Ab Initio Local Energy and Local Stress: Essence of the Method and Recent Applications to Surfaces, Defects, and Interfaces

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First-principles plane-wave methods based on density-functional theory (DFT) such as ultrasoft pseudopotential and projector augmented wave (PAW) methods coupled with efficient iterative ground-state computations enable us to deal with various defects, surfaces and interfaces in materials. In the plane-wave methods, total energies E_{tot} and stress tensors $\sigma_{\alpha\beta}$ are given as integrated or averaged quantities in the supercell, and we cannot obtain local distribution of energies or stresses. If we use empirical interatomic potentials, we can obtain such local distributions, while the quantitative accuracy is limited. If we could obtain the local distribution of energies and stresses by the first-principles plane-wave methods, it should greatly contribute to the understanding of the nature of defects, surfaces and interfaces and the local mechanical properties. We are engaged in the development of the computational technique for such local energies and local stresses within the plane-wave DFT framework. In this paper, we explain the essence of our scheme and show recent applications to surfaces, defects, and grain boundaries (GBs) in metals and precipitate/metal interfaces [1-5].

Historically, the schemes to obtain energy density $\varepsilon(\vec{r})$ [6] and stress density $\tau_{\alpha\beta}(\vec{r})$ [7] were proposed within the plane-wave DFT framework. These densities are defined as real-space cell-periodic functions as follows:

$$E_{tot} = \int_{V} \varepsilon(\vec{r})\, d\vec{r}\,, \qquad \sigma_{\alpha\beta} = \frac{1}{V}\frac{\partial E_{tot}}{\partial \varepsilon_{\alpha\beta}} = \frac{1}{V}\int_{V} \tau_{\alpha\beta}(\vec{r})\, d\vec{r} \qquad (1)$$

However, these densities have inherent gauge-dependent problems [6,7], preventing practical applications. The kinetic terms in the energy and stress densities have the freedom of selection of symmetric or asymmetric forms, resulting in the dependence of density values on this selection, namely the non-uniqueness of density values. The differences between the symmetric and asymmetric forms in the kinetic energy and stress densities are proportional to $\nabla^2\rho(\vec{r})$ and $\nabla_\alpha\nabla_\beta\rho(\vec{r})$, respectively, where $\rho(\vec{r})$ is the valence-electron density distribution. The integrations of these terms inside the supercell V are exactly zero. We define local regions V_i for which the gauge-dependent terms $\nabla^2\rho(\vec{r})$ and $\nabla_\alpha\nabla_\beta\rho(\vec{r})$ are also integrated to be zero as

$$\int_{V_i} \nabla^2 \rho(\vec{r})\, d\vec{r}^3 = \int_{S_i} \nabla\rho(\vec{r})\cdot\vec{n}_\perp\, dS = 0 \qquad (2)$$

$$\int_{V_i} \nabla_\alpha\nabla_\beta \rho(\vec{r})\, d\vec{r}^3 = \int_{S_i} \nabla_\beta\rho(\vec{r})\,\vec{e}_\alpha\cdot\vec{n}_\perp\, dS = 0 \qquad (3)$$

By integrating the energy and stress densities for such local regions, we can obtain unique local energy and local stress without the gauge-dependent problem of the kinetic terms, because the gauge-dependent terms are integrated to be zero in each local region.

We have coded the energy and stress densities within the PAW-GGA method in QMAS package developed in AIST [8]. To decide the local regions, we adopt two schemes. One is the layer-by-layer method [1] for layered supercells such as surface slabs and cells for stacking faults. By the two-dimensional periodicity of each layer, Eqs. (2) and (3) can be expressed as one-dimensional equations for integrated charge profile on each plane, leading to atomic-layer regions bounded by flat planes. The other is the Bader integration for general systems. The final form of Eq. (2) means that the surface integration of the normal component of the gradient of the electron density on the region surface should be zero. This condition can be satisfied by the Bader atomic region decided so that the term $\nabla\rho(\vec{r})\cdot\vec{n}_{\perp}$ is zero on the region surface [9]. Note that the diagonal sum of Eq. (3) is equivalent to Eq. (2). In this way, we can obtain the local energy and diagonal sum of local stress tensor for each atomic Bader region as unique physical quantities. We utilize the Yu-Trinkle algorithm [10] for the Bader partitioning of the data on uniform FFT mesh as used in their similar local-energy method.

We have examined layer-by-layer stresses of an Al(111) surface, and found the surface-stress oscillation, correlated with Friedel-like in-plane charge oscillation [1]. For (111) surfaces of fcc late transition metals, we have found large tensile stresses on the top layer. The comparison with the tight-binding model (Friedel model) has shown that the origin of the tensile stress is the *d*-band width reduction due to the coordination number reduction [2]. For stacking faults in fcc metals, we have observed the energy increases at the atomic layers of hcp-like stacking, of which the magnitude and extent have correlation with the electronic structure. For a tilt GB in Al, there occur covalent-like reconstructed bonds with increased charge density between interface atoms with reduced coordination numbers. The local energies at such atoms clearly show the remarkable local stability, while the EAM potential cannot reproduce this phenomenon [3]. The examination of <110> tilt GBs in bcc Fe has shown the presence of two kinds of interface atoms. One with an expanded atomic volume shows a high local energy, a high tensile stress, and an enhanced magnetic moment, while the other with short interfacial bonds shows a lower local energy, a compressive stress and a reduced magnetic moment [4]. The local energy analysis is also effective to understand the impurity-segregation mechanism. For a Fe/TiC interface, the local energy and local stress are quite effective to understand the bonding nature and misfit stresses [5].

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