# Development of a First-Principles Code for Materials Science: Local Energy-Density and Stress-Density Calculations and XANES/ELNES Calculations by the PAW Method

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## Introduction

The projector augmented wave (PAW) method [1] is the most advanced plane-wave method within density-functional theory (DFT) for the total energy, atomic structures and various properties of materials. By recovering the true oscillation of valence wave functions near nuclei via projection, this method has both accuracy as the FLAPW method and efficiency as the ultrasoft pseudopotential method. We are developing new package software QMAS (Quantum MAterials Simulator) [2] for the PAW method so as to attain more efficient parallel computations and to deal with a wider range of materials properties than the conventional package software. In this paper, we present new functionalities in QMAS for materials science researches: local energy-density and stress-density schemes [3] and full-PAW XANES/ELNES (X-ray absorption near edge structure/electron energy-loss near-edge structure) calculations [4,5].

## Energy-Density and Stress-Density Schemes

In plane-wave schemes based on DFT, physical quantities such as energy and stress are given as the integral or average throughout the supercell. If such quantities are given in each local region in the supercell, defective systems such as surfaces and boundaries could be deeply analyzed. Historically, local energy-density [6] and stress-density [7] schemes have been proposed within plane-wave pseudopotential methods. However, practical applications have not been performed enough, due to the difficulty of the gauge-dependent problem. Recently, we have clarified the formulation of the energy density and stress density in the PAW method for the first time [3], and proposed that local energy and local stress can be given as unique physical quantities if the densities are integrated within proper local regions where the gauge-dependent terms are integrated to be zero. This strategy has been successfully applied to each atomic layer of Al (111) surfaces [3]. In this paper, we present applications to grain boundaries in metals. For general defective systems, it is necessary to define local regions to satisfy the condition for the gauge-dependent problem. We adopt atom-centered regions via fuzzy-Voronoi [8] or Bader integration schemes [9] for such local regions.

**Full-PAW XANES/ELNES Calculations**

XANES and ELNES are able to provide sensitive information on chemical bonding, valence states and coordination in materials. It is essential to perform quantitative simulations of the spectra to elucidate the local atomic and electronic structures from the observed spectra. For this purpose, the band-structure methods [10] such as OLCAO or FLAPW+lo methods have an advantage that various physical quantities can be derived in the same theoretical framework. Recently XANES/ELNES codes using the pseudopotential method have been developed [11], where large supercells to prevent unphysical interactions among core holes are attained. However, in such a scheme, the reconstruction of true all-electron valence wave functions from pseudo-wave functions based on the concept of the PAW approach is necessary. Thus we have developed the code for *full*-PAW calculations of XANES/ELNES in QMAS, where the theoretical threshold energy is also obtained within the PAW framework due to the concept in [12]. In this paper, we show that our full-PAW scheme can provide XANES/ELNES spectra as well as the chemical shift in the threshold energy, more accurately than the psudopotential method, and with much smaller computational efforts than the FLAPW method.

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