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A Mortar Spectral Element Method for Full-Potential Electronic Structure Calculations

Yichen Guo[1], Lueling Jia[1,*], Huajie Chen[2], Huiyuan Li[3] and Zhimin Zhang[1,4]

[1] *Beijing Computational Science Research Center, Beijing, 100193, P.R. China.*

[2] *School of Mathematical Sciences, Beijing Normal University, Beijing, 100875, P.R. China.*

[3] *State Key Laboratory of Computer Science/Laboratory of Parallel Computing, Institute of Software, Chinese Academy of Sciences, Beijing, 100190, P.R. China.*

[4] *Department of Mathematics, Wayne State University, Detroit, MI 48202, USA.*

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Abstract. In this paper, we propose an efficient mortar spectral element approximation scheme for full-potential electronic structure calculations. As a subsequent work of [24], the paper adopts a similar domain decomposition that the computational domain is first decomposed into a number of cuboid subdomains satisfying each nucleus is located in the center of one cube, in which a small ball element centered at the site of the nucleus is attached, and the remainder of the cube is further partitioned into six curvilinear hexahedrons. Specially designed Sobolev-orthogonal basis is adopted in each ball. Classic conforming spectral element approximations using mapped Jacobi polynomials are implemented on the curvilinear hexahedrons and the cuboid elements without nuclei. A mortar technique is applied to patch the different discretizations. Numerical experiments are carried out to demonstrate the efficiency of our scheme, especially the spectral convergence rates of the ground state approximations. Essentially the algorithm can be extended to general eigenvalue problems with the Coulomb singularities.

AMS subject classifications: 65N25, 35Q40, 35P30

Key words: Kohn-Sham equation, full-potential calculations, mortar spectral element method, exponential order of convergence.

*Corresponding author. *Email addresses:* ycguo@csrc.ac.cn (Y. Guo), lljia@csrc.ac.cn (L. Jia), chen.huajie@bnu.edu.cn (H. Chen), huiyuan@iscas.ac.cn (H. Li), zmzhang@csrc.ac.cn; ag7761@wayne.edu (Z. Zhang)

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1 Introduction

The Schrödinger wave equation is the quantum mechanical law determining the behavior of matter. Numerical solution of the Schrödinger equation is challenging since many-body problems would lead to high computational cost, especially for large scale systems. Several highly successful approximations have been made for efficient implementations [25, 33], among which Kohn-Sham density functional theory (DFT) achieves so far the best compromise between accuracy and efficiency when dealing with condensed matter systems [18, 22]. Therefore the Kohn-Sham equations play an essential role in the study of electronic structures of materials.

In this paper, we consider the following Kohn-Sham equations for a system containing N_n nuclei and N_e electrons,

$$\begin{cases} \left(-\frac{1}{2}\Delta + V_{\rm ne} + V_H(\rho_u) + V_{\rm xc}(\rho_u)\right) u_i = \lambda_i u_i, \quad i = 1,2,\cdots,N_e/2, \quad \text{in } \mathbb{R}^3, \\ \int_{\mathbb{R}^3} u_i u_j = \delta_{i,j}, \qquad\qquad\qquad\qquad\qquad\qquad i,j = 1,2,\cdots,N_e/2, \end{cases} \tag{1.1}$$

where the k-th nucleus is located at $\boldsymbol{R}_k \in \mathbb{R}^3$ and has charge $Z_k \in \mathbb{N}_+$. $\delta_{i,j}$ is the Kronecker delta. We assume in this paper that N_e is even for considering a system without the spin polarization effects and consider $N_{\rm e}/2$ eigenpairs. In (1.1), ρ_u is the electron density defined by

$$\rho_u(\boldsymbol{x}) = 2\sum_{i=1}^{N_e/2} |u_i(\boldsymbol{x})|^2, \quad u = (u_1, u_2, \cdots, u_{N_e/2}). \tag{1.2}$$

$V_{\rm ne}$ is the singular Coulomb interaction between electrons and nuclei,

$$V_{\rm ne}(\boldsymbol{x}) = -\sum_{k=1}^{N_n} \frac{Z_k}{|\boldsymbol{x} - \boldsymbol{R}_k|}.$$

$V_H(\rho_u)$ is the Hartree potential given by

$$V_H(\rho_u) = \int_{\mathbb{R}^3} \frac{\rho_u(\boldsymbol{y})}{|\boldsymbol{x} - \boldsymbol{y}|} d\boldsymbol{y}. \tag{1.3}$$

$V_{\rm xc}(\rho_u)$ is the exchange-correlation potential [22]. (1.1) is a nonlinear eigenvalue problem since the potentials V_H and $V_{\rm xc}$ depend on the eigenfunctions. Physically, the problem is considered in $\mathbb{R}^3$. In practice, owing to the exponential decay of the eigenfunctions of (1.1) on the whole space [1, 17], it is feasible to restrict the computations to a properly bounded domain $\Omega \subset \mathbb{R}^3$ by imposing appropriate boundary conditions.

Developments in various numerical algorithms and large-scale computations have made great contributions to the popularity of Kohn-Sham density functional theory. The singular Coulomb potential in the Kohn-Sham equations introduces a cusp in the eigenfunctions at each atomic position. The cusps hinder classic numerical methods with