

## Towards Translational Invariance of Total Energy with Finite Element Methods for Kohn-Sham Equation

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**Abstract.** Numerical oscillation of the total energy can be observed when the Kohn-Sham equation is solved by real-space methods to simulate the translational move of an electronic system. Effectively remove or reduce the unphysical oscillation is crucial not only for the optimization of the geometry of the electronic structure, but also for the study of molecular dynamics. In this paper, we study such unphysical oscillation based on the numerical framework in [G. Bao, G. H. Hu, and D. Liu, *An h-adaptive finite element solver for the calculations of the electronic structures*, Journal of Computational Physics, Volume 231, Issue 14, Pages 4967-4979, 2012], and deliver some numerical methods to constrain such unphysical effect for both pseudopotential and all-electron calculations, including a stabilized cubature strategy for Hamiltonian operator, and an *a posteriori* error estimator of the finite element methods for Kohn-Sham equation. The numerical results demonstrate the effectiveness of our method on restraining unphysical oscillation of the total energies.

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**Key words:** Translational invariance, adaptive finite element methods, Kohn-Sham equation, unstructured mesh.

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## 1 Introduction

Density functional theory (DFT) [11] has been becoming one of the most important models for the electronic structure calculations. In DFT, the Kohn-Sham equation [14] plays a crucial role in both theoretical and numerical studies [19].

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Lots of research has been done towards the numerical methods for Kohn-Sham equation. For example, the plane-wave expansion methods [16, 32], the real-space methods including the finite difference methods [7, 8], the finite element methods [23, 29], the discontinuous Galerkin methods [18], etc. Among these methods, the plane-wave pseudopotential (PWP) methods have been well developed and widely applied in the computational chemistry community. One of the main advantages of plane-wave expansion methods is that the plane-wave basis functions are independent of the ionic positions. Hence no Pulay corrections [25] is needed on the calculation of the ionic force. Although the real-space methods have a lot of advantages such as the flexibility on handling various boundary conditions and complex practical domains, all these methods suffer from the numerical oscillation of the total energy when simulating the translational or/and rotational move of the electronic systems in the domain.

To explain the numerical oscillation of the total energy, let us consider an electronic structure system with  $N_{nuc}$  atoms in the domain. By real-space methods, the Hamiltonian operator is discretized based on a mesh of the computational domain, i.e., the Hamiltonian operator needs to be evaluated pointwisely. It can be imagined that when a different mesh is used, or the molecule moves, the evaluation of the Hamiltonian would not be consistent with the previous one. It is acceptable in the calculations if the inconsistency is sufficiently small. This happens when all terms in the Hamiltonian are smooth and vary gently. However, once there is singularity in the Hamiltonian, and such singularity does not resolved well by the numerical methods, this kind of inconsistency could be large enough to qualitatively affect the numerical result such as the ground-state total energy of the system and the derived intermolecular force from Hellman-Feynman theorem [9]. Unfortunately, the Coulomb interaction between the electron and nucleus, which is called the external potential in the Hamiltonian, is quite singular. For example, the external potential in the Kohn-Sham equation for system we discussed can be given as

$$V_{ext}(\vec{x}) = - \sum_i^{N_{nuc}} \frac{Z_i}{|\vec{x} - \vec{R}_i|}, \quad i = 1, 2, \dots, N_{nuc},$$

where  $Z_i$  and  $\vec{R}_i$  stand for the  $i$ -th nucleus charge and position, respectively. Besides the external potential, the kinetic energy operator could also behave singular in the vicinity of the nucleus because the wavefunctions vary dramatically in the same area. Large numerical error will be introduced if we evaluate these terms inadequately. Furthermore, when we use a fixed uniform mesh to partition the domain, and let the electronic structure do a translational move in the domain, the numerical error from the inadequate discretization will appear periodically with the period the mesh size. Consequently, the total energy of the system obtained from the calculation will also oscillate periodically with the same period, which is called egg-box effect. This is not physical because nothing is changed in the system but the position of the electronic structure, so the total energy should be kept as a constant theoretically. This numerical oscillation is unacceptable since it will affect the evaluation of ground-state total energy, and the calculation of the ionic force