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Numerical Analysis of Finite Dimensional Approximations in Finite Temperature DFT

Ge Xu[1], Huajie Chen[1,*] and Xingyu Gao[2]

[1] *School of Mathematical Sciences, Beijing Normal University, Beijing 100875, China.*
[2] *National Key Laboratory of Computational Physics, Institute of Applied Physics and Computational Mathematics, Beijing 100088, China.*

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Abstract. In this paper, we study numerical approximations of the ground states in finite temperature density functional theory. We formulate the problem with respect to the density matrices and justify the convergence of the finite dimensional approximations. Moreover, we provide an optimal a priori error estimate under some mild assumptions and present some numerical experiments to support the theory.

AMS subject classifications: 65N15, 65N25, 35P30, 81Q05

Key words: Finite temperature density functional theory, Mermin-Kohn-Sham equation, density matrix, a priori error estimates.

1 Introduction

Density functional theory (DFT) [22, 23] has been the most widely used method in electronic structure calculations, which achieves the best compromise between accuracy and computational cost among different approaches [5, 27, 29, 34]. While the standard DFT models are in principle for systems at zero temperature, a finite temperature DFT model was proposed [30] for systems where the temperature effects on electrons are not negligible. The finite temperature DFT can be viewed as an extension of DFT by including the electron entropy into the total energy, which considers the electrons within a canonical ensemble [34]. It has not only been successfully applied to many practical simulations (see, e.g. [24, 41]), but also used to resolve the "charge sloshing" phenomenon in self-consistent field iterations for metallic systems by smearing the integer occupation numbers into fractional ones (see, e.g. [28, 31]).

*Corresponding author. *Email addresses:* gao_xingyu@iapcm.ac.cn (X. Gao), chen.huajie@bnu.edu.cn (H. Chen), gexu@mail.bnu.edu.cn (G. Xu)

The finite temperature DFT model is usually formulated by the so-called Mermin-Kohn-Sham (MKS) equation [29, 30, 33]: Find the chemical potential $\mu \in \mathbb{R}$, the orbitals and occupation numbers $(\phi_i, \lambda_i) \in H^1(\mathbb{R}^3) \times \mathbb{R}$ $(i = 1,2,\ldots)$ satisfying

$$\left(-\frac{1}{2}\Delta + v_{\text{ext}} + v_{\text{H}}(\rho) + v_{\text{xc}}(\rho)\right)\phi_i = \lambda_i \phi_i, \tag{1.1a}$$

$$\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \tag{1.1b}$$

$$\rho = \sum_i f_i |\phi_i|^2, \tag{1.1c}$$

$$f_i = \left(1 + e^{\frac{(\lambda_i - \mu)}{(k_{\text{B}} T)}}\right)^{-1}, \tag{1.1d}$$

$$\sum_i f_i = N \tag{1.1e}$$

with k_{B} the Boltzmann constant and T the electron temperature of the system. The chemical potential μ is actually determined by the constraint (1.1e) that the sum of occupation numbers equals the electron number. In Eq. (1.1a), the potential includes the external potential v_{ext} representing the nuclear attraction, the Hartree potential $v_{\text{H}}(\rho) = \int_{\mathbb{R}^3} \rho(r)/|\cdot - r| \, \mathrm{d}r$ representing the mean-field electron repulsion, and the exchange-correlation potential $v_{\text{xc}}(\rho)$ [29]. The Mermin-Kohn-Sham equation is a nonlinear eigenvalue problem, as the operator depends on both the eigenvalues and eigenfunctions to be solved. This is usually solved by a self-consistent field (SCF) iteration algorithm in practice. We note that the standard Kohn-Sham equations will be recovered at the zero temperature limit, which gives the occupation numbers $f_i = 1$ when $i \leq N$ and $f_i = 0$ when $i > N$ under the gap condition $\lambda_N < \lambda_{N+1}$.

Validation of numerical results is a fundamental issue, particularly the discretization error resulting from the choice of a finite basis set. For standard DFT models like orbital-free and Kohn-Sham models, there are many works on the numerical analysis in the past decade [3, 4, 9–11, 18, 25, 42, 44]. The extension of the existing analysis to the finite temperature DFT model presents additional complexity, as it requires the consideration of a significantly bigger set of orbitals and occupation numbers. To the best of our knowledge, there is very limited work devoted to its mathematical and numerical analysis. In [36], the existence and uniqueness of solutions for the MKS equations were proved by using the Banach's fixed point theorem under the condition that the coupling constant is sufficiently small. In [12], the existence and uniqueness were justified with the assumption the absence of exchange correlation potential, by using the Schauder's fixed point theorem. In [14], the invariance of the energy functional and existence of the minimizer of an ensemble Kohn-Sham model were studied, by involving a pseudo-eigenvalue matrix. In [13], a similar problem, the Schrödinger-Poisson equation was considered and the a priori error estimate was derived. We mention that for general MKS equation, the convergence analysis and error estimates under the energy norm are still missing.