \mathcal{T}_{\Phi_0} \), namely, there exists a positive constant \( \gamma \) depending on \( (\Lambda_0, \Phi_0) \) such that

\[
\inf_{\psi \in \mathcal{T}_{\Phi_0}} \sup_{\Gamma \in \mathcal{T}_{\Phi_0}} \frac{\langle \mathcal{L}'_{\Phi_0}(\Lambda_0, \Phi_0) \Psi, \Gamma \rangle}{\| \Psi \|_{1,\Omega} \| \Gamma \|_{1,\Omega}} \geq \gamma. \quad (2.12)
\]

We see that Assumption **A2** implies Assumption **A1** and the commonly used \( X_\alpha \) and LDA exchange-correction energy satisfy Assumption **A2** [5, 8]. We shall mention that none of the above assumptions will be used in our convergence analysis of finite dimensional approximations in Section 4.1.
Remark 2.1 It is open whether Assumption A3 holds for some solutions of Kohn–Sham models, though it may hold for semiconductors and “closed shell” atoms and molecules. We see that the following assumption
\[
\langle L'_{\Phi}(\Lambda, \Phi) \Psi, \Psi \rangle \geq \gamma \| \Psi \|_{1,\Omega}^2 \quad \forall \, \Psi \in T_{\Phi}, \tag{2.13}
\]
which implies (2.12), is employed in [6, 29]. Note that (2.13) is equivalent to (2.12) when \((\Lambda, \Phi)\) is the ground state solution of (2.5).

The following lemma will be used in our analysis of the local uniqueness of discrete solution.

Lemma 2.1 Let \(y_1 = (\Lambda_1, \Phi_1)\) and \(y_2 = (\Lambda_2, \Phi_2) \in Y\) satisfy \(\|y_1\|_Y + \|y_2\|_Y \leq \bar{C}\). If Assumption A1 is satisfied, then there exists a constant \(C_F\) depending on \(\bar{C}\) such that
\[
\|F(y_1) - F(y_2)\| \leq C_F \|y_1 - y_2\|_Y \quad \forall \, y_1, y_2 \in Y. \tag{2.14}
\]
Moreover, if Assumption A2 is satisfied, then there is a constant \(C'_F\) such that
\[
\left\| F_{y_1} - F_{y_2} \right\| \leq C'_F \left( \|y_1 - y_2\|_Y^2 + \|y_1 - y_2\|_Y^2 \right) \quad \forall \, y_1, y_2 \in Y. \tag{2.15}
\]

Proof To prove (2.14), it is sufficient to show that
\[
\left( A_{\Phi_1} \Phi_1 - A_{\Phi_2} \Phi_2, \Gamma \right) \leq C \|\Phi_1 - \Phi_2\|_{1,\Omega} \|\Gamma\|_{1,\Omega} \quad \forall \, \Gamma \in \mathcal{H}. \tag{2.16}
\]
which together with (2.9) indeed implies (2.14). Using the Hölder inequality and the Sobolev inequality, we have for \(i = 1, 2, \cdots, N\) that
\[
\left( -\frac{1}{2} \Delta + V_{\text{loc}} \right) \phi_{1,i} - \left( -\frac{1}{2} \Delta + V_{\text{loc}} \right) \phi_{2,i}, v \right)
\leq \frac{1}{2} \|\phi_{1,i} - \phi_{2,i}\|_{1,\Omega} \|v\|_{1,\Omega} + \|V_{\text{loc}}\|_{0,\Omega} \|\phi_{1,i} - \phi_{2,i}\|_{0,3,\Omega} \|v\|_{0,6,\Omega}
\lesssim \|\phi_{1,i} - \phi_{2,i}\|_{1,\Omega} \|v\|_{1,\Omega} \quad \forall \, v \in H^1_0(\Omega)
\]
and hence
\[
\left( -\frac{1}{2} \Delta + V_{\text{loc}} \right) \Phi_1 - \left( -\frac{1}{2} \Delta + V_{\text{loc}} \right) \Phi_2, \Gamma \right)
\lesssim \|\Phi_1 - \Phi_2\|_{1,\Omega} \|\Gamma\|_{1,\Omega} \quad \forall \, \Gamma \in \mathcal{H}. \tag{2.17}
\]
Due to
\[
\left( V_{n\ell} \Phi_1 - V_{n\ell} \Phi_2, \Gamma \right) = \sum_{i=1}^{N} \left( \sum_{j=1}^{M} (\xi_j, \phi_{1,i} - \phi_{2,i}) \xi_j, \gamma_i \right),
\]

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we obtain
\[
\left( V_{nl} \Phi_1 - V_{nl} \Phi_2, \Gamma \right) \lesssim \sum_{i=1}^{N} \| \phi_{1,i} - \phi_{2,i} \|_{0, \Omega} \| \gamma_i \|_{0, \Omega}
\]
\[
\lesssim \| \Phi_1 - \Phi_2 \|_{1, \Omega} \| \Gamma \|_{1, \Omega} \quad \forall \, \Gamma \in \mathcal{H}.
\]  
(2.18)

Obviously
\[
(E'(\rho_{\Phi_1}) \Phi_1 - E'(\rho_{\Phi_2}) \Phi_2, \Gamma) \lesssim \| \Phi_1 - \Phi_2 \|_{1, \Omega} \| \Gamma \|_{1, \Omega} \quad \forall \, \Gamma \in \mathcal{H}
\]
when \( p_1 = 0 \) in Assumption A1. If Assumption A1 is satisfied for \( p_1 \in (0, 2] \), then there exists \( \delta_i \in [0, 1] \) such that
\[
(E'(\rho_{\Phi_1}) \Phi_1 - E'(\rho_{\Phi_2}) \Phi_2, \Gamma) = \sum_{i=1}^{N} \int_{\Omega} (E'(\rho_{\Phi_1}) \phi_{1,i} - E'(\rho_{\Phi_2}) \phi_{2,i}) \gamma_i
\]
\[
= \sum_{i=1}^{N} \int_{\Omega} (E'(\rho_{\xi}) + 2\xi^2 \mathcal{E}''(\rho_{\xi})) (\phi_{1,i} - \phi_{2,i}) \gamma_i
\]
\[
\leq \sum_{i=1}^{N} \| E'(\rho_{\xi}) + 2\xi^2 \mathcal{E}''(\rho_{\xi}) \|_{0,3/p_1, \Omega} \| \phi_{1,i} - \phi_{2,i} \|_{1, \Omega}
\]
\[
\sum_{i=1}^{N} \| \rho_{\xi} \|_{0,3, \Omega} \| \phi_{1,i} - \phi_{2,i} \|_{1, \Omega} \| \gamma_i \|_{1, \Omega}
\]
\[
\lesssim \| \Phi_1 - \Phi_2 \|_{1, \Omega} \| \Gamma \|_{1, \Omega},
\]  
(2.19)

where \( \xi = (\xi_1, \xi_2, \ldots, \xi_N) \) with \( \xi_i = \delta_i \phi_{1,i} + (1 - \delta_i) \phi_{2,i} \), and the Hölder inequality, the Sobolev inequality, and the fact
\[
\| \rho_{\xi} \|_{0,3, \Omega} \lesssim \| \rho_{\Phi_1} \|_{0,3, \Omega} + \| \rho_{\Phi_2} \|_{0,3, \Omega} \lesssim \| \Phi_1 \|_{1, \Omega}^2 + \| \Phi_2 \|_{1, \Omega}^2 \leq \tilde{C}^2
\]
are used.

For Coulomb term, we obtain from the Young’s inequality and the Hölder inequality that
\[
\| r^{-1} \ast (\rho_{\Phi_1} - \rho_{\Phi_2}) \|_{0, \infty, \Omega} \lesssim \| r^{-1} \|_{0, \Omega} \| \rho_{\Phi_1} - \rho_{\Phi_2} \|_{0, \Omega} \lesssim \| r^{-1} \|_{0, \Omega} \| \Phi_1 - \Phi_2 \|_{1, \Omega},
\]
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where \( \hat{\Omega} = \{ x - y : x, y \in \Omega \} \). Since
\[
\int_{\Omega} \left( (r^{-1} \ast \rho_{\Phi_1}) \phi_{1,i} - (r^{-1} \ast \rho_{\Phi_2}) \phi_{2,i} \right) v
= \int_{\Omega} (r^{-1} \ast \rho_{\Phi_1}) (\phi_{1,i} - \phi_{2,i}) v + \int_{\Omega} r^{-1} \ast (\rho_{\Phi_1} - \rho_{\Phi_2}) \phi_{2,i} v
\leq \| r^{-1} \ast \rho_{\Phi_1} \|_{0, \infty, \Omega} \| \phi_{1,i} - \phi_{2,i} \|_{0, \Omega} \| v \|_{0, \Omega}
+ \| r^{-1} \ast (\rho_{\Phi_1} - \rho_{\Phi_2}) \|_{0, \infty, \Omega} \| \phi_{2,i} \|_{0, \Omega} \| v \|_{0, \Omega}
\lesssim \| \phi_{1,i} - \phi_{2,i} \|_{1, \Omega} \| v \|_{1, \Omega} + \| \Phi_1 - \Phi_2 \|_{1, \Omega} \| v \|_{1, \Omega}
\quad \forall v \in H^1_0(\Omega)
\]
holds for \( i = 1, 2, \cdots, N \), we have
\[
\left( (r^{-1} \ast \rho_{\Phi_1}) \Phi_1 - (r^{-1} \ast \rho_{\Phi_2}) \Phi_2, \Gamma \right) \lesssim \| \Phi_1 - \Phi_2 \|_{1, \Omega} \| \Gamma \|_{1, \Omega}
\quad \forall \Gamma \in \mathcal{H}. \quad (2.20)
\]
Taking (2.17), (2.18), (2.19), (2.20) and definition (2.6) into account, we then arrive at (2.16).

If Assumption A2 holds, then following [6, Lemma 4.5] we obtain for \( \Psi = (\psi_1, \psi_2, \cdots, \psi_N), \Gamma = (\gamma_1, \gamma_2, \cdots, \gamma_N) \in \mathcal{H} \) that
\[
| (\mathcal{E}'(\rho_{\Phi_1}) \Psi, \Gamma) - (\mathcal{E}'(\rho_{\Phi_2}) \Psi, \Gamma) | = \int_{\Omega} \int_0^1 2\mathcal{E}''(\rho_{\Phi(t)})
\times \left( \sum_{i=1}^N \phi_i(t) (\phi_{1,i} - \phi_{2,i}) \right) \left( \sum_{i=1}^N \psi_i \gamma_i \right) dt
\lesssim \int_{\Omega} \int_0^1 (1 + \rho_{\Phi(t)}^{\alpha-1}) \rho_{\Phi(t)}^{1/2} \rho_{\Phi_1-\Phi_2}^{1/2} \rho_{\Psi}^{1/2} \rho_{\Gamma}^{1/2} dt
\]  
(2.21)
and
\[
\sum_{i=1}^N \left( \phi_{1,i} \mathcal{E}''(\rho_{\Phi_1}) \sum_{j=1}^N \phi_{1,j} \psi_j, \gamma_i \right) - \sum_{i=1}^N \left( \phi_{2,i} \mathcal{E}''(\rho_{\Phi_2}) \sum_{j=1}^N \phi_{2,j} \psi_j, \gamma_i \right)
= \int_{\Omega} \int_0^1 \left[ \mathcal{E}''(\rho_{\Phi(t)}) \left( \sum_{i=1}^N \phi_i(t) \psi_i \right) \left( \sum_{i=1}^N (\phi_{1,i} - \phi_{2,i}) \gamma_i \right)
\right.
\left. + \mathcal{E}''(\rho_{\Phi(t)}) \left( \sum_{i=1}^N (\phi_{1,i} - \phi_{2,i}) \psi_i \right) \left( \sum_{i=1}^N \phi_i(t) \gamma_i \right) + \mathcal{E}''(\rho_{\Phi(t)})
\times \left( \sum_{i=1}^N \phi_i(t) (\phi_{1,i} - \phi_{2,i}) \right) \left( \sum_{i=1}^N \phi_i(t) \psi_i \right) \left( \sum_{i=1}^N \phi_i(t) \gamma_i \right) \right] dt
\lesssim \int_{\Omega} \int_0^1 (1 + \rho_{\Phi(t)}^{\alpha-1}) \rho_{\Phi(t)}^{1/2} \rho_{\Phi_1-\Phi_2}^{1/2} \rho_{\Psi}^{1/2} \rho_{\Gamma}^{1/2} dt, \quad (2.22)
\]
where \( \Phi(t) = \Phi_1 + t(\Phi_2 - \Phi_1) \) with \( t \in [0, 1] \).
For all $0 < \alpha \leq 1/2$, we have

\[
\int_0^1 \rho_{\Phi(t)}^{a-1/2} dt = \int_0^1 \left( \sum_{i=1}^N \phi_{1,i}^2 + 2t \sum_{i=1}^N \phi_{1,i}(\phi_{2,i} - \phi_{1,i}) + t^2 \sum_{i=1}^N (\phi_{2,i} - \phi_{1,i})^2 \right)^{a-1/2} dt
\]

\[
= \int_0^1 \left( \sum_{i=1}^N \phi_{1,i}^2 + \sum_{i=1}^N (\phi_{2,i} - \phi_{1,i})^2 \left( t + \frac{\sum_{i=1}^N \phi_{1,i}(\phi_{2,i} - \phi_{1,i})}{\sum_{i=1}^N (\phi_{2,i} - \phi_{1,i})^2} \right)^2 \right)^{a-1/2} dt
\]

\[
\leq \int_0^1 \left| t + \frac{\sum_{i=1}^N \phi_{1,i}(\phi_{2,i} - \phi_{1,i})}{\sum_{i=1}^N (\phi_{2,i} - \phi_{1,i})^2} \right|^{2a-1} \times \left( \sum_{i=1}^N (\phi_{2,i} - \phi_{1,i})^2 \right)^{a-1/2} dt \leq \frac{1}{\alpha 2^{2a}} \rho_{\Phi_1-\Phi_2}^{a-1/2},
\]

which together with the fact that $0 \leq \rho_{\Phi(t)} \leq 2(\rho_{\Phi_1} + t^2 \rho_{\Phi_1-\Phi_2})$ implies that for all $0 < \alpha \leq 1$

\[
\int_\Omega \int_0^1 \left( 1 + \rho_{\Phi(t)}^{a-1/2} \right)^{1/2} \rho_{\Phi(t)}^{1/2} \rho_{\Phi_1-\Phi_2}^{1/2} \rho_{\Psi}^{1/2} \rho_{\Gamma}^{1/2} dt \leq \int_\Omega \left( \rho_{\Phi_1-\Phi_2}^{a/2} + \rho_{\Phi_1-\Phi_2} \right) \rho_{\Psi}^{1/2} \rho_{\Gamma}^{1/2}
\]

\[
\lesssim \|\rho_{\Phi_1-\Phi_2}\|_{0,6/a,\Omega} \|\rho_{\Psi}\|_{0,12/(6-a),\Omega} \|\rho_{\Gamma}\|_{0,12/(6-a),\Omega} + \|\rho_{\Phi_1-\Phi_2}\|_{0,3,\Omega} \|\rho_{\Psi}\|_{0,3,\Omega} \|\rho_{\Gamma}\|_{0,3,\Omega}
\]

\[
\lesssim (\|\Phi_1 - \Phi_2\|^2_{\Omega} + \|\Phi_1 - \Phi_2\|^2_{1,\Omega}) \|\Psi\|_{1,\Omega} \|\Gamma\|_{1,\Omega}. \quad (2.23)
\]

Similar arguments to that in (2.20) yield that

\[
\sum_{j=1}^N |D(\phi_{1,j}\psi_j, \phi_{1,i}v) - D(\phi_{2,j}\psi_j, \phi_{2,i}v)|
\]

\[
\leq \sum_{j=1}^N |D(\phi_{1,j}\psi_j - \phi_{2,j}\psi_j, \phi_{1,i}v)| + \sum_{j=1}^N |D(\phi_{2,j}\psi_j, \phi_{1,i}v - \phi_{2,i}v)|
\]

\[
\lesssim \sum_{j=1}^N \|\phi_{1,j} - \phi_{2,j}\|_{1,\Omega} \|\psi_j\|_{1,\Omega} \|v\|_{1,\Omega} + \sum_{j=1}^N \|\phi_{1,j} - \phi_{2,j}\|_{1,\Omega} \|\psi_j\|_{1,\Omega} \|v\|_{1,\Omega}
\]

\[
\lesssim \|\Phi_1 - \Phi_2\|_{1,\Omega} \|\Psi\|_{1,\Omega} \|v\|_{1,\Omega} \quad \forall \, \psi \in \mathcal{H}, \, \forall \, v \in H^1_0(\Omega). \quad (2.24)
\]
Therefore, taking (2.10), (2.11), (2.21), (2.22), (2.23) and (2.24) into account, we get

\[
\langle (F_{y_1} - F_{y_2})((\psi, \Psi)), (\xi, \Gamma) \rangle 
\lesssim (\|y_1 - y_2\|^2_Y + \|y_1 - y_2\|^2_Y)\| (\psi, \Psi) \|_Y \| (\xi, \Gamma) \|_Y \ orall (\psi, \Psi), (\xi, \Gamma) \in Y,
\]

which implies (2.15) and completes the proof. \(\Box\)

3 Finite dimensional approximations

For the sake of generality, we will not concentrate on any specific approximation, rather we shall study approximations in a class of finite dimensional subspaces \(S_n \subset X (n = 1, 2, \cdots)\) that satisfy

\[
\lim_{n \to \infty} \inf_{\psi \in S_n} \| \psi - \phi \|_{1,\Omega} = 0 \ \forall \phi \in X, \quad (3.1)
\]

where \(X\) is some Banach space containing the eigenfunctions of (2.1), say, \(H^1_0(\Omega)\) or \(H^1_\#(\Omega)\).

Assumptions (3.1) is apparently very mild and satisfied by several typical finite dimensional subspaces used in practice, for instance, spaces spanned by plane wave bases [7], spaces spanned by wavelets [3, 15], and piecewise polynomial finite element spaces [11]. As a result, we may investigate all these kinds of finite dimensional approximation approaches in computational either physics or quantum chemistry in a unified framework. For convenience, here and hereafter we consider the case of \(X = H^1_0(\Omega)\) only.

We see that finite dimensional subspaces

\[
\mathcal{H}_n \equiv \{ \Phi_n \in S_n \cap \mathcal{C}_9 : \inf_{\Psi \in \mathcal{H}_n \cap \mathcal{C}_9} E(\Psi) = \min_{\Psi \in \mathcal{H}_n \cap \mathcal{C}_9} E(\Psi) \}.
\]

The existence of a minimizer of (3.3) can be obtained by similar arguments to that in the proof of Theorem 4.1 (c.f., also, [6, 8]). However, the uniqueness is unknown even up to a unitary transform. Therefore we define the set of finite dimensional ground state solutions:

\[
\mathcal{G}_n = \left\{ \Phi_n \in \mathcal{H}_n \cap \mathcal{Q} : E(\Phi_n) = \min_{\Psi \in \mathcal{H}_n \cap \mathcal{Q}} E(\Psi) \right\}.
\]
Given \( n \geq 1 \), any minimizer \( \Phi_n = (\phi_{1,n}, \phi_{2,n}, \cdots, \phi_{N,n}) \) of (3.3) solves
\[
\begin{align*}
\left\{ (A_{\phi_n} \phi_{i,n}, v) = \left( \sum_{j=1}^{N} \lambda_{i,j,n} \phi_{j,n}, v \right) \quad \forall \; v \in S_n, \; i = 1, 2, \cdots, N, \\
\int_{\Omega} \phi_{i,n} \phi_{j,n} = \delta_{ij}
\right\}
\tag{3.4}
\end{align*}
\]
with the Lagrange multiplier
\[
\Lambda_n = (\lambda_{i,j,n})_{i,j=1}^{N} = \left( \int_{\Omega} \phi_{j,n} A_{\phi_n} \phi_{i,n} \right)_{i,j=1}^{N}.
\tag{3.5}
\]
Define the set of finite dimensional ground state eigenpairs
\[
\Theta_n = \left\{ (\Lambda_n, \Phi_n) \in \mathbb{R}^{N \times N} \times (\mathcal{H}_n \cap \mathbb{Q}) : \Phi_n \in \mathcal{G}_n \text{ and } (\Lambda_n, \Phi_n) \text{ solves (3.4)} \right\}.
\]
Proposition 2.2 and (3.5) imply that the finite dimensional approximations are uniformly bounded
\[
\sup_{(\Lambda_n, \Phi_n) \in \Theta_n, n \geq 1} (\|\Phi_n\|_{1, \Omega} + |\Lambda_n|) < C
\tag{3.6}
\]
for some constant \( C \).

We then address the Galerkin discretization of (2.8). Let
\[
Y_n = \mathbb{R}^{N \times N} \times \mathcal{H}_n
\]
and \( F_n : Y_n \rightarrow Y_n^* \) be an approximation of \( F \) defined by
\[
\langle F_n((\Lambda_n, \Phi_n)), (\xi_n, \Gamma_n) \rangle = \langle F((\Lambda_n, \Phi_n)), (\xi_n, \Gamma_n) \rangle \quad \forall \ (\Lambda_n, \Phi_n), (\xi_n, \Gamma_n) \in Y_n.
\]
Then discrete problem (3.4) can be rewritten as
\[
F_n((\Lambda_n, \Phi_n)) = 0 \in Y_n^*. \tag{3.7}
\]
We also denote the derivative of \( F_n \) at \((\Lambda_n, \Phi_n) \in Y_n \) by \( F_n'((\Lambda_n, \Phi_n)) : Y_n \rightarrow Y_n^* \) as follows:
\[
\langle F_n'((\Lambda_n, \Phi_n))(\eta_n, \Psi_n), (\xi_n, \Gamma_n) \rangle = \langle \mathcal{L}_{\phi_n}'((\Lambda_n, \Phi_n)) \Psi_n, \Gamma_n \rangle - \sum_{i,j=1}^{N} (\mu_{i,j,n} \phi_{j,n}, \gamma_{i,n}) + \sum_{i,j=1}^{N} \chi_{i,j,n} \int_{\Omega} (\psi_{i,n} \phi_{j,n} + \phi_{i,n} \psi_{j,n}).
\]
Given \( (\Lambda, \Phi) \in \mathcal{S}^{N \times N} \times \mathbb{Q} \), we define
\[
X_\Phi = \mathcal{S}^{N \times N} \times (S_\Phi \oplus T_\Phi) \subset Y
\]
with the induced norm \( \|(\mu, \Psi)\|_{X_\Phi} = |\mu| + \|\Psi\|_{1, \Omega} \) for each \((\mu, \Psi) \in X_\Phi \) and
\[
X_{\Phi,n} = \mathcal{S}^{N \times N} \times (\mathcal{H}_n \cap (S_\Phi \oplus T_\Phi)).
\]
We shall derive the existence of a unique local discrete solution \( y_n \in X_{\Phi_{0,n}} \) of (3.4) in the neighborhood of \( y_0 \equiv (\Lambda_0, \Phi_0) \), where \( \Lambda_0 = (\lambda_{0,i,j})_{i,j=1}^{N} \) and \( \Phi_0 = (\phi_{0,1}, \phi_{0,2}, \cdots, \phi_{0,N}) \).
Lemma 3.1 $F'_{y_0} : X_{\phi_0} \rightarrow X^*_{\phi_0}$ is an isomorphism.

Proof It is sufficient to prove that equation

$$F'_{y_0}((\mu, \Psi)) = (\eta, g)$$

(3.8)

is uniquely solvable in $X_{\phi_0}$ for every $(\eta, g) \in X^*_{\phi_0}$. To this end we define the following bilinear forms $a_{\phi_0} : \mathcal{H} \times \mathcal{H} \rightarrow \mathbb{R}$ and $b_{\phi_0}, c_{\phi_0} : \mathcal{H} \times \mathbb{R}^{N \times N} \rightarrow \mathbb{R}$ by

$$a_{\phi_0}(\Psi, \Gamma) = (\mathcal{L}_{\phi_0}(\Lambda_0, \Phi_0)\Psi, \Gamma),$$

$$b_{\phi_0}(\Psi, \chi) = \sum_{i, j=1}^{N} \chi_{ij}(\phi_{0,i}, \psi_{j}),$$

$$c_{\phi_0}(\Psi, \chi) = \sum_{i, j=1}^{N} \chi_{ij}(\phi_{0,i}, \psi_{j}) + (\phi_{0,i}, \psi_{j}).$$

Using (2.10), we may rewrite (3.8) as follows: find $\mu \in S^{N \times N}$ and $\Psi \in S_{\phi_0} \oplus T_{\phi_0}$ such that

$$\begin{cases}
a_{\phi_0}(\Psi, \Gamma) - b_{\phi_0}(\Gamma, \mu) = (g, \Gamma) & \forall \Gamma \in S_{\phi_0} \oplus T_{\phi_0}, \\
c_{\phi_0}(\Psi, \chi) = \sum_{i, j=1}^{N} \chi_{ij}\eta_{ij} & \forall \chi \in S^{N \times N}.
\end{cases}$$

(3.9)

For any given $\chi \in S^{N \times N}$, we can choose $\Psi = \Phi_0\chi$, and thus

$$c_{\phi_0}(\Psi, \chi) = 2 \sum_{i, j=1}^{N} |\chi_{ij}|^2.$$  (3.10)

where $\Phi_0^T \Phi_0 = I^{N \times N}$ is used. Note that a simple calculation leads to

$$||\Psi||_{1, \Omega} = ||\Phi_0\chi||_{1, \Omega} \lesssim \left( \sum_{i, j=1}^{N} |\chi_{ij}|^2 \right)^{1/2} ||\Phi_0||_{1, \Omega}. \quad (3.11)$$

By taking into account (2.3), (3.10) and (3.11), we obtain

$$\inf_{\chi \in S^{N \times N}} \sup_{\Psi \in S_{\phi_0}} \frac{c_{\phi_0}(\Psi, \chi)}{||\Psi||_{1, \Omega} \left( \sum_{i, j=1}^{N} |\chi_{ij}|^2 \right)^{1/2}} \geq \kappa_c,$$  (3.12)

where $\kappa_c > 0$ is independent of $\chi$. Hence, there exists a unique solution $\Psi_S \in S_{\phi_0}$ such that

$$c_{\phi_0}(\Psi_S, \chi) = \sum_{i, j=1}^{N} \chi_{ij}\eta_{ij} \quad \forall \chi \in S^{N \times N}.$$
Therefore (3.9) is equivalent to: find $\Psi_0 \in T_{\Phi_0}$ such that
\[ a_{\Phi_0}(\Psi_0, \Gamma) = (g, \Gamma) - a_{\Phi_0}(\Psi_S, \Gamma) \quad \forall \Gamma \in T_{\Phi_0}. \tag{3.13} \]

The unique solvability of (3.13) is a direct consequence of (2.12).

Using similar arguments to that from (3.10) to (3.12), we get
\[
\inf_{\chi \in \mathcal{S}_{N \times N}} \sup_{\Psi_1 \in \mathcal{S}_{\Phi_0}} b_{\Phi_0}(\Psi_1, \chi) \geq \kappa_b,
\]
where $\kappa_b > 0$ is independent of $\chi$. This implies that equation
\[ b_{\Phi_0}(\Gamma, \mu) = a_{\Phi_0}(\Psi_0 + \Psi_S, \Gamma) - (g, \Gamma) \quad \forall \Gamma \in S_{\Phi_0}. \]

We have proved that for any $(\Gamma, g) \in X^*_0$ in (3.9), there exists a unique solution $(\mu_S, \Psi_0 + \Psi_S)$. This indicates that $F'_{y_0}$ is an isomorphism from $X_{\Phi_0}$ to $X^*_0$ and completes the proof. \(\square\)

Note that $F'_{y_0} : X_{\Phi_0} \to X^*_0$ being an isomorphism is equivalent to the following inf-sup condition
\[ \inf_{y_1 \in X_{\Phi_0}} \sup_{y_2 \in X_{\Phi_0}} \frac{\langle F'_{y_0} y_1, y_2 \rangle}{\|y_1\|_{X_{\Phi_0}} \|y_2\|_{X_{\Phi_0}}} = \beta > 0 \tag{3.14} \]

with the constant satisfying $\beta^{-1} = \|F'_{y_0}^{-1}\|$.

For any $\Phi \in Q$, we define
\[ Q^\Phi = \{ \Psi \in Q : \|\Psi - \Phi\|_{0, \Omega} = \min_{U \in \mathcal{O}_{N \times N}} \|\Psi U - \Phi\|_{0, \Omega} \}. \]

In our analysis, we need the following lemma, whose proof is referred to [6].

**Lemma 3.2** If $\Phi \in Q$, then $\Psi \in Q^\Phi$ can be represented by
\[ \Psi = \Phi + S(W) \Phi + W, \]
where $W \in T_\Phi$ and $S(W) \in \mathcal{S}_{N \times N}$ satisfying
\[ |S(W)| = |(I_{N \times N} - W^T W)^{1/2} - I_{N \times N}| \leq \|W\|_{0, \Omega}^2 \leq \|\Psi - \Phi\|_{0, \Omega}^2. \tag{3.15} \]

Before giving a discrete counterpart with Lemma 3.1, we also need to introduce two projections. First, we define the projection $\tilde{\Pi}_n : Q \to \mathcal{H}_n \cap Q$ such that
\[ \|\tilde{\Pi}_n \Phi - \Phi\|_{1, \Omega} = \min_{\Psi \in \mathcal{H}_n \cap Q} \|\Psi - \Phi\|_{1, \Omega} \quad \forall \Phi \in Q. \]

To project further into $X_{\Phi,n}$, we then define $\Pi_n : \mathcal{S}_{N \times N} \times Q \to X_{\Phi,n}$ by
\[ \Pi_n(\Lambda, \Phi) = (\Lambda, (\tilde{\Pi}_n \Phi) \tilde{U}) \quad \forall (\Lambda, \Phi) \in \mathcal{S}_{N \times N} \times Q, \]

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Finite dimensional approximations of Kohn-Sham models

\[ \mathcal{U} = \arg \min_{\mathcal{U} \in \mathcal{O}^{N \times N}} \| (\Pi_n \Phi) \mathcal{U} - \Phi \|_{0, \Omega}. \]

From Lemma 3.2, we see that \( \Pi_n : S^{N \times N} \times \mathbb{Q} \to X_{\Phi, n} \) is well-defined.

**Lemma 3.3** If Assumption A2 is satisfied, then there exists \( n_0 > 1 \) such that \( F'_{n, \Pi_n y_0} : X_{\Phi_0, n} \to X_{\Phi_0, n}^* \) is an isomorphism for all \( n \geq n_0 \). Moreover, there is a constant \( M > 0 \) such that

\[ \| F'_{n, \Pi_n y_0} - I \| \leq M \quad \forall \ n \geq n_0. \]

**Proof** We first prove that

\[ \lim_{n \to \infty} \| \Pi_n y - y \|_{X_\Phi} = 0 \quad \forall \ y \equiv (\Lambda, \Phi) \in S^{N \times N} \times \mathbb{Q}. \] (3.16)

Using the fact that \( \Phi \in \mathbb{Q} \) and \( (\Pi_n \Phi) \mathcal{U} \in \mathbb{Q}^\Phi \), we have

\[ | \mathcal{U} - I | = \| (\Pi_n \Phi) \mathcal{U} - \Pi_n \Phi \|_{0, \Omega} \leq \| (\Pi_n \Phi) \mathcal{U} - \Pi_n \Phi \|_{1, \Omega} \]

\[ + \| \Pi_n \Phi - \Phi \|_{0, \Omega} \lesssim \| \Pi_n \Phi - \Phi \|_{1, \Omega}, \]

which implies

\[ \| (\Pi_n \Phi) \mathcal{U} - \Phi \|_{1, \Omega} \leq \| \Pi_n \Phi - \Phi \|_{1, \Omega} + \| (\Pi_n \Phi) \mathcal{U} - \Pi_n \Phi \|_{1, \Omega} \]

\[ \leq \| \Pi_n \Phi - \Phi \|_{1, \Omega} + | \mathcal{U} - I | \cdot \| \Pi_n \Phi \|_{1, \Omega} \]

\[ \lesssim \| \Pi_n \Phi - \Phi \|_{1, \Omega}. \] (3.17)

Let \( \Phi^n \equiv (\phi^n_1, \phi^n_2, \ldots, \phi^n_N) = \arg \min_{\Psi \in \mathcal{P}_n} \| \Psi - \Phi \|_{1, \Omega} \), we may estimate \( \| \Pi_n \Phi - \Phi \|_{1, \Omega} \) as follows:

\[ \| \Pi_n \Phi - \Phi \|_{1, \Omega} \leq \sum_{i=1}^N \| \frac{Q_n \phi^n_i}{\| Q_n \phi^n_i \|_{0, \Omega}} - \phi_i \|_{1, \Omega} \]

\[ \leq \sum_{i=1}^N \left( \| Q_n \phi^n_i - \phi_i \|_{1, \Omega} + \| \frac{Q_n \phi^n_i}{\| Q_n \phi^n_i \|_{0, \Omega}} - Q_n \phi^n_i \|_{1, \Omega} \right) \]

\[ \leq \sum_{i=1}^N \left( 1 + \frac{\| Q_n \phi^n_i \|_{1, \Omega}}{\| Q_n \phi^n_i \|_{0, \Omega}} \right) \| \phi_i - Q_n \phi^n_i \|_{1, \Omega}, \]

where \( Q_n \) is the Gram-Schmidt orthogonal operator:

\[ Q_n \phi^n_i = \phi^n_i - \sum_{j=1}^{i-1} \frac{(Q_n \phi^n_j, \phi^n_i)}{(Q_n \phi^n_j, Q_n \phi^n_j)} Q_n \phi^n_j \quad i = 1, \ldots, N. \]
Note that
\[
\|\phi_i - Q_n\phi_i^n\|_{1,\Omega} \leq \|\phi_i^n - \phi_i\|_{1,\Omega} + \sum_{j=1}^{i-1} \frac{\|Q_n\phi_j^n\|_{1,\Omega}}{\|Q_n\phi_j^n\|_{0,\Omega}} \times \left( \left( Q_n\phi_j^n, \phi_j^n - \phi_i \right) + \left( Q_n\phi_j^n - \phi_j, \phi_i \right) \right)
\]
\[
\leq \left( 1 + \sum_{j=1}^{i-1} \frac{\|Q_n\phi_j^n\|_{1,\Omega}}{\|Q_n\phi_j^n\|_{0,\Omega}} \right) \|\phi_i - \phi_i^n\|_{1,\Omega} + \sum_{j=1}^{i-1} \frac{\|Q_n\phi_j^n\|_{1,\Omega}}{\|Q_n\phi_j^n\|_{0,\Omega}} \|\phi_j - Q_n\phi_j^n\|_{1,\Omega},
\]
we conclude
\[
\|\tilde{\Pi}_n\Phi - \Phi\|_{1,\Omega} \lesssim \|\Phi^n - \Phi\|_{1,\Omega} = \inf_{\Psi \in \mathcal{H}_n} \|\Psi - \Phi\|_{1,\Omega}.
\] (3.18)
Using (3.17), (3.18) and the definition of \(\Pi_n\), we arrive at
\[
\|\Pi_n y - y\|_{X_\Phi} \lesssim \inf_{\Psi \in \mathcal{H}_n} \|\Psi - \Phi\|_{1,\Omega},
\] (3.19)
which together with (3.2) leads to (3.16).

We then show the invertibility of \(F_{0,y_0} : X_{\Phi_0,n} \to X_{\Phi_0,n}^*\). We obtain from (3.14) that
\[
\sup_{y_2 \in X_{\Phi_0}} \frac{\langle F_{0,y_0} y_1, y_2 \rangle}{\|y_1\|_{X_{\Phi_0}} \|y_2\|_{X_{\Phi_0}}} \geq \beta \quad \forall \ y_1 \in X_{\Phi_0}.
\]
Let \(P_{n,\Phi_0} : S_{\Phi_0} \oplus T_{\Phi_0} \to \mathcal{H}_n \cap (S_{\Phi_0} \oplus T_{\Phi_0})\) be a projection operator satisfying
\[
(\nabla \Phi_1, \nabla (\Phi_2 - P_{n,\Phi_0} \Phi_2)) = 0 \quad \forall \ \Phi_1 \in \mathcal{H}_n \cap (S_{\Phi_0} \oplus T_{\Phi_0}).
\]
Set
\[
\eta_n = \sup_{\Psi \in S_{\Phi_0} \oplus T_{\Phi_0}, \|\Psi\|_{1,\Omega} \leq 1} \|\Psi - P_{n,\Phi_0} \Psi\|_{0,\Omega},
\]
we have (see, e.g., [37])
\[
\|\Psi - P_{n,\Phi_0} \Psi\|_{0,\Omega} \lesssim \eta_n \|\Psi\|_{1,\Omega} \quad \forall \ \Psi \in S_{\Phi_0} \oplus T_{\Phi_0} \quad \text{with} \quad \lim_{n \to \infty} \eta_n = 0.
\] (3.20)
Let \(P_n = (I, P_{n,\Phi_0})\), we obtain from definition (2.10) and (3.20) that
\[
\langle F'_{y_0,y_1}, P_n y_2 \rangle = \langle F'_{y_0,y_1}, y_2 \rangle - \langle F'_{y_0,y_1}, y_2 - P_n y_2 \rangle
\]
\[
= \langle F'_{y_0,y_1}, y_2 \rangle + \frac{1}{2} (\nabla \Phi_1, \nabla (\Phi_2 - P_{n,\Phi_0} \Phi_2)) - \langle F'_{y_0,y_1}, y_2 - P_n y_2 \rangle
\]
\[
\geq \langle F'_{y_0,y_1}, y_2 \rangle - c \|y_1\|_{X_{\Phi_0}} \|y_2\|_{0,\Omega} - P_n y_2\|_{0,\Omega}
\]
\[
\geq \langle F'_{y_0,y_1}, y_2 \rangle - c \eta_n \|y_1\|_{X_{\Phi_0}} \|y_2\|_{X_{\Phi_0}},
\]
which implies that there exists $\tilde{n}$ such that for all $n \geq \tilde{n}$, there holds

$$\sup_{y_2 \in X_{\Phi_0,n}} \frac{\langle F'_{y_0} y_1, y_2 \rangle}{\|y_1\|_{X_{\Phi_0}} \|y_2\|_{X_{\Phi_0}}} \geq \frac{\beta}{2} \quad \forall \ y_1 \in X_{\Phi_0,n},$$

or equivalently

$$\inf_{y_1 \in X_{\Phi_0,n}} \sup_{y_2 \in X_{\Phi_0,n}} \frac{\langle F'_{y_0} y_1, y_2 \rangle}{\|y_1\|_{X_{\Phi_0}} \|y_2\|_{X_{\Phi_0}}} \geq \frac{\beta}{2}.$$

Thus $F'_{n,y_0}$ is an isomorphism from $X_{\Phi_0,n}$ to $X^*_{\Phi_0,n}$ satisfying

$$\|F'_{n,y_0}^{-1}\| \leq 2\beta^{-1} \quad \forall \ n \geq \tilde{n}.$$

Note that $F'_{n}$ satisfies the following discrete Hölder condition

$$\|F'_{n,y_0} - F'_{n,\Pi_n y_0}\| \lesssim \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}} + \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}}^2.$$

It follows from (3.16) that there exists $n_0 > \tilde{n}$ such that the inf-sup constant of $F'_{n,\Pi_n y_0}$ is uniformly away from zero for all $n \geq n_0$. This completes the proof.

\[\square\]

**Theorem 3.1** If Assumption A2 is satisfied, then there exist $\delta > 0$, $n_1 > n_0$ such that (3.4) has a unique local solution $y_n = (\Lambda_n, \Phi_n) \in X_{\Phi_0,n} \cap B_{\delta}(y_0)$ for all $n \geq n_1$.

**Proof** The idea is to construct a contractive mapping whose fixed point is $y_n$. We rewrite (3.7) as

$$F_n(y_n) - F_n(\Pi_n y_0) = -F_n(\Pi_n y_0).$$

Using (2.14), we have

$$\|F_n(\Pi_n y_0)\|_{X_{\Phi_0,n}} = \|F(\Pi_n y_0)\|_{X_{\Phi_0,n}} - F(y_0)\|_{X_{\Phi_0,n}} X_{\Phi_0} \leq \|F(\Pi_n y_0) - F(y_0)\|_{X_{\Phi_0,n}} \lesssim \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}}.$$

From Lemma 3.3, we may define the map $\mathcal{N} : B_R(\Pi_n y_0) \cap X_{\Phi_0,n} \rightarrow X_{\Phi_0,n}$ by

$$F'_{n,\Pi_n y_0}(\mathcal{N}(x) - \Pi_n y_0) = -F_n(\Pi_n y_0) - (x - \Pi_n y_0)
\times \int_0^1 (F'_{n,\Pi_n y_0 + t(x-\Pi_n y_0)} - F'_{n,\Pi_n y_0}) dt$$

when $n \geq n_0$.

We will show that $\mathcal{N}$ is a contraction from $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ into $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ if $R$ is chosen sufficiently small and $n$ is large enough.
First, we prove that $\mathcal{N}$ maps $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ to $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ for sufficiently small $R$. Note that $F_n'_{\Pi_n y_0}$ is an isomorphism on $X_{\Phi_0,n}$ if $n$ is sufficiently large. For each $x \in B_R(\Pi_n y_0)$, we have $\mathcal{N}(x) - \Pi_n y_0 \in X_{\Phi_0,n}$ and
\[
\|\mathcal{N}(x) - \Pi_n y_0\|_{X_{\Phi_0}} \leq M \left( \|F_n(\Pi_n y_0)\|_{X_{\Phi_0,n}} + R \int_0^1 \|F_n',_{\Pi_n y_0+t(x-\Pi_n y_0)} - F_n',_{\Pi_n y_0}\| dt \right) \leq CM \left( \|\Pi_n y_0 - y_0\|_{X_{\Phi_0}} + R(R^\alpha + R^2) \right).
\]
Since $CM(\|\Pi_n y_0 - y_0\|_{X_{\Phi_0}} + R^{1+\alpha} + R^3)$ can be estimated by $R$ when $R$ is sufficiently small and $n$ is sufficiently large, we have that $\mathcal{N}(x) \in B_R(\Pi_n y_0)$. It is clear that $R$ can be chosen independently of $n$.

Next, we show that $\mathcal{N}$ is a contraction on $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$. If $x_1, x_2 \in B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$, then
\[
F_n',_{\Pi_n y_0} (\mathcal{N}(x_1) - \mathcal{N}(x_2)) = (x_1 - x_2) \int_0^1 (F_n',_{\Pi_n y_0} - F_n',_{x_1+t(x_2-x_1)}) dt.
\]
Thus, $\|\mathcal{N}(x_1) - \mathcal{N}(x_2)\|_{X_{\Phi_0}}$ can be estimated as
\[
\|\mathcal{N}(x_1) - \mathcal{N}(x_2)\|_{X_{\Phi_0}} \leq M\|x_2 - x_1\|_{X_{\Phi_0}} \int_0^1 \|F_n',_{\Pi_n y_0} - F_n',_{x_1+t(x_2-x_1)}\| dt \leq CM(R^\alpha + R^2)\|x_1 - x_2\|_{X_{\Phi_0}}.
\]
We obtain for sufficiently small $R$ that $CM(R^\alpha + R^2) < 1$ and hence $\mathcal{N}$ is a contraction on $B_R(\Pi_n y_0)$.

We are now able to use Banach’s Fixed Point Theorem to obtain the existence and uniqueness of a fixed point $y_n$ of map $\mathcal{N} : B_R(\Pi_n y_0) \cap X_{\Phi_0,n} \rightarrow B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$, which is the solution of $F_n(y_n) = 0$. This completes the proof.

\section{4 Numerical analysis}

In this section, we shall prove the convergence of finite dimensional approximations and derive various error estimates under different assumptions.

\subsection{4.1 Convergence}

The purpose of this subsection is to prove the convergence of the numerical ground state solutions, for which we need to introduce the following distances between two sets. We define the distance between two subsets $A, B \subset Y$ by
\[
\mathcal{D}(A, B) = \sup_{(\Lambda, \Phi) \in A} \inf_{(\mu, \Psi) \in B} (|\Lambda - \mu| + \|\Phi - \Psi\|_{1,\Omega})
\]
and the distance between two sets $M, N \subset \mathcal{H}$ by

$$d_{\mathcal{H}}(M, N) = \sup_{\Phi \in M} \inf_{\Psi \in N} \|\Phi - \Psi\|_{1,\Omega}.$$  

**Theorem 4.1** There hold

$$\lim_{n \to \infty} D(\Theta_n, \Theta) = 0, \quad (4.1)$$

$$\lim_{n \to \infty} E_n = \min_{\Psi \in \mathcal{Q}} E(\Psi), \quad (4.2)$$

where $E_n = E(\Phi_n)$ for any $\Phi_n \in \mathcal{G}_n$.

**Proof** Let $(\Lambda_n, \Phi_n) \in \Theta_n$ for $n = 1, 2, \ldots$. Given any subsequence $\{\Phi_{n_k}\}$ of $\{\Phi_n\}$ with $1 \leq n_1 < n_2 < \cdots < n_k < \cdots$, we obtain from the Banach–Alaoglu Theorem and (3.6) that there exist $\Phi \in \mathcal{H}$ and a weakly convergent subsequence $\{\Phi_{n_k}\} \subset \{\Phi_n\}$ such that

$$\Phi_{n_k} \rightharpoonup \Phi \text{ in } \mathcal{H}. \quad (4.3)$$

Next we shall prove $\Phi \in \mathcal{G}$ and

$$\lim_{j \to \infty} \|\Phi - \Phi_{n_{k_j}}\|_{1,\Omega} = 0, \quad (4.4)$$

$$\lim_{j \to \infty} E\left(\Phi_{n_{k_j}}\right) = \min_{\Psi \in \mathcal{Q}} E(\Psi). \quad (4.5)$$

From (4.3) and Proposition 2.3, we have

$$\liminf_{j \to \infty} E\left(\Phi_{n_{k_j}}\right) \geq E(\Phi). \quad (4.6)$$

Note that (3.2) implies that $\{\Phi_{n_{k_j}}\}$ is a minimizing sequence for $E(\Psi)$ and the Rellich theorem shows that

$$\int_{\Omega} \phi_{i,n_{k_j}} \phi_{j,n_{k_j}} \to \int_{\Omega} \phi_i \phi_j \quad j \to \infty.$$ 

Therefore $\Phi \in \mathcal{Q}$ is a minimizer of $E(\Psi)$, which together with (4.6) leads to

$$\lim_{j \to \infty} E\left(\Phi_{n_{k_j}}\right) = E(\Phi) = \min_{\Psi \in \mathcal{Q}} E(\Psi). \quad (4.7)$$

This further implies (4.5) and $\Phi \in \mathcal{G}$.

Since $H_0^1(\Omega)$ is compactly imbedded into $L^p(\Omega)$ for $p \in [2, 6)$, we have that $\phi_{i,n_{k_j}} \to \phi_i$ strongly in $L^p(\Omega)$ as $j \to \infty$ for $i = 1, 2, \ldots, N$. This indicates that $\{\rho_{\Phi_{n_{k_j}}}\}$ converges to $\rho_\Phi$ strongly in $L^q(\Omega)$ for $q \in [1, 3)$, from which we obtain that

$$\lim_{j \to \infty} \int_{\Omega} V_{\text{loc}}(x) \left(\rho_{\Phi_{n_{k_j}}}(x) - \rho_\Phi(x)\right) dx = 0,$$

$$\lim_{j \to \infty} \int_{\Omega} \left(E\left(\rho_{\Phi_{n_{k_j}}}\right) - E(\rho_\Phi(x))\right) dx = 0,$$
and
\[ \lim_{j \to \infty} D \left( \rho_{\Phi_{nk_j}}, \rho_{\Phi_{nk_j}} \right) = D(\rho_{\Phi}, \rho_{\Phi}). \quad (4.8) \]

Consequently, we can get from (4.7) to (4.8) that each term of \( E(\cdot) \) converges and in particular
\[ \lim_{j \to \infty} \sum_{i=1}^{N} \| \nabla \phi_{i, nk_j} \|_{0, \Omega}^2 = \sum_{i=1}^{N} \| \nabla \phi_i \|_{0, \Omega}^2. \]

Using (4.3) and the fact that \( \mathcal{H} \) is a Hilbert space under norm \( \left( \sum_{i=1}^{N} \| \nabla \phi_i \|_{0, \Omega}^2 \right)^{1/2} \),
we obtain (4.4). If \((\Lambda, \Phi)\) solves (2.5), then
\[ \lim_{j \to \infty} |\Lambda_{nk_j} - \Lambda| = 0 \]
is a direct consequence of (2.7), (3.5) and (4.4). Hence we arrive at (4.1). This completes the proof. \( \square \)

Remark 4.1 Theorem 4.1 states that all the limit points of finite dimensional approximations are ground state solutions. We note that [31] gave the convergence of ground state energy approximations only while we provide further convergence of approximations of both eigenvalues and eigenfunctions.

4.2 Error estimates for the energy approximation

We shall derive the quadratic convergence rate of ground state energy approximations, which is a generalization and improvement of [6, 31].

Theorem 4.2 Let \( E \) be the ground state energy of (2.4) and \( E_n \) be the ground state energy of (3.3), namely, \( E = E(\Phi) \) for all \( \Phi \in \mathcal{G} \) and \( E_n = E(\Phi_n) \) for all \( \Phi_n \in \mathcal{G}_n \). If Assumption A1 holds, then
\[ |E - E_n| \lesssim d_H(\mathcal{G}, \mathcal{H}_n). \quad (4.9) \]

Proof We see from the definition of ground state energies \( E \) and \( E_n \) that
\[ 0 \leq E_n - E \leq E(\Psi) - E \quad \forall \Psi \in \mathcal{H}_n \cap \mathcal{Q}. \]

Following [6, 29], if Assumption A1 holds, we obtain from the Taylor expansion that for any \( \Psi \in \mathcal{Q} \), there holds
\[ E(\Psi) - E(\Phi) = (E'(\Phi), \Psi - \Phi) + \frac{1}{2}(E''(\xi)(\Psi - \Phi), \Psi - \Phi), \quad (4.10) \]
where \( \xi = \Phi + \delta(\Psi - \Phi) \) with \( \delta \in [0, 1] \). Since \( \Phi \) is a ground state solution, we get from (2.5) that
\[ (E'(\Phi), \Psi - \Phi) = 2(\Phi \Lambda, \Psi - \Phi) = 2(\Phi UU^T \Lambda U, \Psi U - \Phi U), \]

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where the orthogonal transform $U$ diagonalizes the Lagrange multiplier $\Lambda$ by

$$U^T \Lambda U = \text{diag}[\tilde{\lambda}_1, \cdots, \tilde{\lambda}_N].$$

Denote $\tilde{\Phi} = \Phi U$ and $\tilde{\Psi} = \Psi U$, we have

$$(E'(\Phi), \Psi - \Phi) = 2 \sum_{i=1}^N \tilde{\lambda}_i \int \tilde{\phi}_i (\tilde{\psi}_i - \tilde{\phi}_i) \lesssim \sum_{i=1}^N \|\tilde{\phi}_i - \tilde{\psi}_i\|_{0,\Omega}^2$$

$$\lesssim \|\tilde{\Phi} - \tilde{\Psi}\|_{1,\Omega}^2 = \|\Phi - \Psi\|_{1,\Omega}^2. \quad (4.11)$$

It is observed by a simple calculation that

$$\langle E''(\xi)\Psi, \Gamma \rangle = 2 \sum_{i=1}^N (A_\xi \psi_i, \gamma_i) + 4 \sum_{i,j=1}^N D(\xi_i \psi_i, \xi_j \gamma_j) + 4 \sum_{i,j=1}^N \int_\Omega E''(\rho_\xi) \xi_i \psi_i \xi_j \gamma_j$$

and hence

$$\langle E''(\xi)(\Phi - \Psi), \Phi - \Psi \rangle \lesssim \|\Psi - \Phi\|_{1,\Omega}^2, \quad (4.12)$$

where the hidden constant depends on the $H$-norm of $\Psi$.

Taking $(4.10)$, $(4.11)$ and $(4.12)$ into account, we have proved that for $\Phi \in G$ there holds

$$E(\Psi) - E(\Phi) \lesssim \|\Phi - \Psi\|_{1,\Omega}^2 \quad \forall \Psi \in H_n \cap Q,$$

which together with the definition of $\tilde{\Pi}_n$ and $(3.18)$ implies

$$0 \leq E_n - E \leq E(\tilde{\Pi}_n \Phi) - E(\Phi) \lesssim \|\tilde{\Pi}_n \Phi - \Phi\|_{1,\Omega}^2 \lesssim d^2_n(G, H_n),$$

where the fact that $\|\tilde{\Pi}_n \Phi\|_{1,\Omega} \lesssim \|\Phi\|_{1,\Omega}$ is used. This completes the proof. $\square$

### 4.3 Error estimates for solutions

In this subsection, we shall derive the a priori error estimates for finite dimensional approximations of Kohn–Sham equations under Assumptions $A2$ and $A3$.

We define bilinear form $a'(\Phi_0; \cdot, \cdot)$ by

$$a'(\Phi_0; \Psi, \Gamma) = \langle L'_\Phi(\Lambda_0, \Phi_0)\Psi, \Gamma \rangle \quad \forall \Psi, \Gamma \in H.$$ 

Obviously, $a'(\Phi_0; \cdot, \cdot)$ is continuous on $H \times H$.

Now we shall introduce the following adjoint problem: for $f \in (L^2(\Omega))^N$, find $\Psi_f \in T_{\Phi_0}$ such that

$$a'(\Phi_0; \Psi_f, \Gamma) = (f, \Gamma) \quad \forall \Gamma \in T_{\Phi_0}. \quad (4.13)$$

Since $L'_\Phi(\Lambda_0, \Phi_0)$ is an isomorphism, $(4.13)$ has a unique solution and

$$\|\Psi_f\|_{1,\Omega} \lesssim \|f\|_{0,\Omega}. \quad (4.14)$$

Let $K: ((L^2(\Omega))^N, \langle \cdot, \cdot \rangle) \to (T_{\Phi_0}, \langle \nabla \cdot, \nabla \cdot \rangle)$ be the operator satisfying

$$\langle \nabla Kw, \nabla v \rangle = (w, v) \quad \forall \ w \in (L^2(\Omega))^N, \forall \ v \in T_{\Phi_0}. \quad (4.15)$$
Then $K$ is compact. Set 

$$\rho_n = \sup_{f \in (L^2(\Omega))^N, \|f\|_{0,\Omega} \leq 1} \inf_{\Psi \in \mathcal{H}_n} \|\nabla ((\mathcal{L}_{\Phi_0}'(\Lambda_0, \Phi_0))^{-1} Kf - \Psi)\|_{0,\Omega},$$

we then have the following estimate (see, e.g., [4])

$$\|\nabla ((\mathcal{L}_{\Phi_0}'(\Lambda_0, \Phi_0))^{-1} Kf - P'_n (\mathcal{L}_{\Phi_0}'(\Lambda_0, \Phi_0))^{-1} Kf)\|_{0,\Omega} \lesssim \rho_n \|f\|_{0,\Omega} \quad \forall f \in (L^2(\Omega))^N$$

(4.16)

with

$$\lim_{n \to \infty} \rho_n = 0,$$

where $P'_n : \mathcal{T}_{\Phi_0} \to \mathcal{T}_{\Phi_0} \cap \mathcal{H}_n$ is the projection operator satisfying

$$(\nabla (\Phi_1 - P'_n \Phi_1), \nabla \Phi_2) = 0 \quad \forall \Phi_2 \in \mathcal{T}_{\Phi_0} \cap \mathcal{H}_n.$$

**Theorem 4.3** If Assumptions A2 and A3 are satisfied, then there exists $\delta > 0$ such that for sufficiently large $n$, (3.4) has a unique local solution $(\Lambda_n, \Phi_n) \in X_{\Phi_0,n} \cap B_\delta(y_0)$ satisfying

$$\|\Phi_0 - \Phi_n\|_{1,\Omega} \lesssim d_H(G, \mathcal{H}_n)$$

(4.17)

and

$$\|\Phi_0 - \Phi_n\|_{0,\Omega} + |\Lambda_0 - \Lambda_n| \lesssim \rho_n \|\Phi_0 - \Phi_n\|_{1,\Omega}$$

(4.18)

with $\rho_n \to 0$ as $n \to \infty$.

**Proof** We obtain from Theorem 3.1 that there exists $\delta > 0$ such that for sufficiently large $n$, (3.4) has a unique local solution $y_n \equiv (\Lambda_n, \Phi_n) \in X_{\Phi_0,n} \cap B_\delta(y_0)$. Hence, we have

$$F_n(y_n) - F_n(\Pi_n y_0) = -F_n(\Pi_n y_0),$$

which leads to

$$F_{n,\Pi_n y_0}'(y_n - \Pi_n y_0) = -F_n(\Pi_n y_0)$$

$$\quad - (y_n - \Pi_n y_0) \int_0^1 (F_{n,\Pi_n y_0}'(y_n - \Pi_n y_0) - F_{n,\Pi_n y_0}'(y_n - \Pi_n y_0)) dt.$$

Using the similar arguments in the proof of Theorem 3.1, we obtain from Lemma 3.3 that for sufficiently large $n$

$$\|y_n - \Pi_n y_0\|_{X_{\Phi_0}} \lesssim \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}} + \|y_n - \Pi_n y_0\|_{X_{\Phi_0}} + \|y_n - \Pi_n y_0\|_{X_{\Phi_0}}^2,$$

which together with (3.16) and the fact that $y_n \in B_\delta(y_0)$ implies that for sufficiently large $n$

$$\|y_n - \Pi_n y_0\|_{X_{\Phi_0}} \lesssim \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}}.$$  

(4.19)
Using (3.19) and (4.19), we conclude
\[ \| y_n - y_0 \| x_{\Phi_0} \lesssim \| y_n - \Pi_n y_0 \| x_{\Phi_0} + \| y_0 - \Pi_n y_0 \| x_{\Phi_0} \lesssim \inf_{\Psi \in \mathcal{H}_n} \| \Psi - \Phi_0 \|_{1, \Omega}, \]
which implies (4.17).
Since there exists \( \delta_i \in [0, 1] \) such that
\[ (\mathcal{E}'(\rho_{\Phi_0}) \phi_{i,n} - \mathcal{E}'(\rho_{\Phi_0}) \phi_{0,i}, \phi_{j,n}) = \int_\Omega (\mathcal{E}'(\rho_\xi) + 2\xi_i^2 \mathcal{E}''(\rho_\xi))(\phi_{i,n} - \phi_{0,i}) \phi_{j,n}, \]
where \( \xi = (\xi_1, \xi_2, \ldots, \xi_N) \) with \( \xi_i = \delta_i \phi_{i,n} + (1 - \delta_i) \phi_{0,i} \), using Assumption A2 we get
\[ (\mathcal{E}'(\rho_{\Phi_0}) \phi_{i,n} - \mathcal{E}'(\rho_{\Phi_0}) \phi_{0,i}, \phi_{j,n}) \lesssim \int_\Omega (\rho_\xi + \rho_\xi^2)(\phi_{i,n} - \phi_{0,i}) \phi_{j,n} \]
\[ \lesssim \| \rho_\xi \|_{0,3/3, \Omega} \| \phi_{i,n} - \phi_{0,i} \|_{0, \Omega} \| \phi_{j,n} \|_{0,6/(3-2\alpha)} \Omega \]
\[ + \| \rho_\xi \|_{0,3, \Omega} \| \phi_{i,n} - \phi_{0,i} \|_{0, \Omega} \| \phi_{j,n} \|_{0,6, \Omega} \]
\[ \lesssim \| \phi_{i,n} - \phi_{0,i} \|_{0, \Omega}. \]
from which we have
\[ (\mathcal{E}'(\rho_{\Phi_0}) - \mathcal{E}'(\rho_{\Phi_0})) \phi_{i,n}, \phi_{j,n}) \]
\[ = (\mathcal{E}'(\rho_{\Phi_0}) \phi_{i,n} - \mathcal{E}'(\rho_{\Phi_0}) \phi_{0,i}, \phi_{j,n}) + (\mathcal{E}'(\rho_{\Phi_0})(\phi_{0,i} - \phi_{i,n}), \phi_{j,n}) \]
\[ \lesssim \| \phi_{i,n} - \phi_{0,i} \|_{0, \Omega}. \]
Note that
\[ \lambda_{i,n} - \lambda_{0,i} = (A_{\Phi_0} \phi_{i,n}, \phi_{j,n}) - (A_{\Phi_0} \phi_{0,i}, \phi_{0,j}) \]
\[ = (A_{\Phi_0}(\phi_{i,n} - \phi_{0,i}), \phi_{j,n} - \phi_{0,j}) + \int_\Omega \sum_{k=1}^n \lambda_{0,ik} \phi_{0,k}(\phi_{j,n} - \phi_{0,j}) \]
\[ + \int_\Omega \sum_{k=1}^n \lambda_{0,jk} \phi_{0,k}(\phi_{i,n} - \phi_{0,i}) + \int_\Omega (\mathcal{E}'(\rho_{\Phi_0}) - \mathcal{E}'(\rho_{\Phi_0})) \phi_{i,n} \phi_{j,n} \]
\[ + D(\phi_{i,n} \phi_{j,n}, \rho_{\Phi_0} - \rho_{\Phi_0}). \]
Hence we conclude that
\[ |\Lambda_n - \Lambda_0| \lesssim \| \Phi_n - \Phi_0 \|_{1, \Omega}^2 + \| \Phi_n - \Phi_0 \|_{0, \Omega}. \] (4.20)
By Lemma 3.2, we decompose \( \Phi_n \) as
\[ \Phi_n = \Phi_0 + S(W) \Phi_0 + W, \] (4.21)
where \( W \in \mathcal{T}_{\Phi_0} \) and \( S(W) \in S^{N \times N} \) satisfying
\[ |S(W)| \leq \| W \|_{0, \Omega}^2 \leq \| \Phi_0 - \Phi_n \|_{0, \Omega}^2. \] (4.22)
Setting $\Psi = \Psi_{\Phi_n - \Phi_0}$ and applying the duality problem of (4.13), we obtain
\[
\|\Phi_n - \Phi_0\|_{0,\Omega}^2 = (\Phi_n - \Phi_0, \Phi_n - \Phi_0) \\
= (\Phi_n - \Phi_0, S(W)\Phi_0) + (\Phi_n - \Phi_0, W) \\
= (\Phi_n - \Phi_0, S(W)\Phi_0) + a'(\Phi_0; \Psi, W),
\]
which together with (4.21) leads to
\[
\|\Phi_n - \Phi_0\|_{0,\Omega}^2 = (\Phi_n - \Phi_0, S(W)\Phi_0) - a'(\Phi_0; \Psi, S(W)\Phi_0) \\
+ a'(\Phi_0; \Psi, \Phi_n - \Phi_0) \\
= (\Phi_n - \Phi_0, S(W)\Phi_0) - a'(\Phi_0; \Psi, S(W)\Phi_0) \\
+ a'(\Phi_0; \Psi - P_n'\Psi, \Phi_n - \Phi_0) \\
+ a'(\Phi_0; P_n'\Psi, \Phi_n - \Phi_0).
\]
Note that from (2.5) and (3.4), we have
\[
2a'(\Phi_0; P_n'\Psi, \Phi_n - \Phi_0) = E''(\Phi_0)(P_n'\Psi, \Phi_n - \Phi_0) \\
- E'(\Phi_n)(P_n'\Psi) + E'(\Phi_0)(P_n'\Psi) \\
+ 2 \sum_{i,j=1}^{N} (\lambda_{ij,n} - \lambda_{0,i}) \int_{\Omega} \phi_{j,n} P_n'\psi_i
\]
while the fact that $\Psi \in \mathcal{I}_{\Phi_0}$ yields
\[
\int_{\Omega} \phi_{j,n} P_n'\psi_i = \int_{\Omega} (\phi_{j,n} - \phi_{0,j})\psi_i + \int_{\Omega} \phi_{j,n}(P_n'\psi_i - \psi_i),
\]
we then come to
\[
\|\Phi_n - \Phi_0\|_{0,\Omega}^2 = (\Phi_n - \Phi_0, S(W)\Phi_0) - a'(\Phi_0; \Psi, S(W)\Phi_0) \\
+ a'(\Phi_0; \Psi - P_n'\Psi, \Phi_n - \Phi_0) \\
- \frac{1}{2} \left( E'(\Phi_n)(P_n'\Psi) - E'(\Phi_0)(P_n'\Psi) - E''(\Phi_0)(P_n'\Psi, \Phi_n - \Phi_0) \right) \\
+ \sum_{i,j=1}^{N} (\lambda_{ij,n} - \lambda_{0,i}) \left( \int_{\Omega} (\phi_{j,n} - \phi_{0,j})\psi_i + \int_{\Omega} \phi_{j,n}(P_n'\psi_i - \psi_i) \right).
\]
Using the Taylor expansion, we have that there exists $\delta \in [0, 1]$ such that
\[
E'(\Phi_n)(P_n'\Psi) - E'(\Phi_0)(P_n'\Psi) - E''(\Phi_0)(P_n'\Psi, \Phi_n - \Phi_0) \\
= E'(\xi)(P_n'\Psi, \Phi_n - \Phi_0) - E''(\Phi_0)(P_n'\Psi, \Phi_n - \Phi_0) \\
\lesssim (\|\Phi_n - \Phi_0\|_{1,\Omega}^2 + \|\Phi_n - \Phi_0\|_{0,\Omega}^2) \|\Phi_n - \Phi_0\|_{0,\Omega}^2. \tag{4.23}
\]
where \( \xi = \Phi_0 + \delta(\Phi_n - \Phi_0) \) and the last inequality is obtained by the similar arguments in the proof of (2.21) or Lemma 4.5 in [6] when \( \Gamma_1 = \Phi_n - \Phi_0, \Gamma_2 = \Phi_n - \Phi_0 \) and \( \Gamma_3 = P'_n \Psi \), and using the fact
\[
\| P'_n \Psi \|_{1,\Omega} \lesssim \| \Psi \|_{1,\Omega} \lesssim \| \Phi_n - \Phi_0 \|_{0,\Omega}.
\]

Taking (4.14), (4.16), (4.22) and (4.23) into account, we obtain that
\[
\| \Phi_n - \Phi_0 \|_{0,\Omega} \lesssim \| \Phi_n - \Phi_0 \|_{0,\Omega}^2 + \rho_n \| \Phi_n - \Phi_0 \|_{1,\Omega} + \| \Phi_n - \Phi_0 \|_{1,\Omega}^2 \| \Phi_n - \Phi_0 \|_{0,\Omega} + |\Lambda_n - \Lambda_0| (\| \Phi_n - \Phi_0 \|_{0,\Omega} + \rho_n),
\]
which together with (4.17) and (4.20) produces
\[
\| \Phi_n - \Phi_0 \|_{0,\Omega} \lesssim \rho_n \| \Phi_n - \Phi_0 \|_{1,\Omega}
\]
when \( n \gg 1 \). This completes the proof. \( \Box \)

**Remark 4.2** Theorem 4.3 shows that under certain assumptions every solution can be approximated with some convergent rate by finite dimensional solutions. We see that [6] provided numerical analysis of plane wave approximations only while our results apply to general finite dimensional discretizations and the analysis is systematic and carried out under very mild assumptions.

**Remark 4.3** If in addition, \( V_{\text{loc}} \in H^1(\Omega), \xi_j \in H^1(\Omega) \) (\( j = 1, 2, \cdots, M \)) and \( E \in C^1([0, \infty)) \cap C^3((0, \infty)) \), then for sufficiently large \( n \), estimates (4.17) and (4.18) are also satisfied with \( \tilde{\rho}_n \to 0 \) as \( n \to \infty \). Here
\[
\tilde{\rho}_n = \sup_{f \in \mathcal{H}, \| f \|_{1,\Omega} \leq 1} \inf_{\Psi \in \mathcal{H}_n} \| \nabla ((L'_{\Phi_0}(\Lambda_0, \Phi_0))^{-1} K f - \Psi) \|_{0,\Omega}
\]
and \( K : (\mathcal{H}, (\nabla \cdot, \nabla \cdot)) \to (\mathcal{H}_0, (\nabla \cdot, \nabla \cdot)) \) satisfying (4.15).

**Remark 4.4** We assume that \( \Omega \) is a convex bounded domain and \( S_n \) is replaced by the standard finite element space \( S^{h,k}_0(\Omega) \) of piecewise polynomials of degree \( k \) (\( k = 1, 2 \)) over a shape-regular mesh with size \( h \). Let \( (\Lambda_{h,k}, \Phi_{h,k}) \in X_{\Phi_0,h} \) be a solution of (3.4) and Assumption A2 hold. Then
\[
|\Lambda_0 - \Lambda_{h,1}| + \| \Phi_0 - \Phi_{h,1} \|_{0,\Omega} + h \| \Phi_0 - \Phi_{h,1} \|_{1,\Omega} \lesssim h^2
\]
when \( h \ll 1 \). If in addition, \( V_{\text{loc}} \in H^1(\Omega), \xi_j \in H^1(\Omega) \) (\( j = 1, 2, \cdots, M \)) and \( E \in C^1([0, \infty)) \cap C^3((0, \infty)) \), then
\[
|\Lambda_0 - \Lambda_{h,2}| + h \| \Phi_0 - \Phi_{h,2} \|_{0,\Omega} + h^2 \| \Phi_0 - \Phi_{h,2} \|_{1,\Omega} \lesssim h^4
\]
when \( h \ll 1 \).

### 5 Numerical examples

In this section, we will report several numerical examples that support our theory. These numerical experiments were carried out on LSSC3 cluster in
the State Key Laboratory of Scientific and Engineering Computing, Chinese Academy of Sciences. Our code is based on the PHG finite element toolbox developed in the State Key Laboratory of Scientific and Engineering Computing, Chinese Academy of Sciences.

In these examples, we solved Kohn–Sham equation (2.5). We chose our computational domain $\Omega$ as $[-10.0, 10.0]^3$. In computation, we used the norm-conserving pseudopotential [32] obtained by fhi98PP software and applied the local density approximation (LDA) for the exchange-correction potential. We applied the standard linear and quadratic finite element discretizations over uniform tetrahedral triangulations. The finite dimensional nonlinear eigenvalue problems were then solved by self consistent field (SCF) iterations [24]. In our computations, more precisely, we choose the Pulay method [27] to mix the density when we carry out the SCF iteration.
Finite dimensional approximations of Kohn-Sham models

Fig. 3 $SiH_4$: errors of the ground state total energy

Fig. 4 $N_2$: errors of the first and second eigenvalues

Fig. 5 $C_2H_4$: errors of the first and second eigenvalues
We present numerical results for \( \text{N}_2 \), \( \text{C}_2\text{H}_4 \) and \( \text{SiH}_4 \) molecules. Since analytical solutions are not available, we use the numerical solutions on a very fine grid for references to calculate the approximation errors.

Let us first come to the ground state total energy approximations. The errors of total energy of \( \text{N}_2 \), \( \text{C}_2\text{H}_4 \) and \( \text{SiH}_4 \) are presented in Figs. 1, 2 and 3, respectively. We can see that convergence rates for linear and quadratic finite elements are \( h^2 \) and \( h^4 \) respectively, which agree well with the results predicted by Theorem 4.2. We then present the approximation errors of the first two eigenvalues for these three molecules, see Figs. 4, 5 and 6. We may see that these results coincide well with our theory (see, e.g., Remark 4.4), too.

6 Concluding remarks

We have analyzed finite dimensional approximations of Kohn–Sham models. We have proved the convergence and shown the a priori error estimates of finite dimensional approximations. As we see, the ground state solutions oscillate near the nuclei [12, 18, 34]. It is natural to apply adaptive finite element discretizations to carry out the electronic structure calculations. Indeed, it is our on-going work to study the convergence and complexity of adaptive finite element methods that will be addressed elsewhere.

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