

Error Estimates of Some Numerical Atomic Orbitals in Molecular Simulations

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Abstract. Numerical atomic orbitals have been successfully used in molecular simulations as a basis set, which provides a nature, physical description of the electronic states and is suitable for $\mathcal{O}(N)$ calculations based on the strictly localized property. This paper presents a numerical analysis for some simplified atomic orbitals, with polynomial-type and confined Hydrogen-like radial basis functions respectively. We give some a priori error estimates to understand why numerical atomic orbitals are computationally efficient in electronic structure calculations.

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1 Introduction

In the *ab-initio* quantum mechanical modeling of many electron systems, Kohn-Sham density functional theory (KS-DFT) [28, 30] achieves so far the best compromise between accuracy and computational cost, and has become the most widely used electronic structure model in molecular simulations and materials science. Let us consider a closed-shell system with M_n nuclei of charges $\{Z_1, \dots, Z_{M_n}\}$, located at the positions $\{\mathbf{R}_1, \dots, \mathbf{R}_{M_n}\}$, and an even number M_e of electrons in the non-relativistic setting. The Kohn-Sham

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ground state energy and electron density of the system can be obtained by minimizing the energy functional

$$E \left[\{\phi_i\}_{i=1}^{M_e/2} \right] = \int_{\mathbb{R}^3} \left(\sum_{i=1}^{M_e/2} |\nabla \phi_i(\mathbf{r})|^2 + v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + e_{\text{xc}}[\rho(\mathbf{r})] \right) d\mathbf{r} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (1.1)$$

with respect to the orbitals $\{\phi_i\}_{i=1}^{M_e/2}$ under constraint $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$, where

$$v_{\text{ext}}(\mathbf{r}) = - \sum_{I=1}^{M_n} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} \quad (1.2)$$

is the electrostatic attraction potential generated by the nuclei, $\rho(\mathbf{r}) = 2 \sum_{i=1}^{M_e/2} |\phi_i(\mathbf{r})|^2$ is the electron density, and $e_{\text{xc}}[\rho]$ is the exchange-correlation energy per volume with electron density ρ by a local density approximation (LDA, see [36]). The Euler-Lagrange equation associated with this minimization problem is the well-known Kohn-Sham equation: Find $\lambda_i \in \mathbb{R}$, $\phi_i \in H^1(\mathbb{R}^3)$ for $i = 1, 2, \dots, M_e/2$, such that $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$ and

$$\left(-\frac{1}{2}\Delta + v_{\text{eff}}[\rho] \right) \phi_i = \lambda_i \phi_i \quad \text{in } \mathbb{R}^3, \quad i = 1, 2, \dots, M_e/2, \quad (1.3)$$

where $\{\lambda_i\}_{i=1}^{M_e/2}$ are the lowest $M_e/2$ eigenvalues, and $v_{\text{eff}}[\rho] = v_{\text{ext}} + v_{\text{H}}[\rho] + v_{\text{xc}}[\rho]$ is the effective potential with $v_{\text{H}}[\rho](\mathbf{r}) = \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$ being the Hartree potential for interactions between electrons and $v_{\text{xc}}[\rho]$ being the exchange-correlation potential [36]. A self-consistent field (SCF) iteration algorithm [33, 36] is commonly resorted to for this nonlinear eigenvalue problem. In each iteration, a new Hamiltonian is constructed from a trial electronic state and a linear eigenvalue problem is then solved to obtain the low-lying eigenvalues. The algorithm requires expansions of the eigenfunctions by a finite set of simple known functions and discretization of the hamiltonian into a finite dimensional matrix. The choice of basis functions is therefore important, which ultimately determines the quality of the approximations.

Linear combination of atomic orbitals (LCAO) methods are the most widely used discretizations by chemists, which capture the essence of the atomic-like features and provide an intuitive description of electronic states. Generally, the atomic orbital basis functions are products of a radial basis function and a spherical harmonic function centered at each nuclear, that is

$$\psi_{Inlm}(\mathbf{r}) = \chi_{Inl}(r_I) Y_{lm}(\hat{\mathbf{r}}_I), \quad I = 1, \dots, M_n, \quad (1.4)$$

where $\mathbf{r}_I = \mathbf{r} - \mathbf{R}_I$, $r = |\mathbf{r}|$, $\hat{\mathbf{r}} = \mathbf{r}/r$, and $Y_{lm}(\hat{\mathbf{r}})$ denotes the spherical harmonic functions on S^2 . The radial basis functions χ_{Inl} depends on not only a site index I , but also an angular momentum quantum number l and a multiplicity index n . Among different basis