



A perturbation-method-based post-processing for the planewave discretization of Kohn–Sham models



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ABSTRACT

In this article, we propose a post-processing of the planewave solution of the Kohn–Sham LDA model with pseudopotentials. This post-processing is based upon the fact that the exact solution can be interpreted as a perturbation of the approximate solution, allowing us to compute corrections for both the eigenfunctions and the eigenvalues of the problem in order to increase the accuracy. Indeed, this post-processing only requires the computation of the residual of the solution on a finer grid so that the additional computational cost is negligible compared to the initial cost of the planewave-based method needed to compute the approximate solution. Theoretical estimates certify an increased convergence rate in the asymptotic convergence range. Numerical results confirm the low computational cost of the post-processing and show that this procedure improves the energy accuracy of the solution even in the pre-asymptotic regime which comprises the target accuracy of practitioners.

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1. Introduction

First-principle molecular simulation is nowadays a major tool in different fields such as chemistry, condensed matter physics and materials science. Its use is motivated by the fact that it enables one to understand and predict the properties of a molecular system, without any empirical parameter except a few fundamental constants of physics (the reduced Planck constant \hbar , the Boltzmann constant k_B , the mass of the electron m_e , the elementary charge e , the dielectric permittivity of the vacuum ϵ_0) and the masses and atomic numbers of the nuclei contained in the system under investigation.

At this level, matter is described as a system of interacting nuclei and electrons. Within the Born–Oppenheimer approximation [1] (made in almost all molecular simulations), nuclei are considered as classical point-like particles and electrons are assumed to be, at each time t , in their ground state. As a consequence, the nuclei dynamics is governed by a classical Hamiltonian

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$$H(\{\mathbf{R}_k\}_{1 \leq k \leq M}, \{\mathbf{P}_k\}_{1 \leq k \leq M}) = \sum_{k=1}^M \frac{|\mathbf{P}_k|^2}{2m_k} + W(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M),$$

where m_k , $\mathbf{R}_k \in \mathbb{R}^3$ and $\mathbf{P}_k \in \mathbb{R}^3$ are respectively the mass, the position and the momentum of the k th nucleus, where M is the total number of nuclei and where W is an effective potential taking into account the presence of the electrons. The bottleneck in first-principle molecular simulation is the evaluation of the potential W for a given nuclear configuration which requires computing the ground state energy of the electrons in the electrostatic potential generated by the nuclei. This quantity can, in principle, be computed by solving the electronic Schrödinger equation. However, as this equation is a (linear) $3\mathcal{N}$ -dimensional partial differential equation, where \mathcal{N} is the number of electrons in the system, this cannot be done by brute force numerical methods when \mathcal{N} exceeds two or three due to the curse of dimensionality. Different approaches have been proposed to compute the electronic ground state energy. The most popular of them can be classified into three groups:

- wavefunction methods, among which are the Hartree–Fock and multiconfiguration self-consistent-field (MCSCF) models (see [4] for a mathematical introduction);
- methods originating from the density functional theory (DFT), namely orbital-free and Kohn–Sham models, that are used and presented in detail hereafter;
- quantum Monte Carlo methods [12,13].

The Kohn–Sham models [7,11] are the most popular approach to date as they offer a good compromise between accuracy and computational cost; they are among the most widely used models in physics and chemistry [2].

The purpose of this article is to present a new post-processing method for periodic Kohn–Sham calculations in plane-wave bases, leading to a significant gain in accuracy at a very limited extra computational cost. This method is based on the observation that the exact Kohn–Sham ground state can be considered as a perturbation of the approximate Kohn–Sham ground state computed in a finite basis set, and in applying first and second-order perturbation theory to the eigenvectors and eigenvalues of the Kohn–Sham operator respectively, in order to improve their accuracies. The specific structure of the problem and the *a priori* error estimates in [3] allow us to identify the leading terms in these first and second-order contributions, which turn out to be easy to evaluate, and discard the other terms, which are very costly or impossible to evaluate, but negligible since proven to be small.

Our approach strongly relies on the fact that the kinetic energy operator which, from a mathematical point of view, is the leading term in the Kohn–Sham Hamiltonian commutes with the orthogonal projection on the discretization space. This is not the case for atomic orbital basis sets methods, but this is the case for other discretizations such as some wavelet methods. The extension of our approach to approximation settings that do not satisfy this commutation property requires additional theoretical investigations and is work in progress.

This article is organized as follows. We first recall in Section 2.1 the mathematical formulation of the Kohn–Sham models for isolated molecular systems. We then present the supercell Kohn–Sham model used in condensed phase modeling and simulation (Section 2.2), and the concept of pseudopotential (Section 2.3). The plane-wave discretization method for the supercell Kohn–Sham model with pseudopotential is discussed in Section 3.1 and the iterative algorithms used to solve the resulting Kohn–Sham equations are detailed in Section 3.2. The *a priori* error estimates our analysis is based upon are reviewed in Section 3.3. We then introduce the post-processing in Section 4. For pedagogical reasons, we derive the expressions of the post-processed eigenfunctions and eigenvalues under the assumptions that all the eigenvalues of the Kohn–Sham operator are non-degenerate. The general case, as well as the proof of Theorem 4.1, which quantifies the improvement of the Kohn–Sham ground state energy obtained by the post-processing in the asymptotic regime, will be detailed in a mathematical analysis oriented paper [5]. In Section 5, we report numerical simulations on a simple system, an alanine molecule, obtained with the KSSOLV package [19], showing that our post-processing method leads to significant gain in accuracy (typically one order of magnitude on the energy) for a small extra cost (a few percent of the overall cost). Numerical simulations with the CO₂ and the benzene molecules were also performed and led to very similar results, and therefore are not presented in this paper.

2. DFT Kohn–Sham models

2.1. Introduction to Kohn–Sham models

Throughout this article, we adopt the system of atomic units for which $\hbar = 1$, $m_e = 1$, $e = 1$, $4\pi\epsilon_0 = 1$. In this system of units, the charge of the electron is -1 and the charges of the nuclei are positive integers.

Let us first consider an isolated molecular system *in vacuo*, consisting of M nuclei of charges $(z_1, \dots, z_M) \in (\mathbb{N} \setminus \{0\})^M$ located at the positions $(\mathbf{R}_1, \dots, \mathbf{R}_M) \in (\mathbb{R}^3)^M$ of the physical space, and of \mathcal{N} electrons. The electrostatic potential generated by the nuclei and felt by the electrons is then given by

$$V_{\text{nuc}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}. \quad (1)$$

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