



Large-scale *ab initio* simulations based on systematically improvable atomic basis



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ABSTRACT

We present a first-principles computer code package (ABACUS) that is based on density functional theory and numerical atomic basis sets. Theoretical foundations and numerical techniques used in the code are described, with focus on the accuracy and transferability of the hierarchical atomic basis sets as generated using a scheme proposed by Chen et al. (2010). Benchmark results are presented for a variety of systems include molecules, solids, surfaces, and defects. All results show that the ABACUS package with its associated atomic basis sets is an efficient and reliable tool for simulating both small and large-scale materials.

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1. Introduction

The density functional theory [1,2] (DFT) based first-principles methods are becoming increasingly important in the research fields of condensed matter physics, material sciences, chemistry, and biology. With the rapid development of supercomputers and the advances of numerical algorithms, nowadays it is possible to study the electronic, structural and dynamical properties of complicated physical systems containing thousands of atoms using DFT. In these cases, the efficiency of widely used plane wave (PW) basis is largely limited, because of its extended nature. Instead, local bases, such as atomic orbitals, are the better choices.

Atomic orbitals have several advantages as basis sets for the *ab initio* electronic structure calculations in the Kohn–Sham scheme [1,2]. First, the basis size of atomic orbitals is much smaller compared to other basis sets, such as PW or real-space mesh. Second, the atomic orbitals are strictly localized and therefore can be combined with either the so-called linear scaling algorithms [3] for electronic calculations, or any other algorithm with a better

scaling behavior than $\mathcal{O}(N^3)$. For example, Lin et al. have recently developed a so-called Pole Expansion and Selected Inversion (PEXSI) technique [4,5], which takes advantage of the sparsity of the Hamiltonian and the overlap matrices obtained with local orbitals, and allows to solve the Kohn–Sham equations with numerical effort that scales as N^α ($\alpha \leq 2$) for both insulating and metallic systems, with N being the number of atoms.

While the analytical Gaussian-type orbitals have been well established for *ab initio* calculations in the quantum chemistry community for decades, the numerically tabulated atomic orbitals are getting more and more popular in the computational physics community. Several first-principles codes based on the numerical atomic orbitals have been developed in recent years, e.g., SIESTA [6], OpenMX [7], FHI-aims [8], to name just a few, which aim at large-scale DFT calculations by exploiting the compactness and locality of numerical atomic orbitals. However, the numerical atomic orbitals must be constructed very carefully to ensure both good accuracy and transferability. Furthermore, it would be highly desirable if the quality of the basis sets can be systematically improved in an unbiased way. Recently, some of us [Chen, Guo, and He (CGH)] proposed a new scheme [9,10] to construct systematically improvable optimized atomic basis sets for DFT calculations. Based on the CGH procedure for basis set generations, we have developed a DFT package [11] from scratch, named

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Atomic-orbital Based Ab-initio Computation at UStc (ABACUS) here in the Key Laboratory of Quantum Information, University of Science and Technology of China (USTC). In the ABACUS package, besides the primary option of using numerical atomic orbitals as basis functions, PW basis can also be employed as an alternative choice. This dual basis feature is very useful for accuracy and consistency checks in benchmark calculations. For both basis set choices, the package uses norm-conserving pseudopotential in the Unified Pseudopotential Format (UPF) that has been used in Quantum ESPRESSO [12]. The UPF pseudopotentials can be generated from the Opium package [13]. Regarding the exchange–correlation functionals, we have implemented the local (spin) density approximation [L(S) DA], and the generalized gradient approximation (GGA) as constructed by Perdew, Burke, and Ernzerhof (PBE). In addition, semi-empirical van der Waals (vdW) corrected DFT scheme as proposed by Grimme (DFT-D2) [14] has also been implemented. Other advanced functionals such as hybrid functionals are currently under development and will be reported in a later work. At the level of local-density approximation (LDA) and generalized gradient approximation (GGA), the ABACUS package can do typical electronic structure calculations, structure relaxations, and molecular dynamics.

In this paper, we first describe the main features of the ABACUS package, as well as the major techniques that are used to implement DFT algorithms with atomic basis sets. In a previous study [9], the CGH orbitals have been demonstrated to be accurate and transferable for the group IV and group III–V semiconductors. Here, we extend the tested systems to a larger range of elements, including the alkali elements, 3d transition metals, group VI and group VII elements, with focus on the structural and electronic properties of molecules, solids, surfaces, and defects. The results demonstrate that ABACUS with the CGH orbitals are highly reliable for both finite and extended systems. In particular, the basis set at the level of double- ζ plus polarization function (DZP) is an excellent choice to compromise between accuracy and computational cost, and can be safely used in production calculations in most situations.

The rest of paper is organized as follows. In Section 2, we introduce the basic algorithms and numerical techniques. In Section 3, we will demonstrate the performance of the ABACUS package, focusing on the accuracy of the atomic orbitals generated using the CGH scheme, for a variety of benchmark systems. The scaling behavior of ABACUS for DFT–LDA calculations as a function of the system size is also presented in this section. Finally, we summarize our work in Section 4.

2. Methods

In this section, we first briefly recapitulate the basic formulation of solving Kohn–Sham equations in atomic basis (Section 2.1) to set up the stage. This is followed by a description of the main techniques used in ABACUS. Topics to be covered include the generation of the CGH atomic orbitals (Section 2.2), the construction of Hamiltonian matrix and overlap matrix (Section 2.3), the solvers for Kohn–Sham equations (Section 2.4), and finally the total energy and force calculations (Section 2.5).

2.1. The Kohn–Sham equation in atomic basis

The central task in DFT calculations is to solve the Kohn–Sham equation [1,2],

$$\hat{H}_{\text{KS}} \Psi_n(\mathbf{r}) = \epsilon_n \Psi_n(\mathbf{r}), \quad (1)$$

where ϵ_n and $\Psi_n(\mathbf{r})$ are the Kohn–Sham eigenvalues and eigenfunctions for state n . Hartree atomic unit ($e = \hbar = m_e = 1$) is used here

and throughout the paper. The Kohn–Sham Hamiltonian \hat{H}_{KS} can be written as,

$$\hat{H}_{\text{KS}} = \hat{T} + \hat{V}^{\text{ext}}(\mathbf{r}) + \hat{V}^H[\rho(\mathbf{r})] + \hat{V}^{\text{xc}}[\rho(\mathbf{r})], \quad (2)$$

where $\hat{T} = -\frac{1}{2}\nabla^2$, $\hat{V}^{\text{ext}}(\mathbf{r})$, $\hat{V}^H[\rho(\mathbf{r})]$, and $\hat{V}^{\text{xc}}[\rho(\mathbf{r})]$ are the kinetic energy operator, the external potential, the Hartree potential, and the exchange–correlation potential, respectively. The Kohn–Sham Hamiltonian \hat{H}_{KS} thus depends on the electron density $\rho(\mathbf{r})$, which can be determined from the occupied Kohn–Sham orbitals

$$\rho(\mathbf{r}) = 2 \sum_{n=1}^{\text{occ.}} |\Psi_n(\mathbf{r})|^2. \quad (3)$$

Here for simplicity we assume that the system is spin-degenerate, and hence the spin index is omitted. Extending the algorithm described here to the spin-polarized case is straightforward and has been implemented in ABACUS.

Norm-conserving pseudopotentials are used to describe the ion–electron interactions. The external potential $\hat{V}^{\text{ext}}(\mathbf{r})$ in Eq. (2) contains the summation of the ion–electron potentials of all atoms plus, when they exist, applied external potentials. Therefore (in the absence of the applied external potential),

$$\hat{V}^{\text{ext}}(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{\alpha i} \hat{v}_{\alpha i}^{\text{ps}}(\mathbf{r} - \boldsymbol{\tau}_{\alpha i} - \mathbf{R}), \quad (4)$$

where $\hat{v}_{\alpha i}^{\text{ps}}$ is a norm-conserving pseudopotential [15] for the i -th atom of element type α , and $\boldsymbol{\tau}_{\alpha i}$ is the atomic coordinate in the cell \mathbf{R} . The pseudopotential can split into a local part of the potential \hat{v}_{α}^L and separable fully non-local potentials [16] $\hat{v}_{\alpha}^{\text{NL}}$,

$$\hat{v}_{\alpha}^{\text{ps}} = \hat{v}_{\alpha}^L + \hat{v}_{\alpha}^{\text{NL}}. \quad (5)$$

The applied external potentials, e.g., electric fields, can be easily added to the local part of the potential, while the non-local pseudopotential can be written as,

$$\hat{v}_{\alpha}^{\text{NL}} = \sum_{l=0}^{l_{\text{max}}} \sum_{m=-l}^l \sum_{n=1}^{n_{\text{max}}} |\chi_{\alpha l m n}\rangle \langle \chi_{\alpha l m n}|, \quad (6)$$

where $|\chi_{\alpha l m n}\rangle$ are non-local projectors, with l , m , n being the angular momentum, the magnetic momentum, and the multiplicity of projectors, respectively. In Eq. (6), l_{max} and n_{max} are the maximal angular momentum and the maximal multiplicity of projectors for each angular momentum channel, respectively.

The Kohn–Sham equation is usually solved within certain basis sets. The ABACUS package offers two choices of basis sets: the PW basis set and the atomic basis set. The advantage to do so is that the results obtained using atomic basis sets can be directly compared to those obtained from PW basis sets for small systems, and thus provides valuable benchmarks for the former. This will be clearly seen in Section 3 where the benchmark results for a variety of systems are presented. However, since the PW algorithm has been well developed and documented, here we only focus on the algorithms of the atomic-basis implementation.

Without losing generality, we consider crystalline systems under periodic boundary conditions. The Kohn–Sham eigenfunctions in Eq. (1) then become Bloch orbitals which, within atom-centered basis set, can be expanded as,

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \sum_{\mu} c_{n\mu, \mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_{\mu}(\mathbf{r} - \boldsymbol{\tau}_{\alpha i} - \mathbf{R}), \quad (7)$$

where $\phi_{\mu}(\mathbf{r} - \boldsymbol{\tau}_{\alpha i} - \mathbf{R})$ are the atomic orbitals centering on the i -th atom of type α in the unit cell \mathbf{R} . The orbital index μ is a compact one, $\mu = \{\alpha, i, l, m, \zeta\}$ with l being the angular momentum, m the magnetic quantum number, and ζ the number of atomic orbitals for a given l . Here n and \mathbf{k} are the band index and Bloch wave vector,

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